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BIOPLASTICS

PLANTS AND CROPS
RAW MATERIALS
PRODUCTS

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BIOPLASTICS

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1 BIOPLASTICS – WHAT DOES IT MEAN, EXACTLY?

1.1 Fundamentals

Plastics are organic polymers[1], which can be processed in various different ways. Their technical properties, such as formability, hardness, elasticity, rigidity, heat resistance and chemical resistance, can be varied across a wide range by selecting the correct raw materials, manufacturing process, and additives. Plastics are lighter and more economical than many other materials. For these reasons, plus their extreme versatility and excellent process ability, they are the material of choice in many industrial and commercial applications [2]. Since the widespread availability of petroleum at the beginning of the 20th century most traditional plastics have been produced using petroleum.

Basically plastic or polymer products differ in whether they are structural polymers or functional polymers.

Structural polymers are those that are used in industrial applications, i. e. what we commonly call plastics.

Functional polymers, however, are used for non-material applications. This may be, for example, the use as a paper additive, adhesives, coating resins, thickeners, flocculants, concrete additives and much more. Even if the amount of biobased raw materials (more on this later) is significantly higher in the functional polymers than for the structural polymers, the main focus of this booklet is on the structural polymers, i. e. the plastic materials that are meant in the following, when using the word “plastics”.

The statistics (2011 figures) are impressive: the plastics industry employs more than 1.45 million people in Western Europe and turns over some 300 billion Euros per annum. Out of the approximately 235 million tonnes of plastics produced annually, worldwide, about one quarter comes from Europe. Its applications are not only in packaging (40 %), construction materials (20 %), but plastic is also needed in automobile production (8 %) and furniture manufacture, as well as in the electronics industry and in the manufacture of domestic equipment of all types [3].

And consumption continues to rise; worldwide from 50 million tonnes p. a. in 1976 to an estimated 330 million tonnes in 2015.

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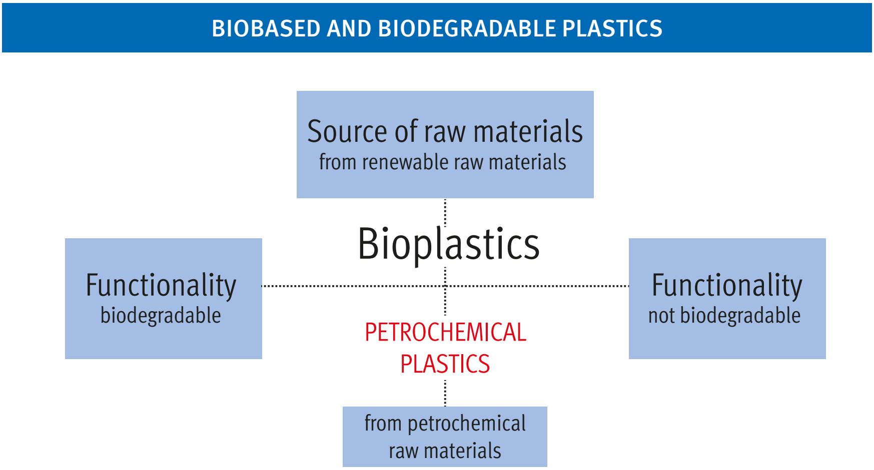
[1] *Polymers (from the Greek Poly = many, meros = particles) are long-chain molecules (macromolecules), that can also be branched. The molecules, entangled like cotton wool, produce a solid material that can be reshaped – i. e. plastic. The precursors of polymers are monomers (mono = one) and oligomers (oligo = few)*

But plastic isn‘t simply plastic. Whilst thermoset resins remain permanently in a rigid state after hardening, thermoplastics can be melted over again, or reshaped by the application of heat. These thermoplastics are the most commonly used and hold an 80 % share of the market. Another group of plastics covers the ductile plastics or thermoplastic elastomers [1].

1.2 Bioplastics = biobased plastics

Bioplastics consist in a large part, or even completely, of renewable resources. Thus bioplastics are biobased plastics. Biodegradable, but petroleum based plastics, are not considered as bioplastics (Fig.1.1).

The first modern plastics from renewable resources, which appeared on the market at the end of the 1980s, were generally biodegradable. The new products were also advertised with this feature. This revealed that the term “bioplastic” was often linked less with the renewable resource base, but more with the property “biodegradation”. From today’s perspective, the biodegradability is not a mandatory criterion for a bioplastic, but merely a special property of some biobased, but also some of petrochemical plastics.


BIOBASED AND BIODEGRADABLE PLASTICS

Source: Engineering Biopolymers (Endres, Siebert-Raths) [5], modified by FNR

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Fig. 1.1: Biobased and biodegradable plastics

2 LEGAL AND REGULATORY BACKGROUND

Most of the comments and data in this section refer to the situation in Germany. They are expanded by those regulations that apply in the EU and the USA.

The German Waste Management legislation requires the manufacture of products which are so designed that during their production and use the amount of waste is minimised. Certain general assumptions include the fact that no noxious by-products or additives must find their way into the natural waste disposal cycle. National and international standards regarding the degradability of polymer materials and products have meanwhile been established to cope with these problems.

2.1 "Biobased" standards and certification

Biobased or biogenic means that the product is wholly or partly made from renewable raw materials [4].

Renewable raw materials in turn are organic raw materials originating from agricultural and forestry production and are used by man for applications outside the food and feed area.

For products that only partly consist of renewable raw materials, it may be necessary (e. g. when issuing certificates) to know the exact biobased ratio. This can be accurately measured using the radiocarbon method. The American standard ASTM D6866 gives guidance on how the carbon content should be determined [90].

The method makes use of the fact that in our atmosphere tiny traces of radioactive carbon isotope ^{14}C (radiocarbon) are constantly formed. ^{14}C is oxidized to $^{14}CO_2$ and ends up in microorganisms and plants through photosynthesis. From there it finds its way into the various biomasses. ^{14}C decays with a half life of about 5,000 years. Therefore, it can be found in fresh biomass, but not in fossil carbon sources, such as petroleum.

between 20 and 40 % Biobased

between 40 and 60 % Biobased

between 60 and 80 % Biobased

more than 80 % Biobased

Fig. 2.1: OK-biobased Logo with indication of the carbon share

When specifying the biobased content, experts discuss two different approaches. On the one hand only the carbon content of the product considered and the biobased content is expressed as a percentage of biobased carbon in the total carbon. The other approach considers the entire biobased mass fraction, including biobased oxygen, hydrogen and biobased nitrogen, in relation to non-biobased content.

Both perspectives have advantages and disadvantages [19] – depending on the perspective of the observer. Therefore, both are considered to be important and necessary.

The certification programmes in question consider the biobased carbon content. Vinçotte in Belgium were the first to offer certification and the use of their “OK-biobased” logo. One to four stars are awarded and displayed on the logo depending on the material’s “biobased” carbon content (Fig. 2.1).

The German certification body DIN CERTCO now also offers such certification where the biobased content is given in percentage groups (Fig. 2.2).

In the USA there is a programme running since a few years and known as “BioPreferred®”. This programme obliges public bodies to purchase products that have the maximum possible content of material from renewable resources. A certification system has evolved from the programme which is based on percentage values determined in accordance with ASTM D6866 and which awards the “USDA CERTIFIED BIOBASED PRODUCT” logo stating the percentage of renewable resources.

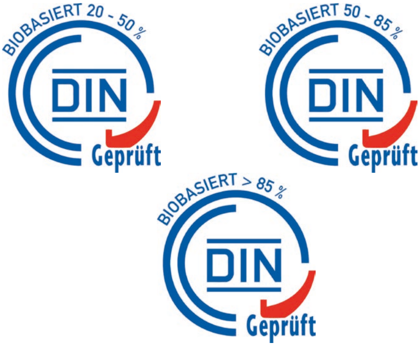

Fig. 2.2: DIN Certified Biobased (DIN CERTCO)

Fig. 2.3: USDA certified biobased product

2.2 Standards and certification regarding “compostability”

A substance or a material is biodegradable if it is broken down by micro-organisms such as bacteria, protozoa[2], fungi, or enzymes. The micro-organisms use the substances as nutrients or a source of energy. The remainder of the broken down substance consists

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[2] *Protozoa are single cell organisms with a cell nucleus, such as paramecia, amoeba etc.*

of carbon dioxide (CO_2), water and mineral salts of the other elements present (mineralisation), [6].

A difference is made between aerobic degradation in the presence of oxygen, as is the case in a compost heap, and anaerobic degradation. In anaerobic degradation there is no oxygen present, as for instance in biogas plants.

Composting is a special case of biodegradation where man takes advantage of the recycling of waste. The requirements of an industrial composting are unlike, for example composting in the garden or a natural degradation in the environment. In industrial composting there are not only technical requirements but also legal issues to consider.

Fig.2.4: Logos for industrial composting (DIN CERTCO)

These standards refer to the compostability of packaging – EN 13432 [83] or more generally to plastics (EN 14995 [84], ASTM D6400 [85]). In Europe DIN CERTCO (Germany) and Vincotte (Belgium) belong to independent certification associations. In the USA this is governed by the BPI (Biodegradable Products Institute). They establish a certificate of conformity for the materials (i.e. an assessment of the material's conformity with the standard) and confirm the manufacturer's right to display a suitable badge or label for compostable products. A material that has the right to carry such a compostability label will completely degrade in the composting installation within 6 to 12 months. Figures 2.4 to 2.6 show the most well-known logos [87, 88, 89].

Fig.2.5: The OK-Compost-Logo (Vinçotte)

Fig. 2.6: The Compostable-Logo from the USA (BPI, US Composting Council)

Compostability in an industrial plant does not automatically mean that the product biodegrades in a home compost heap. For disposal together with garden compost only plastic products are suitable that are proven to almost completely biodegrade at less than 30 degrees Celsius within one

Fig. 2.7: Logo for garden composting (DIN CERTCO)

year. Here also, DIN CERTCO and Vinçotte offer certification (according to the Australian Standard AS 5810) and offer a corresponding logo.

The compostability standard laid down in EN 13432 is backed up by other legal framework conditions. These include the EU Packaging Directive 94/62/EG and the draft for an EU Biowaste Directive.

2.3 Relevant German laws and regulations

In Germany there are a number of laws and regulations that are also relevant for products from biobased plastics. In addition to the “Altfahrzeug-Verordnung” (ELV – Ordinance on the transfer, return and environmentally sound disposal of old vehicles) and the “Elektro- und Elektronikgeräte-Gesetz” (Act Governing the Sale, Return and Environmentally Sound Disposal of Electrical and Electronic Equipment), currently the mainly packaging ordinance is (“Verpackungsverordnung” – on the avoidance and recovery of packaging waste). Last amended in April 2008, the ordinance regulates how to deal with used packaging. For certified compostable plastic packaging a temporary derogation was introduced: These packages were exempted from the obligations according to §6 of the regulation and the DSD (Dual System Germany) fees. The manufacturers and distributors had to make sure, however, that a high percentage as possible of the packaging was supplied for recycling [1]. Since 01.01.2013 this special regulation is no longer valid, i.e. if it is to be disposed of by the Duales System appropriate fees must also be paid for compostable packaging .

With the amendment of the Biowaste Ordinance (BioAbf – regulation on the recycling of biowaste in agricultural, forestry and horticultural soils) in mid-2012, however, composting was severely limited as a disposal option for biobased products, many of which are in fact biodegradable.

At the time of going to press (Spring 2014) a series of additional or supplementary provisions is in preparation. As part of the “Kreislaufwirtschaftsgesetz” (Waste Management Act) it is assumed that recycling of waste or residual materials will gain considerably in importance. In this regard it is to be expected that the ordinance is being replaced by a more complex law. This will mean that not only packaging but also other plastic products such as household wares, stationery, CDs, etc. are collected as recyclables. This will significantly increase the volume of this “value material stream” significantly, and possibly even double it.

