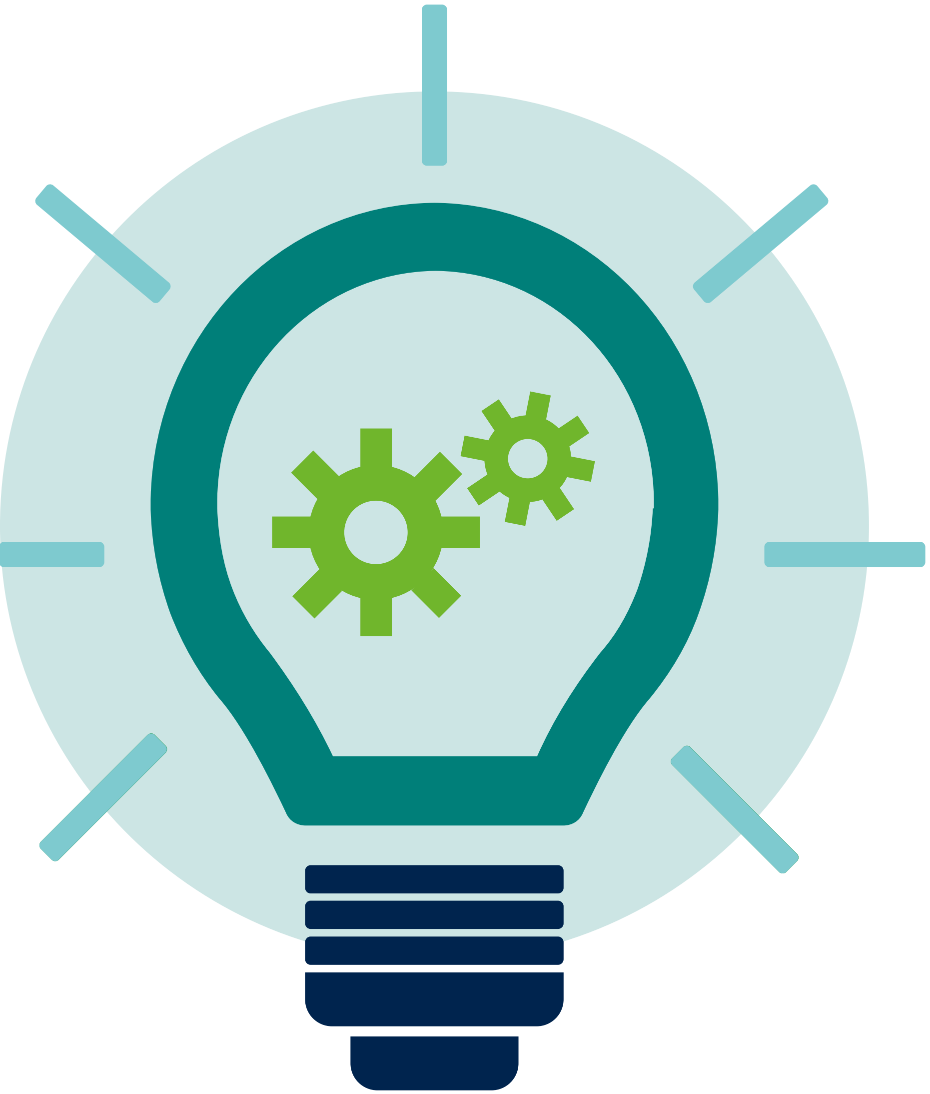
TransBiB
Boost. Industrial. Bioeconomy.



Bioeconomy in the plastics industry

Training on definitions, materials and technologies

Discover – Develop – Connect

Gefördert durch:
Bundesministerium für Wirtschaft und Energie
aufgrund eines Beschlusses des Deutschen Bundestages

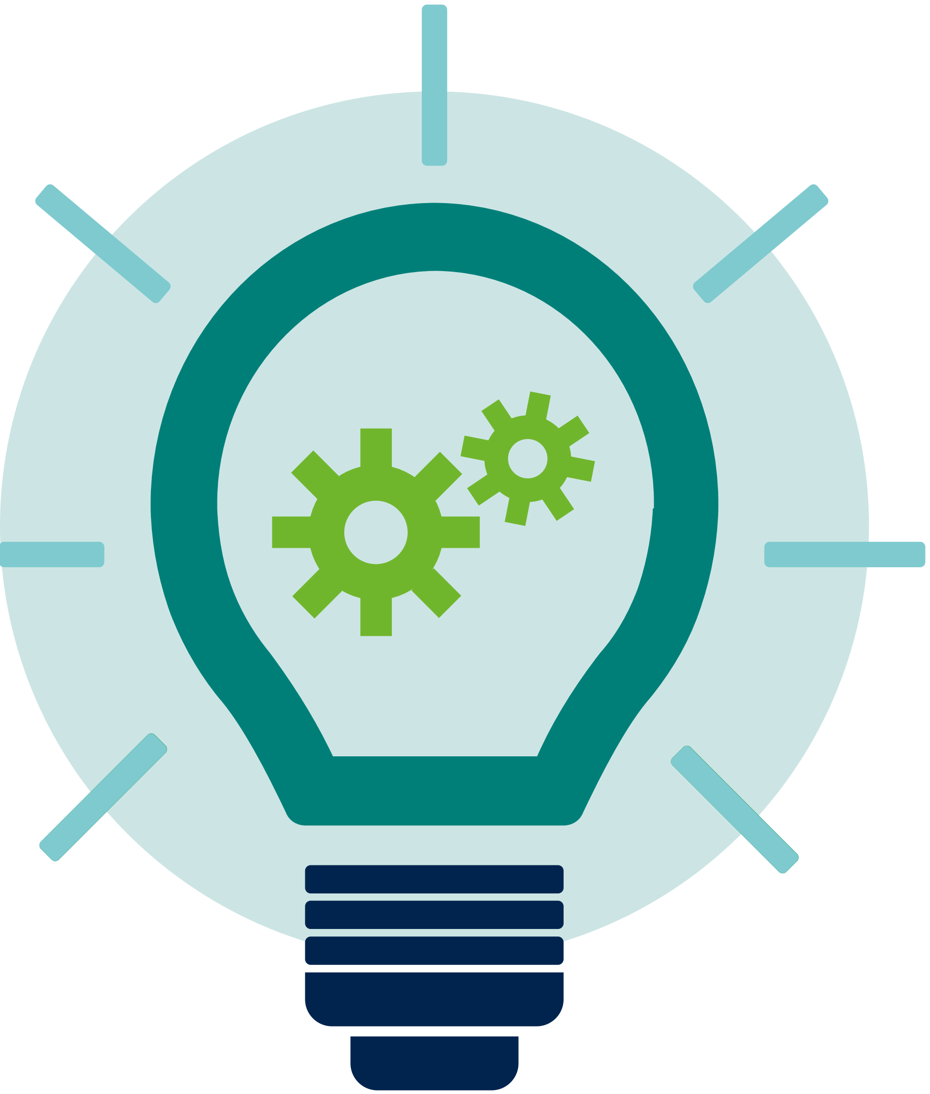
Content

Bioplastics

- Degradability
- Ressources
- Drop-in
- Biobased carbon sources
- Biobased plastics
- Enzymatic degradation

Modified biomass

- Starch
- Cellulose
- Polyhydroxyalkanoates



Bioplastics

Origin, properties & use cases

Discover – Develop – Connect

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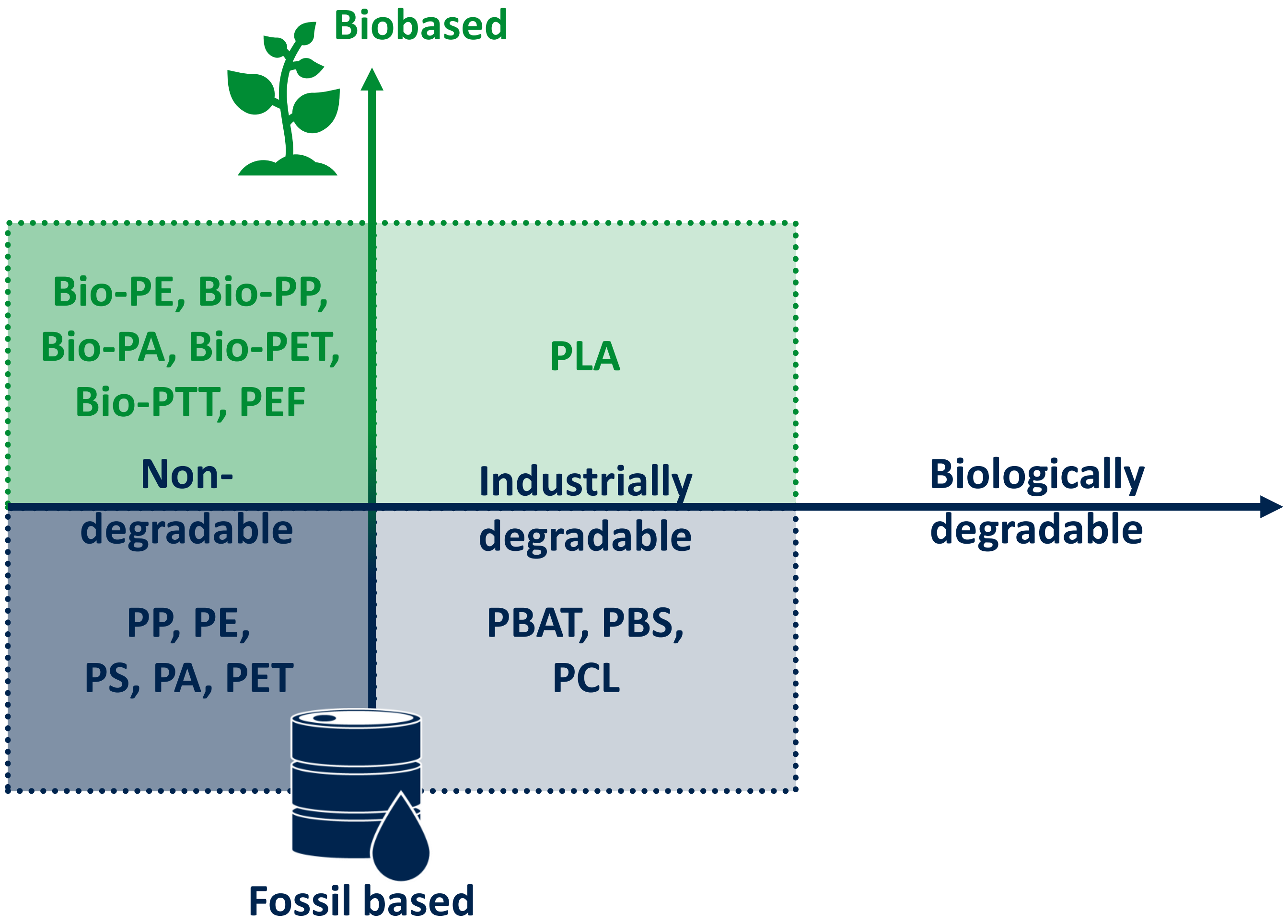
Classification by origin & degradability



PA	Polyamide
PBAT	Polybutylene (adipate-co-terephthalate)
PBS	Polybutylene succinate
PCL	Polycaprolactone
PE	Polyethylene
PEF	Polyethylene furanoate
PET	Polyethylene terephthalate
PHA	Polyhydroxyalkanoate
PLA	Polylactic acid
PP	Polypropylene
PS	Polystyrene
PTT	Polytrimethylene terephthalate

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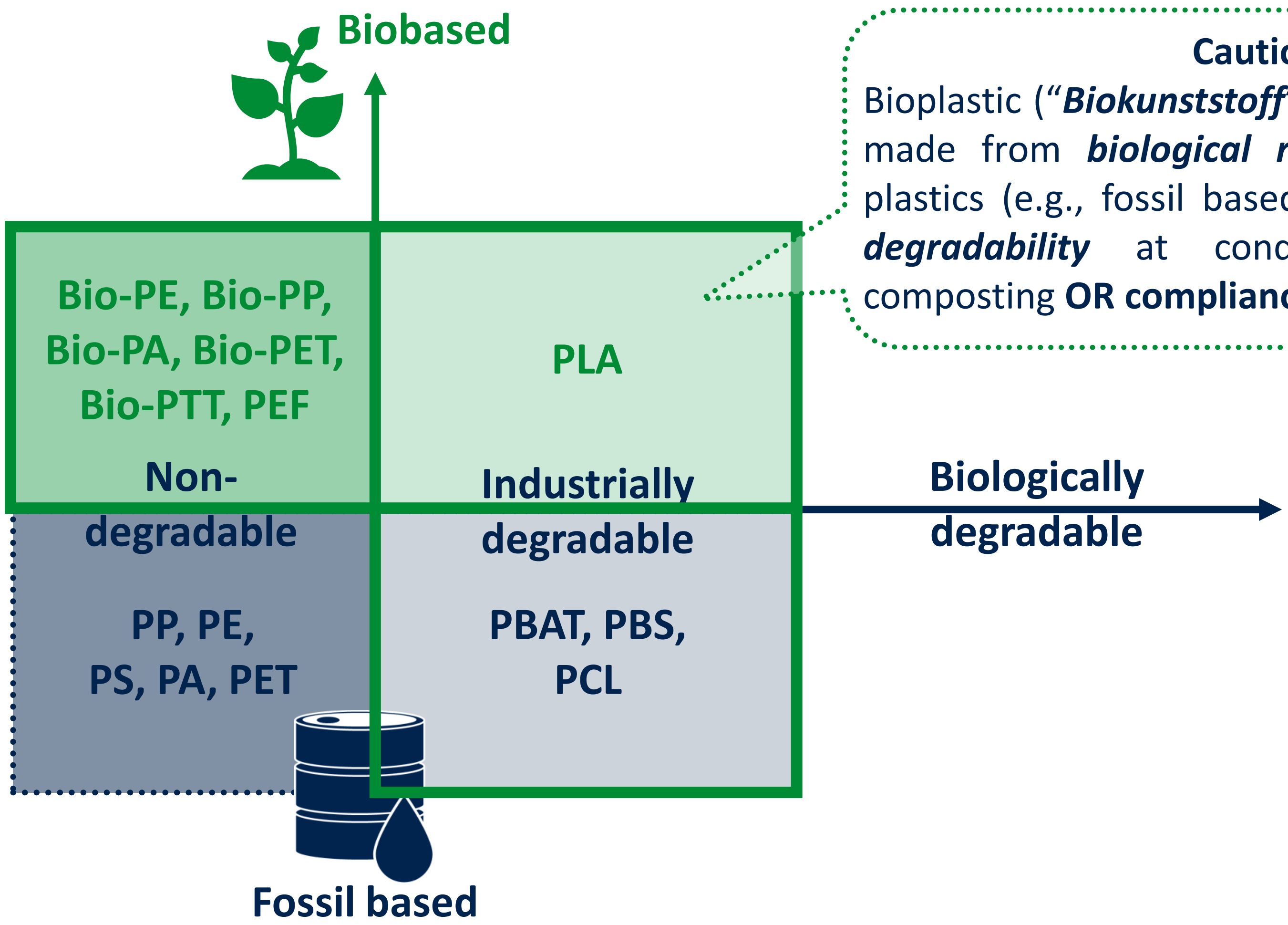

Caution!
Bioplastic ("***Biokunststoff***") may refer to plastics made from ***biological ressources*** as well as plastics (e.g., fossil based) providing ***biological degradability*** at conditions of industrial composting **OR compliance with both criteria**!

