BIODEGRADABLE PLASTICS: Problems and Prospects

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OUTLINE OF PRESENTATION

1. Rationale
2. Definition of important terms
3. Types and examples of commercial plastics
4. Some data on bioplastic production
5. Physical tests for plastic biodegradability
6. Recycling of plastics
7. Summary and recommendations

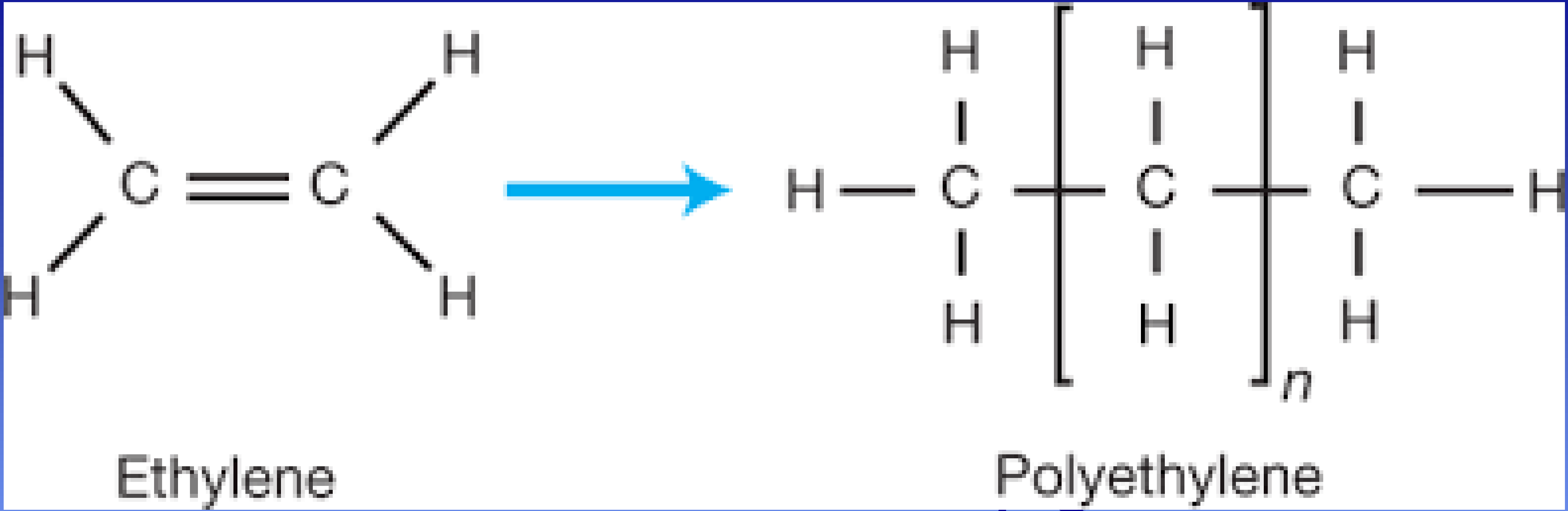

Plastic Pollution

Quotes on Plastic from Sir David Attenborough (2017)

- “More than eight million tons of plastic reaches the sea every year. There will be more plastic than fish in the sea by 2050, and 99 per cent of the planet’s seabirds will have eaten some.”

- “Humans are already eating plastic from the sea too. The average person who eats seafood swallows up to 11,000 pieces of microplastic every year, according to a study by researchers at the University of Ghent. As Prince Charles put it at a recent Our Ocean summit, “plastic is very much on the menu.”

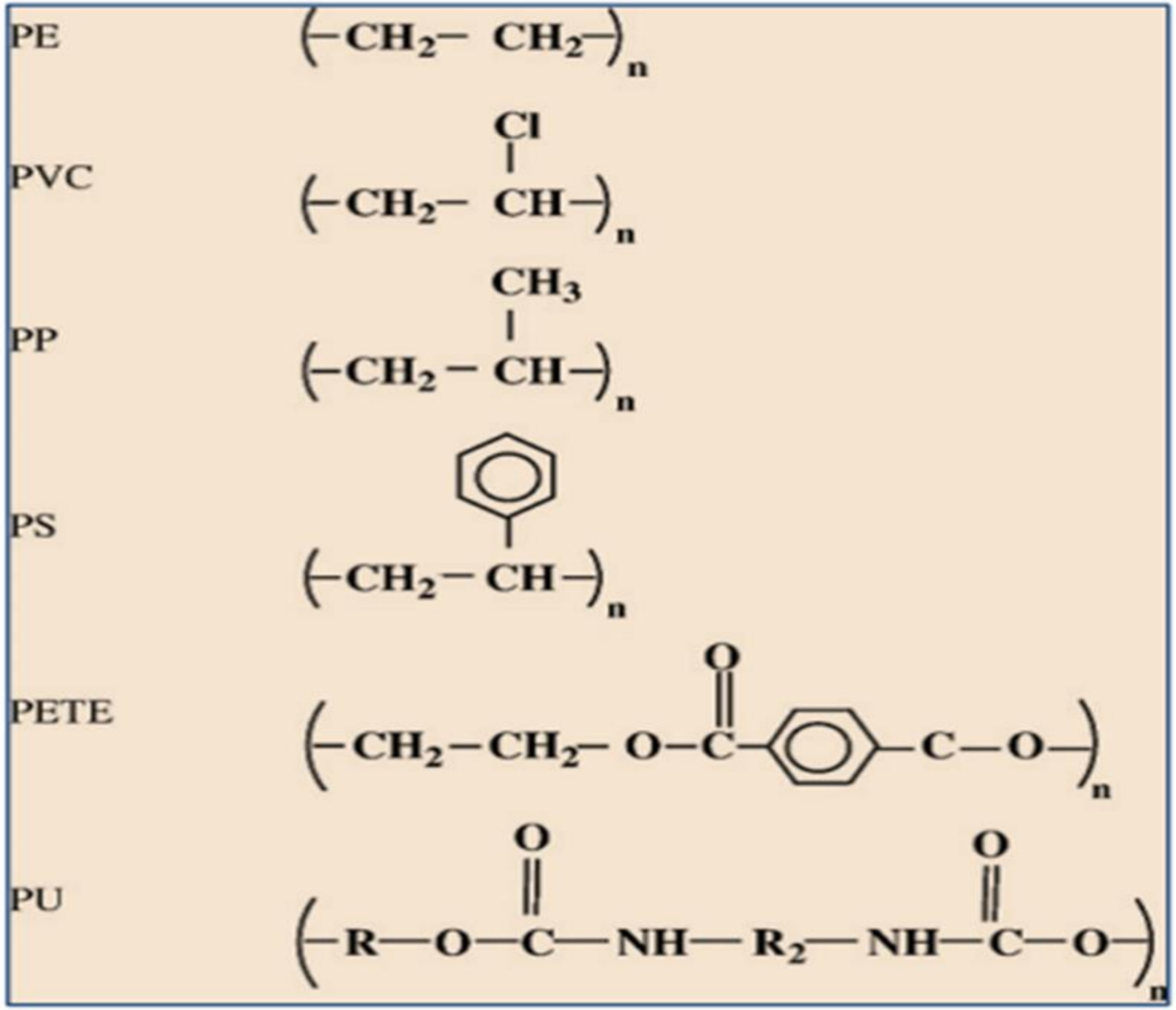
Plastic is a synthetic polymer consisting of carbon, hydrogen, oxygen, chloride and nitrogen. It is derived from fossil sources such as oil, coal and natural gas. Examples are polyethylene (PE), polyethylene terephthalate (PET), nylons, polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyurethane (PU) .Due to inefficient disposal methods for these materials, they often end up as environment pollutants, posing an ever-increasing ecological threat to all inhabitants of our planet.



Polymerization reaction of ethylene into polyethylene (PE)

Fossil-Based Plastics

Fossil- or petrochemical-based plastics utilize fossil feedstocks like petroleum and natural gas. About 7% of all petroleum is converted into plastics. Examples of fossil-based plastics are polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) and polystyrene (PS). Although these materials are predominantly made from fossil feedstock, they could also be produced from biomass which would describe them as bio-based.