3 RENEWABLE RESOURCES

3.1 Introduction

Biobased plastics can be produced from a wide range of plant-based raw materials. On the one hand natural polymers, i. e. macromolecules that occur naturally in plants etc., are used, and on the other hand smaller molecules, such as sugar, disaccharides and fatty acids (plant oils), are used as the basic raw materials in the production of bioplastics. All of these renewable resources can be obtained, modified and processed into biobased plastics.

3.2 Natural polymers

By natural polymers (biopolymers) we mean polymers synthesised by any living organism. These may be, for example, polysaccharides, proteins or lignin that act as energy reserves or have a structural function for the cells or the whole organism [2].

Many of the naturally occurring biopolymers briefly summarised below can be used for the manufacturer of biobased plastics, (but certainly not all of them).

3.2.1 Polysaccharides (carbohydrates)

Among the most important biopolymers are the polysaccharides (multiple or many sugars). α-polysaccharides for instance fill an energy storage role in starch. β-Polysaccharides act as structural substances, for example in cellulose, the main component in the cell walls of plants.

3.2.2 Proteins

Proteins are biopolymers built up of amino acids. They exist in all living creatures and serve to move substances around the body, or act as a substance that provides a structural framework, as signal sources, or as catalysts.

Proteins include casein from the milk of mammals. Gluten is a mixture of different proteins that is found in the seeds of grain crops. Collagen is a structural protein of the connective tissue (e. g. skin, teeth, sinews, ligaments or bones) in many higher life forms. Collagen is the main basic material for the manufacture of gelatine.

3.2.3 Lignin

Lignin is a 3-dimensional cross-linked aromatic macromolecule. The solid, colourless substance is contained in the cell walls of plants and causes the lignification (turning into wood) of grasses, shrubs, bushes and trees etc. Alongside cellulose, lignin is the most common organic substance on earth. As a by-product of the pulp and paper industry around 50 million tonnes of lignin are produced each year [13]. The majority of it is burned for energy recovery.

3.2.4 Natural rubber

Natural rubber is an elastic biopolymer from plants – mainly latex from specific trees.

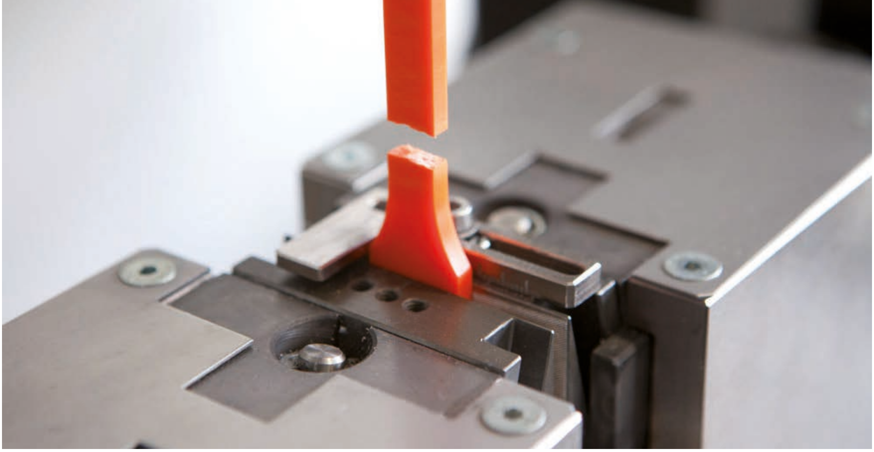

Fig. 3.1: Material test with a bioplastic test rod

Alongside the rubber tree, latex is also obtained from other trees such as bullet wood (Manilkara bidentata) or gutta percha. Natural rubber is the most important raw material used in the production of vulcanised rubber.

3.2.5 Other

An interesting group of biopolymers are the polyhydroxyalkanoates – polyesters (PHAs) that are formed in certain micro-organisms as an energy reserve (cf. chapter 4.2.5).

3.3 Other biogenic materials

3.3.1 Plant oils

Vegetable oils typically consist of glycerine and different fatty acids. Alongside their use in human and animal food, as lubricants or energy sources, a number of vegetable oils can also be used as raw material for the manufacture of bioplastics.

The vegetable oils used to produce bioplastics, will be covered in chapter 4.

3.3.2 Monomers

In addition to the substances listed above there is also a range of monomers and dimers that can be used for the production of biobased plastics.

Alongside polysaccharides these are monosaccharide sugars such as glucose and fructose (both $C_6H_{12}O_6$) or disaccharides such as sucrose ($C_{12}H_{22}O_{11}$).

Certain bivalent alcohols which can also be used (partly) in the production of biobased plastics are able themselves to be produced from renewable raw materials for a few years now biobased 1,3-propanediol has been sold as bio-PDO, and 1,4-butanediol will soon be marketed as bio-BDO produced from renewable resources such as maize starch [14, 15].

An important area, which has been a significant object of research in recent times, is succinic acid ($C_4H_6O_4$), which can also be made by fermentation, using starch and various oligosaccharides. (Details in chapter 4.3.1)

An important monomer used for PLA, one of the most significant bioplastics on the market today, is lactic acid (Details in chapter 3.4.1).

The world's most commonly produced plastic is polyethylene (PE) Its ethylene monomer is today mainly obtained by way of steam-cracking carbonates such as naphtha, or also ethane, propane and liquefied gas. By dehydrating bio-ethanol based on sugar cane a biobased ethylene for the production of bio-polyethylene can be obtained (see chapter 4.3.5).

3.3.3 Other

A current trend is biomass gasification to synthesis gas. By a subsequent chemical or biotechnological conversion of the synthesis gas biopolymer monomers can be produced. However, both ways are still in the research stage. A chemical route could, via conversion of synthesis gas to ethanol and finally to ethylene, lead to polyethylene (see previous paragraph and chapter 4.3.5). Currently, however, it is rather the biotechnological way that is intensely pursuing the possible uses of synthesis gas as a carbon source for microorganisms, which can be formed by fermentation of polymer monomers [2, 16, 17].

4 BIOBASED PLASTICS

4.1 Introduction

Plastics have not always been produced from fossil materials such as petroleum. Quite the contrary – the first plastics were already biobased.

Celluloid is regarded as the world's first "plastic", discovered in 1855 by the Englishman Alexander Parkes and initially sold under the name Parkesine [18]. The publication at the time of a prize competition gave the legendary boost to the development of plastics that could be used in place of costly ivory for the production of billiard balls. Celluloid, made from cellulose nitrate and camphor, set the pace and was quickly adopted for other applications such as picture graphic film, decorative manufactured goods, spectacle frames, combs, table-tennis balls and other products [1].

Casein is the protein component in the milk of higher mammals that is not found in whey. From the end of the 19th century until the 1930s casein was one of the raw materials for the plastic called galalith, which was used among other things for making buttons, personal decorative items, and also as an insulation material in electrical installations. [2].

During the second decade of the 20th century Henry Ford in the USA experimented with wheat and soya. One of the first series applications was a starter box for the 1915 Model T Ford. Following this, Ford attempted several applications for products made


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Fig. 4.1: Hair pin 1920/1950 made from celluloid

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Fig. 4.2: Buttons 1920/1940 made from casein

from soy oil, such as paints and lacquers, a substitute for rubber, and for upholstery fabrics.

These early “biobased plastics” were soon forgotten in the age of the petroleum boom. Only from 1980, and increasing at the turn of the century, did bioplastics become once again a focus of research and development. The principal interest at that time was biodegradability and compostability. Meantime it became clear that compostability is only a sensible option where it offers some additional benefit, and where it is not just another method of disposal.

The renaissance of bioplastics began with plastics based on starch (starch blends and also starch raw materials). Starch, after hydraulic cracking into glucose (previously also dextrose), is also used as a raw material in fermentation processes. In this way new bioplastics such as PLA and PHA are produced (see chapter 4.3.1 and 4.2.5). Sugar is also the raw material for the latest generation of bioplastics including the biobased polyolefins PE and PVC, (and soon to come is PP) as well as the partially biobased polyester PET, (see chapter 4.3.5 and 4.3.1), which however are not all biodegradable.

Further examples of partially biobased plastics are certain bio-polyamides (see chapter 4.3.2). A whole range of producers offer polyamide 6.10 where the dicarboxylic acid (via sebacic acid) required for its production is produced from castor oil or soy oil, the diamine, however, is of petrochemical origin.

Blends of biobased and petrochemical plastics are, for example, mixtures of PLA (100 % bio) and PBAT (polybutylene adipate terephthalate, a petroleum based but compostable copolyester).

Even where it is the declared aim of many companies and researchers to produce plastics totally based on renewable resources, any approaches in the direction of partially biobased plastics are a step in the right direction (see also chapter 4.3).

4.2 Modified natural polymers

4.2.1 Polysaccharide-based plastics

4.2.1.1 Thermoplastic starch

To produce thermoplastic starch (TPS) starch grains are destructured by an extrusion process [2, 4]. Starch consists of two components, the branched polymerised amylopectin, which is the principal component and which encases the unbranched amylose [1]. In order to destructure the starch it must be subjected to sufficient mechanical energy and heat in the presence of so-called plasticisers. The best plasticiser for starch is water at a concentration of 45 %. Other plasticisers are glycerine, sorbitol, etc.

4.2.1.2 Cellulose-based plastics

Cellulose is the principal component of cell walls in all higher forms of plant life, at varying percentages. It is therefore the most common organic compound and also the most common polysaccharide (multi-sugar).

Cellulose is unbranched and consists of several hundred (up to ten thousand) glucose molecules (in a glucosidic bond) or cellobiose units. The cellulose molecules bind together with higher structures that often have a static function as tear-resistant fibres in plants [2, 5, 21].

In cotton wool the cellulose content reaches about 95 %, in hardwood from 40 to 75 %, and in soft woods it is between 30 to 50 %. Cellulose is, in terms of quantity, the most significant renewable raw material resource – globally about 1.3 billion tonnes are obtained each year for technical applications. Furthermore cellulose can be used industrially in the form of cellulose regenerates and cellulose derivatives (Fig. 4.4).


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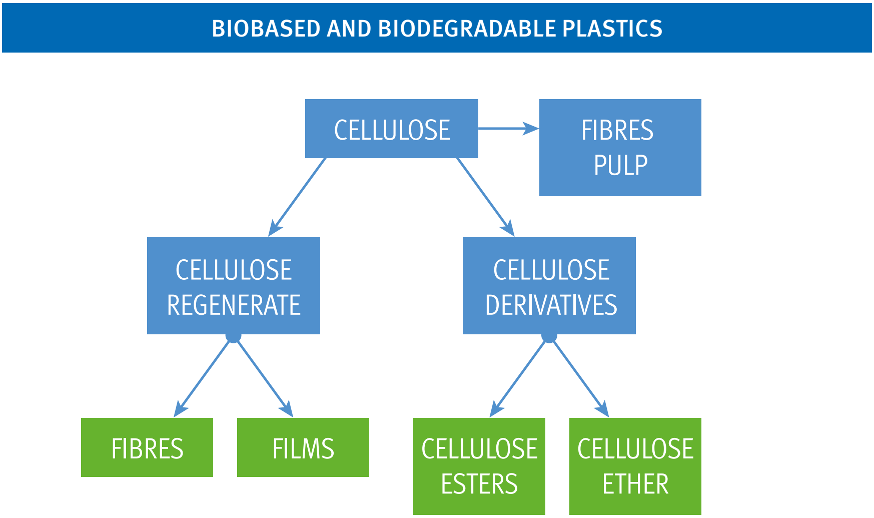
Fig. 4.3: Cellophane – a crystal clear cellulose product

Cellulose regenerate

If cellulose is chemically dissolved and newly restructured in the form of fibres or film it is known as a cellulose regenerate. The most well-known members of this group



Source: Engineering biopolymers (Endres, Siebert-Raths) [5], modified by FNR

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Fig. 4.4: Cellulose-based polymer materials (Picture: according to [5])

of materials are viscose, viscose silk, rayon or artificial silk, and a few more in the area of fibres and textiles. Cellulosic chemical fibres (mainly Rayon and Lyocell) build the lion's share (30 % in Germany and globally 9 %, 2011) of chemical fibres.

