Combattere lo spreco alimentare

Recupero di biomasse di scarto per la produzione di bioplastiche microbiche

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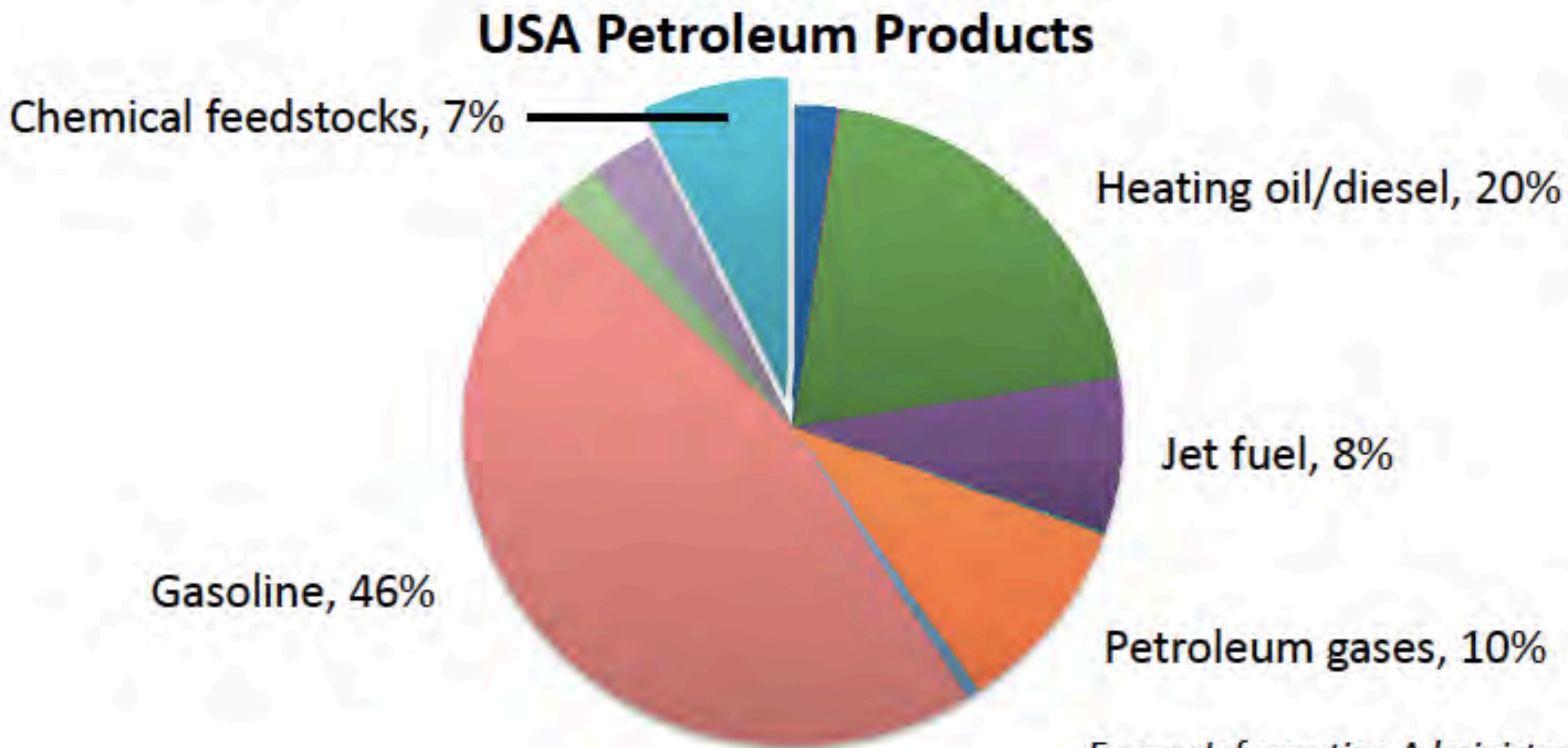
Biorefineries

- Chemical refineries convert petroleum into fuels and other chemical products
- A biorefinery should be able to supply equivalent products from agricultural feedstocks



Energy Information Administration, 2008 data

New materials?