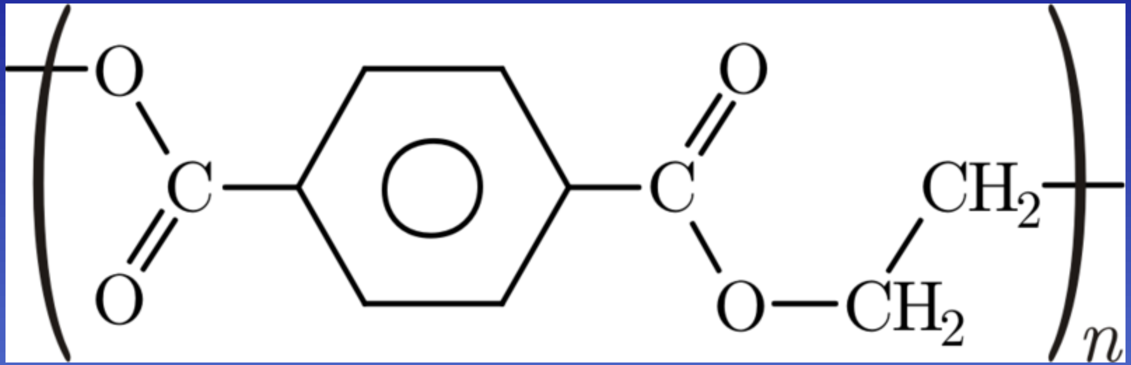


Chemical structures of fossil-based plastics Polyethylene (PE), Polyvinyl chloride (PVC), Polypropylene (PP), Polystyrene (PS), Polyethylene Terephthalate (PET) and Polyurethane (PU)

Thermoplastics - polymers that do not change their chemical composition when heated and can, therefore, undergo molding multiple times. These include the common plastics polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polytetrafluoroethylene (PTFE) with molecular weights in the range of 20,000 to 500,000 AMU.

Thermosetting Polymers - remain solid and can not be melted nor modified. The chemical change here is irreversible, and hence these plastics are not recyclable because they have a highly cross-linked structure, whereas thermoplastics are linear. Examples include phenol-formaldehyde, polyurethanes, etc.

Problems with Conventional Plastic



- Pros
  - Cheap and Easy to Manufacture
  - Good Commercial Properties
- Cons
  - Complex entanglements of polymer chains (usually PET or PBT) make it hard to decompose
  - Relies heavily on petrochemicals
  - Needs processing
  - Recycling requires energy and money
  - Releases toxic chemicals
  - Fragmentation or Cyclization occurs
  - 200 million tons produced each year and most of it is not recycled

Biomass - substance of biological origin except geological formations and fossilized biological matter.

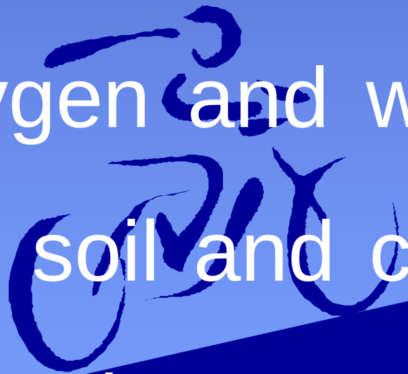
Biodegradation - biological decomposition in the presence of microorganisms.

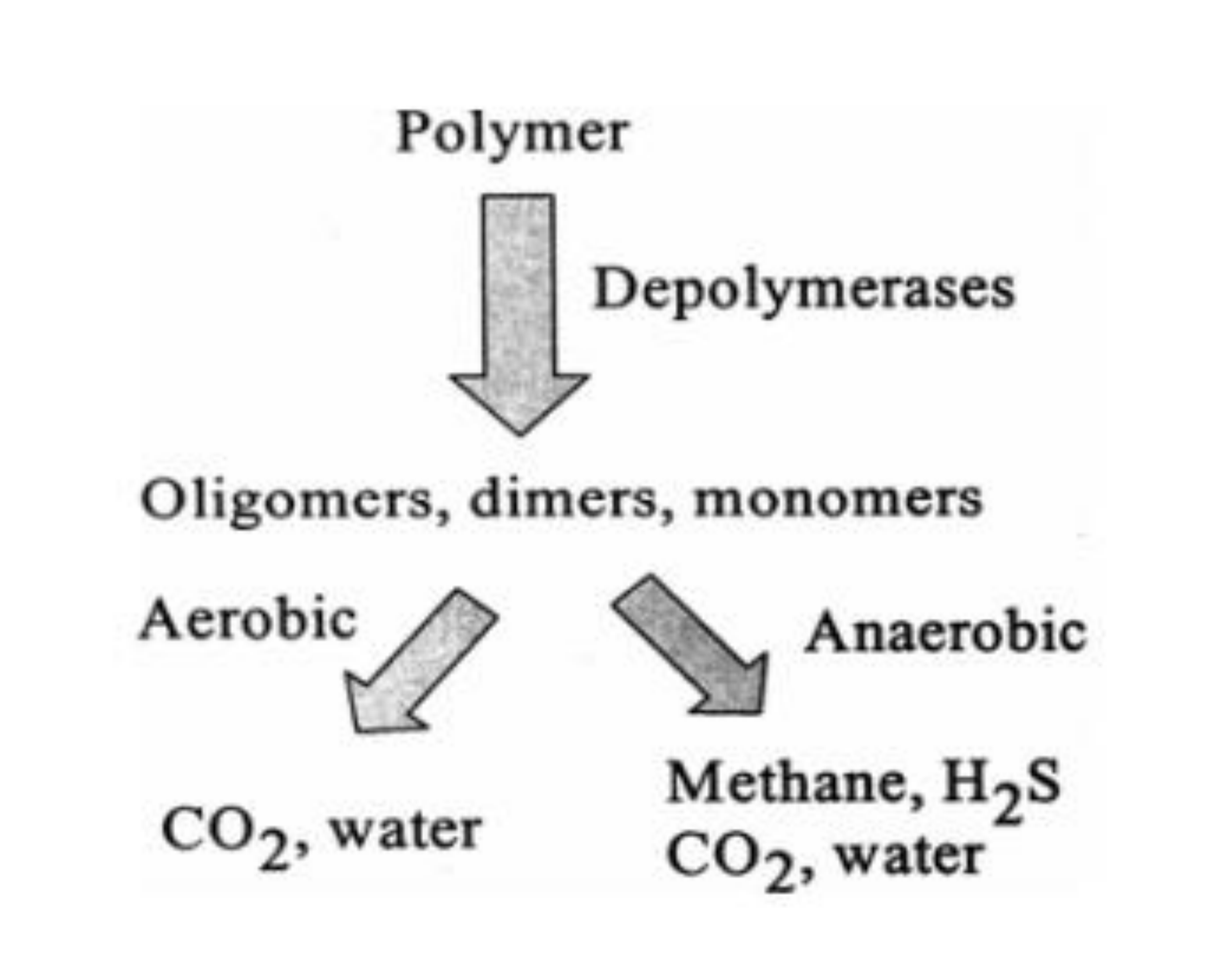
Aerobic decomposition – biological decomposition in the presence of oxygen or air, where carbon is converted to carbon dioxide and biomass.

Anaerobic decomposition – biological decomposition in the absence of oxygen or air, where carbon is converted to methane and biomass.

Biodegradable

Biodegradable materials can be broken down by microorganisms (bacteria or fungi) into water carbon dioxide (CO_2) and methane (CH_4) and microbial biomass. Biodegradability depends on environmental conditions, e.g. temperature, presence of microorganisms, as well as of oxygen and water. Both extent and rate of biodegradability vary with soil and climate, properties of the water medium, as well as composting conditions.





Reaction pathways during biodegradation of polymers

$$C_{polymer} + O_2 \xrightarrow{a} C_{biomass} \xrightarrow{b} CO_2 + H_2O$$

$$\text{Biodegradation } \% = \frac{C_{evolved\ as\ CO_2}}{C_{polymer}} \times 100$$

Compostable bio-plastics are decomposed biologically in a composting process at a similar rate to other compostable materials, without leaving visible toxic remainders. A plastic is designated bio-compostable based on standard measurements of its total biodegradability and disintegration degree, as well as ecological toxicity of its degraded materials.