In the field of film are cellulose hydrate and also cellulose film, known by the original brand name of Cellophane [5].

Cellulose derivatives

With regard to industrial use cellulose derivatives (including biobased plastics) play an important role. They are classified into two main groups – cellulose ethers and cellulose esters [5].

Cellulose esters here have a considerably higher importance for the plastics industry. The first thermoplastic material was celluloid, produced from 75 % cellulose nitrate (obtained from nitric acid and cellulose) and 25 % camphor.

Basically cellulose esters occur by the esterification of cellulose with organic acids. The most important cellulose esters from a technical point of view are cellulose acetate (CA with acetic acid), cellulose propionate (CP with propionic acid) and cellulose butyrate (CB with botanic acid).

4.2.2 Protein-based plastics

Another group of bioplastics that can be produced from animal or plant proteins (see also chapter 3.2.2) is casein. Casein is one of the bioplastics made from animal protein, and was already a significant player at the beginning of the age of plastics (see chapter 4.1). To make a casein plastic the basic casein, obtained from skimmed milk and plasticised, is processed to form a cross-linked plastic by the action of formaldehyde and the removal of water. In this context the term casein-formaldehyde is commonly used. Because of their comparably low technical characteristics casein plastics are used today only in small niche markets [5].

A different type of protein-based plastic is gelatine. It is used, in addition to the well-


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Fig. 4.5: Swiss army penknife, grip made from cellulose butyrate


© Michael Thielen

Fig. 4.6: Transparent dice made from cellulose acetate

known applications, as a nutritional supplement and also as a binding agent or capsule for pharmaceutical tablets [5]. In the majority of cases gelatine is produced from collagen (see chapter 3.2.2).

4.2.3 Lignin-based plastics

It is possible to change the properties of the lignin polymers by modification. Thus both thermoplastic and thermoset materials can be produced. In the field of thermoplastics lignin can be used as a blending partner for plastics (PE, PVC, PA) or composites reinforced with natural fibers.

The most well-known bioplastic based on lignin (chapter 3.2.3) is sold under the name of “liquid wood” [13, 25] and is easy to process in injection moulding machines (chapter 5.3.3). This bioplastic is also sold containing natural fibres (flax, hemp) to increase its strength [92]. In the field of thermoset resins formulations using lignin are being developed for phenolic, epoxy and polyurethane resins [2, 26, 27].


© Tecnaro

Fig. 4.7: Loudspeaker housing made from a lignin-based bioplastic

4.2.4 Natural rubber and thermoplastic elastomers

A very popular “relation” of plastics is rubber. Other associated terms are natural latex, caoutchouc and elastomers. Even though most of the worlds demand for rubber is today produced from petrochemicals (synthetic rubbers, mainly from styrene and butadiene), the trend is moving back to the use of materials from renewable resources. Even today about 40 % of the demand on rubber is covered by caoutchouc [28].

By natural rubber (caoutchouc[3]) we mean polymers that are based on plant products, and principally latex. In nature this latex sap runs from damaged areas of the tree‘s bark and so acts as a protective substance for the tree by closing off damaged areas and preventing bacterial contamination. In sustainable cultivated plantations the sap is obtained by making deliberate slits in the bark. The crude latex with sulphur rubber is produced by vulcanising [2].

In addition to rubber, which has been known as a biological material for many decades, there are the so-called thermoplastic elastomers (TPE). These plastics, which are also very elastic, are not cross-linked and so can be remelted (thermoplastics). There is a whole range of biobased or partially biobased types available.

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[3] *Indian: “the tree that weeps” from cao = tree, and ochu = tears*

An important group here are the thermoplastic polyurethanes (TPU, or occasionally TPE-U). Their range of applications goes from the soles of shoes, and other shoe parts, to film and the soft component of hard-soft bonded parts such as tooth-brush handles. For details of biobased polyurethanes (see chapter 4.3.3).

Fig. 4.8: Walking shoes with partially biobased polyurethane (TPU)

Thermoplastic ether-ester elastomer (TPC-ET) with hard sections produced from petrochemical polybutylene terephthalate (PBT) and soft sections that contain a polyether produced using biobased 1,3 propanediol (cf. chapter 3.3.2), is suitable for technical applications such as airbag covers in passenger cars. A version exhibited in 2010 consists of 35 % by weight of renewable raw materials [23].

A 100 % biobased TPE is a block copolymer (polyether block amide) that in 2010 was presented for, among other things, ski boots. The TPE material consists of 100 % biobased polyamide 11 (cf. chapter 4.3.2) and biobased polyether [24].

4.2.5 Polyhydroxy alkanoates

Starch and other substances that supply carbonates can also be converted into bioplastics by fermentation and the action of micro-organisms. Examples are the polyhydroxy alkanoates (PHA) or the polyhydroxy fatty acids, a family of polyesters. Special bacteria are able to produce these molecules as intracellular reserves [5]. Here the micro-organisms store a particularly high level of energy reserves (up to 80 % of their own body weight) for when their sources of nutrition become scarce. By “farming” this type of bacteria, and feeding them on sugar or starch (mostly from maize), or at times on plant oils or other nutrients rich in carbonates, it is possible to obtain PHS‘s on an industrial scale. The family of polyhydroxyalkanoates includes polyhydroxy butyric acid (PHB) and polyhydroxybutyrate, polyhydroxyvalerate (PHV), poly-3-hydroxybutyrate-co-valerate (PHBV) and others [5].

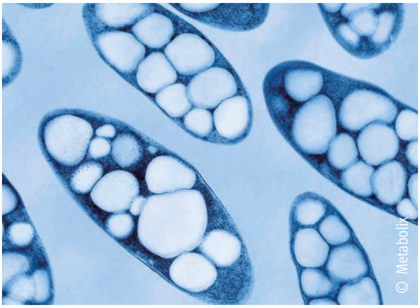


Fig 4.9: Electron microscope image of bacteria with stored PHA particles

PHAs are mainly film and injection moulding grades and are now increasingly available as extrusion and blow moulding grades. A Japanese supplier in 2010 showed a particle foam (similar to Styropor®) and made from PHBH [30].

4.3 Synthesised biobased polymers from synthesised biobased monomers

4.3.1 Biobased polyesters

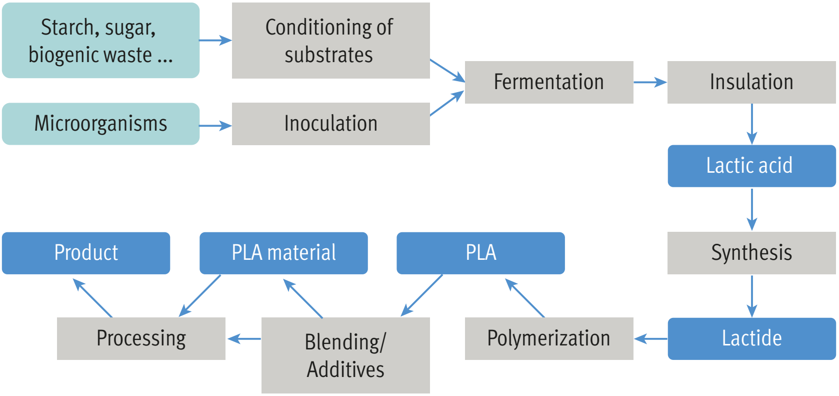
Polylactic acid (PLA)

In this group of materials PLA (polylactide, polylactic acid) is today's most important bioplastic on the market [5]. PLA is based on lactic acid, a natural acid, and is mainly produced by fermentation of sugar or starch with the help of micro-organisms.

The world's first large PLA production unit with a capacity of 140,000 tonnes per annum began production in the USA in 2002. Industrial PLA production facilities can now be found in the Netherlands, Japan and China. Plants are being planned. In Guben, on the German-Polish border, a pilot plant with a capacity of 500 tonnes per annum was installed in 2011.

PLA, as it exits the reactor, is not an easily processed plastic. Hence, as is usual with most plastics, raw PLA polymer is adapted to specific applications by compounding with suitable additives or by copolymerisation,

PROCESS STEPS FOR GENERATING POLYLACTIDE MATERIALS AND COMPONENTS



Source: Technical Biopolymere (Endres, Siebert-Raths) [5], modified by FNR

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Fig. 4.10: Manufacture of PLA products

or is blended with other plastics (bioplastics or traditional plastics).

Advantages of polylactide plastic are its high level of rigidity, transparency of the film, cups and pots, as well as its thermo plasticity and good processing performance on existing equipment in the plastics converting industry. Nevertheless PLA has some disadvantages: as its softening point is around 60 °C the material is only to a limited extent suitable for the manufacture of cups for hot drinks [1]. Modified PLA types can be produced by the use of the right additives or by combinations of L- and D-lactides (stereocomplexing), which then have the required rigidity for use at higher temperatures [34]. A second characteristic of PLA together with other bioplastics is its low water vapour barrier. Whilst this characteristic would make it unsuitable, for example, for the production of bottles, its ability to “breathe” is an advantage in the packaging of bread or vegetables.

Transparent PLA is very similar to conventional mass produced plastics, not only in its properties but it can also be processed on existing machinery without modification. PLA and PLA-blends are available in granulate form, and in various grades, for use by plastics converters in the manufacture of film, moulded parts, drinks containers, cups, bottles and other everyday items [1]. In addition to short life packaging film or deep drawn products (e.g. beverage or yoghurt pots, fruit, vegetable and meat trays) the material also has great potential for use in the manufacture of durable items. Examples here are casings for mobile phones (possibly strengthened with natural fibres), desktop accessories, lipstick tubes, and lots more. Even in the automotive industry we are seeing the first series application of plastics based on PLA. Some Japanese car manufacturers have developed their own blends which they use to produce dashboards [35], door tread plates, etc.


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Fig. 4.11: Transparent PLA film for packaging vegetables

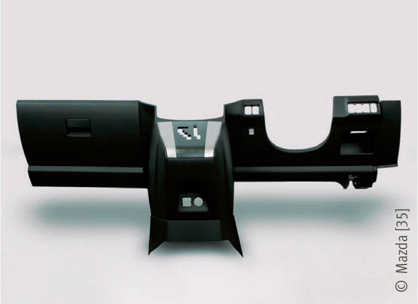

© Mazda [35]

Fig. 4.12: Lower dashboard panel made from a PLA blend

Fibres spun from PLA are even used for textile applications. On the market we can already find all kinds of textiles from articles of clothing through children's shoes to car seat covers.


© Inomata

Fig. 4.13: Baby's shoes made from a PLA/PET blended fabric and soles made from a soft PLA compound [36]

Polyethylene terephthalate (PET)

PET, since the second half of the 20th century, has been a mass-produced plastic. A real boom began in 1975 with its use by the big North American soft drinks companies to make "easy-to-grip" and "unbreakable" beverage bottles.

PET is a thermoplastic polyester that is produced by polycondensation of monoethylene glycol (or ethylene glycol, a bivalent alcohol, a diol) and terephthalic acid or dimethyl terephthalate.

Since 2010 the first beverage bottles have been supplied made from partially biobased PET [37]. The monoethylene glycol (about 30 % by weight) is obtained from sugar cane molasses. The terephthalic acid is in this application still produced from petrochemical resources. At about the same time a Japanese automobile group also announced that it was producing partially biobased PET [38].

