

# Bio-based plastics: status, challenges and trends

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## Abstract

The increasing concern about diminishing fossil resources and the impacts of the global warming is driving the growth of the new bioeconomy. Bioplastics, thermoplastic biopolymers that are either biodegradable or at least partly bio-based, are one of the fastest growing markets. The average growth rates over the past years have constantly been double-digit. Though the production capacities are small, currently approximately 0.5% of the global plastics productions, recent market forecasts expect a sharp rise in the upcoming three years. Due to identical property profiles and established recycling processes, the largest growth is expected for partly bio-based conventional plastics, especially for bio-PET.

This development was made possible by numerous innovations in the fields of chemical catalysis, biotechnology, and plastics engineering. It reflects an ongoing change in the bio-plastic industry, which increasingly focuses on the production of durable, bio-based plastics, after years of concentration on biodegradable plastics used for niche applications. But also the markets for bio-based and biodegradable plastics are expected to continue their rapid growth.

This article reviews advances in production processes and material properties of selected bio-based plastics. It focuses on the most important bio-based plastics with established production and commercial applications. It furthermore provides an overview of new applications, and trends, as well as of major producers.

**Keywords:** *Bio-based plastics, biopolymers, renewable resources, bioeconomy*

## Zusammenfassung

### Bio-basierte Kunststoffe: Status, Herausforderungen und Trends

Die zunehmende Besorgnis über abnehmende fossile Ressourcen und die Auswirkungen der Klimaerwärmung fördert das Wachstum der Bioökonomie. Der Markt für Biokunststoffe, thermoplastische Biopolymere, die entweder biologisch abbaubar oder wenigstens teilweise bio-basierten Ursprungs sind, ist einer der am schnellsten wachsenden. Obwohl die Produktionskapazitäten von Biokunststoffen gegenwärtig noch klein sind, ca. 0,5 % der globalen Kunststoffproduktion, gehen aktuelle Marktprognosen von einem sprunghaften Anstieg in den kommenden drei Jahren aus. Aufgrund identischer Eigenschaften und etablierter Recyclingprozesse wird das größte Wachstum für bio-basierte konventionelle Kunststoffe wie bio-PET erwartet.

Möglich wurde diese Entwicklung durch Innovationen in den Bereichen der chemischen Katalyse, der Biotechnologie und der Kunststofftechnik. Sie spiegelt einen andauernden Wandel der Kunststoffindustrie wider, die sich zunehmend auf die Produktion nicht bio-abbaubarer Biokunststoffe konzentriert, nachdem der Fokus viele Jahre lang auf biologisch abbaubaren Kunststoffen für Nischenanwendungen lag. Aber auch für die Märkte der bio-abbaubaren Biokunststoffe wird erwartet, dass das schnelle Wachstum ahnält.

Dieser Artikel gibt einen Überblick über ausgewählte bio-basierte Kunststoffe mit Schwerpunkt auf Fortschritten in den Bereichen Produktion und Materialeigenschaften. Er konzentriert sich auf die wichtigsten bio-basierten Kunststoffe mit bereits etablierter Produktion und kommerziellen Anwendungen. Darüber hinaus werden neue Anwendungen, aktuelle Trends und wichtige Produzenten vorgestellt.

**Schlüsselwörter:** *Bio-basierte Kunststoffe, Biopolymere, Nachwachsende Rohstoffe, Bioökonomie*

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## 1 Introduction

Steadily growing since 1950, the worldwide production of plastics materials has reached 288 million tons in 2012 (Plastics Europe, 2013). Germany is one of the most important actors on the plastic markets and the biggest manufacturer and processor of plastics in the EU. In 2012, the German plastic industry produced 19.5 million tons of plastics and generated a revenue of 25.1 billion euros (Plastics Europe Deutschland, 2013).

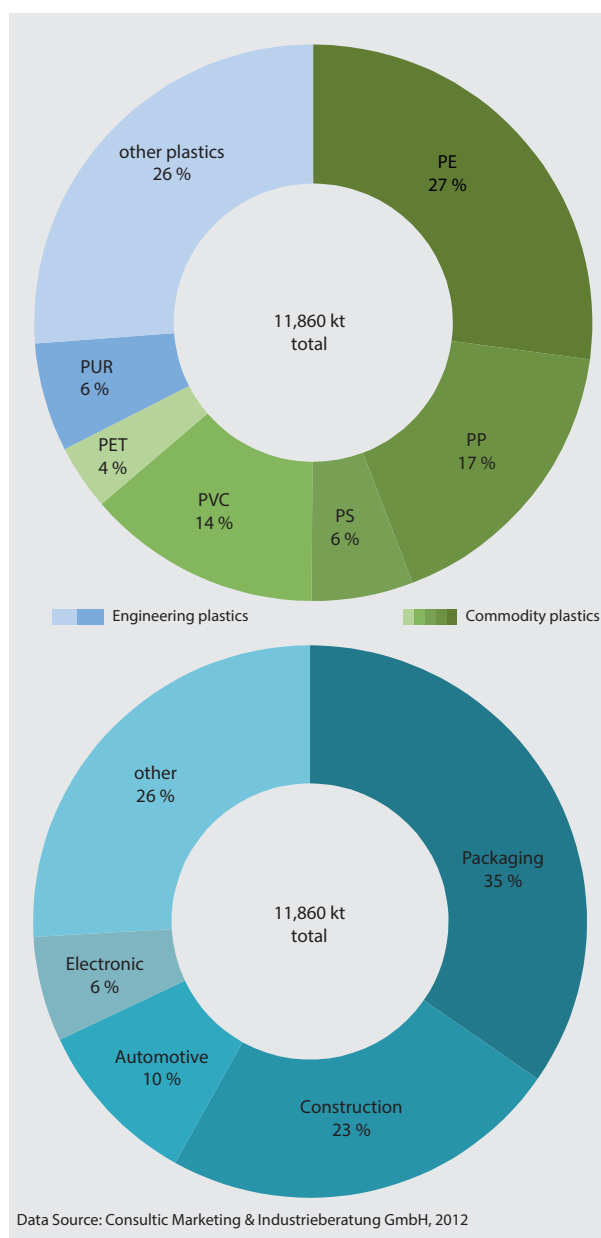
Large amounts of petroleum, approximately 7% of the global production, are used for the production of plastics (Bozell, 2008). Consequently, today's (renewable) energy debate is also impacting the plastics industry. The challenges are well known and essentially the same that underlie the energy debate. Namely fossil resources, especially petroleum and gas, are of finite availability and have volatile and steadily increasing prices. An additional pressure on decision makers is generated by the growing political and public concern about the environmental impacts related with the increasing utilization of plastics.