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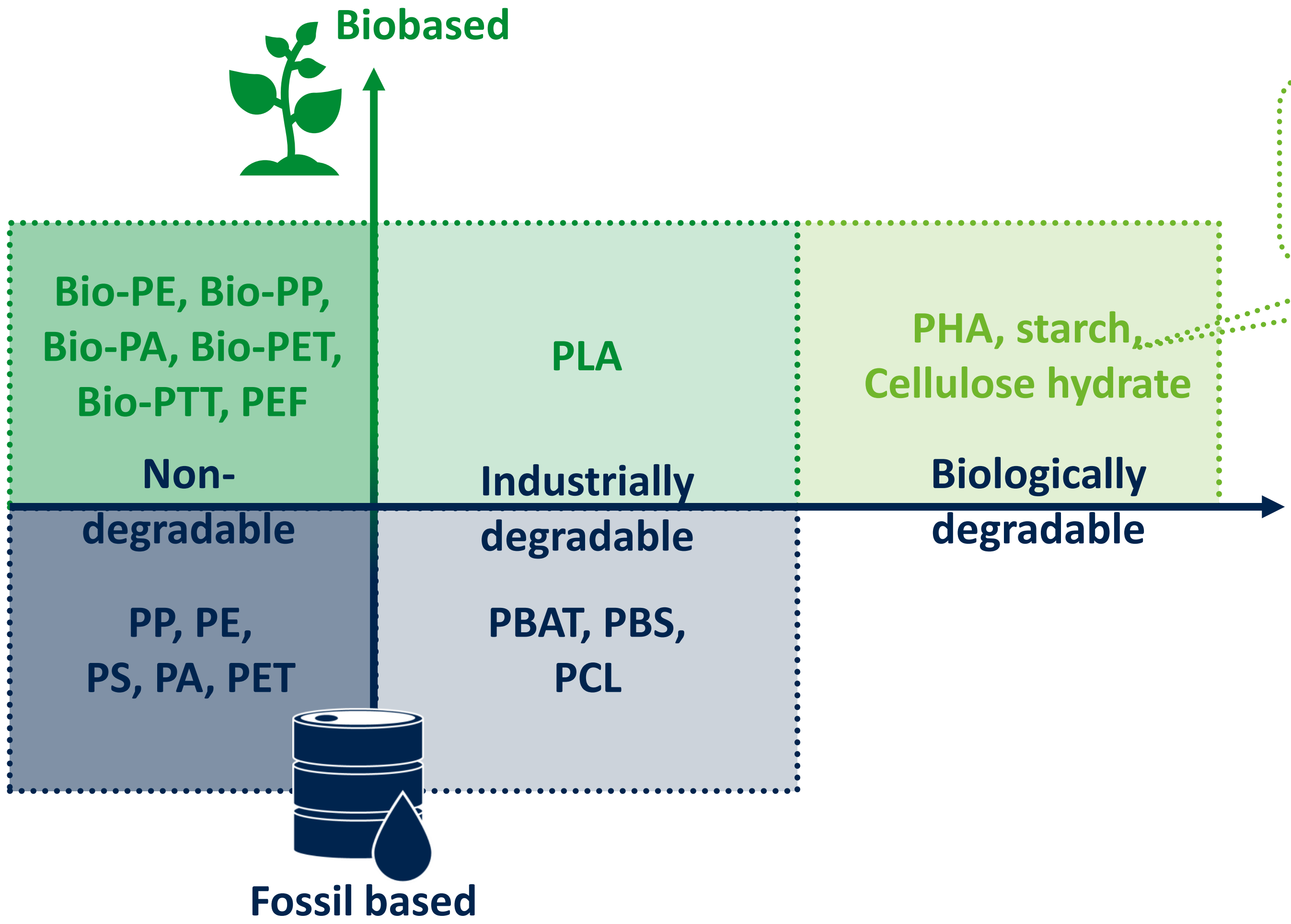

Non-modified natural biopolymers (= natural polymers) are no plastics![1]

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[1] EU SUPD Art. 3 (40)

Classification by raw material

1. Generation (Edible)

Raw materials are obtained from **edible biomass**.

Starch: Corn, wheat, potatoes, tapioca, etc.

Glucose: sugar cane, sugar beet, etc.

Plant oil: Soybeans, sunflowers, castor beans, rapeseed, oil palms etc.

Classification by raw material

1. Generation (Edible)

Raw materials are obtained from **edible biomass**.

2. Generation (Non-edible)

Raw materials are obtained from non-**edible biomass**.

Starch: Corn, wheat, potatoes, tapioca, etc.

Glucose: sugar cane, sugar beet, etc.

Plant oil: Soybeans, sunflowers, castor beans, rapeseed, oil palms etc.

Lignocellulose: By-productus or waste from agriculture and forestry (e.g., bagasse, straw etc.)

Municipal waste: organic waste, waste water etc.

Classification by raw material

1. Generation (Edible)

Raw materials are obtained from **edible biomass**.

2. Generation (Non-edible)

Raw materials are obtained from non-**edible biomass**.

3. Generation (Non-edible & bodenunabhängig)

Raw materials are obtained from non-edible, soil-independent cultures.

Starch: Corn, wheat, potatoes, tapioca, etc.

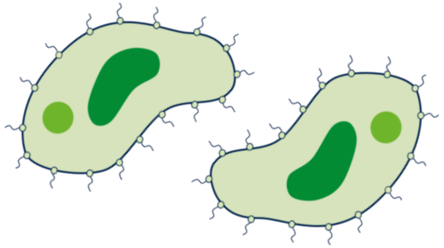
Glucose: sugar cane, sugar beet, etc.

Plant oil: Soybeans, sunflowers, castor beans, rapeseed, oil palms etc.

Lignocellulose: By-productus or waste from agriculture and forestry (e.g., bagasse, straw etc.)

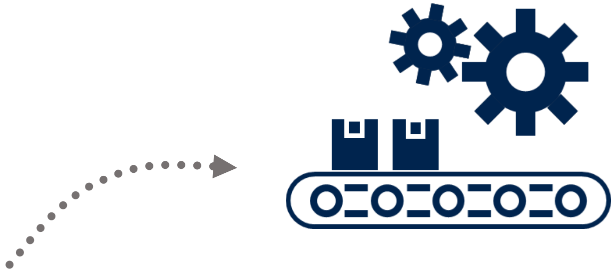
Municipal waste: organic waste, waste water etc.

Microorganisms: Microalgae, bacteria, fungi, yeasts etc.



Bioplastics in the process chain

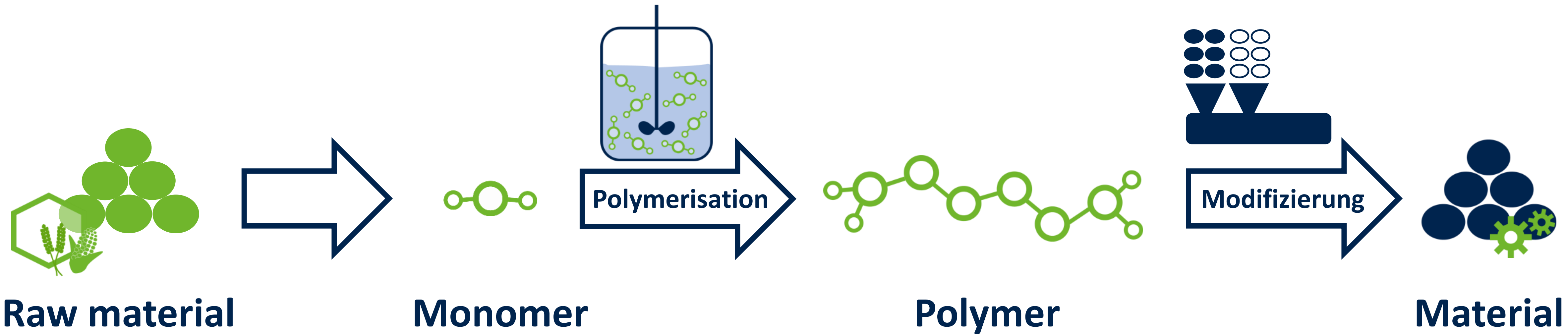
Drop-in bioplastics are plastics, whose **chemical structure is identical** to that of conventional (petrochemical) plastics.



The basic chemicals for the production of drop-in bioplastics are produced from **renewable raw materials** (renewable sources, e.g., sugar cane) instead of petrochemicals (fossil source).

The **same machines and processes** can be used for further processing into end products as for their fossil-based counterparts.

Drop-in solutions



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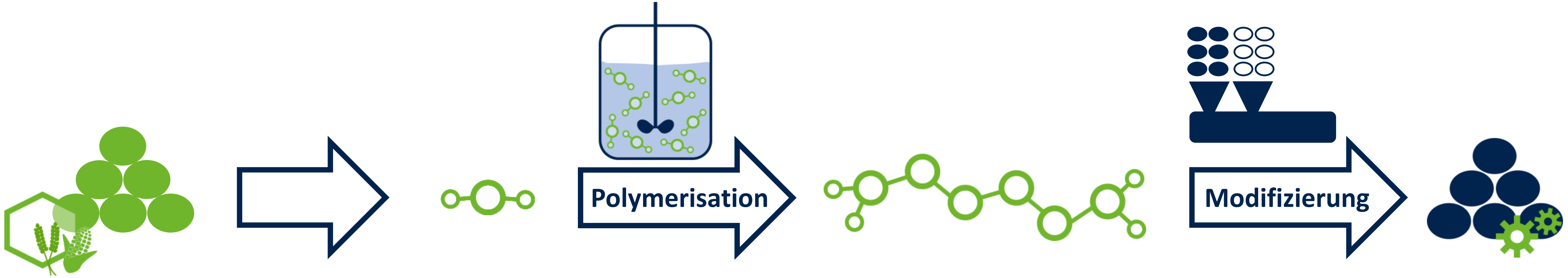


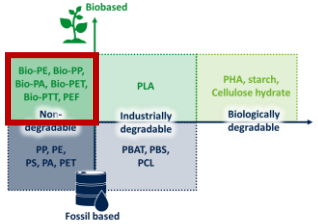
Raw material | **Monomer** | **Polymer** | **Material**

Biobased hydrocarbons (e.g., oils, fats)

Polymerizable biomass (e.g., lactides, diacids)

Biological polymers (e.g., starch, cellulose, rubber)

Biobased carbon sources



sugar cane

- **Brasil** (favorable climatic conditions and established production)
- ✓ **High sugar content**
- ✗ **Environment** Rainforest deforestation for agricultural land