© Coca-Cola

Fig. 4.14: Partially biobased PET

Terephthalic acid as the second component of PET (and other plastics) using renewable resources had been regarded as too elaborate and costly. Now, however, there are apparently clear routes to the economic production of biobased terephthalic acid [39].

Regardless of whether PET is partially or totally produced from renewable resources, chemically the material is identical to conventional PET and can thus be recycled together with conventional PET.

Polyethylene Furanoate (PEF)

A 100 % biobased alternative to PET could be Polyethylene Furanoate (PEF). 2,5 Furan Dicarboxylic acid (FDCA) can be polymerized with ethylene glycol to produce Polyethylene Furanoate. A technology was developed in the Netherlands to produce FDCA from biomass [95].

Polytrimethylterephthalate (PTT)

Polytrimethylterephthalate (PTT), which is also partially biobased, is certainly not as well known, or has the same market importance as PET. PTT has however, as a partially biobased plastic, been on the market much longer than (partially) biobased PET.

Similarly to PET, PTT is also produced using terephthalic acid (until now made from petrochemical resources, – but in future also to be biobased?), or dimethyl terephthalate and a diol. In this case it is a biobased 1,3 propanediol, also known as bio-PDO (cf. chapter 3.2.2).

PTT was first launched onto the market mainly in the form of spun fibres and textiles. Because they are particularly soft and yet can bear heavy wear the principal area of application was for domestic carpets and carpets for the automobile industry.

But PTT is also suitable for injection moulding applications and quite comparable to polybutylene terephthalate (PBT). With a high quality surface finish, and low shrink and deformation performance, the material is ideal for, amongst other things, electrical and electronic components such as plugs and housings, or also for air breather outlets on car instrument panels [41, 42].

Biobased alkyde resins

Alkyde resins are used mainly as functional polymers in the field of paints and lacquers, but also as a filler compound used by decorators etc. They are polyesters that are produced by polycondensation of polyvalent alcohols (e. g. glycerine or glycol) with dicarboxylic acids (e. g. phthalic acid, adipinic acid, succinic acid, maleic acid or their anhydrides) [2]. Because amongst the polyvalent alcohols, as well as the dicarboxylic acids, there are some that can be produced from renewable resources, biobased or partly biobased alkyde resins can be produced and some are already available on the market.

Alkyde resins are principally used as raw materials in paints that are compatible with other coating materials.

In addition they are used in the production of printing inks, adhesives, insulating material, jointing compounds, as a textile enhancer and as a floor covering. This latter application, mainly known as linoleum, has been produced from linseed oil for decades by a complex process.

If vegetable oils (again, primarily linseed oil) are provided with crosslinking additives (siccatives), varnishes (colourless protective coatings with quick-drying oils), which are used as paints and binders for printing inks, can be produced.

Furthermore by dimerization of vegetable oil-based fatty acids dimer fatty acids are produced, which then can be converted with polyols into the alkyde resin, to be used as binders in paints and varnishes.

Biobased polysuccinates

Other bio-polyesters are, for example, polybutylene succinate (PBS), a biodegradable bioplastic that is produced from butanediol (e. g. bio-BDO) and succinic acid, and which can also be produced in a biobased form (see chapter 2.3.2).

Fig. 4.15: Packaging made from polybutylene succinate (PBS)

With polybutylene succinate adipate (PBSA), in addition to the succinic acid, adipinic acid is polymerised within the compound. This plastic too can be biobased to a greater or less degree depending on the origin of the monomer.

Other biobased polyesters

Other (fully or partially) biobased polyesters are polybutylene terephthalate (PBT) made from terephthalic acid or terephthalic acid methyl ester, and biobased butanediol (bio-BDO). PBT is seen as a “technical brother” of PET, which is preferred for use as packaging.

First positive results have been achieved with regard to producing the very successful biodegradable plastic PBAT (polybutylene adipate terephthalate) from renewable resources [9].

In addition, there are other vegetable oil-based polyesters that can be used for the production of printing inks, adhesives, insulating materials and casting materials, as well as an agent for textile finishing and as a floor covering. The latter, usually referred to as linoleum, has been produced for decades following a complex process, using linseed oil.

Unsaturated polyester resins

Unsaturated polyester resins (UP) are known for example in boat building and the repair of damaged bodywork on a car. They are also usually reinforced with (or filled with), for example, fibreglass in the form of

Fig. 4.16: Speedboat made from partially biobased UP resin

sheet moulding compounds (SMC) or bulk moulding compounds (BMC) and principally used in the construction of new vehicles.

Polyester resins are condensation products from bivalent or polyvalent alcohols (e.g. glycols or glycerine) and dicarboxylic acids [2], and as described above (see also chapters 3.3.2 and 4.3) can be produced from renewable resources. Today there is a whole range of partially biobased UP resins on the market [55, 56].

4.3.2 Biobased polyamides

Polyamides are plastics that are particularly suitable for fibres and technical applications. The most well known examples, which caused a sensation in the first half of the last century, are Nylon® and Perlon®. Polyamides today are used for demanding injection moulding applications, extruded products, hollowware and textiles for the manufacture of clothing, decorative materials and technical fabrics.

Bio-polyamides are totally or partially biobased depending on whether the dicarboxylic acid, the diamine, or both are produced from renewable resources.

An economically important dicarboxylic acid to produce bio-polyamides is sebacic acid, which can be produced for example from castor oil. With this monomer, partially biobased polyamides such as PA 4.10 or PA 6.10 are possible. Here the "10"-component is the biobased part. Both partially biobased PA 4.10 and also PA 6.10 are commercially available.

© Philipp Thielen

Fig. 4.17: Wall fixing plugs made from partially biobased PA 6.10

A further example is PA 10.10, which is also commercially available. Here too the first "10"-component is biobased. The base material 1.10 diaminodecane can also be obtained from the castor oil plant, so that PA 10.10 is also 100 % biobased.

The also completely biobased PA 11 has already been on the market for more than 60 years. It can be made from the castor oil plants, is totally biobased and is suitable, thanks to its special chemical and general


© Arkema

Fig. 4.18: Fuel injector nipple made from 100 % biobased PA 11

resistance, for biofuel pipework and other components.

In addition to those mentioned here there are plenty more biobased polyamides [47].

4.3.3 Biobased polyurethane

Polyurethanes are produced by a reaction between polyols and diisocyanates and can be hard and brittle, elastic, foamed or compact. They may be used in thermoplastic or thermosetting form.

Because polyols can be obtained from plant oils such as castor oil or soya oil, there are already a large number of partially biobased polyurethanes on the market. While castor oil already contains OH groups, polyols made from vegetable oils, such as rapeseed, sunflower or soya oil are produced by epoxidation of unsaturated fatty acids and the subsequent addition of multiple alcohols on the ring opening of epoxides.

© Ford Motor Company

Fig. 4.19: Car seat made from soya foam

So-called thermoplastic polyurethane, TPU (TPE-U), as a member of the elastomer group, has already been mentioned in chapter 4.2.4.

Another important group of polyurethanes comes in the form of foams used in automobile manufacture. As a pioneer in this field one of the big North American automobile groups has, for a number of years, been using polyurethane foam where the polyol is produced based on soya. Under the title “Sleeping on Sunflowers” a German manufacturer for mattresses advertises foam that is produced based on vegetable oil.

4.3.4 Biobased polyacrylates

Acrylic plastics include, as an example, PMMA (polymethyl methacrylate) which is also known as Plexiglas® or acrylic glass. Scientists from the university of Duisburg in Essen have discovered an enzyme that allows them to produce a precursor of methylmethacrylate (MMA) which in turn serves as a monomer for the production of PMMA and is based on a biotechnical process using natural raw materials such as sugar, alcohol or fatty acids [49].

Furthermore there are currently efforts being made to be able to use a biobased version of the platform chemical (platform chemicals are standard chemicals that can be used for a variety of purposes) 3-hydroxypropionic acid for the production of further raw materials to make acrylic plastics [50].

4.3.5 Biobased polyolefins

Among the most important and most commonly used plastics are polyolefins (polyethylene PE and polypropylene PP). They are easily recognized by the fact that their density is less than 1 g/cm^3 – i. e. they float in water. Both PE and PP can be produced from renewable resources [51].

Bio-polyethylene (BIO-PE)

Polyethylene (PE) is the simplest and at the same time most common plastic with a global capacity of 80 million tonnes p. a. (2008 [51]). There are numerous possible applications, going from film (pouches, bags, shrink film) through blow-moulded hollowware such as shampoo bottles and petrol canisters, to barrels, automobile fuel tanks, or injection moulded parts such as tubes and profile sections.

Polyethylene can be produced petrochemically by polymerisation of ethylene gas. Another way in which the monomer ethylene can be produced is by dehydration of ethanol. This method was used at the beginning of large scale PE production in the first half of the 20th century, before the availability of petrochemically produced ethylene gas [2].

Having in mind the production of plastics from renewable resources this process has once again attracted interest. For instance in Brazil bio-ethanol has been produced for many years from sugar cane by a fermentation process. This bio-ethanol can now be used for the production of ethylene and hence bio-polyethylene. In 2010 in Brazil a production plant with an annual capacity of 200,000 tonnes was installed.

Bio-polypropylene (Bio-PP)

Biobased polypropylene can, like bio-PE, be produced from bio-ethanol but the process is much more complex. Polypropylene (PP) is considerably younger than PE and is used in numerous technical applications. Global production in 2008 was in the order of 44 million tonnes [51].

To produce bio-PP there are several ways of obtaining the propylene monomer C_3H_6 from renewable resources [52]. A large Brazilian producer of polyolefins has announced the start-up in 2013 of a bio-PP plant but without saying which method will be used to produce the plastic [54].

4.3.6 Biobased polyvinyl chloride

Ethylene from bio-ethanol can also be also used for the production of partially biobased polyvinyl chloride (PVC). Similar to bio-PE and bio-PE PP efforts can be found primarily in Brazil [53].

4.3.7 Epoxy resins

Another thermoset resin which is used in boat building but also in the aerospace sector, racing cars, for tennis racquets or wind powered installations is epoxy resin. Such expoxy resins are often reinforced with fibreglass, carbon fibres, aramid fibres (Kevlar®, Twaron®) but also with natural fibres.

The possible ways of producing expoxy resins are very different and complex. Thus, for the production of biobased epoxy resins, epoxidized vegetable oils, primarily linseed oil, is used. Applications can be found in structural polymers and epoxy foams as well as functional polymers (e. g. epoxy resins for adhesives and coatings).

Epichlorhydrin is easy to obtain from biobased glycerine, a by-product from biodiesel production [57]. It is already being produced on an industrial scale.

An alternative way to produce 100 % biobased epoxy resin was presented at the beginning of 2011 [58]. The researchers produced a polyamine from grape seed oil which is then used as a hardener for a reaction with epoxidized linseed oil.

4.3.8 Other biobased plastics

As has been clearly shown there are many plastics that can be fully or partially biobased because there is a wealth of monomers, platform chemicals or other substances, the so-called chemical building blocks, which can be obtained from renewable resources. These are, for example, the bio-PDO and bio-BDO diols, monoethylene glycol, sebacic acid, succinic acid, terephthalic acid, itaconic acid and many more. Every step taken to replace fossil-based carbonates with "young" carbonates from renewable resources is a step in the right direction.

4.4 Bioplastics from waste

A much-discussed topic is the potential conflict involving the possible use of food or animal feed resources for the production of bioenergy or biofuel. And even though the requirement would be a lot smaller, this applies also to the industrial use of materials from renewable resources for bioplastics (more in chapter 8.3).

