Biobased and biodegradable polymers: definition, production, performances

Prof. PATRIZIA CINELLI

patrizia.cinelli@unipi.it

Tel. +39-0502217869

University of Pisa

Department of Civil and Industrial Engineering

Outline

Recover Project: short overview

Circular Economy Principles, Bio Plastic market overview,

Bio-polymers: Definition, Biobased, Biodegradable
Plastic degradation(aerobic, anaerobic):
Dependence from chemical structure, polymer characteristics

Main sustainable Polymers:
Synthetic Polymers: Poly lactic acid, Polyhydroxyalkanoates, polybutylene succinate,
Natural Polymers: Thermo plastic Starch, chitin, chitosan

RECOV3R

PROJECT DETAILS

48 Months

17 Partners

7 Countries (Belgium, Germany, Ireland, Italy, Portugal, Spain, United Kingdom)

5.8 Million € (ca. 4.4 M€ EC contribution)

Call: **BBI-2019-SO2-R3** - Apply microorganisms and/or enzymes to resolve end-of-life issues of plastics

Enzymes + microorganisms + insects + earthworms
Plastics for food packaging and agriculture

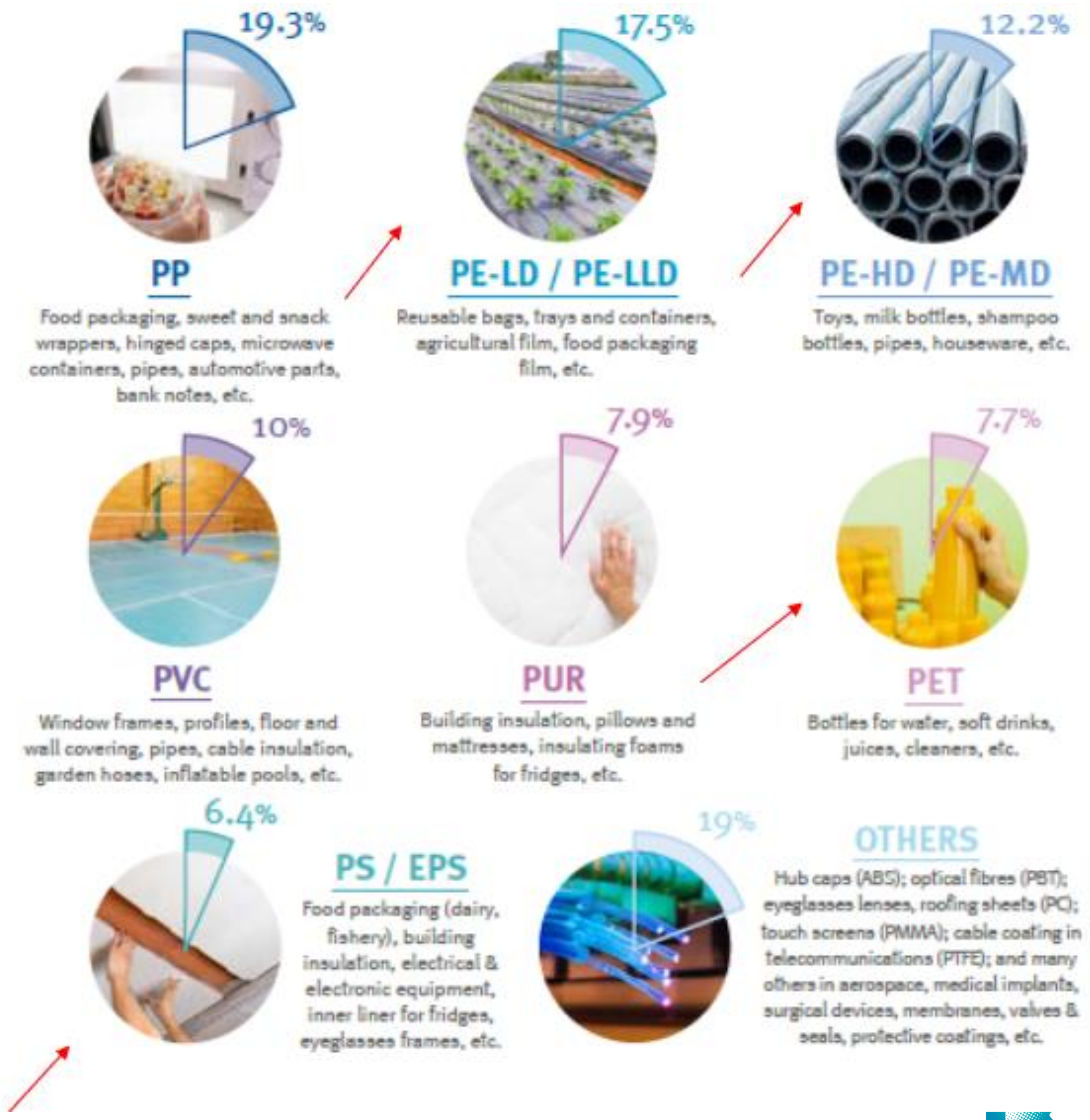
RECOV3R

PROJECT CONSORTIUM

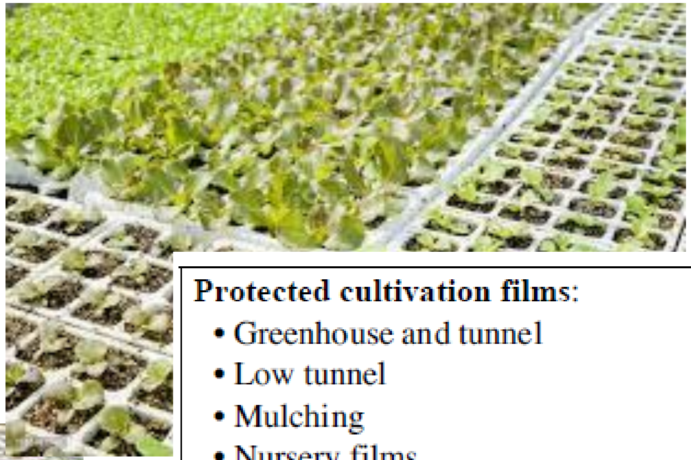
Participant name	Short name
Universidad De Almería	UAL (Coo.)
Università Di Pisa	UNIPI
Asociación Agraria Jóvenes Agricultores España	ASAJA
BRUNEL University	BRUNEL
Universidad Miguel Hernández De Elche	UMH
Albstadt-Sigmaringen University	ASU
NATURPLÁS PLÁSTICOS AGRICOLAS, S.L.	NATURPLAS
ASA SPEZIALENZYME GMBH	ASA
NUTRINSECT SRL	NUTRINSECT
IRIS Technology Solutions, S.L.	IRIS
Organic Waste Systems N.V	OWS
IDELUX Environnement	IDELUX
FEMTO ENGINEERING SRL	FEMTO
Ingredient Odyssey LDA - Entogreen	ENTO
CARTON BROS. - MANOR FARM	MANOR
ENCO ENGINEERING SRL	ENCO
S.A. Agricultores de la Vega de Valencia	SAV

5 HES, 1 Association, 1 NGO, 7 SMEs, 3 large enterprises (2 BIC members)

PLASTIC WASTE ISSUE



PLASTIC IN AGRICULTURE

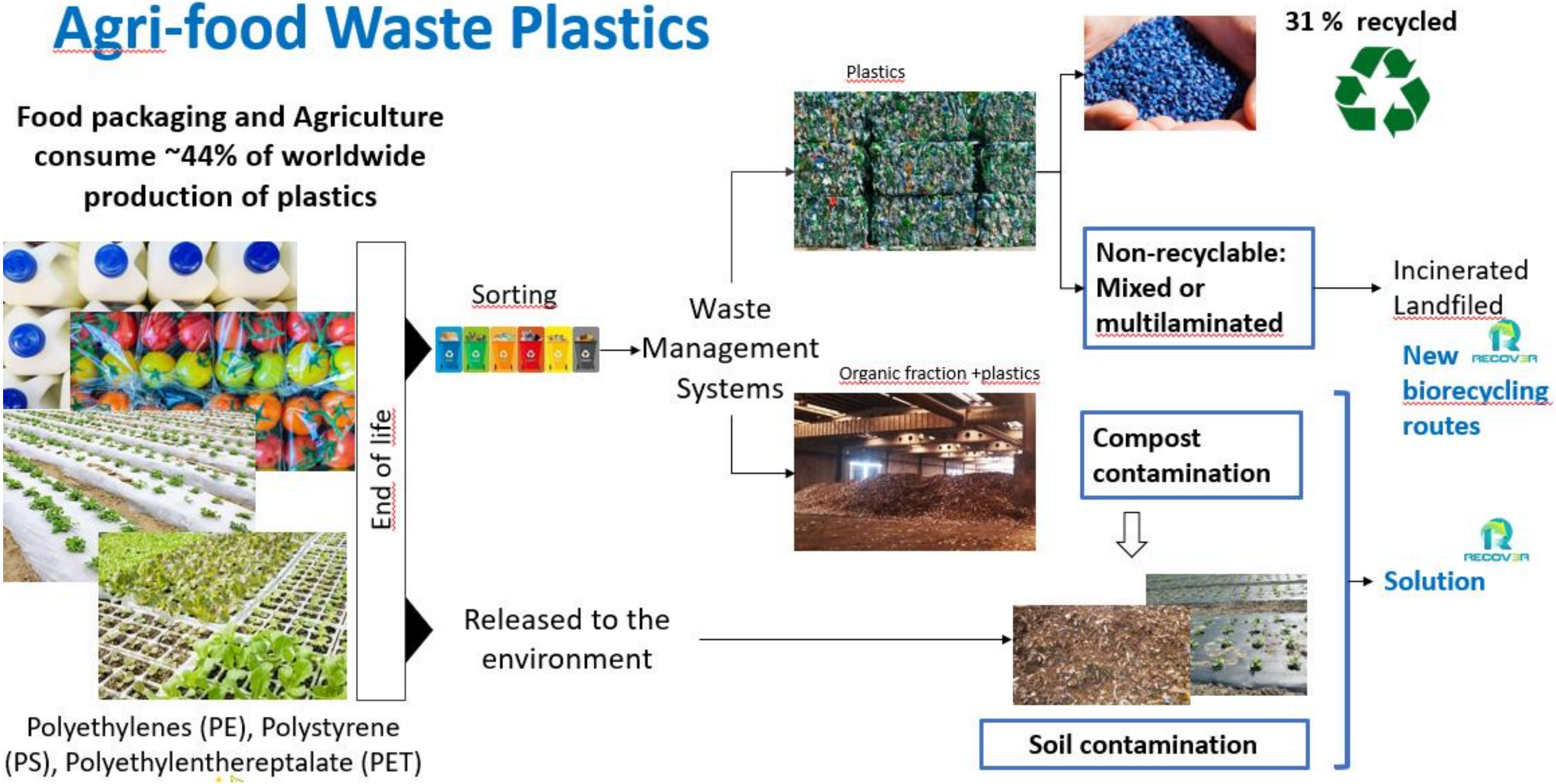


Protected cultivation films:	**Nets:**	**Packaging:**
• Greenhouse and tunnel	• Anti-hail	• Fertilizer sacks
• Low tunnel	• Anti-bird	• Agrochemical cans
• Mulching	• Wind breaking	• Containers
• Nursery films	• Shading	• Tanks for liquid storage
• Direct covering	• Nets for olives and nut picking	• Crates
• Covering vineyards and orchards		
	Piping, irrigation /drainage:	**Other:**
	• Water reservoir	• Silage films
	• Channel lining	• Fumigation films
	• Irrigation tapes and pipes	• Bale twines
	• Drainage pipes	• Bale wraps
	• Microirrigation	• Nursery pots
	• Drippers	• Strings and ropes

A wide range of plastics are used in agriculture, including, polyolefins (polyethylenes (PE), Polypropylene (PP), Polystirene, Ethylene-Vinyl Accetate Copolymer (EVA) and less frequently, Poly-vinyl chloride (PVC), Polycarbonate (PC) and poly-methyl-methacrylate (PMMA).

Source: https://www.plasticseurope.org/en/about-plastics/agriculture

Agri-food Waste Plastics

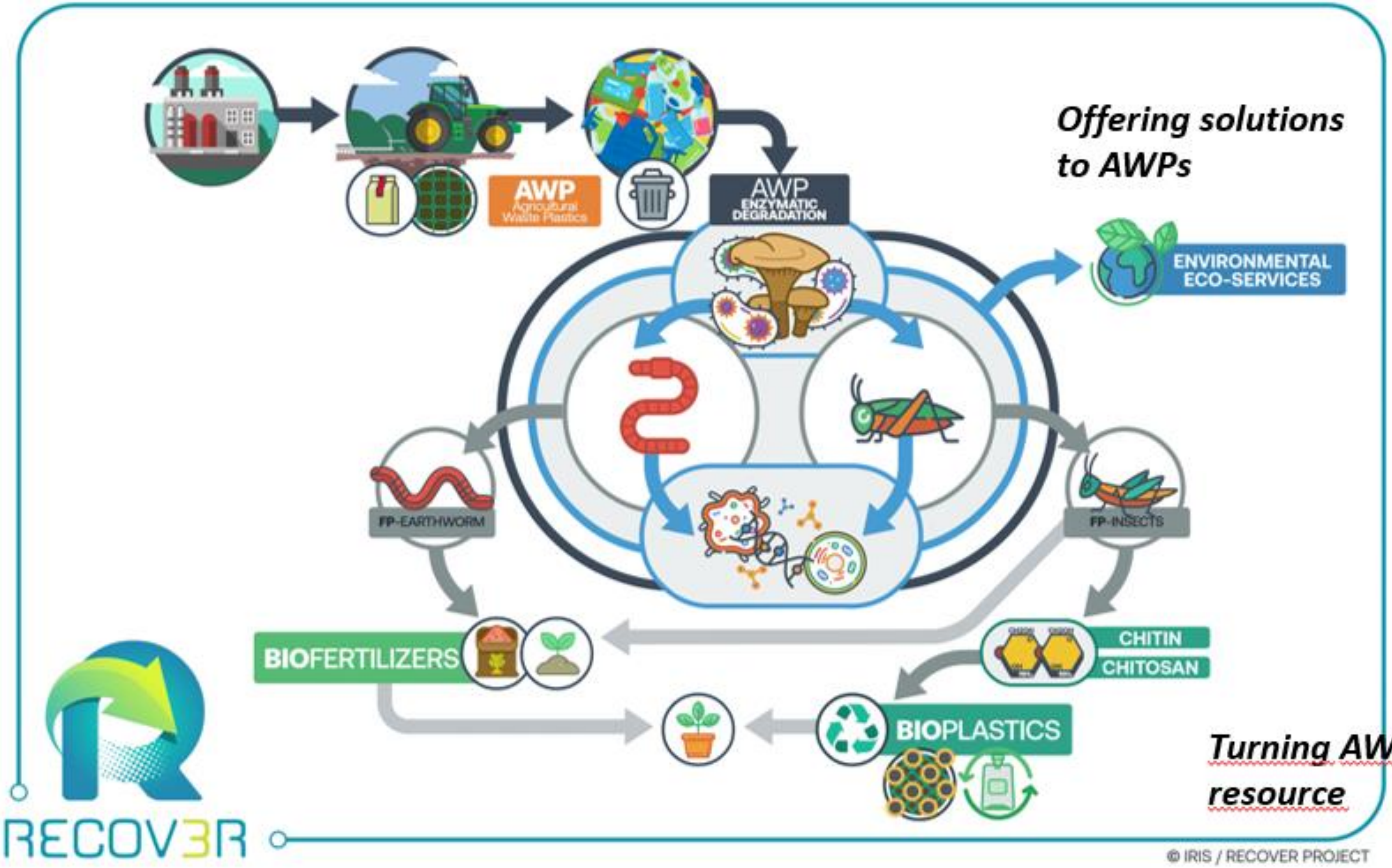


Recover solutions & innovations

Agri-food Waste Plastics (AWPs)

Combining new enzymes, microorganisms, insects & earthworms

Products

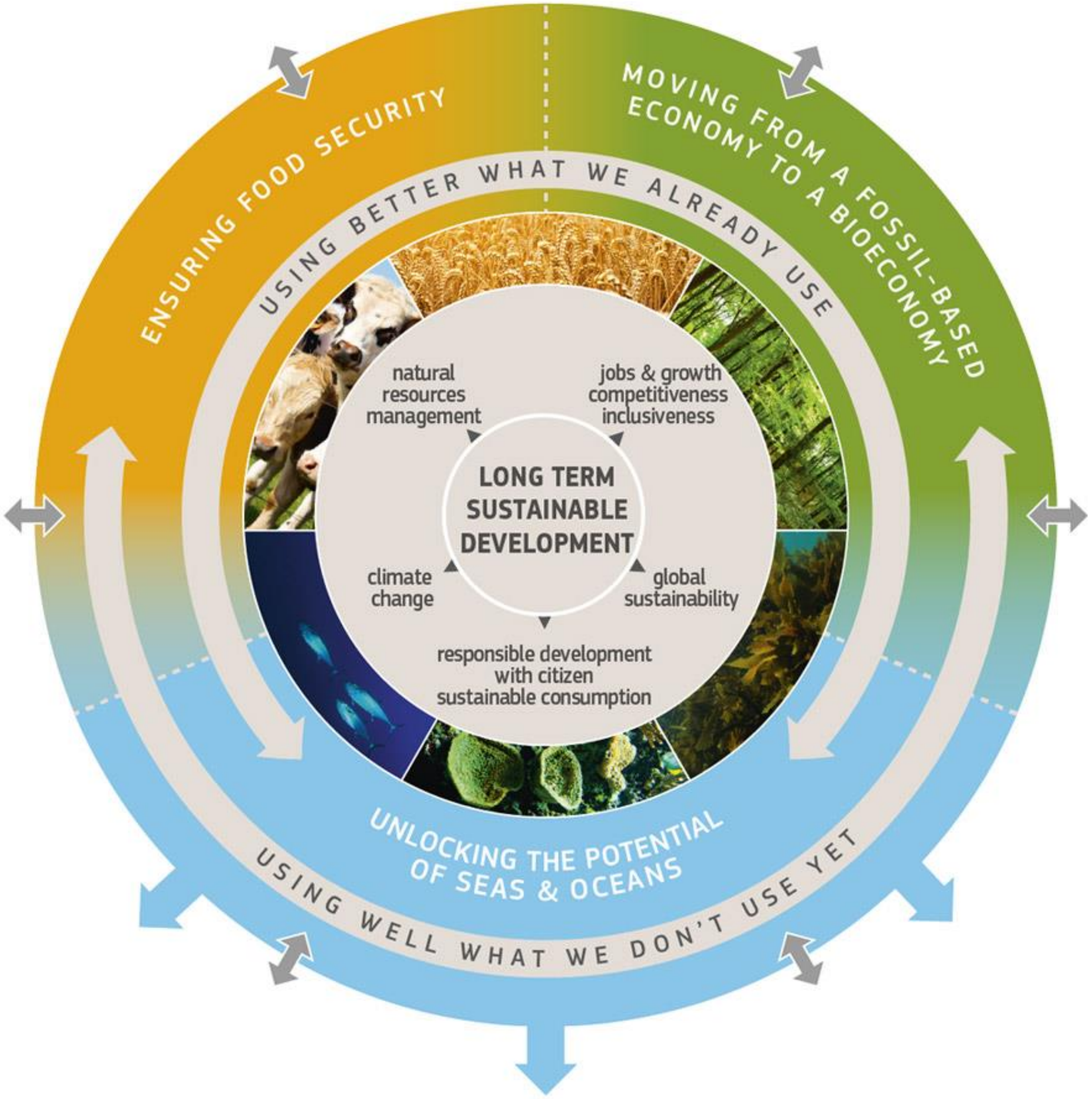


Offering solutions to AWPs

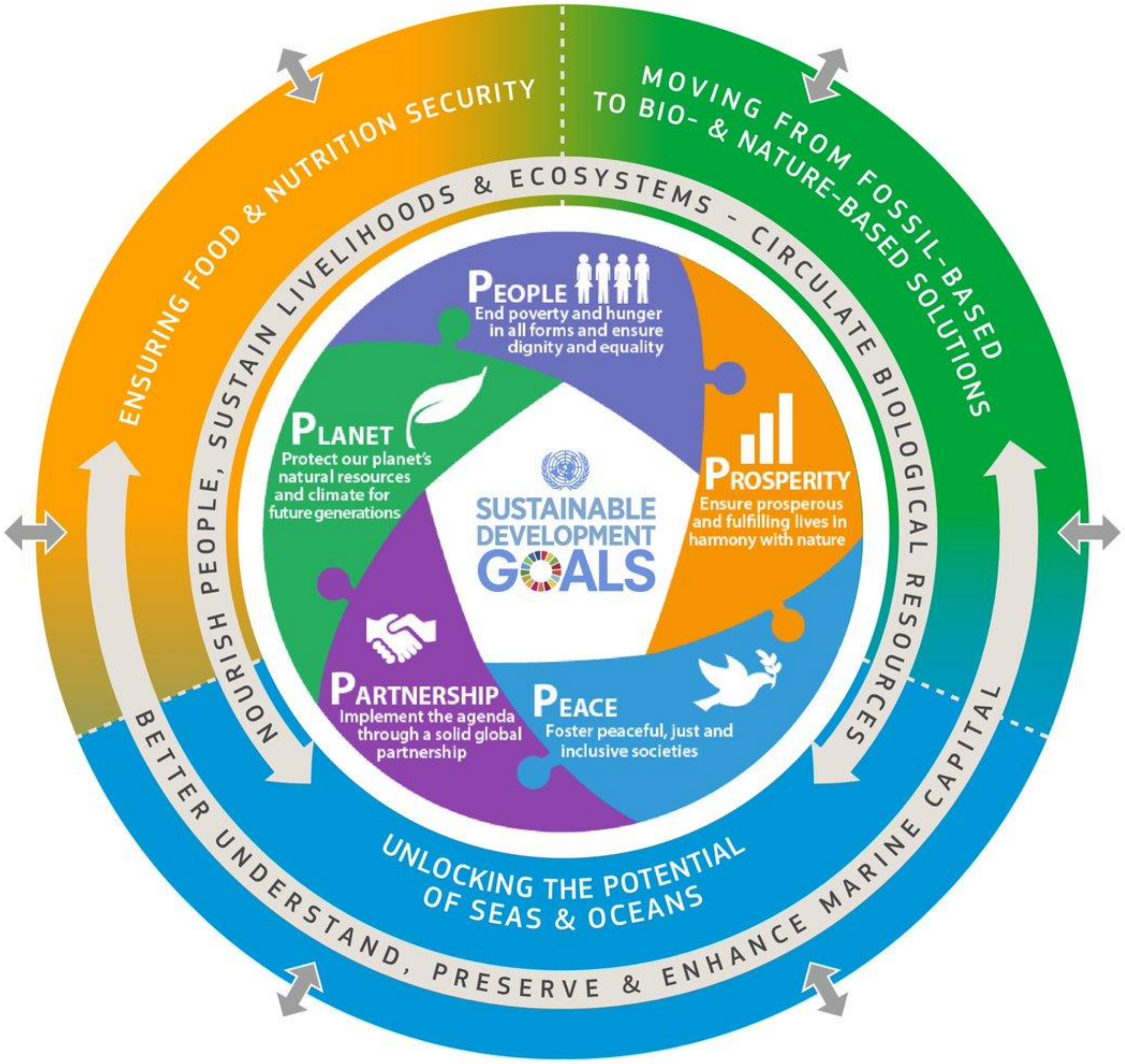
Turning AWPs a resource

RECOV3R

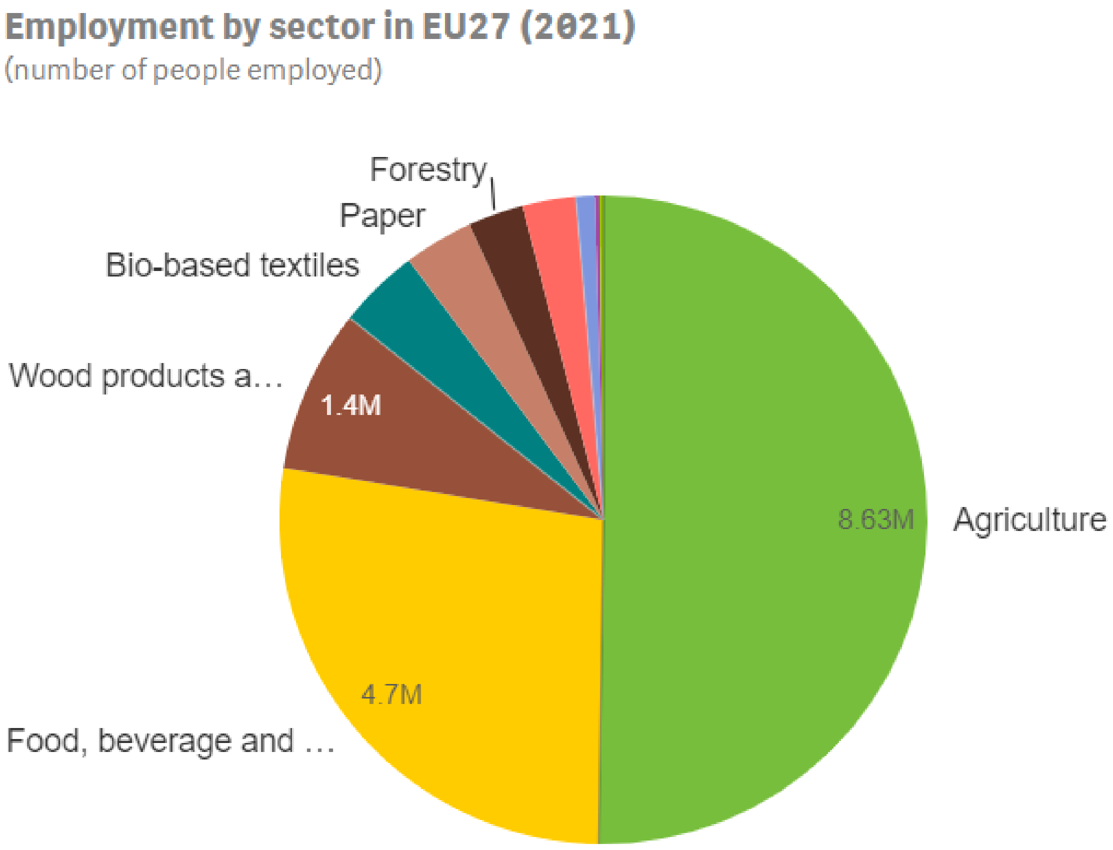
CIRULAR ECONOMY, BIOECONMY

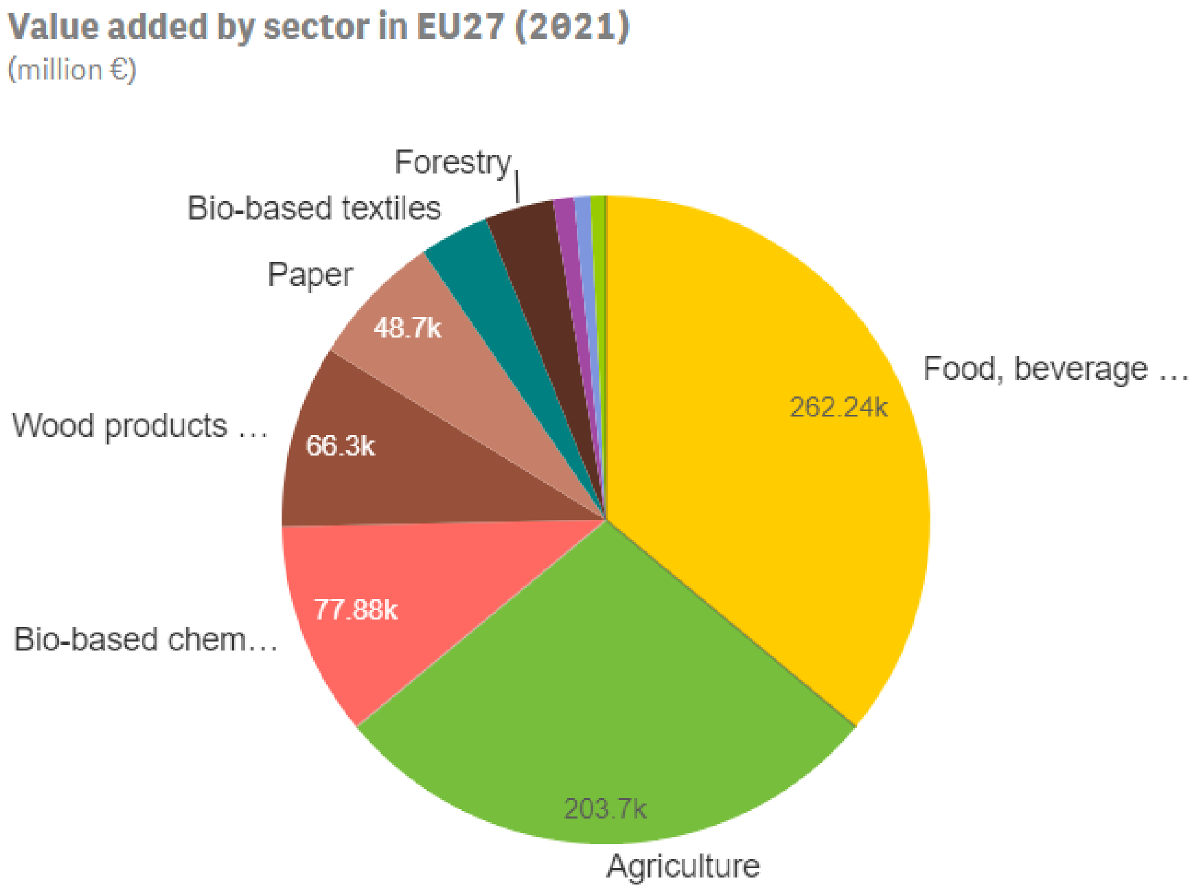


A SUSTAINABLE AND CIRCULAR BIOECONOMY FOR EUROPE

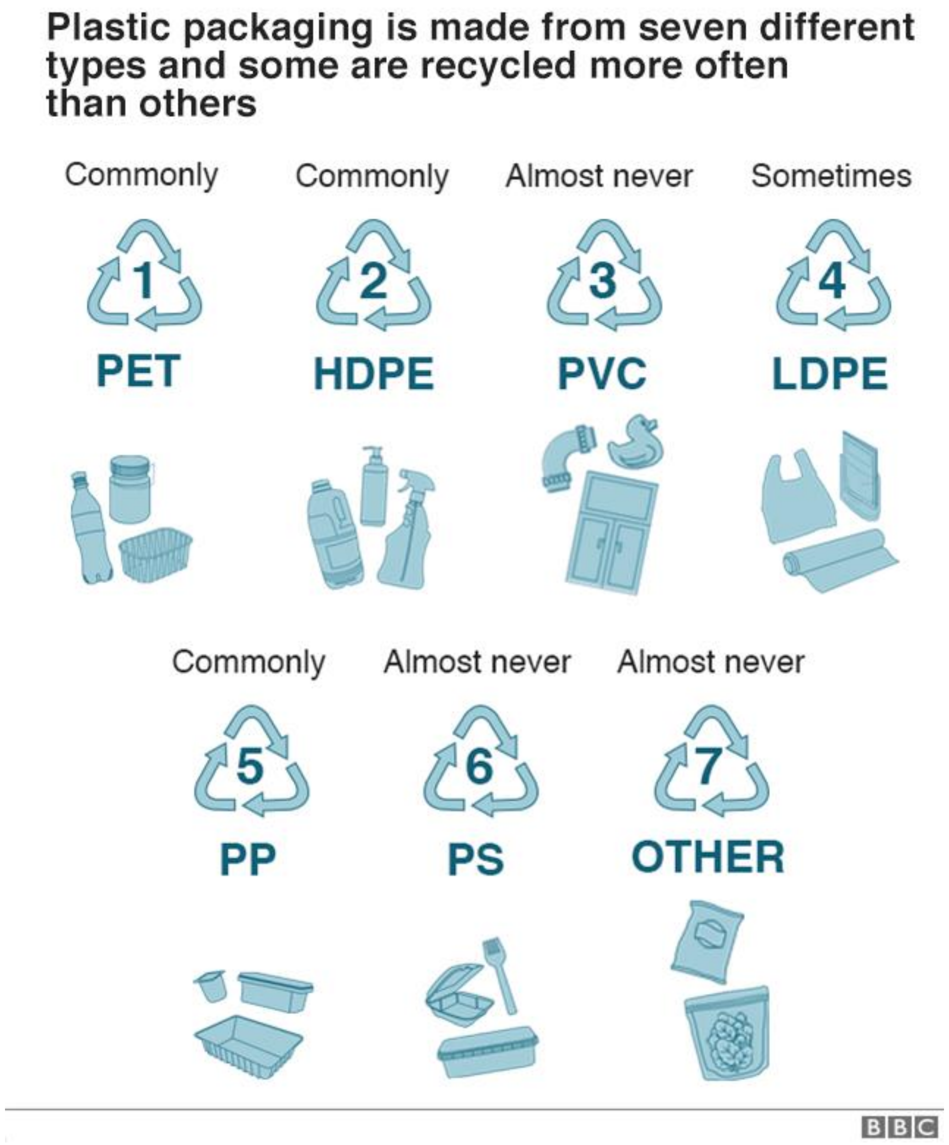


BIOECONOMY SECTORS





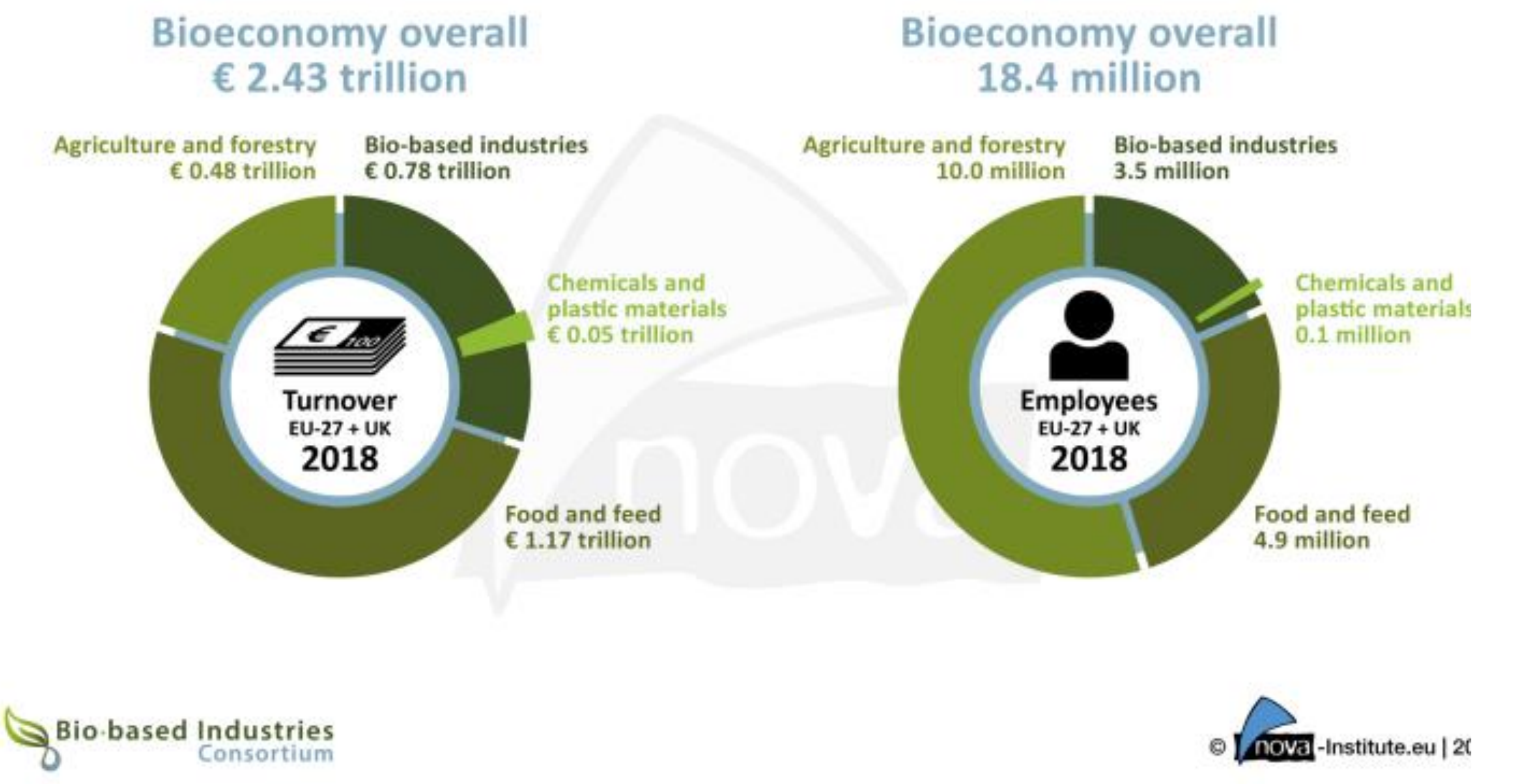
Plastic materials for packaging - Recyclable