Although energy is the primary issue when it comes to the impacts of the depletion of fossil resources, the size of the challenge for the plastic industry is bigger than it might seem. Unlike for the energy issue, there is only one renewable alternative for the production of plastics and bulk chemicals, and that is the use of biomass. The approach of using biomass for the production of plastics is not a new one. The production of the first modern artificial polymer, celluloid, and the vulcanization of rubber, were already sophisticated and quite mature processes at the beginning of the last century. However, in the course of the petrochemical revolution, the markets for plastics based on renewable resources have lost their importance to the petroleum based plastics we are using today.

Though the physical and functional diversity of plastics seems enormous, 64% of the processed volume is accounted by five commodity plastics, namely polyethylene (PE), polypropylene (PP), poly(vinylchloride) (PVC), poly(styrene) (PS), and poly(ethylene terephthalate) (PET) (Figure 1). The remaining volume is accounted for by other engineering plastics like polyamides and polyurethanes and others. The largest share of the processed volume of plastics is used in the packaging and construction sector, followed by automotive and electronics applications.

Plastics have become an essential part of modern life and offer great economic, ecologic, and social benefits: Examples are functional packagings that reduce food spoilage, lightweight plastic components that lower the fuel consumption of vehicles and aircrafts, and highly efficient insulation foams that enable us to build zero-energy buildings. Except the lack of renewability of their precursors there is nothing wrong with the plastics we are using today.

Thus, changing the raw material base to bio-based feedstocks represents an appealing solution for many in the plastic industry. Accordingly, many companies have outlined the production of bio-based plastics as an objective in the past three decades. The result of the related research activities is a



**Figure 1**  
In Germany processed plastics 2011 – above: by type;  
below: by sector

very diverse range of “bioplastics” which make it difficult to define general characteristics. For clarity here a basic definition: A bioplastic is a plastic material that is either bio-based (partially or completely), biodegradable or features both properties. The focus of this review is in bio-based plastics which are necessarily at least partly derived from renewable resources but do not have to be biodegradable.

The first bio-based products introduced to the markets were poly(hydroxyalkanoate) produced by ICI (Great Britain) in the 1980s. Their development was driven by the increasing demand for biodegradable plastics for packaging and agricultural applications. Due to high prices and the lack of essential properties required for main applications, these first products never penetrated important markets. However,

the interest in bio-degradable products remained high and the number of applications rapidly grew beyond the originally very limited number of simple packaging applications. Biodegradable products with improved material properties were developed in the 1990s. Some of these were completely petroleum-derived, which gave rise to some irritations among consumers.

In the late 1990s, the interest in bioplastics shifted towards the use of renewable raw materials. In 2001, *Nature-Works LLC* was the *first* company that produced a completely bio-based plastic (poly(lactic acid)) in large quantities (USA, 140ktpa). Since then, the production of many bio-based plastics has been demonstrated at pilot and demo scale. Some of the products are conventional plastics like PE and PVC, others are partly bio-based (e.g. polyols, polyamides), and some of them are entirely new plastics such as poly(lactic acid). Partly bio-based plastics often require petrochemical monomers that cannot be resembled by bio-based replacements, at least not at a reasonable price. Today's bio-based plastics are sophisticated materials which could technically be a substitute for around 90% of the plastics we use today (Shen et al., 2010).

At present, however, high price levels and low production capacities of bio-based plastics prevent deeper market penetration. According to a recent forecast, the production capacities of bio-based plastics approximately correspond to 0.5% of the global plastic production (European Bioplastics, Institute for Bioplastics and Biocomposites, 2013; Plastics Europe, 2013). Though this is a rather small share, numerous commercial successes and ongoing commercializations impressively show the rapidly progressing change in the plastic industry towards bio-based products. If this development continues, bio-based plastics are likely to become an important pillar of the future bio-economy.

This article reviews recent advances in the development, production, and application of a selection of bio-based

plastics including novel plastics, like thermoplastic starch and poly(lactic acid), as well bio-based versions of conventional plastics. The key selection criteria for the bio-based plastics discussed, are expected med-term production volumes and usage. Important progress in the development and diversification of material properties of novel bio-based plastics is described and compared with the properties of the conventional plastics they could substitute.

## 2 Production of bio-based plastics

Bio-based plastics can be obtained via three principal routes (Figure 2). The first approach is by modification of natural polymers while preserving the polymer backbone (mainly) intact. This is the most important approach today, used for the production of starch and cellulose-based plastics and for various other bio-based polymers and fibers used in non-plastic and non-food applications.

The second way comprises a two-step biomass conversion approach starting with the production of bio-based precursors (monomers) by means of biochemical and/or chemical transformation followed by the polymerization of the monomers in the final step (both steps are normally complex and can be divided in several sub-steps). If the monomers obtained are bio-based versions of conventional monomers they are called drop-in (replacements). Conventional plastics produced using drop-in monomers are advantageous, because they cannot be distinguished, neither structurally nor by performance, from their petrochemical counterparts. Hence, they can readily enter existing processing and recycling systems. A good example is bio-based PE prepared from bio-ethanol derived ethylene.

Bio-based monomers that have new structures or have not been applied to the markets in the past are also used to produce plastics. These "novel" bio-based plastics often have