To keep the future space requirements as low as possible, research and industry are intensely trying to find ways to use mainly agricultural residue and waste materials for the future production of bioplastics. The bioplastics so produced are described in chapters 4.2 and 4.3. They therefore are not a "further" class of bioplastics.

The challenge also consists in developing production, processing and marketing structures all along the value-added chain such that a balance is ensured between economics and security of supply based on the premise of an acceptable provision of nutrition and considering the sustainability aspects of the bioplastic. Of particular importance here is also the use of all possibilities to reduce the required land area for the production of bioplastics through increased resource and material efficiency.

An example can be seen in the Netherlands where there is a flourishing potato industry (for chips). When peeling and slicing the potatoes on an industrial scale there is, in addition to the peels a large amount of water used during the processes. This process water, like the peels and other waste, has a high percentage of useable starch. So there are now companies in the Netherlands that produce plastics from the starch so obtained. Similar approaches to the use of process water containing starch and associated waste are also established in several other parts of the world.

In New Zealand and the Netherlands polyhydroxyalkanoate (PHA) is experimentally produced on a laboratory scale. The "food" for the PHA-producing bacteria is here recovered from municipal wastewater. [33].

A few years ago a large brandowner took the used frying oil from his production line for shaped potatoes and used it as a "food source" for PHA producing micro-organisms. Thus old frying fat became a high quality plastic material [22, 59].

Black liquor, a waste product of the pulp industry contains lignin (cf. chapter 3.2.3 and 4.2.3) and so called tall oils. The products from the tall oil find manifold uses in the processing industry. Such tall oil fatty acids (TOFA) can generally be used for the same purposes as other fatty acids They are applied as raw materials for coatings, polyamide resins for the printing and adhesive industries and epoxy resins. Tall oil in the rubber industry can be used as emulsifiers in the production of synthetic rubber. Dimer fatty acids, from tall oil fatty acids, can also be reacted with diamines to produce polyamides.

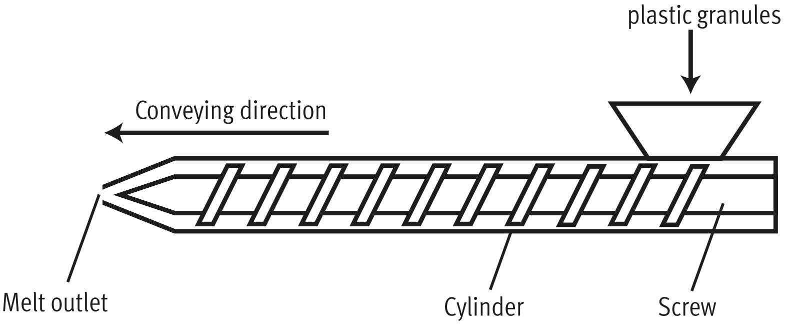
5 METHODS OF PROCESSING PLASTICS

5.1 Introduction

Fig. 5.1: Plastifying screws for plastics

In this book the principal focus will be on thermoplastics, i.e. plastics that become soft again (plasticised) at elevated temperatures and so can be remelted and given new shapes. In most cases the melting, or more correctly plastification, is done in screw feed units (see sketch in Fig. 5.2). In this way, using a machine comparable to a domestic mincer, in addition to external electrical heating additional heat is usually applied through dissipation. The raw plastic in granulate form is loaded into the machine via a cone-shaped funnel and conveyed by the rotating screw of the plastifying unit (Fig 5.2). It is melted, homogenised and then delivered to the mould via a so-called injection nozzle.

SKETCH OF A PLASTIFYING UNIT



Source: Michael Thielen

Fig. 5.2: Sketch of a plastifying unit

5.2 Compounding

A polymer only becomes a “plastic” if it can be converted into a product using conventional processes. Like most “conventional plastics”, most bioplastics emerging from the reactor as “raw plastics” cannot as a rule be converted to end products. They must be correctly adapted to the specific application by compounding. Compounding means preparing for use, and describes the enhancing process that raw plastics go through, being blended with certain additives (e.g. fillers or other additives) to optimise their properties for the planned application [2]. Such additives can be processing aids, UV stabilisers, impact resistance modifiers, plasticisers, colour pigments and many more. The objective is to adapt the mechanical or thermal properties of the plastic to suit the end product and to make the plastic processable.

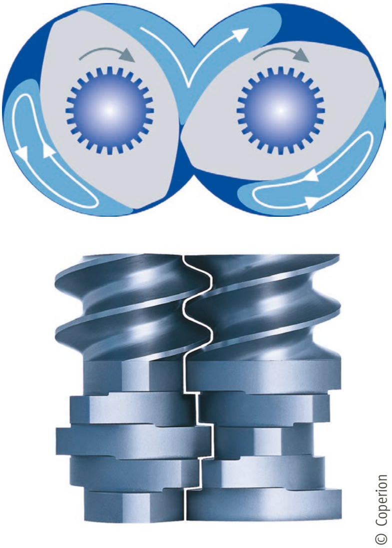

© Coperion

Fig. 5.3: *Principle of a synchronized twin screw extruder*

Compounding is often done in a twin screw extruder specially built for this purpose (more on extruders in chapter 5.3.1), and where the components can be particularly thoroughly mixed together and homogenised. (Fig. 5.3).

5.3 Further processing

The compounds, ready for further processing, are now converted, in a wide range of processes, into components or finished products. To do this in most cases existing plastic processing machines and installations can be used. It is generally only a matter of adjusting the process parameters such as temperature, pressure etc. Hygroscopic materials, i.e. those that tend to absorb moisture from the atmospheric air, must be pre-dried using appropriate equipment.

5.3.1 Extrusion

Extrusion (from the Latin extrudere = push out, drive out) means a continuous plastifying, conveying and pushing out of a thermoplastic material through a specifically shaped die. In this way continuous products such as piping, engineering profiles, film or plate can be produced. Such semi finished products may be, for example, thicker film that can be further processed by thermoforming (chapter 5.3.5).

A way of improving the mechanical properties of extruded film is by stretching immediately after extrusion (in-line stretching). The molecules are oriented such that the tensile strength and rigidity are increased. Stretching can be in one direction (e.g. lateral stretching) or in both lateral and longitudinal directions. An example here is biaxial oriented PLA film (BoPLA) [60].

By adding a foaming agent a foam extrudate can also be produced. Such semi finished products may be, for example, thicker film that can be further processed by thermoforming (chapter 5.3.5).

And finally extruders may also be part of an installation for complex processes such as film blowing (chapter 5.3.2) or extrusion blow moulding (chapter 5.3.4).

5.3.2 Blown film extrusion

In order to blow thin film an extruder is combined with a ring nozzle. The plastified mass of material is, between the extruder and the nozzle, formed into a tube and forced upwards through the nozzle. There the tube-shaped melt is air blown to a much higher diameter than the original, and pulled upwards at a higher speed. It is not only the biaxial pull but also the moment of cooling that determine the thickness of the film.

The tube is laid flat and then rolled up either as a tubular film or slit along the side to make a flat film. It is not unusual to see this type of film blowing installation as a 10 metre high tower.


© Der Grüne Punkt – Duales System Deuts nd GmbH

Fig. 5.4: Blown film extrusion

By installing several extruders for different types of plastic, multi-layer film can be produced. Each plastic takes on a specific role, such as firmness, a barrier function, the ability to be welded etc.

Products made from blown film are, for example, packaging, rubbish sacks and bags for biological waste, hygienic foil for nappies, mailing pouches, disposable gloves and shopping bags [1].

5.3.3 Injection moulding

Almost all sizes and shapes of plastic parts can be made by injection moulding. A screw plastifier softens the plastic as the screw moves slowly back during the melt process to enable a shot of melted plastic to build up in front of the screw tip. Once the quantity needed for one shot is reached the screw moves forward and presses the melt through the pre-heated nozzle and under pressure through the feed channel to the cavity of the cold mould, the so-called "tool". The plastic now cools down in the tool and is ejected as a finished moulded part [1].

The possible applications for injection moulding are almost endless. Some examples are ball-point pens, rulers and other office accessories, disposable cutlery, garden furniture, car bumpers, beverage cases, knobs and handles, small mechanical parts, and lots more.

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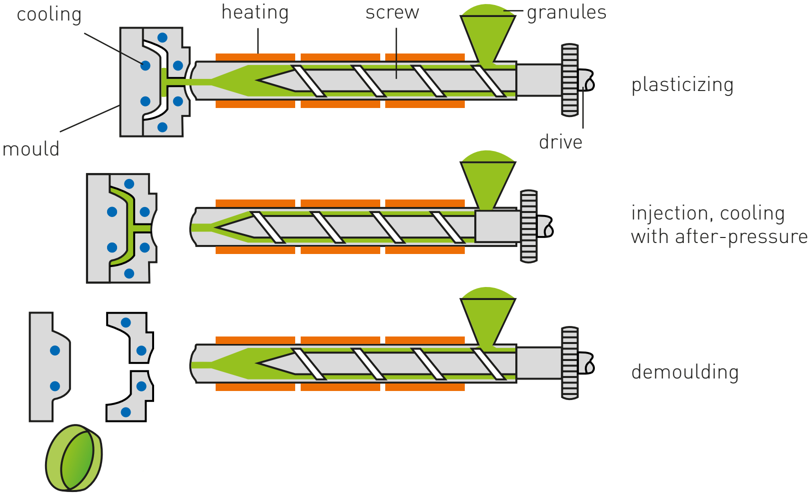
Fig. 5.5: Injection moulding machine

INJECTION MOULDING



Source: lerntagebuch.ch – Injection molding

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Fig. 5.6: The injection moulding process

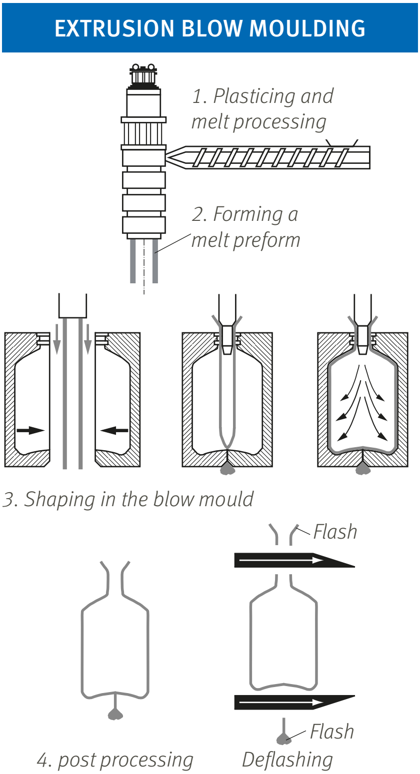
5.3.4 Blow moulding

Plastic hollow articles are generally produced by blow moulding. There are various processes available but the most commonly used are extrusion blow moulding and stretch blow moulding [61].

In extrusion blow moulding the tubular thermoplastic melt is produced in an extruder from where it is ejected vertically downwards through an annular die to create a soft “preform”. A mould consisting of two vertical halves (the blow mould) is clamped around the freely suspended preform and squeezes this at both ends (top and bottom). Now the preform is inflated through a blow pin or needle and pressed against the cold walls of the blow mould tool, where it cools and becomes harder, taking shape of the mould.

Typical areas of application for this process are bottles (shampoo, ketchup, dish soap etc.) canisters, barrels tanks and also games and sports equipment such as kayaks or kids’ plastic cars.

An early extrusion blow moulded packaging made from bioplastics was a shampoo bottle made from a polyhydroxyalkanoate (PHA) in the 1990s. The latest examples are a small bottle made from bio-PE for a probiotic drink from a major supplier of dairy products [62].