- **Less than 30% of plastic waste is collected for recycling**
- **95% of the value of plastic packaging materials (70-105 billion €) is annually lost after a very short first use cycle**
- **Even Biobased and Compostable plastic can be recycled**

RECOV3R

An “environmentally friend” plastic (BIOPLASTIC) is the winning alternative, being biobased, biodegradable or recyclable



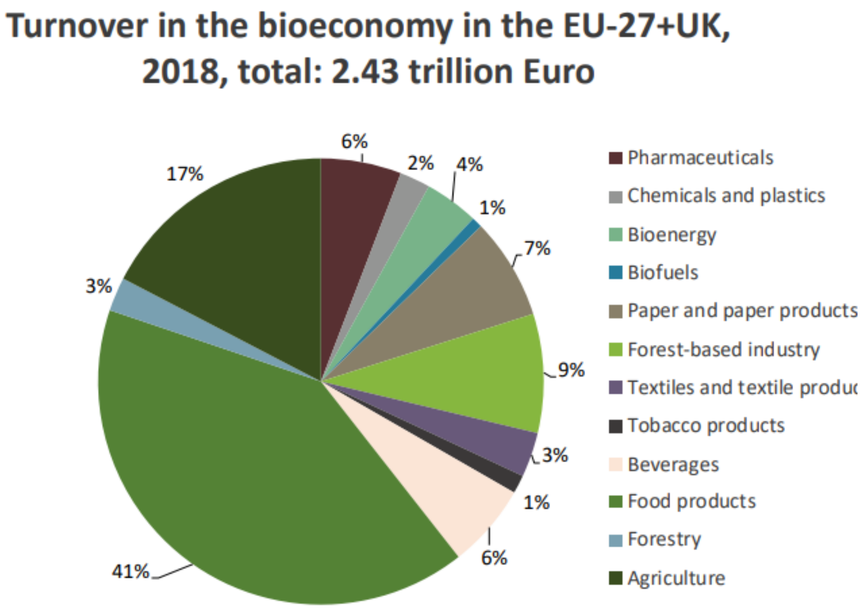


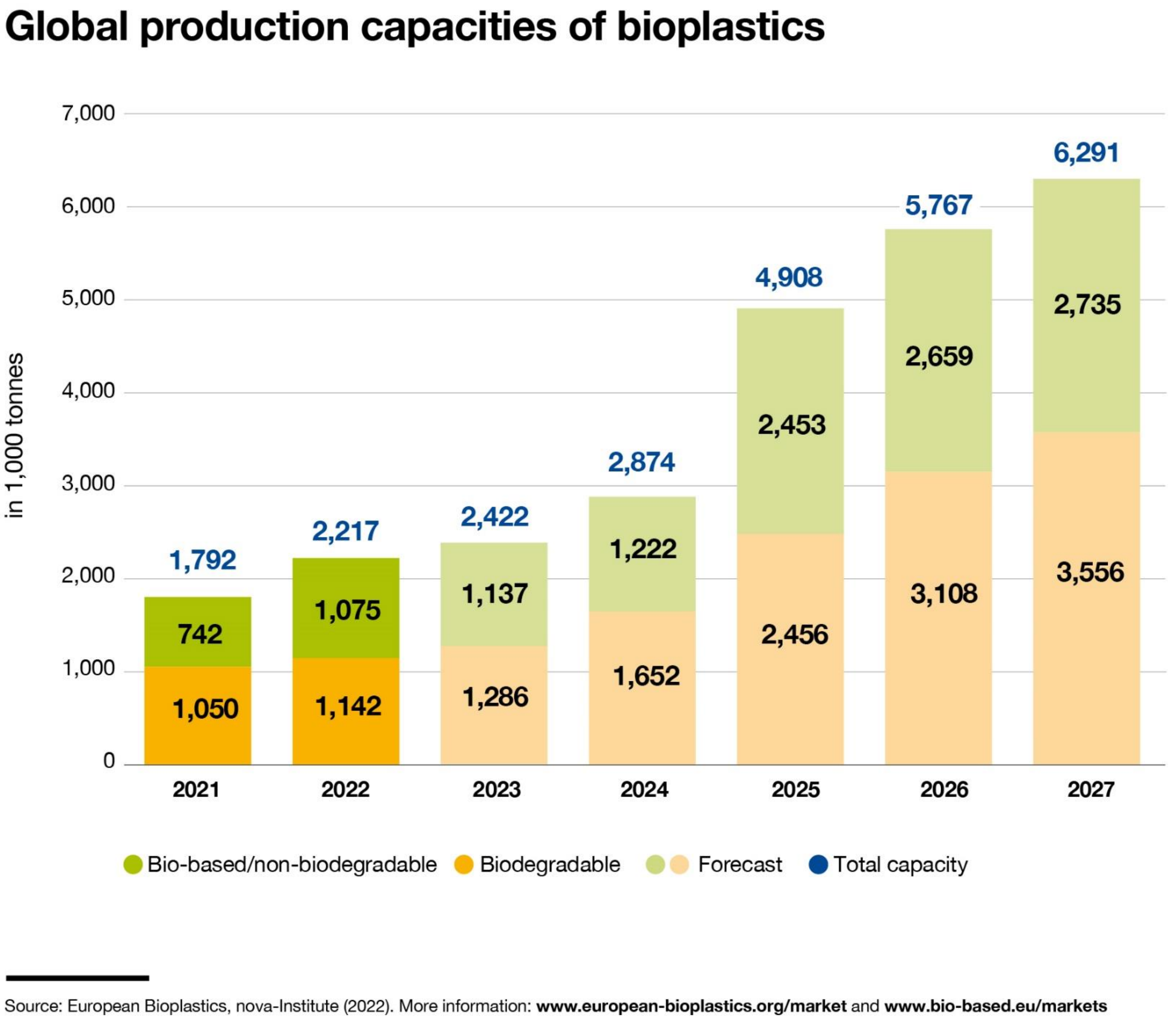
Figure 1 Overall turnover and employment of the bioeconomy and its bio-based industries in the EU-27 (+UK) in 2018

The European bio-economy sectors are worth more than €2 trillion in annual turnover and account for 18 million jobs in the EU

(https://biconsortium.eu/sites/biconsortium.eu/files/downloads/European%20Bioeconomy%20in%20Figures%202008%20-%202018.pdf)

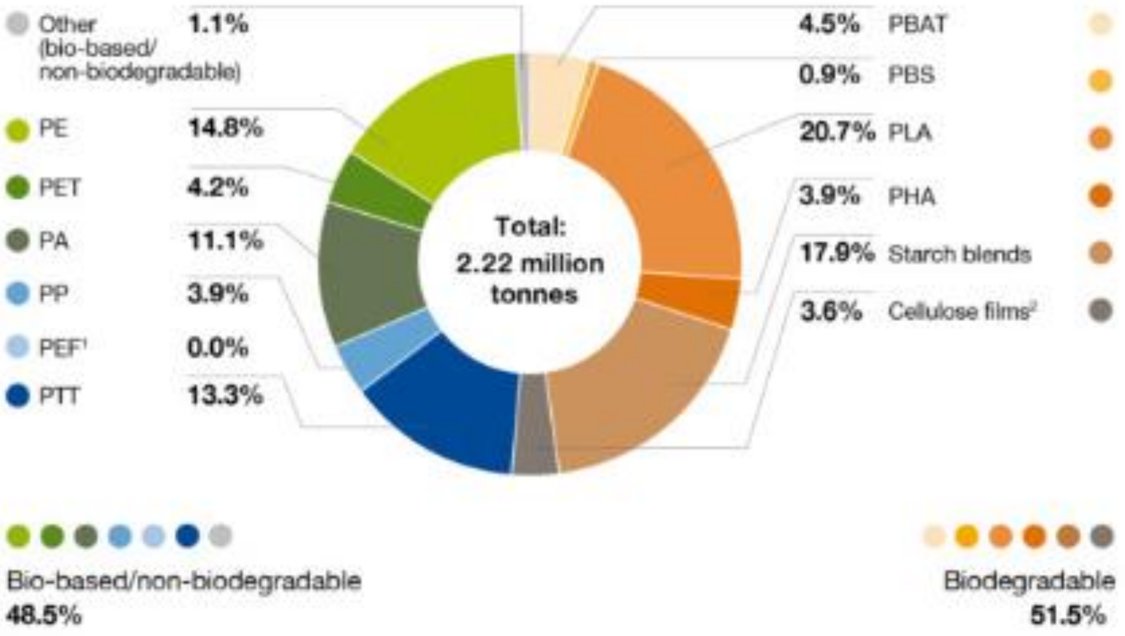
Bioplastic Market

According to the latest market data compiled by European Bioplastics in cooperation with the nova-Institute, global bioplastics production capacities are set to increase from around 2.23 million tonnes in 2022 to approximately 6.3 million tonnes in 2027.



BIOPLASTICS

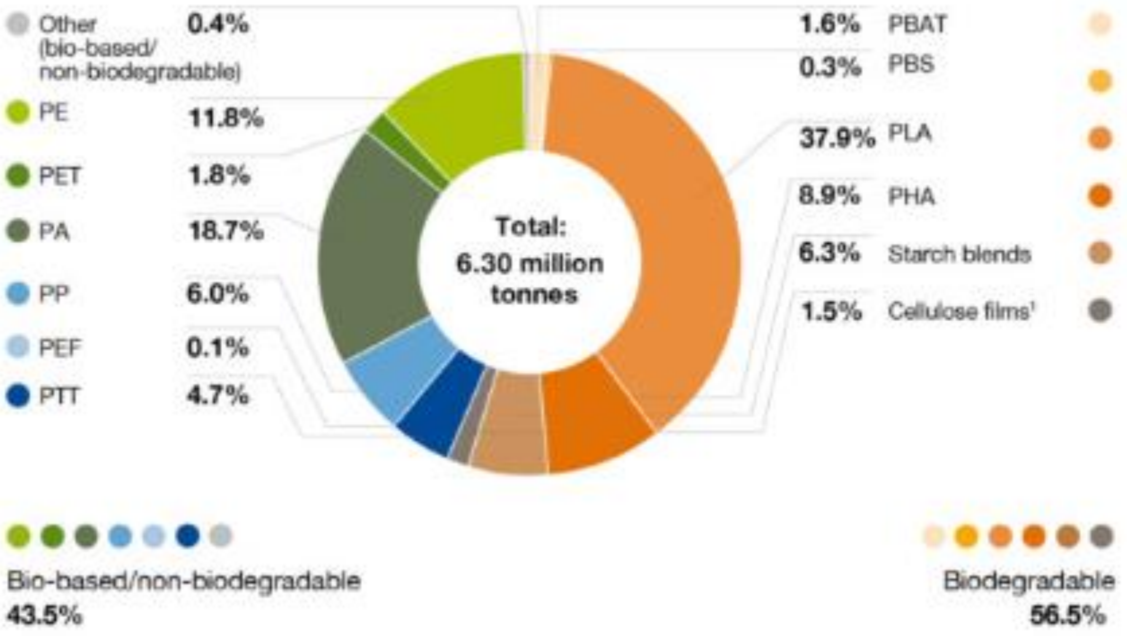
Global production capacities of bioplastics 2022
(by material type)



[1] PEF is currently in development and predicted to be available at commercial scale in 2023. [2] Regenerated cellulose films

Source: European Bioplastics, nova-Institute (2022). More information: **www.european-bioplastics.org/market** and **www.bio-based.eu/markets**

Global production capacities of bioplastics 2027
(by material type)

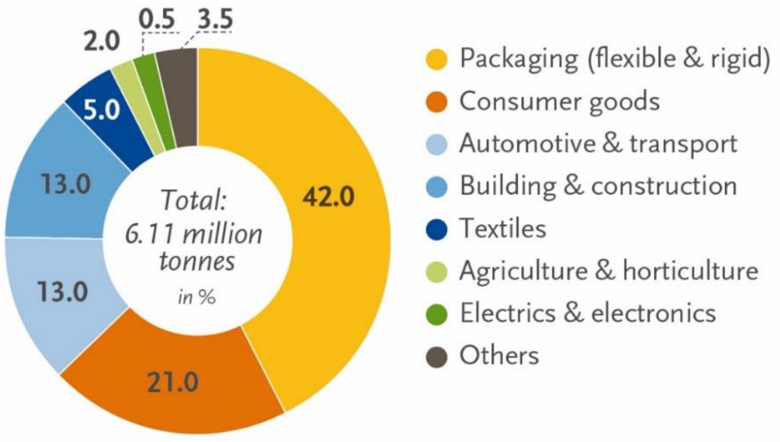


[1] Regenerated cellulose films

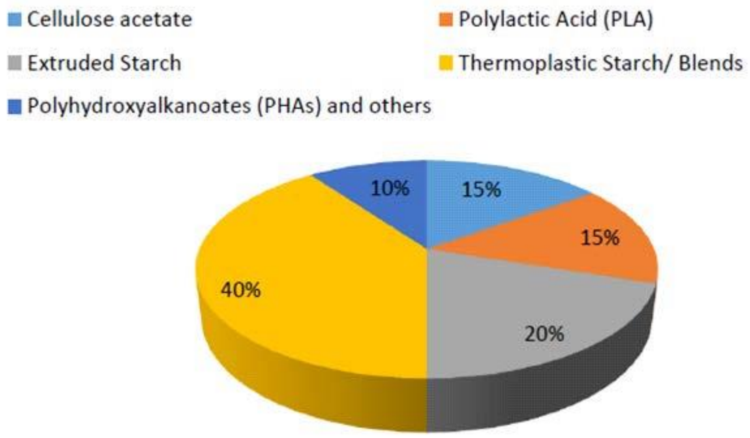
Source: European Bioplastics, nova-Institute (2022). More information: **www.european-bioplastics.org/market** and **www.bio-based.eu/markets**

BIOPLASTICS APPLICATIONS

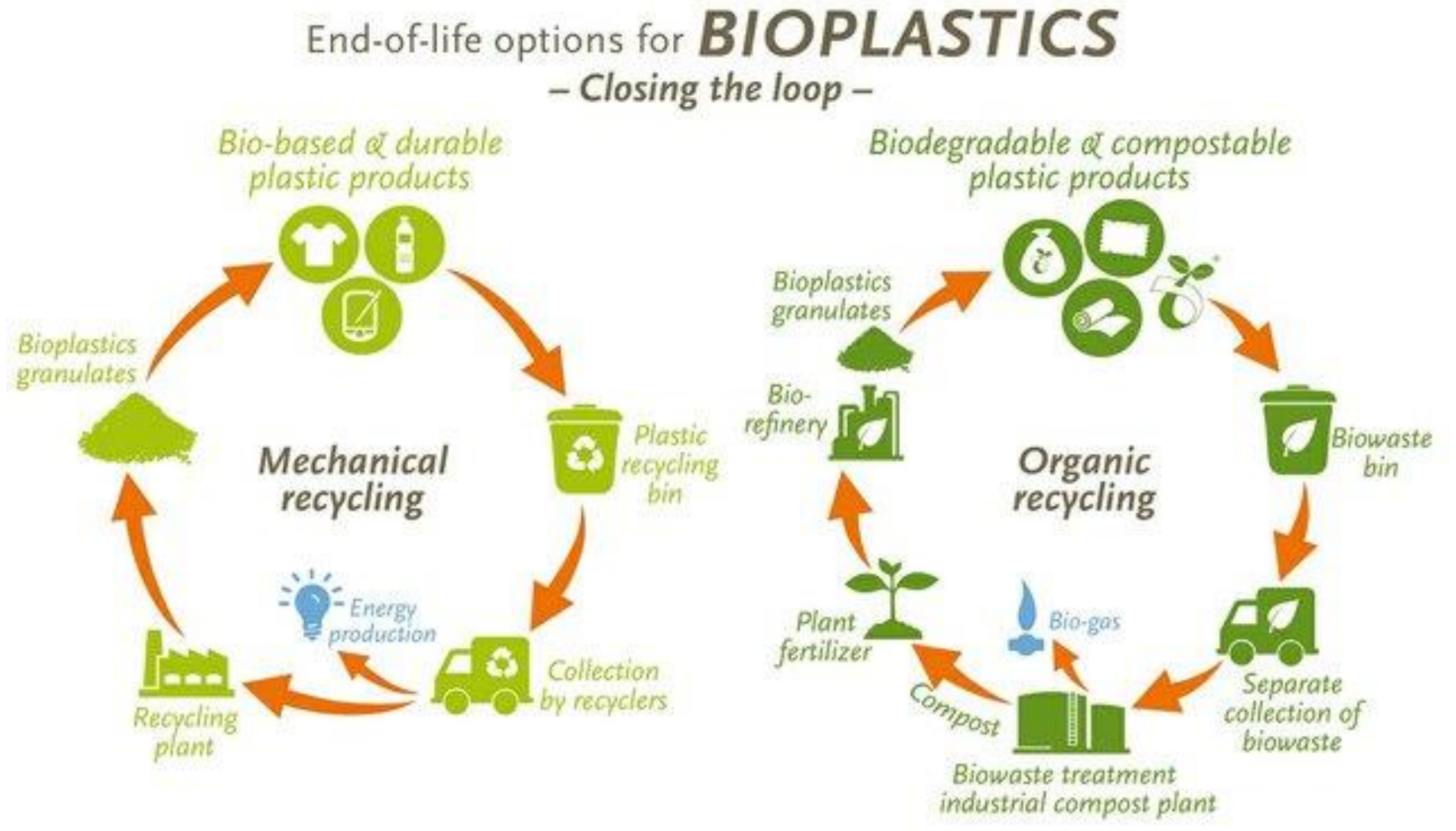
Global production capacities of bioplastics in 2021 (by market segment)



Source: European Bioplastics, nova-Institute (2016). More information: **www.bio-based.eu/markets** and **www.european-bioplastics.org/market**



- A big bioplastics market segment will be occupied by Packaging.
- Packaging industry produces large volumes of plastic, an improper disposal causes environmental disasters.
- As a result, bioplastics in this field will be the winning alternative since, being biodegradable, they are characterized by a sustainable disposal.



End-of-life options for BIOPLASTICS
– Closing the loop –
Bio-based & durable plastic products
Plastic recycling bin
Collection by recyclers
Energy production
Recycling plant
Bioplastics granulates
Mechanical recycling
Biodegradable & compostable plastic products
Biowaste bin
Separate collection of biowaste
Biowaste treatment industrial compost plant
Bio-gas
Compost
Plant fertilizer
Bio-refinery
Bioplastics granulates
Organic recycling

BIOPLASTICS AND BIOPOLYMERS… WHAT ARE THE DIFFERENCES?

- The main commercially available polymers derive from fossil fuels and they are difficult to recycle and / or reuse.

- The use of biodegradable and compostable materials from renewable sources is expected to contribute to sustainability and to reduce the environmental impact associated with the disposal of petroleum-based polymers.

- A bioplastic is a substance made from organic biomass sources.

- A polymeric substance to be termed "bioplastics", according to the European Bioplastics Association[1], must possess at least one of the following characteristics:

»Derived partly from renewable sources.
»Being biodegradable.

[1] http://www.european-bioplastics.org

European Bioplastics	**Biobased:** material or product (partly) derived from biomass (plants). Bioplastic: The term bio-plastics encompass a whole family of materials that are bio-based, biodegradable, or both.
SPI Plastic Industry Trade Association, Bioplastics Council	**Bioplastics:** plastic that is biodegradable, has bio-based content, or both. **Biodegradable Plastic:** a plastic that undergoes biodegradation (a process in which the degradation results from the action of naturally-occurring micro-organisms such as bacteria, fungi, and algae) as per accepted industry standards. As of 2008, accepted industry standard specifications are: ASTM D6400, ASTM D6868, ASTM D7081 or **EN 13432** (see Table 1.4). **Biobased content:** Fraction of the carbon content that is new carbon content made up of biological materials or agricultural resources versus fossil carbon content. Biobased content is measured following the procedures set by ASTM D6866.

Parliament seals ban on throwaway plastics by 2021

March 2019

•Single-use plastic cutlery, cotton buds, straws and stirrers to be banned by 03.07 2021

•90% collection target for plastic bottles by 2029

•More stringent application of the "polluter pays" principle

The following products will be banned in the EU by 2021:

•Single-use plastic cutlery (forks, knives, spoons and chopsticks)
•Single-use plastic plates
•Plastic straws
•Cotton bud sticks made of plastic
•Plastic balloon sticks
•Oxo-degradable plastics and food containers and expanded polystyrene cups

New recycling target and more responsibility for producers
Member states will have to achieve a 90% collection target for plastic bottles by 2029, and plastic bottles will have to contain at least 25% of recycled content by 2025 and 30% by 2030.

Ref: EU restrictions on certain single-use plastics, Information and resources on the new EU rules on single-use plastics
https://environment.ec.europa.eu/topics/plastics/single-use-plastics/eu-restrictions-certain-single-use-plastics_en#:~:text=The%20EU%20is%20acting%20against,of%20the%20EU%20Member%20States.

Plastic Banned or under discussion

Plastic cotton swab sticks, cutlery, plates, straws, drink stirrers, and sticks for balloons will need to be made with more sustainable materials by 2021. Single-use plastic drink containers will be allowed only if their caps remain attached. Plastic bottles will also need to be made of at least 30% recycled plastic by 2030.

For products without cheap and easy nonplastic alternatives, such as wet wipes and fishing gear, the focus is on limiting use. Producers of these products will be obliged to help cover cleanup costs and to promote awareness of litter and waste management options.

Now the ban has passed the union level, the individual countries within the EU have two years to transpose the legislation into their national law

ITEM	ACTION
Balloon sticks	Ban
Cutlery, plates & straws	
Cotton swab sticks	
Drink bottles	Allowed only if caps remain attached
Drink cups	Reduce use
Food containers	
Cigarette butts	Awareness, cleanup efforts
Bags	
Snack bags & wrappers	
Wet wipes & sanitary items	

https://cen.acs.org/policy/legislation-/EU-adopts-plastics-ban/97/i21

Understanding Biobased Carbon Content Measurement

- Biobased carbon testing is able to distinguish biobased from non-biobased products

- The terms biobased and non-biobased are applicable to carbon-containing products

- A product's biobased carbon content is reported as a fraction of total organic carbon content (TOC) and not on its weight according to ASTM D6866

- A product's biobased carbon content can be reported as a fraction of total carbon content (TC) according to other standardized methods such as ISO 16620-2 and CEN 16640.

BIOBASED – Materials that are derived in whole or in part from biomass resources are biobased. Biomass resources are organic materials that are available on a renewable or recurring basis such as crop residues, wood residues, grasses, and aquatic plants. Corn ethanol is a well-known example of a biobased material derived from biomass resources.

BIOBASED PRODUCT – Any product that contains some amount of biobased material within it is technically a biobased product. The term is typically applied only to materials containing carbon.

NON-BIOBASED PRODUCT – Any product that does not contain any biobased materials in it is a non-biobased product, but the term is typically applied only to materials containing carbon. Products made entirely from petrochemical resources are referred to as non-biobased products. Glass, however, is not generally referred to as non-biobased material since it doesn't contain any carbon.

RECOV3R

BIOBASED POLYMERS

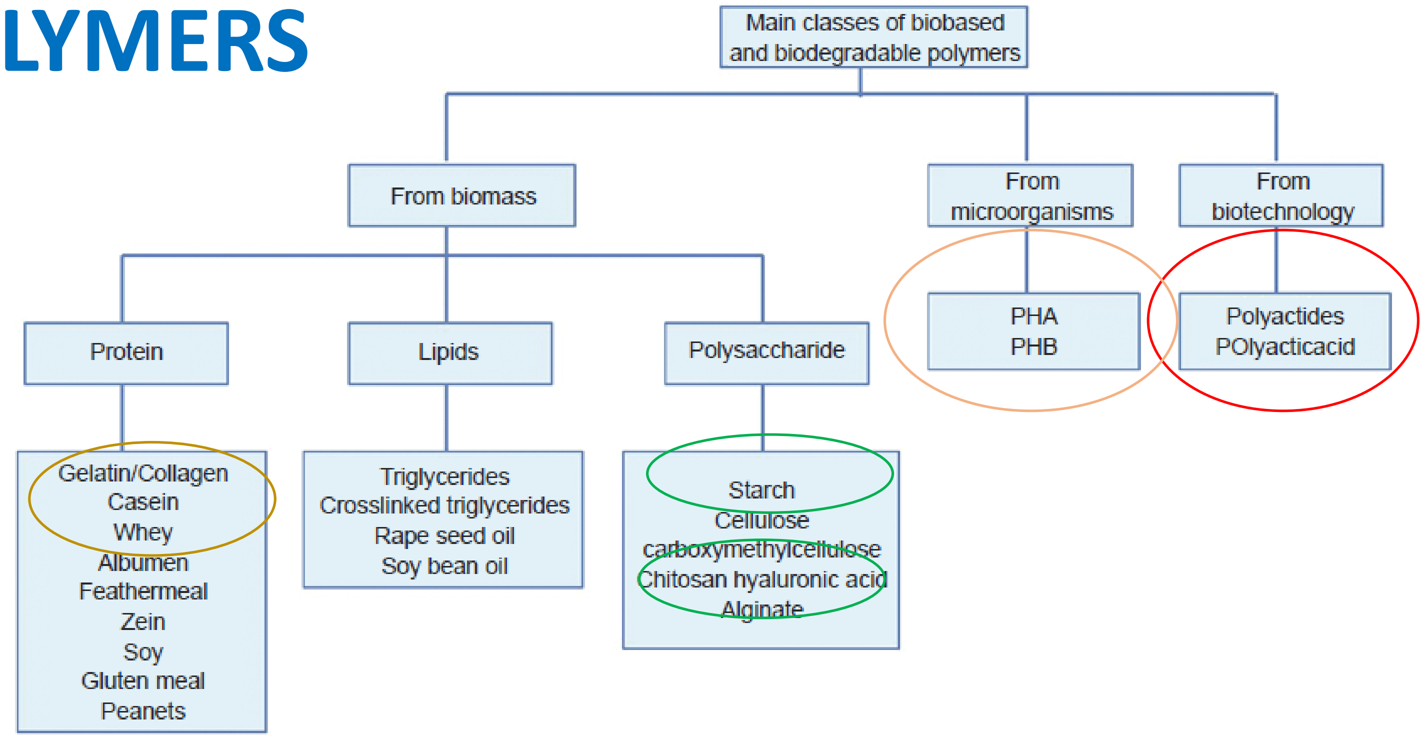


Figure 1. Different classes of polymers which are biobased and biodegradable (therefore not including biodegradable plastics from petrochemical resources and non biodegradable partly or fully biosourced plastics)

- From natural bio-based polymers (starch, cellulose, hemicellulose, chitosan, proteins, and their derivatives by chemical modification) pectin, alginate,

-Production of bio-based monomers by fermentation/conventional chemistry followed by polymerization (polylactic acid, polybutylene succinate, polyethylene)

-Production of bio-based polymers by bacteria (polyhydroxyalkanoates).

BIOBASED LOGOS

Label	Biobased content range
One star ☆	20% < Biobased < 40%
Two star ☆☆	40% < Biobased < 60%
Three stars ☆☆☆	60% < Biobased < 80%
Four stars ☆☆☆☆	Biobased > 80%

OK biobased VINÇOTTE	OK biobased VINÇOTTE	OK biobased VINÇOTTE	OK biobased VINÇOTTE
between 20 and 40 % Biobased	between 40 and 60 % Biobased	between 60 and 80 % Biobased	more than 80 % Biobased

BIOBASED 20 - 50 % DIN Geprüft

BIOBASED 50 - 85 % DIN Geprüft

BIOBASED > 85 % DIN Geprüft

http://www.dincertco.de.
http://www.okcompost.be

In the context of the "Lead Market Initiative for Europe" the European Commission created the Mandate M/429 addressed to the European Standardization bodies (CEN, CENELEC and ETSI) for the development of horizontal European standards for bio-based products. CEN initiated a new Technical Committee CEN/TC411 on "Bio-based products", which started working in the beginning of October 2011.

The main active institutes in this field are Vinçotte (Belgium) and Din Certco (Germany). They both have a ranking system based on the bio-based carbon content

a) バイオマスプラ

b)

USDA CERTIFIED BIOBASED PRODUCT
PRODUCT 57%

European Commission, "Mandate addressed to CEN, CENELEC and ETSI for the elaboration of a standardisation programme for bio-based products", M/429.

