

Bioplastics and Biodegradable polymers



UNIVERSITY OF LISBON
INTERDISCIPLINARY STUDIES
ON SUSTAINABLE ENVIRONMENT AND SEAS

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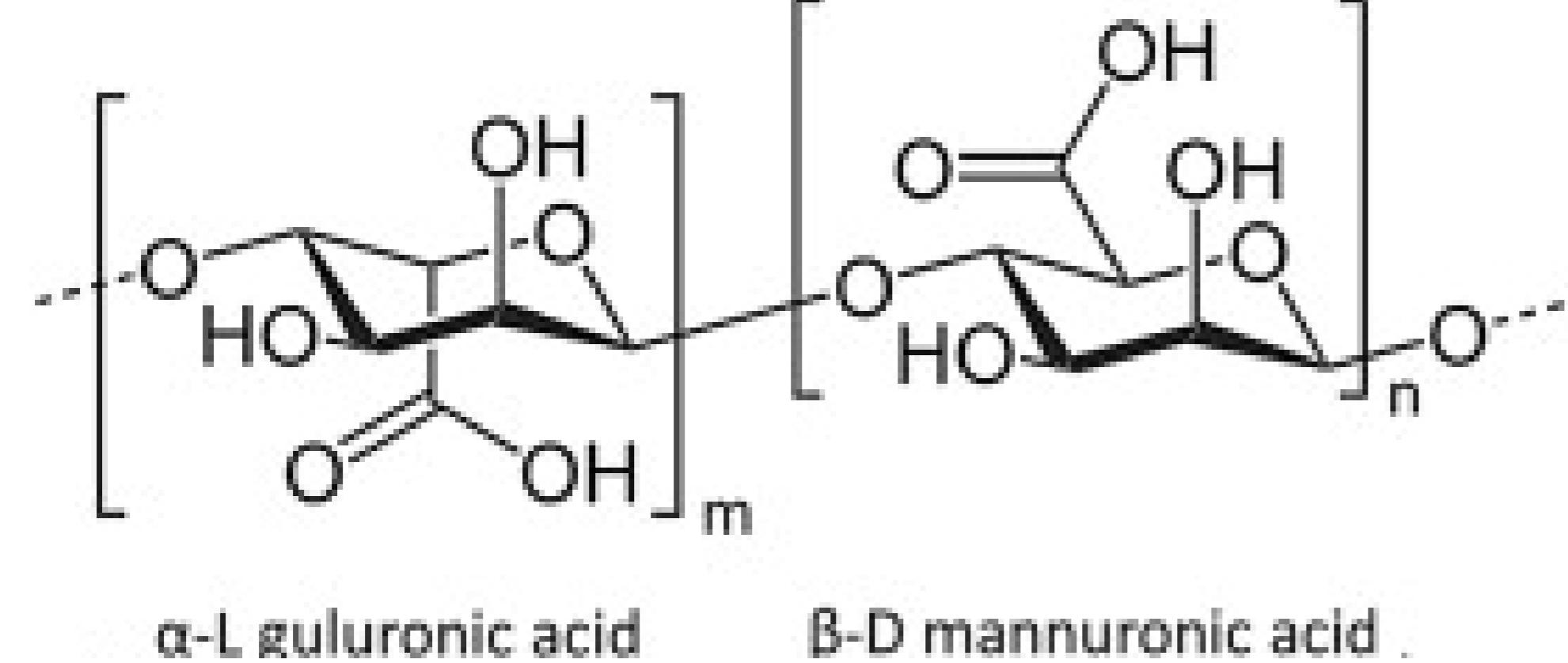
www.ulisses.ulisboa.pt



Summary

- **Bioplastics vs Biodegradable plastics**
- **Biodegradation in several environments**
- **Types of biodegradable polymers**
- **Sources**
- **Main properties**
- **Examples and applications**

- Biodegradable polymers: high molecular weight molecules (macromolecules)
- Macromolecules made up of the covalent bond of low molecular weight molecules (monomers)



α -L guluronic acid

β -D mannuronic acid

Alginic acid

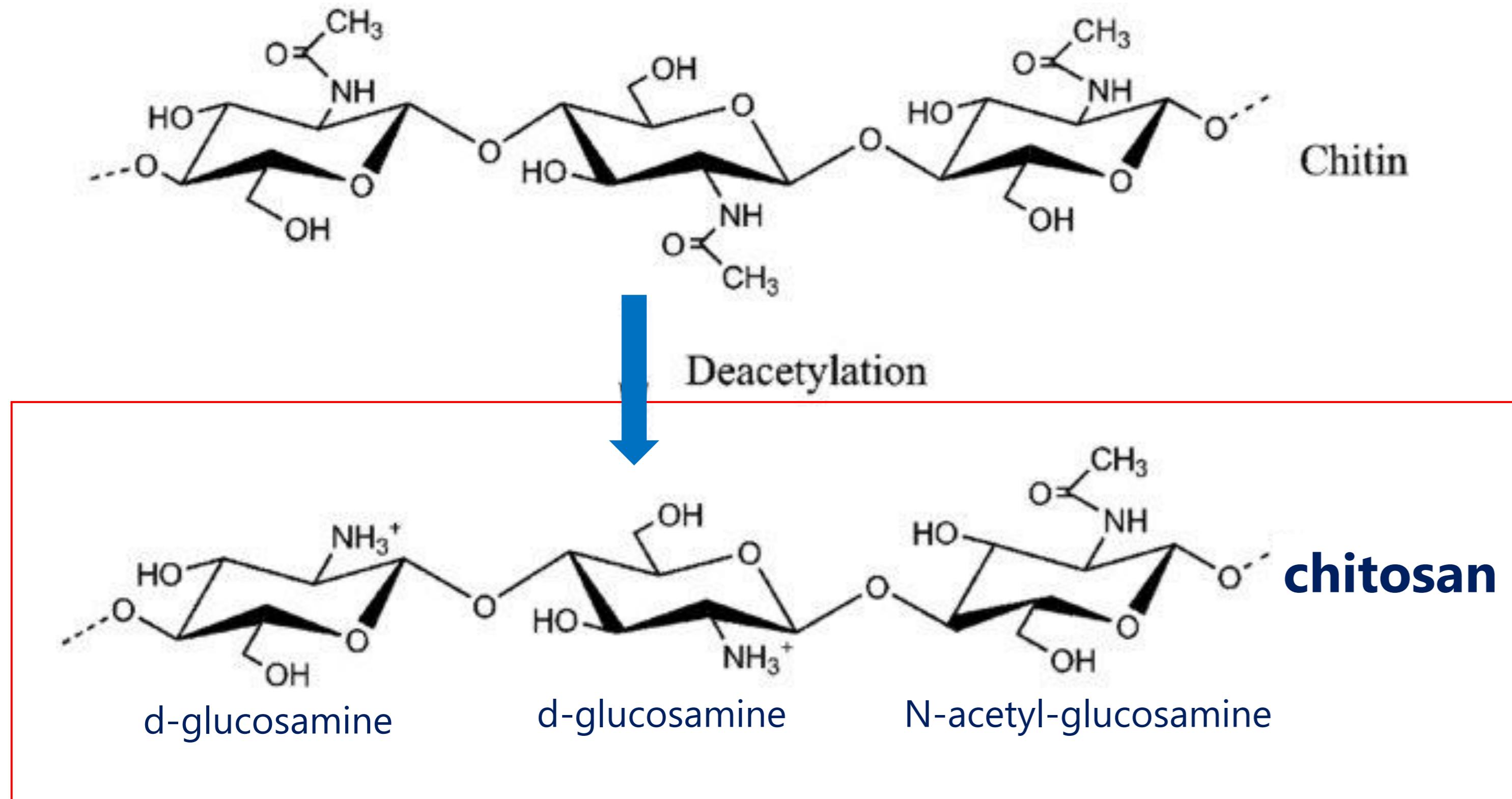
Feedstock (source)



Algae



Alginic acid powder



Feedstock (source)



Sea food shells



Chitosan powder

Biodegradation

- Biodegradation is the conversion of substrates (in this case polymers) by naturally occurring organisms (mainly microorganisms) into water, carbon dioxide, methane, biomass and minerals.
- A material or product is called **biodegradable under specific environmental conditions** if it is able to undergo, within a given time, a certain degradation process that is caused by biological activity and can be measured by a standardized test method
- The property of biodegradation does not depend on the source of a material. Instead, it is rather depended on its chemical structure.