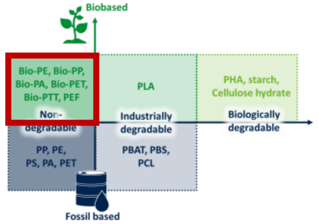
corn

- **USA** (generally where sugar cane cannot be grown/harvested)
- ✗ **Efficiency** Prior transformation of starch into sugar necessary
  Food competition, especially due to misguided subsidies for the fuel industry

sugar beet

- **Europe** (suitable for temperate climate)
- ✓ **High yield per area**

Biobased carbon sources



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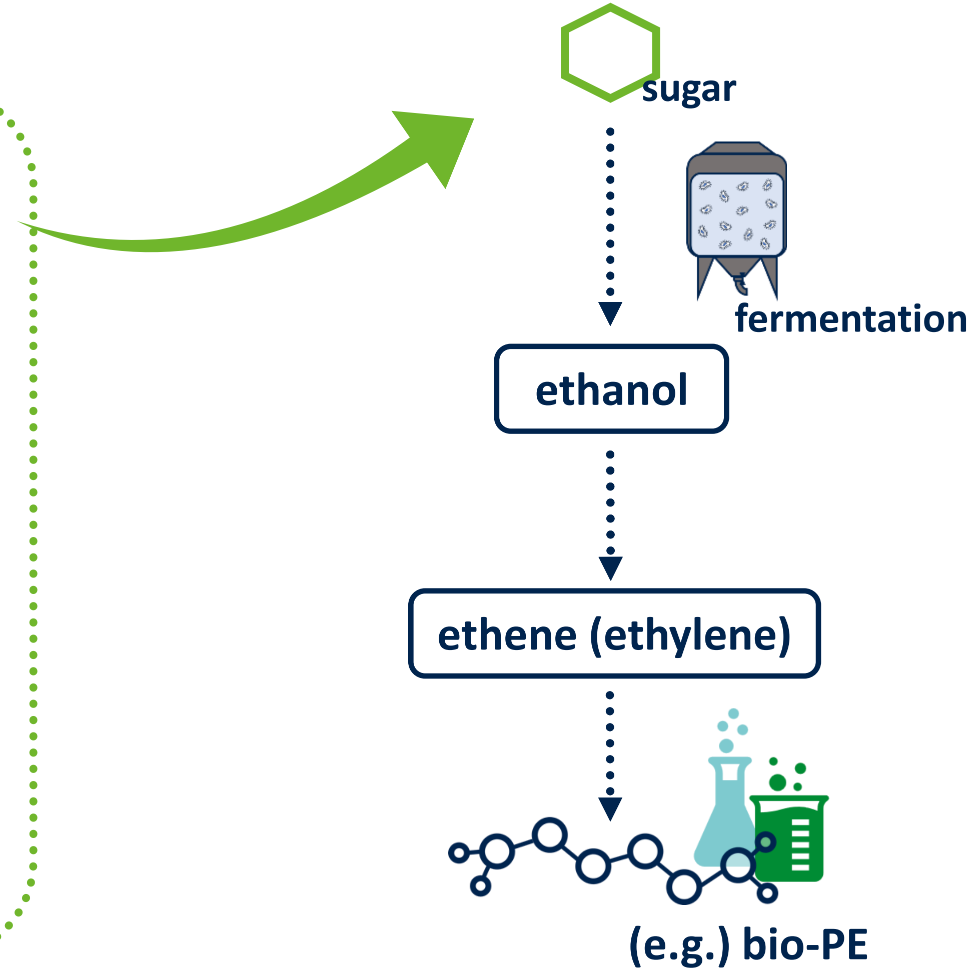

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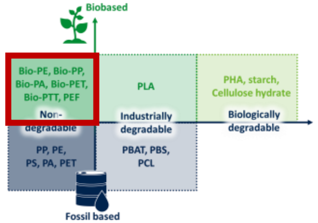
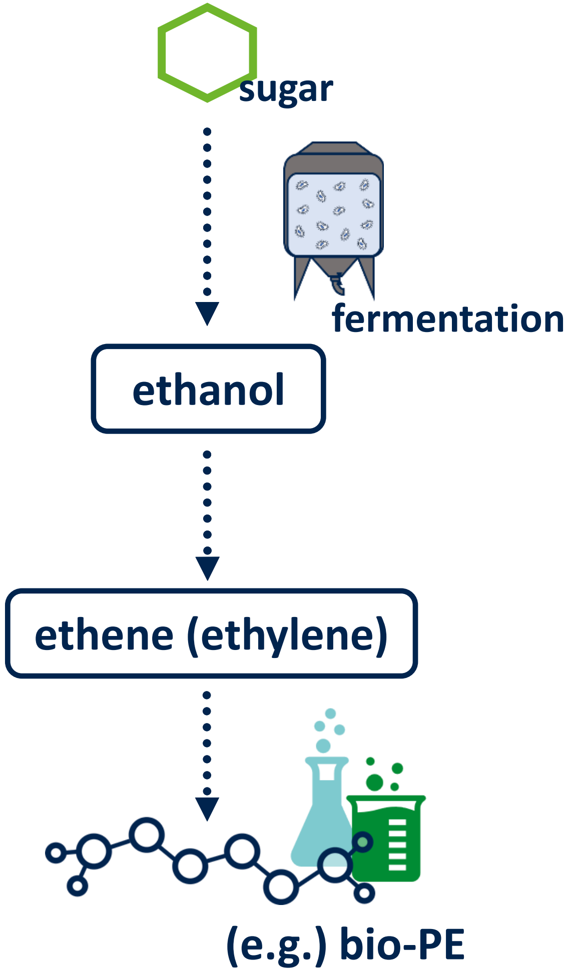
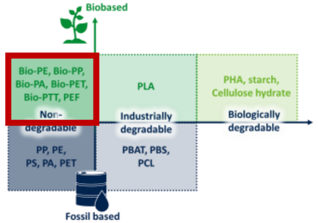


- **Raw material availability: Regionality** (short transport routes) and **available quantity** of raw material have a decisive influence on the **costs** and implementation of a transformation
- **Sustainability:** the use of **non-edible biomass** (2. generation) and side or waste streams limits fear of **food security and land use**
- **CO_2 balance:** biobased polymers such as bio-PE possess significantly **lower CO_2 footprints**, than their fossil-based counterparts



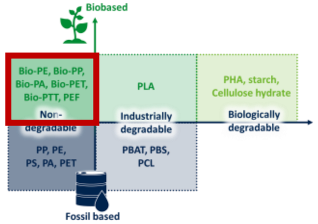
Biobased plastics | PA



Polyamides (technical thermoplastics, nylon)

- PAs are formally produced from **condensation of a carboxylic acid and an amine** (amide bond)
- Industrially most relevant are **PA 6.6 und PA 12**
- **high strength and rigidity** with good abrasion and wear resistance
- **divers applications,** e.g., as fibers

Biobased plastics | PA



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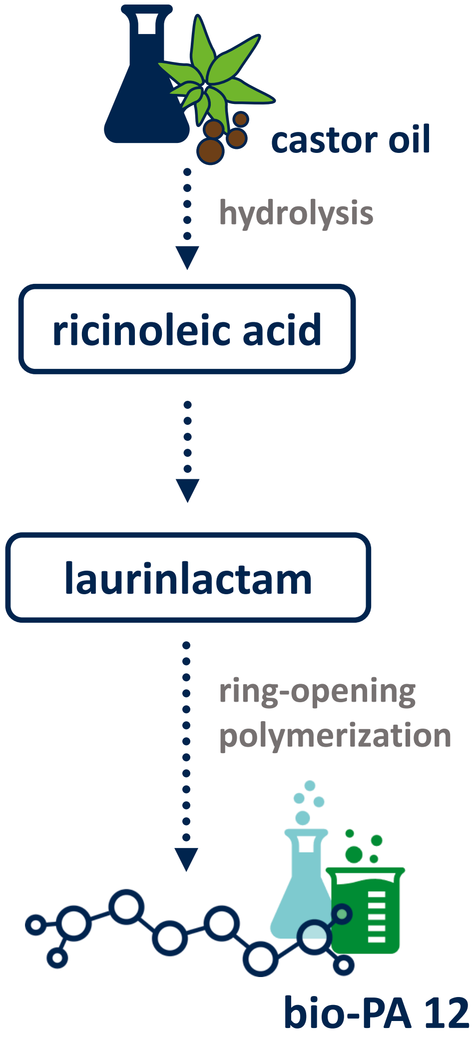
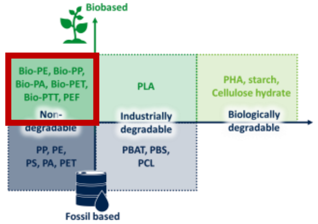
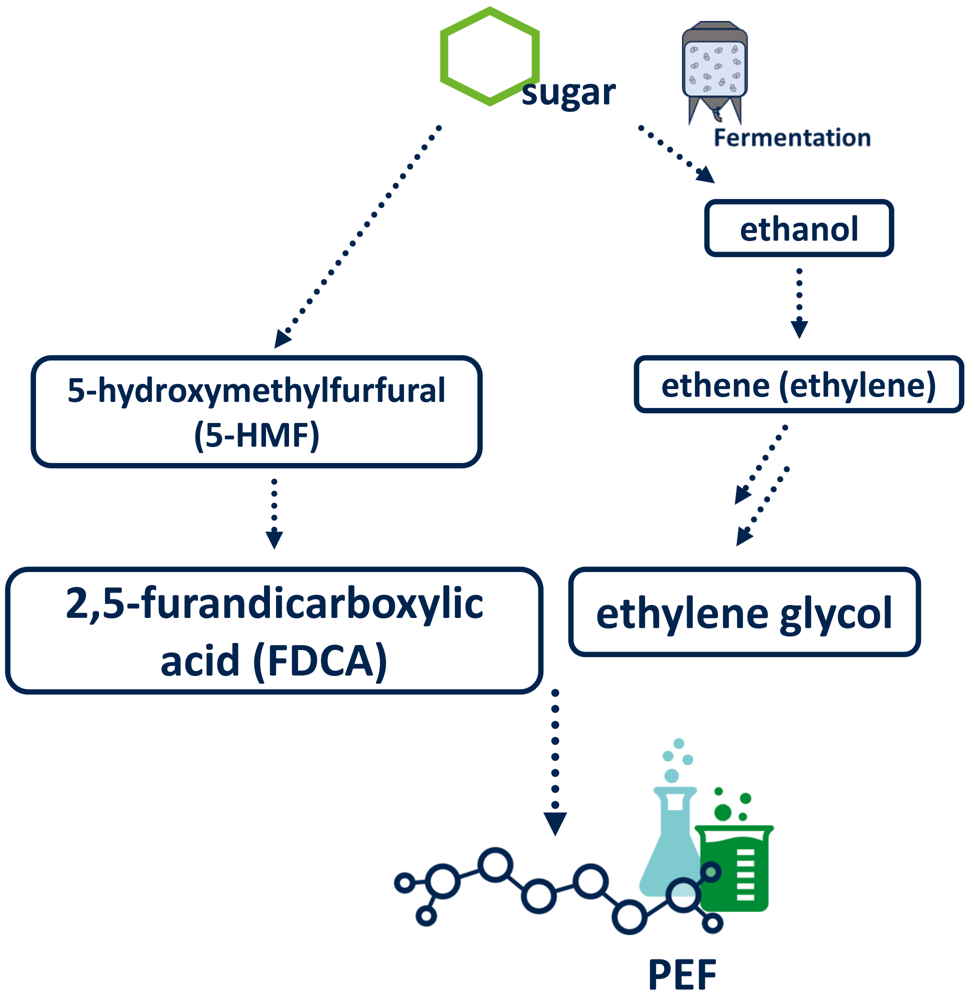


Biobased plastics | PEF



Polyethylenfuranoate (PEF) – biobased PET-alternative (technical thermoplastics)

- Aromatic polyester: comparable with PET
- Educts: **2,5-furandicarboxylic acid (FDCA) and ethylene glycol (MEG)**
- FDCA is produced from sugar (fructose)
- Ethylene glycol could be synthesized from sugar as well to a produce a **fully biobased PEF**
- **Industrial application** as bottles, films and fibers



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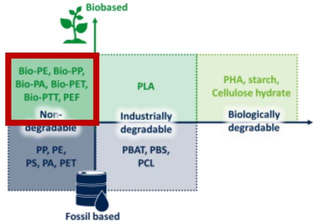

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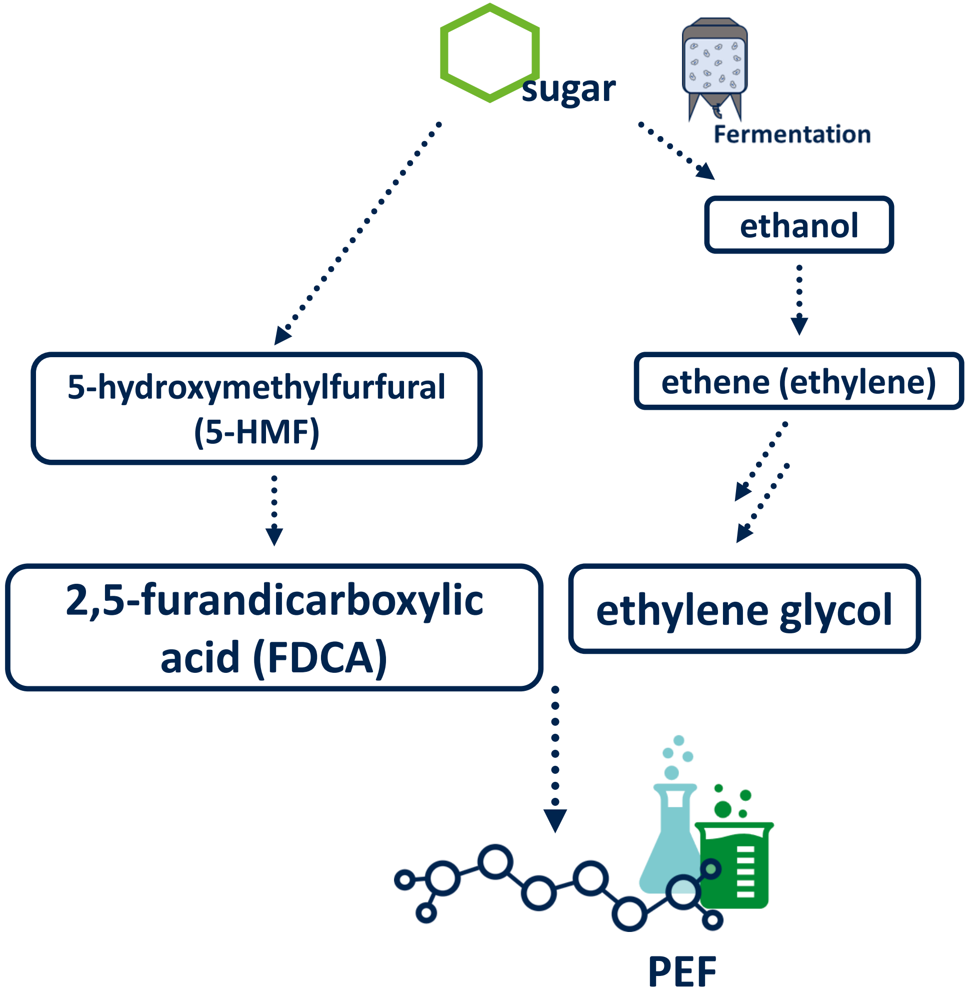
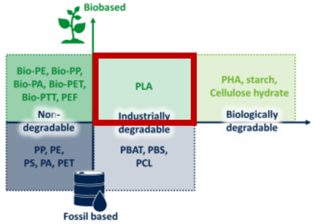
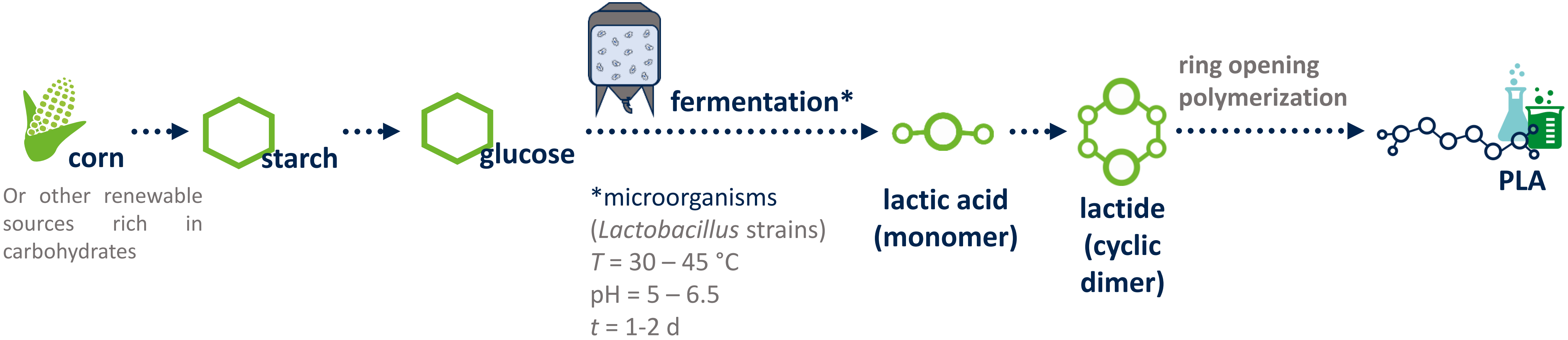
Comparison with PET