Biobased / Biodegradable LOGOS

BIOBASED 50 - 85 %
DIN Geprüft
8C084/8C085

BIOBASED 20 - 50 %
DIN Geprüft
8C083

BP バイオマスプラ
No.299/No.300

GreenPla
Biodegradable Plastics

HOME
OK compost
S534
VINÇOTTE

BPI ®

COMPOSTABLE
IN INDUSTRIAL FACILITIES
Check locally, as these do not exist in many communities. **Not suitable for backyard composting.** CERT # 10528580

recyclable
certified at WMU

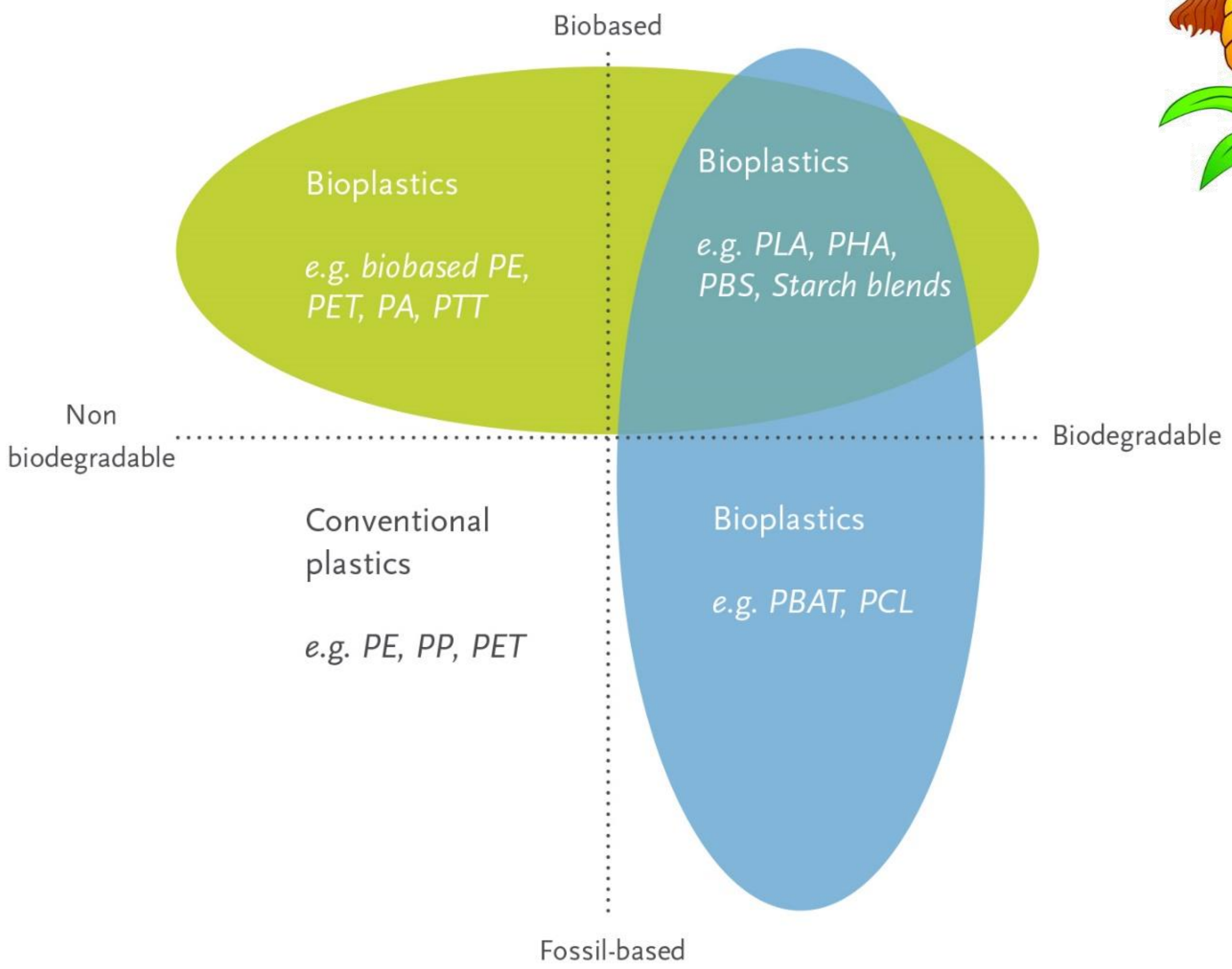
OK compost
S534
VINÇOTTE

RECOV3R

Many times the bioplastic and biopolymer terms are used as synonyms but the two terms are not equivalent:

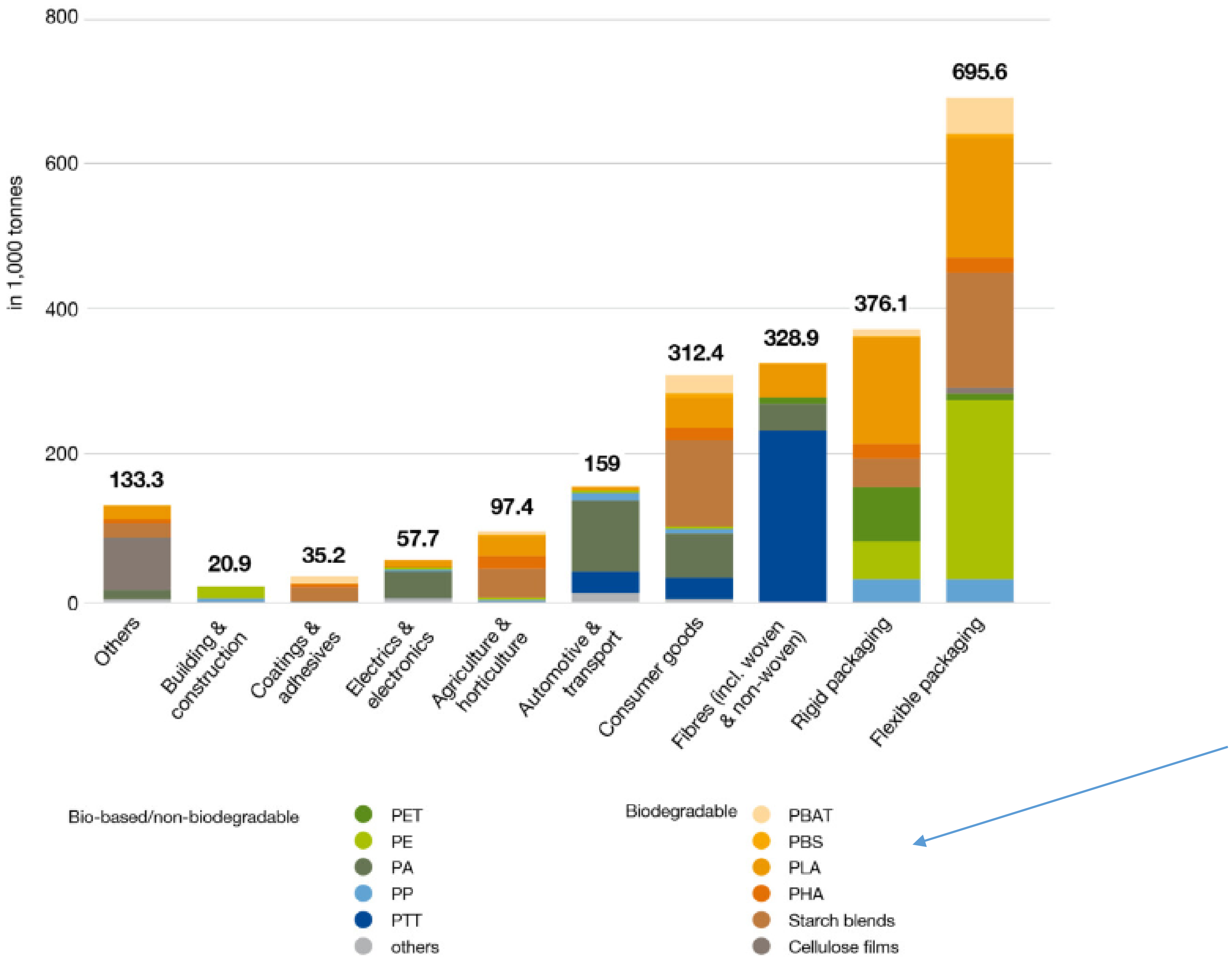
- The term Biopolymer is referred to a biodegradable polymer produced from renewable sources.

- The term bioplastics is referred to a biodegradable polymer not necessarily derived form renewable sources.



- ✓ PLA (polylactic acid)
- ✓ PHAs (polyhydroxyalkanoates)
- ✓ PBS (Polybutylene Succinate)
- ✓ Starch

Global production capacities of bioplastics 2022 (by market segment)



Source: European Bioplastics, nova-Institute (2022). More information: **www.european-bioplastics.org/market** and **www.bio-based.eu/markets**

BIODEGRADABILITY

"Biobased" is different from "biodegradable"

- The property of biodegradation does not depend on the resource basis of a material but is rather linked to its chemical structure. 100% biobased plastics may be non-biodegradable, and 100% fossil based plastics can biodegrade

- Biodegradation is a chemical process during which microorganisms convert materials into natural substances such as water, CO_2, compost.

- The process of biodegradation depends on the surrounding environmental conditions (e.g. location or temperature), on the material and on the application.

- Macroscopically, degradation occurs through changes and deterioration of the key materials properties (cracking, breakage, fragmentation). These changes are mainly due to the shrinkage of polymer chains

BIODEGRADABILITY

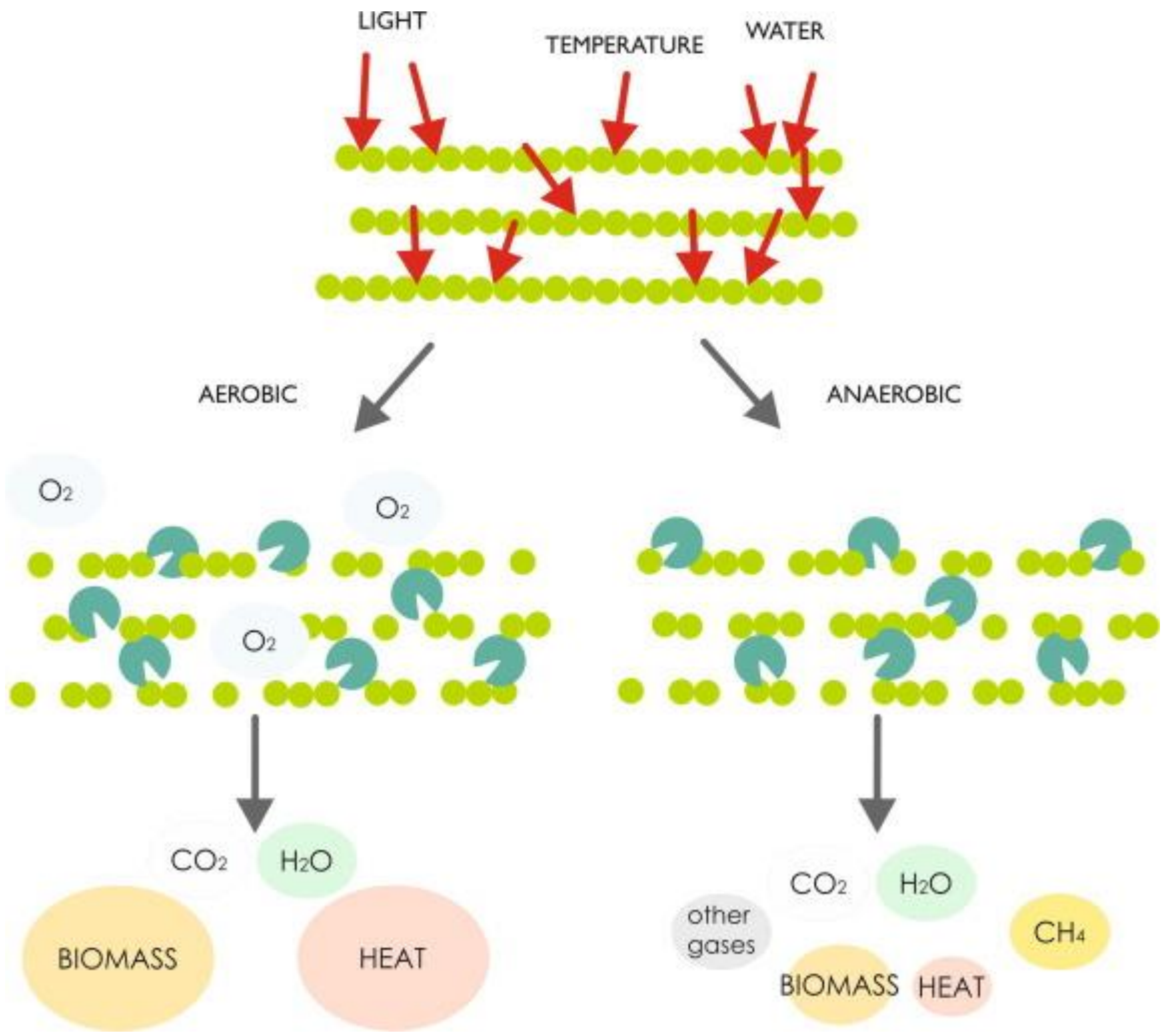
- **Aerobic**

  Hydrocarbon Polymer + O_2 = CO_2 + H_2O + biomass + residue

- **Anaerobic**

  Hydrocarbon Polymer = CH_4 + CO_2 + H_2O + biomass + residue

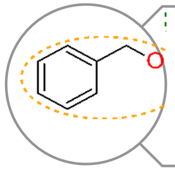
$$Mineralization\ (\%) = 100 \cdot \frac{CO_2\ from\ sample - CO_2 from\ blank}{Th\ CO_2}$$


LIGHT
TEMPERATURE
WATER
AEROBIC
ANAEROBIC
O2
O2
O2
CO2
H2O
BIOMASS
HEAT
CO2
H2O
other gases
CH4
BIOMASS
HEAT

RECOV3R

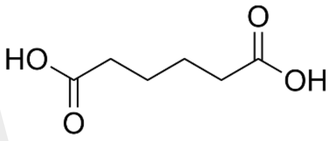
BIODEGRADABILITY FACTORS

Chemical Structure: A polymer with a more complex chemical structure (for example lignin has a lot of aromatics group and ramification point) biodegrades slowly.



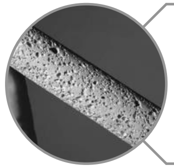
Functional Groups: Esters, amines and urethane bonds are more hydrophilic, hence more hydrolysable and more degradable.

Segmental Mobility: Polymers with high flexibility degree are easily degraded. Examples are PBA (polybutylenadipate) and PBS (polybutylensuccinate)

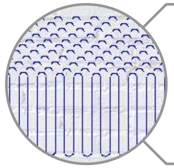


Adipic acid

Molecular Weight: A high molecular weight is detrimental for the degradation.



Surface Features: If polymer surface is irregular and porous, the polymer is more susceptible to microbial attack and sensible to degradation.



Crystallinity: If the polymeric chains are arranged in an orderly manner (more crystalline polymers) the degradation process is hindered.

Normative, regulations

- **EN 13431:2000** - Packaging. Requirements for Packaging Recoverable in the Form of **Energy Recovery** Including Specification of Minimum Inferior Calorific Value.

- **EN 13432:2000** - Packaging. Requirements for Packaging Recoverable Through Composting and Biodegradation. Test Scheme and Evaluation Criteria for the Final Acceptance of Packaging.

- **CR 13695-1** - Packaging. Requirements for Measuring and Verifying the Four Heavy Metals (Cr, Rd, Hg, Pb) and Their Release into the Environment, and Other Dangerous Substances Present in Packaging.

- **EN 13427:2000** - Packaging. Requirements for the Use of European Standards in the Field of Packaging Waste ("Umbrella Norm").
- **EN 13428:2000** - Packaging. Requirements Specific to Manufacturing and Composition. Prevention by Source Reduction.
- **EN 13429:2000** - **Packaging. Reuse**
- **EN 13430:2000** - Packaging. Requirements for Packaging Recoverable by **Material Recycling.**

RECOV3R

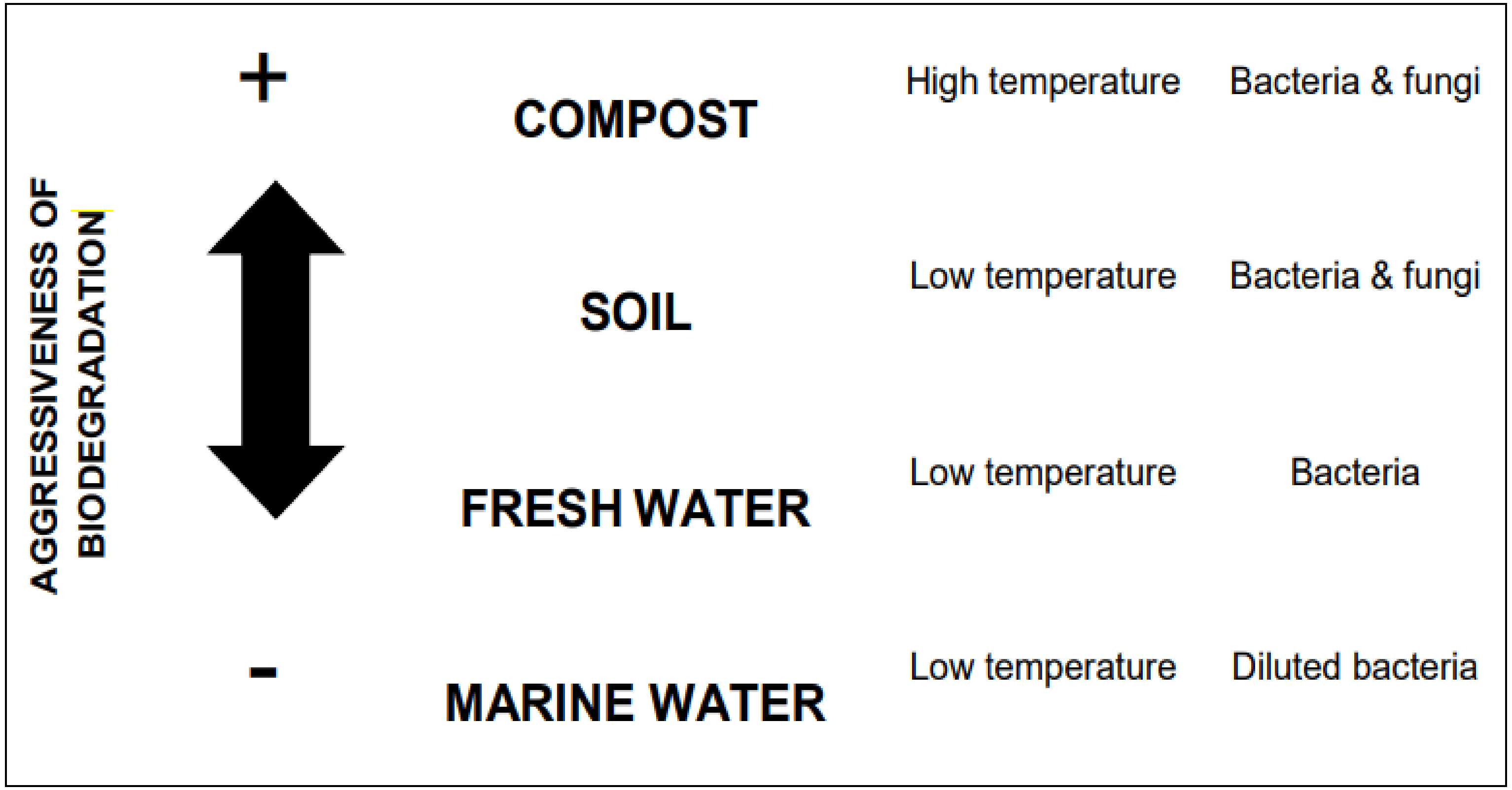
COMPOSTING

Composting can reduce the volume of organic waste quite significantly, while the compost produced can be used for agricultural and horticultural purposes.
About 50% of all domestic waste comprises organic material, a percentage that is set to grow in the future owing to the growing popularity of biodegradable products (packaging material, disposable cutlery and plates

Products featuring the “OK compost INDUSTRIAL” label are guaranteed as biodegradable in an industrial composting plant.

This applies to all components, inks and additives.

General characterization:
dry matter, volatile solids, organic carbon contents are required and the quantification of the actual thickness of the material/packaging.

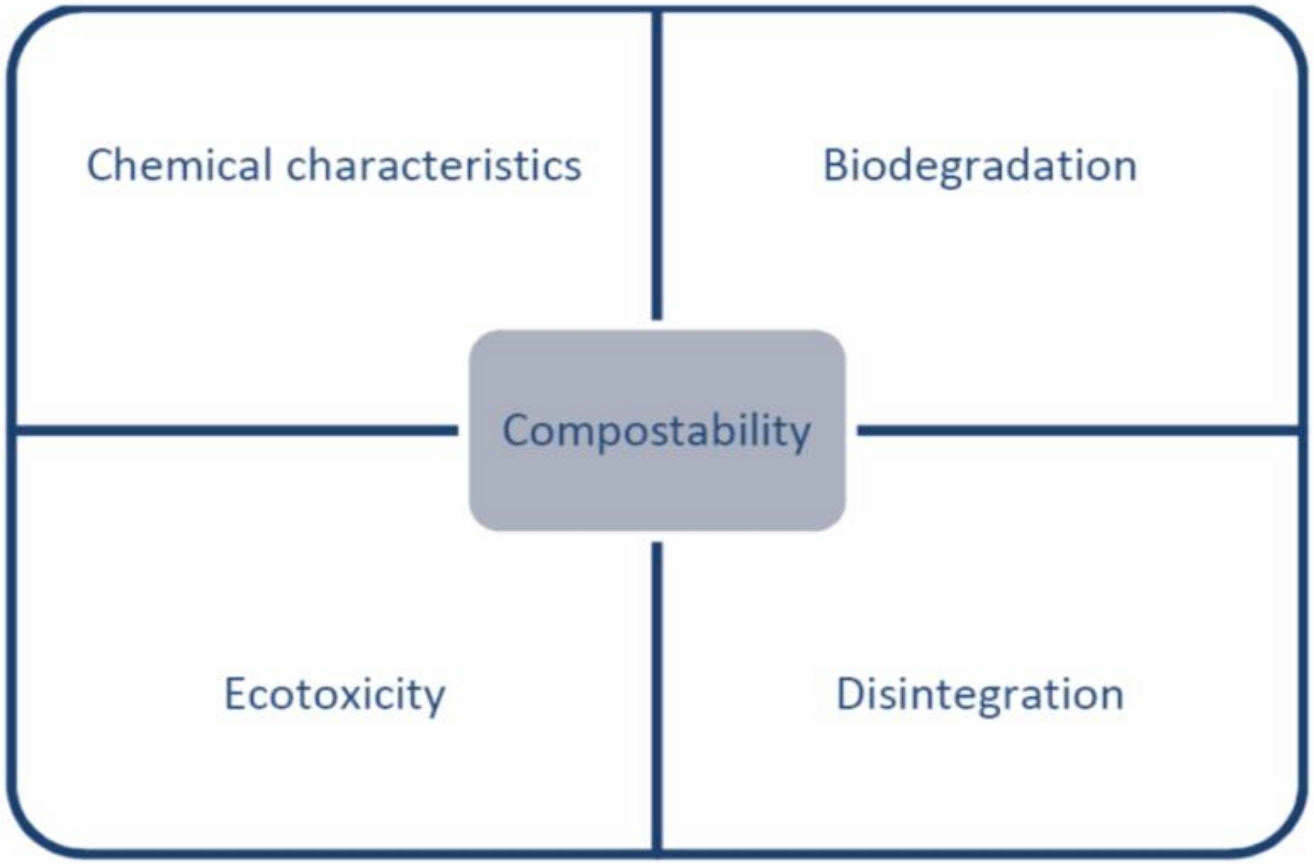


Low levels of heavy metals concentrations, in particular for Arsenic, Cadmium, Chrome, Copper, Mercury, Molybdenum, Nickel, Lead, Selenium and Zinc, and Fluorine content have to comply with specified limit values defined by EN 13432.

EN 13423-2000

The reference point for the certification programme is the harmonised EN **13432-2000 standard** "Packaging—Requirements for packaging recoverable through composting and biodegradation—Test scheme and evaluation criteria for the final acceptance of packaging".

Characterization, biodegradability, disintegration, and compost quality/ecotoxicity.
For the compost quality or ecotoxicity test, physical and chemical parameters such as density, total dry and volatile solids, salt content, and pH, have to be determined to show that the tested packaging does or does not have negative effects on the compost quality.
Only the plant growth test, based on OECD 208 guideline, is included in EN 13432-2000 for ecotoxicity.
The results (germination numbers and plant biomass growth) of the compost with the tested material and the blank compost are compared.



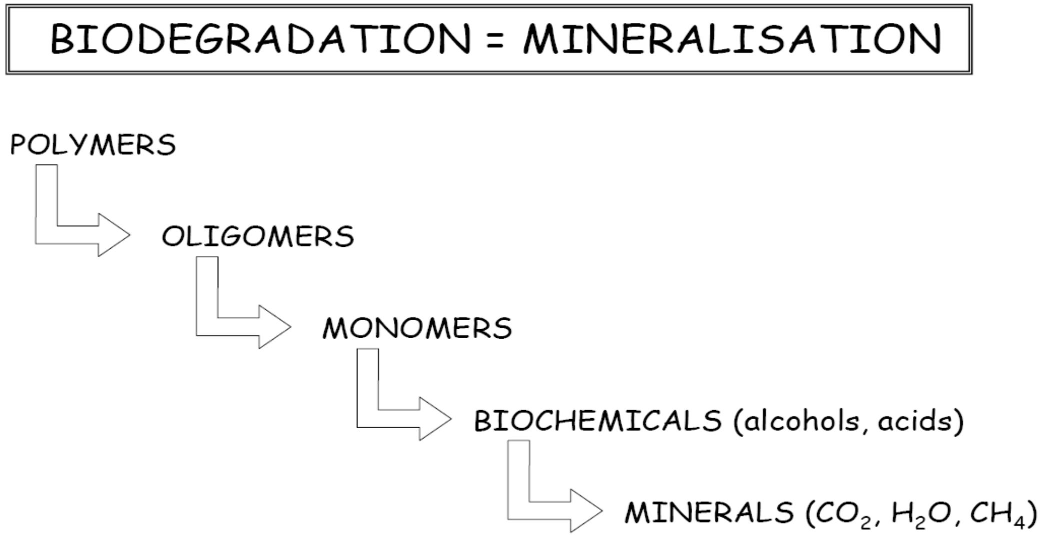
RECOV3R

EN 13423-2000

A product can be defined as compostable as required by EN 13432 (2000) if it respects specific characteristics:

- The product must contain at least 50% organic matter and may not exceed the heavy metal limits specified in the standard.

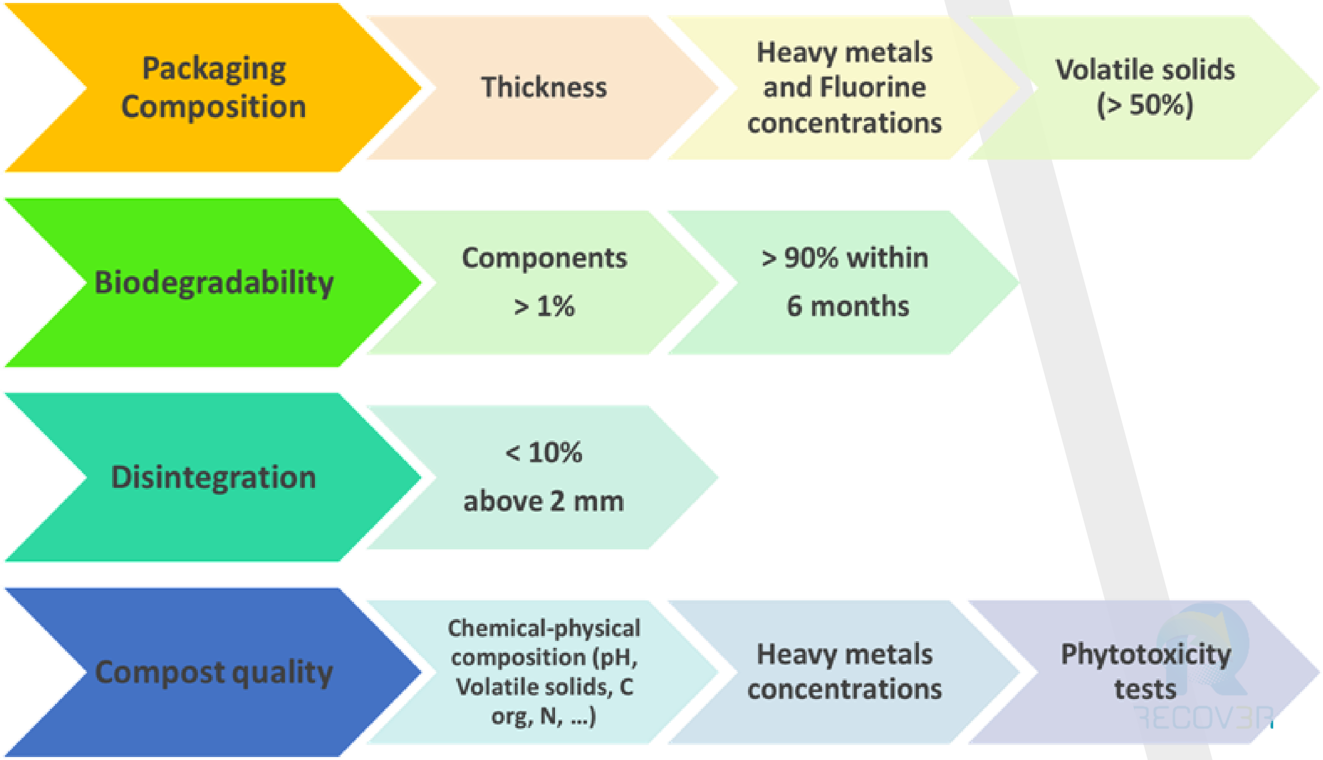
- The products should mineralize for at least 90% within 6 months under controlled composting conditions, where mineralization is defined as the conversion of the organic C to CO_2 and biomass, this characteristic is linked to the chemical composition of the sample.



EN 13423-2000

The product, in the form which enters the market, should, within a timeframe of 12 weeks, fragment in parts smaller than 2 mm under controlled composting conditions. It has to be outlined that this requirement refers to the physical form of the product instead of to the chemical composition. These characteristics are connected mostly to the thickness and the physical construction (e.g. laminate, coating, etc.) of the sample, and can result tricky to be met also for packaging based on biodegradable materials. The mass of residues above 2 mm must be less than 10% of the original mass.

The compost obtained at the end of the composting trial, that can also contain some no degraded residuals from the product, must not have any negative effects to the germination and growth of plants



Certification, Logos

In Europe there are several certification logos used by institutes for industrial compost-ability. One of them is the ‘Seedling’ logo of European Bioplastics, issued by the certification institutes of Din Certco (Germany) and the Ok Compost of Vinçotte (Belgium)

Certification, Logos

Concerning home compostability there is currently no international norm in place which defines the criteria to be adopted. Organizations which have defined criteria for home compostability include:

Vinçotte (Belgium) with the OK Compost Home programme

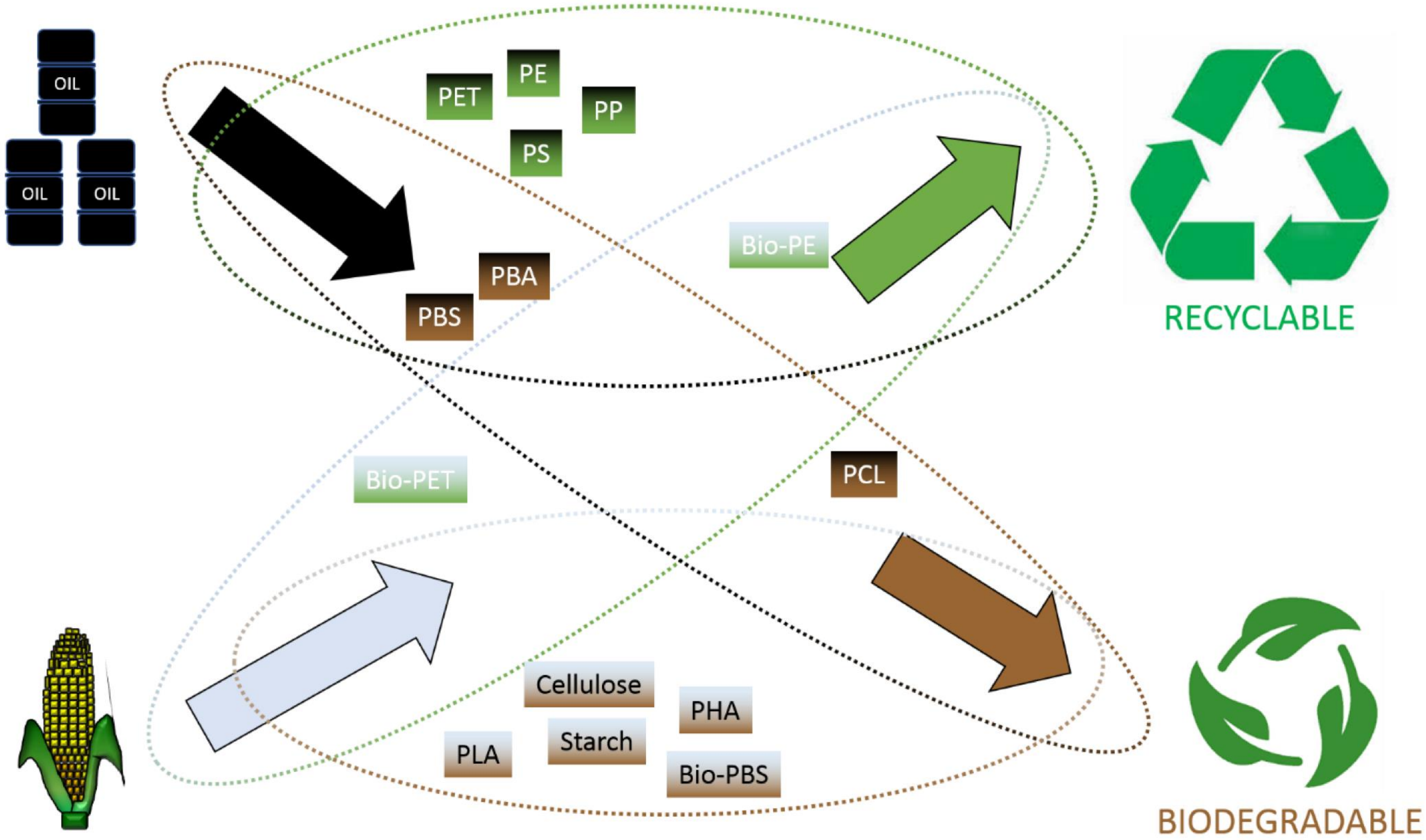
Biodegradation shall be tested at ambient temperature (between 20°C and 30°C).

