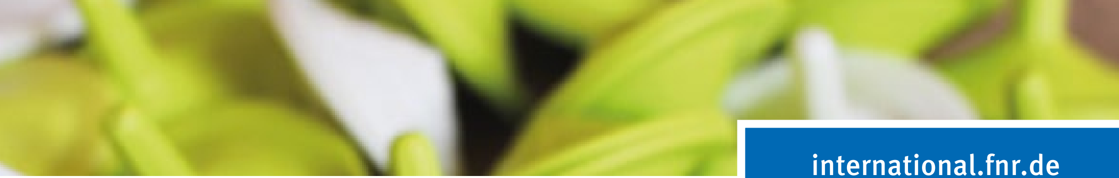


international.fnr.de

# BIOPLASTICS

PLANTS
RAW MATERIALS
PRODUCTS

With support from

Federal Ministry
of Food
and Agriculture

by decision of the
German Bundestag

FNR
Fachagentur Nachwachsende Rohstoffe e.V.

# IMPRINT

**Published by**
Fachagentur Nachwachsende Rohstoffe e. V. (FNR)
Agency for Renewable Resources
OT Gülzow, Hofplatz 1
18276 Gülzow-Prüzen
Tel.: +49 3843/6930-0
Fax: +49 3843/6930-102
info@fnr.de
international.fnr.de

With support from the Federal Ministry of Food and Agriculture,
based on a decision of the Parliament of the Federal Republic of Germany

**Text**
Dr. Michael Thielen, bioplastics MAGAZINE

**Editing**
Fachagentur Nachwachsende Rohstoffe e. V. (FNR),
Department of Public Relations

**Pictures**
Title: FNR/Britta Autzen
So far as the picture makes no indication to the contrary:
Fachagentur Nachwachsende Rohstoffe e. V. (FNR)

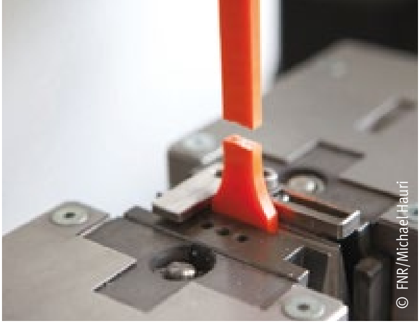
**Design/Implementation**
www.tangram.de, Rostock

**Printed by**
www.mkl-druck.de, Ostbevern

Printed on 100 % recycling paper using vegetable oil-based colours

Order no. 237
3rd revised edition
FNR 2020

# BIOPLASTICS




# CONTENTS


© Sergey Nivens/Fotolia.com


© FNR/Britta Autzen

# 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.

Plastic or polymer products are used as structural polymers in material applications, which we commonly refer to as 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 are impressive: the plastics industry employs more than 1.6 million people in European Union and turns over some 360 billion Euros per annum. Out of the approximately 359 million tonnes of plastics produced annually, worldwide, about one fifth comes from Europe and again a quarter of them from Germany. Its applications are not only in packaging (40 %), construction materials (20 %), but plastic is also needed in automobile production (10 %) and furniture manufacture (statistics status 2019), as well as in the electronics industry and in the manufacture of domestic equipment of all types [3]. And consumption continues to rise.

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] 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)*

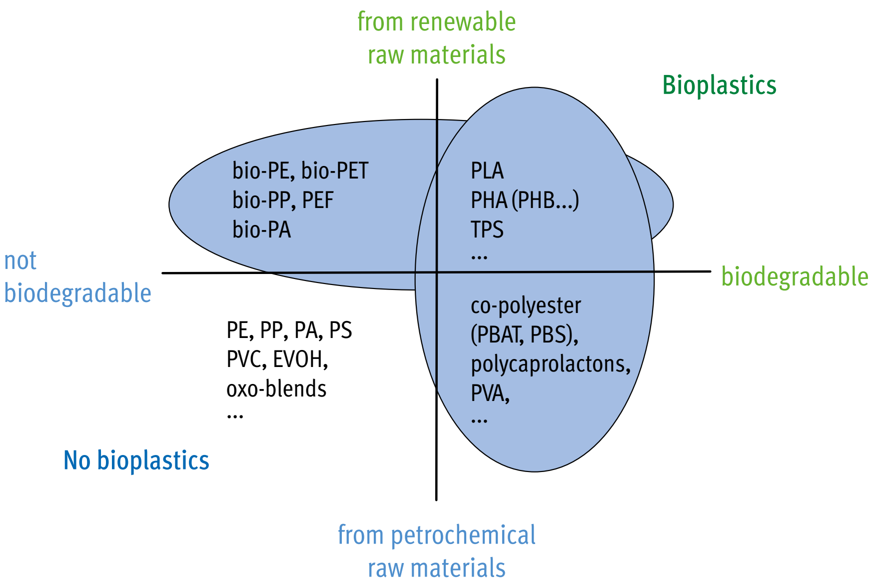
## 1.2 Bioplastics = biobased plastics

Biobased plastics consist in a large part, or even completely, of renewable resources. They are often referred to briefly as bioplastics.

The first modern plastics from renewable resources, which appeared on the market at the end of the 1980s, were usually biodegradable. This revealed that the term "bioplastic" was often linked less with the renewable resource base, but with the property "biodegradable".

From to-day'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 M. Thielen



*Fig. 1.1: Biobased and biodegradable plastics*

## 1.3 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 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 [65].

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.

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 [14] – 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. TÜV Austria (formerly Vinçotte) offers certification with the OK-biobased logo, in which the biobased carbon content is marked with one to four stars (* 20–40 %/** 40–60 %/*** 60–80 %/**** more than 80 %) (Fig. 1.2).

*Fig. 1.2: OK-biobased Logo*

The German certification body DIN CERTCO now also offers such certification where the biobased content is given in percentage groups (Fig. 1.3).

In the USA there is a programme running since a few years and known as “BioPreferred®”. This programme obliges public

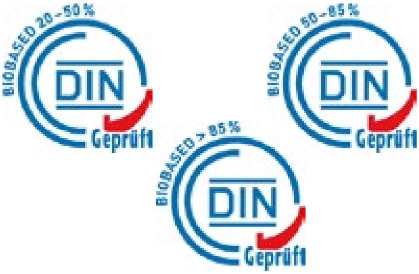



*Fig. 1.3: DIN Certified Biobased (DIN CERTCO)*

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.

In the meantime, consideration is also being given in Germany as to how the public sector can be encouraged to make greater use of products that are manufactured to a large extent from renewable raw materials.

# 2 RENEWABLE RESOURCES

## 2.1 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.

## 2.2 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 manufacturing of biobased plastics.

### 2.2.1 Polysaccharides (carbohydrates)

Polysaccharides (multiple sugars or polysaccharides) include some of the most important organic compounds. Cellulose, the main component of plant cell walls, is an unbranched biopolymer consisting of several hundred to tens of thousands of glucose building blocks. In the plant, these high-molecular chains combine to form higher structures, which, as tear-resistant fibres, also have static functions [2, 5, 16]. The cellulose content of cotton fibres is 88–96 % [2], wood consists of 41–52 % cellulose [97].

Starch is formed as an energy storage in plants. It consists of two components, branched amylopectin and unbranched amylose.

An important non-plant polysaccharide is chitin. In fungi, it is a main component of the cell walls, in articulates (including insects and arachnids) it is a main component of the exoskeleton.

### 2.2.2 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.

Fig. 2.1: Starch from potatoes and cereals

### 2.2.3 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 [8]. The majority of it is burned for energy recovery.

### 2.2.4 Natural rubber

Natural rubber is an elastic biopolymer, mainly made from latex from specific trees, such as the rubber tree, bullet wood (Manilkara bidentata) or gutta percha. Natural rubber is the most important raw material for the production of rubber, which is made from it by vulcanization.

### 2.2.5 Other

An interesting group of biopolymers are the polyhydroxyalkanoates – polyesters (PHAs), which are formed in certain microorganisms as an energy reserve (cf. chapter 3.2.5).

## 2.3 Other biogenic materials

### 2.3.1 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 fatty acids in particular are also an interesting source of raw materials for the production of bioplastics.

### 2.3.2 Carbohydrates

In addition to the substances mentioned above, a number of other carbohydrates such as monosaccharides (such as glucose and fructose) or disaccharides (such as sucrose) can serve as starting materials for the production of biobased plastics.

Certain bivalent alcohols which can also be used in the production of biobased plastics can be produced from renewable raw materials themselves. For a few years now biobased 1,3-propanediol has been sold as bio-PDO, and 1,4-butane-diol will soon be marketed as bio-BDO produced from renewable resources such as maize starch [9, 10].

An important component used in the production of bioplastics is succinic acid ($C_4H_6O_4$), which can also be produced by fermentation from starch and different oligosaccharides.

The currently economically most important monomer is lactic acid, from which polylactide (PLA), i.e. polylactic acid, is produced (see chapter 3.3.1).

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 bioethanol based on sugar cane a biobased ethylene for the production of bio-polyethylene can be obtained (see chapter 3.3.4).

## 2.4 Where do the raw materials come from?

### 2.4.1 Agricultural and forestry raw materials

A frequently held discussion is the potential conflict of the use of food or feed for the production of bioenergy or biofuels. Although on a much smaller scale, this also applies to the industrial use of renewable resources e.g. for bioplastics. Thus, the question of the availability of agricultural land is raised again and again and, in this context, hunger in the world is discussed. Since this is a very sensitive topic, a few facts and figures are to be compiled here.

It is important to note in this context that we are talking about a low market volume for bioplastics in the coming years. Only for longer-term scenarios double-digit market shares will be achieved. Accordingly, we should be aware that this discussion is primarily concerned with the long-term availability of agricultural land for the sustainable production of raw materials for bioplastics. In order to get a feeling for the magnitude of the land required in the long term, it should be borne in mind that currently between 3 and 4% of the crude oil demand is used for the production of plastics. The largest part of the oil used is therefore used for energy [55].

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 [57, 58]. According to the estimates in chapter 7.2 it can be assumed that for 2024 the forecast world production capacity for bioplastics will require around 1 million hectares of agricultural land. This represents about 0.02% of the agricultural land used worldwide, i.e. around 4.7 billion hectares [57].

In the future, forestry will play an increasingly important role as a raw material supplier for bio-based plastics. The big advantage: the use of cellulose and increasingly also lignin does not lead to a competitive situation with food and animal feed.

### 2.4.2 Use of residual and waste materials

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 challenge 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 food and considering the sustainability aspects of the bioplastic.

An example can be seen in the Netherlands where there is a flourishing potato and potato processing industry (French fries). The industrial peeling and cutting of potatoes involves the use of large amounts of process water. This water, like the peels and other waste, contains a high proportion of usable starch. In the Netherlands and Germany, for example, there are companies that produce plastic from starch obtained in this way.

In New Zealand and the Netherlands, polyhydroxyalkanoate (PHA) has been produced at laboratory scale on a trial basis, with municipal wastewater serving as the source of "food" for the PHA-producing bacteria. [25, 69].

A few years ago, a large manufacturer of branded goods successfully put the fat discarded after being used to fry potato chips to use as "food" for PHA-producing microorganisms. In this way, discarded deep-frying fat was turned into a high-quality plastic material [41]. A Czech/Chinese company is currently developing the industrial-scale conversion of used frying fat from catering establishments into PHA bioplastics [70].