ASTM D5210 – Standard Test Method for Determining the Anaerobic Biodegradation of Plastic Materials in the Presence of Municipal Sewage Sludge

ASTM D6400 – Standard Specification for Compostable Plastics (USA)

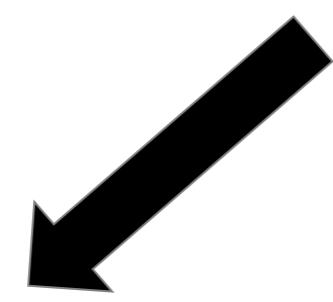
ASTM D5988 – Standard Test Method for Determining Aerobic Biodegradation in Soil of Plastic Materials

ISO 14852 – Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium

UNI EN 14995 - Standard Specification for Compostable Plastics (Europe)

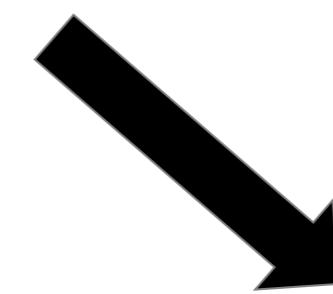
Biodegradable polymers

They may or may not originate from renewable sources



Bio-based

Polymers in which 100% of its carbon comes from renewable sources



Oil-based

Produced with petrochemical based monomers

However:

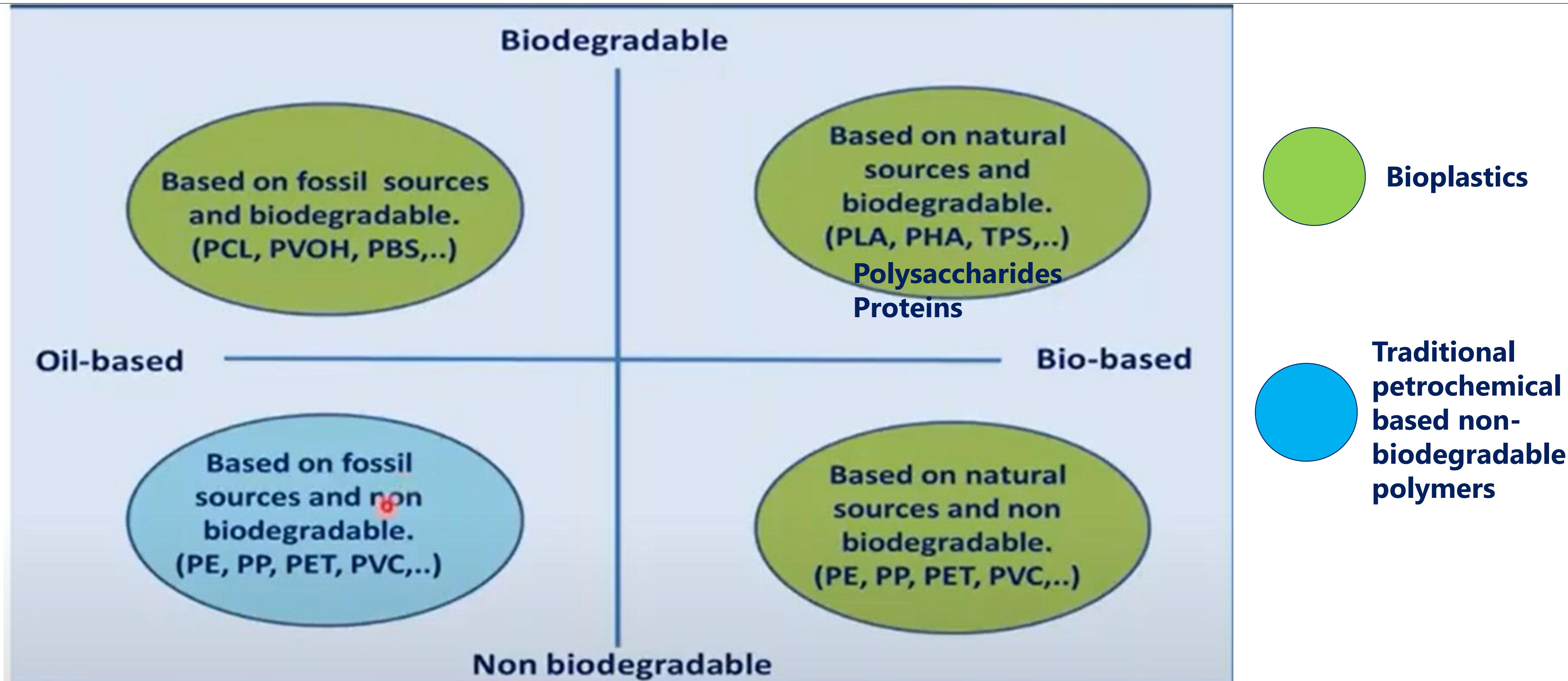
The term "bio-based" does not equal "biodegradable"

There are "bio-based" polymers that are not "biodegradable"

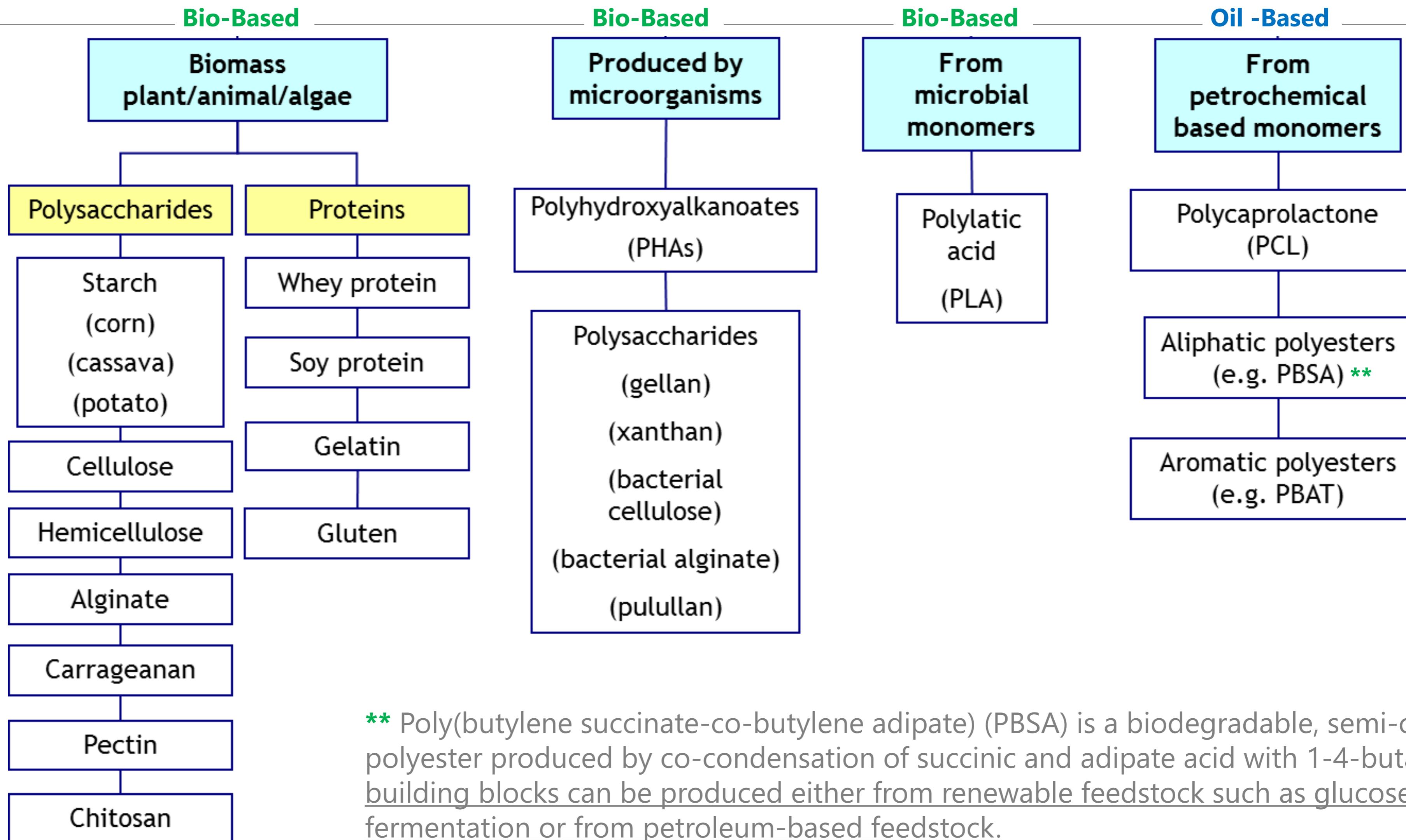
In addition:

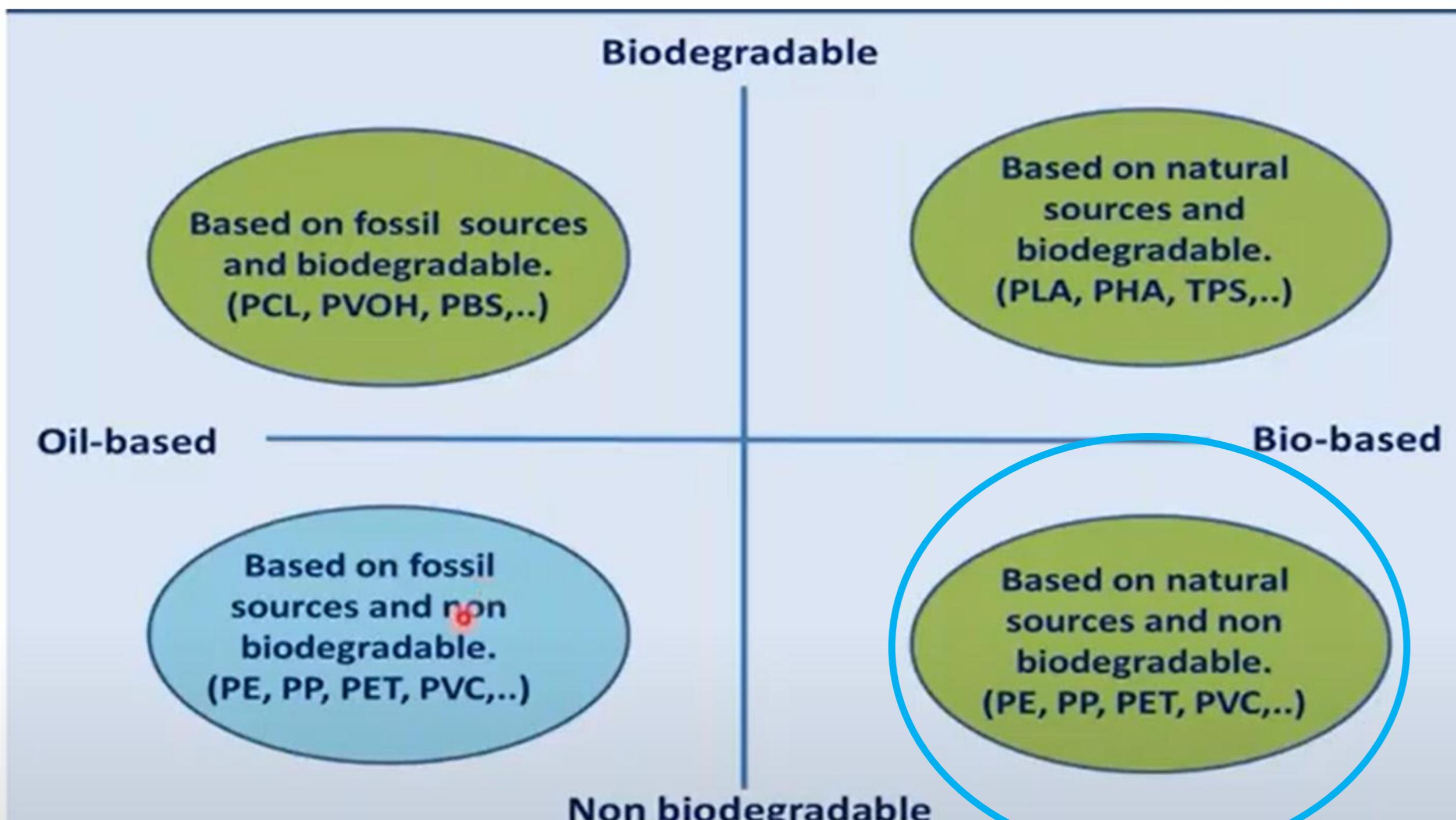
Bioplastics is a term that includes: (i) polymers extracted directly from biomass, (ii) produced by microorganisms, (iii) synthetized with monomers produced by microorganisms or (iv) oil-based biodegradable polymers.