The temperature must be kept below 30°C for the duration of the test.

The required percentage of biodegradation is exactly the same as specified in EN 13432 namely absolute or relative 90 %.

The period of application for the biodegradation test specified in the test methods shall be maximum of 12 months

MAIN BIOBASED BIODEGRADABLE POLYMERS



RECOV3R

PHYSICAL PARAMETERS

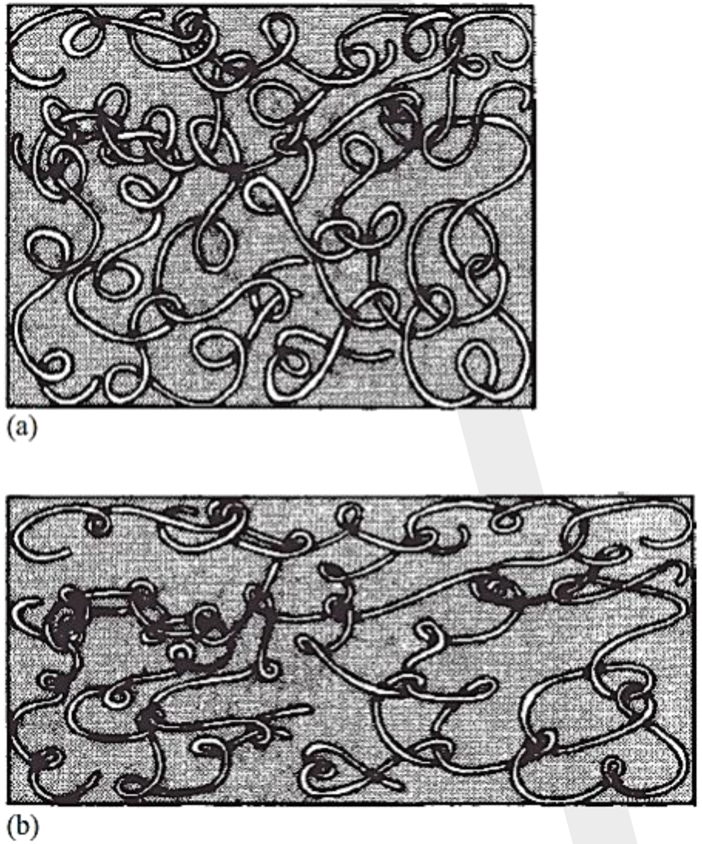
- A polymer is formed by long molecular chains; the arrangement of these chains influences the morphology and the mechanical properties of the polymer.

- A completely casually and disordered arrangement of the polymer chains is related to an amorphous polymer. However, there are micro volumes within which macromolecules have a certain order like crystals; these micro volumes, named crystallites, are dispersed in an amorphous matrix (semi crystalline polymers).

- When an amorphous polymer is stretched, the molecules may be preferentially aligned along the stretch direction giving to the final material isotropic mechanical properties.

- Many polymers crystallize if they are cooled from melt. In this case we may say that they are crystalline but unoriented in the macroscopic sense.

- Increasing the crystallinity increases the mechanical strength, the temperature of use and the density of the polymer.



Schematic diagrams of **(a)** unoriented amorphous polymer and **(b)** oriented amorphous polymer (From: An Introduction to the mechanical properties of solid polymers / I. M. Ward and J. Sweeney. – 2nd ed.

In summary: for a polymer to crystallize the molecule must have a regular structure.

Some amorphous polymers are similar to glass; they are transparent and relatively fragile (glassy state). With heating, going from the glassy state to the rubbery state is called a glass transition.

The main physical parameters that affect the mechanical and morphological characteristics of a polymer are those related to the achievement of particular characteristics temperatures. For example to crystallize a polymer, the temperature must be kept below the crystal melting point and sufficient time must be given for the long molecules to arrange in order in the solid state.

The temperatures that characterizes a polymer are:

- Glass Transition Temperature (T_g)
- Melting Temperature (T_m)
- Crystallization Temperature (T_c)

PLA

- PLA (Poly Lactic Acid) bioplastics are being used in a broad range of markets and applications. Is extremely versatile: it can be injection molded into plastic parts; extruded into sheet or film; foamed; thermoformed into packaging items.

- PLA 2003D and PLA4032D (with around 3% of D-units) are commercially used. The 2003D is used principally for injection molding and thermoforming whereas the 4032D for films.

- PLA main producers are:

» Total® / Corbion®

» NatureWorks®

» Sulzer®

TOTAL | Corbion

NatureWorks

SULZER

PHAs

- PHAs can be incorporated into packaging components such as coatings, laminations and biodegradable printing inks. Additionally, PHA structures can include rigid thermoplastics, thermoplastic elastomers and grades useful in waxes, adhesives and binders. The cost is around 7-15 €/Kg.

- PHAs main producers are:

» Imperial Chemical Industries

ICI

» BP

bp

» Biomer

BIOMER biodegradable polymers

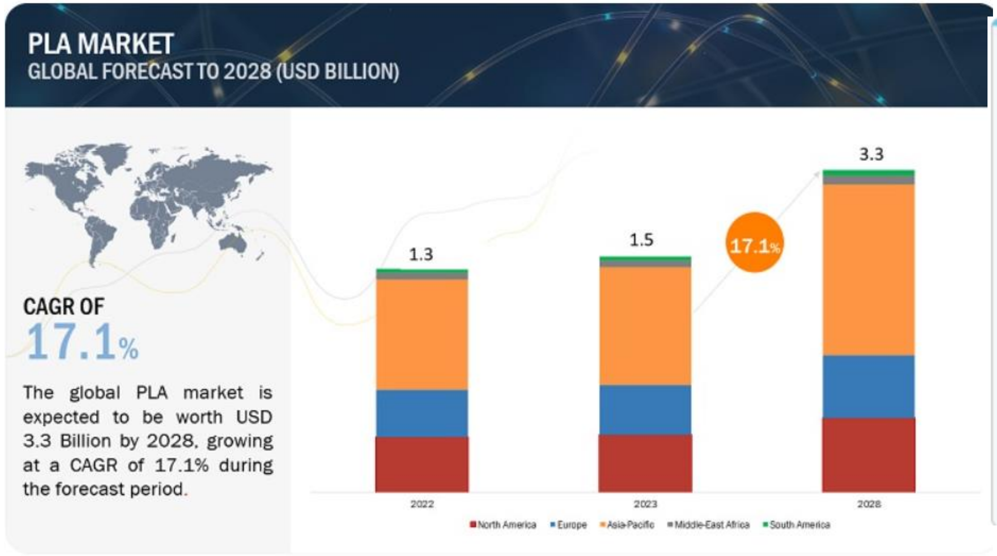
» Kaneka

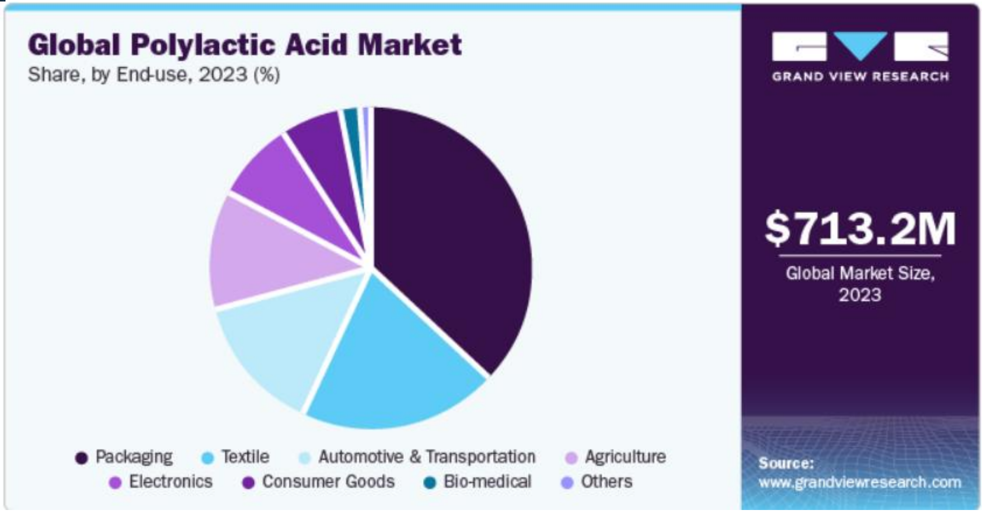
Kaneka

RECOV3R

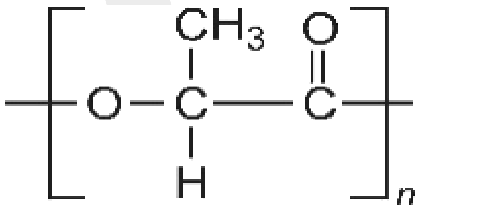
POLYLACTIC ACID (PLA)

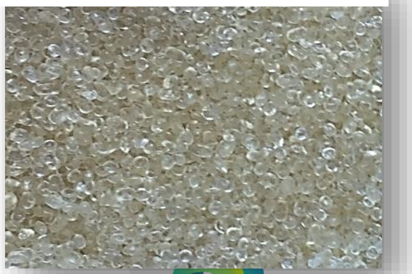
- Poly(lactic acid) (PLA) is a biodegradable and biobased thermoplastic aliphatic polyester with some properties similar to polyethylene (PE), polypropylene (PP) and polystyrene (PS).
- It derives from renewable resources such as corn starch (in the United States and Canada), tapioca roots, chips (mostly in Asia), or sugarcane (in the rest of the world).
- Polylactic Acid (PLA) Market. The global polylactic acid (PLA) market was valued at USD 1.5 billion in 2023 and is projected to reach USD 3.3 billion by 2028, growing at 17.1% CAGR from 2023 to 2028





Monomeric Unit





POLYLACTIC ACID (PLA)

The Polylactic Acid Market is projected to reach USD 1.9 billion by 2026, at a CAGR of 12.2%.
(Compound Annual Growth Rate, CAGR)

Note: e-estimated p-projected.
Source: Expert Interviews, Secondary Sources, and MarketsandMarkets Analysis

PLA bioplastics: applications & markets

Automotive

For interiors & under-the-hood parts.

- High heat resistance
- Durable
- Hydrolytic stability

Packaging & disposables

Yoghurt pots, coffee cups & lids, disposable serviceware.

- Transparent
- Compostable
- Biobased & recyclable

Consumer goods

Sunglasses, serviceware, toys.

- High heat resistance
- Excellent surface appearance
- Durable
- Good impact resistance

Building & construction

Foam for insulation, fibers for carpets & furnishings.

- High heat resistance
- Durable
- Weavable

Consumer electronics

Injection molded casings & housings.

- High heat resistance
- Excellent surface appearance
- Durable
- Good impact resistance

Sportswear & goods

Fibers for apparel, foam for surfboards & helmets, molded parts for equipment.

- High heat resistance
- Good breathability
- Soft & tactile feel
- Washable & durable

The basic building block of PLA is the lactic acid (LA).

It is a simple chiral molecule which exists as two enantiomers, L- and D-lactic acid, optically active.

To produce PLA are using renewable resources like :

Corn starch, sugar cane, sugar beets, wheat.

2.2 kg of corn are needed to produce 1 kg PLA

RECOV3R

POLY LACTIC ACID (PLA)

PLA is a highly transparent and rigid material with a relatively low crystallization rate that makes it a promising candidate for the fabrication of biaxially oriented films, thermoformed containers and stretch-blown bottles

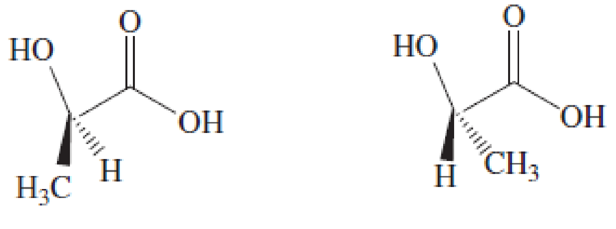
The building block of PLA is lactic acid (2-hydroxypropionic acid) which can exist as optically active D- or L-enantiomers

The range of application of PLA is severely limited because of glass transition temperature (around 55–60°C) thus research was focused on the study of PLA crystallization kinetics, Tm is usually about 170 °C

PLA possesses high strength, good crease-retention, grease and oil resistance and excellent aroma barrier properties. Additionally, the decomposition of PLA occurs by hydrolysis, followed by biodegradation via bacteria. Major limitations of PLA are due to its high brittleness, low toughness and low tensile elongation.
Mechanical parameters indicated that PLA is a brittle material (tensile strength = 32 MPa) with high Young modulus (2.3 GPa) and low percentage elongation of break (EB) (5%).

At temperature higher than glass transition only the PLA crystalline phase can confer useful mechanical properties. Increasing the crystallization speed of PLA is thus desired

Lactic acid is optically active and thus it has a L or D form.
The maximum attainable crystallinity level is obtained by minimizing the amount of the other lactide and mesolactide in the lactide used as the major monomer.



D-lactic acid   L-lactic acid

Figure 1 Stereoisomers of lactic acid.

POLY LACTIC ACID (PLA)

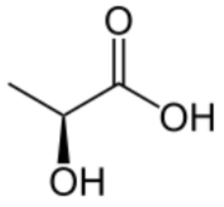
For semi-crystalline PLA, the Tm is a function of the different processing parameters and the initial PLA structure.

Tm increases with the molecular weight (Mw) until a maximum value. Besides, the crystallinity decreases with increasing Mw.

Tg is also determined by the proportion of the different types of lactide.

Tm depends on the presence of meso-lactide in the structure which produces a Tm reduction.

Property	L-PLA	DL-PLA
Glass Transition Temperature (T_g)	60 – 65 °C	50 – 60 °C
Melting Point (T_m)	184 °C	Amorphous
Specific Gravity	1.24	1.25
Tensile Strength (MPa)	55.2 – 82.7	27.6 – 41.4
Elongation (%)	5 – 10	3 – 10
Modulus (MPa)	2758 – 4137	1379 – 2758
Inherent viscosity (dl/g)	0.90 – 1.2	0.55 – 0.75



L-Lactic Acid

Molecular formula	$C_3H_6O_3$
Molar mass	90.08 g/mol
Density	1.209 g/mL
Melting point	L: 53 °C D: 53 °C D/L: 16.8 °C
Boiling point	122 °C at 15 mmHg

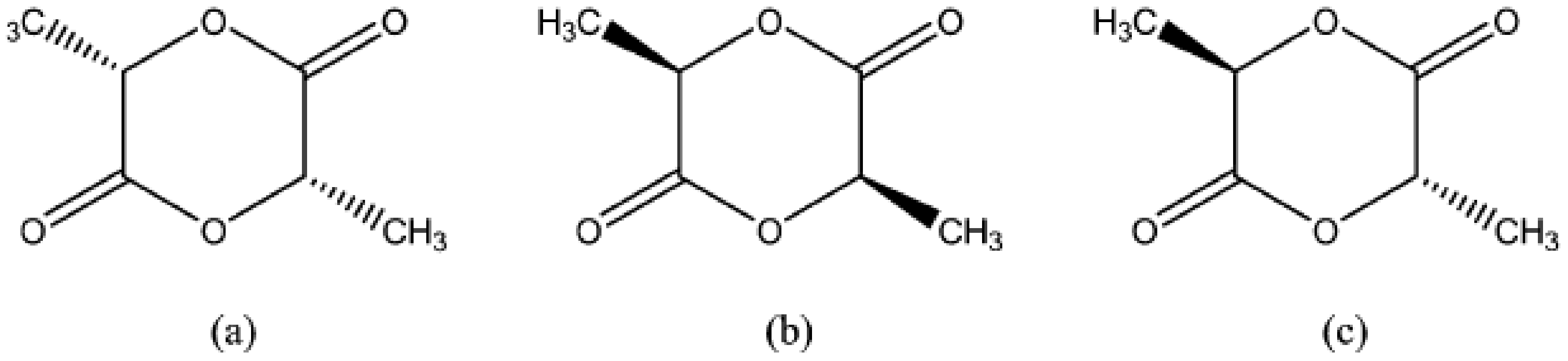


Fig. 4 Chemical structures of dimeric (a) D-lactide, (b) L-lactide and (c) *meso*-lactide.

POLY LACTIC ACID

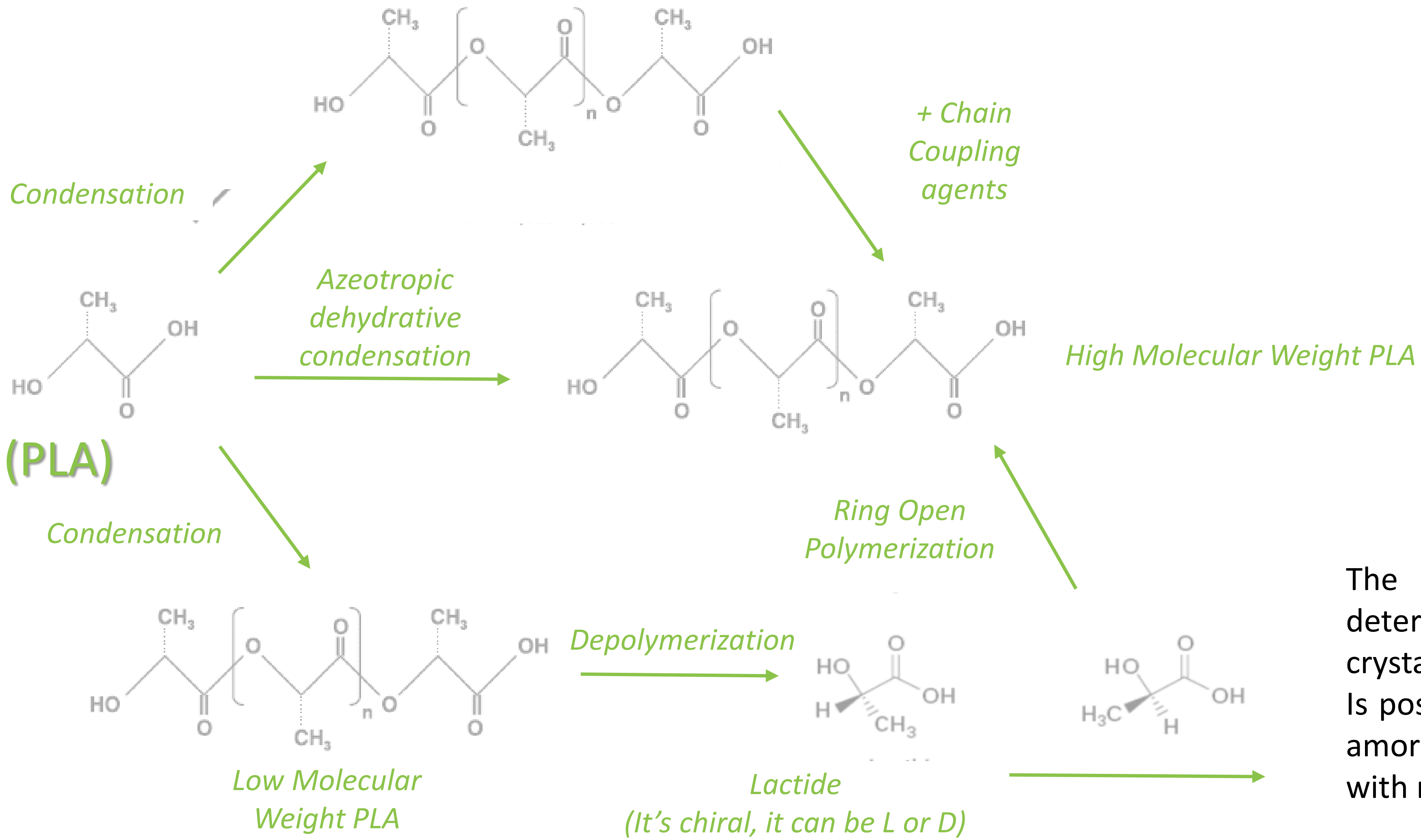
Lactic acid is a chiral molecule existing as two stereoisomers, L- and D-lactic acid which can be produced by different ways, i.e., biologically or chemically
Synthesized

Biologically
lactic acid is obtained by fermentation of carbohydrates by lactic bacteria belonging mainly to the genus Lactobacillus, or fungi.
This fermentative process requires a bacterial strain but also a carbon source (carbohydrates), a nitrogen source (yeast extract, peptides…), and mineral elements to allow the growth of bacteria and the production of lactic acid. The lactic acid as-formed exists almost exclusively **as L-lactic acid** and leads to poly(L-lactic acid) (PLLA) with low molecular weight by polycondensation reaction

Chemically
the chemical process could lead to various ratio of L- and D-lactic acid. The chemical reactions, leading to the formation of a cyclic dimer, the lactide, as an intermediate step to the production of PLA, could lead to long macromolecular chains with L- and D-lactic acid monomers.

RECOV3R

SINTHESYS OF POLYLACTIC ACID (PLA)

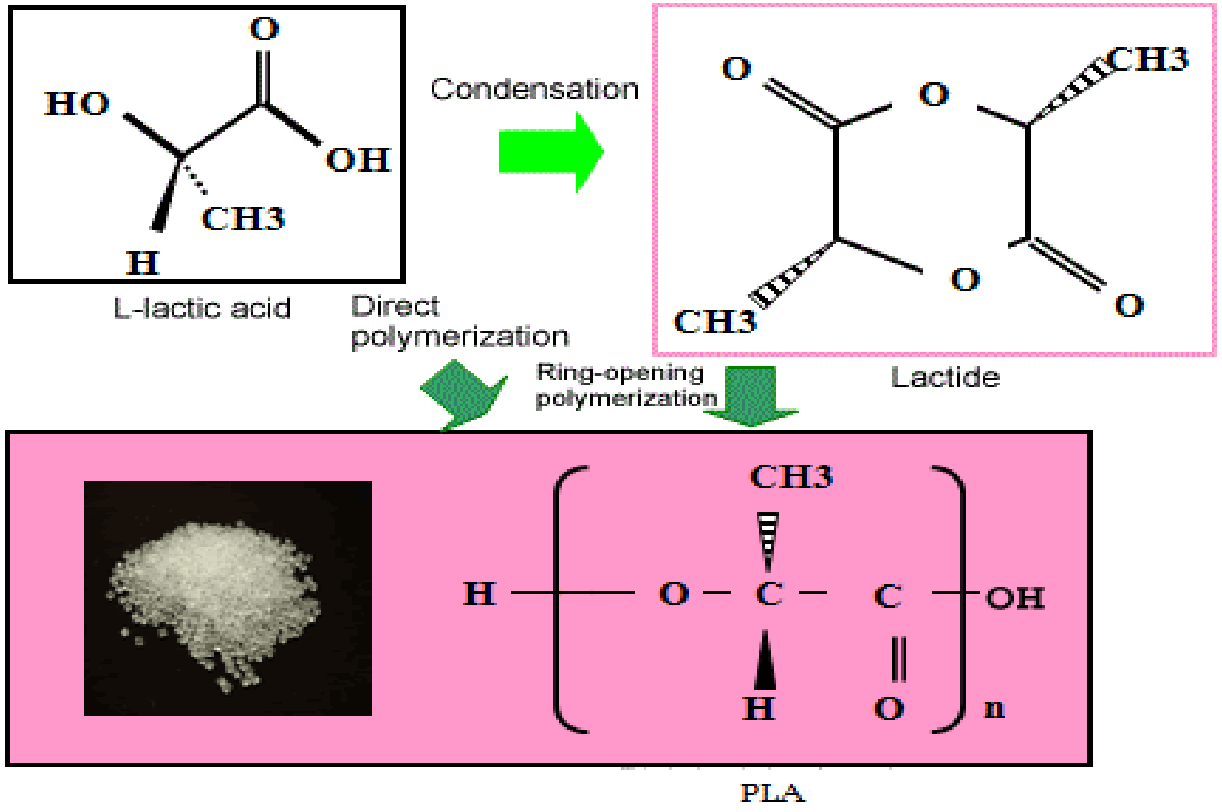


The ratio of D- and L-lactide determines the degree of crystallinity of the polymer.
Is possible to obtain either a totally amorphous PLA than a polymer with more than 40% of crystallinity.

Production of PLA

There are two methods for manufacturing polylactic acid from lactic acid: the first method uses the cyclic lactic acid dimer called lactide as an intermediate stage; the second method is direct polymerization of lactic acid.

The method using the lactide intermediary yields polylactic acid with greater molecular weight.



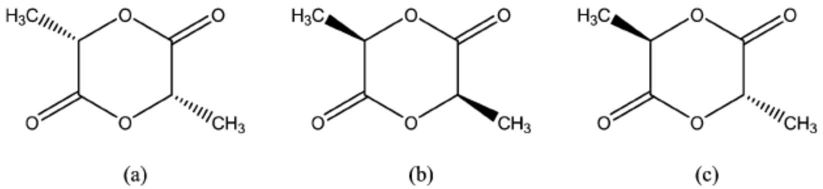
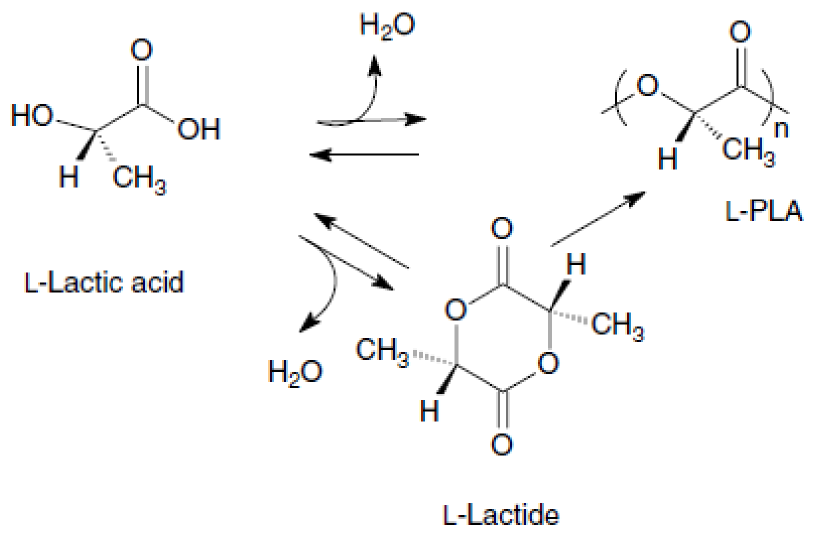


Fig. 4 Chemical structures of dimeric (a) D-lactide, (b) L-lactide and (c) *meso*-lactide.

Cargill Dow LLC has developed a patented, low-cost continuous process for the production of lactic acid-based polymers

The process combines the substantial environmental and economic benefits of synthesizing both lactide and PLA in the melt rather than in solution and, for the first time, provided a commercially viable biodegradable commodity polymer made from renewable resources.

The process starts with lactic acid produced by fermentation of dextrose, followed by a continuous condensation reaction of aqueous lactic acid to produce low molecular weight PLA prepolymer.



The low molecular weight oligomers are converted into a mixture of lactide stereoisomers using a catalyst to enhance the rate and selectivity of the intramolecular cyclization reaction.

The molten lactide mixture is then purified by vacuum distillation.

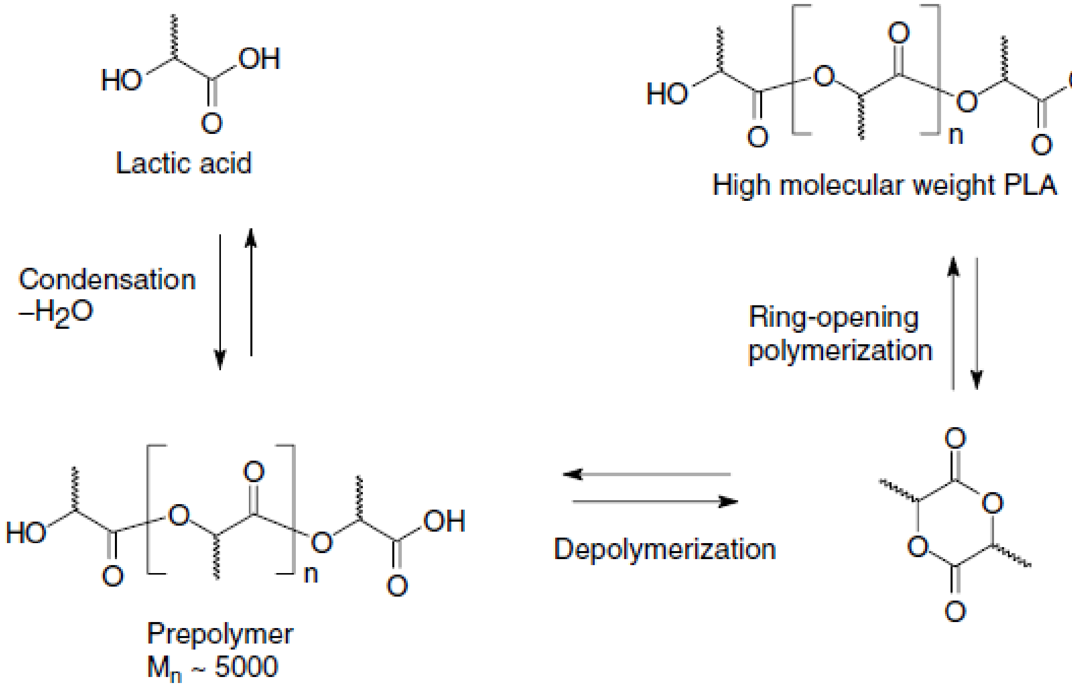


FIGURE 16.2
Schematic of PLA production via prepolymer and lactide.