- Better O_2-, CO_2- and H_2O-barrier properties
- High tensile strength
- Low melting point
- Higher glass temperature



Biobased plastics | PLA





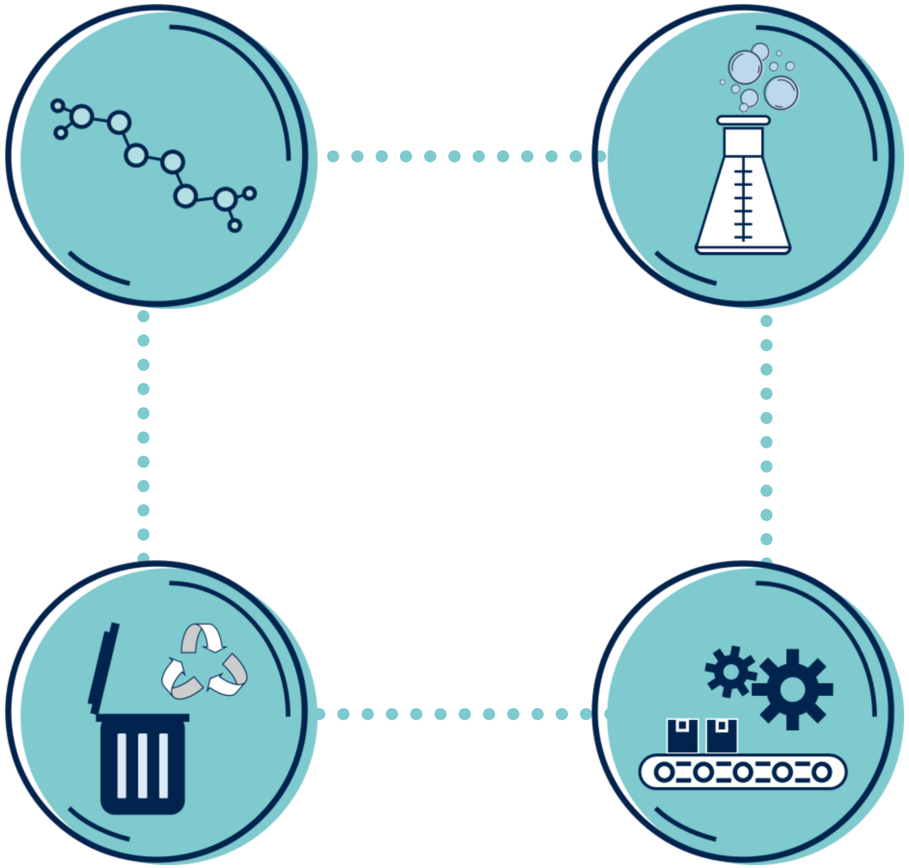
Polylactid (technical thermoplastics)

- PLA belongs to the **polyesters**
- Production is usually based on **starch-rich plants**
- Extracted starch is converted into sugar (glucose) that is transformed into lactic acid (monomer) by **fermentation**

PLA – Polylactic acid

Chemical properties:

Lactic acid is a hydroxycarboxylic acid (an acid group and an alcohol in the molecule structure). It occurs in two enantiomeric forms: **L- and D-lactic acid**. PLA has **hydrophobic properties** due to its nonpolar polymer chain, but is less hydrophobic than PE.



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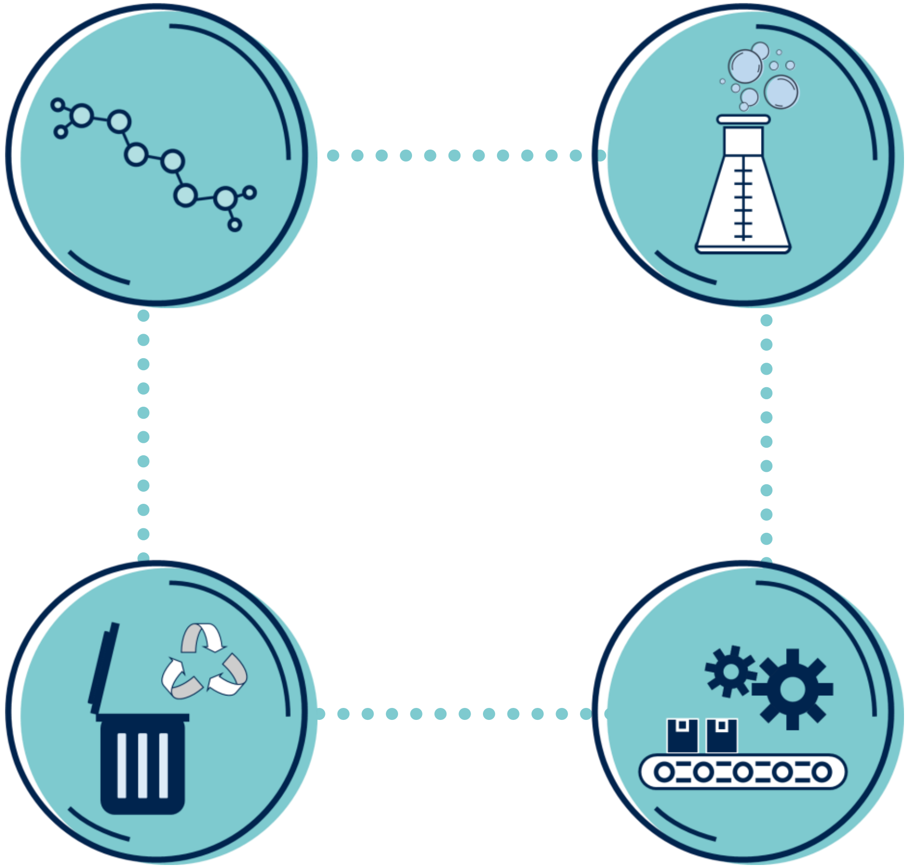

Production:

Lactic acid monomer (L- and D-lactic acid) can be produced by **fermentation from carbohydrates** such as sugar or starch. Polymerization takes place either by **direct condensation or ring opening condensation**, starting from lactide (dimer).

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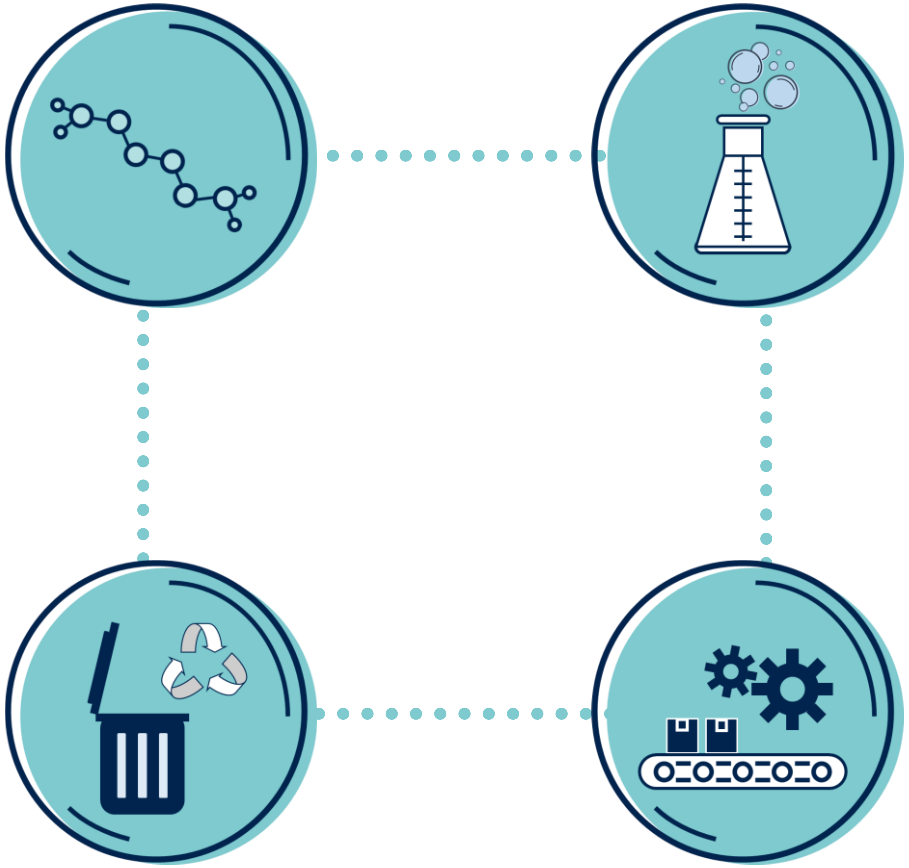

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Degradability:

PLA is **not biodegradable or only to insufficient degree at ambient temperature** or uncontrolled environmental conditions! **Industrial composting conditions** are required instead. In addition, the degree of crystallinity affects biodegradability.

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1,5 – 3,0 €/kg

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Processing:

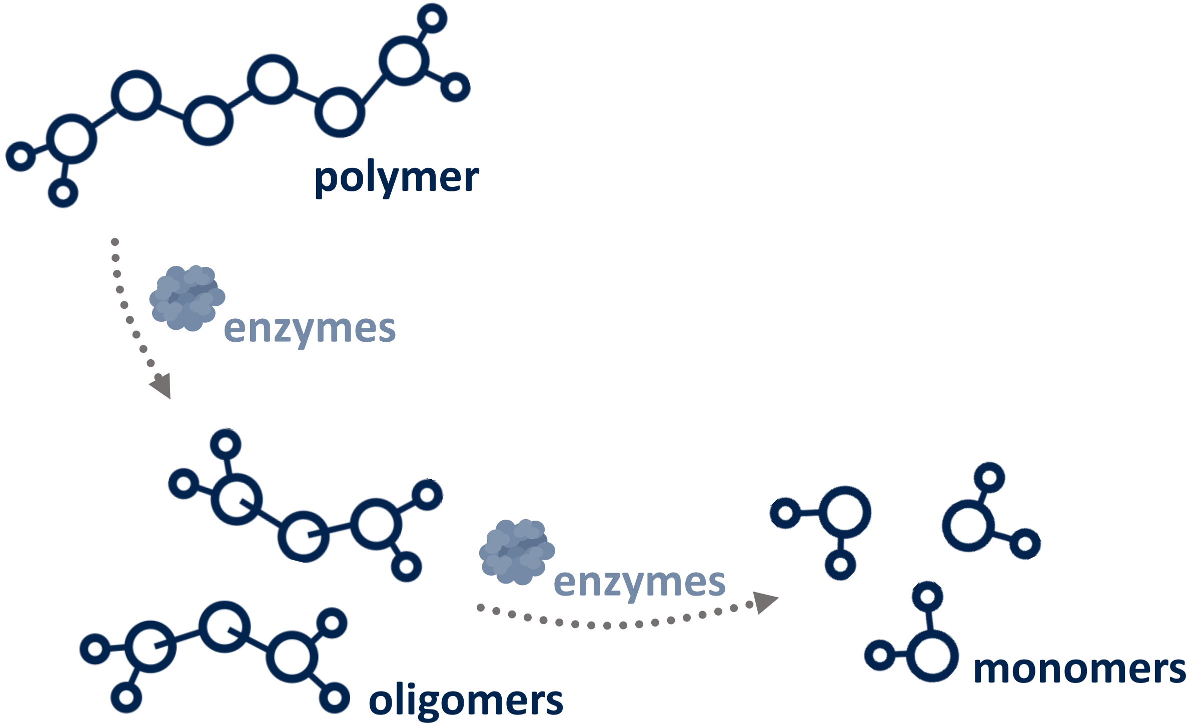
Modifications are possible via the ratio of PLLA and PDLA, the **chain length** of the polymers and their **crystallinity** as well as through adition of **additives, fillers or reinforcing materials**. The **processing temperature** is approximately **150 – 180 °C**.