Biodegradable or Compostable?

Compostable plastics are a subgroup of biodegradable plastics and are biologically decomposed under composting conditions and within the relatively short period of a composting cycle.

Compostable always means biodegradable.

Biodegradable does not necessarily mean compostable.

The term **bioplastic** (or bio-plastic) refers to either the bio-based origin of a plastic or to the biodegradable character of a plastic. Bio-based and biodegradable are not synonymous.

*Partly based on van den Oever et al. (2017)

Bio-based bioplastics are defined as “plastics” in which 100% of the carbon is derived from renewable agricultural and forestry resources, such as corn starch, soybean protein and cellulose.

Lactic Acid Polymerization

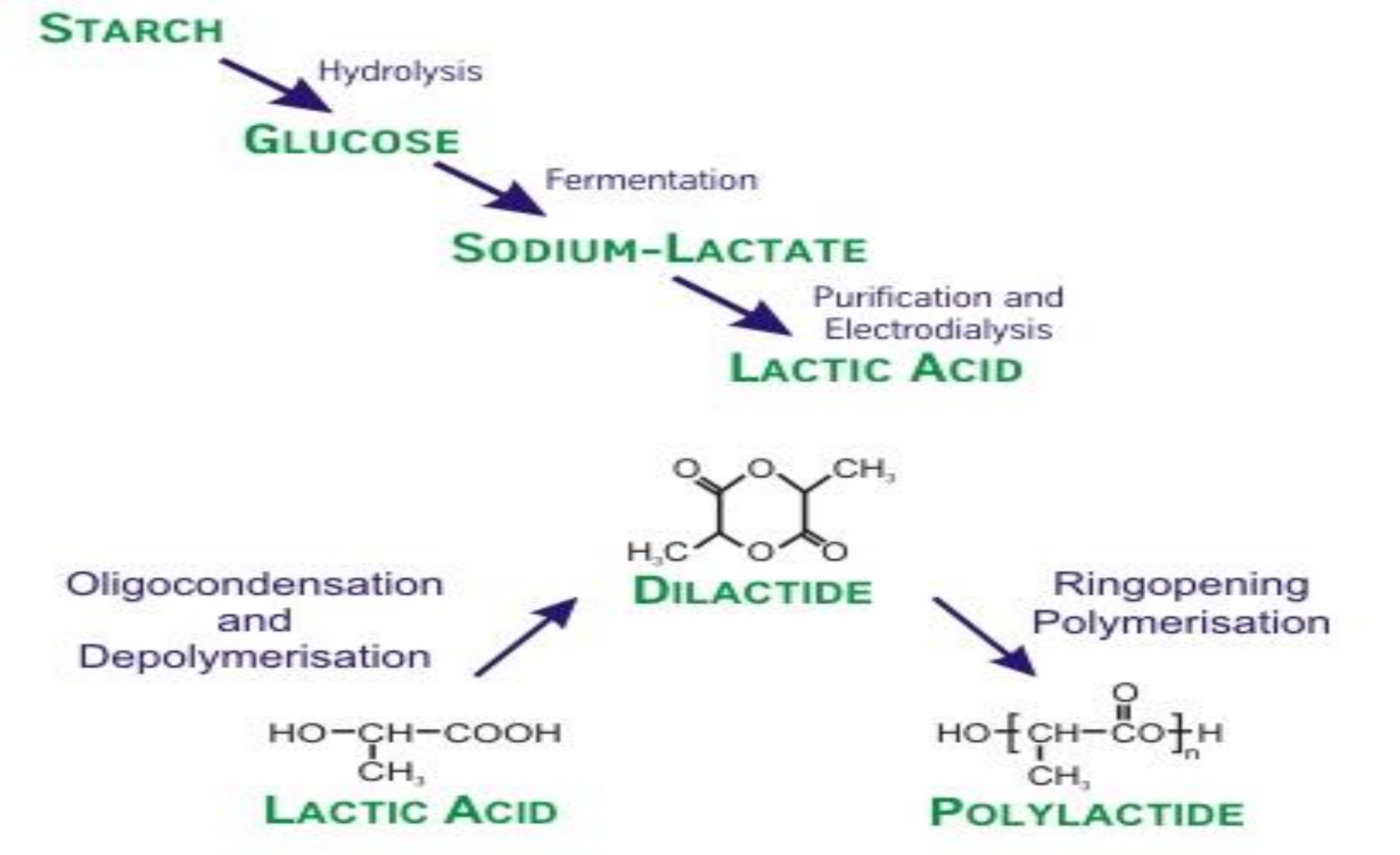
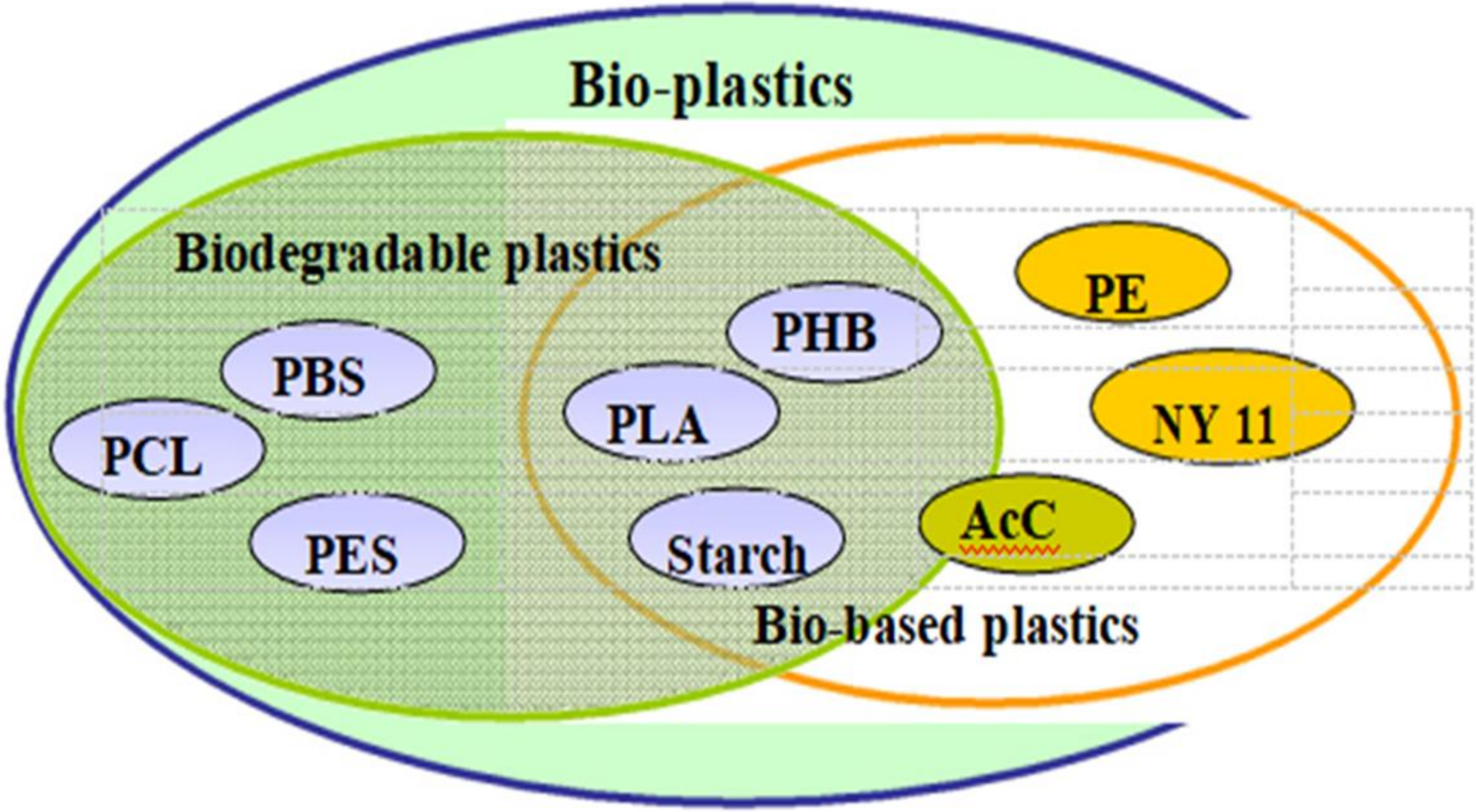


Figure 1. Bio-plastics comprised of biodegradable plastics and bio-based plastics.