Black liquor, a waste product of the pulp industry contains lignin (cf. chapter 3.2.3) and so-called tall oils. The products from the tall oil distillation 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 serve 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.

Another trend is biomass gasification (anaerobic digestion) to synthesis gas. Biopolymer monomers can be produced by subsequent chemical or biotechnological conversion of the synthesis gas thus obtained. However, both methods are still in the research stage. One chemical route could lead via the conversion of synthesis gas to ethanol and finally to ethylene and then to polyethylene (cf. chapter 3.3.4). At present, however, the biotechnological route is being intensively pursued, which uses synthesis gas as a carbon source for microorganisms for the fermentative production of polymer monomers [2, 11, 12].

The production of biobased polyoleofins (PE, PP) (see also chapter 3.3.4) from bionaphtha was announced in 2018 by a Finnish chemical company in cooperation with plastics and product manufacturers. Bio-Naphta is either a by-product of the production of biobased diesel fuel, or it is made from sustainably produced vegetable oils and from used cooking oils. After the start of a pilot plant in autumn 2018, the parallel production of biobased polypropylene and polyethylene on a commercial scale at a German location was announced in June 2019. In March 2020, the announcement of the production of biobased polypropylene in Belgium followed [98, 99, 100, 101, 102].

# 3 BIOBASED PLASTICS

## 3.1 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 [13]. 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].


*Fig. 3.1: Hair pin 1920/1950 made from celluloid*

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].


*Fig. 3.2: Buttons 1920/1940 made from casein*

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 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 3.3.1 and 3.2.5). Sugar is also the raw material for the latest generation of bioplastics including the biobased polyolefins PE, PP and PVC, as well as the partially biobased polyester PET, (see chapter 3.3.4 and 3.3.1), and the newly developed polyethylene furanoate (PEF, see chapter 3.3.1) which however are not all bio-degradable.

Further examples of partially biobased plastics are certain bio-polyamides. A whole range of raw material suppliers 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 (see chapter 3.3.2).

Blends of biobased and petrochemical plastics are, for example, mixtures of PLA (100 % biobased) 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.

## 3.2 Modified natural polymers

### 3.2.1 Polysaccharide-based plastics

#### 3.2.1.1 Thermoplastic starch

Thermoplastic starch (TPS) is produced by an extrusion process that destructures starch grains [1, 2]. In order to destroy the starch, i.e. to destroy its granular structure and crystallinity, it must be subjected to sufficient mechanical energy and heat in the presence of so-called plasticisers or softening agents [15]. Suitable plasticizers are e.g. water (at a concentration of below 45 %), glycerine and sorbitol.

#### 3.2.1.2 Cellulose-based plastics

Cellulose can be used industrially in the form of cellulose regenerates and cellulose derivatives (Fig. 3.4).

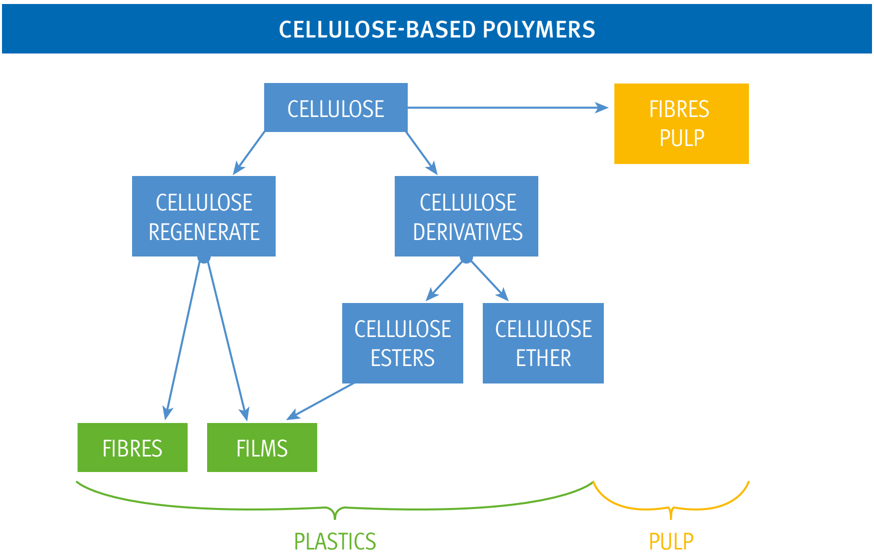
**Cellulose regenerate**

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 of materials are viscose, viscose silk, rayon,


lyocell or artificial silk, and a few more in the area of fibres and textiles. The global share of cellulosic manufactured fibres was 9.2 % (6.8 million tons) in 2018 [17].

In the field of films, the most well-known regenerated cellulose is cellulose hydrate or Cellophane (formerly a brand name) (see fig. 3.3) [5].

*Fig. 3.3: Cellophane – a crystal clear cellulose product*




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



*Fig. 3.4: Cellulose-based polymers*

**Cellulose derivatives**

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

Cellulose esters, the most important group, also include celluloid, which was produced from 75 % cellulose nitrate (obtained from nitric acid and cellulose) and 25 % camphor.

Basically, cellulose esters are produced by esterification of cellulose with organic acids. The most important cellulose esters from a technical point of view are cellulose acetate (CA), cellulose propionate (CP) and cellulose butyrate (CB), with CA having the greatest market significance.


*Fig. 3.5: Swiss army knife, grip made from cellulose butyrate*


*Fig. 3.6: Transparent dice made from cellulose acetate*

## 3.2.2 Protein-based plastics

One of the protein-based plastics is casein (see chapter 2.2.2), which already had a certain importance at the beginning of the age of plastics (see chapter 3.1). To make a casein plastic the basic casein, obtained from skimmed milk and plasticised, is processed to form a cross-linked plastic by the use 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 were used only in small niche markets until recently [5].

More recent approaches use, among other things, milk that is not suitable for human consumption to extract casein from it. From this casein fibres and textiles [71] or water-soluble films, e. g. for dishwasher tabs [72] can be made.

A different type of protein-based plastic is gelatine (see chapter 2.2.2). In addition to the well-known applications, such as a nutritional supplement, it is also used as a binding agent or capsule for pharmaceutical tablets [5].

## 3.2.3 Lignin-based plastics

It is possible to change the spectrum of 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 fibres.


*Fig 3.7: Loudspeaker housing made from a lignin-based bioplastic*

The most well-known bioplastic based on lignin (chapter 2.2.3) is sold under the name of "liquid wood" [20, 109] and is easy to process in injection moulding machines (chapter 4.3.3). This bioplastic is also sold containing natural fibres (flax, hemp) to increase its strength [67]. In the field of thermosets, formulations with lignin are developed for phenolic, epoxy and polyurethane resins [2, 21, 22].

### 3.2.4 Natural rubber and thermoplastic elastomers

A very popular "relative" of plastics is rubber. Other associated terms are natural latex, caoutchouc and elastomers. Even though more than half of the world 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 natural rubber [23].

By natural rubber (caoutchouk[2]) 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. Rubber is produced by vulcanising crude latex with sulphur [2].

As an alternative raw material source for natural latex, the root of the Russian dandelion is also being investigated today [73].

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 grades available [74, 75].

An important group here are the thermoplastic polyurethanes (TPU). 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 (see chapter 3.3.3.).

[2] *Indian: „the tree that weeps" from cao = tree, and ochu = tears*

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 (bio-PDO, cf. chapter 2.3.2), is suitable for technical applications such as airbag covers in passenger cars, air ducts up to furniture, sports articles and fibres [18].


*Fig. 3.8: Walking shoes with partially biobased polyurethane (TPU)*

A 100 % biobased block copolymer (polyether block amide) was presented in 2010 for, among other things, ski boots. The TPE material consists of biobased polyamide 11 (cf chapter 3.3.2) and biobased polyether [19].

## 3.2.5 Polyhydroxyalkanoates

Starch and other substances that supply carbohydrates can also be converted into bioplastics by fermentation through micro-organisms. Examples are the polyhydroxyalkanoates (PHAs) or the polyhydroxy fatty acids, a family of polyesters. As in many mammals, including humans, that hold energy reserves in the form of body fat there are also bacteria that hold intracellular reserves of polyhydroxyalkanoates [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, or on plant oils or other nutrients rich in carbon, it is possible to obtain PHAs on an industrial scale.


*Fig. 3.9: Electron microscope image of bacteria with stored PHA particles*

Today those most economically interesting PHAs are PHB or copolymers such as PHBV (poly-3-hydroxy butyrate-covalerate), PHBH (poly-3-hydroxy butyrate-co-3-hydroxyhexanoate) or PHBHV, which was used for a shampoo bottle in markets including Germany and the USA in the 1990s, but later disappeared from the market.

Processable polyhydroxyalkanoates are generally obtained by removing the biopolymer from the bacterial cell material and cleaning and compounding it. PHAs are mainly film, extrusion and injection moulding grades and are now increasingly available as blow moulding grades too. A Japanese company in 2010 showed a particle foam made from PHBH (similar to Styrofoam®) [24].

A special feature of all currently available polyhydroxyalkanoates is the fact that they biodegrade completely and relatively quickly in an industrial composting plant (see chapter 6.4) or biogas installation, as well as on a home compost heap, in the soil or in fresh and seawater.

A number of companies worldwide are working on the large-scale production of various polyhydroxyalkanoates [76]. Among them are also efforts to produce PHA from used cooking fat [70], or from $CO_2$ and $CH_4$ (methane).

## 3.3 Biobased polymers synthesised from biobased monomers

### 3.3.1 Biobased Polyesters

**Polylactide (PLA)**
In this group of materials PLA (polylactide, polylactic acid) is one of today's most important bioplastics 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.

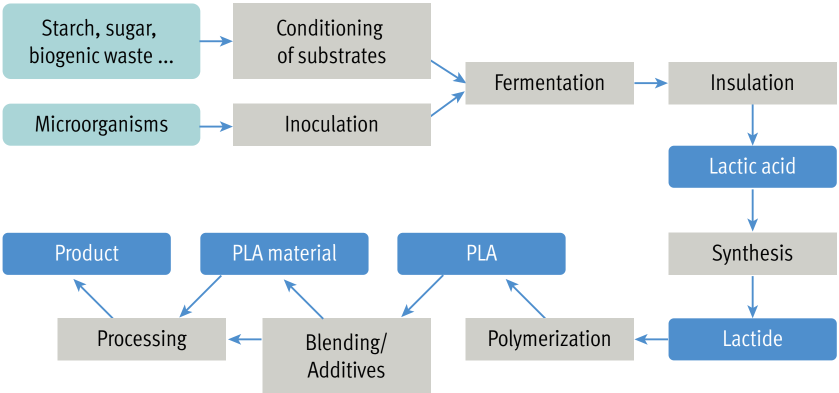
The world's first larger PLA production unit with a capacity of 150,000 tonnes per annum began production in the USA in 2002. The second largest plant with a capacity of 75,000 tonnes went into operation in Thailand at the end of 2018. Further industrial PLA production plants are planned or under construction (e.g. in China).

PLA is, as it exits the reactor, 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 or blended with other plastics (bioplastics or traditional plastics).

Transparent PLA is very similar to conventional commodity 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].

Advantages of the polylactide plastic are its high level of rigidity, transparency of the film, cups and pots, as well as its thermoplasticity 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 certain additives or by a combination of L- and D-lactides (stereocomplexing), which then have the required morphology for use at higher temperatures [26]. Since 2017 heat resistant PLA grades have been commercially available.