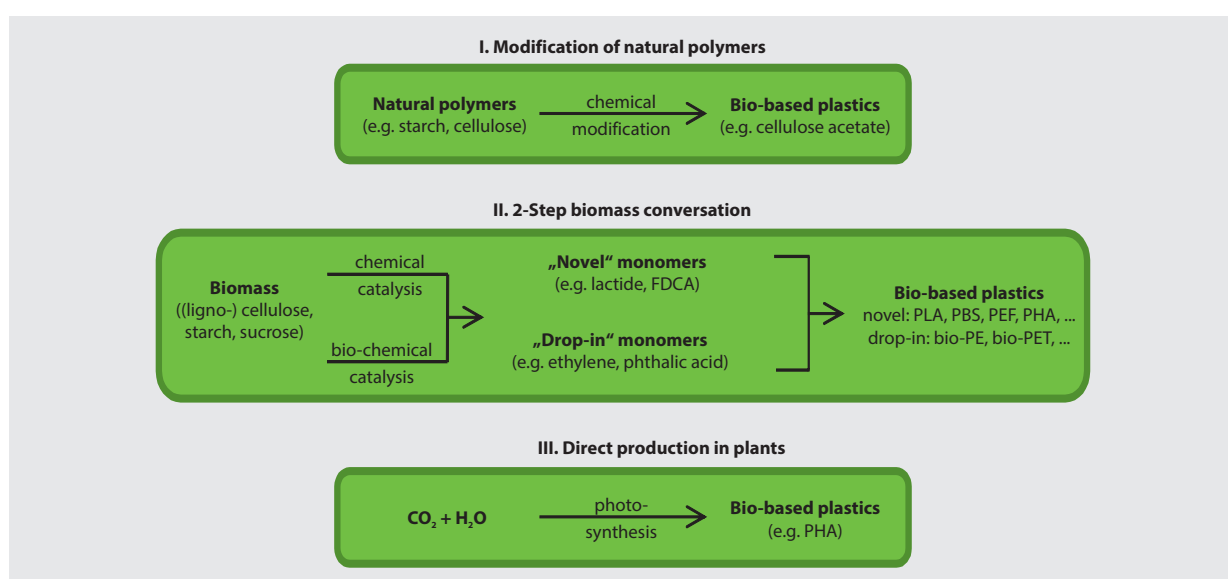


Figure 2

Principal routes to bio-based plastics

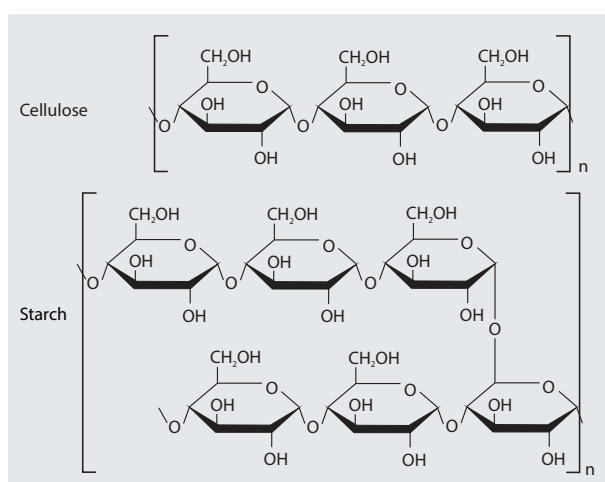
different properties. Compared to the standard plastics which they could replace, they often show an improved functionality and thus additional markets and applications. However, in contrast to drop-in plastics, novel bio-based plastics require the development and implementation of new recycling systems.

This second approach to bio-based plastics is constantly gaining importance due to the advancements in the chemical and bio-technological production of monomers.

The third route comprises the production of a polymeric material, which can be used as a plastic without further modification, directly in microorganisms or plants. Because of the progress in genetic engineering and biotechnology which enables to move genes responsible for the production of a polymer like poly(hydroxyalkanoate) (PHA) from bacteria into crops, this route is becoming more feasible. However, as favorable as direct production of bio-based plastics via photosynthesis may seem, as complex are the related environmental and regulatory issues. Although this route has been intensively studied for many years now, no notable quantities of bio-based plastics have been produced accordingly.

## 2.1 Plastics from natural polymers

Polymers are very common in nature and used in many industrial processes. By the annually produced volume, cellulose, chitin, and lignin are most abundant. Currently, lignin and chitin have no notable commercial applications as plastic materials, but their use as filler for rubber and thermoplastics and as prepolymers is being intensively studied (Chen et al., 2012; Doherty et al., 2011; Hatakeyama H and Hatakeyama T, 2010; Nandanwar et al., 2012; Srinivasa and Tharanathan, 2007).



**Figure 3**  
Structure of cellulose and starch

Among the natural polymers, only cellulose and starch are used for the industrial production of bio-based plastics. Their production is in accordance with route I (Figure 2). Though their monomeric building blocks are very similar (Figure 3),

they exhibit very different properties. Starch and cellulose have in common that they cannot be processed as a thermoplastic material without prior modification.

### 2.1.1 Plastics from starch

Starch is a polysaccharide produced by green plants for the storage of energy. Due to its semi-crystalline structure, which undergoes thermal degradation before the melting point is reached, native starch cannot be applied to thermoplastic processing.

A bio-based plastic that is based on starch is thermoplastic starch (TPS). It can be prepared from starch granules by mixing and heating them in the presence of one or more plasticizers, typically water and glycerol, in a process called destructurization. TPS is an attractive bio-based material because starch is cheap, biodegradable, and abundantly available in large volumes. Furthermore, TPS is processable with common equipment. However, TPS is very hydrophilic which renders it unsuitable for applications in humid environments (Liu et al., 2009). This currently limits the applicability of TPS to niche products like fast dissolving dishwasher tabs or adhesive tapes. Several solutions to improve the properties of TPS were developed including the use of less volatile and less water sensitive plasticizers like sorbitol or xylitol and the addition of suitable hydrophobic fillers like lignin (Fang and Hanna, 2000; Kaewtatip and Thongmee, 2013; Li and Huneault, 2011; Rahmat et al., 2009).

Blending TPS and starch with hydrophobic plastics has extended their use as plastic materials. The hydrophobic component prevents the direct uptake of water and increases the water resistance significantly. Via the variation of the plasticizer content the material properties can be adjusted. Because most hydrophobic polymers are incompatible with starch, the maximum starch content of blends is limited to approximately 25 to 30%. Higher contents can be achieved by reactive blending in the presence of compatibilizers, which covalently link the components (Kalambur and Rizvi, 2006). Blends with conventional and bio-based polymers have been intensively investigated (Nayak, 2010; van der Burgt et al., 1996; Willett and Shogren, 2002).

Today, various commercial grades are available. Primarily, these are polyester-based blends used for short-lived biodegradable products like bags, packaging films, agricultural mulch films and protection foams. But also non-biodegradable starch-polyolefin blends have been commercialized. Cereplast (USA) offers PE and PP TPS blends that are targeted for long-term applications in automobiles, consumer-goods, and construction. They offer significantly lower carbon footprints than the pure polyolefins. Besides several companies with pilot/demo scale plants (< 10 ktpa) the most important producers of starch plastics are Novamont (Italy, 120 ktpa) and Rodenberg (Netherlands, 47 ktpa).