<https://biplasticseurope.eu/about>

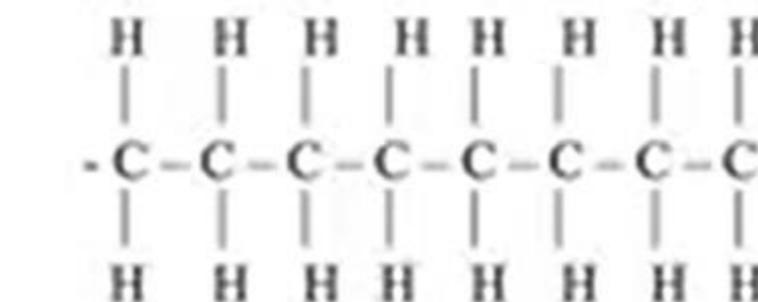


Biodegradable Polymers

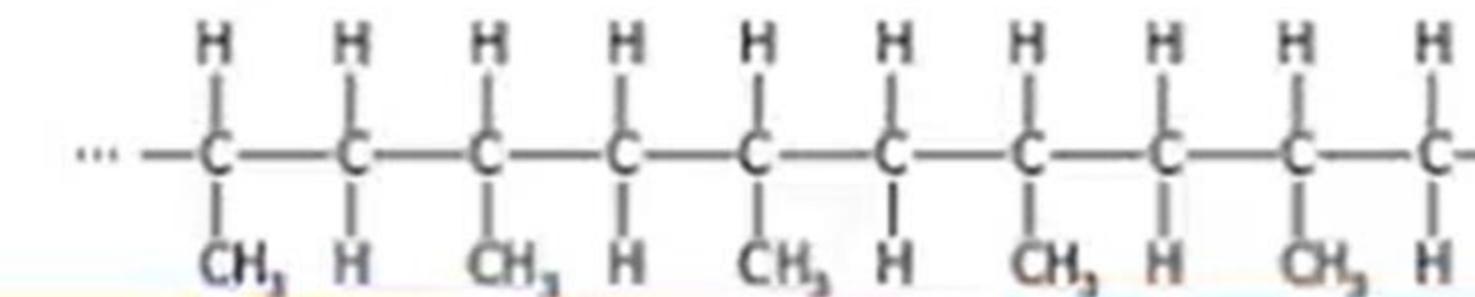




Bio-PE: Ethylene is obtained by the catalytic dehydration of bio-ethanol, followed by normal polymerizations.



Bio-PP: the ethylene obtained from bio-ethanol is dimerized to produce n-butene. The n-butene is then reacted with the ethylene to produce bio-PP. A similar production route is possible using butanol from sugar fermentation.



Frequently used bio-based or biodegradable polymers

Abbreviation	Name	Bio-based	Biodegradable
PA	Polyamide	✓	
PBAT	Polybutylene adipate terephthalate		✓
PBS	Polybutylene succinate	✓	✓
PCL	Polycaprolactone		✓
PE	Polyethylene	✓/✗	
PET	Polyethylene terephthalate	✓/✗	
PHA	Polyhydroxyalkanoate	✓	✓
PHVB	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)	✓	✓
PLA	Polylactic acid	✓	✓

Biodegradation



proven biodegradability



proven biodegradability
under certain conditions
or for certain grades



biodegradability not proven



MARINE ENVIRONMENT

Temperature 30°C,
90% biodegradation within
a maximum of 6 months
(Certification: TÜV AUSTRIA OK
biodegradable MARINE (ISO under
preparation))



FRESH WATER

Temperature 21°C,
90% biodegradation within
a maximum of 56 days
(Certification: TÜV AUSTRIA OK
biodegradable WATER)



SOIL

Temperature 25°C,
90% biodegradation within
a maximum of 2 years
(Certification: TÜV AUSTRIA OK
biodegradable SOIL; DIN Certco
DIN-Geprüft biodegradable in soil)



HOME COMPOSTING

Temperature 28°C,
90% biodegradation within
a maximum of 12 months (Certification:
TÜV AUSTRIA OK compost HOME; DIN
Certco DIN-Geprüft Home
Compostable)



LANDFILL

No standard specifications or
certification scheme available,
since this is not a preferred
end-of-life option



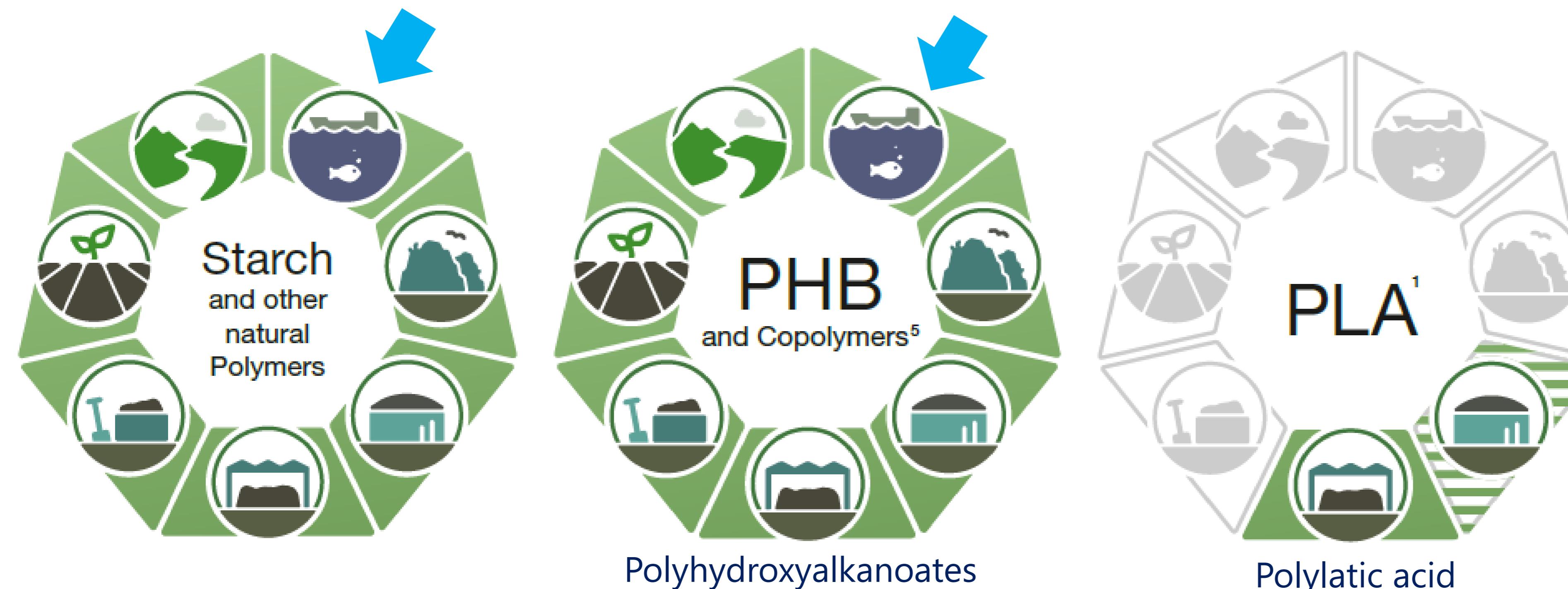
ANAEROBIC DIGESTION

Termophilic 52°C / mesophilic 37°C;
standard specification not yet
available, but 90% generally
considered as completely
biodegradable