## PROCESS STEPS FOR GENERATING POLYLACTIDE MATERIALS AND COMPONENTS




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



*Fig. 3.10: Manufacture of PLA products*

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.

In addition to short life packaging film or thermoformed 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 baby toys, 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 [27], door tread plates, etc.

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


*Fig. 3.11: Baby toys made from PLA*


*Fig. 3.14: Baby's shoes made from a PLA/PET blended fabric and soles made from a soft PLA compound [28]*


*Fig. 3.12: Transparent PLA film for packaging vegetables*


*Fig. 3.13: Lower dashboard panel made from a PLA blend*

**Polyethylenterephthalat (PET)**

Since the second half of the 20th century, PET 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 made from partially biobased PET [29, 30]. The monoethylene glycol (about 30 % by weight) is obtained from sugar cane molasses. The terephthalic acid in this case is still produced from petrochemical resources.


*Fig. 3.15: Beverage bottles made from partially biobased PET*

The production of purified terephthalic acid (PTA) as the second component of PET (and other plastics) using renewable resources had been regarded as too elaborate and costly. Now, however, there are first approaches to the economic production of biobased terephthalic acid via Bio-Paraxylene (Bio-PX) [31, 77, 78].

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 [68].

Despite the differences between PEF and PET, their chemical similarity means that the PEF production process closely resembles that of PET and other polyesters. Processing can also typically be carried out on the same equipment that is used for PET, other polyesters and often even other plastics. In many cases, the only changes required are to the process parameters, in addition to minor adjustments to the machines, of the kind that are usually made when changing between different materials.

Due to the lower melting point of PEF, it can typically be processed at lower processing temperatures than PET, saving energy costs while at the same time offering a sufficiently wide processing window as to ensure smooth operation. In addition, PEF is similar enough to PET to be recycled using the same processing steps followed in the many PET recycling processes.

Compared to PET, PEF has a 10 times higher oxygen and $CO_2$ barrier and a water vapour barrier that is twice as high. The glass transition temperature (+12 °C) and the modulus of elasticity of PEF (+60 %) are also higher than those of PET. These advantageous properties will enable new packaging options and additional functions in cases where PET does not meet the requirements [79].

### Polytrimethylene terephthalate (PTT)

Polytrimethylene terephthalate (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), or dimethyl terephthalate and a diol. In this case it is a biobased 1,3 propanediol (bio-PDO, see chapter 2.3.2).

### Biobased Polysuccinate

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


*Fig. 3.16: Packaging made from polybutylene succinate (PBS)*

When producing polybutylene succinate adipate (PBSA), in addition to the succinic acid, adipic 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.

### Biobased polycarbonate

Biobased 'polycarbonate' refers to a partially biobased and durable engineering plastic belonging to the polycarbonate family (formally, polycarbonate is also a polyester) produced from isosorbide, which in turn is obtained from sorbitol. Sorbitol is the sugar alcohol of glucose $C_6H_{14}O_6$ [85]. It is therefore a widely available raw material.

Aliphatic polycarbonate (APC), or, to be more precise, cycloaliphatic polycarbonate is made from isosorbide, $CO_2$ and biobased succinic acid. The double ring structure of the isosorbide mimics the bisphenol A structure in the molecular structure, resulting in material properties comparable to those of conventional polycarbonates [103].

The material combines the positive properties of polycarbonate (PC) (impact strength) and polymethyl methacrylate (PMMA) (scratch resistance) and is also characterized by a reduced tendency to yellowing [86, 87]. In addition, it offers good optical (transmission and UV resistance) and mechanical properties as well as heat resistance.

It is suitable for applications such as touchscreens, where a high degree of scratch resistance and impact strength in combination with a good optical surface are important. In vehicle interior trim and covers as well as exterior parts such as radiator grilles, the material's exceptional high-gloss surface makes additional painting unnecessary [88].


*Fig. 3.17: Automotive interior trim in piano lacquer look*

**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.

In the meantime, initial success has also been achieved in producing the biodegradable plastic PBAT (polybutylene adipate terephthalate), partly from renewable raw materials [7]. PBAT is very successful on the market.

In addition, there are other vegetable oil-based polyesters that can be used to produce printing inks, adhesives, insulating materials, encapsulation compounds, as textile finishing agents and as floor coverings. The latter, usually referred to as linoleum, has been produced from linseed oil using complex processes for decades.

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


*Fig. 3.18: Speedboat made from partially biobased UP resin*

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 2.3.2, 3.3) can be produced from renewable resources. Today there is a whole range of partially biobased UP resins on the market [37, 38].

## 3.3.2 Biobased Polyamides

Polyamides are plastics that are particularly suitable for fibres and technical applications. The most well known examples, which attracted attention in the first half of the last century, are Nylon® and Perlon®. Today polyamides are used for demanding injection moulding applications, extruded products, hollow articles and textiles for the manufacture of clothing, decorative materials and technical fabrics.

Polyamides are usually produced from dicarboxylic acids and diamines. Biopolyamides are completely or partially biobased, depending on whether the dicarboxylic acid, the diamine or both are produced from renewable resources.

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


*Fig. 3.19: Wall fixing plugs made from partially biobased PA 6.10*

A further example is PA 10.10, which is also commercially available. Here the first “10”-component is biobased too. The base material 1,10 diaminodecane (or decamethylene diamine) can also be obtained from the castor oil plant, so that PA 10.10 is also 100 % biobased.


*Fig. 3.20: Fuel injector nipple made from 100 % biobased PA 11*

The completely biobased PA 11, which has already been on the market for about 70 years. It can only be made from castor oil and is therefore totally biobased. Thanks to its special chemical and general resistance it is suitable for biofuel pipework and other components.

In addition to those mentioned here there are still some more biobased polyamides [32].

## 3.3.3 Biobased Polyurethanes

Polyurethanes are produced by a reaction between polyols and diisocyanates. These materials can be hard and brittle, elastic, foamed or compact. Polyurethane can be a thermoplastic or thermosetting material.


*Fig. 3.21: Car seat made from soy foam*

Since polyols can also be produced from vegetable oils from castor, rapeseed, sunflower or soy, a large number of partially biobased polyurethanes are already sold on the market today. While fatty acids from castor oil already contains OH groups, polyols from vegetable oils such as rapeseed, sunflower or soybean oil are produced by epoxidizing the unsaturated fatty acids and then adding multiple alcohols via the ring opening of the epoxides.

So-called thermoplastic polyurethane, TPU, as a member of the elastomer group, has been discussed in chapter 3.2.4.

Another important group of polyurethanes are the foams used in the automotive industry. A major North American automobile manufacturer has already been pioneering the use of polyurethane foam based on a polyol derived from soy for a number of years now.

In addition, the first efforts to produce diisocyanates from renewable raw materials have met with success. An aliphatic polyisocyanate based on a 70 % biobased pentamethylene diisocyanate (PDI trimer) was presented in 2017. It is used as a hardener component for lightfast polyurethane coating systems [80].

### 3.3.4 Biobased Polyolefins

Among the most important and most commonly used plastics are polyolefins (polyethylene PE and polypropylene PP). They are easily recognised by the fact that their density is less than 1 g/cm³ – i.e. they float in water. Both PE and PP can be produced from renewable resources [33].

**Bio-polyethylen (Bio-PE)**

Polyethylene (PE) is the simplest and at the same time most common plastic with a global capacity of 110 million tonnes [33]. There are numerous possible applications, going from film (pouches, bags, shrink film) through blow-moulded hollow articles 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 by polymerisation of petrochemically produced ethylene gas. Another possibility to produce the monomer ethylene is by dehydrogenation of ethanol. This method was already 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].

With regard to the production of plastics from renewable raw materials, this process has gained interest again. For instance, in Brazil bioethanol has been produced for many years from sugar cane by a fermentation process. This bioethanol can now be used for the production of ethylene and hence bio-polyethylene. The production of 1 ton of green PE is the equivalent of capturing 3.09 tons of carbon dioxide from the atmosphere. In 2010 in Brazil a production plant with an annual capacity of 200,000 tonnes was installed.


*Fig. 3.22: Toy made from bio-PE*

**Bio-polypropylene (Bio-PP)**

Polypropylene (PP) is also used for many technical applications. The annual production capacity worldwide is about 56 million tonnes (2018) [104]. Like bio-PE, biobased polypropylene can be produced from bioethanol, but the process is much more complex.

There are several possibilities for producing the monomer propylene from renewable resources [34]. One large Brazilian producer of polyolefins announced they had started up production at a bio-PP plant, without, however, providing details of how the plastic will be produced.

In 2018, a Finnish chemical company announced that it would use biobased raw materials such as used cooking oils and sustainably produced vegetable oils to produce the raw materials for Bio-PP on a commercial scale. In autumn 2019 and spring 2020, several plastic producers announced the large-scale production of bio-PP based on it (see chapter 2.4.2) [98, 99, 100, 101, 102].

A Japanese company announced the development of biobased polypropylene in 2019. Its method involves fermenting various types of biomass, mainly non-edible plants, to isopropanol (IPA), which is then dehydrated to produce propylene [36].

### 3.3.5 Biobased Polyvinylchloride

Ethylene from bioethanol can also be used for the production of partially biobased polyvinyl chloride (PVC). Appropriate efforts were made around 10 years ago, mainly in Brazil. [35].

A Belgian chemical company launched partially biobased PVC on the market in early 2020, which is also produced using biobased ethylene [110].

Research is more active, however, in the field of plasticizers for fossil-based PVC. Many conventional plasticizers, especially the so-called phthalates, are hazardous to health and can, for example, have a disruptive effect on hormone balance [81]. New, biobased alternatives to conventional plasticizers in PVC are now being developed, for example on the basis of PHA [81, 82].

### 3.3.6 Biobased Epoxy Resins

Another thermoset resin which is used in boat building, but also in aerospace, automobile racing, for the production of tennis rackets or wind turbines are epoxy resins. Such epoxy resins are often reinforced with reinforcing fibres such as glass fibres, carbon fibres, aramid fibres (Kevlar®, Twaron®), but also with natural fibres.

The possible ways of producing epoxy resins are very different and complex. For example, epoxidized vegetable oils, mainly linseed oil, are used to produce biobased epoxy resins. Applications include structural polymers and epoxy foams as well as functional polymers (e.g. epoxy resins for adhesives and coatings).

Epichlorohydrin is also frequently used, which can be produced from biobased glycerine, a waste product of biodiesel production [39]. 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 [40]. The researchers produced a polyamine from grape seed oil which is then used as a hardener for a reaction with epoxidized linseed oil.

### 3.3.7 Other biobased plastics

As can be seen so far 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. These monomers or building blocks are mostly used for biobased polyamides and polyesters.

As a fast-growing source of renewable biomass, algae have aroused the interest of many researchers. The first products are already available on the market. Some companies are using algae as a filler material. Two North American manufacturers announced as early as in 2015 that they planned to produce the world's first flexible foams using algae products as fillers [83].

Another company, located in Mississippi (USA), uses algae biomass, which is extracted from freshwater sources around the world to produce EVA foams, a process that at the same time serves to cleanse these sources. To manufacture the flexible, pliable foam, the extracted algal biomass is dewatered and dried, polymerized and finally mixed with other ingredients. The biobased content (algae content) of the end product is between 15 and 60 %, depending on the formulation and application [84].