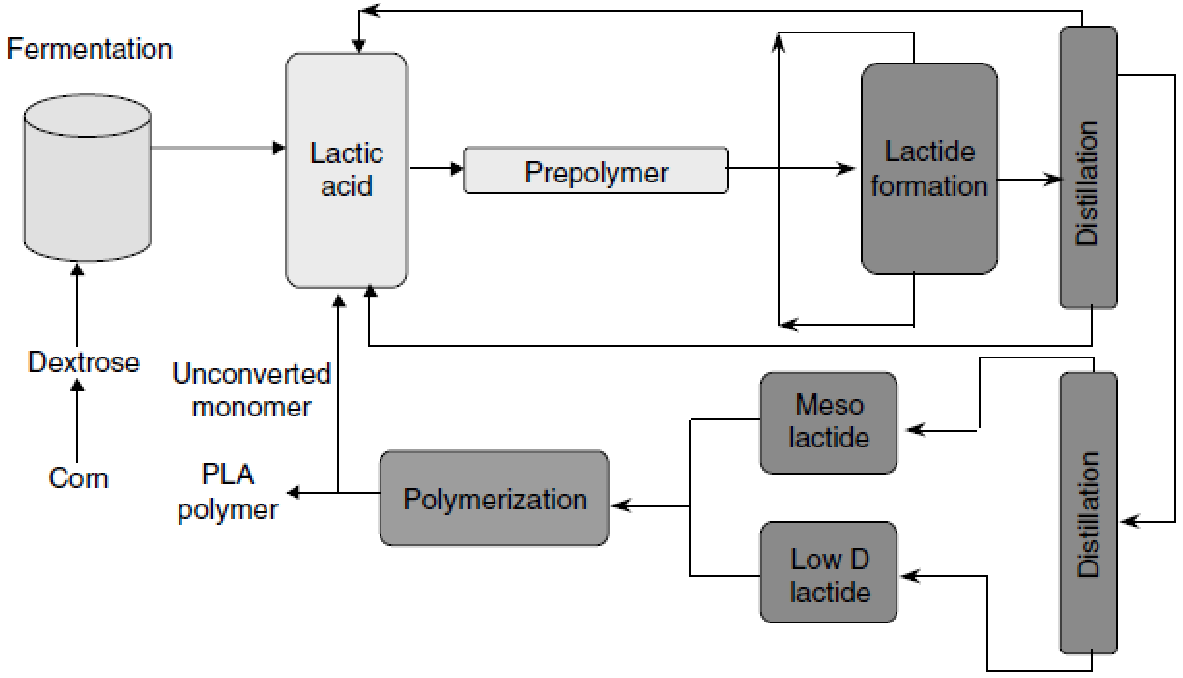


FIGURE 16.3
Nonsolvent process to prepare polylactic acid.

Finally, PLA high polymer is produced using an organo tin-catalyzed, ring-opening lactide polymerization in the melt, completely eliminating the use of costly and environmentally unfriendly solvents.

After the polymerization is complete, any remaining monomer is removed under vacuum and recycled to the beginning of the process

Properties of Extrusion/Thermoforming and Injection Molding Grades of NatureWorks PLA

	PLA Polymer 2000D[a]	ASTM Method	PLA Polymer 3010D[b]	ASTM Method
Physical Property				
Specific gravity (g/cc)	1.25	D792	1.21	D792
Melt index, g/10 min (190°C/2.16 kg)	4–8	D1238	10–30	D1238
Clarity	Transparent		Transparent	
Mechanical Properties				
Tensile strength at break, psi (MPa)	7,700 (53)	D882	7,000 (48)	D638
Tensile yield strength, psi (MPa)	8,700 (60)	D882		
Tensile modulus, kpsi (GPa)	500 (3.5)	D882		
Tensile elongation (%)	6.0	D882	2.5	D638
Notched izod impact, ft-lb/in (J/m)	0.24 (0.33)	D256	0.3 (0.16)	D256
Flexural strength, psi (MPa)			12,000 (83)	D790
Flexural modulus, kpsi (GPa)			555 (3.8)	D790

[a] 2000D is a product of Cargill Dow LLC designed as an extrusion/thermoforming grade; properties typical of extruded sheet.

[b] 3010D is a product of Cargill Dow LLC designed as an injection molding grade; properties typical of injection molded tensile bars.

Table 2 Potential food application of PLA based packaging materials.

Type of food	Film properties	Commercial manufacturer
Bottled water	Moisture, light and gas barrier	Biota™
Bottled juice	Moisture, light and gas barrier, inert to migration of flavor	Noble™
Milk	Moisture, light and gas barrier	
Yoghurt	Mechanical strength, barrier of oxygen, carbon dioxide, moisture and grease	Dannon™
Cheese	Moisture, light and gas barrier	
Butter/Margarine		
Mushroom	Mechanical strength, balanced gas and moisture barrier; protection against crushing/bruising	

Table 3 Comparison of thermal properties (heating rate 10°C/min) of PLA and synthetic polymers.*

Sample	$M_n \times 10^3$	T_g (°C)	T_m (°C)	T_c (°C)
Polyethylene terephthalate (PET)	100	90.5	257.7	216.6
Polyethylene	103		98.8	76.7
Polystyrene (atactic)	99	98.5		
PLA (L-form)	150	66.9	179.8	–
PLA (DL-form)	250	53.1	–	–

*Authors unpublished data.

Table 4 Comparison of water vapor and oxygen transmission rate of PLA and synthetic polymers.*

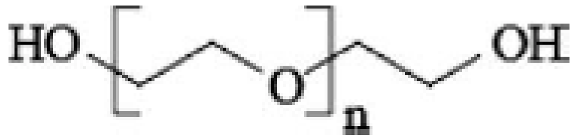
Sample	Thickness (mm)	WVTR [g(m²/d)]	Permeability coefficients [kg/m/(m²/s/Pa)]	OTR [cc(m²/d)]	Permeability coefficients [kg/m/(m²/s/Pa)]
PET	18	3.48	2.82×10^{-15}	9.44	6.95×10^{-19}
PS	18	5.18	4.18×10^{-15}	531.58	3.91×10^{-17}
PLA	20	15.30	1.34×10^{-14}	56.33	4.33×10^{-18}

Table 6 Characteristics of typical bioresorbable PLA based polymers.

Polymer	T_m (°C)	T_g (°C)	Modulas (GPa)	Degradation time (months)
Poly(lactic acid) (L-form)	173–178	60–65	2.7	>24
Poly(lactic acid) (DL-form)	Amorphous	55–60	1.9	12–16
Poly(DL lactic acid-co-glycolic acid) (75/25)	Amorphous	50–55	2.0	4–5
Poly(DL lactic acid-co-glycolic acid) (50/50)	Amorphous	45–50	2.0	1–2

PLA can be plasticized using oligomeric lactic acid (o-LA)

Citrate ester



Low molecular weight polyethylene glycol (PEG)

Epoxidized soybean oil

The effect of plasticization increases the chain mobility and then favors the PLA organization and crystallization. After plasticization, a crystallinity ranging between 20 and 30 % is obtained.

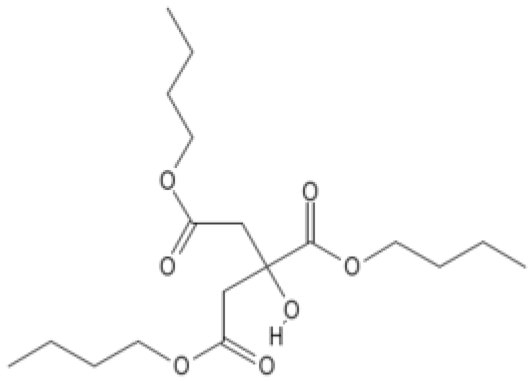
PLA presents a medium water and oxygen permeability level comparable to polystyrene. These different properties associated with its tunability and its availability favor its actual developments in different packaging applications (trays, cups, bottles, films…)

Regarding biodegradation in compost, adequate conditions are only found in industrial units with a high temperature (above 50 °C) and a high relative humidity (RH%) to promote chain hydrolysis.

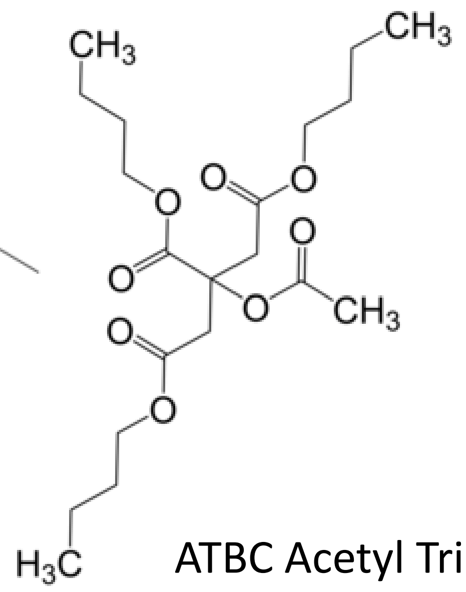
Table 1 Mechanical and thermal performance of PLA plasticized with different modifiers

Modifiers	M_W (g mol^{-1})	Conc. (wt%)	T_g (°C)	E^a (MPa)	ε^a (%)	σ^a (MPa)
PLA[54,55]	137 000	100	59	1720	7	51.7
Triethyl citrate[54]	276	20	32.6		382	12.6
Tributyl citrate[54]	360	20	17.6		350	7.1
Acetyl triethyl citrate[54]	318	20	30		320	9.6
Acetyl tributyl citrate[54]	402	20	17		420	9.2
Poly(oxyethylene)[55]	10 000	21	31	320	7	49
Poly(ε-caprolactone)[55]	10 000	20	35	961	25	19
Glycerol[51]	92.09	20	53		—	—
PEG monolaurate[51]	400	20	21		142	—
Plasticized TPS[51]	—	25	—		2.9	30.2
PEG[62]	1500	10	34.3	1750	150	15.1
PEG[62]	1500	20	23.2	1460	150	14.6

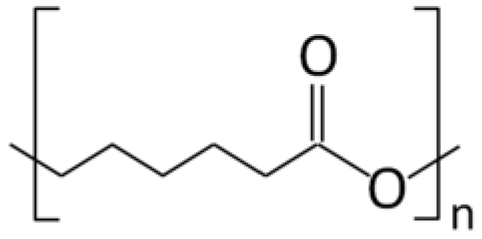
[a] Tensile modulus (E), tensile stress at yield (σ), and elongation at break (ε).



TriButylCitrate



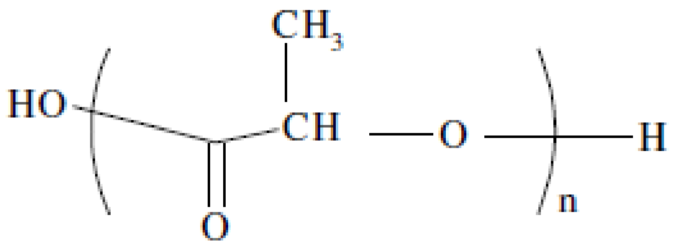
ATBC Acetyl TriButylCitrate



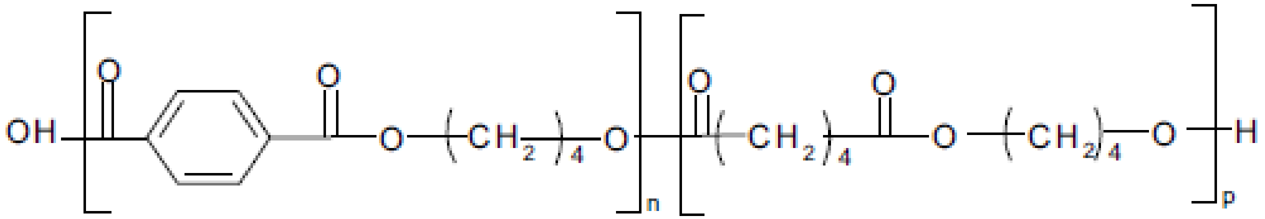
PCL (Poly caprolactone)

Melt-compounding of biodegradable polymer blends based on commercial aliphatic polyesters such as poly (lactic acid) (PLA), poly(ε-polycaprolactone) (PCL), poly(3-hydroxybutyrate) (PHB), poly(butylene-adipate- *co*-terephtalate) (PBAT), poly(butylene succinate) (PBS), and also thermoplastic starch (TPS) or natural rubber (NR), gained much attention from researchers, which is related to their relatively easy processing, suitable usage properties and good quality/ price ratio of the final products.

a: *PLA*



b: *PBAT*



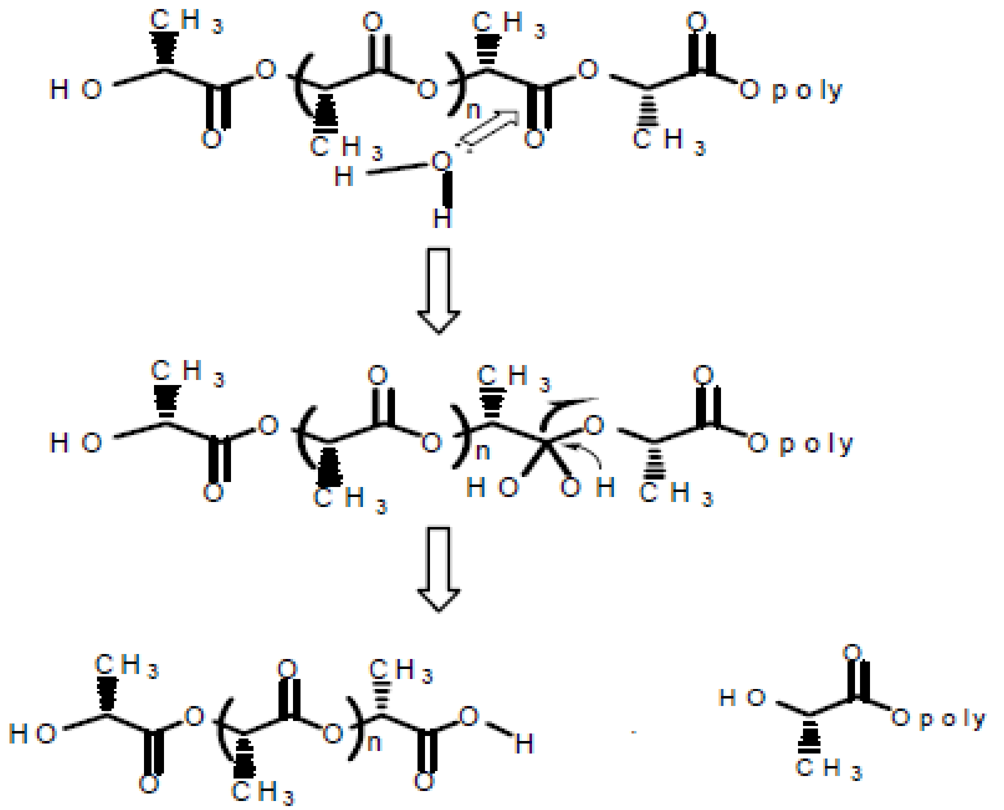
PLA is biodegraded in Industrial Composting 58 °C, 50% RH

PLA degradability is driven by the hydrolysis and cleavage of the ester linkages in the polymer backbone

Under conditions of high temperature and high humidity, as in active compost, for example, PLA will degrade quickly and disintegrate within weeks to months.

The primary mechanism of degradation is hydrolysis, followed by bacterial attack on the fragmented residues.

The environmental degradation of PLA occurs by a two-step process. During the initial phases of degradation, the high molecular weight polyester chains hydrolyze to lower molecular weight oligomers. The rate of hydrolysis is accelerated by acids or bases and is dependent on moisture content and temperature.



Scheme 1 PLA hydrolysis and molecular weight loss

Stage	Molecular Weight	Rate of MW Decrease	Weight Loss	Hydrolysis Reaction	Degradation Mechanism
First stage	High	Slow (rate determined)	None	Nonenzymatic	Bulk
	Critical (M_n: 10,000 – 20,000)		Onset		
Second stage	Low	Rapid	Rapid	Nonenzymatic and enzymatic	Bulk and surface

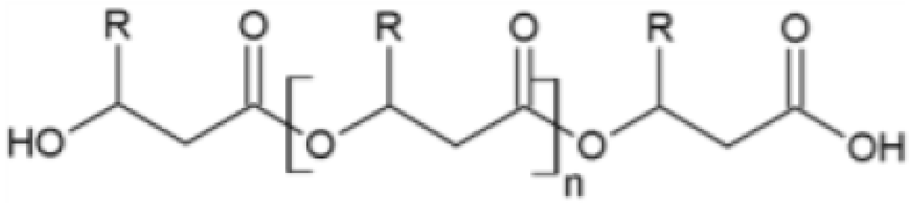
Article dimensions, crystallinity, and blends will affect the rate of degradation.
PLA products rapidly degrade in both aerobic and anaerobic composting conditions

Polylactic Acid is a little bit more brittle than ABS for 3D prototyping but it has some advantages as well. For a full comparison of the two plastics as they relate to 3D printing

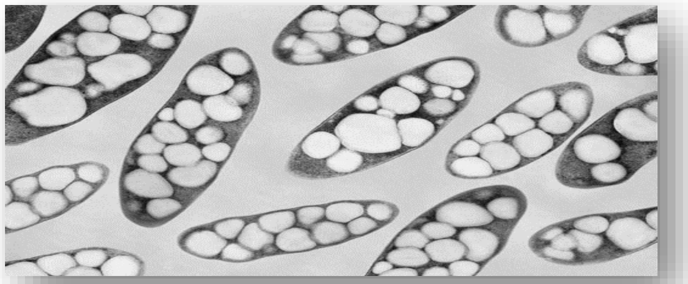
RECOV3R

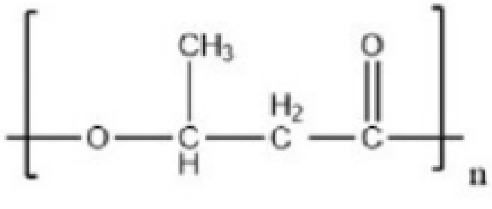
POLYHYDROXYALKANOATES (PHAs)

- Beijerinck in 1888 first observed the PHA as granules in the bacterial cells.
- Later on, Lemoigne in 1926 discovered PHA in *Bacillus megaterium* in the form of poly (3-hydroxybutyrate) (PHB), the most well-known scl-PHA member, characterized as a stiff and brittle material and difficult to be processed due to its semi-crystalline isotactic nature.
- Polyhydroxyalkanoates (PHAs) are natural polymers (polyesters) synthesized by numerous bacteria as energy reserve and present in the form of granules in the cell cytoplasm
- Poly-hydroxyalkanoates are synthesized and accumulated by about 300 different microbial species covered in more than 90 kinds of Gram-positive and Gram-negative bacteria, such as Bacillus, alcaligene latus, Rhodococcus, Rhodospirillum, Pseudomonas, Alcaligenes, Azotobacter, Rhizobium.
- When bacterial cells are temporarily free of one or more nutrients such as nitrogen (N), sulphur (S), phosphorus (P), magnesium (Mg) or oxygen (O), their metabolism does not work normally. In this circumstance the cell can accumulate nutrient reserves: phosphorus in the form of polyphosphate (poly P) and carbon in the forms of polyhydroxyalkanoate (PHAs).
- Industrial production of polyhydroxyalkanoates is based on the fermentation of microbial cultures on substrates such as sugars (glucose) or carbohydrate compounds (corn).



General strucure of PHAs

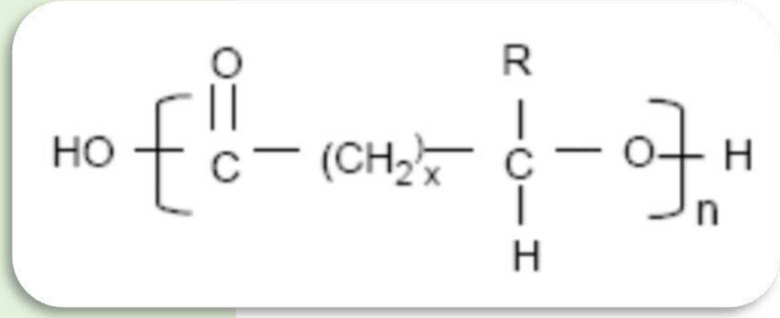




P3HB

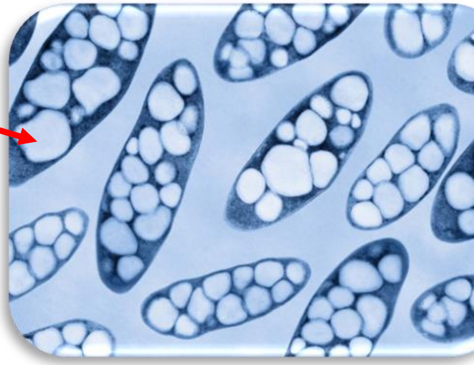
POLYHYDROXYALKANOATES (PHAs)

Polyhydroxyalkanoates (PHAs) are thermoplastic polyester synthesized from different bacterias. A wide variety of prokaryotic organisms accumulate PHA from 30 to 80 % of their cellular dry weight.



PHAs have **good thermal properties**
(melting point at 160-180°C) good processability
Good resistance in a large temperature's range
from -30°C to +120°C.

PHAs



Biotechnological studies revealed that PHB is produced under balanced growth conditions when the cells become limited for an essential nutrient but are exposed to an excess of carbon.

Depending on the carbon substrates and the metabolism of the microorganism, different monomers, and thus (co)polymers, could be obtained.

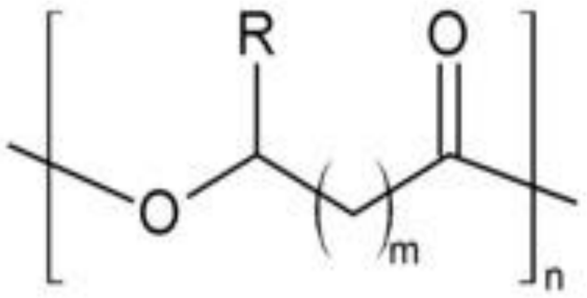
In marine and terrestrial environments PHAs are biodegradable

POLYHYDROXYALKANOATES (PHAs)

The multiplicity of polyhydroxyalkanoates is due to the type of branching R present in the molecule that may be linear or branched, saturated or unsaturated, with aromatic or halogenated substituents.
The number of -CH2- groups and the number of monomers present influence PHAs the physical characteristics of PHAs.

m=1	R= hydrogen	3-hydroxypropionate	(3HP)
	methyl	**3-hydroxybutyrate**	**(3HB)**
	ethyl	**3-hydroxyvalerate**	**(3HV)**
	propyl	3-hydroxyhexanoate	(3HH)
	pentyl	3-hydroxyoctanoate	(3HO)
	heptyl	3-hydroxydecanoate	(3HD)
	nonyl	3-hydroxydodecanoate	(3HDD)
m=2	R= hydrogen	4-hydroxybutyrate	(4HB)
m=3	R= hydrogen	5-hydroxyvalerate	(5HV

Monomeric Unit



m is the number of groups CH2, ***n*** is the number of monomers ranging from 100 to 30000, and ***R*** is the side chain

POLYHYDROXYALKANOATES (PHAs)

The main biopolymer of the PHA family is the poly hydroxybutyrate homopolymer (PHB),

but also different poly(hydroxybutyrate-cohydroxyalkanoates) copolyesters exist such as:
poly(hydroxybutyrate-co-hydroxyl valerate) (PHBV),
poly(hydroxybutyrate-co-hydroxyhexanoate) (PHBHx),

Table 2.2 Main PHA abbreviations

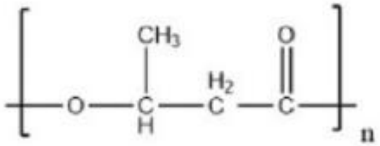
Conventional abbreviations (short)	Full abbreviations	Structures
PHB	P(3HB)	Homopolymer
PHV	P(3HV)	Homopolymer
PHBV	P(3HB-co-3HV)	Copolymer
PHBHx	P(3HB-co-3HHx)	Copolymer
PHBO	P(3HB-co-3HO)	Copolymer
PHBD	P(3HB-co-3HD)	Copolymer
PHBOd	P(3HB-co-3HOd)	Copolymer

poly(hydroxybutyrate-co-hydroxyoctanoate) (PHBO), and poly(hydroxybutyrateco-hydroxyoctadecanoate) (PHBOd)

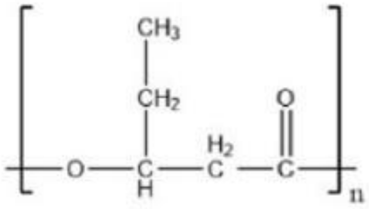
Table 2.1 Main PHAs homopolymer structures based on the Fig. 2.11

Chemical name	Abbreviation	x value	R group
Poly(3-hydroxypropionate)	P(3HP)	1	Hydrogen
Poly(3-hydroxybutyrate)	P(3HB)	1	Methyl
Poly(3-hydroxyvalerate)	P(3HV)	1	Ethyl
Poly(3-hydroxyhexanoate) or poly (3-hydroxycaproate)	P(3HHx) or P(3HC)	1	Propyl
Poly(3-hydroxyhexanoate)	P(3HH)	1	Butyl
Poly (3-hydroxyoctanoate)	P(3HO)	1	Pentyl
Poly (3-hydroxynonanoate)	P(3HN)		Hexyl
Poly(3-hydroxydecanoate)	P(3HD)	1	Heptyl
Poly(3-hydroxyundecanoate) or	P(3HUD)or P(3HUd)	1	Octyl
Poly(3-hydroxydodecanoate)	P(3HDD) or P(3HDd)	1	Nonyl
Poly(3-hydroxyoctadecanoate)	P(3HOD) or P(3HOd)	1	Pentadecanoyl
Poly(4-hydroxybutyrate)	P(4HB)	2	Hydrogen
Poly(5-hydroxybutyrate)	P(5HB)	2	Methyl
Poly(5-hydroxyvalerate)	P(5HV)	3	Hydrogen

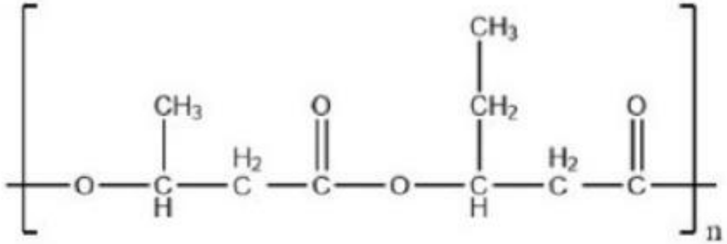
RECOV3R



P3HB

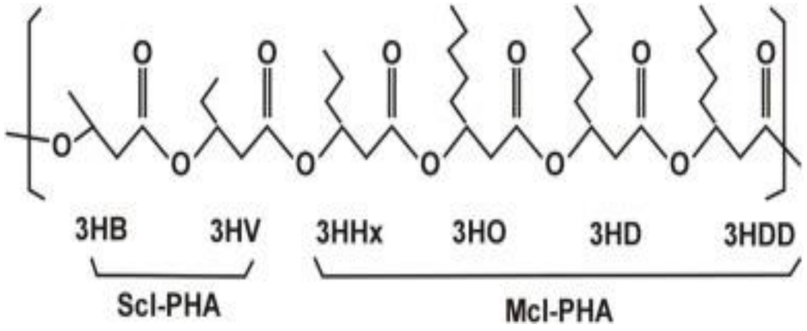


PHV



PHBV

The chain-length of the volatile fatty acids is of great influence on the composition and properties of PHA. In mixed culture PHA production, for example, P3HB is brittle and stiff and has limited applications. The incorporation of 3HV into P3HB results in a more flexible and tougher PHA, also less permeable to oxygen, making it suitable for food packaging.



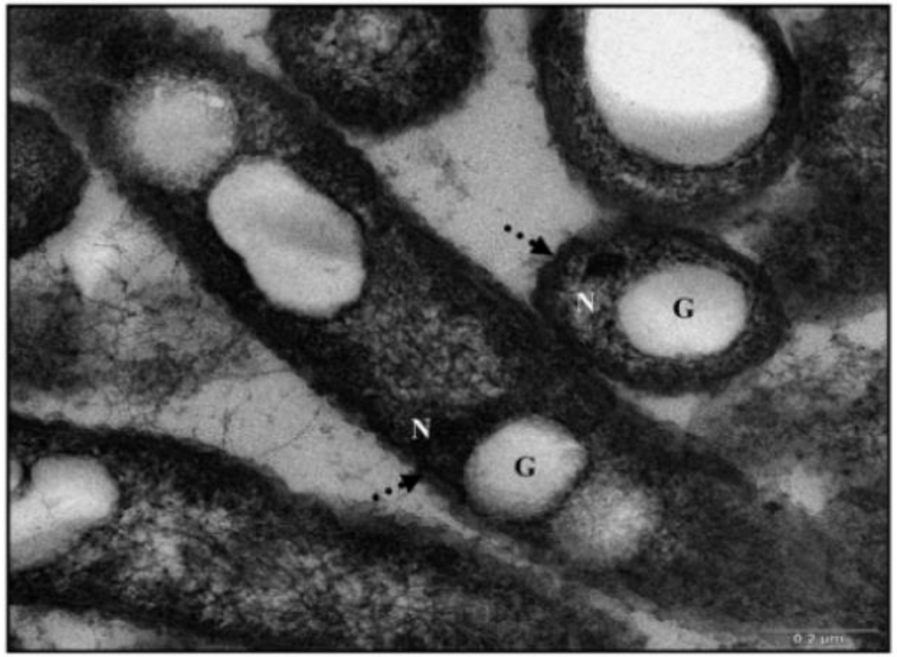
- **short-chain-length PHAs *(scl-PHAs)*** consist of 3–5 carbon atoms;
- **medium-chain-length PHAs *(mcl-PHAs)*** consist of 6–14 carbon atoms.

The number of -CH_2 groups and the number of monomers affect the physical characteristics of PHAs.
mcl-PHAs have a much lower level of crystallinity, tensile strength, melting point than scl-PHAs and are more flexible.
So, the introduction of different HA monomers such as 3-hydroxyvalerate (3HV) or 3-hydroxyhexanoate (3HHx) into the chain increases elasticity.

PHAs Natural Producers

- ✓ Prokaryotes include bacterias and archaea
- ✓ *Bacillus*
- ✓ *Alcaligenes*
- ✓ *Azotobacter*
- ✓ ***Ralstonia eutropha***
- ✓ *Vibrio*
- ✓ *Enterobacter*
- ✓ *Cupriavidus*
- ✓ *Methylobacterium*

The cost of PHA production is mainly affected by downstream process
and therefore, the development of PHA extraction methods is required to m
the overall process much simpler and cheaper. Improved bioseparation syste
are essential for biotechnology as separation is the limiting parameter for
success of biological processes. The recovery system may affect the amour
product recovery, the convenience of the subsequent purification steps and
quality of the final product. Cell separation from fermentation broth is
preliminary step of the recovery method.