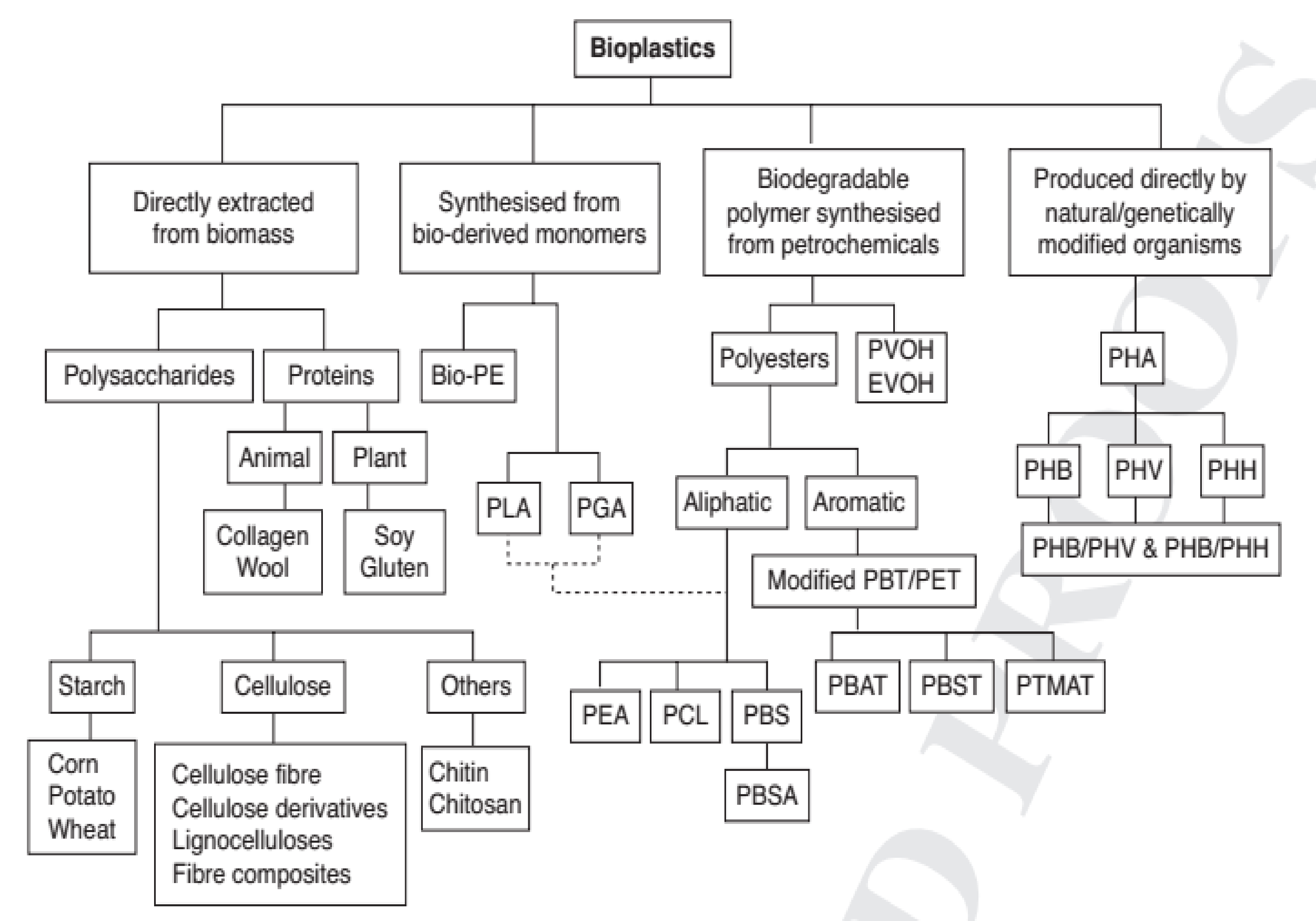


Ref: Tokiwa et al. (2009)

	Petrochemical	Partly bio-based	Bio-based
Non-biodegradable	PE, PP, PET, PS, PVC	Bio-PET, PTT	Bio-PE
Biodegradable	PBAT, PBS(A), PCL	Starch blends	PLA, PHA, Cellophane

Figure 1. Diagram indicating positioning of bio-based versus petrochemical plastics and biodegradable versus non-biodegradable plastics.

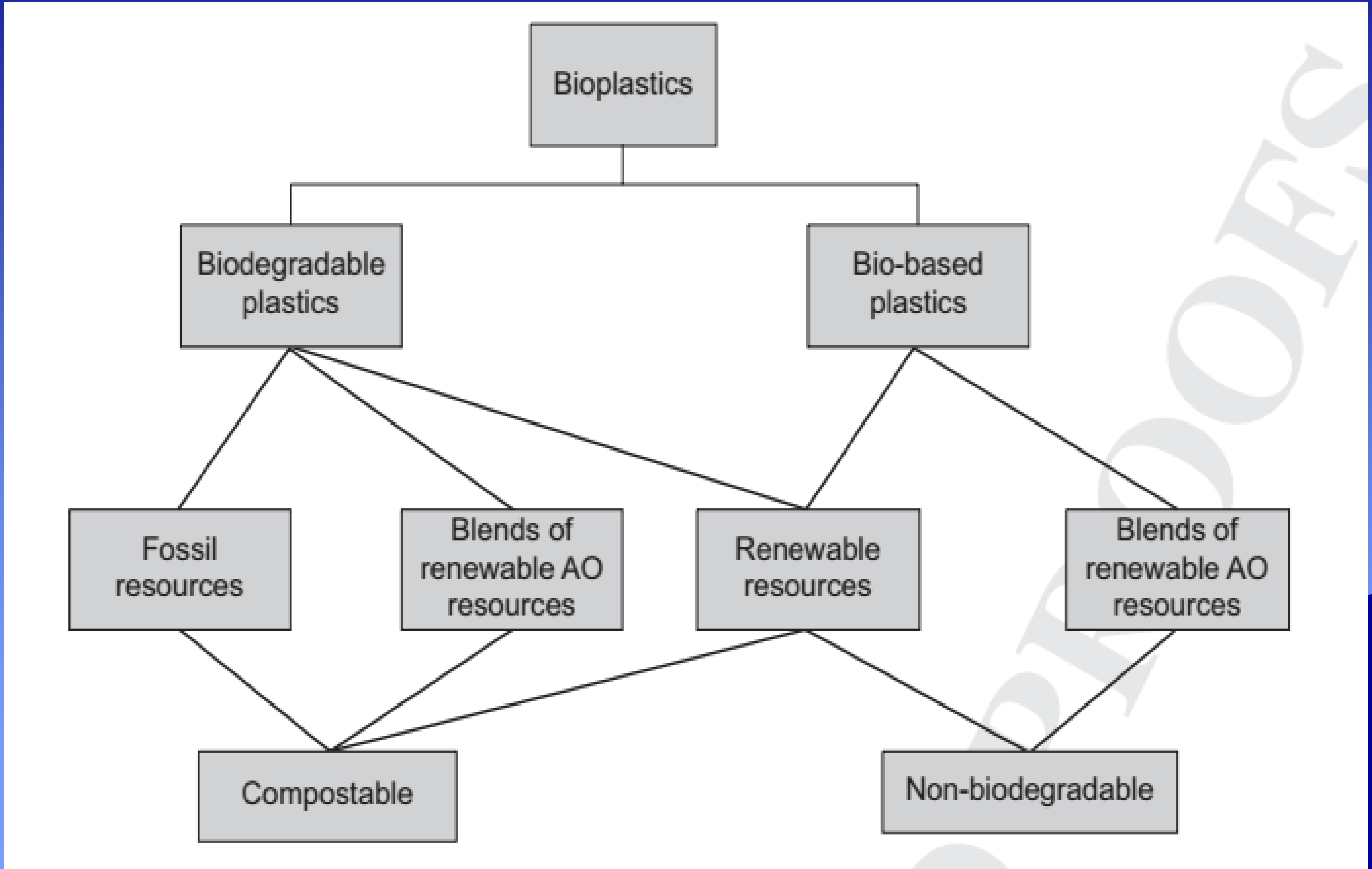
Classification of Bioplastics based on origin and method of production