In addition, there are many other approaches to produce bioplastics or building blocks from the most diverse, sometimes exotic-looking sources of raw materials. Examples include whey, chicory roots or sunflower seed shells, as well as slaughterhouse waste, feathers or the shells of crustaceans.

Any approach to replace fossil-based carbon with "young" carbon from a renewable resource is a step in the right direction.

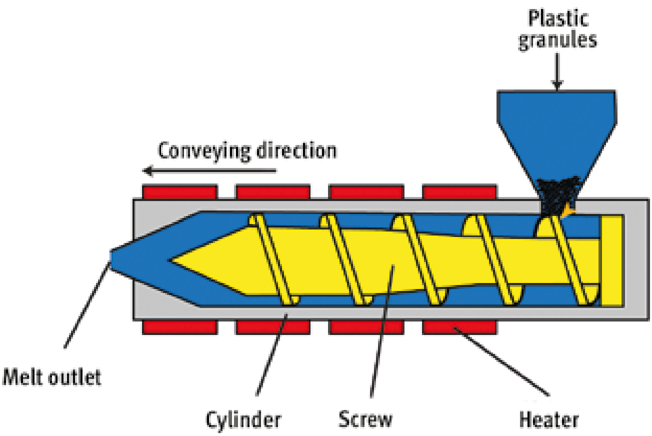
# 4 METHODS OF PROCESSING PLASTICS

## 4.1 Introduction

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. 4.2). 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. It is melted, homogenised and then delivered to the mould via a so-called injection nozzle.


*Fig 4.1: Plastifying screws for plastics*

**SKETCH OF A PLASTIFYING UNIT**



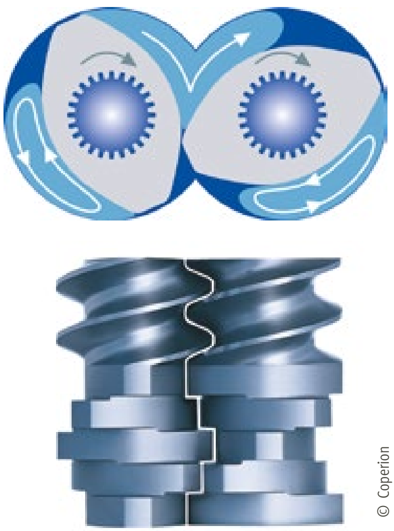

Source: Michael Thielen



*Fig. 4.2: Sketch of a plastifying unit*

## 4.2 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. 4.3: Principle of a synchronized twin screw extruder*

Compounding is often done in a twin-screw extruder specially built for this purpose, and where the components can be particularly thoroughly mixed together and homogenised. (Fig. 4.3).

## 4.3 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.

### 4.3.1 Extrusion

Extrusion 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 (see chapter 4.3.5).

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) [42].

By adding a foaming agent a foamed extrudate can also be produced (see chapter 4.3.6).

And finally extruders may also be part of an installation for complex processes such as film blowing (chapter 4.3.2) or extrusion blow moulding (chapter 4.3.4).

## 4.3.2 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.

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.


*Fig. 4.4: Blown film extrusion*

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].

## 4.3.3 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.

*Fig. 4.5: Injection moulding machine*

### 4.3.4 Blow moulding

Plastic hollow articles are mostly produced by blow moulding. There are various processes available but the most commonly used are extrusion blow moulding and stretch blow moulding. [43, 45].

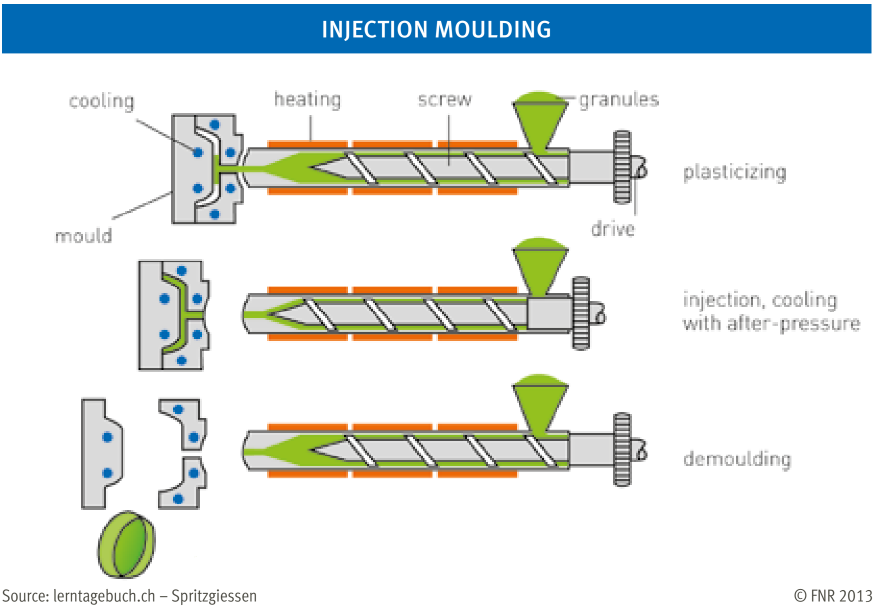


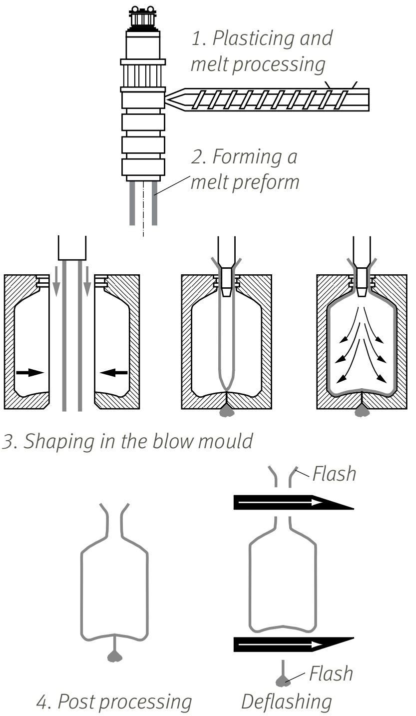

*Fig. 4.6: The injection moulding process*

In extrusion blow moulding the thermoplastic melt is produced in an extruder from where it is ejected vertically downwards through an annular die to create a soft tubular “preform”. A mould consisting of two vertical halves (the blow mould) is closed 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 on the shape of the mould. The blow mould is opened and the plastic hollow article is removed. Finally, the remnants (known as the flash) cut from the squeezed ends are removed.

© Ferbedo

*Fig. 4.8: Kid‘s ride-on truck made of bio-PE*

**EXTRUSION BLOW MOULDING**




Source: Blasformen von Kunststoffhohlkörpern (Thielen, Hartwig, Gust) [43]

© FNR 2020

*Fig. 4.7: Extrusion blow moulding*

Typical areas of application for this process are bottles (shampoo, ketchup, detergents etc.), canisters, barrels, tanks and also leisure and sports equipment such as kayaks or kid’s ride-on cars, plus lots more.

In the 1990s, an extrusion-blowmoulded shampoo bottle made from a polyhydroxyalkanoate (PHA) was introduced to the market. The most recent examples include a kid‘s ride-on truck made from Bio-PE [44].

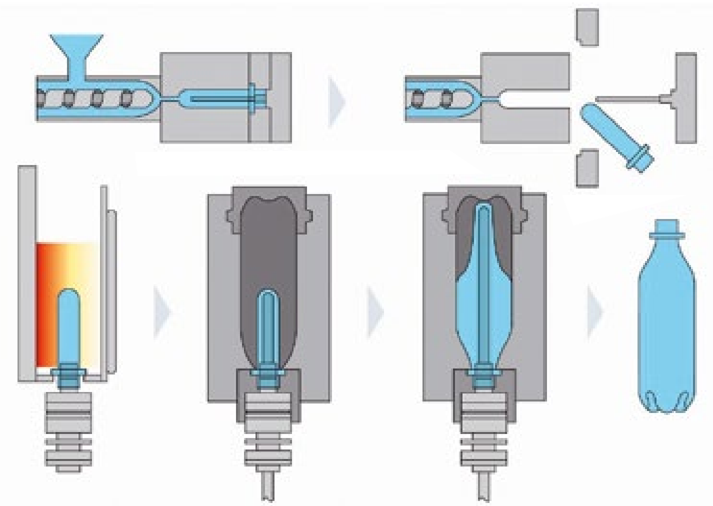
A different process to the versatile extrusion blow moulding technique is stretch blow moulding which is used almost exclusively for the manufacture of (beverage) bottles. Here a small preform that resembles a test tube with a screw thread at the neck is first injection moulded.

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.

Bioplastics that can be processed by stretch blow moulding include Bio-PET, PEF and PLA.


*Fig. 4.9: Preforms and bottles (left to right: PLA, PP, PET)*

**STRETCH BLOW MOULDING**



Source: KHS Corpoplast



*Fig. 4.10: Stretch blow moulding*

### 4.3.5 Thermoforming

By thermoforming (also 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]. Heat and high-pressure air are used, and sometimes a vacuum, plus where required a mould to help stamp the three dimensional shape.


*Fig. 4.11: Thermoformed meat packaging made from PLA*

The film is drawn from a large roll or in-line directly from an extruder and fed 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 station the film is held firm by clamping frames. Where necessary a stamping 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 ejected from the mould tool and at the next station is punched out of the remaining flat film.

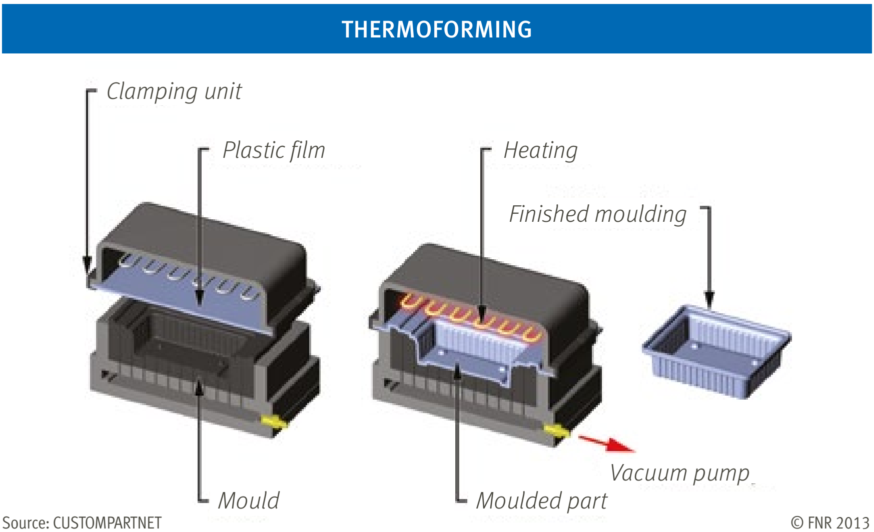



*Fig. 4.12: Thermoforming*

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.

### 4.3.6 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. hydrocarbons) are added to the plastic which vaporise during the polymerisation process and so form the typical gas bubbles. Chemical foaming is similar to the use of baking soda. Chemical foaming agents are often solids that are added to the plastic and which break down at higher temperatures, releasing gases [46]. And in mechanical foaming gas is simply blown into the plastic melt as it is being agitated (cf. whipped cream).

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 3.3.3).