INDUSTRIAL COMPOSTING

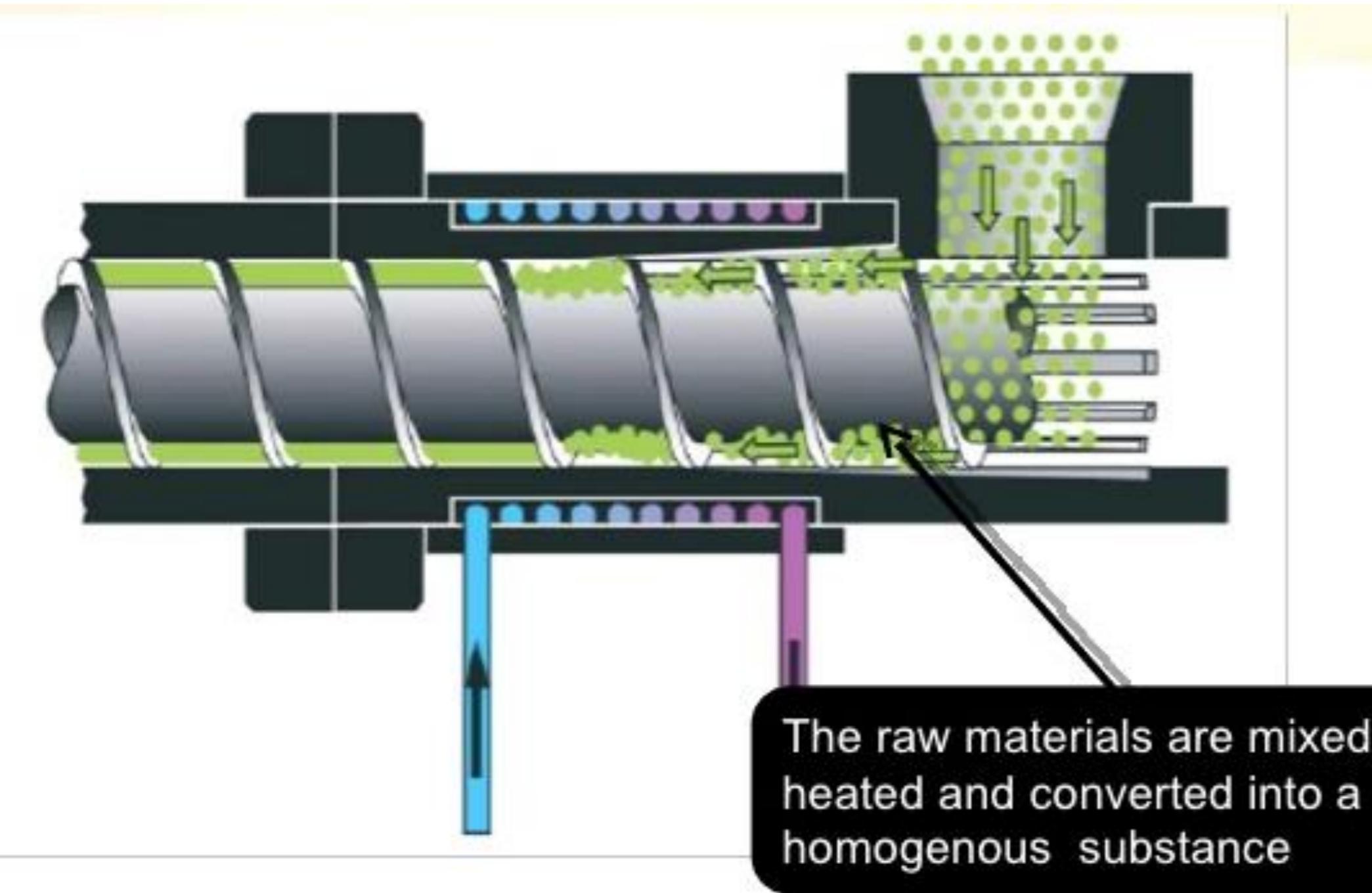
Temperature 58°C,
90% biodegradation within
a maximum of 6 months
(Standard: EN 13432)



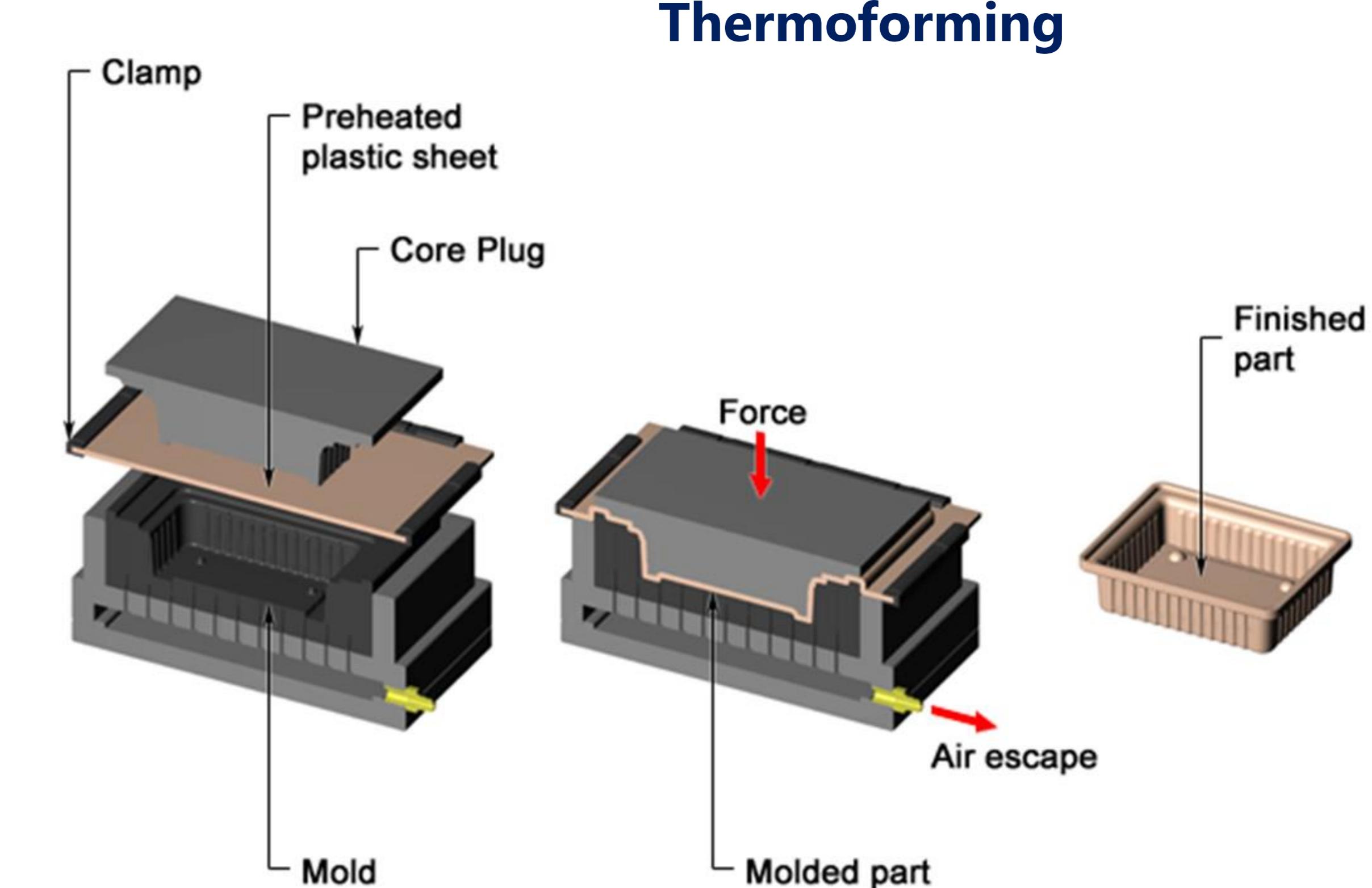
Biodegradable-Polymers-in-Various-Environments.pdf