PBT-polybutyl terephalate	PBSA-polybutylene succinate adipate	PBS-polybutylene succinate
PBAT-polybutylene adipate/terephthalate	PCL-polycaprolactone	PGA-polyglycolic acid
PHA-polyhydroxyalkanoates	PHB-polyhydroxybutyrate	PHH-polyhydroxyhexanoate
PHV-polyhydroxyvalerate	PLA-polylactic acid	PVOH-polyvinylalcohol
PTMAT-polymethylene adipate/terephthalate	PBS-polybutyllene succinate	Bio-PE-polyethylene from bio-ethanol
PEA-polyester amide	EVOH-poly(ethylene vinylalcohol)	

NOTE: Bioplastics can also be produced as co-polymers or bio-composites using two or more of these materials

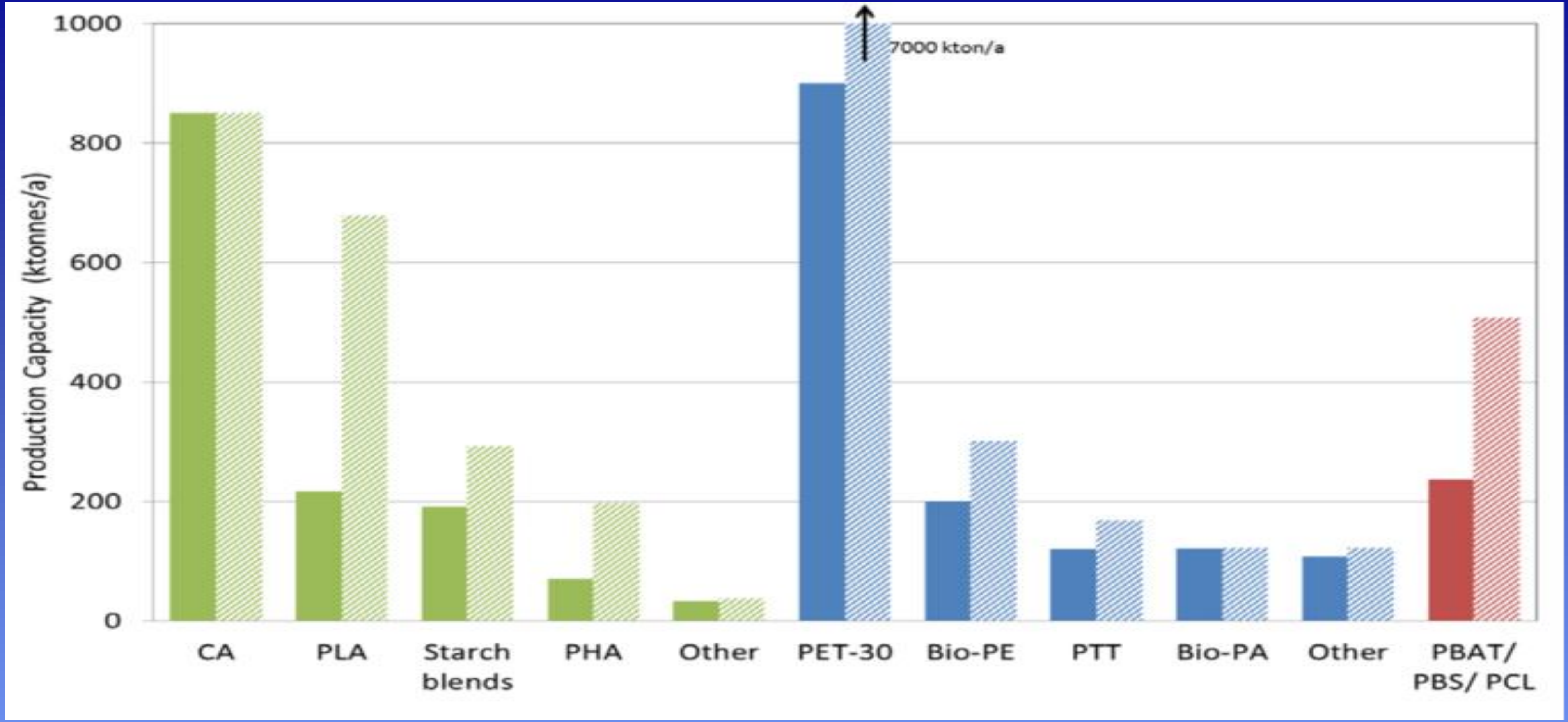
Types of Bioplastics



Biodegradable bio-plastics are fully degraded by microorganisms, without leaving toxic remainders. The term “biodegradable” refers to materials that can disintegrate or break down naturally into biogases and biomass (mostly carbon dioxide and water) as a result of being exposed to microorganisms and humidity

Commercial Bioplastics

- Starch-based plastics
- Polylactide-based plastics (PLA)
- Polyhydroxyalkanoate-based plastics (PHB, PHBV, etc.)
- Aliphatic-aromatic-polyester-based plastics
- Cellulose-based plastics (cellophane, etc.)
- Lignin-based plastics



Global production capacity data in 2015/2016 (solid bars) and announced production capacities for 2020 (shaded bars) of bio-based biodegradable polymers (Green), bio-based non-biodegradable (drop in) polymers (Blue) and fossil-based biodegradable polymers (Red) (van den Oever et al., 2017).

Business Forecast for Bioplastic Production in Asia

- “Biodegradable, compostable” polymers (such as PLA, PBS, PBAT, PHAs) are expected to contribute about 25% to the Asian production of bio-based polymers in 2021. However, that means that about 75% of the total bio-based production in Asia will be focusing on durable polymers.

  As leading countries China, Japan, Malaysia, South Korea, Taiwan and Thailand are in the focus of the report with their activities in bio-based LA, PLA, PBS(X), PE, PHAs and PA.