*Fig. 4.13: Particle foam made of a PLA/PBAT-Blend*

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) have been successful in penetrating the market [47]. 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. For some years now, a particle foam made of a PLA/PBAT blend has also been available (fig. 4.13) [89].

Particle foams made from pure PBAT and blends with other bioplastics were presented by a Chinese company in 2019 [105].

### 4.3.7 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.

### 4.3.8 Thermoset processing

Unlike thermoplastics, thermoset resins are cross-linked plastics that cannot be shaped under the influence of heat or be remelted. 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.

### 4.3.9 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..

### 4.3.10 Joining of plastics

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].

In contrast to welded films, peel films have a predetermined breaking point along the sealed seam to allow the upper film to be pulled away from the lower one with little force – peeling. This consumer-friendly sealing technology has become indispensable in many food packages (sausage, meat, coffee and snacks). The technical feasibility of peel films made of biobased plastics, such as PLA, is currently being investigated.

# 5 APPLICATIONS

Bioplastics are used today in numerous applications. Chapter 7 examines the recent market statistics in some detail.

## 5.1 Packaging

Alongside simple, foamed packaging chips (loose fill) based on starch (Fig. 5.1), 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].

First packaging applications of bioplastics were 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), cups for dairy produce, 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].



*Fig. 5.1: Starch-based packaging flakes*

Coating of paper and cardboard laminates with bioplastics leads to new packaging with good moisture and fat or oil resistance [48].

In the USA a mineral water bottle made from PLA bioplastic was launched as early as 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 since 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 in the long run as a selling point.

The packaging sector is still considered to have huge growth potential for bioplastics. Even though the disposal of used packaging made of these plastics can be carried out in various ways (see chapter 6), it should be borne in mind that disposal via composting is not possible in Germany due to legal regulations.

Catering products are usually as short-lived as packaging. Once used, cups, plates and cutlery, together with the adhering food leftovers, end up in the trash, which quickly accumulates in large quantities at parties and other large events. Tableware made of biobased and compostable plastic, offers an alternative. This means that catering products can be recycled together with the food leftovers (where permitted).


*Fig. 5.2: Thin fruit bags are suitable for use for collecting biowaste*

*Fig. 5.3: Fruit net made from bioplastics*


*Fig. 5.4: Tubes made from bio-PE*


*Fig. 5.5: Catering-Service ware made from PLA*

## 5.2 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. 5.6) 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. 5.7) are also cost savers and can be used for tying up tall-growing plants such as tomatoes or for other fixing purposes. 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, bioplastic alternatives can be disposed of on the normal compost together with plant waste [1].

Compostable, pre-sown seed strips and encapsulation for active substances are commonly 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 centres. Film, woven fabric and nets made from biodegradable plastics are used to hold back recently laid roadside banks and similar, and prevent soil erosion until they are stabilised by plants.



*Fig. 5.6: Mulch film*

*Fig. 5.7: A net vine clip made of a wine pomace biocomposite holds a net to protect ripening grapes*

## 5.3 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, 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 jars for powders or cremes are just as readily available, as are 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.

## 5.4 Consumer electronics

In contrast to the medical area, or in horticulture, 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.

In 2015, a Japanese smartphone was equipped with a touch panel front screen made of an isosorbide-based bioplastics (see chapter 3.3.1 – Biobased polycarbonate). Compared to glass, this material is characterized by its good impact resistance and is partly biobased. Today, a wide range of electronic devices from computer mice and keyboards to headphone components


*Fig. 5.8: Smartphone with isosorbide based bioplastics in the touch panel*

© FKuR/Fujitsu | allefarben-foto

*Fig. 5.9: Computer keyboard with a cellulose plastic based lower housing and a hand-rest (black) made from lignin-based plastic*

*Fig. 5.10: Computer mouse made from PLA*

with housings or components made of bio-based plastics are already available on the market.

## 5.5 Automobile manufacture

As mentioned in chapter 3.1 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. Since 2011, Ford has been using soy-based polyol as a polyurethane component for seats, headrests or armrests in all vehicles built in North America.

Another pioneer in this process is Toyota. In the "Prius", one of the Japanese manufacturer's first hybrid vehicles, a spare wheel cover made from PLA with kenaf reinforcement was introduced. In a hybrid limousine from Toyota, which is only available in Japan, as well as in Honda, the seat covers and carpets were made of partially bio-based PET for the first time [49].

In the engine compartment plastics based on renewable resources are also used. Polyamide 11 made from castor oil has been used in automotive applications for more about 70 years and is eminently suitable for fuel lines and connectors, especially for the very aggressive bioethanol (E10 etc.) and biodiesel fuels. In 2013 Mercedes presented an A-Class model in which a completely biobased PA 4.10 was used to produce the engine compartment cover [90].

A partially biobased polyester-elastomer was the basis for the development of a fully functional steering wheel with integrated airbag, which consists of more than 50% renewable raw materials [50].

The isosorbide-based bioplastic, which has already been mentioned several times, is used by Mazda, among others, as an unpainted high-gloss component in the radiator grille [88].


*Fig. 5.11/5.12: Mazda CX-5: Radiator grille Mazda CX-5 made from isosorbide-based plastic*

Research work on the so-called "bioconcept car", which serves as a model for the testing of various biobased, partially fibre-reinforced car body components [66], shows that load-bearing body parts can also be produced from biobased materials.


*Fig. 5.13: Car door made of natural fibre reinforced plastic*

## 5.6 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.

The examples of the various applications are almost endless and go from children's shoes or bathing suits and wedding dresses to men's business shirts and haute couture apparel.

In fact, textiles made from renewable resources are almost as old as the human race: linen, cotton and other natural fibres have a long history. 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.

An Austrian supplier of cellulose-based viscose fibres, Modal fibres and Lyocell fibres received further international certifications in 2019 from an independent Belgian research laboratory, confirming that these fibre products are biodegradable in industrial composting as well as in soil, fresh and sea water [106].


*Fig. 5.14: T-Shirt made from 100 % biobased PET*

## 5.7 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.


*Fig. 5.15: Carpet made from PTT-fibres*


*Fig. 5.16: PLA based edge banding*

Biobased plastics are also finding their way into the furniture industry. In 2019, a PLA-based edge banding for furniture boards was launched in the USA (Fig. 5.16). An Italian company introduced a chair in 2017 and a modular storage system made of PHA in 2019 (Fig. 5.17).

In 2013, several Stuttgart university institutes presented a moss façade module for outdoor use based on thermoformed PLA-based elements (Fig. 5.18). The moss takes up fine dust as fertiliser and converts it into plant mass. In addition, 1 cm³ of moss has a surface area of 0.17 m². This surface enlargement by a factor of 30 also provides high sound absorption [91].


*Fig. 5.17: Modular storage system made of PHA*

*Fig. 5.18: Bioplastics facade*

## 5.8 Sport and play

Plastic is the most commonly used material for toys and many leisure products. Plastics continue to take precedence over wood, cardboard and textiles (including plush), which, ultimately, are also very often made of synthetic fibres. Since toys should be as healthy and sustainable as possible, the first responsible manufacturers of plastic toys have started to switch to plastics derived from biobased materials.

Baby toys made of PLA, bio-PE or starch-based bioplastics have been launched in the market. Beach toys are available that are made from bio-PE or PHA, with PHA offering the added advantage that it is claimed to be biodegradable in seawater if accidentally “lost”.

Further examples are building blocks made of bioplastics filled with wood fibre or wood flour or toy cars and tractors made from Bio-PE or WPC.


*Fig 5.19: Click-system elements made of PLA/PHA blend*

There is even a range of toddlers' ride-on cars now available that is made of Bio-PE (see Fig. 4.8).

And since 2018, a well-known Danish manufacturer of children's building bricks has been producing certain elements – the soft trees and bushes – from bio-PE.

The number of applications is also steadily increasing in the sports and leisure sector. The handle of a Nordic Walking pole made of partially biobased polyamide 6.10 was presented back in 2009, as were ski boots as well as sports shoes with parts made of biobased elastomers targeted at a wide range of sports. The sports range is complemented by eyewear and sunglasses with high-quality optical "lenses" made of clear biobased polyamide.

The ball used for the 2010 Soccer World Cup was largely made of a biobased elastomer (Fig. 5.21).


*Fig. 5.20: Building bricks made of wood-filled Bio-PE*


*Fig. 5.21: World Cup 2010 ball made of biobased elastomer [107]*

## 5.9 Household

Desk utensils can be made from PLA. Adhesive tapes made of cellulose materials or biaxially oriented PLA (BoPLA) are now also combined with other biobased adhesives.

In 2017, a grain mill was introduced with a housing consisting of a special blend based on PLA/PHA (Fig. 5.23).

Further examples include food storage containers made of bio-PE or PLA/PHA blends, glue sticks with bio-PE housings, highlighter markers and much more.


*Fig. 5.22: Desk utensils made from PLA*


*Fig. 5.23: Grain mill with PLA/PHA blend housing*

# 6 RECYCLING – RECOVERY – DISPOSAL

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. Of course here too, as with other valuable materials, closed cycles should be aimed for.

According to the German Circular Economy Act (Kreislaufwirtschaftsgesetz, KrWG) amended in 2012, circular economy is defined as "avoidance and recycling of waste".

In the recovery of bioplastics, the focus should always be on recycling both the stored biobased carbon as well as the stored energy in technical cycles. Bioplastics in particular enable the intelligent use of resources and ensure high added value in a low-carbon economy.

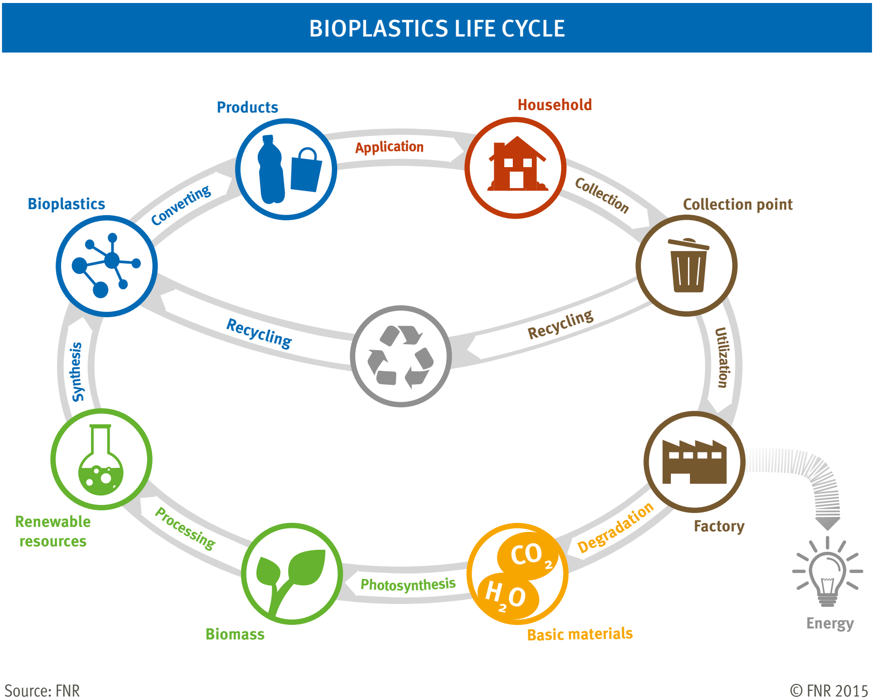



*Fig. 6.1: Bioplastics life cycle*

## 6.1 Relevant German laws and regulations

In Germany there are a number of laws and regulations that are also relevant for products made of biobased plastics. In addition to the End-of-Life Vehicles Ordinance (AltfahrzeugV), the Battery Act (BatterieG) and the Electrical and Electronic Equipment Act (ElektroG), these is currently mainly the Packaging Act (VerpackG).