Source: Blow molding of hollow plastic articles (Thielen, Hartwig, Gust), 2006

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Fig. 5.7: Extrusion blow moulding (graph from [61])

A different process to the versatile extrusion blow moulding technique is stretch blow moulding which is used almost exclusively for the manufacture of (beverage) bottles. Here a small preform that resembles a test tube with a screw thread at the neck is first injection moulded.

This preform is then, in a separate machine, heated in a radiation oven, following which it is sealed in a mould and stretched laterally by a stretching rod. Its diameter is also stretched, by high pressure air. This biaxial stretching of the molecules gives the plastic a high degree of rigidity and firmness such that thin-walled containers can be produced.

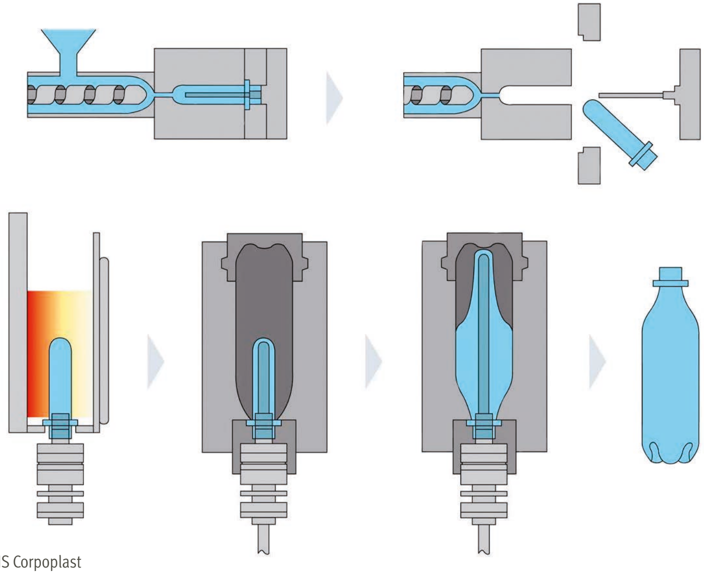
A bioplastic that is ideally suited for this process is PLA.

Fig. 5.8: Preforms and bottles (from left to right: PLA, PP, PET)

5.3.5 Thermoforming

By thermoforming (previously known as hot forming, deep drawing or vacuum deep drawing) we refer to the production of three dimensional moulded parts from semi-finished flat plastic material (film, plate etc.) [2, 69]. Heat and high pressure air are used, and sometimes a vacuum, plus where required a mould to help stamp the three dimensional shape.

STRETCH BLOW MOULDING



Source: KHS Corpoplast

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Fig. 5.9: Stretch blow moulding

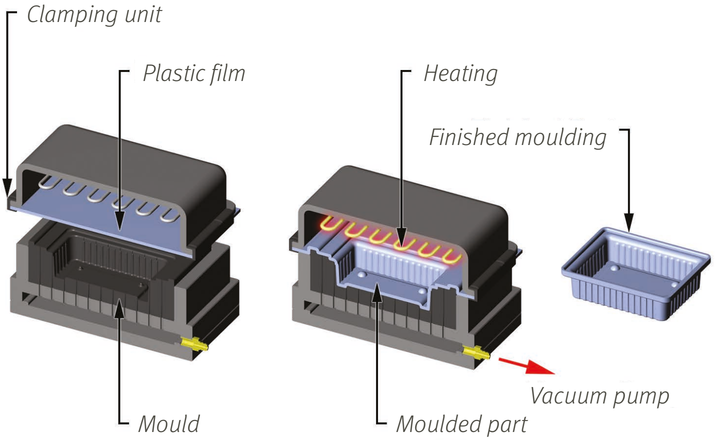
The film is drawn from a large roll, or fed in-line directly from an extruder and on to the automatic moulding unit where it is taken through in an indexed motion. At a heating station the film is heated up by radiation on one or both sides. In the tool or an initial blast of air is used to roughly shape the desired contour. Then high pressure air is applied on one side and a vacuum is drawn on the opposite side in order to bring the film swiftly and firmly against the cold surface of the mould. The cooled film, now rigid again, is punched out of the remaining flat film.

Typical applications are chocolate box inserts, blister packaging, yoghurt or margarine tubs, drinking cups, meat trays, clamshell packs, and other similar packaging applications. Larger parts such as sand boxes and kids' paddling pools, and through to technical parts for cars, can be made using the thermoforming process.


© DuPont (links), Ilip (rechts)

Fig. 5.10: Thermoformed packaging made from PLA

THERMOFORMING



Source: CUSTOMPARTNET

© FNR 2013

Fig. 5.11: Thermoforming

5.3.6 Foams

With the objective of making moulded parts that are particularly light, that have good heat and noise insulation, or good mechanical damping, or simply to save on material, plastics can be foamed.

During foaming the porous structure is generated by a physical, chemical or mechanical process. In physical foaming low boiling point liquids (e.g. volatile organic compounds) are added to the plastic which vaporize during the polymerization process and so form the typical gas bubbles. Alternatively a chemical foaming agent is added to the plastic and will break down at higher temperatures, releasing gases [64]. And in mechanical foaming gas is simply blown into the plastic melt as it is being agitated. (cf. whipped cream).

Fig. 5.12: PLA particle foam

Now we find different plastic products depending on the way that they are processed. Using an extruder, panels or profile sections with a consistent cell structure, or possibly with a foamed core and compact outer faces (integral foam), are produced [1]. Extruded foam panels or film can also be further processed by thermoforming. An example is seen in foamed PLA meat trays.

With polyurethane the foam structure is created by elimination of water (water vapour, steam) through the reaction of polyol with isocyanate (see also chapter 4.3.3).

Another interesting area is particle foams. Known as EPS (expanded polystyrene, and also under the trade name Styropor® (BASF)), particle foams made from PLA (E-PLA) and polyhydroxyalkanoate (PHA) have been successful in penetrating the market [65]. Here tiny spheres are loaded with a foaming agent (e.g. pentane or sometimes CO_2). A mould is filled to a certain volume with these spheres and then heated. The spheres grow larger and melt together as a result of the high pressure.

5.3.7 Casting

There are also certain bioplastics that cannot be processed, as discussed above in a thermoplastic process. Film made from cellulose acetate cannot be extruded or blown, but has to be cast.

5.3.8 Thermoset processing

Unlike thermoplastics, thermoset resins are cross-linked plastics that cannot be shaped under the influence of heat, or be re-melted. Thermoset resin systems are usually made of several components, which initially show quite a low viscosity and cure by the cross linking reaction. Thermosetting (or thermoset) moulding compounds are often made of the resin, fillers and/or reinforcing fibres. These compounds can be processed further depending on the resin filler, and according to various methods. These include the pressing of SMC (sheet moulding compound) – and BMC (Bulk Moulding Compound), hand lay-up, spray-up, filament winding, prepreg, pultrusion, resin transfer moulding (RTM = Resin Transfer Moulding) and many more.

5.3.9 Other plastic processing methods

In addition to the processes described briefly here there is a whole range of other plastic processes but which so far have been rarely used or used very specifically for bioplastics. These include rotational moulding for the production of very large and thick walled hollow parts such as large underground tanks. In calendering a plastic compound is fed into a large rolling mill and pressed into a film format. Other processes include, for example, die casting, injection-compression moulding etc.

5.3.10 Joining plastic together

Semi-finished products or component parts made from thermoplastics can be fixed together in various ways (joining). The use of adhesives must be one of the most well-known joining processes. Under the influence of pressure and heat thermoplastics can also be welded together. Thus tubes and piping can be joined, or containers, packaging, shopping bags, carrier bags, pouches and sacks can be so produced. The principal of plastics processing based on welding is widely used in many variants and the use of a film welding device to pack food in PE film pouches has, for instance, already found its way into many homes [1].

6 APPLICATIONS

Bioplastics are used today in numerous applications. Chapter 8 examines the recent market statistics in some detail.

6.1 Packaging

Alongside simple, foamed packaging chips (loose fill) based on starch (Fig. 6.1), which can also be coloured and used as children's toys, there is now a huge number of packaging items made from bioplastics. Technically almost everything can be done: bioplastics can be blown as film or multilayer film, or extruded as flat film. They can be thermoformed and are able to be printed, glued and converted into packaging components in numerous ways. In short: packaging manufacturers and packers can process bioplastics on almost all of their usual machines with no problems [1].


© iStockphoto

Fig. 6.1: Starch based packaging flakes

Established packaging applications for bioplastics are shopping bags, which also have a secondary use as a bag to collect compostable kitchen and garden waste. Further applications are thermoformed inserts for chocolate boxes, trays for fruit, vegetables, meat and eggs (also foamed), tubs for dairy produce, margarine and sandwich -spread, bottles, nets or pouches for fruit and vegetables. Blister packs, where the film is closely formed to follow the profile of the packaged product, can also be produced. For use in the cosmetics business there are jars and tubes. Packaging materials made from bioplastics with barrier properties, impenetrable to odours and with good performance on the machines are available now, and are also the subject of continuous ongoing development [1].

Coating of paper and cardboard laminates with bioplastics leads to new packaging with good moisture and fat or oil resistance [66].

In the USA a mineral water bottle made from PLA bioplastic had been launched in

2005. This was followed by a range of other bottles for water, milk and juice in North America, Europe, Australia, New Zealand and other regions. Many of these bottles have disappeared from the market for various reasons. Whilst the bottles were initially promoted for their biodegradability it soon became clear that this could not last forever as a selling point.

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Fig. 6.2: Compostable bags are suitable for use for collecting biowaste

Fig. 6.3: Fruit net made from bioplastics

Fig. 6.4: PLA bottles

No wonder that it was the packaging industry that quickly recognized the huge potential for bioplastics. Users, packers, and brand owners are taking advantage of their user-friendly credentials. Disposal of used packaging made from bioplastic can be carried out in various ways (cf. chapter 7).

As a rule catering products are short-lived, like packaging. Once they have been used cups, plates and cutlery are thrown into the rubbish bin with any waste food clinging to them, and during festivals and other large scale events soon build up into considerable amounts. Here biobased plastics offer not only real ecological alternatives. They are also compostable and so can be disposed of together with the food remnants.

© Huhtamaki, Novamont

Fig. 6.5: Catering-Serviceware

6.2 Horticulture and agriculture

In addition to the extensive advantages already mentioned for bioplastics, their biodegradability also plays a special and important role in gardening and agriculture. By using them sensibly the gardener or farmer could save himself a great deal of work. Mulch film (Fig. 6.6) made from biodegradable plastic can be ploughed in after use and does not have to be laboriously picked up and disposed of as contaminated plastic waste at a rather high cost. Plant pots and seed trays break down in the soil and are no longer seen as waste. Plant trays for flowers and vegetable plants, made from the right plastic, can be composted in the domestic compost heap together with kitchen and garden waste [1].

Bioplastic twine, ties and clips (Fig. 6.7) are also cost savers and can be used for tying up tall plants such as tomatoes. Whilst materials currently used have to be picked up by hand after the harvest, or disposed of together with the green waste at higher cost, bioplastics alternatives can be disposed of on the normal compost together with plant waste [1].

Bioplastic, compostable, presown seed strips and encapsulation for active substances are used. Degradable film and nets are used in mushroom growing as well as for wrapping the roots of trees and shrubs ready for sale in garden centers. Film, woven fabric and nets made from bioplastics are used to hold back recently laid roadside banks and prevent soil erosion until they are stabilized by plants.