Some of biodegradable polymers are of Thermoplastic

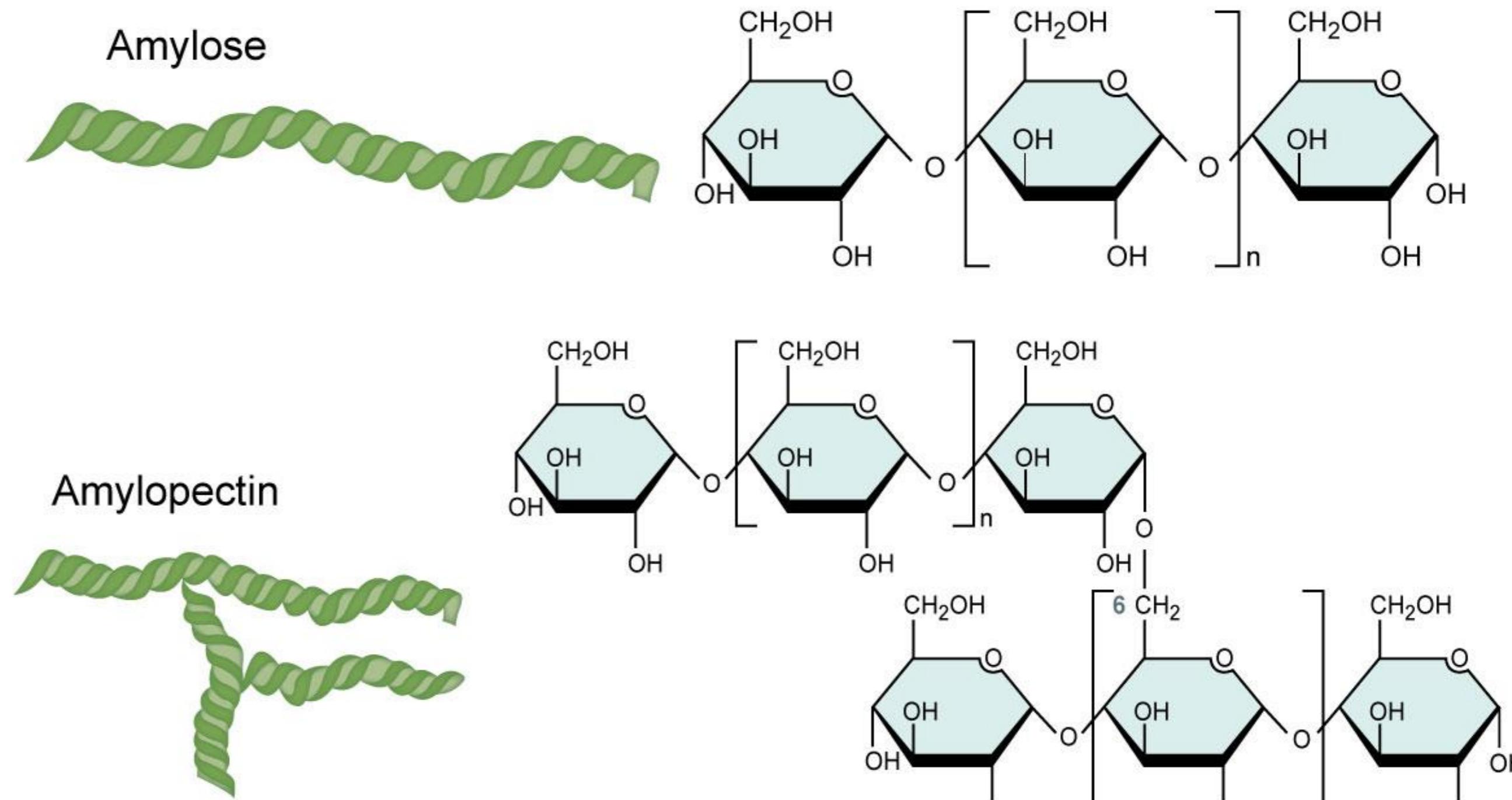
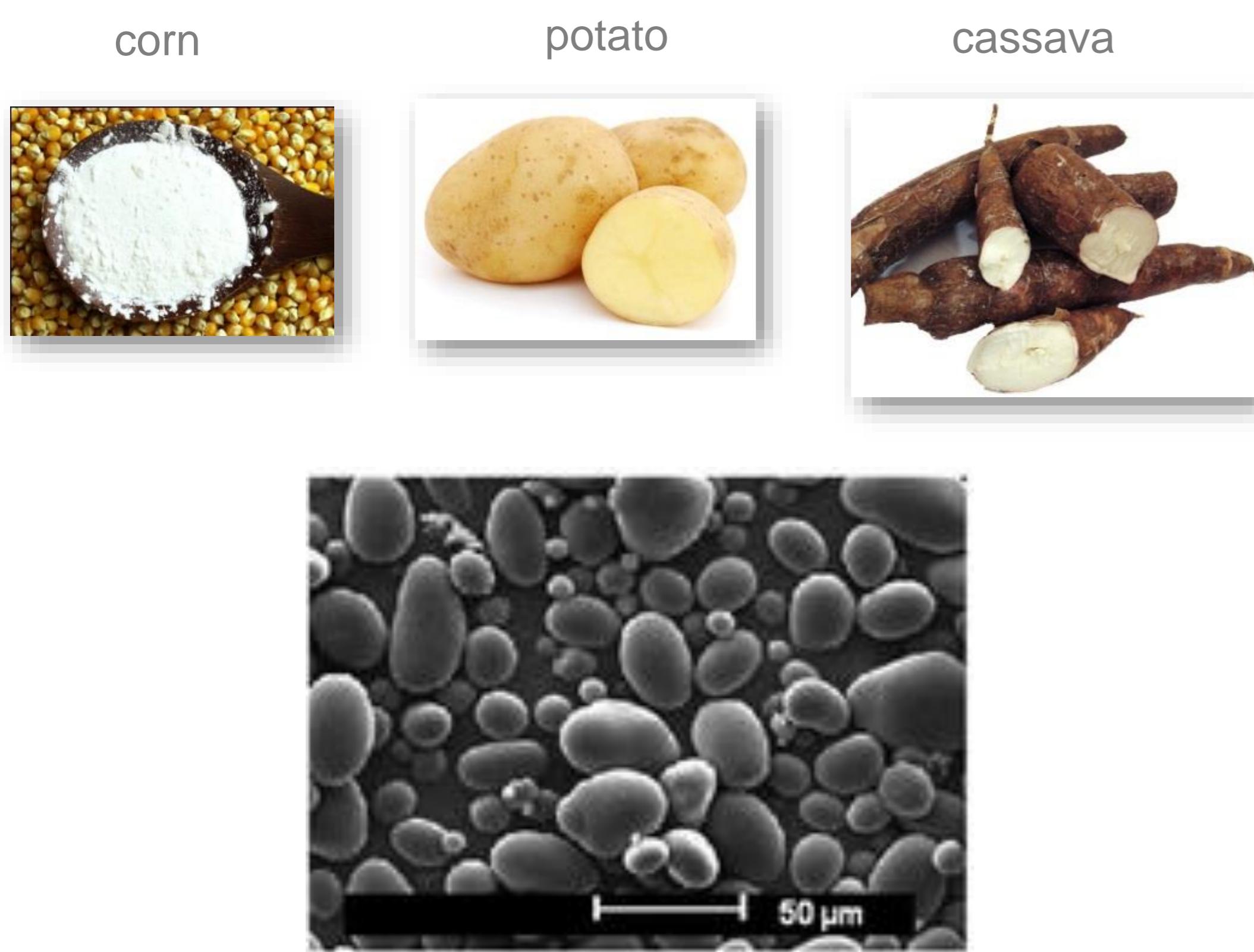
Extrusion