### 6.1.1 German Packaging Act

The German Packaging Act (VerpackG) regulates the introduction of packaging on the market and the handling of used packaging. It came into force on 01.01.2019 and has replaced the Packaging Ordinance (VerpackV) which was valid until then.

According to § 21, section 1, sentence 2 of the Packaging Act, the use of renewable raw materials is to be promoted in addition to the use of recyclates. For the collection and disposal of used sales packaging, the companies must calculate and collect fees in such a way that there are incentives to produce packaging from renewable raw materials. The legal objective is to “promote” this packaging within the scope of an “overall ecological” development (see [51]).

In addition to known packaging materials such as paper, cardboard or wood, this also includes plastic packaging that is at least partially made from renewable (biobased) raw materials. Such products, which include various polymers and packaging applications, have considerable economic and ecological potential in terms of sustainable development. Here § 21 (1, 2) of the Packaging Act (see [51]) may provide assistance.

### 6.1.2 German Ordinance on Biowaste

With the amendment of the German Ordinance on Biowaste (BioAbfV – Ordinance on the Utilisation of Biowaste on Soils Used for Agriculture, Forestry and Horticulture) in mid-2012, composting as a disposal option for biodegradable plastic products was severely restricted. As a result, only a few products, such as certified compostable organic waste bags or coffee capsules, are currently allowed in the organic waste bin in Germany, and only where the competent local authorities do not impose any further restrictions.

## 6.2 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 Circular Economy Act (KrWG) defines recycling as – “any recovery process by which waste is processed into products, materials or substances either for the original purpose or for other purposes. It includes the processing of organic materials, but does not include energy recovery and processing into materials intended for use as fuel or for filling of voids. – Composting is thus considered as a recycling process, but it is considered separately here under the aspect of “biological treatment”.

Sorting of the waste as pure as possible is an essential prerequisite for the recycling processes presented here.

### 6.2.1 Material recycling

Material recycling, physically or mechanically, is in simple terms, the shredding, cleaning, remelting, and regranulating 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 and quality. Extremely pure waste such as production waste (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 "downcycling". 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 shopping bag, then a rubbish sack and finally 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 recycled. In some cases, depending on the circumstances, additional steps are required.

It may however, be necessary e. g. for PLA to go through an additional step of polycondensation, or a special crystallisation stage.

A material recycling of so-called drop-in bioplastics (Bio-PE, Bio-PP, Bio-PA, Bio-PET, etc.) is completely unproblematic, even together with the petroleum-based types, as these are chemically absolutely identical. The material recycling of new types of bioplastics, such as PLA, is also technically feasible. Due to the currently still too small quantities, however, this is not yet economically feasible. Small quantities of such bioplastics (PLA, PHA) also do not pose a problem of contamination when co-recycling with mass plastics [108].

### 6.2.2 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 recovery.

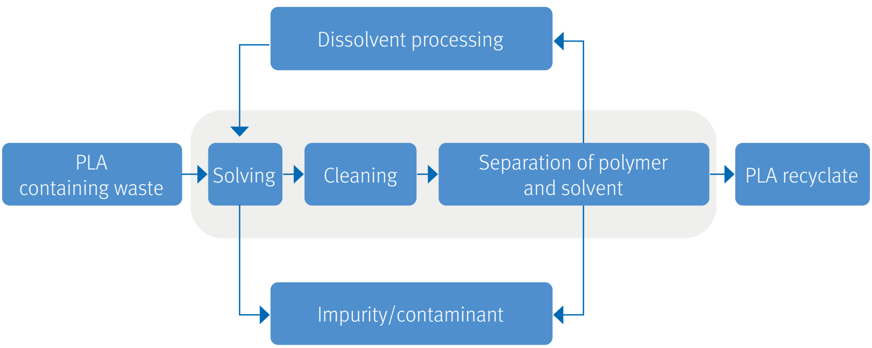
Another approach is the solvent-based recycling of PLA. This has already proven successful for conventional thermoplastics (PET, PS, ABS, PA, PVC etc.) and produces very pure and high-quality polymer recyclates from contaminated and heterogeneous waste. Waste is treated with a specific solvent that is capable of selectively extracting PLA from waste mixtures, composite packaging and PLA blends (SustRecPLA Process, see Fig. 6.2) [92].

Another example is the chemical recycling of PLA. In installations such as are currently operating in USA and Belgium the polylactic acid is reconverted into lactic acid and can then be converted into new PLA or be used for other purposes [93, 94].

## 6.3 Energy recovery

Bioplastics can, after use and after being recycled a maximum number of times, still be burned and the stored 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.

**SUSTRECPLA PROCESS**




Source: Fraunhofer IVV



*Fig. 6.2: SustRecPLA Process*

## 6.4 Biological treatment

### 6.4.1 Composting

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

There are plenty of examples where biodegradability, or disposal by composting, does in fact bring additional benefits.

At events catering cutlery, tableware and food remnants can be taken together to a composting facility (where it is permitted and a respective infrastructure is available).

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 green plant residues. 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 (see chapter 5.2).

**Definition, standards and certification: "compostable"**

A substance or a material is biodegradable if it is broken down by micro-organisms such as bacteria, protozoa[3], fungi, or enzymes. The micro-organisms use the substances as nutrients or a source of energy. The remainder of the broken-down substance consists of carbon dioxide ($CO_2$), water and mineral salts of the other elements present (mineralisation), [6].

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 any case, it should be borne in mind that the energy content stored in the plastic, which becomes waste heat during composting, cannot be used and is therefore lost.

Particularly with regard to environmental degradability, there is currently much discussion about degradation in soil as well as in fresh and sea water. It should be noted that degradability in these environments cannot provide solutions to the issues of littering (careless disposal), marine pollution from plastic waste, including the microplastic problem. All this is a question of the behaviour of the population and waste management in certain countries, which cannot be solved by special materials.

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

Plastic products intended to be industrially composted must first be certified in accordance with the standards, e.g. EN 13432 [59] or more generally to plastics (EN 14995 [60], ASTM D6400 [61]). In Europe DIN CERTCO (Germany) and TÜV Austria (Belgium) belong to independent certification associations. In the USA this is governed by the BPI (Biodegradable Products Institute). If the set standard values for the time-dependent conversion of carbon into $CO_2$, the loss of physical properties such as weight and size as well as the toxicological properties of produced composts are complied with, a corresponding registered label may be awarded. A material that has the right to carry such a compostability label will completely degrade in the composting installation within 6 to 12 weeks.

As mentioned at the beginning of this chapter, the German Biowaste Ordinance (BioAbfV) currently permits only a few products in the biowaste collection bins for industrial composting. Figures 6.3 to 6.5 show the most well known logos [62, 63, 64].

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

*Fig. 6.3: Logo for industrial composting (European Bioplastics)*

*Fig. 6.4: Logo for industrial composting (DIN CERTCO)*

*Fig. 6.5: OK-Compost-Logo (TÜV Austria)*

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.

*Fig. 6.6: Logo for garden composting (DIN CERTCO)*

### 6.4.2 Anaerobic digestion

Another possibility of utilization is biogasification, also called Anaerobic Digestion (AD) or fermentation. Here, microorganisms decompose biogenic material in the absence of oxygen, i.e. under anaerobic conditions [52].

Biological waste, such as from the organic waste bin or liquid manure from agricultural production, is suitable for fermentation. The methane gas produced during the fermentation process can also be used to generate energy. The fermentation residues are reused in different ways (e.g. composting, fertilisation, drying and incineration).

The possibilities of converting waste from biodegradable plastics in biogas plants into methane that can be used as energy are currently investigated intensively.

# 7 MARKET

## 7.1 Introduction

For several years now, renewable raw materials have been used in large quantities for the production of plastics, especially in the field of functional polymers (see chapter 1) [53].

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.

Until a few years ago the bioplastics market was mainly characterised 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 years this situation has changed significantly. The market is now dominated by so-called drop-in bioplastics. These are biobased or partially biobased “conventional” plastics such as bio-polyethylene (PE), bio-polyamide (PA), bio-polyethylene terephthalate (PET). The speed with which this fundamental change swept the market was made possible, on the one hand, by the fact that several globally active companies, especially in the food packaging sector (beverage bottles), switched to the use of these bioplastics to package their products. On the other hand, these drop-in bioplastics were produced in comparatively large quantities from the very beginning at large plants. As these drop-in bioplastics have the same properties as their petroleum-based counterparts, they must compete directly on price with their conventional, petro-based siblings, which means that mass production at large-capacity plants plays an important role in their market launch [54].

## 7.2 Market overview

Every year, various institutions publish up-to-date market overviews and forecasts. These include, for example, the “Biopolymers facts and statistics” [95] report from the Institute for Bioplastics and Biomaterials at the University of Applied Sciences and Arts Hannover (IfBB) and the “Bioplastics market data” [96] published by the European Bioplastics Association, which are compiled in cooperation with the nova-Institut.

As can be seen in Fig. 7.1, production capacities for bioplastics are expected to increase to more than 2.4 million tonnes by 2024 [96].

Fig. 7.2 shows the types of bioplastics represented in these market figures. It shows

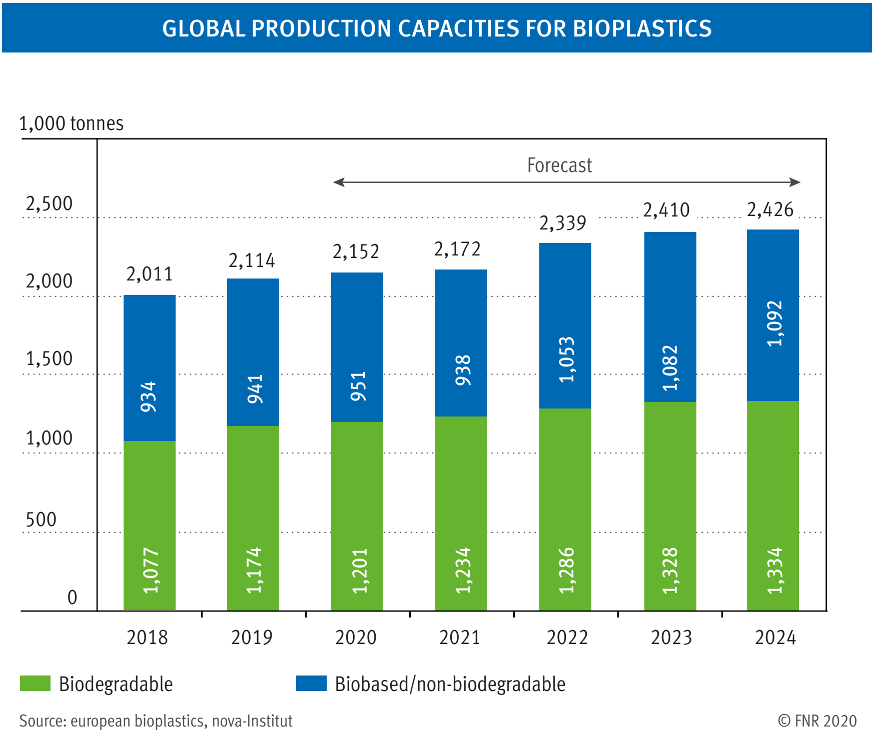
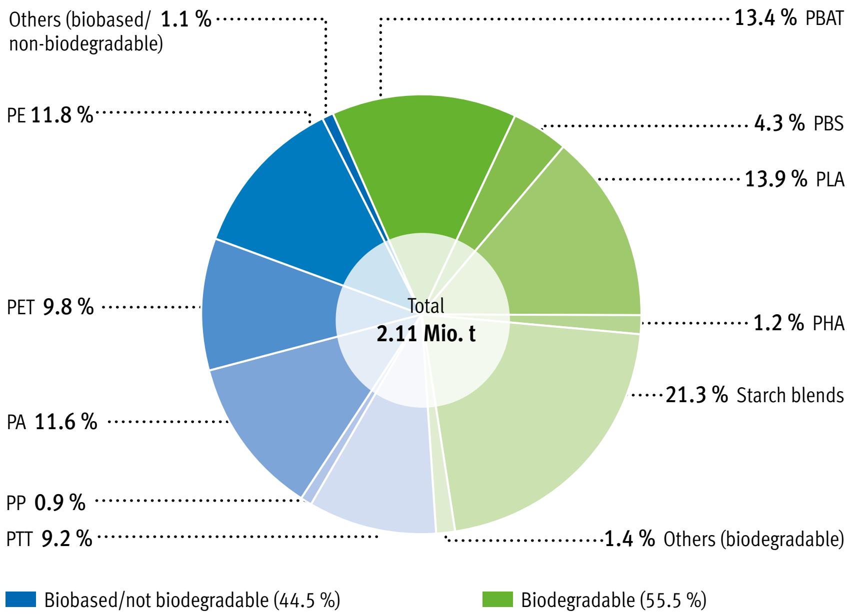