- Before 1940 approx. 80 % of commercially available biodegradable plastic and its monomers were discovered and described
- 1938 Polyethylen
- In the 70s:
  - Oil crises (1973)
  - Set point for further development
- In the 80s:
  - Oil crises (1980) – pilot plants for bioplastics
  - Oxodegrable products – inhibited the further development?

Source: NARAYAN R. et al. 1994
www.n24.de 2010-02-17

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Definition of Bioplastic

- Up to now not fixed (CEN/TC 249/WG 17 planed release 2010)
- According to European Bioplastics:

  Plastic based on renewable resources

  Biodegradable polymers which meet all criteria of scientifically recognized norms for biodegradability and compostability of plastics and plastic products (EU: EN 13432 / EN 14995, US: ASTM D-6400, ISO 17088).
- NOT oxodegradable!

european bioplastics

Source: www.european-bioplastics.org 2010-02-17

BACKGROUND

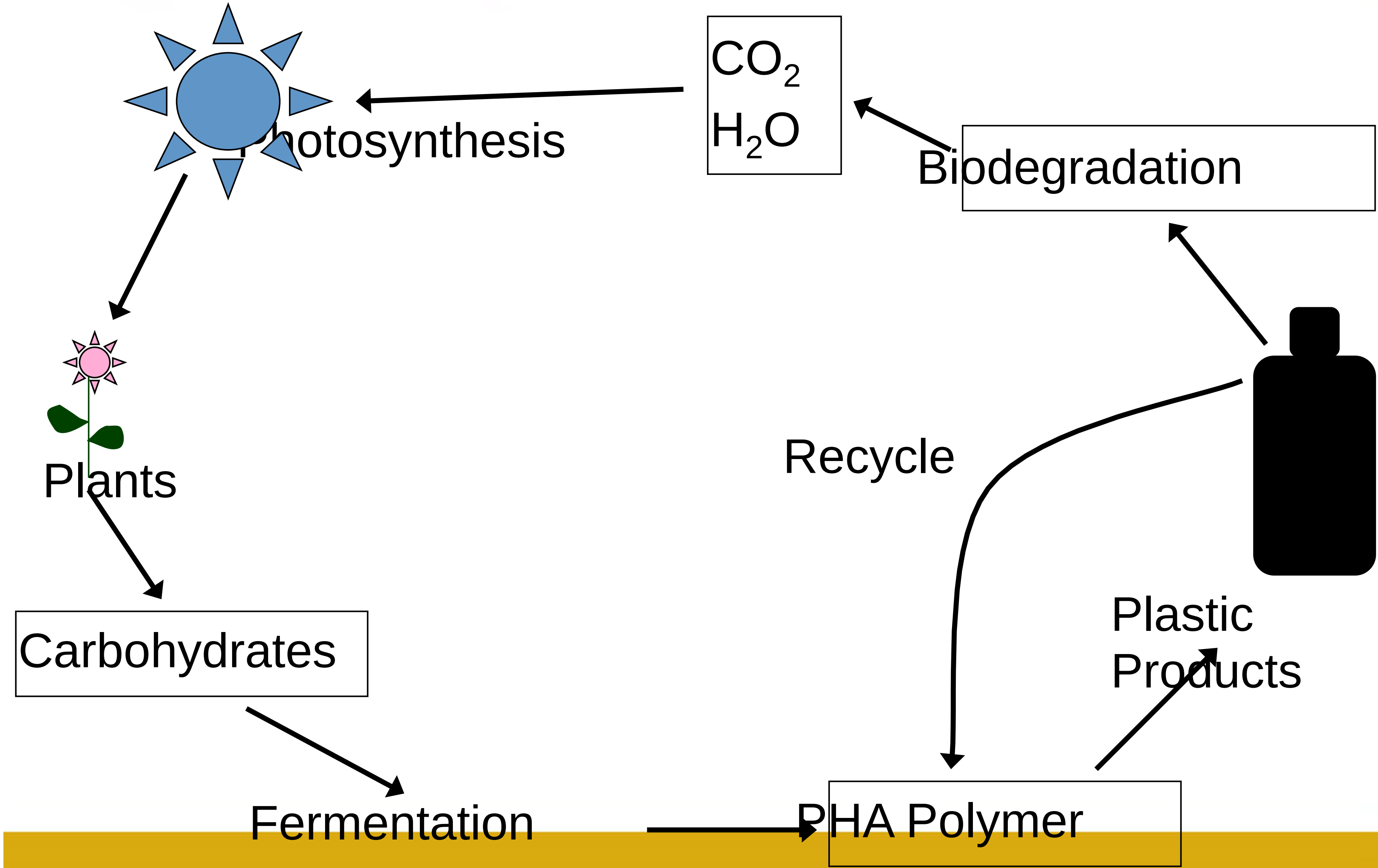
- **What are Bioplastics?**
  – Degradable polymers that are naturally degraded by the action of microorganisms such as bacteria, fungi and algae