Properties & applications of PLA

- Non-toxic
- Biocompatible
- Moderate barrier properties against water vapor (slightly lower than PET) -> can be improved as a blend or with a coating
- Transparent
- Good mechanical strength -> but very brittle

- Suitable **for extrusion** and **injection molding**: films, foils, fibers and sheets
- 3D printing (additive manufacturing)
- **Packaging** for food contact (e.g., for disposable packaging)
- **Medical implants**

Enzymatic plastics degradation



- Polymers such as PET and PLA, which contain **ester bonds** in their chemical structure, **can be degraded enzymatically.**
- **Various enzymes** from cutinases, lipases, laccases, esterases and PETases are **capable of hydrolyzing ester bonds.**
- They originate from various microorganisms (bacteria, algae, fungi)
- **During hydrolysis, the molecular weight decreases continuously:** first oligomers (short chain polymers) are formed followed by degradation to monomers.
- Biobased polymers can ultimately be degraded to CO_2 and H_2O (e.g., PLA).

Enzymatic plastics degradation

- The activity of enzymes for degradation can be tailored by ***Protein Engineering***.
- A **material-specific binding of the enzymes**[1] to the polymer can further increase degradation.[2],[3]

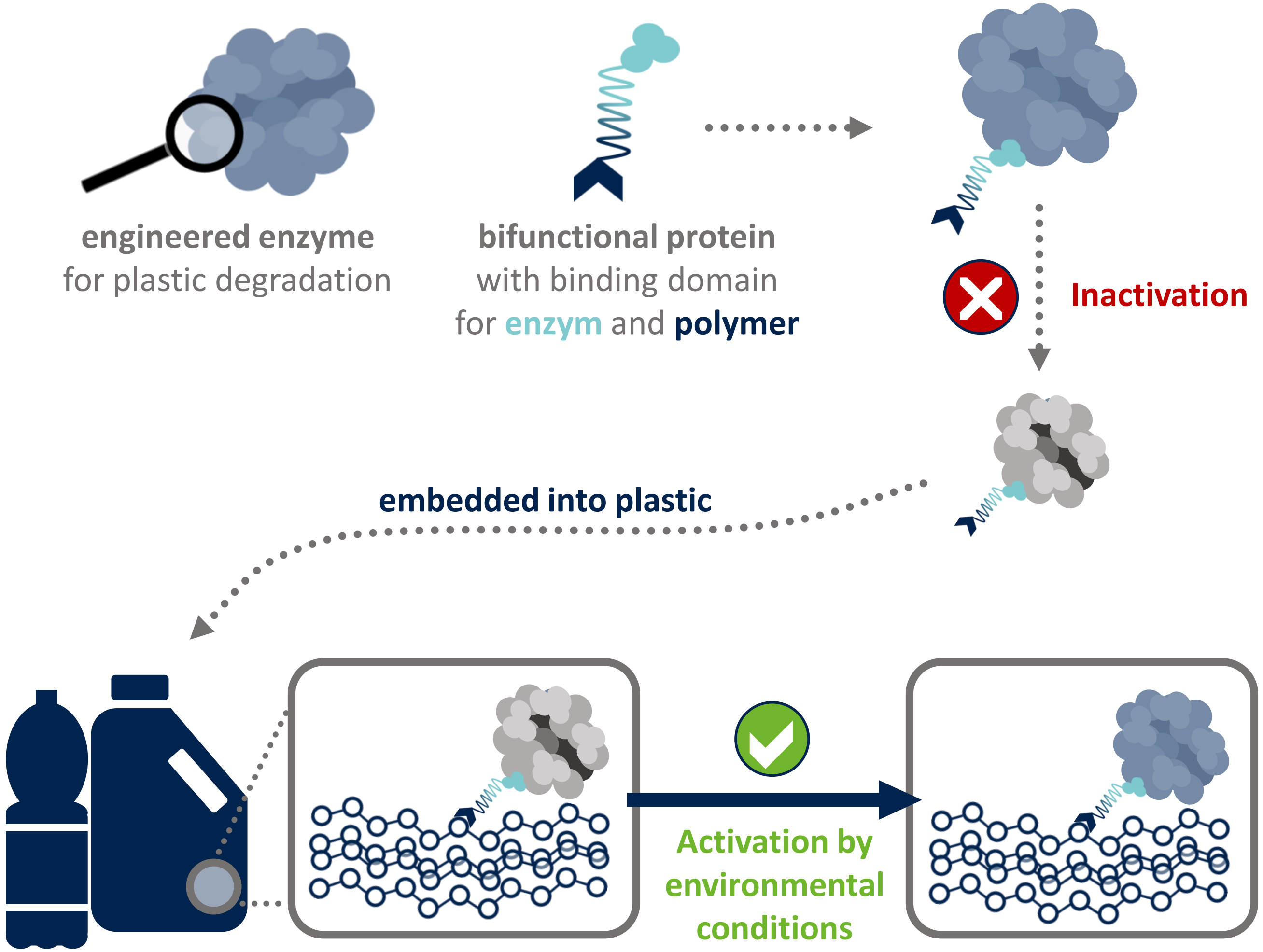
engineered enzyme
for plastic degradation

bifunctional protein
with binding domain
for enzym and **polymer**

[1] *Chem. Soc. Rev.* **2024**, 53, 6445-6510.
[2] *Angew. Chem. Int. Ed.* **2024**, *136*, e202317419.
[3] *ACS Catal.* **2023**, 13, 12746-12754.

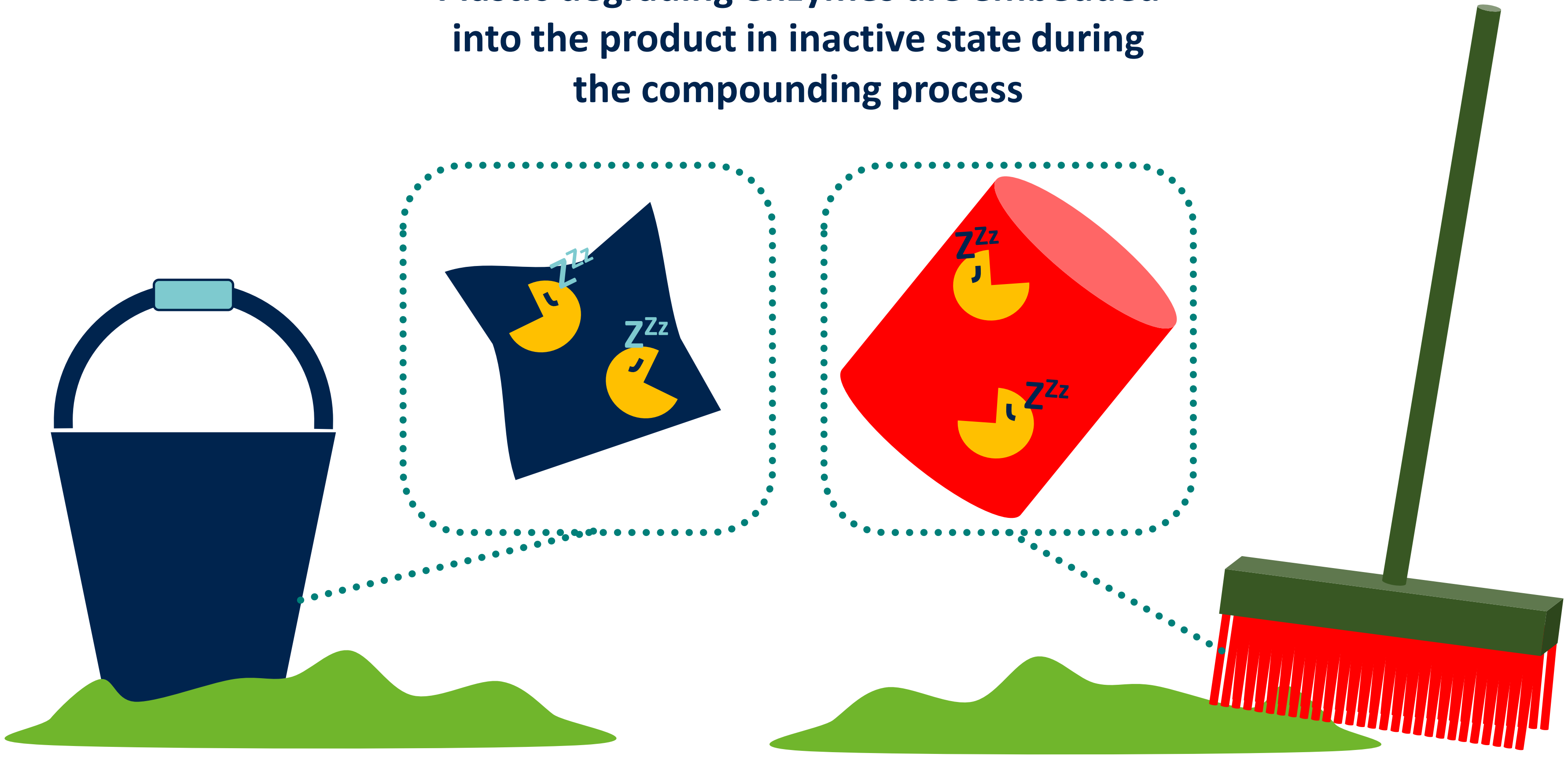
Enzymatic plastics degradation

- The activity of enzymes for degradation can be tailored by ***Protein Engineering***.
- A **material-specific binding of the enzymes**[1] to the polymer can further increase degradation.[2],[3]
- Enzymes can be introduced **into material in an inactive form** to ensure **programmed degradation** under specific conditions.
- **Challenges** include the prevailing environmental conditions, the **crystallinity of the polymer** and slow degradation, which contrasts with the rapidly growing amount of plastic waste.



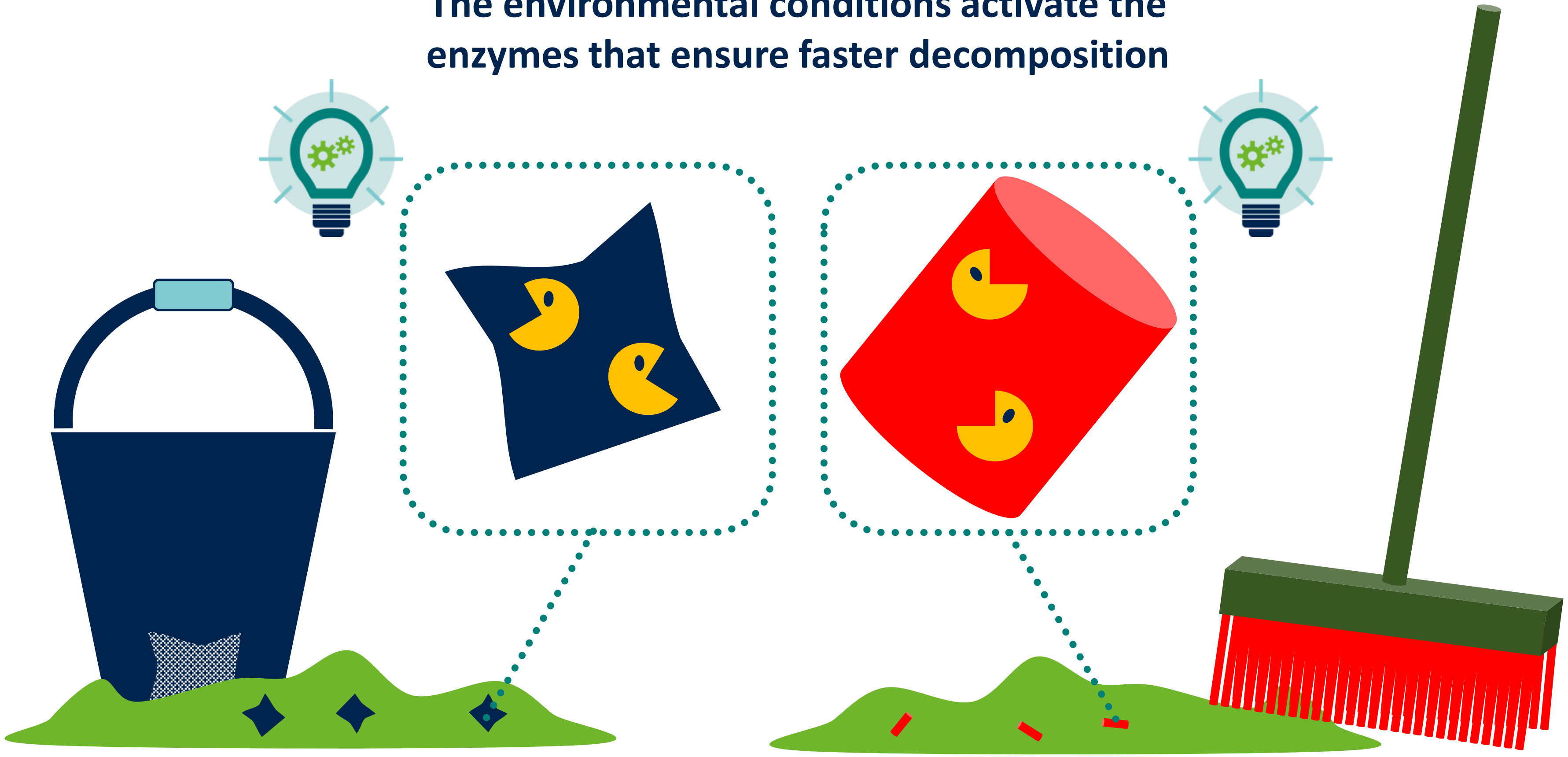
Use Case: Programmed plastic degradation

Plastic degrading enzymes are embedded into the product in inactive state during the compounding process