*Fig. 7.1: Global production capacities for bioplastics (Values estimated from 2020 onwards)*

the production capacities for bioplastics broken down by plastic type for 2019.

Despite the market growth rates described above, bioplastics are still at the beginning of their development. With a total market for plastics of an estimated 348 million tonnes in 2017 [3], bioplastics will account for no more than 2 % in quantitative terms in the next few years. From a purely technical point of view, however, up to 90 % of all plastics could be converted from fossil to renewable sources. In the short and medium term, however, this conversion will not be possible due to economic hurdles and the short-term unavailability of biomass [56].

MARKET SHARES OF THE DIFFERENT TYPES OF BIOPLASTICS




Source: european bioplastics, nova-Institut



*Fig. 7.2: Market shares of the different types of bioplastics (2019)*

# 8 ANNEX

## 8.1 Internet links

| | |
|---|---|
| www.fnr.de | FNR – General Information |
| www.biowerkstoffe.fnr.de | FNR – Information about bioplastics |
| www.bmel.de | BMEL – Information on on the biobased economy and renewable resources |
| www.european-bioplastics.org | Information of the European trade association |
| www.bio-based.eu | News portal |
| www.bioplasticsmagazine.com | Trade magazine and News portal |
| www.materialdatacenter.com | Biopolymer database |

## 8.2 Bibliography


[1] Lörcks, J.: Biokunststoffe, Broschüre der FNR, 2005

[2] N. N.: Wikipedia, Internet access 01/2020

[3] N. N.: Plastics – the Facts 2019, An analysis of European plastics production, demand and waste data, Plastics Europe, Brüssel, 2019

[4] DIN CEN/TR 16208:2011-07 (D) „Biobasierte Produkte – Übersicht über Normen; Deutsche Fassung CEN/TR 16208:2011“

[5] Endres, H.-J.; Siebert-Raths, A.: Technische Biopolymere, Carl Hanser Verlag, 2009

[6] N. N.: DIN EN ISO 14855-1

[7] N. N.: Leistungsfähig und bioabbaubar, Presseinformation P-09-445, BASF 2009

[8] Kamm, B.; Kamm, M.; Schmidt, M.; Hirth, T.; Schulze, M.: Lignocellulose-based Chemical Products and Product Family Trees. In: Kamm, B.; Gruber, P.R.; Kamm, M. (Hrsg.): Biorefineries – industrial processes and products. Status quo and future directions. Wiley-VCH, Weinheim 2006, ISBN 3-527-31027-4, S. 67–84

[9] N. N.: www.duponttateandlyle.com, Internet access 01/2020

[10] N. N.: https://bioplasticsnews.com/wp-content/uploads/2018/08/bio-bdo-novamont.pdf, Internet access 01/2020

[11] N. N.: www.clib2021.de, Internet access 02/2012

[12] Raschka, A.: Machbarkeits- und Potenzialstudie zu den Nutzungsmöglichkeiten von biomassebasiertem Synthesegas, http://nova-institute.eu/project/machbarkeits-und-potenzialstudie-zu-den-nutzungsmoglichkeiten-von-biomassebasiertem-synthesegas/, Internet access 01/2020

[13] Worden, E. C.: Nitrocellulose industry. New York, Van Nostrand, 1911, S. 568. (Parkes, Englisches Patent 2359 aus dem Jahr 1855)
[14] Carus, M.; Scholz, L.: How to Measure the Bio-based Content, bioplastics MAGAZINE, Vol. 5, Issue 03/2010
[15] Bastioli, C.: Basics of Starch-Based Materials, bioplastics MAGAZINE, Vol. 4, Issue 05/2009
[16] Zepnik, S.; Kesselring, A.; Kopitzky,R.; Michels, C.: Basics of Cellulosics, bioplastics MAGAZINE, Vol. 5, Issue 01/2010
[17] N. N.: Weltproduktion von Chemiefasern, https://www.ivc-ev.de/de/weltproduktion-von-chemiefasern-balkendiagramm, Internet access 02/2020
[18] N. N.: Steigerung der Leistungsfähigkeit von biobasierten Kunststoffen, http://www.dupont.de/produkte-und-dienstleistungen/plastics-polymers-resins/thermoplastics/brands/hytrel-thermoplastic-elastomer/products/hytrel-rs-biobased-polymers.html, Internet access 09/2019
[19] N. N.: www.pebax.com, Internet access, 01/2020
[20] Fink, H.-P.: Basics of Lignin, MAGAZINE, Vol. 6, Issue 01/2011
[21] Fink, H.-P.; Engelmann, G.; Ebert, A.: Lignin als Polymerwerkstoff, FNR-Fachgespräch Stoffliche Nutzung von Lignin, Berlin, 03/2009
[22] N. N.: Stoffliche Nutzung von Lignin, Gülzower Fachgespräche, Band 31, FNR, 2009
[23] N. N.: www.wdk.de, Internet access 01/2020
[24] N. N.: Bio-Based Biodegradable PHA Foam, bioplastics MAGAZINE, Vol. 5, Issue 01/2010
[25] Fernyhough, A.: From Waste 2 Gold: Making bioplastic products from biomass waste streams, bioplastics MAGAZINE, Vol. 2, Issue 04/2007
[26] N. N.: High heat becomes a reality (2017), https://www.total-corbion.com/about-pla/performance/, Internet access 09/2019
[27] N. N.: Mazda introduced 'Biotechmaterial' for interior applications, bioplastics MAGAZINE, Vol. 3, Issue 02/2008
[28] Inomata, I.: The Current Status of Bioplastics Development in Japan, bioplastics MAGAZINE, Vol. 4, Issue 01/2009
[29] N. N.: The Coca-Cola PlantBottle, bioplastics MAGAZINE, Vol. 5, Issue 06/2010
[30] N. N.: Bio-PET, bioplastics MAGAZINE, Vol. 5, Issue 06/2010
[31] Morgan, K.: Completing the Puzzle: 100 % plant-derived PET, bioplastics MAGAZINE, Vol. 6, Issue 04/2011
[32] Thielen, M.: Basics of bio-polyamides, bioplastics MAGAZINE, Vol. 5, Issue 03/2010
[33] Mostyn, T.: Global polyethylene capacity growth to be led by Asia and North America, https://www.hydrocarbonengineering.com/petrochemicals/22042019/global-polyethylene-capacity-growth-to-be-led-by-asia-and-north-america/, Internet access 10/2019

[34] N. N.: Mitsui Chemicals working on commercialisation bio-PP, https://www.bioplasticsmagazine.com/en/news/meldungen/20190930Mitsui-Chemicals-working-on-commercialisation--bio-PP.php, Internet access 10/2019
[35] N. N.: Solvay Indupa will produce bioethanol-based vinyl in Brasil, Solvay Presse-Information, 12/2007
[36] Smith, C.: Braskem commits to producing bio-based polypropylene, Plastics News online, 28.10.2010
[37] Mannermaa, T.: The First Step to Sustainable Composites, bioplastics MAGAZINE, Vol. 6, Issue 03/2011
[38] N. N.: Full System Ahead: The Rise of Bio-Based Thermoset, bioplastics MAGAZINE, Vol. 6, Issue 03/2011
[39] Boonyaporn, P.: Enabling Sustainable Epoxy Resins, European Coatings Journal 04 – 2019
[40] Stemmelen, R. et al.: A Fully Biobased Epoxy Resin from Vegetable Oils, Journal of Polymer Science Part A: Polymer Chemistry, 49: 2434–2444. doi: 10.1002/ pola.24674
[41] Verlinden, R.; Hill, D.; Kenward, M.; Williams, C.; Piotrowska-Seget, Z.; Radecka, I.: Production of polyhydroxyalkanoates from waste frying oil by Cupriavidus necator, www.amb-express.com/content/1/1/11, Internet access 12/2011
[42] N. N.: How to Produce BOPLA Films, bioplastics MAGAZINE, Vol. 5, Issue 06/2010
[43] Thielen, M.; Hartwig, K.; Gust, P.: Blasformen von Kunststoffhohlkörpern, Carl Hanser Verlag, 2. Auflage 2019
[44] Petrascheck, E.: You never forget your first car, bioplastics MAGAZINE, Vol. 14, Issue 03/2019
[45] Yoder, L.; Plastic Technologies, Inc.: Basics of Stretch Blow Moulding, bioplastics MAGAZINE, Vol. 6, Issue 04/2011
[46] Oberbach, K.; Baur, E.; Brinkmann, S.; Schmachtenberg, E.: Saechtling Kunststoff-handbuch, Carl Hanser Verlag, München, Wien, 2004
[47] N. N.: Kaneka @ Foam Expo Europe 2018, http://www.kaneka.be/news/kaneka-foam-expo-europe-2018, Internet access 10/2019
[48] Manjure, S.: PLA for Paper Coating, bioplastics MAGAZINE, Vol. 6, Issue 05/2011
[49] N. N.: Toyota setzt auf Biokunststoff, http://nachrichten.rp-online.de/auto/toyota-setzt-auf-biokunststoff-1.2509333, Internet access 01/ 2020
[50] Gaumann, U.: Biobased polymers for automotive safety components, bioplastics MAGAZINE, Vol. 8, Issue 01/2013
[51] Kaeb, H.: Infopapier: Biobasierte Kunststoffverpackungen im Verpackungsgesetz (FNR) https://biowerkstoffe.fnr.de/fileadmin/biopolymere/dateien/pdfs/Infopapier-Systeme-final.pdf, Internet access 01/2020