Though starch based plastics have developed a high market penetration, the production capacities are not expected to grow as fast as expected for other bio-based plastics because many issues exist in using high amounts of

starch (>30%) without compromising the material properties, even in reactive blends.

### 2.1.2 Plastics from cellulose

Like starch, cellulose degrades prior to melting. But, because of a high degree of crystallinity, it is more stable than starch and cannot be dissolved or plasticized with common solvents or plasticizers. For the production of a plastic material the cellulose, usually in the form of pulp, has to be chemically modified. The most important thermoplastic cellulose material is cellulose acetate (CA) (Balsler et al., 2000). Since its first commercial production in the early 20th century, CA has been an important plastic material, until it was replaced by less expensive petrochemical plastics. CA is prepared by acetylation of the hydroxyl groups of pulp with acetic anhydride. Depending on the origin of the anhydride CA can be fully or partly bio-based.

The thermal and mechanical properties and the bio-degradation rate of CA, depend on the degree of acetylation (Chandra and Rustgi, 1998). CA is predominantly used for fiber applications (textiles and cigarette filters). Niche plastic-applications include spectacle frames, handles and casings of other high-value products, as well as polarized films, which are used for LCD displays.

The industrial derivatization of pulp is a mature and sophisticated process, which is performed under harsh conditions. Recent research has focused on alternative solvents, such as ionic liquids (Gericke et al., 2012), the expensive recovery of these solvents remains the major drawback of these techniques.

Major producer of cellulosic polymers is Eastman Chemical (USA), further producers are Innovia Films Ltd (UK), and FKuR (Germany). Only a small share of the CA production (800 ktpa) is used for plastics applications. Due to the high price and the niche character of most applications, a significant change of the production capacities cannot be expected in the close future.

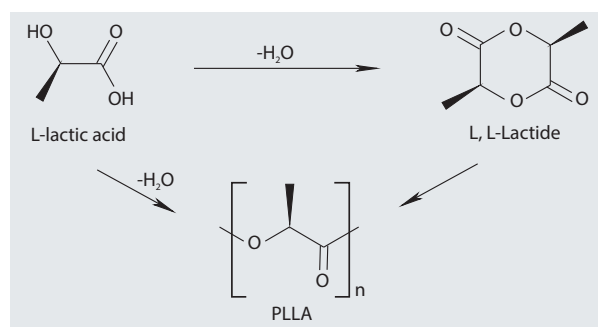
## 2.2 Bio-based polyesters

Polyesters are one of the structurally and functionally most versatile groups of polymeric materials and formed when dicarboxylic acids and di-functional alcohols or hydroxy acid are polymerized. These monomers are quite abundant in nature and can be produced via various fermentative pathways, which were intensively studied and reviewed in the last years (Bechthold et al., 2008; Gandini et al., 2009; van Haveren et al., 2008).

Depending on the utilized monomers and on the process conditions, polyesters with a large spectrum of properties, ranging from stiff to soft, can be prepared. An important feature of many polyesters is their ease of degradation due to the hydrolysis of the ester linkage, which is the reason for their biodegradability. Advances in biotechnology and chemical catalysis have enabled the production of various fully and partly bio-based polyesters. Currently the most important fully bio-based polyester is PLA.

### 2.2.1 Poly(lactic acid)

PLA plastics are amorphous or semi-crystalline polyesters, that can be produced from the renewable fermentation product lactic acid (LA). The LA molecule has an asymmetric carbon atom and therefore occurs in two forms. L-LA is present in many organisms. The enantiomer D-LA (mirror image of L-LA), however, is very rare in nature (Chahal and Starr, 2000). PLA can be prepared via direct condensation of LA or via ring opening polymerization (ROP) of the cyclic lactic acid dimers, L,L-, D,D-, and D,L-lactide (Lim et al., 2008). The products of both routes are generally referred to as PLA (Figure 4).



**Figure 4**  
Synthesis of lactide and poly(lactic acid)

According to a commonly adopted and more specific nomenclature, the polycondensation products of LA are called poly(lactic acid), and the products prepared by ROP of lactides are called polylactides.

Besides being biodegradable, a major advantage of PLA is the possibility to process the plastic on common process equipment. The thermal and mechanical properties of PLA properties depend on the ratio and the distribution of L- and D-LA in the polymer chains.

Both, amorphous and semi crystalline PLAs, show a glass transition temperature ( $T_g$ ) between 50 and 70°C.  $T_g$  is an important parameter. It is defined as the temperature above which the amorphous regions of a plastic change from brittle to rubbery or liquid-like. Accordingly, native PLAs are brittle at room temperature. PLA solely consisting of L-LA blocks is semi-crystalline due to the high structural regularity. The crystalline regions (up to 37%) provide additional mechanical strength, especially at elevated temperatures (Perego et al., 1996). The melting temperature of the crystals is typically around 180°C (Lim et al., 2008). An important property of a semi-crystalline thermoplastic is the rate at which it recrystallizes upon cooling from the melt. Fast and spontaneous crystallization is required for many plastic applications with short cycle times (e.g. injection molding). Pure PLLA crystallizes spontaneously, but the rate of crystallization decreases with increasing D-LA content (Saeidlou et al., 2012). Less pure PLLA thus often contains a quasi-amorphous phase and overall shows inferior mechanical properties.

In order to control the PLA crystallinity, several nucleating agents have been investigated. Besides a variety of nanoparticles, talc and nano-clay have proven to be very

good nucleating agents for PLA. Below 90% L-LA content PLLAs remain amorphous (Saeidlou et al., 2012). Because the monomers L-LA and D-LA are enantiomers, PDLA plastics feature the same properties like the corresponding PLLAs.

If both, L-LA and D-LA chain structures are present in a PLA plastic, strong interactions between these complementary structures can cause the formation of a very stable stereo complex. The effect is most pronounced in PLAs that contain equimolar amounts of L- and D-LA, e.g. in 1:1 blends of pure PLLA and PDLA (stereo complex PLA (scPLA)). Compared to PLLA, scPLA shows a significantly higher melting temperature of 210 to 240 °C and spontaneous and fast crystallization (Ikada et al., 1987).