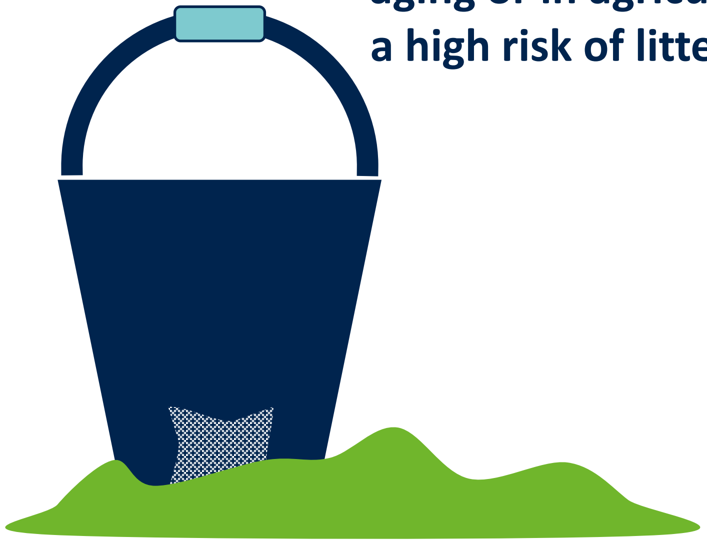
Use Case: Programmed plastic degradation

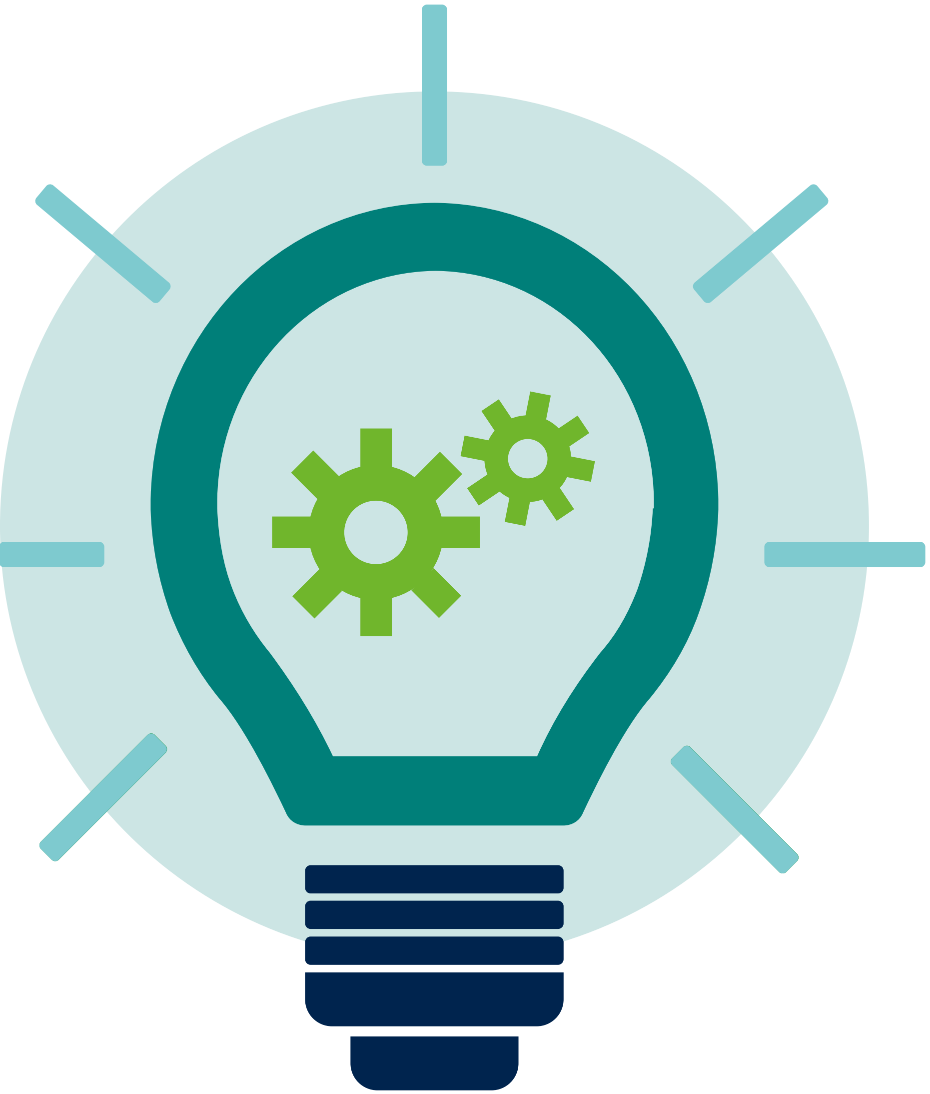
The environmental conditions activate the enzymes that ensure faster decomposition



Use Case: Programmed plastic degradation

This programmed degradation is particularly interesting for applications in which fragments inevitably end up in the environment (e.g., through aging or in agricultural applications) or where there is a high risk of littering, i.e., disposal in the environent.





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Modified biomass

Properties, processing and recycling

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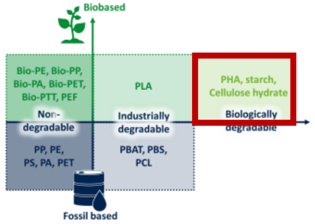
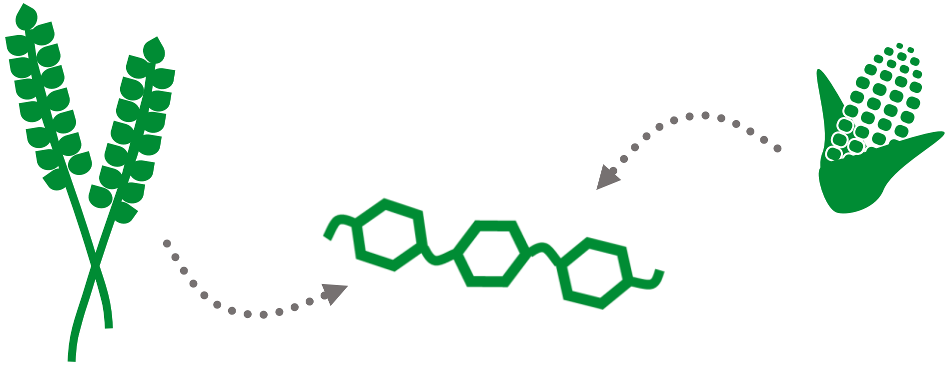
Natural, biobased & biodegradable

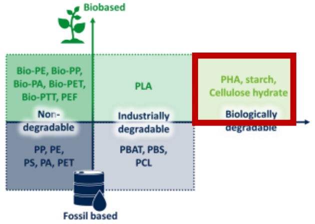


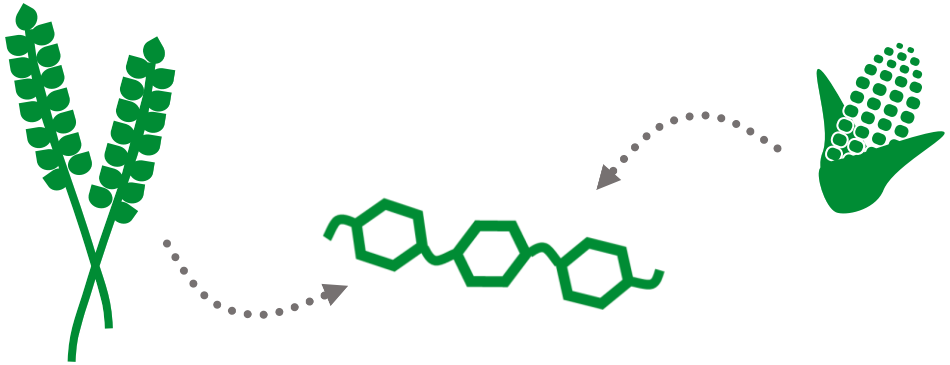


- A wide variety of **natural polymers** exists in nature.
- By definition, **(chemically) unmodified natural polymers** are **not plastic!** (and therefore do not form microplastics)[1].
- Often, these polymers are **polysaccharides (sugar polymers)**
- **Natural polymers** provide an **inherent biological degradability.**

[1] EU SUPD Art. 3 (40)

Natural, biobased & biodegradable





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Industrial applications include for example:

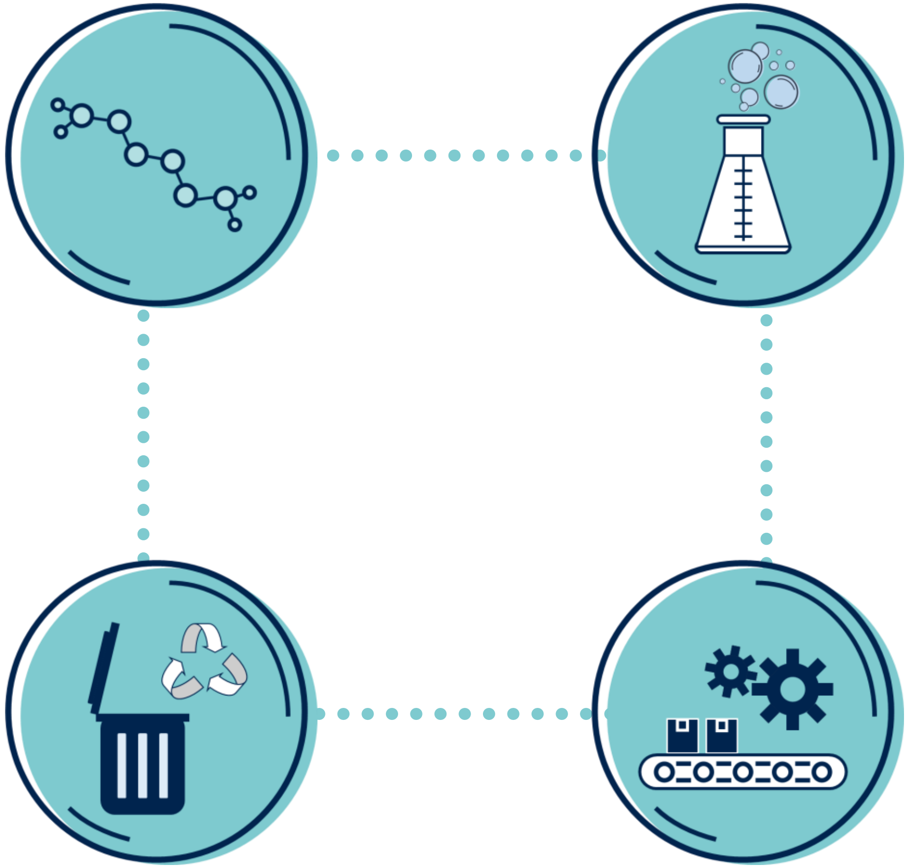
- **Pectin** (sugar polymer from plant-based raw materials; apple or beet pulp) is used as a gelling agent.
- **Chitin** (sugar polymer found in fungi or shells of insects/crustaceans) serves as basis for **chitosan**, which is suitablefor production of fibers, foams and films.
- **Cellulose** from wood and cellulose-rich plants – these include bast plants such as hemp, flax, kenaf and ramie; cotton consists almost entirely of cellulose
- **Starch –** Sugar polymer from starch-rich plants such as corn and potatoes

[1] EU SUPD Art. 3 (40)

Thermoplastic starch (TPS)

Chemical properties:

Starch consists of **sugar molecules** that are linked either as linear chains (amylose) or highly branched structures (amylopectin). Due to their **moisture-absorbing properties**, starch is usually **used in blends** of starch and additives (e.g., glycerin).



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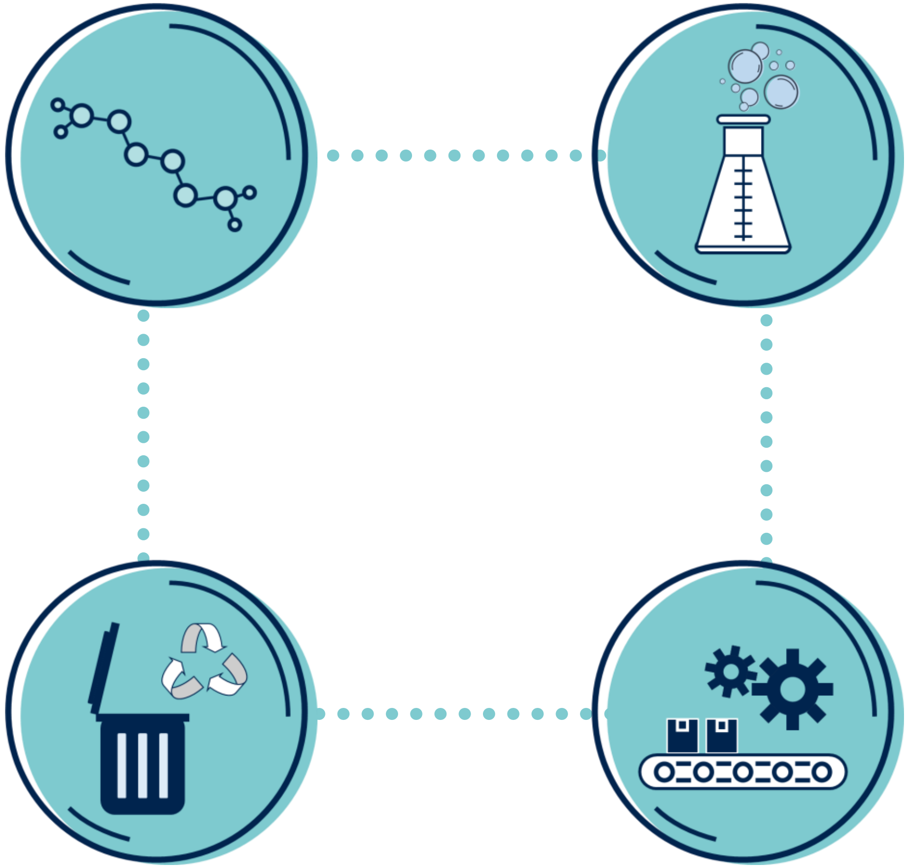

Production:

Starch can be extracted from various plants (e.g., corn, wheat, potatoes, tapioca). The extracted starch granules are **destructured** by **adding water** and **thermomechanical processing** in the extruder. Both water content and shear influence the mechanical properties of the product.