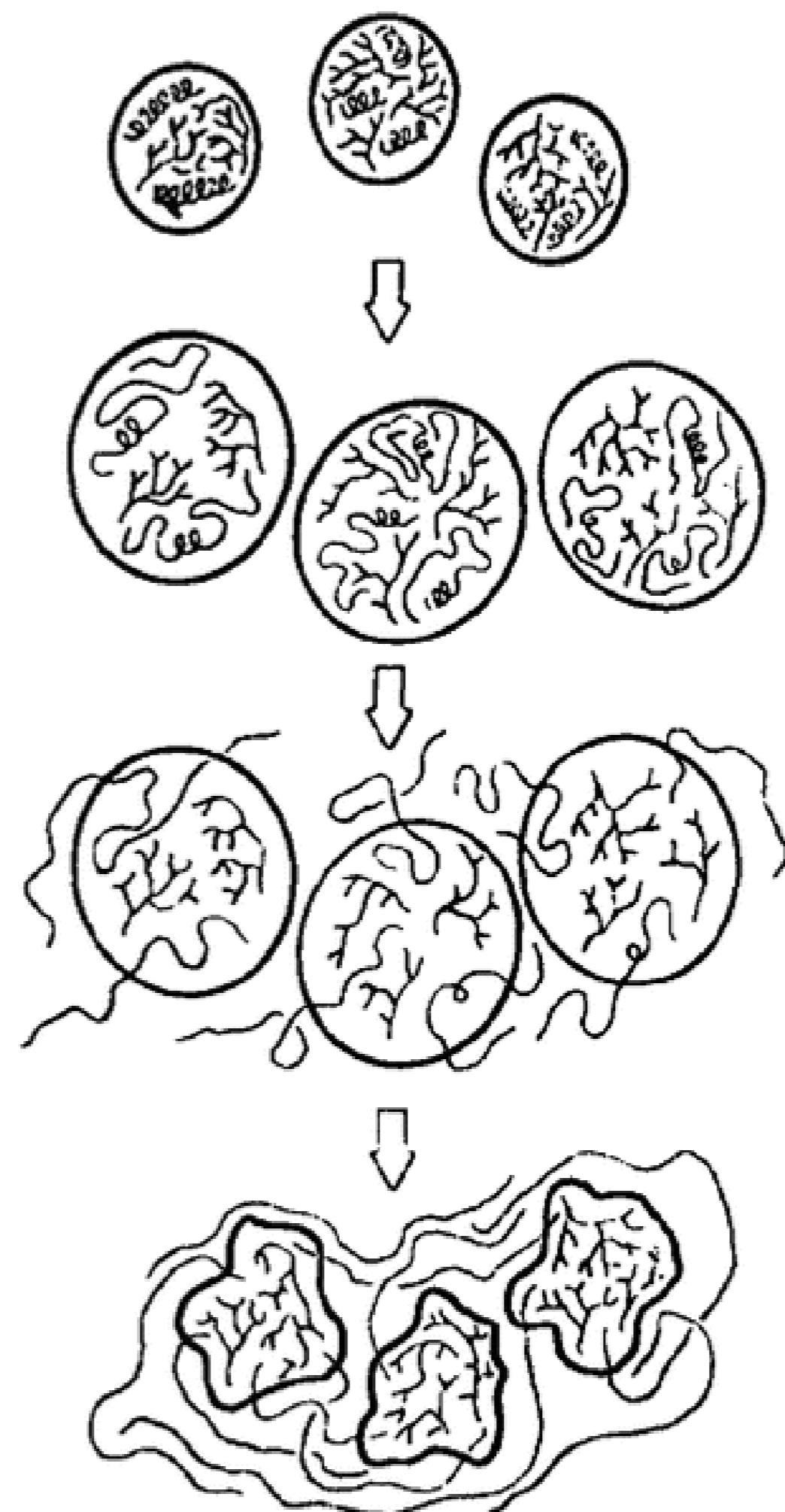
Thermoforming



Starch



Starch Gelatinization

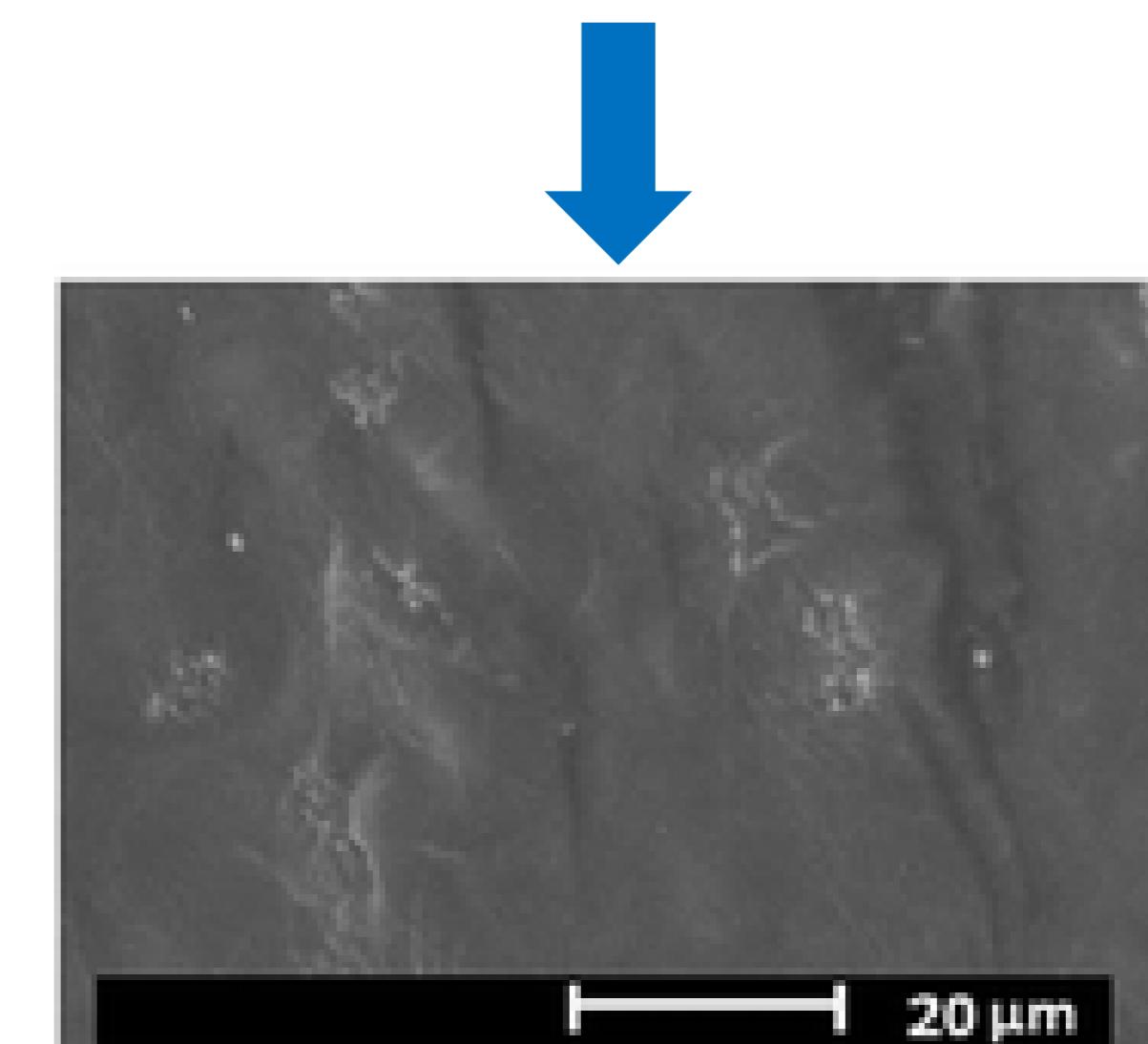
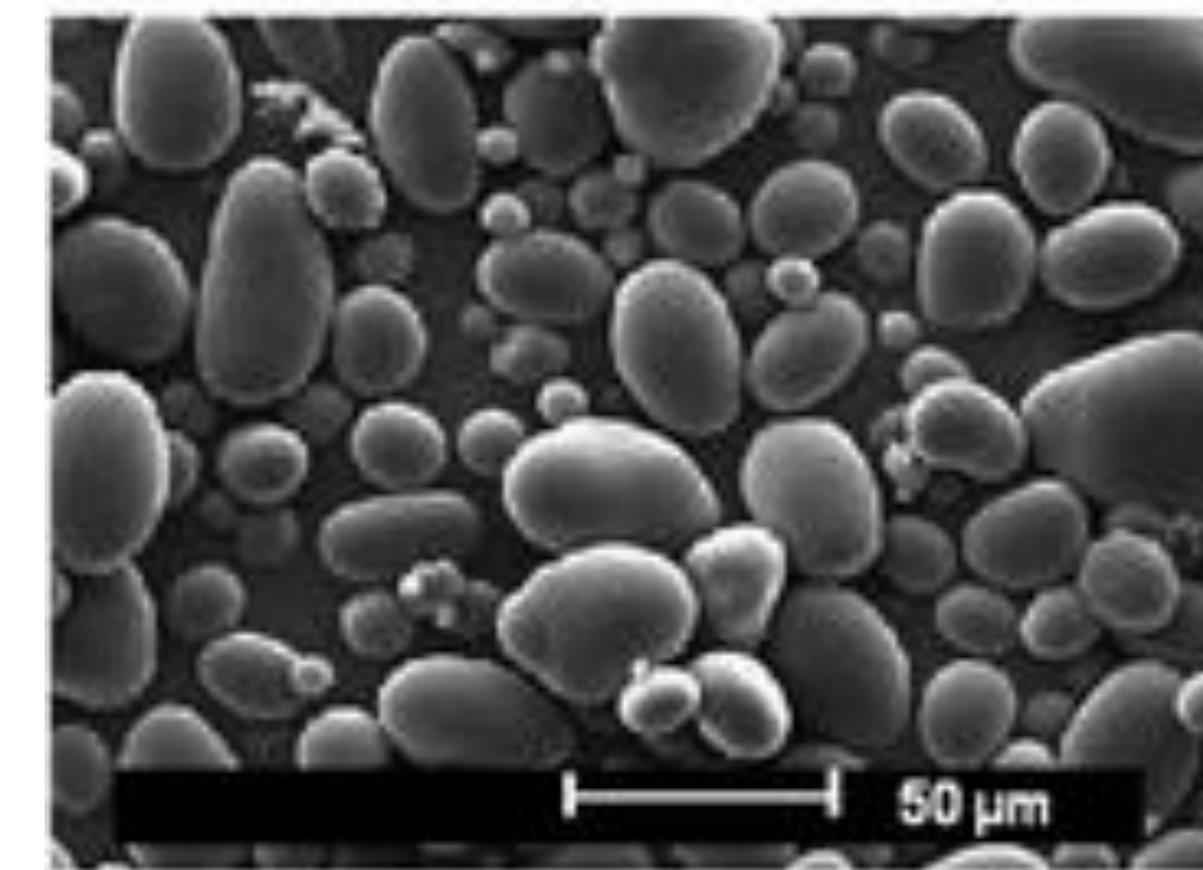


Raw starch granules made up of amylose (helix) and amylopectin (branched)

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

Addition of heat and more water cause more swelling. Amylose begins to diffuse out of granules.

Granules, now containing mostly amylopectin, have collapsed and are held in a matrix of amylose forming a gel



Starch based items

Trays



Foams



Films



Non-biodegradable Polystyrene foams vs biodegradable starch foams
<https://www.youtube.com/watch?v=wdWRx05P4I0>

Polyhydroxyalkanoates (PHAs)



Produced by bacteria

Accumulated inside cells in granules

Energy reserves

Carbon sources: sugars, volatile organic acids, glycerol (preferably present in residues and by-products)

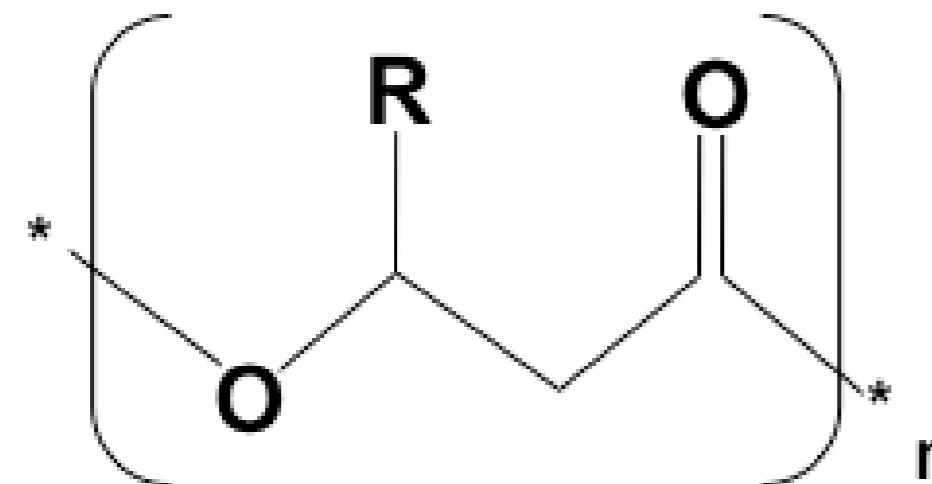
- **Thermoplastic**
- **Hydrophobic**



PHAs after extraction and purification

Polyhydroxyalkanoates (PHAs)