Several scPLA production techniques have been developed, including the application of chiral catalysts, melt and solvent blending (Auras et al., 2004; Ovitt and Coates, 2002). Stereocomplex technology significantly improves PLA heat stability and enables to replace PS and PP and other plastics in applications like hot beverage cups and microwave safe packaging. Besides crystallinity control, various plasticization and processing techniques have been investigated in order to overcome the inherent brittleness of PLA (Anderson et al., 2008; Liu and Zhang, 2011). An often observed disadvantage was that improvements in either impact strength or the tensile modulus usually came along with reduction in modulus or tensile strength.

New additives and processing technologies have expanded the number of PLA applications, which today go well beyond the initial scope of biodegradable packagings. They now include many durable applications like bottles, casings of IT-products, cellular phones, films, and textiles (Jamshidian et al., 2010). A bio-materials initiative launched by IBM is currently developing a PLA-ABS blend (30% PLA) that could replace polycarbonate/acrylonitrile butadiene styrene (PC/ABS), the predominantly used plastic material in IT-products. The remaining technical challenge is to achieve adequate flame retardancy.

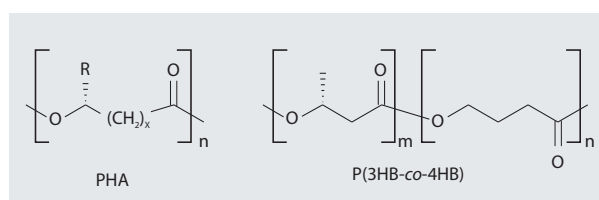
Several companies in Belgium, China, Japan, Switzerland, and the Netherlands have installed small PLA production capacities (several ktpa). NatureWorks LLC remains the world's only large-scale commercial producer of PLA (USA, 140 ktpa). However, the Dutch lactide producer Purac, is providing Lactides (Thailand, 75 ktpa) for PLA production, has started up the world's first D, D-lactide production in 2009 (Spain, 5 ktpa). It is currently used in the production of heat resistant scPLA foam which could be a biodegradable substitute for expandable polystyrene. Though PLA prices have significantly fallen in the last years, they are still not competitive with commodity plastics. NatureWorks LLC assumes to reach cost parity with PET and PS due to an increased economy of scale by 2015.

### 2.2.2 Poly(hydroxyalkanoate)

PHAs are a group of naturally occurring, amorphous or semi-crystalline polyesters, that are biocompatible and fully biodegradable (Chen, 2010). PHAs can be produced via bacterial fermentation of renewable feedstocks or in geneti-

cally engineered plants according to route II or III (Figure 2) (Braunegg et al., 1998). The generic chemical structure is shown in Figure 5.

More than 150 different PHA monomers, hydroxyalkanoic acids that differ in the length of spacer (X) and type of side group (R), have been identified in PHAs (Steinbüchel and Valentin, 1995). PHA production using microorganisms comprises three basic steps (Suriyamongkol et al., 2007). The fermentation step is usually a two-stage fed batch process, which is followed by a solvent based extraction-precipitation step. After drying, the purified PHA plastic is ready for use. The properties of PHAs strongly depend on their molecular structure and composition. The simplest PHA, poly(3-hydroxybutyrate) (P3HB) is very crystalline (up to 60%) and shows thermal and mechanical properties that can be compared to PP and PE. However, they show a slow crystallization behavior and the elongation at break, a measure of the flexibility, is two orders of magnitude lower compared to PP (Marchessault and Yu, 2005).



**Figure 5**  
Poly(hydroxyalkanoate) left: generic structure;  
right: PHA-copolymer

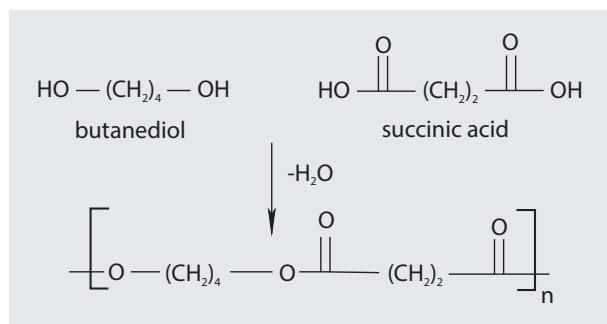
By using mixed cultures, genetically engineered organisms and by varying the carbon sources used in the fermentation process, the final product properties of PHAs can be tailored (Madison and Huisman, 1999). Important progress has been made in fine-tuning the properties of PHA-copolymers comprised of 3-hydroxybutyrate and 3-hydroxyvalerate or 3-hydroxyhexanoate and 4-hydroxybutyrate. They are more flexible than P3HB and can be adjusted to match the property profile of commodity plastics like PP, PE and PET (Laycock et al., 2013; Marchessault and Yu, 2005).

Meredian PHA is currently operating and expanding the world's largest plant (USA, 15 ktpa, 30 ktpa by 2014). Several commercial PHA grades, optimized for a broad range of applications, including injection molded items, films, foams, and fibers, are currently available. According to the manufacturers, PHA production capacities are currently about 35 ktpa. At the current stage of commercialization, the produced grades are mainly used for product development. A project that could have an important impact on the demand for PHAs is a replacement for PC/ABS (50% PHA) in housings, also investigated by the aforementioned bio-materials initiative.

However, PHA are still among the most expensive bio-based plastics. An important cost driver is the energy intensive extraction and purification step, which adversely is also in contradiction with the principles of green chemistry (Koller et al., 2005)

### 2.2.3 Poly(butylene succinate)

Poly(butylene succinate) (PBS) (Figure 6) is a semi-crystalline, completely biodegradable polyester that is produced by polycondensation of succinic acid and 1,4-butanediol (BDO) (Xu and Guo, 2010).