Thermoplastic starch (TPS)

Chemical properties:

Starch consists of **sugar molecules** that are linked either as linear chains (amylose) or highly branched structures (amylopectin). Due to their **moisture-absorbing properties**, starch is usually **used in blends** of starch and additives (e.g., glycerin).

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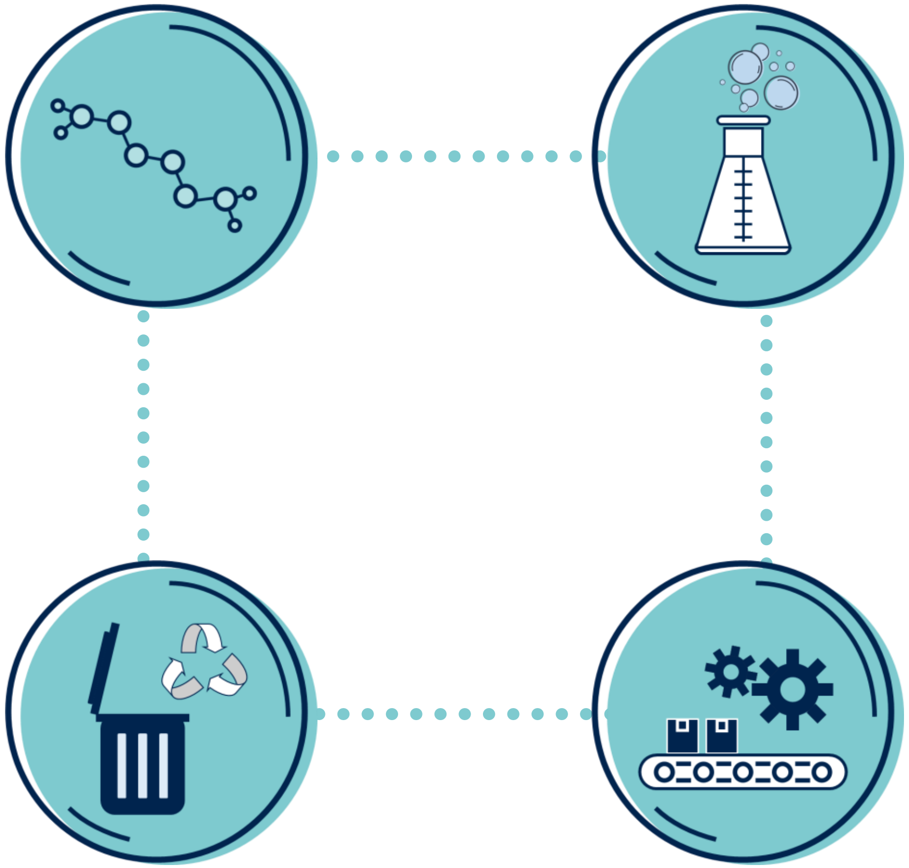

Disposal / recycling:

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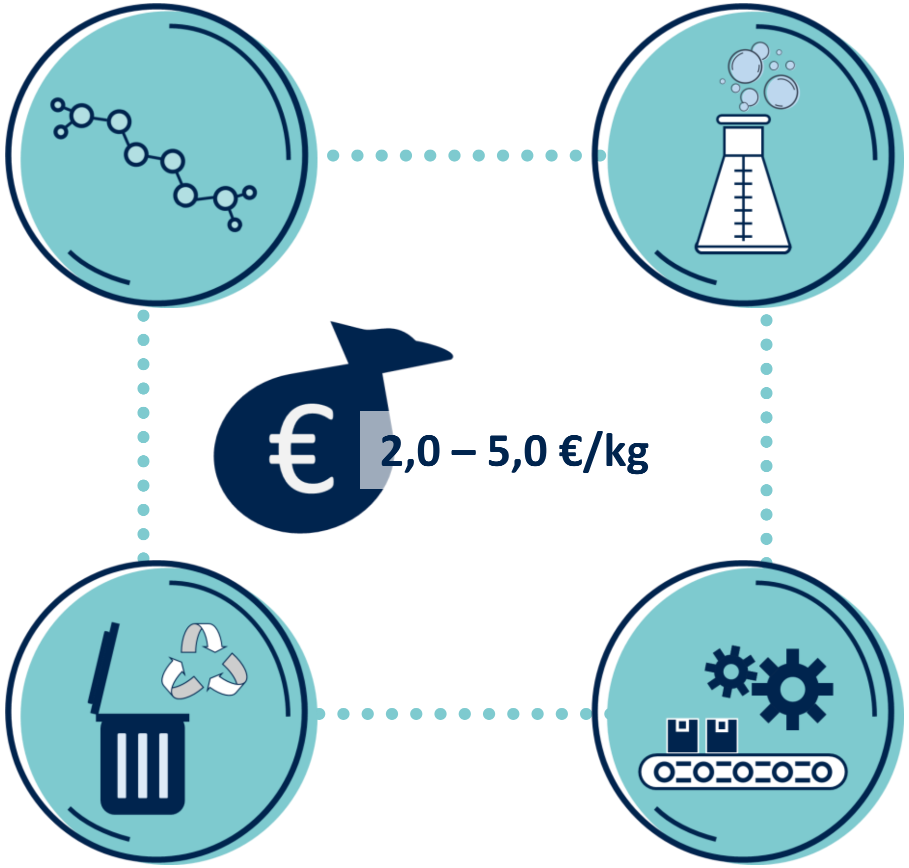

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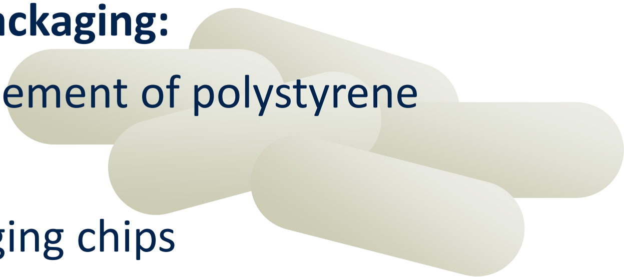
Processing:

The **processing temperature** is approx. **120 – 180 °C** (use of plasticizers such as glycerin is necessary). At higher temperatures, discoloration and degradation must be expexted. For modified starch and starch blends, the processing temp. Varies depending on the type of modification/polymer added (up to max. 200 °C). **Extrusion is carried out at 140 – 190 °C.**

Properties & applications of TPS

- Suitable for **food contact**
- Generally hydrophilic; absorbs moisture/water vapor
- Hydrophobicity can be increased through modification
- Relatively low mechanical strength; **brittle**
- Modifications can improve/increase mechanical strength
- Suitable for blends with other polymers
- Can be used in **injection molding**

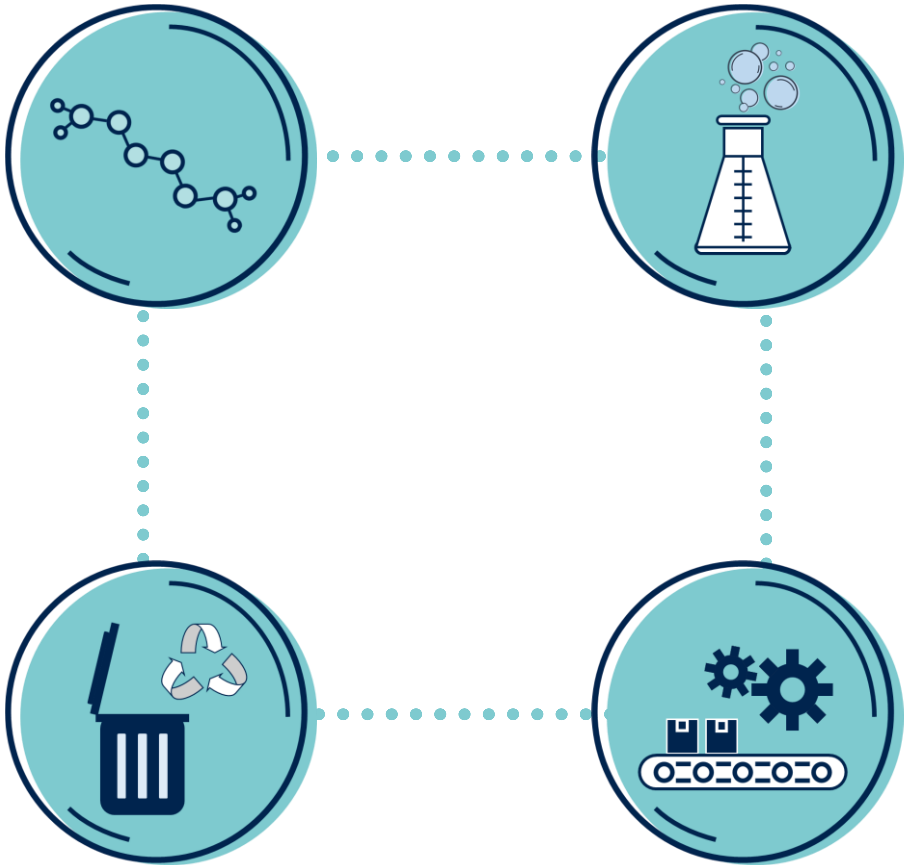
- **Film/foil**: food packaging; shopping bags
- **Coatings**
- **Agriculture**
  - Mulch films
- **Single use/disposable applications** (e.g., disposable tableware and cutlery)
- **Foam packaging:**
  - Replacement of polystyrene foams
  - Packaging chips



Celluloses

Chemical properties:

If the chemical structure remains unmodified, the material is called **regenerated cellulose;** if it is altered, it is referred to as **derivative**. Typical examples are cellulose hydrate (cellulose film) and cellulose acetate (thermoplastic).



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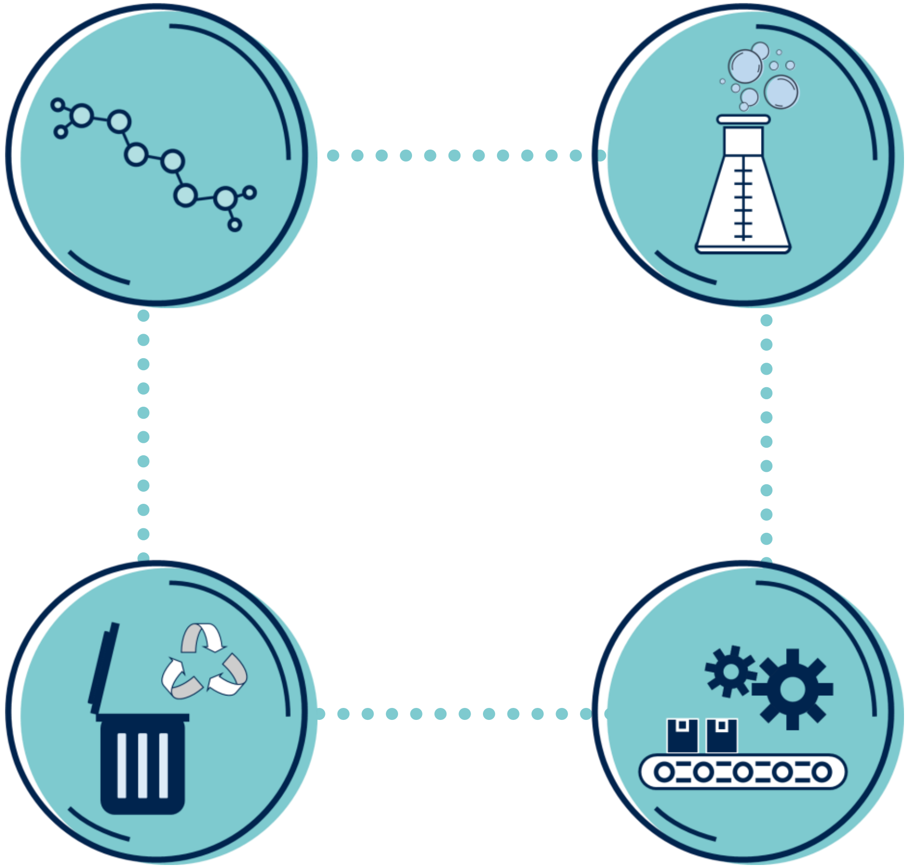

Production:

Cellulose is a **component of plant cells** and is therefore obtained from biomass such as wood and straw. **Cellulose acetate** is produced by partial **acetylation** using acetic acid (anhydride). **Microcristalline cellulose** is produced by the **hydrolysis** of purified cellulose with strong acids. **Nanocellulose** is celllulose (fibers, crystals) that has been mechanically or enzymatically processed to **nanodimensions**.