PHA extraction

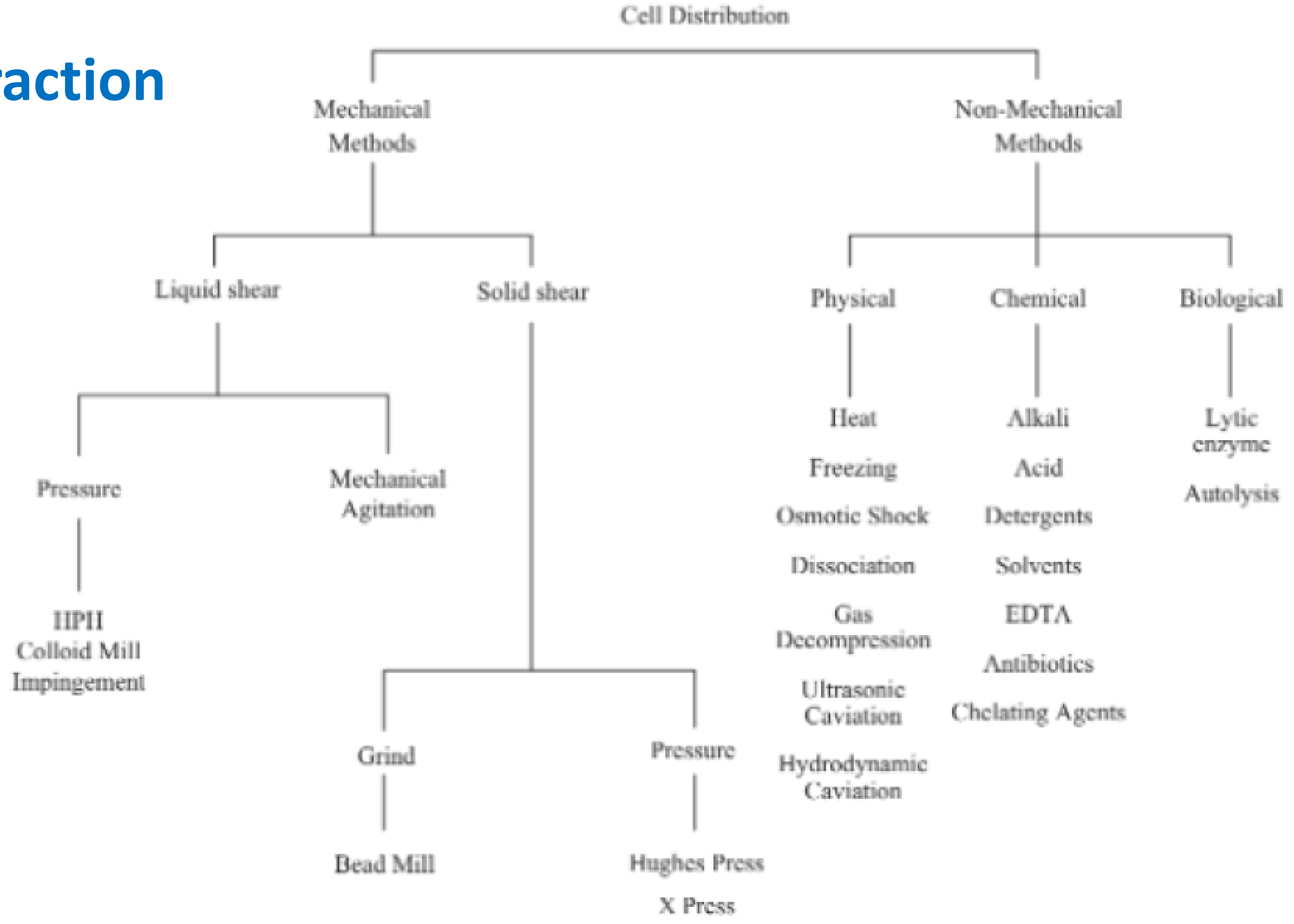


Figure 1 : *Classification of different recovery methods to extract PHA from the cell*

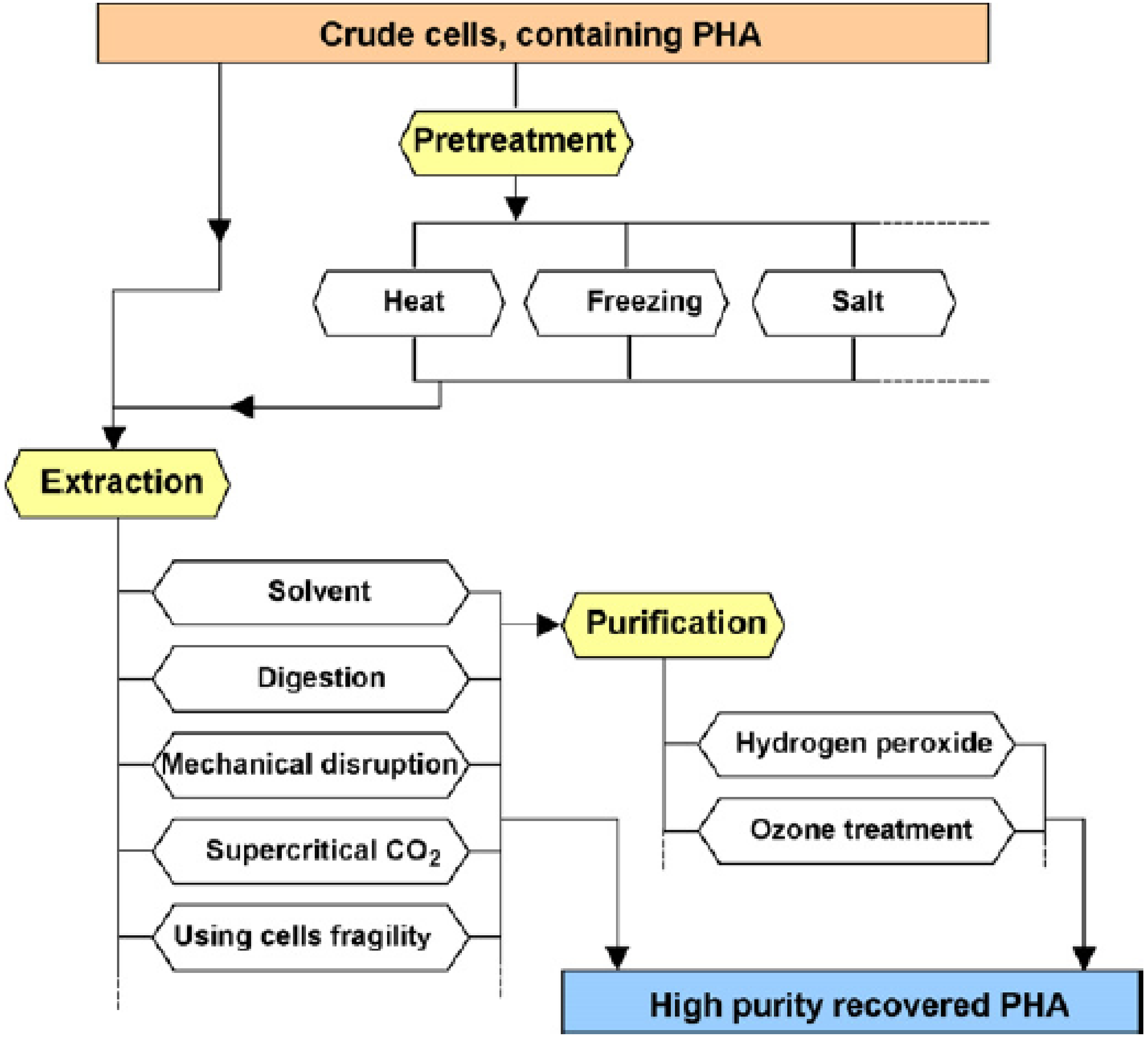
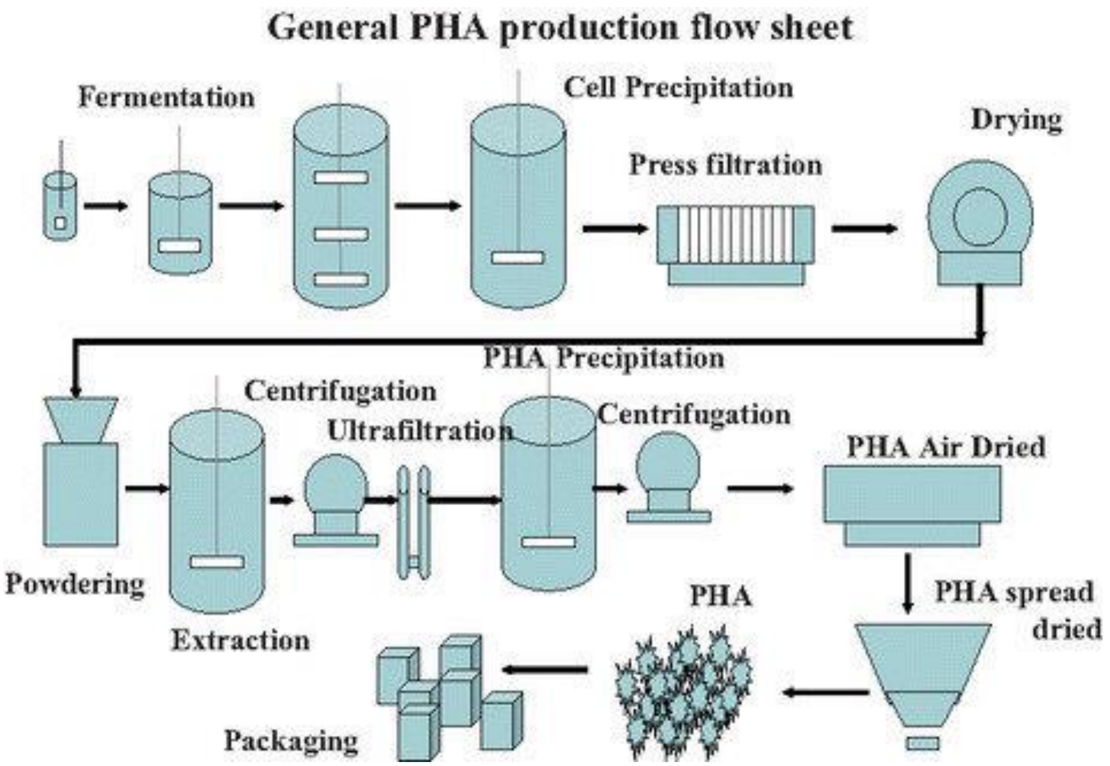


Fig. 3. Purification strategy of PHAs. The recovery of PHAs could be composed of three steps pretreatment, extraction, and purification.



RECOV3R

POLYHYDROXYALKANOATES (PHAs)

Biologically produced, poly3hydroxybutyrate P(3HB) is a semi-crystalline isotactic stereo regular polymer with 100% R configuration that allows a high level of degradability.

The Mw of P(3HB) produced from wild type bacteria is usually in the range of $1 \cdot 10^4$-$3 \cdot 10^6$ g/mol with a polydispersity of around two. The glass transition temperature of P(3HB) is around 2°C while the melting temperature is near 180°C, as measured by calorimetric analysis.

The densities of crystalline and amorphous P(3HB) are 1.26 and 1.18 g/cm3, respectively.
Mechanical properties like the Young's modulus (3.5 GPa) and the tensile strength (43 MPa) of P(3HB) material are close to those of isotactic polypropylene. The extension to break (5%) for P(3HB) is however markedly lower than that of polypropylene (400%).

Table 1. Range of typical properties of PHA's

Property* [units]	Values
T_g [°C]	2
T_m [°C]	160–175
X_{cr} [%]	40–60
E [GPa]	1–2
σ [MPa]	15–40
ε [%]	1–15
WVTR [g·mm/m^2·day]	2.36
OTR [cc·mm/m^2·day]	55.12

*T_g: glass transition temperature, T_m: melting temperature, X_{cr}: crystallinity degree, E: Young's modulus, σ: tensile strength, ε: elongation at break, WVTR: water vapour transmission rate; OTR: oxygen transmission rate.

PHA technical substitution potential

Where:
++ represents the completely substitution;
+ represents the partial substitution;
- represents no substitution

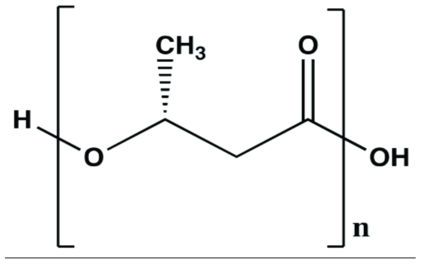
	PVC	PE-HD	PE-LD	PP	PS	PMMA	PA	PET	PBT	PC	POM	PUR	ABS
P(3HB)	+	+	+	+	+	-	-	+	+	-	-	-	+
P(3HB-co-3HHx)	+	+	+	+	-	-	-	-	-	-	-	+	-

PHAs properties

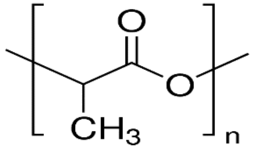
Table 24.4 Comparison of the properties of the main biodegradable polyesters

Property/Material	PHB	PLA	PCL	PEA
Physical Properties				
Density (g/ml)	1.25	1.25	1.10	1.05
Thermal Properties				
Melting temperature (°C)	165	151	62	114
Glass transition temperature (°C)	–5	58	–60	–32
Degree of crystallinity (%)	40–60	0–2	60–70	30–36
Mechanical Properties				
Young's modulus (MPa)	1000–1200	2000–2100	180–240	250–270
Tensile strength (MPa)	15–20	16–103	13–15	18
Elongation at break (%)	14–16	8–10	Higher than 600	400–460
Barrier Properties				
WVTR at 25 °C (g/m^2·day)	20	170	180	700
Surface Properties				
Surface tension (mN/m)	60	50	53	62
Polar component	32	14	12	24
Biodegradability				
Biodegradation 60 days (%)	100	100	100	100

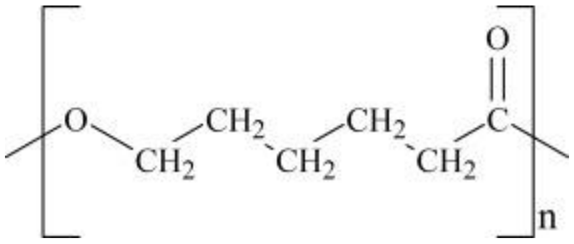
Source: Adapted from [41].



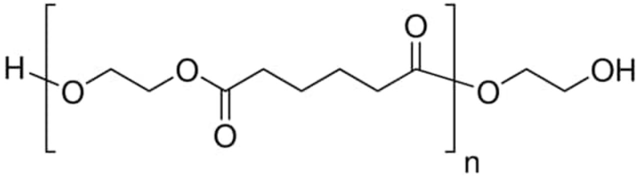
Poly hydroxybutyrate



Poly lactic acid



Polycaprolactone



Poly EthyleneAdipate

PHA processing, thermal degradation

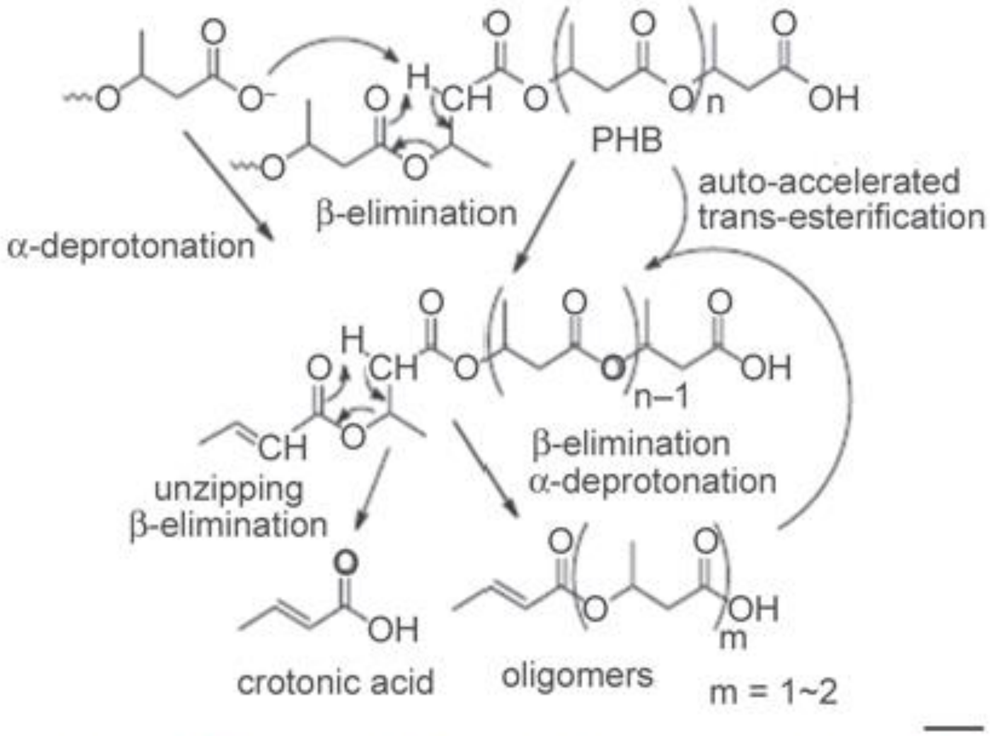


Figure 4. Mechanism of thermal degradation for PHB

PHB thermally decomposes at temperatures just above its melting point.
A short exposure of PHB to temperature near 180°C could induce a severe degradation accompanied by production of the degraded products of olefinic and carboxylic acid compounds, e.g., crotonic acid and various oligomers: through the random chain scission reaction that involves a cis-elimination reaction of β- CH and a six-member ring transition.
The most common mechanisms are summarised in Figure 4.

During processing, the degradation of the chains may be reduced by the addition of a lubricant that prevents the degradation of the chains in processing, so that the material can be processed at 170– 180°C, because PHB is sensitive to high processing temperatures.

This leads to a decrease in the molecular weight, as well as a reduction in the melt viscosity.
The crystallization temperature shifts to lower values, and crystallization takes longer.

PHA processing

PHAs can be processed mainly via injection moulding, extrusion and extrusion bubbles into films and hollow bodies.

The use of co-polymers were chosen in order to improve the flexibility for potential packaging applications, it leads to decrease of the glass transition and melting temperatures.

In addition, *the HV broadens the processing window since there is improved melt stability at lower processing temperatures*.

They have observed that the complex viscosity decreased with increasing temperature due to a decrease in molecular weights of the samples.
These results suggest that processing the co-polymer below 160°C would be beneficial with low screw speed.
The mechanical results indicate all PHBV materials had high elastic modulus and flexural strength with low tensile strength and elongation at break.
The water vapour transmission rate (WVTR) results indicated the polymer to be very hydrophilic, resulting in higher water transmission rates.

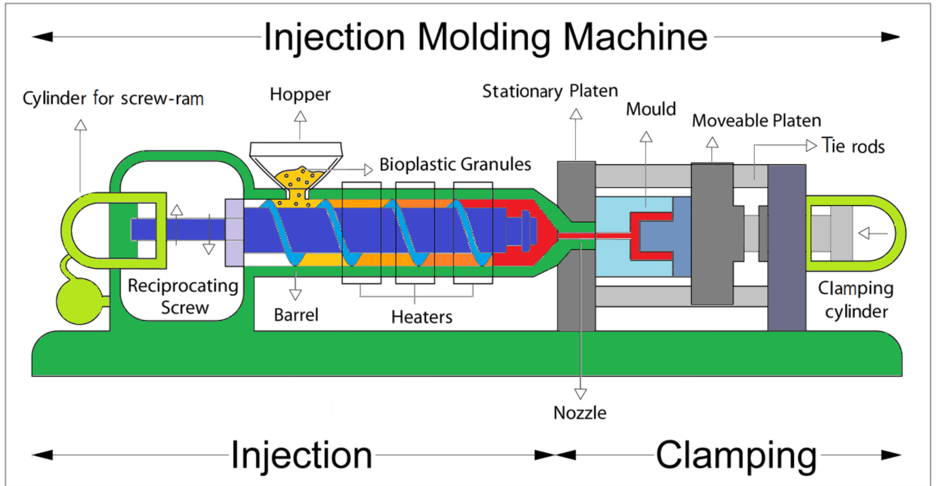
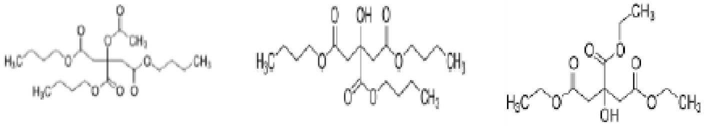


Table 2 Effect of plasticizing modifiers on the glass transition temperature and mechanical properties of PHBV

Sample	Modifier concentration (wt%)	M_W (g mol^{-1})	T_g (°C)	ε (%)	TS (MPa)
PHBV[83]	100	680 000	−6.6	6	43.1
Soy oil[83]	20	814.3	−3.4	3	33.7
Epoxidized soy oil[83]	20	874.2	−19.0	7.2	22.1
Dibutyl phthalate[83]	20	278.2	−28.5	10	11.7
Triethyl citrate[83]	20	276.1	−30.0	10	10.9
Epoxy soyate[88]	20	—	—	7.51	13.8
Soy oil[88]	10	—	—	5.09	18.7
Epoxidized linseed oil[88]	10			7.46	19.6



ATBC **TBC** **TEC**

Fig.1. Chemical structure of ecological plasticizers

Table 1. Properties of the used plasticizers

Plasticizer	Molecular weight (g mol^{-1})	Density (g L^{-1})	Solubility parameters
Tributyl citrate (TBC)	360.44	1.043	18.8 (J cm^{-3})$^{1/2}$ [21]
Tributyl *o*-acetylcitrate (ATBC)	405.5	1.045 – 1.055	18.7 (J cm^{-3})$^{1/2}$ [21]
Triethyl citrate (TEC)	276.28	1.137	22.7- 23.8 MPa$^{1/2}$ [20,22]

Table 5. Challenge and Prospects of PHAs

PHAS challenges	PHAs prospects
High cost of production and extraction	– Reduction in cost related to the use of substrate for bacteria growth coming from by products or waste materials. – Increase PHAs production by use of mixed culture or modified bacteria or microalgae. – Optimisation of PHA extraction processes.
Quality of PHA	– Optimisation of the quality and uniformity of PHAs produced in mixed culture.
Mechanical properties	– Better understanding of PHAs kinetics of crystallization and proper choice of additives (nucleating agents, plasticizers) to achieve stability in mechanical properties, and improvement in elongation at break.
Production of blends and composites	– Optimisation in the use of PHAs in blends with other biodegradable polymers achieving a reduction in cost of the final product while still maintaining the outstanding properties of PHAs in terms of barrier properties, Modulus, high biodegrability in different environments.
Blends with natural additives	– PHAs in processing are very sensitve to water presence, but proper drying of natural additives and proper choice of compatibilizers is promising for the preparation of blends of PHAs and natural polymers (starch, proteins, etc.) which can achieve the production of plastic items with high biodegradability, for example also in marine environment.

RECOV3R

“MARINE POTS"
Performance evaluation

Monitoring of the plants’ growth

In Marine Water





In Dunes




Tirreno sea, in Tuscany, Italy. Posidonia oceanica planting, for coast restoration

Performance evaluation of "terrestrial pots"

outdoors

buried

greenhouse

PHBV and wood Fibres

Table 5. Challenge and Prospects of PHAs

PHAS challenges	PHAs prospects
High cost of production and extraction	– Reduction in cost related to the use of substrate for bacteria growth coming from by products or waste materials. – Increase PHAs production by use of mixed culture or modified bacteria or microalgae. – Optimisation of PHA extraction processes.
Quality of PHA	– Optimisation of the quality and uniformity of PHAs produced in mixed culture.
Mechanical properties	– Better understanding of PHAs kinetics of crystallization and proper choice of additives (nucleating agents, plasticizers) to achieve stability in mechanical properties, and improvement in elongation at break.
Production of blends and composites	– Optimisation in the use of PHAs in blends with other biodegradable polymers achieving a reduction in cost of the final product while still maintaining the outstanding properties of PHAs in terms of barrier properties, Modulus, high biodegrability in different environments.
Blends with natural additives	– PHAs in processing are very sensitve to water presence, but proper drying of natural additives and proper choice of compatibilizers is promising for the preparation of blends of PHAs and natural polymers (starch, proteins, etc.) which can achieve the production of plastic items with high biodegradability, for example also in marine environment.

RECOV3R

STARCH

- Starch is a basic component of MaterBi® (produced by Novamont), used for production of biodegradable materials. As blown films it is known as biodegradable shoppers replacing traditional polyethylene bags.

- Plantic™ produces a water-soluble starch/PVOH compound with silicate nanoclay added. It is used captively to make thermoformed candy trays. Recently, Plantic developed grades for blown film.

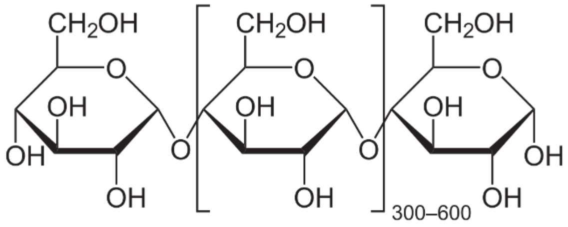
- Rodenburg Biopolymers produces Solanyl® (made from potato waste). Solanyl® is principally marketed for nursery pots and other horticultural applications.

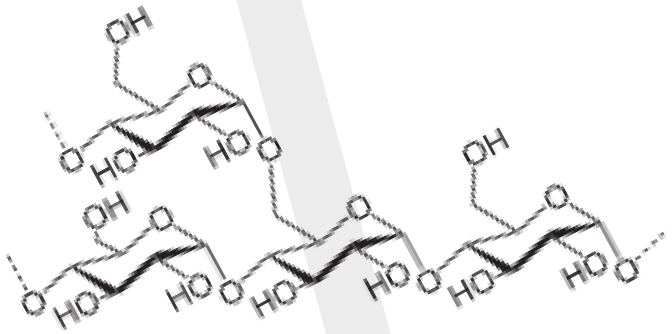
- EarthShell Corporation uses reclaimed starch from the commercial processing of potatoes and French fries. This maximizes the efficiency of potato processing and reduces costs. Limestone, recycled fiber are the other ingredients. Many food containers like trays, cups, plates, wraps etc are produced with this material.

Starch is composed of two polymers

Amylose (about 20%)

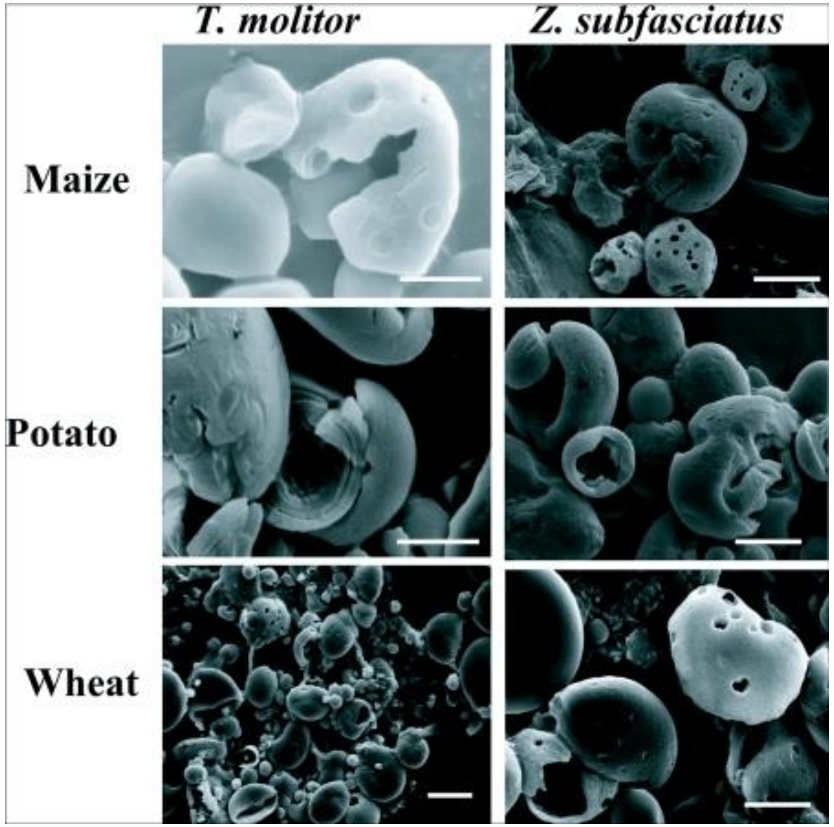
Amylopectin (about 80%)



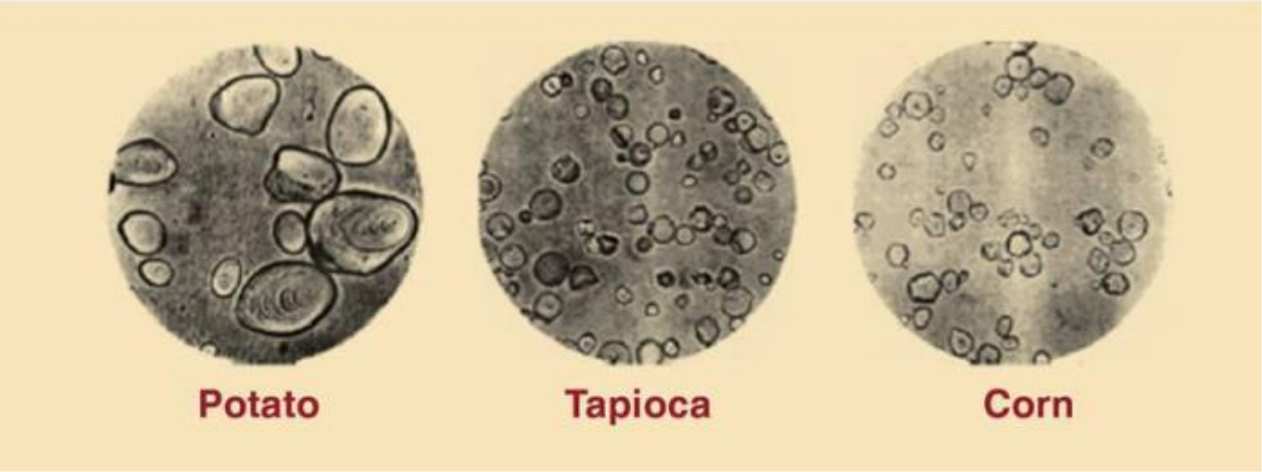


In both cases these are glucose polymers that differ from one another to the structure.

STARCH



DIFFERENT STARCH GRANULES



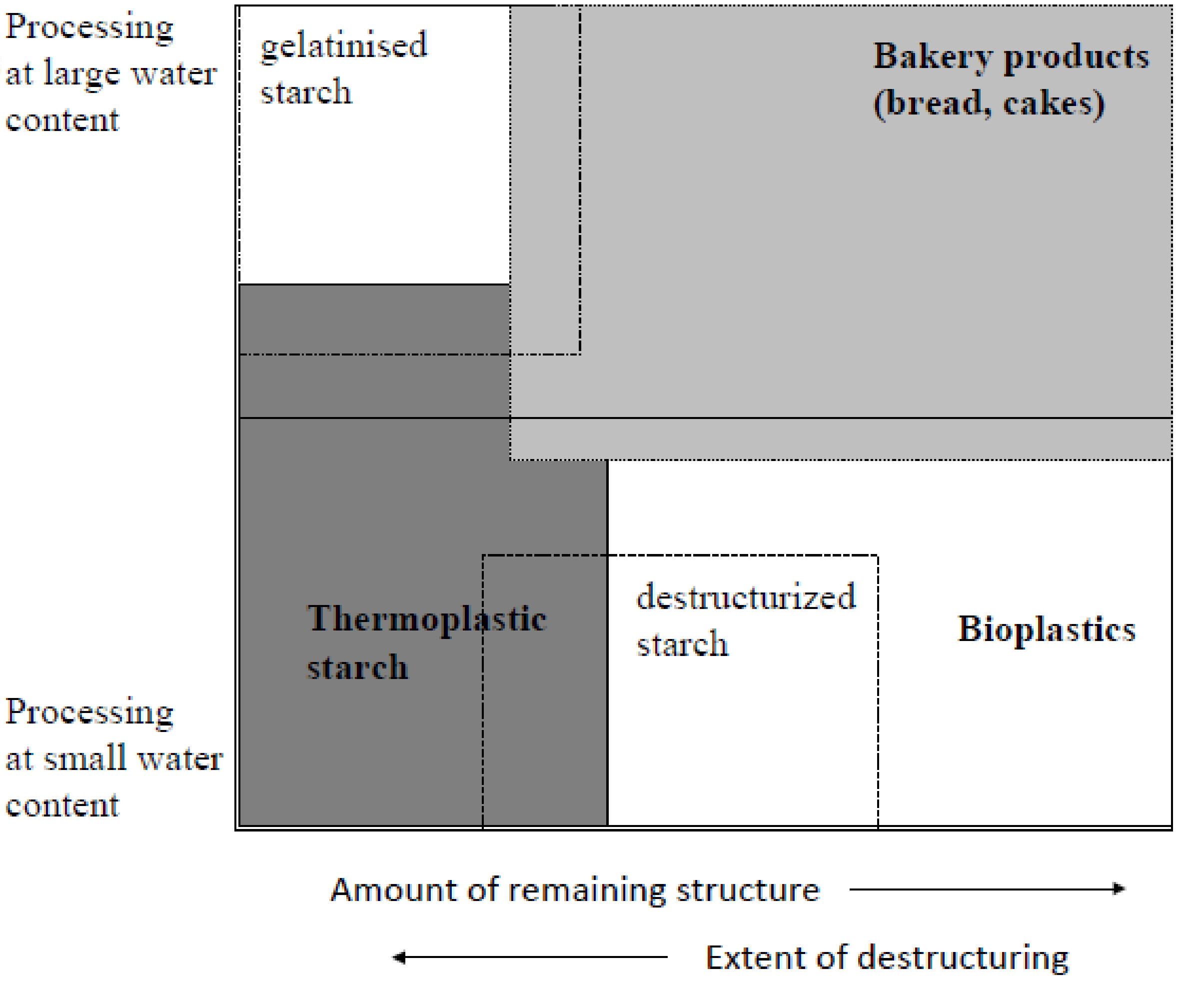
Starch has different proportions of amylose and amylopectin ranging from about 10–20% amylose and 80–90% amylopectin depending on the source.