Ref: Bioplastics industry in Asia 2017

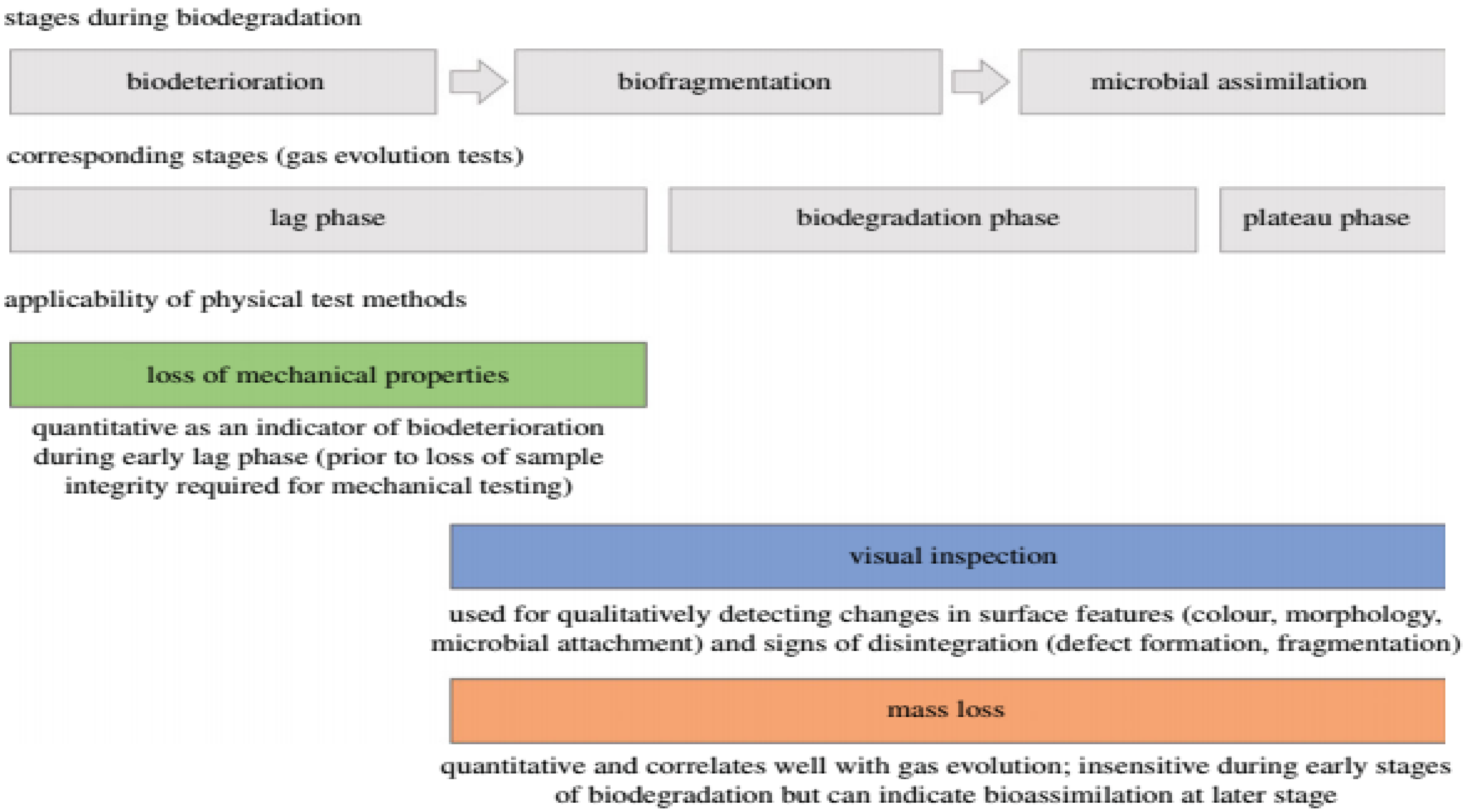


Figure 1. Physical test methods for the evaluation of plastic biodegradation, and their relation to different stages of polymer breakdown and corresponding stages observed using gas (CO_2 and CH_4) evolution tests.

Filipino firm produces additive to make plastic items biodegradable

- ITDI-DOST has verified the claim that a unique additive produced by a local company makes plastic materials biodegradable and has issued Environmental Technology Verification-013 for the additive, BioMate®, which is manufactured by First In Colours, Inc. (FIC), a sister company of Chemrez Technologies Inc. This is the first such additive in the P75 billion Philippine plastics film and bags industry to be verified by the ITDI as making plastics both photo and biodegradable – although many imported additives sold in the local market have made similar claims

- Polyolefin plastics formulated with BioMate® undergo a 2-step degradation process; first by photodegradation and then biodegradation," said FIC's Operations Mgr. If exposed outdoors, films with BioMate will become brittle in 30-45 days and embrittlement continues until films are small enough for bacteria and microorganisms to consume (within 9-12 months). Indoors, shelf life of plastics with BioMate is 6 to 9 months.

Ref: Manila Bulletin (J. Loyola) May 31, 2010

OXO-BIODEGRADABLE PLASTICS - The new process of OXO-degradation is based on adding a very small amount of pro-degradation chemical into the manufacturing process, thereby changing the behavior of the plastic. Degradation begins when the programmed service life is over (as controlled by the additive formulation) and the product is no longer required.

Photodegradable bioplastic has light sensitive groups connected to the backbone of the polymer. Exposure to UV radiation for a long time can disintegrate its polymeric structure, allowing further bacterial degradation. Absence of sunlight in landfills, however, keeps this plastic virtually non-degraded.

Evaluation of biodegradation-promoting additives for plastics (done in Michigan, U.S.A.)

- The effect of biodegradation-promoting additives on the biodegradation of polyethylene (PE) and polyethylene terephthalate (PET) was evaluated in a 3-year study. Biodegradation was evaluated in compost, anaerobic digestion, and soil burial environments. None of the five different additives tested significantly increased biodegradation in any of these environments. Thus, no evidence was found that these additives promote and/or enhance biodegradation of PE or PET polymers

- (Selke et al., 2015)

Degradation behavior of fossil-based and bio-based plastics during composting (done in Czech Republic)

Commercial bioplastics and a PE plastic with additives (claimed to be degradable) were used for the 3-month study. The research was carried out in real conditions in the Central Composting Plant in Brno, Czech Republic. SEM analysis of the samples was done in order to analyze microstructure and morphology of specimens, validating dispersion results. The samples certified as compostable have degraded in real composting conditions. Samples (4–7) showed significant erosion on surface when subjected to the SEM analysis. PE plastic with degradation additives, which were labeled by their producers as 100% degradable, did not show any visual signs of degradation.

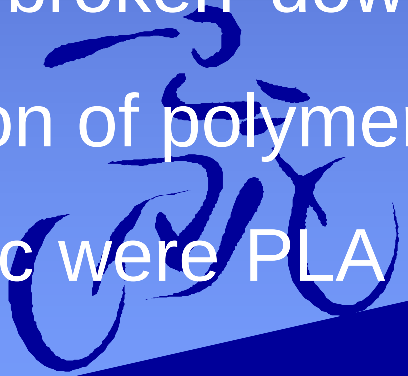
Adamcova et al., 2018

Biodegradable plastics offer a promising solution to the present plastic pollution problem because they can be derived from renewable feedstocks, thereby reducing greenhouse gas emissions. Bio-plastics such as polyhydroxy alkanoates (PHA) and polylactic acid (PLA) can be produced by microbial processes using agricultural substrates. Biodegradable plastics offer many advantages such as increased soil fertility, low accumulation of plastic waste in the environment and reduction in waste management costs.

Furthermore, biodegradable plastics can be recycled to useful metabolites (monomers and oligomers) by microorganisms and enzymes. A second strategy involves degradation of some petroleum-derived plastics by biological processes. A typical example can be seen in the case of some aliphatic polyesters such as PCL and PBS that can be degraded with enzymes and microorganisms. Polycarbonates (particularly the aliphatic types) possess some degree of biodegradability.

Recycling

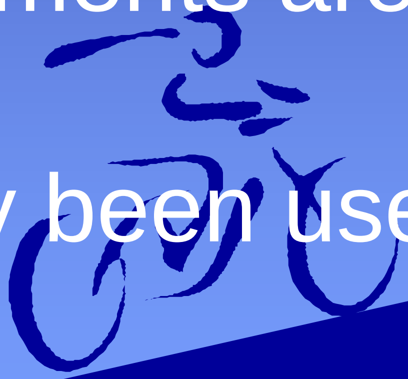
Material recycling is defined as the reprocessing of a used product material into a new product. An example is plastic which after use can be collected, sorted and reprocessed into new products). This type of recycling is called mechanical recycling. Another option is chemical recycling where materials are broken down to monomers which can be used again for the production of polymer. An example is the Loopla process developed by Galactic were PLA is hydrolysed to lactic acid (Looplife, 2016).



Plans to build Philippine Roads using 'Plastic Asphalt'

“San Miguel Corp. plans to collaborate with U.S.-based Dow Chemical Company in creating 'plastic asphalt'. Initial testing will be done on parking lots, municipal roads and sidewalks. This project will be done on a massive scale once all safety and quality requirements are met.”

This same technology has already been used in Thailand, India and Indonesia.



SUMMARY

Plastics are polymers that are unchanged chemically when heated and can be molded multiple times. Most fossil-based plastics (PE, PET, PVC, etc.) are non-biodegradable, although some (polyesters, etc.) are biodegradable and fully degraded into CO_2, methane and microbial biomass. Bio-based plastics (PLA, PHA, cellophane, etc.) are mainly biodegradable although a few, such as bio-PE, are non-biodegradable. For environmental reasons, plastics should also be compostable and are fully degraded by composting under recommended conditions.