Homopolymers



Copolymers

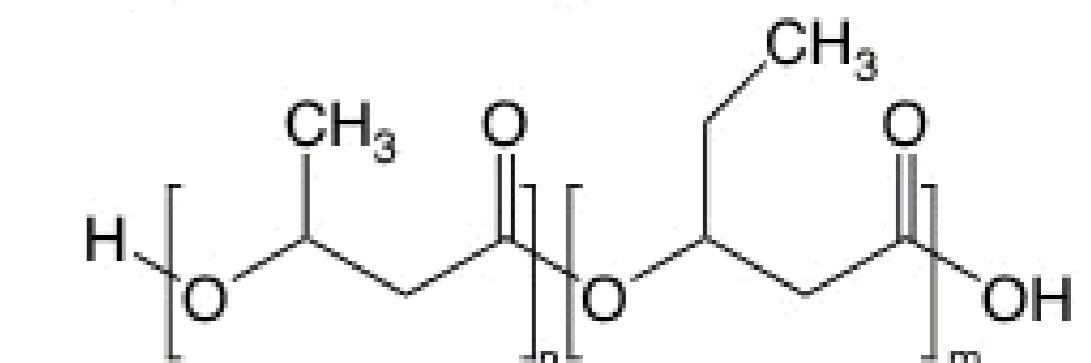
R group	Chemical Name
Hydrogen	Poly-3-hydroxypropionate
Methyl	Poly-3-hydroxybutyrate
Ethyl	Poly-3-hydroxyvalerate
Propyl	Poly-3-hydroxyhexanoate
Pentyl	Poly-3-hydroxyoctanoate

PHA synthesized

PHBV

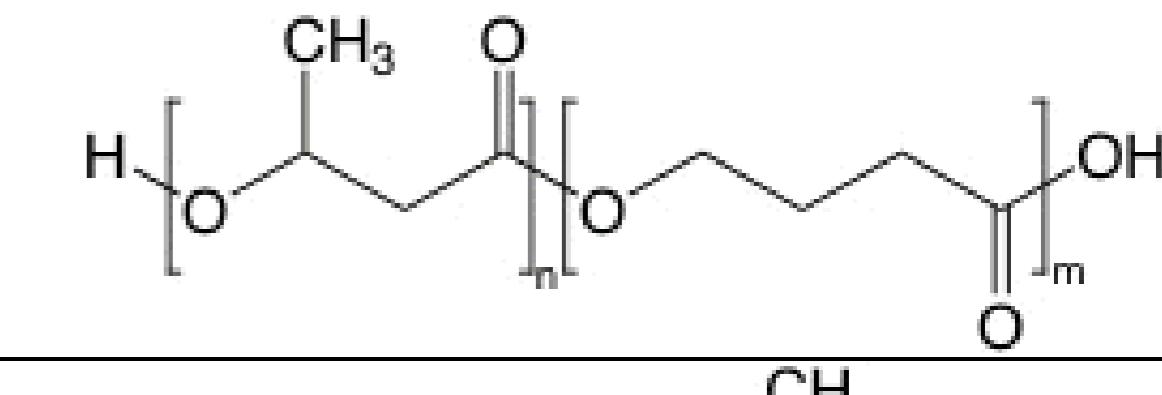
[poly(3-hydroxybutyrate-co-3-hydroxyvalerate)]

PHA chemical structure



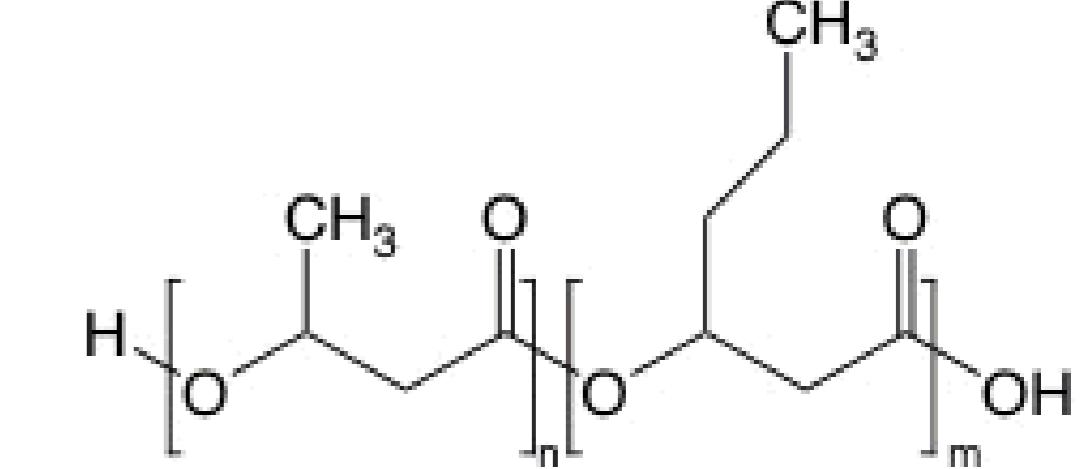
P3HB4HB

[poly(3-hydroxybutyrate-co-4-hydroxybutyrate)]



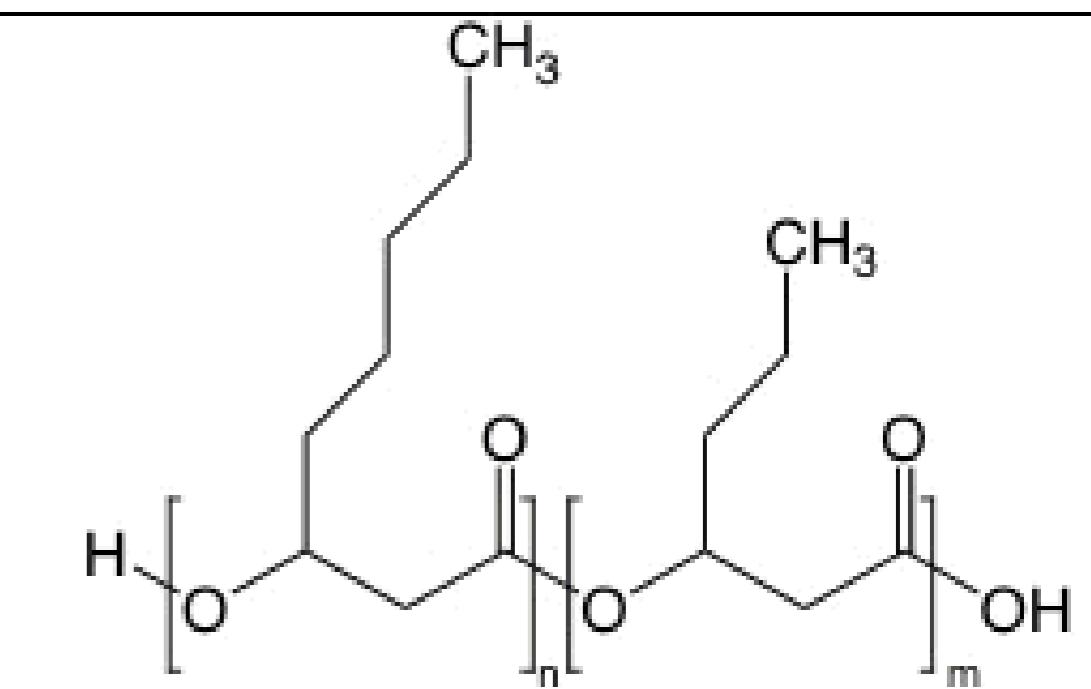
PHBHHx

[poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)]



PHOHHx

[poly(3-hydroxyoctanoate-co-3-hydroxyhexanoate)]

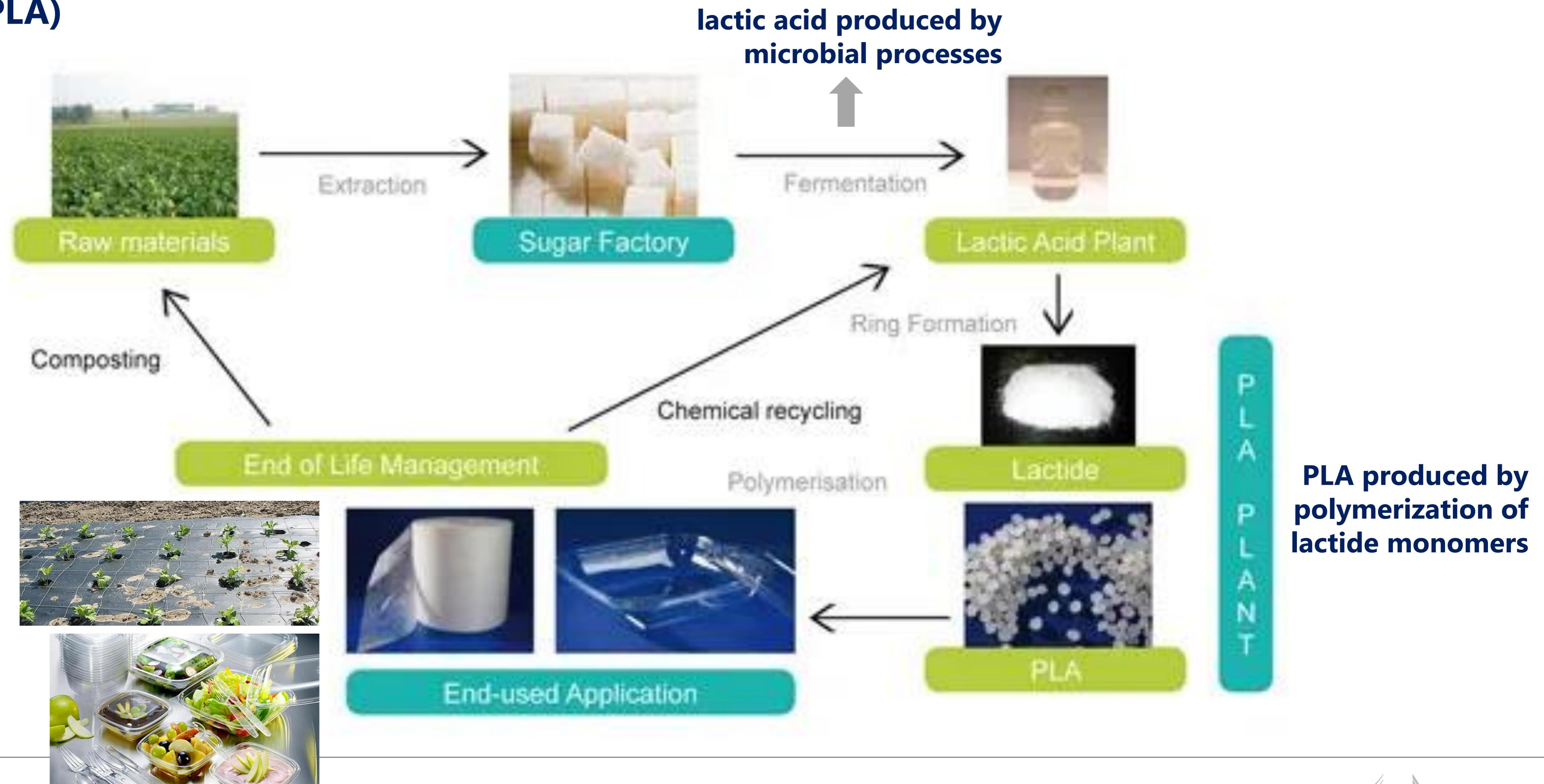


Polyhydroxyalkanoates (PHAs) applications



Polylactic Acid (PLA)