Starch Source	% Amylose
Waxy Rice	0
High Amylose Corn	70
Corn	28
Cassava	17
Waxy Sorghum	0
Wheat	26
Sweet Potato	18
Arrowroot	21
Sago	26
Potato	20

STARCH

- It has a low cost, is available in huge quantities, produced from renewable resources and completely biodegradable.
- Starch is a semicrystalline polymer, it represents the major form of stored carbohydrate in plants.
- Neat starch has an high glass transition temperature, and its relative large modulus and strength is accompanied by poor deformability and impact resistance due to the limited conformational mobility of its stiff chains.
- On the other hand, it is sensitive to water, its processing is difficult and its properties are usually inferior to commodity polymers.
- Depending on the amount of water used during processing, starch is ether gelatinized (large amount of water) or melted (small water contents)

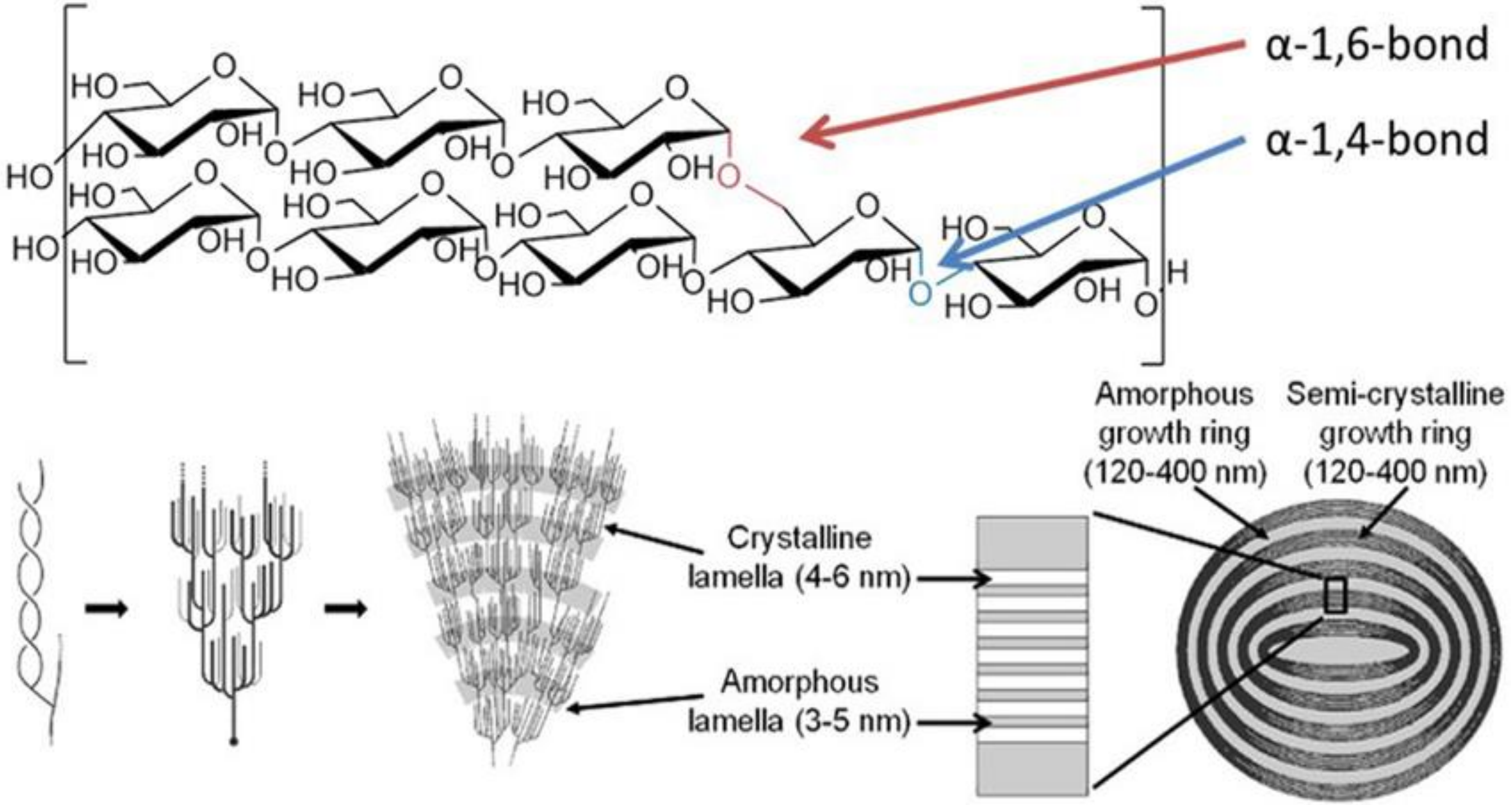
Structure-Property Correlations in Thermoplastic Starch Blend and Composites



STARCH

Amylose is soluble in water and forms a helical structure.
Starch occurs naturally as discrete granules since the short-branched amylopectin chains are able to form helical structures which crystallize.

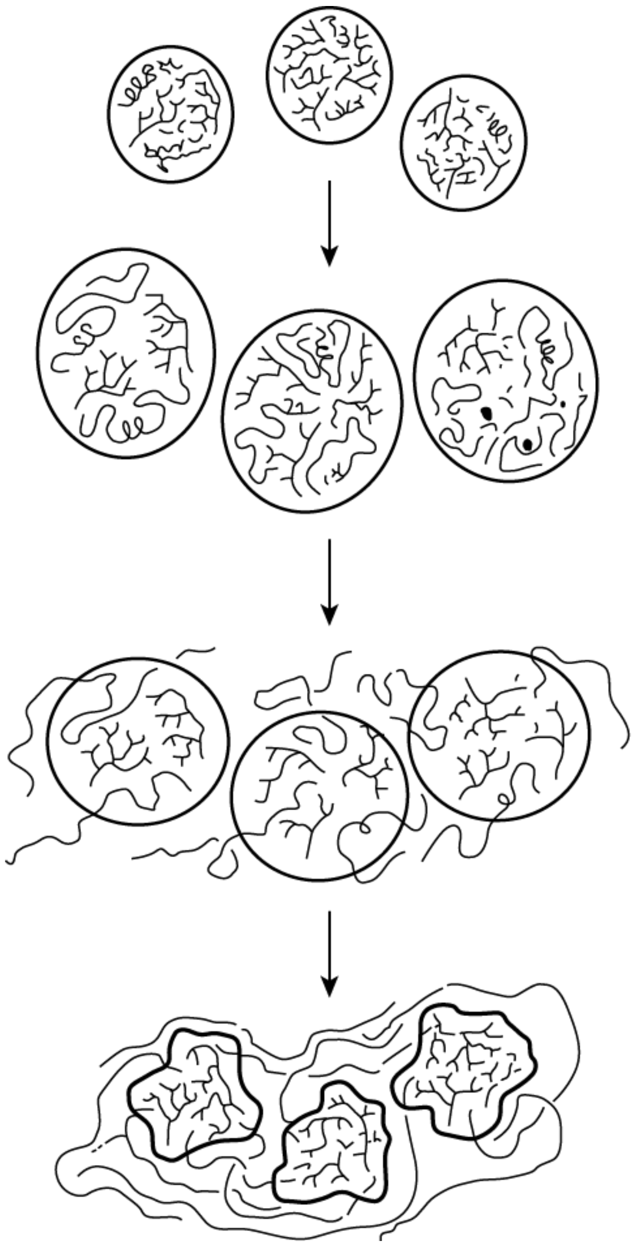
The starch granule organization consists in alternation of crystalline and amorphous areas leading to a concentric structure.
The amorphous areas are mainly constituted of amylose chains and amylopectin branching points. The crystalline parts are mainly composed of amylopectin side chains.



STARCH

Because of numerous intermolecular hydrogen bonds existing between the chains, the melting temperature (Tm) of starch is higher than its degradation temperature, to elaborate a plastic-like material, it is necessary to introduce high water content or/and some non-volatile plasticizers (glycerol, sorbitol,…) which decrease the glass transition temperature (Tg) and the Tm.

The increase of water (polyols) and temperature induces an irreversible swelling process named ‘‘gelatinization’’.
During gelatinization, the amylose is well solubilized, the granular semi-crystalline structure disappears, and the granules swell rapidly.
This phenomenon occurs at a given temperature defined as ‘‘gelatinization temperature’’ (Tgel) which depends on the starch botanical origin.



Raw starch granules made up of amylose (helix) and amylopectin (branched).

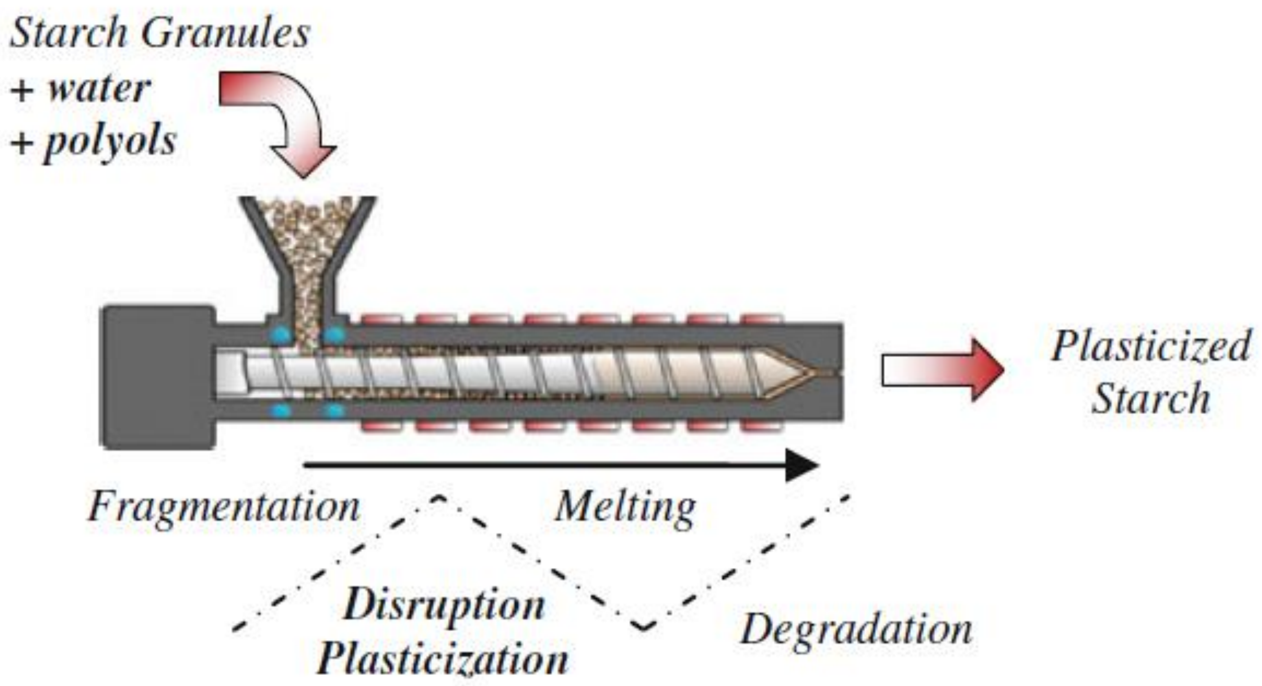
Addition of water breaks up amylose crystallinity and disrupts helices.
Granules swell.

Addition of heat more water causes more swelling.
Amylose begins to diffuse out of granule.

Granules, Now containing mostly amylopetin, have collapsed and are held in a matrix of amylose forming a gel.

STARCH Processing

The starch melting process is often carried out in association with plasticizers to obtain a homogeneous molten phase. During the thermo-mechanical process, e.g.,
extrusion, different and successive phenomena occur.
The disruption of starch granules being dependent on the specific mechanical
energy provided during processing, this material could be described as a ‘‘thermomechanical- plastic’’ material.
During processing, amylose and amylopectin degradation occurs and this phenomenon is obviously dependent on the thermal and mechanical energy brought to the system.



STARCH

One of the disadvantages of TPS is its brittleness caused by its relatively high Tg and lack of a sub-Tg main chain relaxation area. During storage, this brittleness increases because of retrogradation.

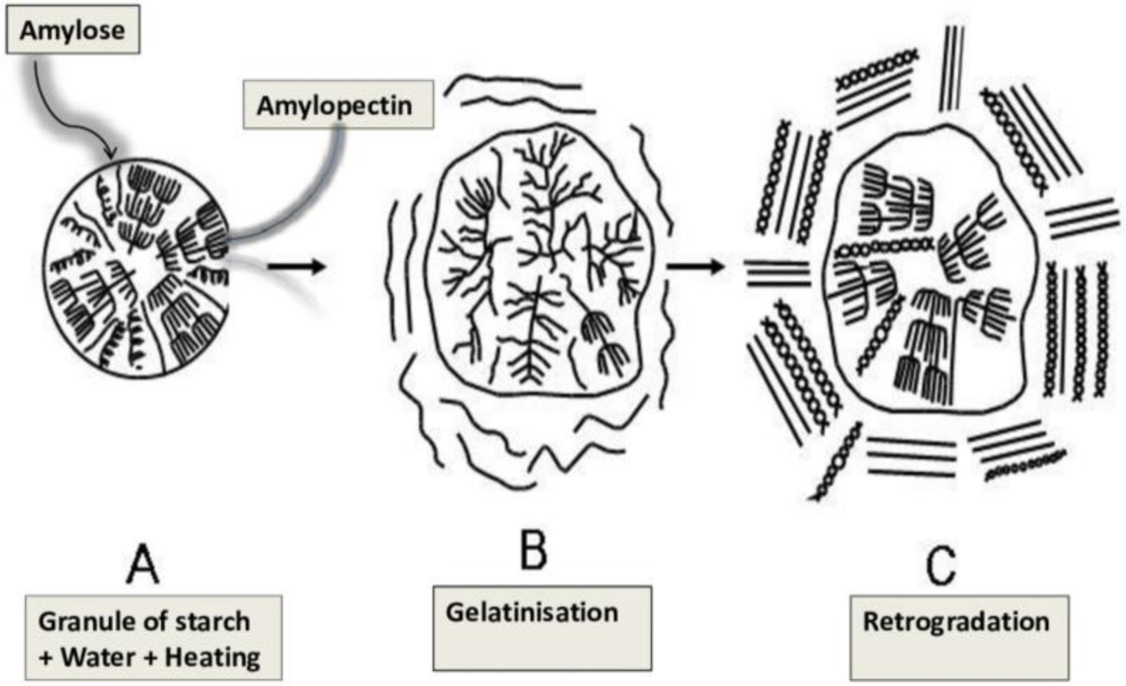
Retrogradation is the change in mechanical properties of TPS caused by the recrystallization process. The recrystallization process is caused by the tendency of macromolecules to form hydrogen bonds during the expulsion of water and/or other solvents.

This process can be divided into the **recrystallization of amylose and the irreversible crystallization of amylopectin.**

Retrogradation is referred to as the **long-term recrystallization of amylopectin because the reversible recrystallization of amylose is slower.**

Above the Tg, further absorption of water increases the mobility of starch until the equilibrium moisture content is reached.

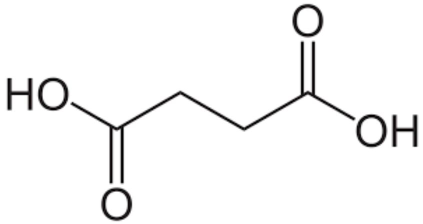
During and after this period, retrogradation takes place and relaxation times increase because of the development of crystallinity.



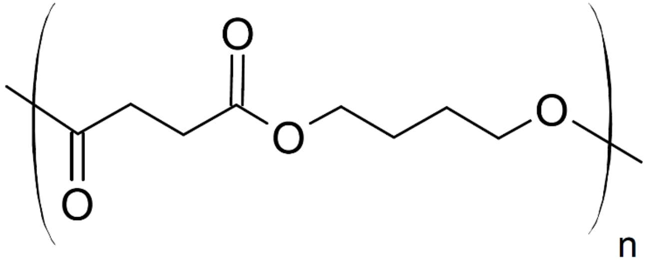
Poly (butylene succinate) (PBS)

PBS is an aliphatic polyester that is attracting increasing attention due to the possibility to be biobased produced, its balanced properties and excellent biodegradability.
This PBS polymer (trade name Bionolle) had a processability similar to the conventional resins, such as polyethylene. For this reason, Bionolle was one of the most suitable materials for processing into films, which was proposed for use in agricultural purposes, shopping bags, compost bags, etc…New possible applications for PBS have been investigated in the last years, for example the development of novel materials for ecological agricultural purpose; in fact, mulching nonwovens and pots produced from nonwovens, can be valid alternatives to polypropylene products.

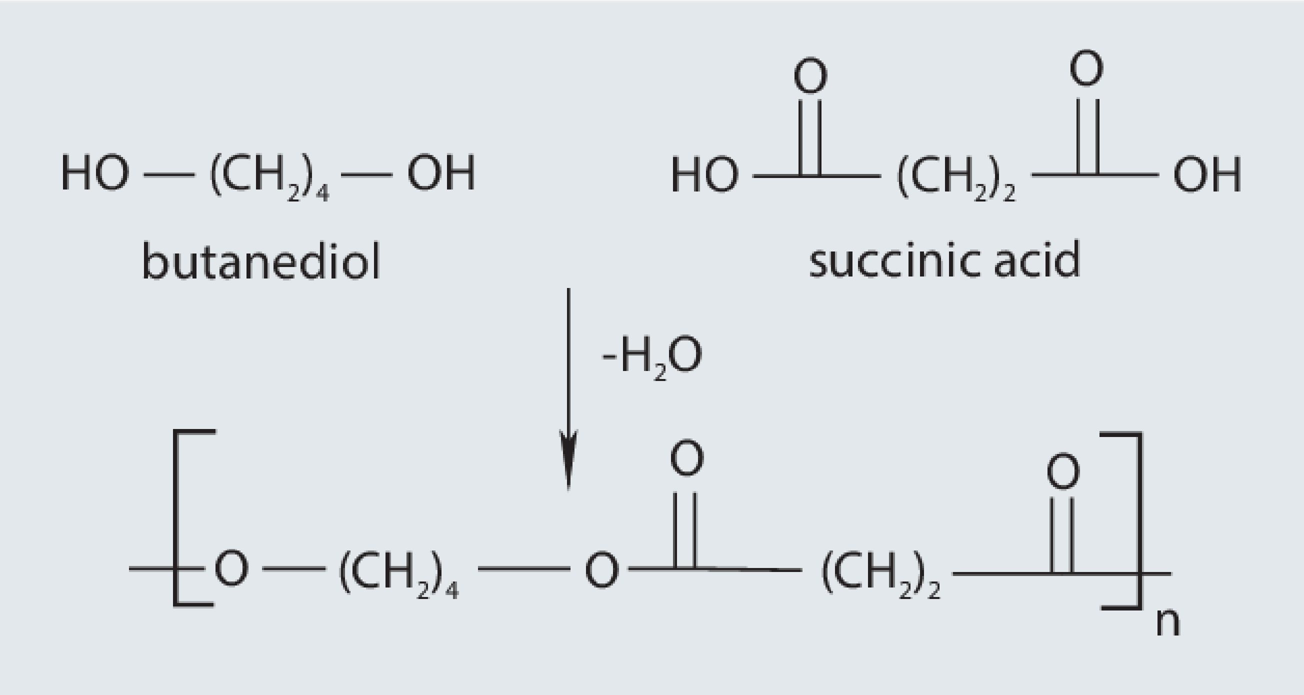
PBS and other aliphatic polyesters were firstly synthesized by the pioneering work of Carothers in 1931.
Massive efforts have been dedicated to the investigation and synthesis of PBS and its copolymers and nowadays, via copolymerization with other dicarboxylic acids or diols, the properties of PBS can be varied in a wide range making PBS a very promising material for various applications.



Succinic acid



For many years, Polybutylene succinate **PBS** and poly (butylene succinate co-adipate) **PBSA** were produced from petrochemical sources by Showa Highpolymer (Shanghai, China)



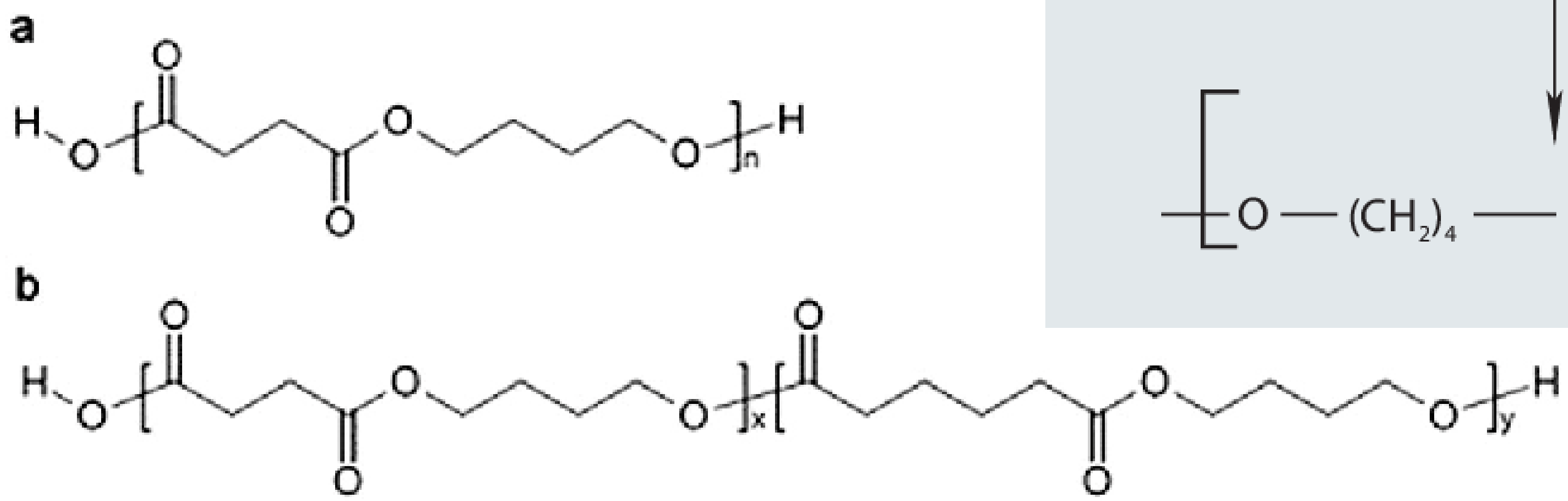


Fig. 1 Chemical structure of PBS (a) and PBSA (b).

Introduced Bio PBS and bio PBSA (PTT MCC Biochem company)

Poly (butylene succinate) (PBS)

PBS is a white crystalline thermoplastic polymer having a density of 1.25 g/cm^3, melting point (T_m) in the range of 90-120 °C and a low glass transition temperature (T_g) of about -45 to –10 °C. It has good mechanical properties and excellent processability.
In fact, PBS can be processed in the field of textiles into melt blow, multifilament, monofilament, nonwoven, flat, and split yarn; it can also be used for the production of injection molded, extruded and blown products

The very good flexibility of PBS coupled with its easy film-forming ability make it particularly suitable for films production

Properties		Test Method	Unit	FD92PM/FD92PB
Density		ISO 1183	g/cm^3	1.24
MFR (190°C, 2.16 kg)		ISO 1133	g/10 min	4
Melting Point		ISO 3146	°C	84
Tensile Modulus	MD	ISO 527-3	MPa	280
	TD			320
Yield Stress	MD	ISO 527-3	MPa	18
	TD			17
Stress at Break	MD	ISO 527-3	MPa	32
	TD			27
Strain at Break	MD	ISO 527-3	%	600
	TD			580
Elmendorf tear strength	MD	ISO 6383-2	N/mm	2
	TD			5
Puncture Impact		PTTMCC method	kJ/m	6

Adipate units act as soft segments leading to a lower glass transition and melting temperature for PBSA versus PBS

- The cost of PBS is around 3.2-4.5 €/Kg.
- Principal PBS producers are: Mitsubishi, Myriant, Reverdia and Hexing Chemical.

RECOV3R

BioPBS™ FZ91PM / FZ91PB Technical Data Sheet

Properties	Test Method	Unit	FZ91PM/FZ91PB
Density	ISO 1183	g/cm^3	1.26
MFR (190°C, 2.16 kg)	ISO 1133	g/10 min	5
Melting Point	ISO 3146	°C	115
Yield Stress	ISO 527-2	MPa	40
Stress at Break	ISO 527-2	MPa	36
Strain at Break	ISO 527-2	%	210
Flexural Modulus	ISO 178	MPa	650
Flexural Strength	ISO 178	MPa	40
Izod Impact Strength (23°C)	ISO 180	kJ/m^2	7
Heat Deflection Temperature (0.45 MPa)	ISO 75-1	°C	95
Rockwell Hardness	ISO 2039-2	R Scale	107

BioPBS™ is bio-based polybutylene succinate (PBS) produced from polymerization of bio-based succinic acid and 1,4-butanediol. Alike LDPE, BioPBS™ is soft and flexible semi-crystalline polyester with excellent properties suitable for injection molding articles for general purpose.

OK COMPOST certified by Vincotte in European Union

BioPBS™ FZ71PM Technical Data Sheet

Properties	Test Method	Unit	FZ71PM
Density	ISO 1183	g/cm^3	1.26
MFR (190°C, 2.16 kg)	ISO 1133	g/10 min	22
Melting Point	ISO 3146	°C	115
Yield Stress	ISO 527-2	MPa	40
Stress at Break	ISO 527-2	MPa	30
Strain at Break	ISO 527-2	%	170
Flexural Modulus	ISO 178	MPa	630
Flexural Strength	ISO 178	MPa	40
Izod Impact Strength (23°C)	ISO 180	kJ/m^2	7
Heat Deflection Temperature (0.45 MPa)	ISO 75-1	°C	95
Rockwell Hardness	ISO 2039-2	R Scale	107

BioPBS™ is bio-based polybutylene succinate (PBS) produced from polymerization of bio-based succinic acid and 1,4-butanediol. Alike LDPE, BioPBS™ is soft and flexible semi-crystalline polyester with excellent properties suitable for cast extrusion and extrusion coating such as compostable paper cups.

OK COMPOST certified by Vincotte in European Union

BioPBS™ FD92PM / FD92PB Technical Data Sheet

Properties		Test Method	Unit	FD92PM/FD92PB
Density		ISO 1183	g/cm^3	1.24
MFR (190°C, 2.16 kg)		ISO 1133	g/10 min	4
Melting Point		ISO 3146	°C	84
Tensile Modulus	MD	ISO 527-3	MPa	280
	TD			320
Yield Stress	MD	ISO 527-3	MPa	18
	TD			17
Stress at Break	MD	ISO 527-3	MPa	32
	TD			27
Strain at Break	MD	ISO 527-3	%	600
	TD			580
Elmendorf tear strength	MD	ISO 6383-2	N/mm	2
	TD			5
Puncture Impact		PTTMCC method	kJ/m	6

OK COMPOST, OK COMPOST HOME and OK Biodegradable SOIL certified by Vincotte in European Union

This is a PBSA

Poly (butylene succinate) (PBS)

Great attention was paid on the production of PBS (traditionally petrochemically derived) by renewable resources and its production starting from sugarcane, cassava and corn (Bio-PBS) has been underway since 2017, making PBS a valid sustainable, biobased and biodegradable plastic alternative.

PBS (and PBSA) are used ad ductility enhancer for PLA.
A highly-biobased and compostable PLA/PBS product, trade name BioFlex® S 5630, was also developed by FKuR Kunststoff GmbH and Fraunhofer UMSICHT; this commercial product can be used for flat sheet extrusion, thermoforming and injection molding.
Just a moderate amount of PBS or PBSA (20 wt%) can turn PLA from brittle to ductile, increasing the elongation break from 25% to more than 200%.
They are compatible during melt processing although they are not miscible at a molecular level
PLA/PBS blends plasticized with isosorbide have been proposed as a novel solution for packaging applications

PBS can be found on the market blended with PLA: for example a commercial PLA/PBS blend used for food service ware is produced by NatureWorks LLC

Poly (butylene succinate) (PBS)

Compared with other biopolymers, PBS has a better eco-efficiency depending on End-of-Life (EOL) options

Various microorganisms are able to degrade PBS and its copolymers, including bacteria and fungi

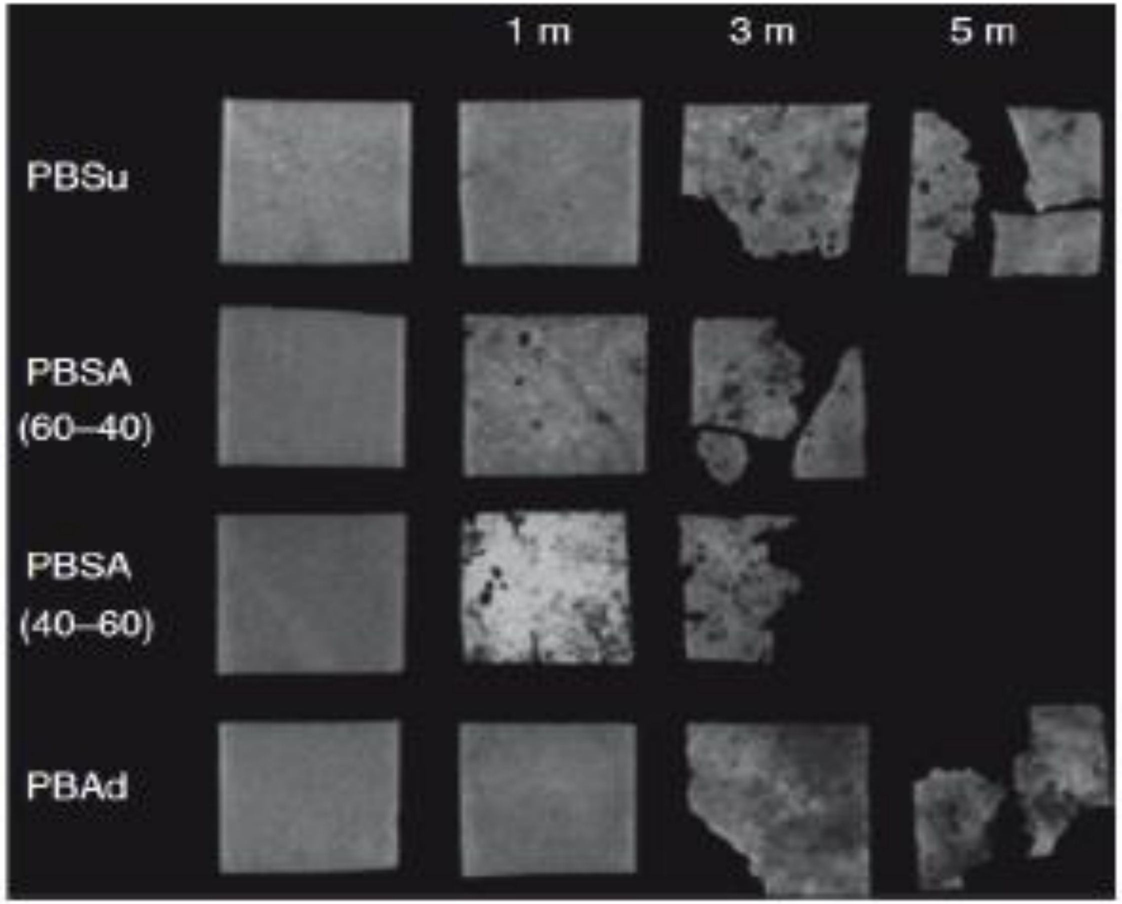
Table 7 Relationship between polymer structures and biodegradability of the aliphatic polyester Bionolle (Fujimaki 1998)

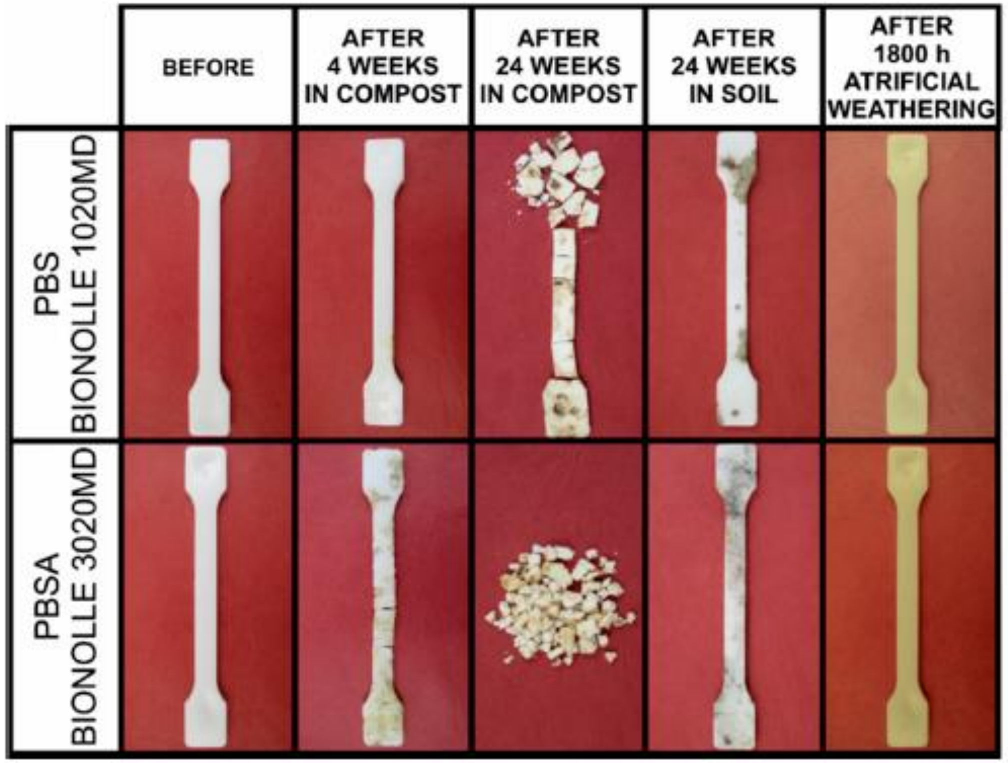
Biodegradability tests	PBS	PBSA	PES
In hot compost	Normal	Rapid	Normal
In moist soil	Normal	Rapid	Normal
In the sea	Slow	(Rapid)	Slow
In water with activated sludge	Slow	Slow	(Rapid)

PBS polybutylene succinate, *PBSA* polybutylene succinate adipate copolymer, *PES* poly(ethylene succinate)

RECOV3R

Poly (butylene succinate) (PBS) Biodegradability





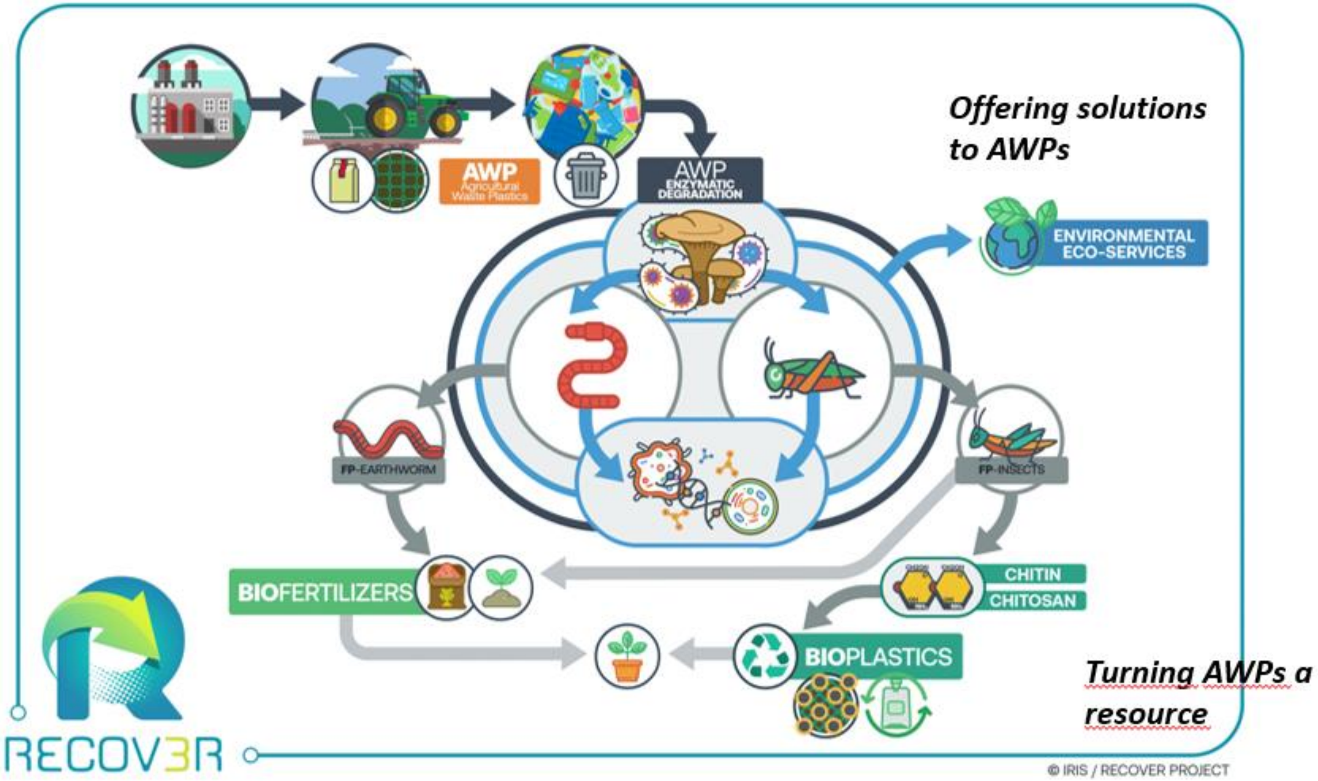
PBS and PBSA based blends after soil burial treatment for 1, 3 and 5 months

Recover solutions & innovations

Agri-food Waste Plastics (AWPs)

Combining new enzymes, microorganisms, insects & earthworms

Products

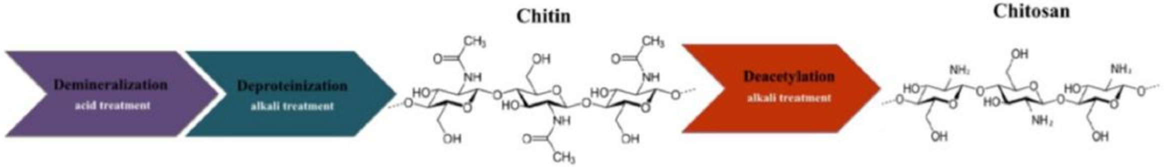


Development of innovative biotic symbiosis for plastic biodegradation and synthesis to solve their end of life challenges in the agriculture and food industries

GA 887648

Chitin and chitosan: Chemical extraction, enzymes, ionic liquids, etc
Work in progress…..