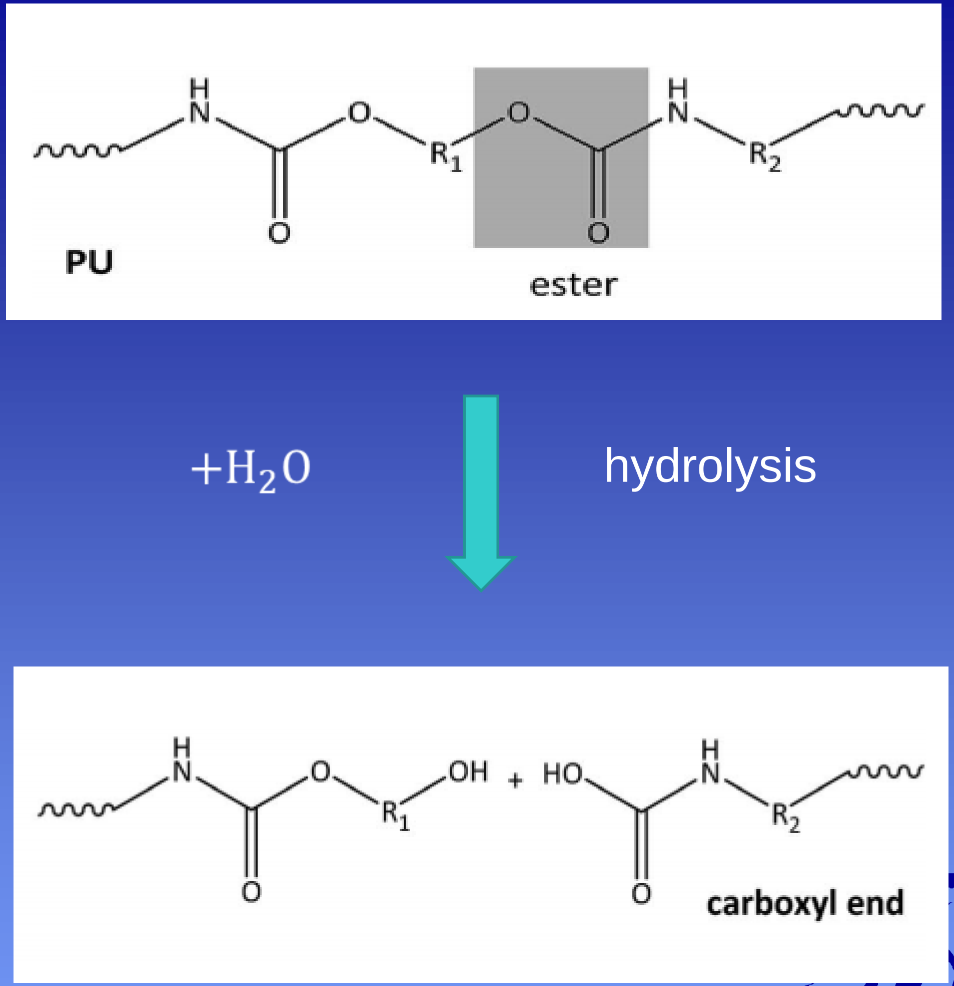
SUMMARY

Some commercial additives have been claimed to be effective in enhancing biodegradability of non-biodegradable plastics. However, recent scientific studies in the U.S.A. and Czech Republic have shown that several of these additives did not perform as claimed under standard biodegradation conditions, such as composting. There is need to test such additives for biodegradability enhancement using standard physical tests for evolution of gases (CO_2 and CH_4), quantitative loss of mass and sample integrity, as well as visual inspection of surface features and disintegration.

Recommendations

1. Government incentives for processors of biodegradable plastic products, e.g. tax reduction/exemption
2. Restricted importation and sale of non-biodegradable, esp. single-use, plastic products
3. Funding and logistical support for R & D on:
 (a) Physico-chemical and biological evaluation of the effectiveness of commercial additives for biodegradation of plastic materials
 (b) Techno-economic feasibility studies on the production of biodegradable plastics from local feedstocks


THANK YOU
for your attention
Sunset view – Sun Moon Beach Resort
(Bagac, Bataan)



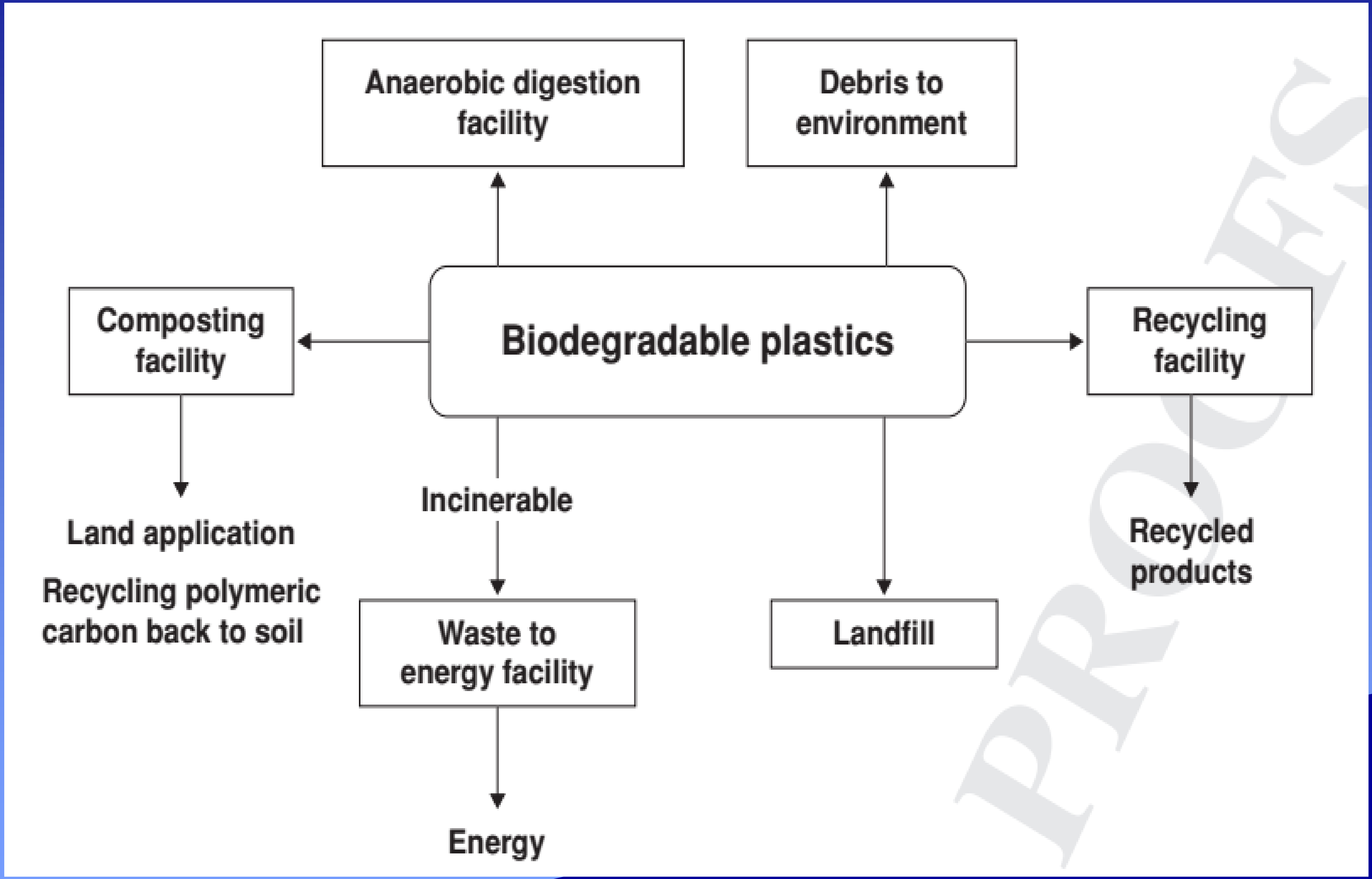
Hydrolytic degradation of the ester bond of PU