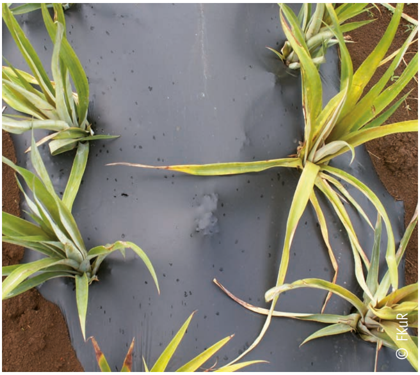
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Fig. 6.6: Mulch film


© Novamont

Fig. 6.7: Plant ties or clips can be disposed of together with green waste

6.3 Medicine and personal care

In the field of medicine special bioplastics have been used for many years. Such bioplastics, that are resorbable, can be applied for several tasks [1]: thermoplastic starch (TPS), for instance, is an alternative to gelatine as a material for pills and capsules. PLA and its copolymers are used as surgical thread, as a carrier for implanted active substances, or to produce resorbable implants such as screws, pins, or plates that are degraded by the metabolism and so make a second surgery for their removal unnecessary.

Special characteristics of certain bioplastics make them a predestined material for hygiene items. These materials allow water vapour to pass through them but remain waterproof and are already widely used as “breathing” biofilm for nappy liners, bed underlays, incontinence products, female hygiene products and disposable gloves [1].

In the huge personal care market more and more bioplastics are finding a use. Lipstick cases and crucibles for powders or creams are just as readily available, as were the first shampoo bottles made from biobased polyethylene. This is only a small selection of the huge number of packaging products already on the market.

6.4 Consumer electronics

In contrast to the medical area, or gardening, applications in the field of consumer electronics, biodegradability is not really an important issue. Here, as with all durable goods, it is the biological origin of the materials used that is the important aspect.

The first electronic equipment of this type and where biobased plastic was used included the Sony Walkman™. PLA was used here as early as 2002.

A very early mobile phone with a housing made from PLA and reinforced with Kenaf – fibres was launched in 2005. Today there are already a huge number of electronic devices on the market, from the computer mouse, through keyboards to headphone parts, all with a housing or components made from biobased plastic.

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Fig. 6.8: Sony Walkman with PLA

Fig. 6.9: Computer keyboard with a cellulose plastic based lower housing and a keypad made from lignin based plastic

Fig. 6.10: Computer mouse made from cellulose acetate

6.5 Automobile manufacture

As mentioned in chapter 4.1 Henry Ford in the USA had already started to experiment at the beginning of the last century with bioplastics based on wheat and soya for applications in automobile manufacture. Today Ford are testing the use of up to 40 % soya based polyol for polyurethane components, firstly for seats, head rests or arm rests. In an initial project with a 2008 Ford Mustang the soya based content of the polyurethane parts was only 5 % by weight [67].


© Hardy Müller

Fig. 6.11: vehicle tailgate made of natural fiber reinforced plastic

Another pioneer in this process is Toyota. In the “Prius”, which is currently one of the most environmentally conscious cars in the world, the spare wheel cover is made from PLA with kenaf reinforcement. At the end of 2011 it was reported that Toyota was to launch a car where the internal surface covering was made from about 80 % bioplastic. The “Sai” hybrid limousine sold in Japan has amongst other things seat covers and carpets made from partly biobased PET [68].

In the engine compartment plastics based on renewable resources are also used. But this too is not new. Polyamide 11 made from castor oil has been used in automotive applications for more than 30 years and is eminently suitable for fuel lines and connectors, especially for the very aggressive bio-ethanol (E10 etc.) and biodiesel fuels.

In November 2012, a fully functional steering wheel with integrated airbag, containing more than 50 % renewable resources, won the 7th “Bioplastics Award”. A biobased polyester elastomer formed the basis for the development of this biobased component of the automotive safety field [69].

The research activities on the so-called “Bioconcept-Car”, a VW Scirocco converted into a racing car, show that not only the interior of vehicles, but also the body is already for the use of biobased components. The Bioconcept-Car represents a model for the testing of partially biobased fibre reinforced body-parts [91].

6.6 Textiles

In the minds of many readers the word "polyester" is automatically linked to textiles and only at closer inspection is it seen as a "plastic". It is therefore no wonder that most bio-polyesters are used to spin fibres and produce textiles. These are mainly PLA and PTT, but also other materials like PPT.


© DuPont

Fig. 6.12: Swimsuit made from PTT fibers


© Olymp

Fig. 6.13: Men's shirt made from a mixed fabric with PLA fibres

The examples of the various applications are almost endless, and go from children's shoes, swimwear, wedding dresses to men's business suits and haute couture apparel. In fact textiles made from renewable resources are almost as old as the human race (linen, cotton etc.). Modern textiles made from renewable resources now however combine their "biological" origin with the technical properties of modern microfibre textiles such as, in particular, good moisture transmission so that sweating is (almost) no longer a problem.

6.7 Construction and housing

Another field of application, where bioplastics are already used in various ways, is the construction and housing sector. Application examples are carpets made from PLA or PTT and other residential and home textiles. Biobased foams such as polyurethane are suitable for the production of upholstered furniture; particle foams made from PLA are used for building insulation. Especially in the field of insulation natural fibre insulation and cellulose-based blow-in insulation materials have already been available on the market for a long time. A large field of application for so-called WPC (Wood Plastic Composites, usually with PP as matrix material) are patio decks and fascia cladding. Bio-PE (and when available Bio-PVC) are ideal materials for water and sewage pipelines.

Biobased functional polymers can be found in paints and varnishes, linseed oil paints, wallpaper paste etc.


© NatureWorks

Fig. 6.14: Carpet made from PLA fibers


© Synbra

Fig. 6.15: PLA particle foam

6.8 Other

The potential use of bioplastics is virtually unlimited. In this section we will be showing just a few of the other examples. The desktop accessories are made from a PLA of Chinese origin and produced in Hungary. In 2010 they were among the five finalists for the Bioplastics Award. Adhesive tape made from cellulose materials or biaxial oriented PLA (BoPLA) have now also been combined with biobased adhesives. In the sport and leisure sector the number of applications is steadily growing. The handle of a Nordic walking pole made of partially biobased polyamide 6.10 was launched in 2009, as were ski boots with certain components made from biobased elastomers. The sports range was also complemented by amongst other things spectacles and sun glasses with high quality optical lenses made from clear bio-polyamide. Children's sand box toys are on the market made from PHA or cotton cellulose, and model railways are enhanced by the addition of small, highly detailed buildings made from PLA.

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Fig. 6.17: Desktop articles made from PLA

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Fig. 6.18: Handle of a Nordic walking pole made from bio-PA 6.10

© BioFactur

Fig. 6.16: Kids' play sand box made from cotton cellulose and other starch based bioplastics

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Fig. 6.19: Ski boot with the upper cuff made from partially biobased elastomer

7 END OF LIFE/DISPOSAL/CLOSED LOOPS

And what happens when these lovely plastic products eventually get broken, worn out, or are simply not required any longer? Here we have a whole range of so-called "end of life" scenarios, which can be used, depending on the material, the application and its condition.

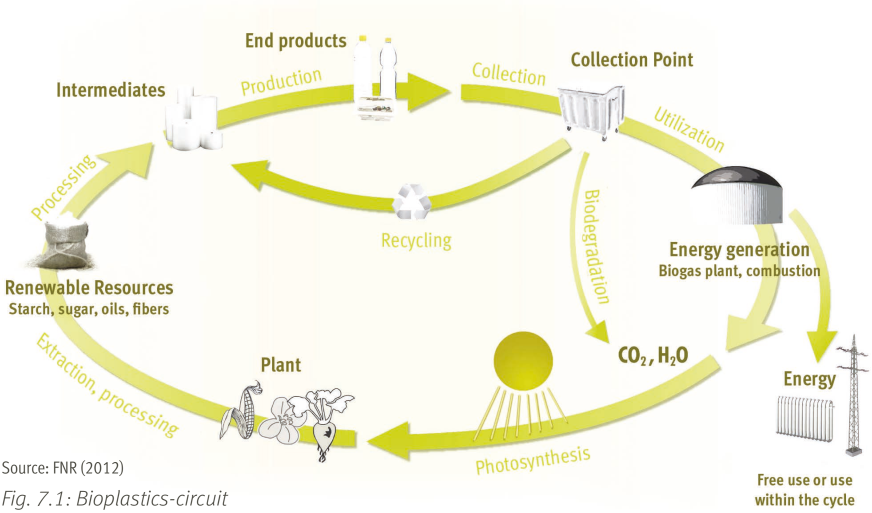
According to the revised Waste Management Act (Kreislaufwirtschaftsgesetz KrWG), that came into force 1st June 2012, the "circular economy" is defined as "the prevention and recovery of waste".

In the recycling of bioplastics it should always be the priority that both the stored biobased carbon and the energy contained are recycled in technical recycling installations. Bioplastics enable intelligent use of resources and ensure a high value in a low-carbon economy.

How bioplastic scrap, after its initial use or application, can be reused depends, as with conventional plastics, on the type of product and the type of plastics in question, as well as the amounts and a suitable recycling system.

The different "end-of-life" scenarios are listed below.

BIOPLASTIC RECYCLING CIRCUIT



Source: FNR (2012)

Fig. 7.1: Bioplastics-circuit

7.1 Recycling

The word “recycling” covers a wide range of general processes in which products that are no longer needed (mainly trash) are converted into a secondary material. The German recycling legislation (KrWG) defines recycling as “Any reclamation process, including product waste, materials or substances, that are prepared for re-use in the same process or other processes. This includes the preparation of organic materials, but does not include energy recycling and the use of such materials as fuels or fillers. Composting is specifically included, but here composting is looked at separately under the aspects of biological treatments.

In the case of material recycling, collection and sorting are to some extent an important prerequisite for the recycling procedures presented here.

7.1.1 Material recycling

Material recycling, including recycling of raw materials, physically or mechanically, is, in simple terms, the shredding, cleaning and re-melting, and re-granulating of plastic waste. In this process the chemical make-up of the material remains unchanged and the secondary raw material can generally be re-used without any losses. Such recyclate, in granulate form can be used for a wide range of new plastic products, depending on its purity quality. Properly and dependably sorted waste material (trimmed edges of film, runners, etc.) are often fed straight back into the same production process. However, very mixed, unsorted and dissimilar plastic waste can, under heat and pressure, often be recycled to make products with undemanding tolerances such as park benches or embankment supports.

Most cases of recycling lie somewhere in between these extremes. If, in a new application, a recycled plastic product is inferior in quality to the products initially produced we talk about “down cycling”. This is something that one tries hard to avoid or to minimise as much as possible.

In ideal cases plastic is used several times in what is known as “cascade recycling”, for instance in a detergent bottle, a rubbish sack, a shopping bag or a park bench. At the end of a cascade recycling loop there is also the possibility of making use of the material for thermal recycling. Most bioplastics can be made ready for use in material recycling. In some cases, depending on the circumstances, additional steps are required. It may, for example, be necessary for PLA to go through an additional step of polycondensation, or a special crystallisation stage.

7.1.2 Chemical recycling

The old plastic material can not only be remelted and regranulated for a new application but in some cases it may also be broken back down into its chemical building blocks (monomers). This is known as chemical recycling or feedstock recycling. A particularly interesting example here is found in the field of bioplastics – namely the chemical recycling of PLA. In installations such as are currently operating in Belgium or California the polylactic acid is reconverted into lactic acid and so can then be converted into new PLA or be used for other purposes

7.2 Energy recovery or thermal recycling

Bioplastics can, after a long useful life, and after being recycled a maximum number of times, still be burned and the stored up energy finally used. The generation of heat and other forms of energy (electricity) by incineration of plastic waste is currently the most commonly used process in Europe for reclaiming the value of such waste, and as long as sufficient quantities are not available for economical material recycling it is, in the view of many experts, the most logical option. The high level of heat generated when incinerating plastics makes them an ideal substitute for coal or heating oil. Whether biobased or obtained from fossil sources there is no technical difference in the value recovery process. In the case of biobased plastics it is possible, however, to obtain renewable energy from the biogenic carbonates – and that is a powerful advantage [73].