[52] de Wilde, B.: Basics of Anaerobic Digestion, bioplastics MAGAZINE, Vol. 4, Issue 06/2009
[53] Schütte, A.: Biobasierte synthetische Polymere – ein Überblick, Dechema, Workshop: Polymermonomere aus nachwachsenden Rohstoffen, 2011
[54] Carus, M. (Hrsg.): Market study on Bio-based Polymers in the world, 2013
[55] Endres, H.-J. et al.: Marktchancen, Flächenbedarf und zukünftige Entwicklungen, KUNSTSTOFFE 09/2011. S. 105ff
[56] Shen, L.; Haufe, J.; Patel, M.: Product overview and market projection of emerging bio-based plastics, PRO-BIB Studie, Universiteit Utrecht, 2009
[57] N. N.: Häufig gestellte Fragen zur Nutzung von landwirtschaftlichen Ressourcen für die Produktion von Biokunststoffen (FAQ Januar 2020), European Bioplastics
[58] Endres, H.-J.; Siebert-Raths, A.: Raw materials and arable land required for biopolymers, Bioplastics Magazine, Vol. 4, Issue 05/09
[59] N. N.: Verpackung – Anforderungen an die Verwertung von Verpackungen durch Kompostierung und biologischen Abbau – Prüfschema und Bewertungskriterien für die Einstufung von Verpackungen, Deutsche Fassung EN 13432:2000
[60] N. N.: Kunststoffe – Bewertung der Kompostierbarkeit – Prüfschema und Spezifikationen, Deutsche Fassung EN 14995:2006
[61] N. N.: ASTM D6400 – 04 Standard Specification for Compostable Plastics
[62] N. N.: Logos Part 1: The “Compostable” logo of European Bioplastics (Basics), bioplastics MAGAZINE, Vol. 1, Issue 01/06
[63] https://www.dincertco.de/de/dincertco/produkte_leistungen/zertifizierung_produkte/umwelt_1/industriell_kompostierbare_produkte/industriell_kompostierbare_produkte.html, Internetzugriff März 2020
[64] N. N.: http://www.tuv-at.be/de/ok-compost/zertifizierungen/ok-compost-seedling/ Internet access 01/2020
[65] N. N.: ASTM D6866: Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis
[66] Habermann, C.: Mobility of the future, bioplastics MAGAZINE, Vol. 8, Issue 01/2013
[67] Ziegler, L. et al.: Biopolymer Composites based on Lignin and Cellulose, bioplastics MAGAZINE, Vol. 6, Issue 01/2011
[68] Mangnus, P.: The world‘s next-generation polyester, bioplastics MAGAZINE, Vol. 7, Issue 04/2012
[69] Korving, L.: High quality PHBV from wastewater (Phario, Netherlands), Vortrag 1st PHA platform World Congress, 2018, Köln
[70] Mynářová, L.: PHA – Circular Economy Concept (Hydal/Nafigate, Czech Republic), Vortrag 1st PHA platform World Congress, 2018, Köln
[71] Thielen, M.: Bioplastic fibres from milk, bioplastics MAGAZINE, Vol. 8, Issue 05/13

[72] Chabance, P.: Packaging made with 100 % bio-based raw material (Lactips), Vortrag, 3. bio!PAC Konferenz, 2019, Düsseldorf
[73] Thielen, M.: Advances in the development of dandelion rubber, bioplastics MAGAZINE, Vol. 14, Issue 02/2019
[74] N. N.: First Bio-based EPDMRubber in the World, bioplastics MAGAZINE, Vol. 6, Issue 06/2011
[75] Bradford, J.: Green Thermoplastic Elastomer (TPE) compounds, bioplastics MAGAZINE, Vol. 11, Issue 05/2016
[76] N. N.: diverse Autoren: Vorträge beim 1st PHA platform World Congress 2018, Köln
[77] N. N.: BP, Virent Inc. and Johnson Matthey join forces to advance bio-paraxylene development, News am 11.03.2019, www.bioplasticsmagazine.com, Internet access 01/2020
[78] Garelik, A.: Making 100 % biobased PET a reality (Anellotech), Vortrag 3. bio!PAC Konferenz, 2019, Düsseldorf
[79] Kemeling, N.; van Berkel J.: PEF, a biobased polyester with a great future, bioplastics MAGAZINE, Vol. 10, Issue 04/2015
[80] N. N.: Pentamethylen-Diisocyanat liefert biobasierten Vernetzer für Polyurethane, www.farbeundlack.de, 16. Januar 2015, Internet access 01/2020
[81] N. N.: Biobasierte Weichmacher für PVC, https://biooekonomie.de/nachrichten/biobasierte-weichmacher-fuer-pvc, 7.12/2018, Internet access 01/2020
[82] Thielen, M.: New amorphous PHA grades as performance additives for PVC and PLA, bioplastics MAGAZINE, Vol. 11, Issue 01/2016
[83] Thielen, M.: Flexible foams with algae, bioplastics MAGAZINE, Vol. 10, Issue 05/2015
[84] Thielen, M.: Barefoot shoe made from algae, bioplastics MAGAZINE, Vol. 12, Issue 04/2017
[85] N. N.: Sorbitol, DocCheck Flexikon, https://flexikon.doccheck.com/de/Sorbitol, Internet access 01/2020
[86] N. N.: Durabio, https://www.mcpp-global.com/de/europa/produkte/brand/durabioTM/ Internet access 06/2019
[87] N. N.: In a world first, Sharp selects bio-based engineering plastic for smartphone front panel, https://www.bioplasticsmagazine.com/en/news/meldungen/20150710Shap-selects-Durabio-for-fron-panel.php, Internet access 06/2019
[88] Thielen, M.: Front grill of Mazda CX-5, bioplastics MAGAZINE, Vol. 13, Issue 01/2018
[89] Sampath, B.: New compostable particle foam, bioplastics MAGAZINE, Vol. 12, Issue 01/2017
[90] Thielen M.: Mercedes engine cover, bioplastics MAGAZINE, Vol. 8, Issue 02/2013
[91] Köhler, C.: Biobased plastics for exterior facades, bioplastics MAGAZINE, Vol. 8, Issue 04/2013

[92] N. N.: Nachhaltige Verwertungsstrategien für Produkte und Abfälle aus biobasierten Kunststoffen – SustRecPLA, https://www.ivv.fraunhofer.de/de/recycling-umwelt/recycling-von-verpackungen/sustrecpla.html, Internet access Juli 2019
[93] Fowler,P.; Kratz, W.; Tschida, R.: Chemically recycling post-consumer PLA, bioplastics MAGAZINE, Vol. 8, Issue 03/2013
[94] Thielen, M.: Capacity for PLA Feedstock Recovery to Expand Significantly, bioplastics MAGAZINE, Vol. 5, Issue 06/2010
[95] N. N.: Biopolymers facts and statistics, https://www.ifbb-hannover.de/files/IfBB/downloads/faltblaetter_broschueren/f+s/Biopolymers-Facts-Statistics-2019.pdf, Internet access 01/2020
[96] N. N.: Bioplastics market data, https://www.european-bioplastics.org/market/, Internet access 01/2020
[97] N. N.: Holz; https://www.chemie.de/lexikon/Holz.html, Internet access 09/2019
[98] Lipponen, K.: IKEA and Neste take a significant step towards a fossil-free future, https://www.neste.com/ikea-and-neste-take-significant-step-towards-fossil-free-future, Internet access 03/2020
[99] Lipponen, K.: Pionierarbeit auch bei biobasierten Kunststoffen, https://www.neste.de/releases-and-news/neste-setzt-auf-kunststoffabfaelle-als-rohstoff-fuer-kraftstoffe-und-kunststoffe, Internet access 03/2020
[100] N. N.: Polyolefins from bio-naphtha/Commercial-scale pilot plant to start-up in autumn, https://www.plasteurope.com/news/IKEA_NESTE_t240099/, Internet access 03/2020
[101] Stark, A.: Neste und Lyondell Basell starten kommerzielle Produktion von biobasierten Kunststoffen, https://www.process.vogel.de/neste-und-lyondell-basell-starten-kommerzielle-produktion-von-biobasierten-kunststoffen-a-840327/, Internet access 03/2020
[102] N. N: Borealis produziert zertifiziertes, erneuerbares Polypropylen in Belgien, https://www.plastverarbeiter.de/96100/borealis-produziert-zertifiziertes-erneuerbares-polypropylen-in-belgien/, Internet access 03/2020
[103] Ravenstijn, J.: Persönliche Information August 2019
[104] N. N.: Polypropylene Market To Reach USD 155.57 Billion By 2026; https://www.globenewswire.com/news-release/2019/08/01/1895698/0/en/Polypropylene-Market-To-Reach-USD-155-57-Billion-By-2026-Reports-And-Data.html, Internet access 02/2020
[105] Yanbo, L.: Lightweighting PBAT based materials, bioplastics MAGAZINE, Vol 14, No. 5, 2019
[106] N. N.: Cellulose based fibers fully biodegradable in water, soil and compost, bioplastics MAGAZINE, Vol. 14, No. 5, 2019

[107] N. N.: Pebax® Rnew selected for the first time in soccer ball!, https://www.arkema.com/export/shared/.content/media/downloads/news-attachments/global/en/press-release/2010/pr-sony-pebax-rnew-soccer-ball-va.pdf, Internet access 10/2019

[108] Hiebel, M. et al.: PLA im Abfallstrom, http://publica.fraunhofer.de/eprints/urn_nbn_de_0011-n-4872829.pdf, Internet access 10/2019

[109] N. N.: www.tecnaro.de, Internet access 01/2020

[110] N. N.: Bio-attributed PVC, https://www.vynova-group.com/bio-attributed-pvc, Internet access 03/2020

## 8.3 List of abbreviations

| | |
|---|---|
| ASTM | American Society for Testing and Materials |
| BMC | Bulk-Moulding-Compound |
| BDO | Butanediol |
| EN | European Norm |
| PA | Polyamid |
| PBAT | Polybutylene adipate terephthalate |
| PBS | Polybutylene succinate |
| PBSA | Polybutylene succinate adipate |
| PBT | Polybutylene terephthalate |
| PC | Polycarbonate |
| PDO | Propanediol |
| PE | Polyethylene |
| PEF | Polyethylene furanoat |
| PET | Polyethylene terephthalat |
| PHA | Polyhydroxyalkanoate |
| PHB | Polyhydroxybutyrate |
| PHBV | Poly-3-hydroxybutyrate-co-valerate |
| PLA | Polylactide (polylactic acid) |
| PP | Polypropylene |
| PTT | Polytrimethylene terephthalat |
| PVC | Polyvinylchloride |
| RTM | Resin Transfer Moulding |
| SMC | Sheet-Moulding-Compound |
| TPE | Thermoplastic Elastomers |
| TPS | Thermoplastic Starch |
| TPU | Thermoplastic Polyurethane |
| USDA | United States Departm. of Agriculture |
| WPC | Wood Plastic Composites |

## 8.4 Index

Fachagentur Nachwachsende Rohstoffe e. V. (FNR)
Agency for Renewable Resources
OT Gülzow, Hofplatz 1
18276 Gülzow-Prüzen
Tel.: +49 3843/6930-0
Fax: +49 3843/6930-102
info@fnr.de
international.fnr.de

Printed on 100 % recycling paper
using vegetable oil-based colours

Order no. 237
www.fnr.de/english_books
FNR 2020

Fachagentur Nachwachsende Rohstoffe e.V.