- Thermoplastic
- Hydrophobic



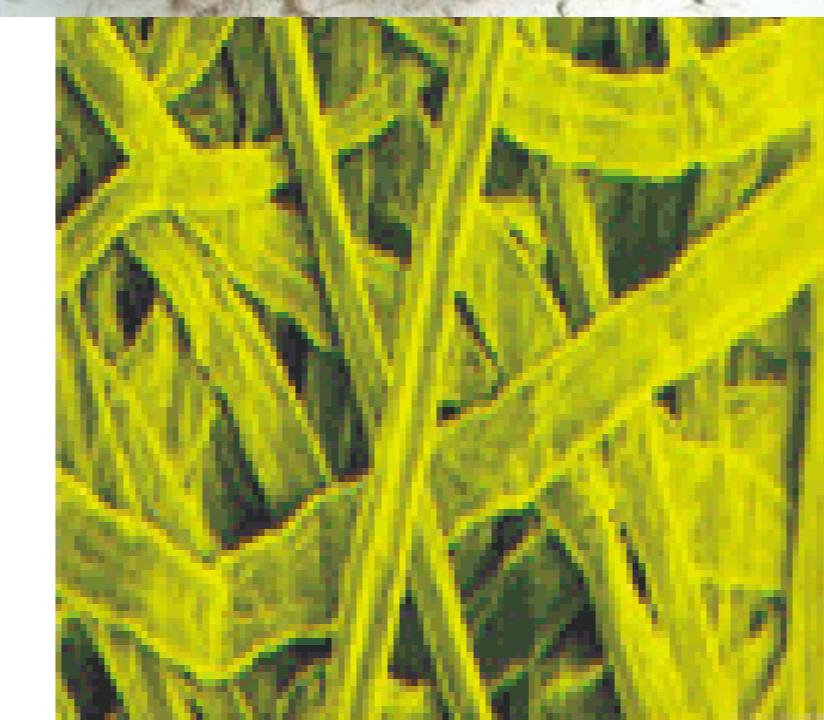
Cellulose



Fibers



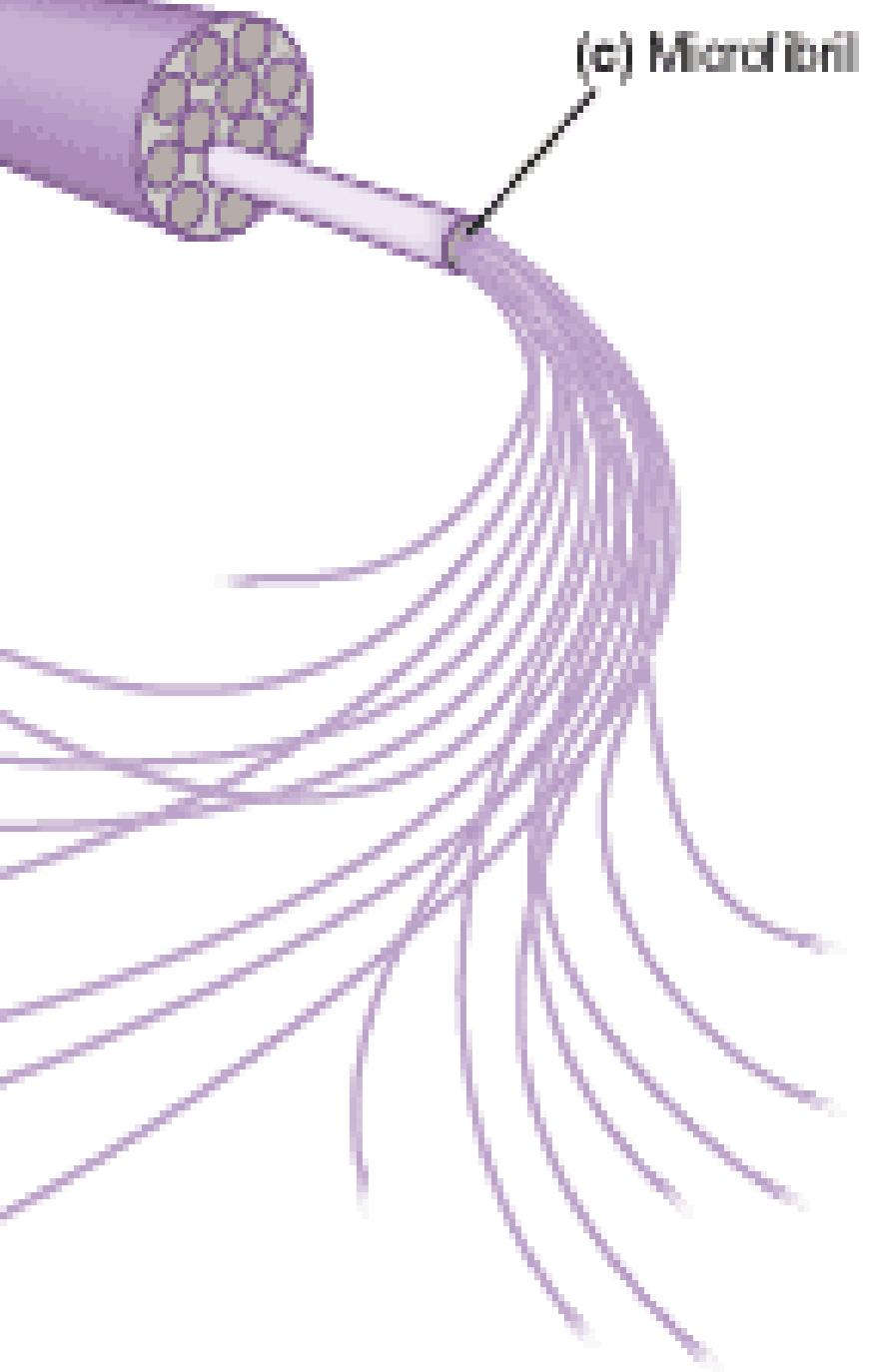
Fibers



(a) Cellulose fibers

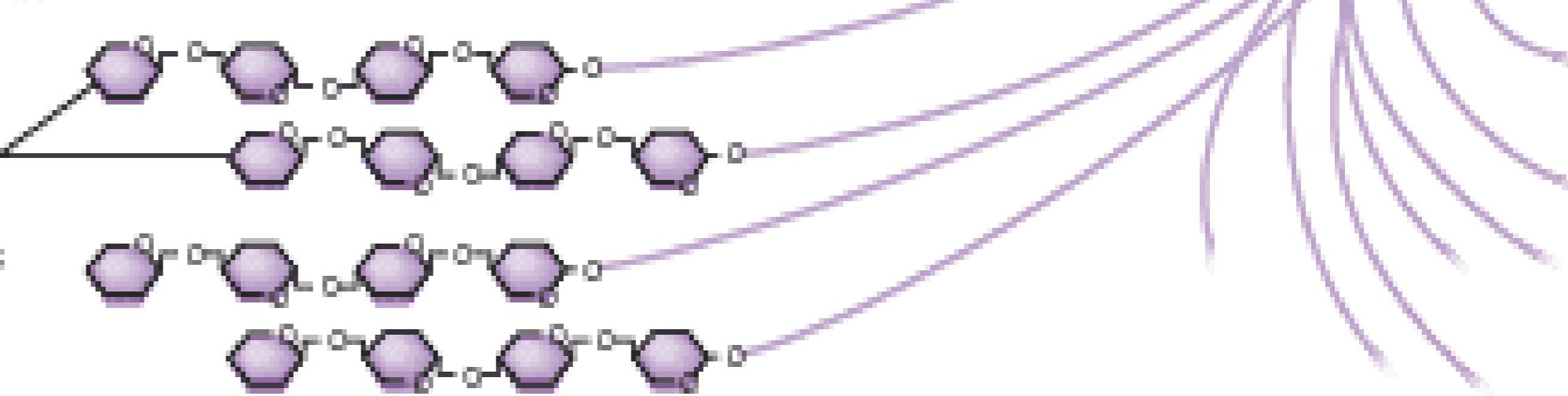


(b) Macrofibril



(c) Microfibril

(d) Chains of cellulose molecules



Further reading

European Project BIO-PLASTICS EUROPE

<https://bioplasticseurope.eu/project>

European Bioplastics association

<https://www.european-bioplastics.org/bioplastics/>



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