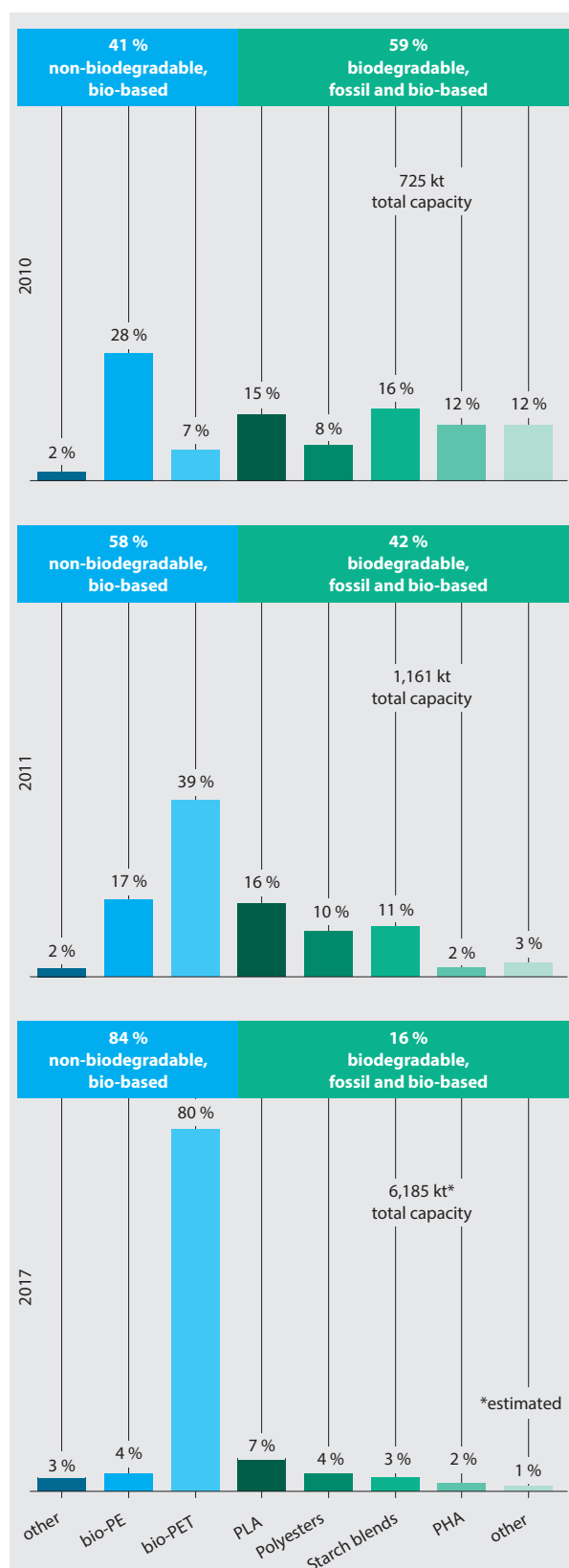


**Figure 6**  
Synthesis of poly(butylene succinate)

Today, PBS is produced in various demo and pilot plants, mainly from petroleum based monomers. The current production capacity is comparatively low (< 20 ktpa). However, bio-based routes to succinic acid and BDO have been extensively investigated (Cheng et al., 2012; Song and Lee, 2006). Several processes have been developed, including the fermentation of carbohydrates using various types of bacteria and fungi. A straight forward route to bio-based BDO is by fermentation of sugars using genetically modified microbes (Yim et al., 2011), demonstrated on a pilot-scale by Genomatica, or via the catalytical hydrogenation of bio-succinic acid (Cukalovic and Stevens, 2008; van Dien, 2013).

PBS is a white thermoplastic material with a low T<sub>g</sub> of -45 to -10°C and a melting point of 90 to 120°C. It generally features good mechanical properties, similar to those of PE and PP (Hwang et al., 2012). Some flexural and barrier properties, however, are not favorable for some applications (Ray and Okamoto, 2003). In order to adjust these properties PBS is usually blended with other thermoplastics, e.g. TPS or PLA, or comonomers like terephthalic acid or adipic acid are incorporated (Xu and Guo, 2010). The addition of nanofillers like clays or carbon nanotubes has also shown to be an efficient way to improve the material properties (Yang et al., 2007). Since the first commercialization in 1994 further PBS grades, homopolymer, copolymer, and blends with other bio-based plastics, have been commercialized. They can be easily processed with conventional polyolefin equipment. Main applications include packaging films and foams, agricultural mulch films, disposable goods, and fibers (Xu and Guo, 2010).

Due to a lack of availability of bio-based succinic acid and BDO in larger volumes, PBS is currently mainly based on fossil resources. However, the bio-based content is expected to increase, because the production capacities of the constituent bio-based monomers are, according to announcements of several companies and joint ventures (Myriant, Reverdia, Bioamber and BASF, CSM Purac and Genomatica), about to be expanded. The shared objective of these working partner-



**Figure 7**  
Global production capacity of bioplastics in 2010, 2011 and 2017

ships is a 100% bio-based PBS for large volume durable markets such as in the automotive interior parts.

### 2.3 Bio-based conventional plastics

The initial focus of bioplastics was on applications that required biodegradability. Accordingly, the production capacities for durable bio-based plastics have remained comparatively low. However, most of the 'commodity' applications of plastics do not require fast degradability but a bio-based origin is increasingly requested. Recent market studies show that the plastic industry responds to the increased demand with shifting the production towards bio-based conventional plastics that are not biodegradable. Besides the expected rapid increase of the total production capacities to about 6.185 ktpa by 2017, Figure 7 shows the shift of the largest segment from biodegradable plastics (59% in 2010) towards bio-based non-biodegradable plastics (84% by 2017) (Data sources: European Bioplastics, Institute for Bioplastics and Biocomposites, 2013; European Bioplastics, Institute for Bioplastics and Biocomposites, 2012; European Bioplastics and University of Applied Sciences and Arts, 2011). Since 2011, the most important bio-based non-biodegradable plastic has been bio-PET, which is expected to grow at an exceptional rate due to the increasing demand for bio-based bottles, and bio-PE. However, though not at the same rate like the drop-in plastics, also the novel biodegradable plastics PLA and PHA are also expected to grow significantly (nova-Institute GmbH, 2013; European Bioplastics, Institute for Bioplastics and Biocomposites, 2012).

#### 2.3.1 Bio-based polyethylene

By the annual production volume, PE is the most important conventional plastic material. It is extensively used in a wide range of applications especially packaging and construction. Conventional PE is produced by radical polymerization of the petrochemically produced monomer ethylene. Alternatively, bio-based ethylene can be prepared from ethanol. This allows the production of bio-based PE using existing polymerization reactors.

Figure 8 shows the reaction scheme of the drop-in approach, which corresponds to route II (Figure 2), starting with the dehydration of ethanol to ethylene and followed by conventional polymerization to PE (Bedia et al., 2011). Via the derivatization of bio-based ethylene, further important bio-based monomers can be obtained (van Haveren et al., 2008). Examples shown are vinylchloride, the precursor of PVC and ethylene glycol, a monomer for used in the production of bio-PET.