- **Benefits Include:**
  - 100 % biodegradable
  - Produced from natural, renewable resources
  - Able to be recycled, composted or burned without producing toxic byproducts

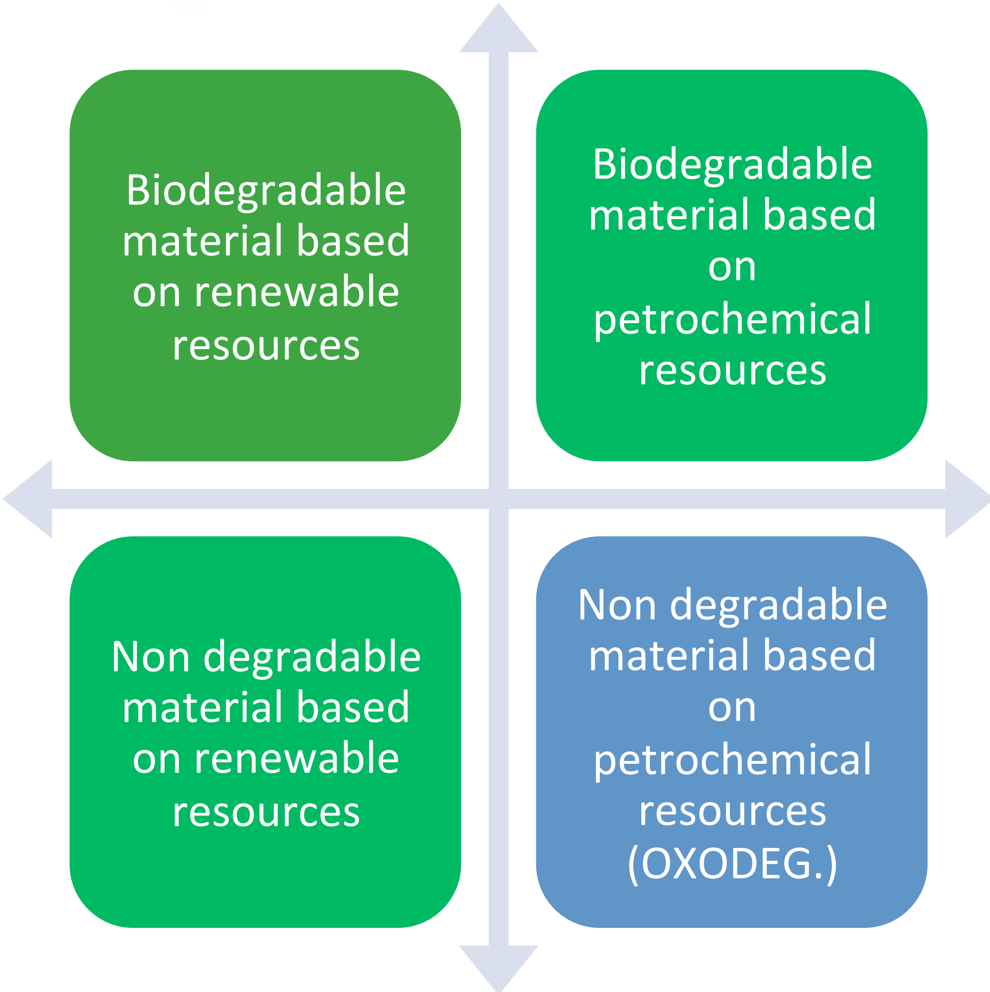
When Plastics are „GREEN"?