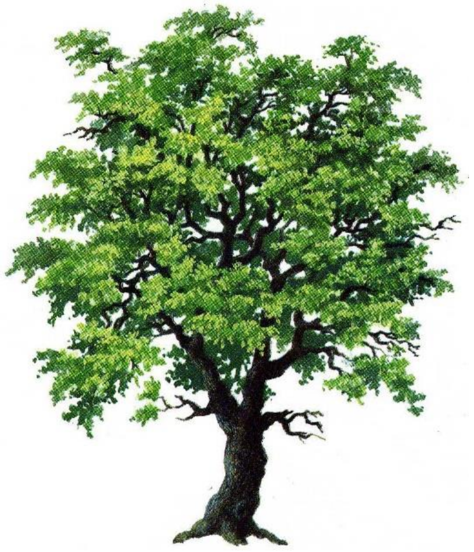
- Pots, sticks or packaging
- Enhanced mulching films
- Food trays, rigid containers, films
- Chitin/chitosan coated films



Nature likes composites too…

POLYSACCHARIDES BIOMATERIAL FOR STRUCTURAL APPLICATION

wood: micro-composite of cellulose in a lignin resin



exoscheleton of arthropodes: micro-composite of chitin fibrils in a protein matrix (containing also calcium carbonate)

The most abundant type of crystalline chitin is the α-chitin

CHITIN CRYSTALS	where	Structural features
α-CHITIN	 krill, insect cuticle, fungal and yeast cell walls	Molecules arranged in antiparallel fashion (strong H bonding)
β-CHITIN	 Squid pens  Tube worms	Molecules arranged in parallel fashion
γ-CHITIN	 Beetle cocoons	Molecules arranged in both parallel and anti-parallel fashion

M Mincea et al., Rev. Adv. Mater. Sci. 30, 2012, 225-242

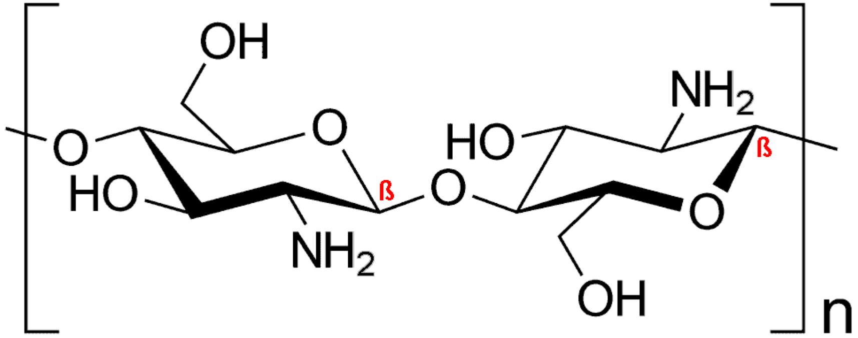
Worldwide chitin based waste material from the fishing industry, exceeds 25 billion tons/year

The processing of 1 kg of shrimp produces 0.75 kg of waste (e.g: chitin containing shells) and 0.25 Kg of final food

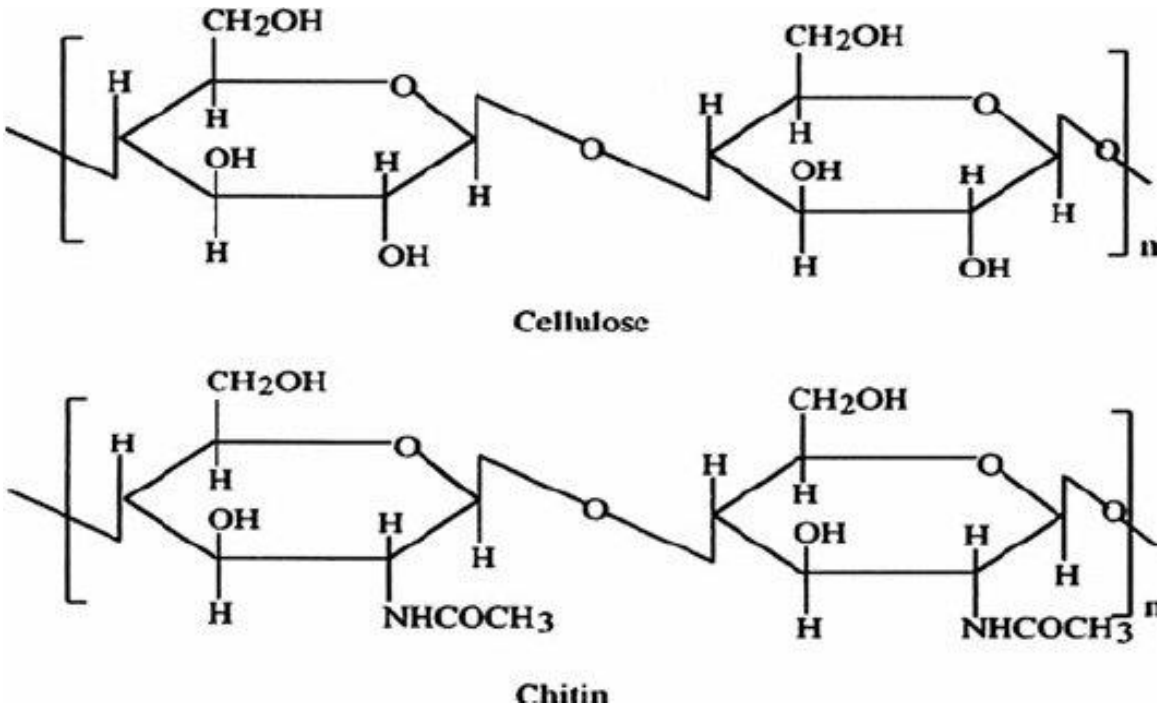
RECOV3R

CHITIN AND CHITOSAN

With an annual production of approximately 1010 – 1020 tons, chitin is considered as one of the most abundant biopolymers on the Earth. Chitin can be present in several materials belonging to exoskeleton of insects (e.g. tubeworms), arthropods (e.g. mollusc, shell oysters, squid pen) and crustaceans (e.g., crabs, lobsters and shrimps). Moreover, chitin is also known as a structural component of cell walls of fungi (mushrooms).

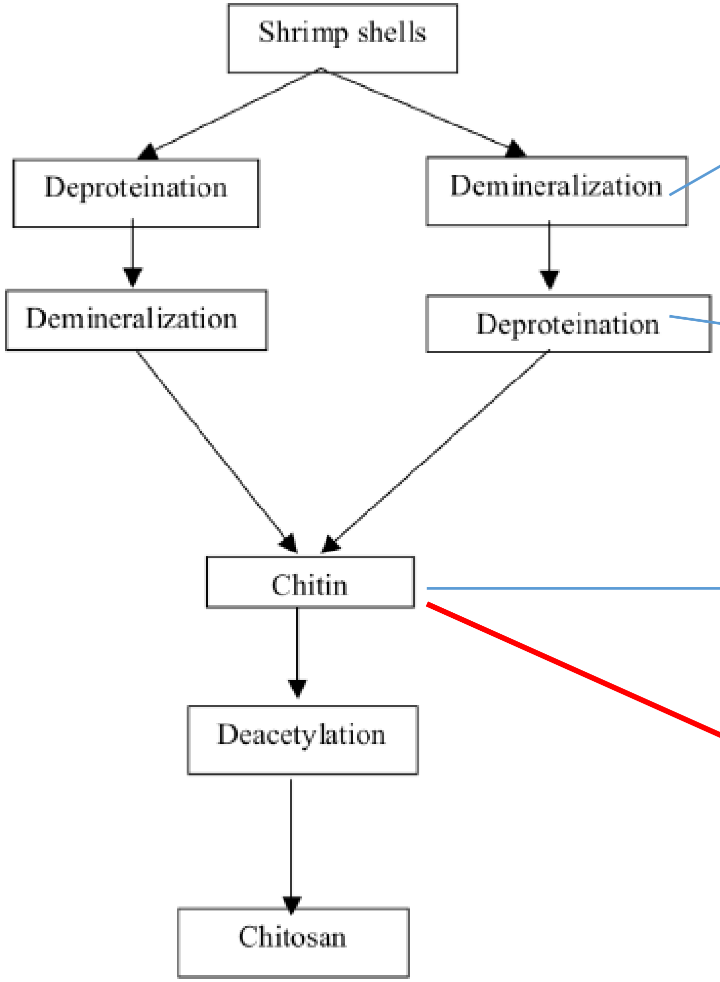


Chitosan



Yadav M, Goswami P, Paritosh K, Kumar M, Pareek N, Vivekanad V, seafood waste: a source for preparation of commercial employable chitin/chitosan materials

CHITIN PURIFICATION



Acid treatment

Basic treatment

Acetylation degree should be higher than 0,9 and molecular weight in the range 1-2,5*10^{6}

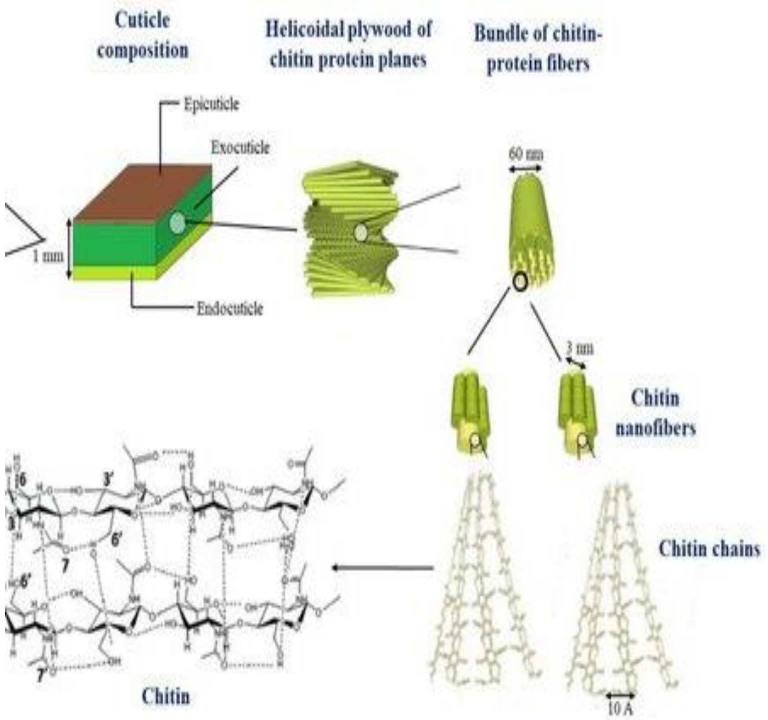
MNV Ravi Kumar, React. Funct. Polym, 46, 2000, 1-27

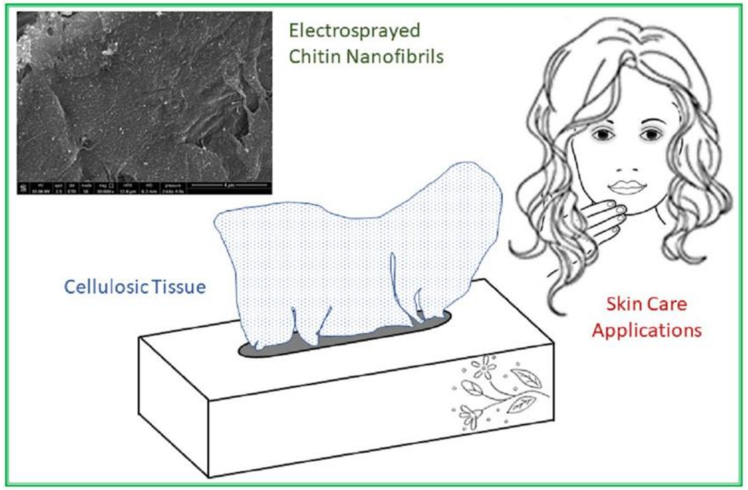
Microfibers based materials

N. Van Toan, The Open Biomaterials Journal, 1, 2009

Chitin and chitosan
Nano chitin fibrils

Chitin is the second most abundant polymerized carbon-based macromolecular material found in nature and can be converted to innovative high-value bio- and eco-compatible materials. Chitin consists of both crystalline and amorphous domains, but the elimination of the amorphous phase results in **chitin nanofibrils (CNs),** which lose their pro-inflammatory and allergenic character and obtain anti-inflammatory, anti-microbial properties.





Cosmetics have recently focused on biobased skin-compatible materials. Materials from natural sources can be used to produce more sustainable skin contact products with enhanced bioactivity.

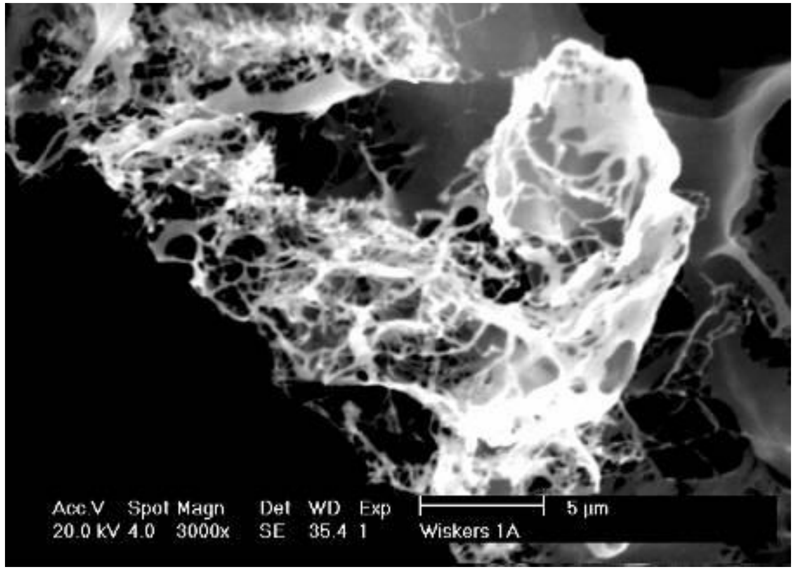
Panariello, L., Coltelli, M.-B, Giangrandi, S., Garrigós, M. C., Hadrich, A., Lazzeri, A., Cinelli, P. (2022) Influence of Functional Bio-Based Coatings Including Chitin Nanofibrils or Polyphenols on Mechanical Properties of Paper Tissues. Polymers, vol. 14, n. 11, June 2022, pag. 2274. https://doi.org/10.3390/polym14112274

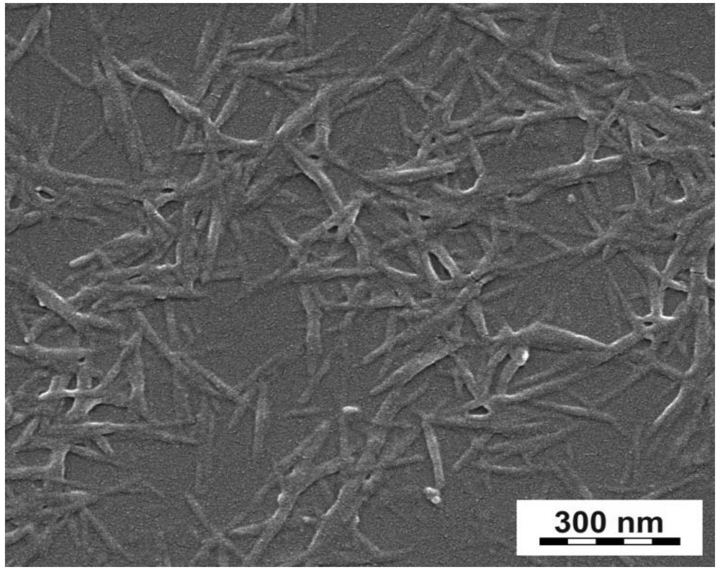
RECOV3R

FROM CHITIN TO NANO-CHITIN

The microfibers contain crystalline nano-fibers. It is possible to produce chitin nano-whiskers by chemical treatment of microfibers.

MAVI SUD plant, Aprilia, (Italy) patented this process. Other producers with similar processes are Celabor (belgium) Texol (Italy) etcd
Nano-chitin is thus available in diluted water suspension for cosmetic applications.





300 nm long and 10 nm wide nano-fibers

Sustainable technologies **for** the production of biodegradable materials based on natural chitin-nanofibrils derived by waste of fish industry, to produce food grade packaging

Production of films for shopping bags

Blown film extrusion in industrial plant

Good processability and tunability of thickness as a function of process parameters.

Shopper based on bio-blend

Bio-blend + chitin nanofibrils + PLA/PBAT

film produced by blown film extrusion in MICROTEC plant based on D material : the colur is slightly browner than the reference BIOCOMP BF 7210, but the transparency is similar.

International Journal of
Molecular Sciences

Article

Chitin Nanofibrils in Poly(Lactic Acid) (PLA) Nanocomposites: Dispersion and Thermo-Mechanical Properties

Maria-Beatrice Coltelli [1,2,*], Patrizia Cinelli [1,2], Vito Gigante [1,2], Laura Aliotta [1,2], Pierfrancesco Morganti [3,4], Luca Panariello [1,2] and Andrea Lazzeri [1,2,*]

Advanced Materials Letters

Research Article 2019, **10**(6), 425-430 Advanced Materials Letters

Chitin Nanofibrils in Renewable Materials for Packaging and Personal Care Applications

Maria-Beatrice Coltelli[1,2*], Vito Gigante[1,2], Luca Panariello[1,2], Laura Aliotta[1,2], Pierfrancesco Morganti[3], Serena Danti[1,2], Patrizia Cinelli[1,2], Andrea Lazzeri[1,2]

CHEMICAL ENGINEERING TRANSACTIONS

VOL. 60, 2017

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Luca Di Palma, Elisabetta Petrucci, Marco Stoller

ISBN 978-88-95608- 50-1; **ISSN** 2283-9216

Degradability and Sustainability of Nanocomposites Based on Polylactic Acid and Chitin Nano Fibrils

Patrizia Cinelli[a,*], Maria Beatrice Coltelli[a], Norma Mallegni[a], Piefrancesco Morganti[b], Andrea Lazzeri[a]

RECOV3R

Example of anti bacterial test on films coated with chitin nanofibrils

Results of antibacterial test on untreated films used as reference

Sample	Recovery after 24 h incubation (cells /cm²)	
	E. coli	S. aureus
PHBV/PBS	15600	687
PBS	5938	156
PLA/PBAT	6130	325

Results of antibacterial tests on films treated with chitin (Aldrich) and chitin (Aldrich) + OLA1350

Sample	Recovery after 24 h incubation (cells /cm²)		Antibacterial activity (R)	
	E. coli	S. aureus	E. coli	S. aureus
PBSA/PHBV + Chitin shrimp 3h 1.5%	12500	356	0.09	0.29
PBSA/PHBV + Chitin shrimp 3h 1.5% + OLA	6875	13	0.35	1.73
PBSA/PHBV + Chitin fungi 3h 1.5% + OLA	10625	58	0.16	1.08
PLA/PBAT + Chitin shrimp 3h 1.5% + OLA	350	38	1.25	0.93
PBS + Chitin shrimp 3h 1.5% + OLA	0.33	3	4.25	2.79
PBS + OLA	17500	1875	0	0

L. Panariello, M.B. Coltelli , A. Harich, F. Braca4 S. Fiori, A. Haviv, F. Miketa, Lazzeri, A. Staebler , V. Gigante, P. Cinelli, Polymer, “Antimicrobial and gas barrier crustaceans and fungal chi-tin-based coatings on biodegradable bioplastic filmsPolymer, MDPI, 2022, under revision.

Formulations based on hot melts

HMC matrix
Technipol®707
PolyButylene Sebacate
Tm: 64°C
Biodegradable
Biobased content: 60% up to 100%

Plasticizers

GLYPLAST OLA2
Lactic Acid Oligomer
Fully biodegradable

GLYPLAST 206/3 NL
Polyester of adipic acid
Insoluble in water

Active Molecules

Celabor Chitosan
from Shrimps

Celabor Glentham Chitin
from Shrimps

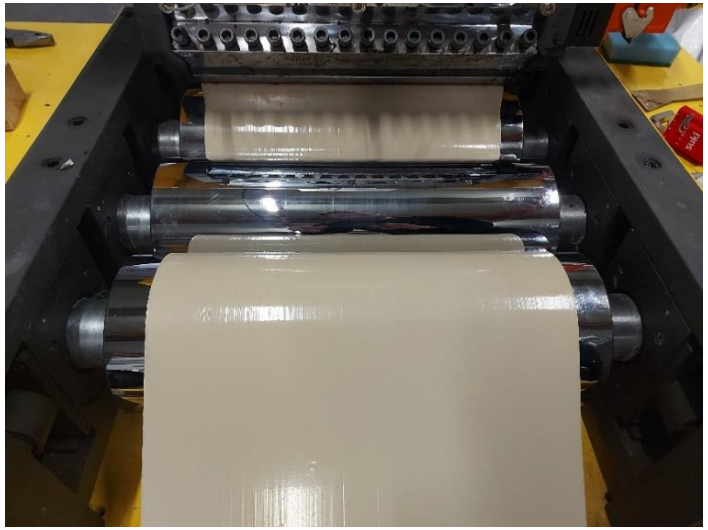
SSICA Cutin
from tomato peels

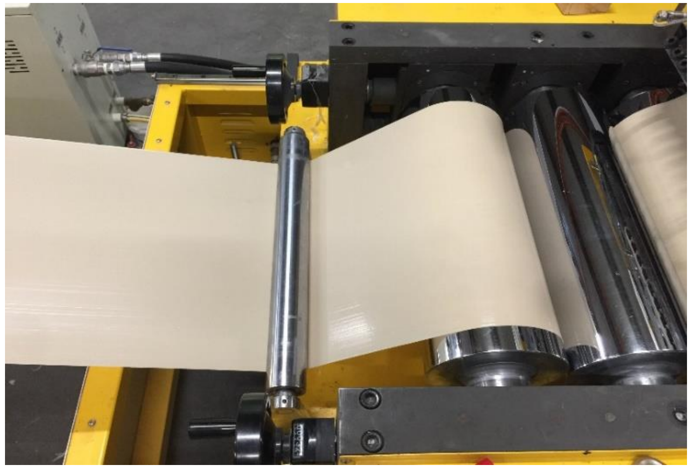
before | Ultraturrax | *after*

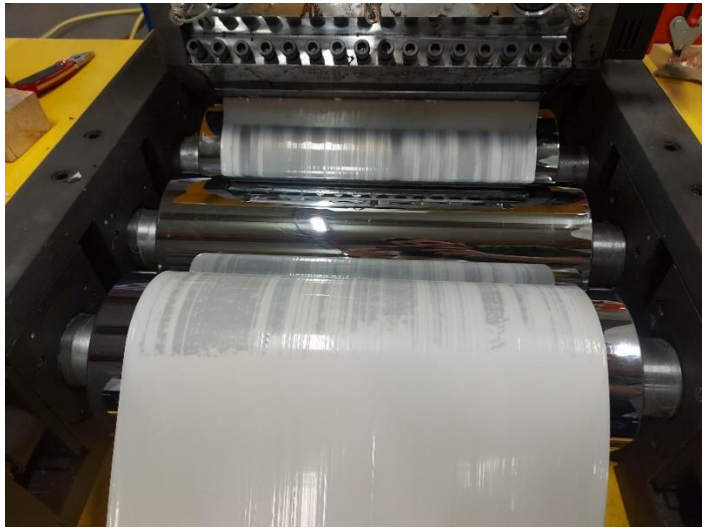
Patent applied: Hot melt biobased polymeric formulations for coating applications containing active biomolecules with antimicrobial and water repellent properties, Patent Application Number 102022000016212; 29 July 2022, UNIPI, INSTM, PLABIO.

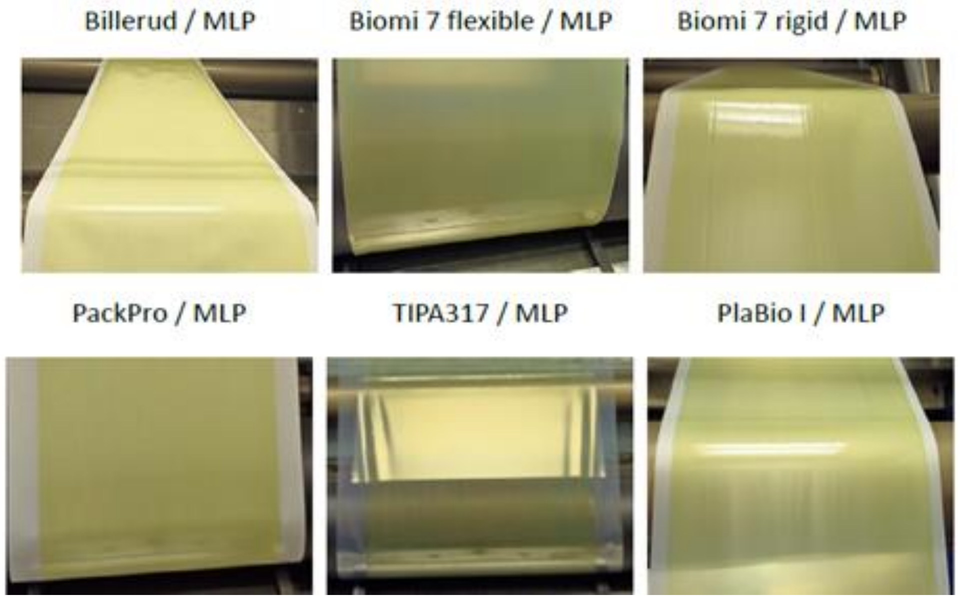
RECOV3R

Prototypes production









HM= Hot melts

Example of anti bacterial test on films coated with chitin nanofibrils

	Judgement for Antibacterial activity (R)	
	E. coli	*S. aureus*
BIO-MI 2 Chitin + OLA	MEDIUM	LOW
BIO-MI 3 Chitin + OLA	MEDIUM	HIGH
BIO-MI 7 Chitin + OLA	MEDIUM	MEDIUM
TIPA 302 + Cutin resin	MEDIUM	MEDIUM
TIPA 317 + Cutin resin	MEDIUM	MEDIUM
TIPA 317 + Chitin resin	LOW	MEDIUM
TIPA 302 + Chitin resin	MEDIUM	MEDIUM

- All the coated samples provided relevant antimicrobial properties both for *E. Coli* and *S. Aureus*;
- The **chitin + OLA** coating on BIO-MI substrates was more effective for *E. Coli* than for *S. Aureus*;

	BIOMI7NEW		BM7N + HM Chitin1		BM7N + HM Chitosan1		BM7N + HM Cutin5	
	lab-scale							
	MD	CD	MD	CD	MD	CD	MD	CD
Elastic Modulus (GPa)	1,00	0,89	0,50	0,42	0,45	0,44	0,35	0,23
Stress at Break (MPa)	30,79	26,42	6,37	7,90	12,18	7,62	15,82	12,54
Elongation at Break (%)	12,37	6,70	2,53	2,62	4,89	2,77	12,90	8,68
Critical Tearing Energy (N/mm)	11,61	60,14	4,62	10,44	7,49	11,44	18,71	24,42
Elmendorf Force (N)	0,26	0,39	0,26	0,21	0,31	0,34	0,42	0,39

CONCLUSIONS

i) Use of biobased resources, in particular those derived from by-products of food and agri-industrial sector, and of bio-based functional molecules can be sustainable (ethic, environment, cost), with synergies and logistic approach.

ii) Biobased polymer requires particular attention in processing and use. Different biopolyesters, and polysaccharides highly differ in properties and biodegradability, but can potentially compete in performances with petro derived polymers.

iii) Use of additives, blending with polymers may allow tuning materials properties, control cost, and degradability

iv) Sustainability and cost depend from raw sources, extraction efficiency, and process ability of the biomolecules.

RECOV3R

Funded projects

Biomass valorization
Protein, cutin, natural fillers

Chitin and chitosan
Packaging, health care

Protein for coating and packaging

PLA, PHA, Packaging

Thank you

Maria J Lopez (UAL)
mllopez@ual.es
Coordinator

Patrizia Cinelli (UNIPI)
patrizia.cinelli@unipi.it
Technical Manager

www. recover-bbi.eu
Website

@RecoverBBI
Twitter

@RecoverBBI
Facebook

Recover- bbi
Linkedin

Ana Plaza (ASAJA)
ana.plaza@asaja.com
Communication and Dissemination Manager

RECOV3R