Pros and Cons of major waste treatment technologies (Ren, 2003)

TECHNOLOGY	PROS	CONS
Recycling	• Reduce amount of wastes for disposal • Save resources and energy in virgin production • Extend product's lifetime, conserve resources	• Not everything economically recyclable • Recycling consume energy, emit pollutants • Recycled product inferior in quality, thus only lower grade application, limited market
Composting	• Reduce load of landfill by digesting organics • End product useful for soil amendment • Need less energy than recycling, incineration	• Economics still unfavorable • Risk of odor and pest problem • No reliable market for end product (compost)

Incineration	• Reduce waste substantially by volume/weight • Generate energy • Need small space, reduce burden of landfill	• High capital and operational costs • Emission of hazardous substances (Dioxin, etc.) • More stringent in operation and control
Land filling	• Final and indispensable disposal of wastes, • Final and indispensable disposal of wastes, • Relatively easy to build and operate	• Suitable sites become scarce worldwide • Cost is increasing significantly due to higher environmental and sanitary requirement • Leachate and gas emission problems

Integration of biodegradable plastics with disposal infrastructures, (Song et.al 2009)



Examples of Biopolymers

Polysaccharides (plant/algal)
< Starch
< Cellulose
< Agar
< Alginate
< Carrageenan
< Pectin
< Various gums (e.g., guar)

Polyesters
< PLA (polyactic acid)
< PHAs ((polyhydroxyalkanoates)

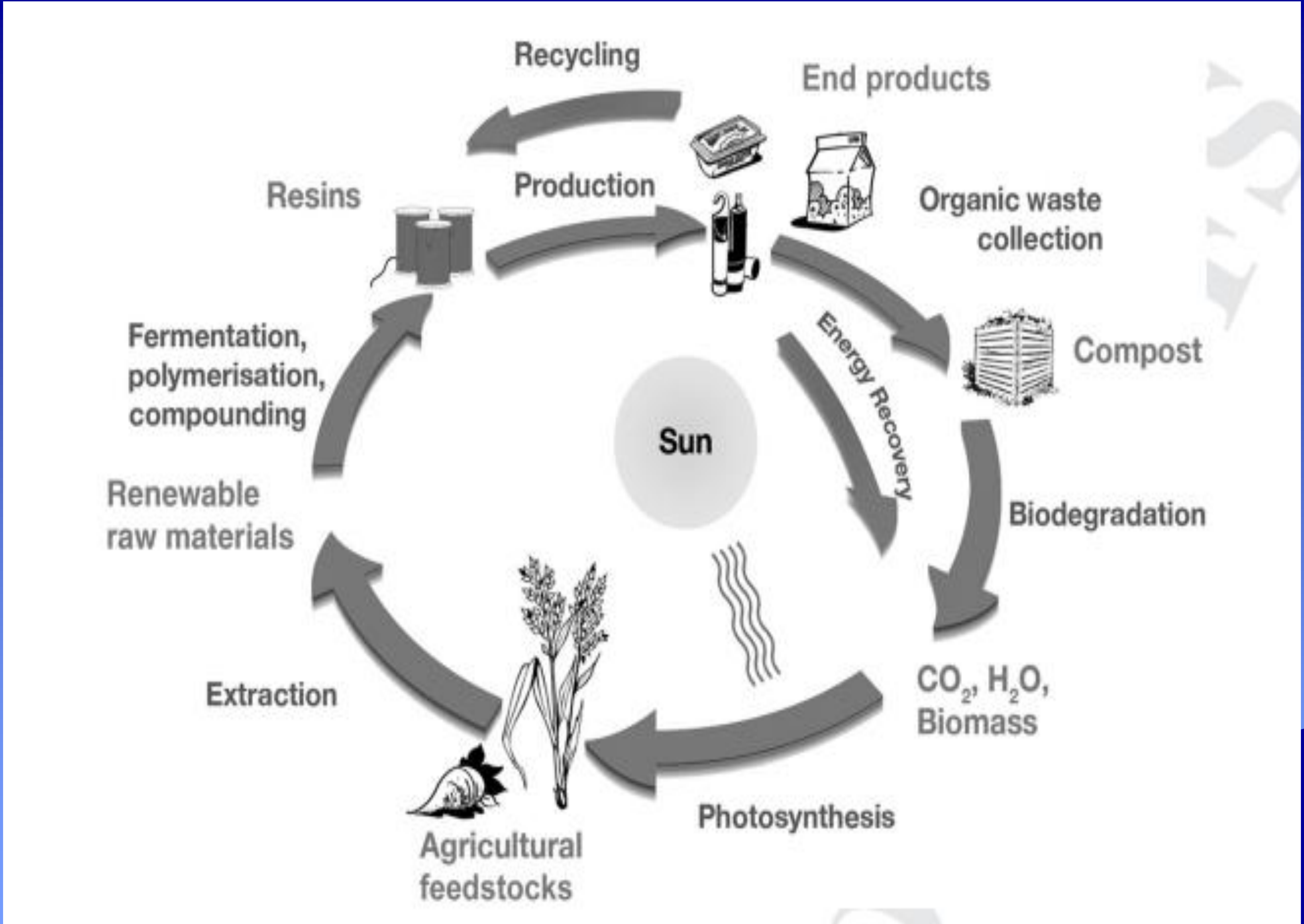
Proteins
< Silks
< Collagen/gelatin
< Elastin (found in cows and pigs)
< Reslin
< Adhesives
< Soy, zein from corn, wheat gluten, casein
< Serum albumin

Table 4. Overview table of suitable fossil and bio-based plastics for different property requirements.

Properties	Fossil plastic	Bio-based plastic
Flexibility and water barrier	PE	Bio-PE
Flexibility	PE	Starch based blends, Biodegradable polyesters
Transparency, stiffness, barrier properties	PET laminate or multilayer oxygen scavenger	PLA provided with SiOx barrier
Transparency, stiffness	PS, PET, PP	PLA
Stiffness	PS, PET	PLA, starch blend, Paperfoam

Table 5. Overview table of suitability of bio-based plastics for different types of applications.

	Film	Rigids (Trays/Cups)	Bottles	Other
PLA	e.g. (cut) vegetables & fruits, flower wraps, bread bags, shrink films. Not for long shelve life products, unless barrier laminates are used.	Salads, vegetables, fruits, dairy products, bakery, drinking cups, meat. Avoid storage of empty trays and cups at high temperatures.	Not a preferred material. Used in small water bottles and chilled, short shelf life juices and dairy products, and wine bottle capsules. Needs barrier materials for further applications.	Compostable teabags and coffee capsules. Coated paperboard (coffee cups) and other service ware. Foamed trays and boxes.
Starch blends	Food waste bags, translucent grocery bags. Vegetables and fruits. Mulch films.	Vegetables and fruits. Coffee capsules	N.a.	Loose fill foams. Service ware. Labels.
Cellulose based	Cellophane, candy wrapping	N.a.	N.a.	Some cellulose acetate in cutlery
Biodegradable polyesters	Grocery bags. Vegetables and fruits. Frozen produce.	Vegetables and fruits (non- transparent)	N.a.	Biodegradable nets. Coated paperboard. Particle foam. Coffee capsules.



Bioplastics lifecycle (European Bioplastics 2008

Renewable

Consumed feedstock is described as renewable when it is derived from resources which are naturally replenished on human timescale, in contrast to fossil oil which requires millions of years to be formed. Bio-based feedstock is renewable as long as new crop cultivation balances harvesting. For instance, peat is not considered renewable due to slow regeneration rate, while tropical hardwood is renewable when well managed.

Cellulose is the most abundant natural polymer on earth and is an almost linear polymer of cellobiose residues. Strongly hydrogen-bonded crystalline microfibrils and fibers are formed due to the regular structure and array of hydroxyl groups. It is mostly of plant origin and a familiar example is paper.