Technically, the depicted routes are not essentially new. The bio-based production of plastics and other chemicals had been common processes in Brazil and India in the 1960s and 1970s (World Bank, 1980). For as long as the price for petroleum was low, the production discontinued and the technology stayed economically unattractive. With the rising price level however, the technology has regained interest and many old processes have been reinvestigated recently (Morschbacker, 2009).

The raw material costs represent the most important part of the production costs of bio-PE. Hence, price and

availability of the raw materials are the key criterions for siting a bio-PE plant.

Braskem, the first producer of bio-PE, has built its large scale production facility (200 ktpa) in Triunfo (Brazil). It utilizes sugar cane ethanol and started production in late 2010. The produced PE grades target applications in packaging (food and cosmetics), toys, and automotive parts. Against the expectations of many, the first production was sold out very fast, although bio-PE was priced at a premium of about 50% compared to conventional PE. Packaging converter Tetra Pak recently, announced plans to use bio-PE for the production of its packaging material factories in Brazil. This initial test would increase the renewable content of about 13 billion packages annually produced in Brazil to up to 82%.

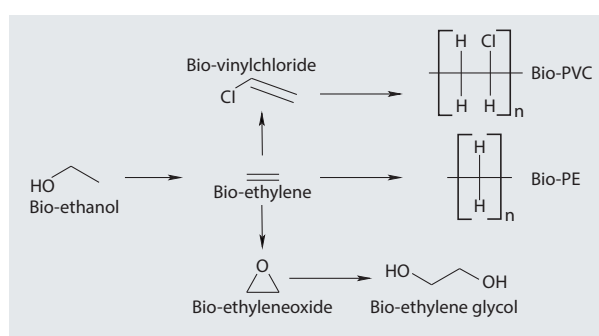


Figure 8

Conversion of ethanol to polyethylene, polyvinylchloride and ethylene glycol

#### 2.3.2 Bio-poly(ethylene terephthalate)

PET is a thermoplastic polyester produced by polycondensation of ethylene glycol (EG) and terephthalic acid (TPA). It is one of the most employed plastics and predominantly used in fiber (textiles) and packaging (bottles and food containers) applications. PET production comprises two steps. The first of these is esterification of TPA with EG, the second is polycondensation, in which PET is formed via a transesterification reaction. High-viscosity PET grades used for bottles or technical yarns are typically produced by chain extension in an additional process step (Rieckmann and Völker, 2004). EG and TPA are typically sourced from petroleum but can alternatively be produced via bio-based routes.

Conventionally, EG is produced via the hydrolysis of ethylene oxide, a product of the catalytical oxidation of ethylene (Figure 8). Provided bio-based ethylene is available, the production of bio-EG is straight forward and can be done in existing plants. As India Glycols demonstrates with its production of bio-EG and other bio-glycols since 1989 (175 ktpa) this route can be technically and economically feasible. The production of bio-based TPA is not as simple. Many processes have been developed and demonstrated at small scale, but none has reached a larger, commercial scale (Dodds and Humphreys, 2013). One of the most advanced processes uses bio-based isobutanol. The related production scheme, depicted in Figure 9, starts with the biotechnological



production of isobutanol which is subsequently transformed via isobutylene and paraxylene into bio-TPA via multiple catalytical conversion steps.

The bio-PET used today is partly bio-based, made of bio-based EG and petroleum-derived TPA. Bio-PET has a bio-based carbon content of 20%. In 2011, the production capacity for bio-based PET reached 620 kt, a 12-fold capacity increase compared to 2010 (Figure 7). Trigger for this sudden and unexpected increase was the great success of the Plant-Bottle, a beverage bottle made of bio-PET, which was introduced by Coca Cola in 2009. Meanwhile other large food manufacturers use the PlantBottle for their products and competitor Pepsi announced to introduce the first fully bio-based bottle, however yet provided only lab-samples of the new bottle.

With the expressed goal of Coca Cola to switch to a fully bio-based bottle by 2020, the bio-PET production capacities are expected to reach 5.000 ktpa by 2016 and to further increase by 2020, (European Bioplastics, Institute for Bioplastics and Biocomposites, 2012; nova-Institute GmbH, 2013). To achieve this goal, Coca Cola cooperates with several renewable chemicals companies and bio-EG plants are being built, e.g. in Taiwan (Greencol, 175 ktpa) or are in planning in Brazil (JBF Industries, 500 ktpa).

The commitment stimulated the development of a bio-based replacement for PET, poly(ethylenefuranoate) (PEF). It can be prepared from EG and 2,5-furandicarboxylic acid (FDCA), a dicarboxylic acid that is structurally comparable with PET. FDCA can be produced from renewable resources. The process, also shown in Figure 9, starts with the conversion of carbohydrates to hydroxymethylfurfural (HMF). Adjacent catalytical oxidations yield FDCA (Bozell and Petersen, 2010). The last step to PEF is a classical polyesterification of FDCA and EG. Because FDCA and TPA have related structures, bio-based TPA can be prepared from FDCA. The missing two carbon atoms in FDCA can be supplied by bio-ethylene (Figure 9) (Eerhart et al., 2012).

This might, however, not be necessary because PEF and PET compete in performance. Regarding the oxygen, carbon

oxide and water barrier properties PEF might even outperform PET which could reduce food spoilage due to shelf life extension (van Es, 2013). Dutch company Avantium currently operates a FDCA pilot plant (40 tpa) and announced plans to build a commercial-scale plant (40-50 ktpa) by 2015.

### 3 Challenges and trends

Since the introduction of the first modern bio-based plastics some 30 years ago, the sector is developing very dynamically. Due to the rising price of petroleum and rapid technological advancement, the initially very high price level was lowered significantly. However, today's bio-based plastics still remain too expensive to compete with conventional plastics.

Though, the most important challenge that has to be addressed in the coming years is the further reduction of the production costs. Economies of scale effects are most important to enable competitive price levels. However, because the supply-chains for bio-based products are typically quite long, their up-scaling is challenging, especially because many of the required technologies have not been tested before.

The feedstock selection will be the most important challenge for three reasons: (1) substrate costs typically account for 40-60% of the total costs of bio-based products (Demain, 2007). (2) the overall yield of the production of bio-based monomers is usually significantly lower than the production of similar petrol based monomers. (3) The simple scale up of the current bio-based plastics production technologies, these usually utilize first-generation feedstocks like sugar cane or corn, are likely to increase the competition of the production of food and bio-based chemicals.