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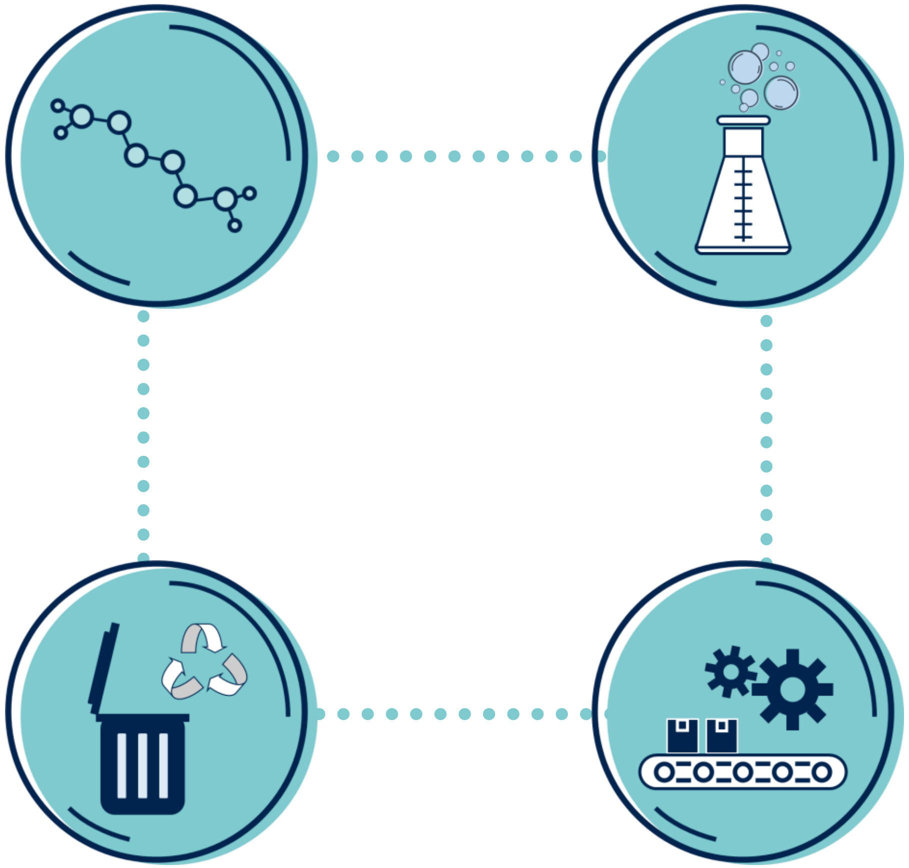
Disposal / recycling:

Cellulose derivatives can be recycled, although the quality and length of the fibers usually decrease with each cycle.
Celluloses (regenerates) are suitable for **home composting and industrial composting** as they can be degraded by various microorganisms and enzymes.



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MCC: 3 – 8 €/kg
CA: 5 – 10 €/kg
NC: 10 – 50 €/kg

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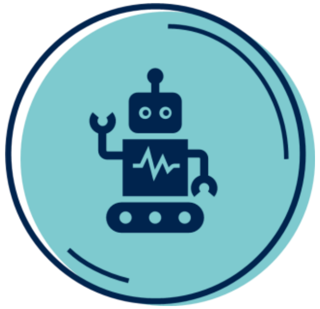
Processing:

Depending on the modification of cellulose, the **processing temperature** is approx. **80 – 200 °C**. Cellulose does not show a sharp melting point, but decomposes at ca. 260 °C.

MCC = Microcristalline cellulose
CA = Cellulose acetate
NC = Nanocellulose

Properties & applications of cellulose

- Suitable for food contact
- Colorless, transparent appearance as cellulose hydrate
- Permeable to water vapor



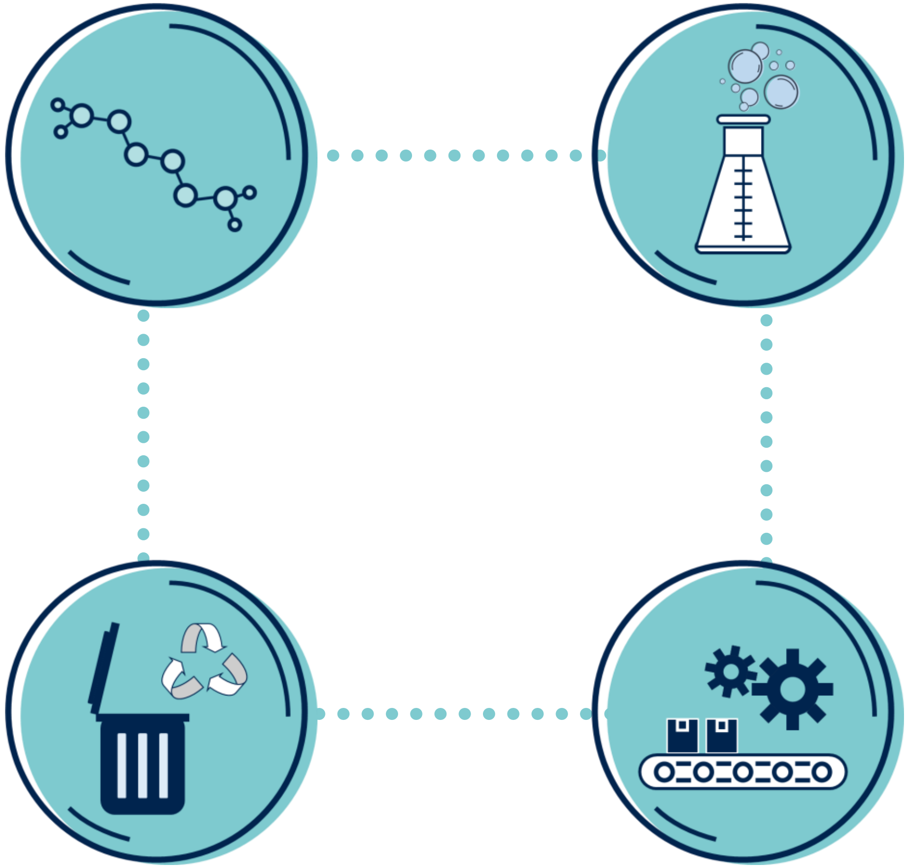
- **Film/foil** (cellulose hydrate)*: food packaging; prevents condensation
- **Coatings**
- **Medical applications** (e.g. wound dressings)
- **Fibers:**
  - Textiles
  - Filters
  - Composite materials

* Known former brand name „Cellophan“

Polyhydroxyalkanoates (PHA)

Chemical properties:

PHAs are water-insoluble, **linear bio-polyesters,** that are formed by many bacteria as reserve substance for carbon and energy (comparable to human fat deposits). Since they can be formed on the basis of different **hydroxycarboxylic acids, PHA is the generic term for a class of substances** that includes e.g., PHB (polyhydroxybutyrate) and PHV (polyhydroxyvaleric acid).



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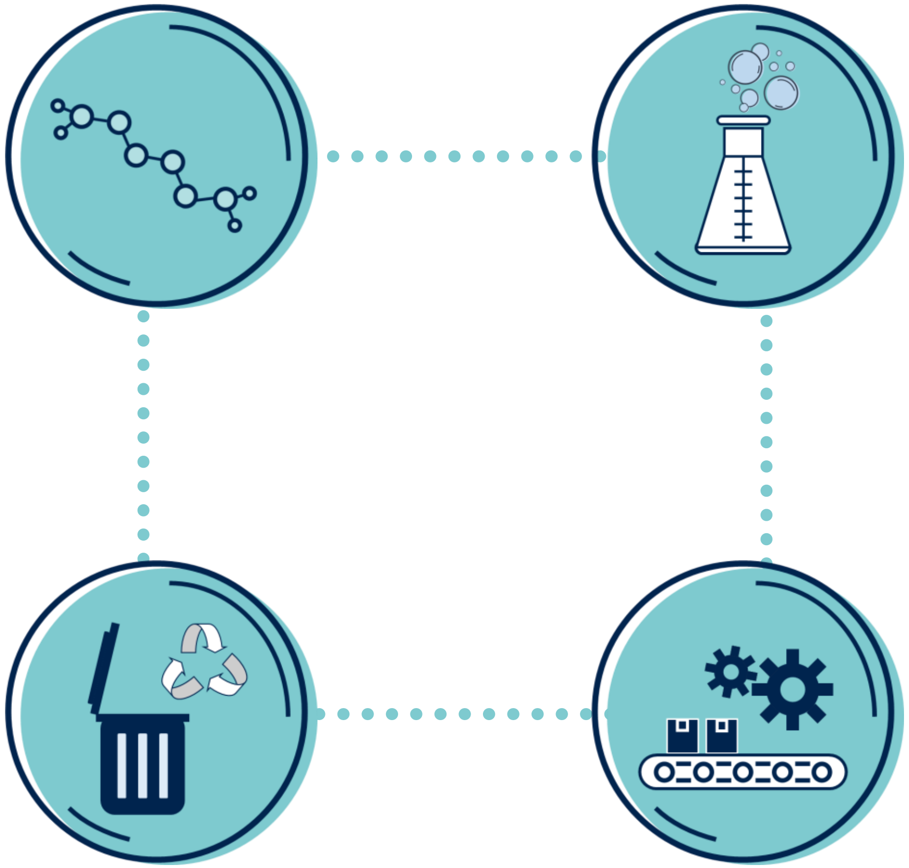

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Generally, no polymerization but an **extraction from cell mass** in the bioreactor is performed.
The type of **PHA** is influenced by the **microorganisms used**, the **biomass (feed)** and the process parameters.

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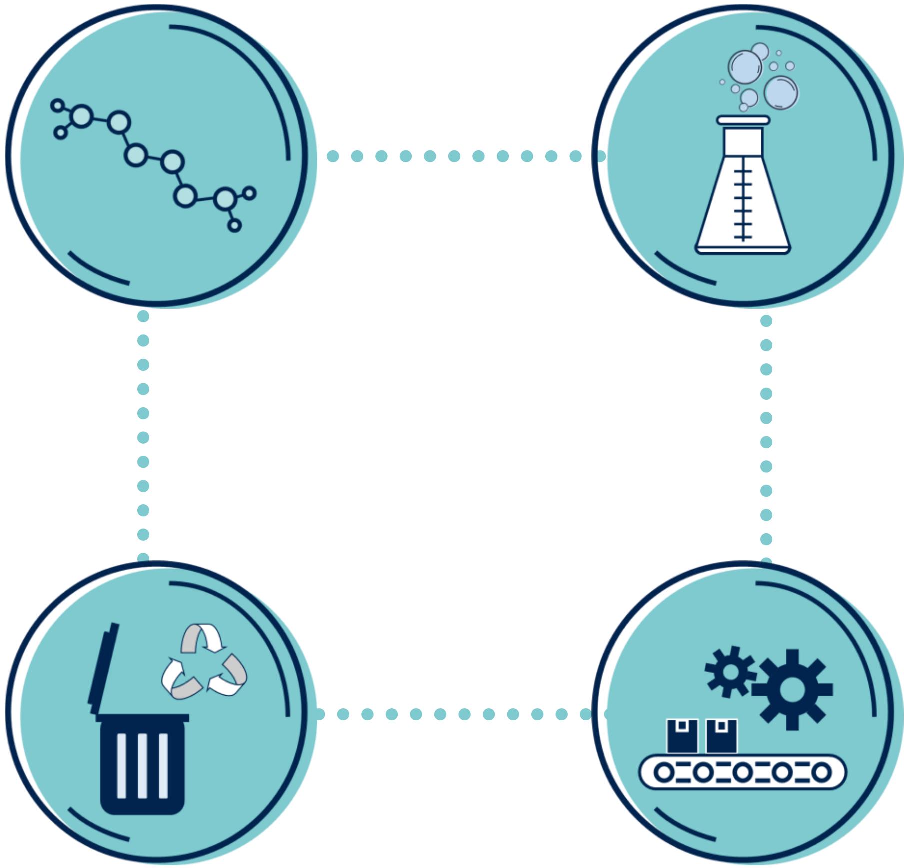

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Due to their ester bonds, PHAs are **biodegradable** (see also surgical suture material). They are suitable for **home composting and industrial composting** as well as for soil and marine environment.

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3,0 – 12,0 €/kg*

Production:

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The type of **PHA** is influenced by the **microorganisms used**, the **biomass (feed)** and the process parameters.

Processing:

Suitable for **thermoplastic applications** in extrusion and injection molding at temperatures of approx. **160 – 190 °C.** Pure **PHB has a high degree of crystallinity** and i therefore brittle and rigid. Copolymers, e.g., with **PHV, increase elasticity** and improve processability.

*cheaper for packaging applications than for medical applications (medical grade)

Properties & applications of PHA

- Non toxic
- Biocompatible
- Good resistance to moisture
- Low permeability to water
- Aroma barrier properties
- Good resistance to UV radiation
- Suitable for **injection molding**
- Suitable for **extrusion (films, hollow bodies)**

- **Food packaging**/disposabel packaging
- Compostable containers
- **Medical applications:**
  - Release of active substances
  - Implants
  - antimicrobial wound sutures
- Hygiene products
- **Cosmetics** (microplastic substitute, thickening agent)

"Bioplastics have the potential to play a significant role in reducing the environmental impact of plastics. However, the industry needs a clear and supportive policy framework to reach its full potential."

Hasso von Pogrell,
Managing Director of European Bioplastics

Discover – Develop – Connect

Your contact and partner regarding bioplastics

Tobias Göbel
SKZ – Das Kunststoffzentrum

transbib@skz.de

Self-check

True or false? Evaluate the following statements based on the content from the recent chapter (solutions are presented on the following slide).

(1) Not only biomass and agricultural waste, but also cell components can serve as raw materials.

(2) The use of biomass in the plastics and packaging industry is a new trend.

(3) Biomass is only suitable for the production of films.

(4) PHA is the generic term for a class of polymers that includes e.g., PHB and PHV.

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Correct! PHAs (polyhydroxyalkanoates) are produced by various microorganisms (bacteria) as energy storage. The type of PHA and the possibility of copolymer formation depend on the bacteria used and, above all, on the fed substrate (e.g., various sugars, short-chain acids or alcohols such as glycerin).

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False! Cellulose hydrate has been used as packaging film for the food industry since the early 20th century. However, awareness of the finite nature and environmental impact of using non-renewable fossil raw materials is now leading to increased attention and a search for bio-based materials.

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False! Biomass can be used to manufacture many products in the plastics and packaging industry. As so-called drop-in solutions, the substances used chemically identical to their fossil-based counterparts.

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Correct! Polyhydroxyalkanoates (PHAs) include polyhydroxybutyrate (PHB) and polyhydroxyvaleric acid (PHV), among others. They are produced by fermentation and belong to the (poly)hydroxycarboxylic acids.

Note

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