7.3 Biological treatment

7.3.1 Composting

Plastics that are biodegradable under certain conditions and are completely broken down by micro-organisms into CO_2, water and a biomass can be composted. Attention should be paid here to the relevant standards such as EN 13432, EN 14855, ASTM D6400 and similar (cf. chapter 2).

There are plenty of examples where biodegradability, or disposal by composting, does in fact bring additional benefits. At large scale events catering cutlery, tableware and food remnants can be taken together to a composting facility. As early as 2005, on the Catholic World Youth Day, there were about 7 million compostable catering units used.

When growing tomatoes in a greenhouse plastic clips have been used for many years to hold the tomato plants firmly against the support canes and allow them to grow upwards. After the tomato harvest these clips, made of compostable plastic, can be disposed of with the unwanted green plant growth. Despite a higher cost of acquisition compared to conventional plastic clips they do offer the grower financial benefits.

As a final example we can once again mention mulch film which, after the harvest, can be ploughed into the ground (cf. chapter 6.2).

7.3.2 Fermentation

Another option for using the energy available is biogasification, also called anaerobic digestion (AD). Here microorganisms digest biogenic material in the absence of oxygen, i.e. under anaerobic conditions [74].

Organic waste such as manure or compost from agricultural production are, due to their high moisture content, particularly suitable for fermentation. The methane gas formed during the fermentation process can also be used for energy. The digestate will continue to be used differently (eg composting, fertilizing, drying and incineration).

The possibility of using the waste from biodegradable plastics in biogas plants and to convert it into useful methane is being intensively investigated at the moment.

8 THE MARKET

8.1 Introduction

Already today large amounts of renewable resources are used for the production of plastics, especially in the area of functional polymers (see chapter 1) [75].

However, considering only the structural polymers, i.e. the “plastics”, mainly dealt with in this brochure, renewable raw materials currently constitute only a very small part of the total raw material base. The bioplastics market currently has therefore only a very small volume of less than 1 % of the total plastics market.

However, the development in recent years has given this market an enormous boost, so that double-digit growth rates are expected in the near future.

Until recent years, the bioplastics market was mainly influenced by bioplastics that take advantage of the natural polymer structures of renewable resources. The main representatives of this group are thermoplastic starch (TPS) and cellulose derivatives.

Over the last three years this situation has changed significantly. In the meantime the market is dominated by so-called “drop in bioplastics”. These are biobased (and partially biobased) standard plastics such as polyethylene (PE), polyamide (PA) or polyethylene terephthalate (PET). This quick change in the market became possible because on the one hand several globally active companies changed their food packaging (and beverage bottles) partially to bioplastics. On the other hand drop-in bioplastics were produced from the start in large scale installations and in suitably large quantities. Because, in comparison with petroleum based plastics, these plastics do not offer any improvement in their performance characteristics they are right from the start in direct price competition with their conventional counterparts which means that the bigger plants play a greater role [76].

8.2 Market overview

In the spring of 2013, two studies were published about the bioplastics market [76], [93]. Based on selected descriptions from these studies, the current market situation and the projected development is illustrated here.

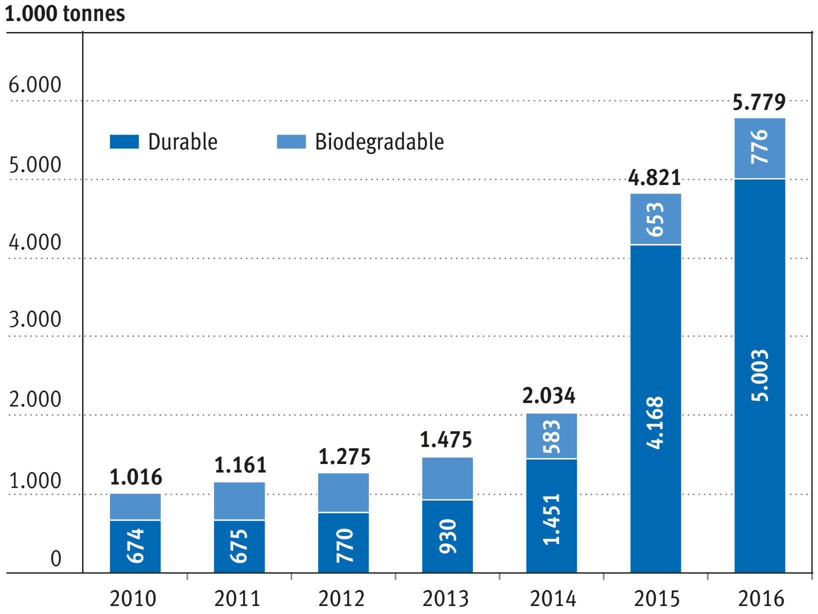
According to estimates of the Institute for bioplastics and biocomposites of the University of Applied Sciences and Arts Hanover (IfBB) the worldwide production capacity of 1 million tonnes was first exceeded in 2010.

As can be seen in Figure 8.1, it is expected that production capacities for bioplastics will rise to more than 5.7 million tonnes by 2016 [93].

However, the graph shows yet another trend, namely the composition of the global production volume: While the proportions of biodegradable and durable bioplastics were almost in balance until 2012, in the following years the proportion of durable bioplastics has grown disproportionately. The production capacity for biodegradable polymers only shows very low growth rates.

The second recent market study [76] also considers, in addition to thermoplastics, thermosetting bioplastics and above all chemical fibres. Thus this study presents higher market figures. The authors of the study have determined production capacities of more than four million tonnes for 2012. By 2016, they predict a capacity of more than 8 million tonnes. Within the framework of this study also the amount of biomass was analysed. In 2012 1.7 million tonnes of biomass were processed into bio-based plastics, in 2016 this will be around 3.5 million tonnes.

GLOBAL PRODUCTION CAPACITY FOR BIOPLASTICS



Source: IfBB, University of Applied Sciences and Arts Hanover [93]

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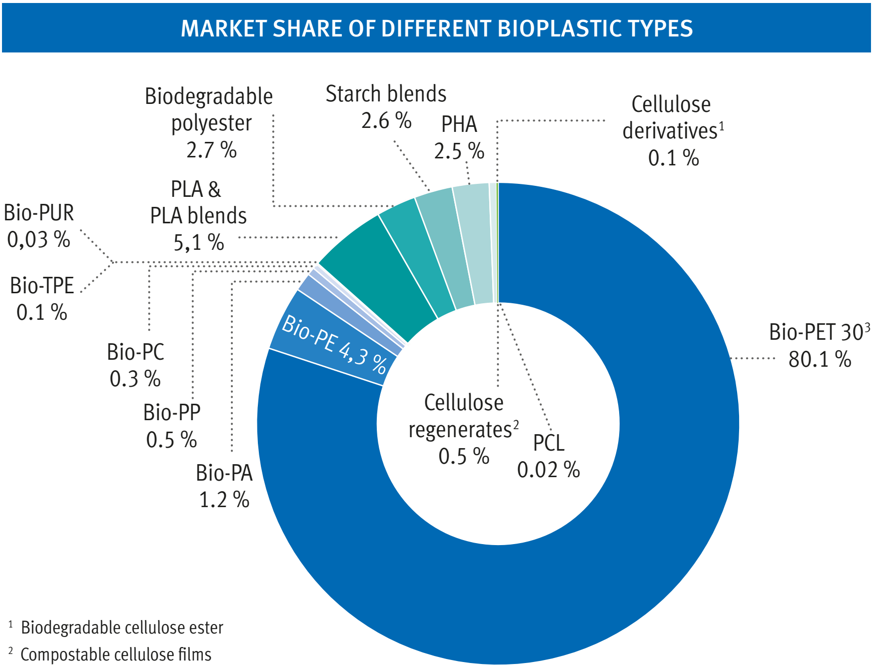
Fig. 8.1: Production capacities for bioplastics broken down by region (estimates for 2016)

Figure 8.2 shows the bioplastic types behind these market figures. The graph shows the production capacity for bioplastics according to types forecasted for 2016. It can be clearly seen that the large expected capacities for drop-in plastics such as Bio-PE and Bio-PET will have a significant impact.

Despite the high market growth described above bioplastics are still in their infancy. With a total market for plastics estimated to be 330 million tonnes in 2015 [79], bioplastics in material applications will amount to no more than 2 % in the next two to three years. From a purely technical point of view up to 90 % of all plastics could be switched from fossil fuels to renewable sources. However, in the short and medium term this conversion will not be possible partly due to economic barriers and to this extent insufficient availability of biomass even at short notice [80].



[1] Biodegradable cellulose ester

[2] Compostable cellulose films

[3] Proportion of renewable raw materials: 30 %

Total for 2016: 5.778 million tonnes

Source: IfBB, University of Hanover [93]

© FNR 2013

Fig. 8.2: Market shares of different types of bioplastics (estimates for 2016)

8.3 Do we in fact have enough agricultural land?

One is constantly hearing the question concerning the availability of agricultural land, and is often discussed in relation to world hunger. Because this is a very sensitive topic we have simply gathered here a few facts and figures.

An important point in this respect is that for the next years we are talking about a low market volume for bioplastics. Only in long-term scenarios are two-digit market shares expected. So we should keep in mind, that this discussion is primarily about the **long term** availability of agricultural land for the sustainable production of raw materials for bioplastics. To get a feeling for the size of agricultural areas needed, one should remember that plastics are accounting for only between 4 % and 7 % of total petroleum consumption. The lion's share of petroleum is thus being used for the purpose of generating energy [78].

Depending on the type of bioplastic, the type of plants used, or the relevant agricultural raw material the average yield is from 2 to 4 tonnes of bioplastics per hectare [81, 82]. According to the estimates in chapter 8.2 it can be assumed that for 2016 the forecast world production capacity for bioplastics will require around 1.1 million hectares of agricultural land. This represents about 0.02 % of the agricultural land used worldwide, i. e. around 5 billion hectares. [94].

Even for long-term scenarios, if the whole world plastics production capacity were to switch to biobased plastics only 4 % to 7 % of the agricultural land available world-wide would be required [72, 78].

9 ANNEX

9.1 Internet links

www.fnr.de	FNR – General Information
www.biowerkstoffe.fnr.de	FNR – Information about bioplastics
www.biopolymernetzwerk.fnr.de	FNR – Information on specific bioplastic topics
www.kommunal.fnr.de	FNR – Information about bioplastics in municipalities
www.aus-natur-gemacht.de	BMEL – Information on biobased economy
www.european-bioplastics.org	Information the European trade association
www.bio-based.eu	News Portal
www.bio-plastics.org	News Portal
www.bioplasticsmagazine.com	Trade Magazine

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9.3 List of abbreviations

ASTM	American Society for Testing and Materials
BMC	Bulk-Moulding-Compound
BDO	Butandiole
DSD	Dual System Germany
EN	European Standard
PBAT	Polybutylenadipatterephthalate
PBS	Polybutylensuccinate
PBSA	Polybutylensuccinatadipate
PBT	Polybutylenterephthalate
PE	Polyethylene
PEF	Polyethylenfuranoate
PET	Polyethylenterephthalate
PHA	Polyhydroxyalkanoate
PHB	Polyhydroxybutyrate
PHV	Polyhydroxyvalerate
PHBV	Poly-3-hydroxybutyrate-co-valerate
PP	Polypropylene
PTT	Polytrimethylenterephthalate
PVC	Polyvinylchloride
PDO	Propandiole
RTM	Resin Transfer Moulding
SMC	Sheet-Moulding-Compound
TPS	Thermoplastic starch
TPU	Thermoplastic polyurethane
USDA	United States Departm. of Agriculture
WPC	Wood Plastic Composites

9.4 Index

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