In order to avoid unsustainable demand, research is currently focusing on lignocellulosic biomass and residue streams from agricultural and food production as feedstocks for bio-based chemicals (FitzPatrick et al., 2010). Although the development of these, so called second-generation technologies,

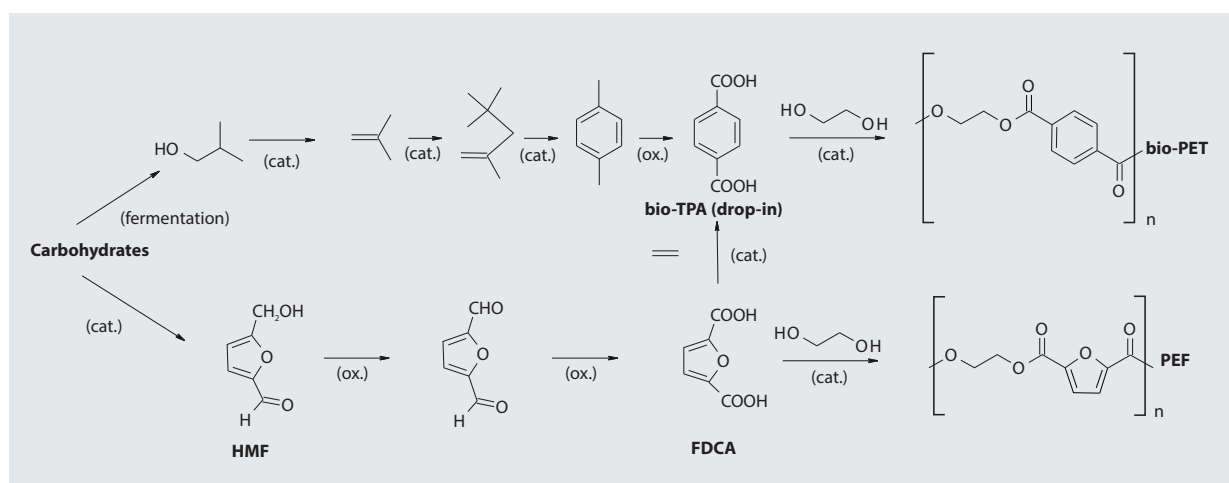


Figure 9

Conversion of sugar to bio-PET and PEF, a novel bio-based plastic that resembles the structure of PET

is progressing, important issues, e.g. the development of efficient lignocellulosic pretreatment, hydrolysis, and downstream technologies, have to be solved (Klein-Marcuschamer et al., 2010). In the meantime, large-scale production capacities are increasingly installed in regions like South America and Asia where low-cost feedstocks, e.g. sugarcane and molasses are available in sufficient quantities. In parallel, new bio-based plastic products and marketing and image campaigns are launched. One of the best indirect results of this trend is the rise of green competition. Bio-PET is nice example for the game-changing impact big players can have on the development of technology, products and markets.

Today's bio-based plastics are predominantly bio-based versions of conventional plastics, mainly PET and PE. By 2016 their share is expected to reach almost 90%. This imbalance is not surprising because the utilization of drop-in replacements does not require any adjustments to existing polymerization and processing equipment. Although drop-in replacements are extending their lead, it remains difficult to predict whether drop-in replacements or novel plastics will finally come out on top. The success of any approach will depend on the final product cost. Bio-ethanol is currently the most versatile starting material for the production of bio-based conventional plastic. However, because the production of ethylene from sugar based ethanol comprises decarboxylation and dehydration steps, the overall process is not very efficient regarding the use of biomass. In contrast, novel monomers can be produced with significant higher atom efficiency. An example is the biotechnological production of succinic acid in which carbon dioxide can be fixated rather than released as a byproduct (Cheng et al., 2012).

Although novel plastics like PLA and PHA can be processed with standard processing equipment, replacing a conventional plastic with a novel plastic is not a simple task. While the basic physical properties of novel plastics have reached a high level of performance, incompatibilities with conventional additives often impair the property profiles. Though an increasing number of additives are available for novel plastics like PLA and PHA, the additives market for bio-based plastics is small and still lacks solutions for important properties, e.g. the flame retardance. With the expected increase of novel plastic production volume, the market for additive is likely to reach a volume that justifies the development and production of new additives.

Novel plastics increasingly occur in existing recycling systems. Although novel plastics are recyclable and their separation technically feasible, existing recycling facilities are not separating them out because they simply lack the critical volume required for individual reclamation. The problem that arises is that novel plastics are claimed to contaminate and impair the performance of recycled conventional plastics (Cornell, 2007; Soroudi and Jakubowicz, 2013). Because this could force waste management companies to reject batches of otherwise recyclable material, it is increasingly demanded to regulate the use of novel plastics, until the required recycling capabilities are installed area-wide.

## 4 Conclusions

Societal demands for sustainable production and consumption, and scientific research are leading to a fast commercialization of new applications for bio-based plastics. They are beginning to change the way plastics are produced. As a result of the rapid pace of the developments, it is likely that bio-based plastics will be commonly found in commodity applications in the near future.

The increasing number of customers that are willing to pay premium prices for green products, have become an important driver for this development. A recent study showed, that product quality (97%) and price (87%) are still influencing the buying behavior of EU citizen more than the impact of a product on the environment (84%) (TNS Political & Social network, 2013). While the gap between the impact of price and of the environmental impacts has decreased compared to earlier studies, the increasing number of companies that are going green with their products might change this trend.

To permanently step out of their green niche, bio-based plastics have to be cost-competitive with their conventional counterparts. Given the current price differences of conventional and bio-based plastics and taking into account the current supply situation with renewable resources, one can assume that bio-based and conventional plastics will be used side by side in the foreseeable future.

### GLOSSARY OF TERMS

BDO	1,4-Butanediol
EG	Ethylene glycol
FDCA	2,5-Furandicarboxylic acid
HMF	Hydroxymethylfurfural
ktpa	kilo tons per year
LA	Lactic acid
PBS	Poly(butylene succinate)
PE	Polyethylene
PEF	Poly(ethylenefuranoate)
PET	Poly(ethylene terephthalate)
PHA	Poly(hydroxyalkanoate)
PLA	Poly(lactic acid)
PP	Polypropylene
PS	Poly(styrene)
PUR	Polyurethane
PVC	Poly(vinylchloride)
ROP	Ring opening polymerization
Tg	Glass transition Temperature
TPA	Terephthalic acid
TPS	Thermoplastic starch

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