Biobased	The production of the building blocks is based on renewable resources; the polymerization of the monomers may occur chemically or biotechnologically.
Biodegradable	The 90% of the carbon of the plastic is metabolized within 180 days. (standardized norm EN-13432)
Compostable	If not more than 10% of the plastic material remain in a sieve of 2mm pore size after 180 days of composting . (standardized norm EN-13432)
Biocompatible	Using standardized methods for assessing the ecotoxicity of the (plastic) material, it must not feature any negative impact on living organisms or the involved environment. (standardized norm ISO 10993)

CARBON CYCLE OF BIOPLASTICS



Definition of Bioplastic

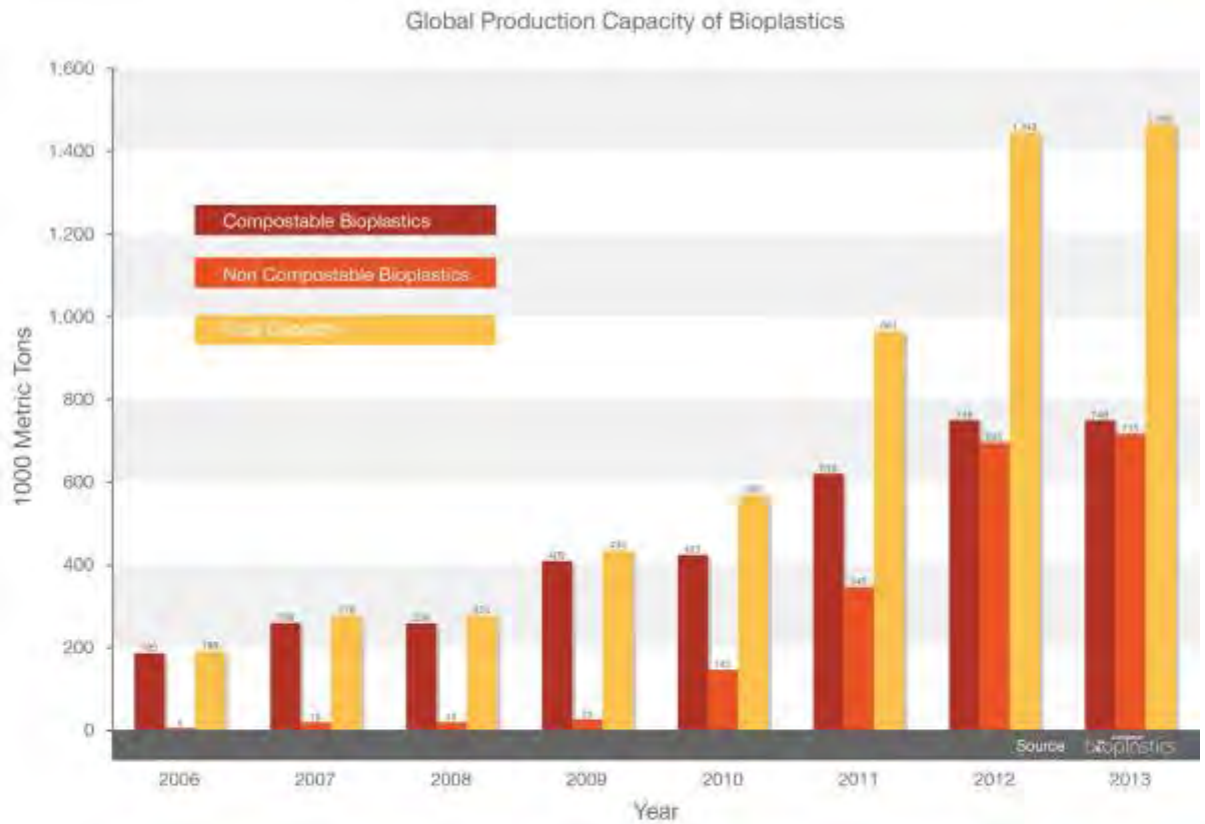


IMPORTANCE

- 2003- North America
  - 107 billion pounds of synthetic plastics produced from petroleum
  - Take >50 years to degrade
  - Improper disposal and failure to recycle → overflowing landfills

Development of the market

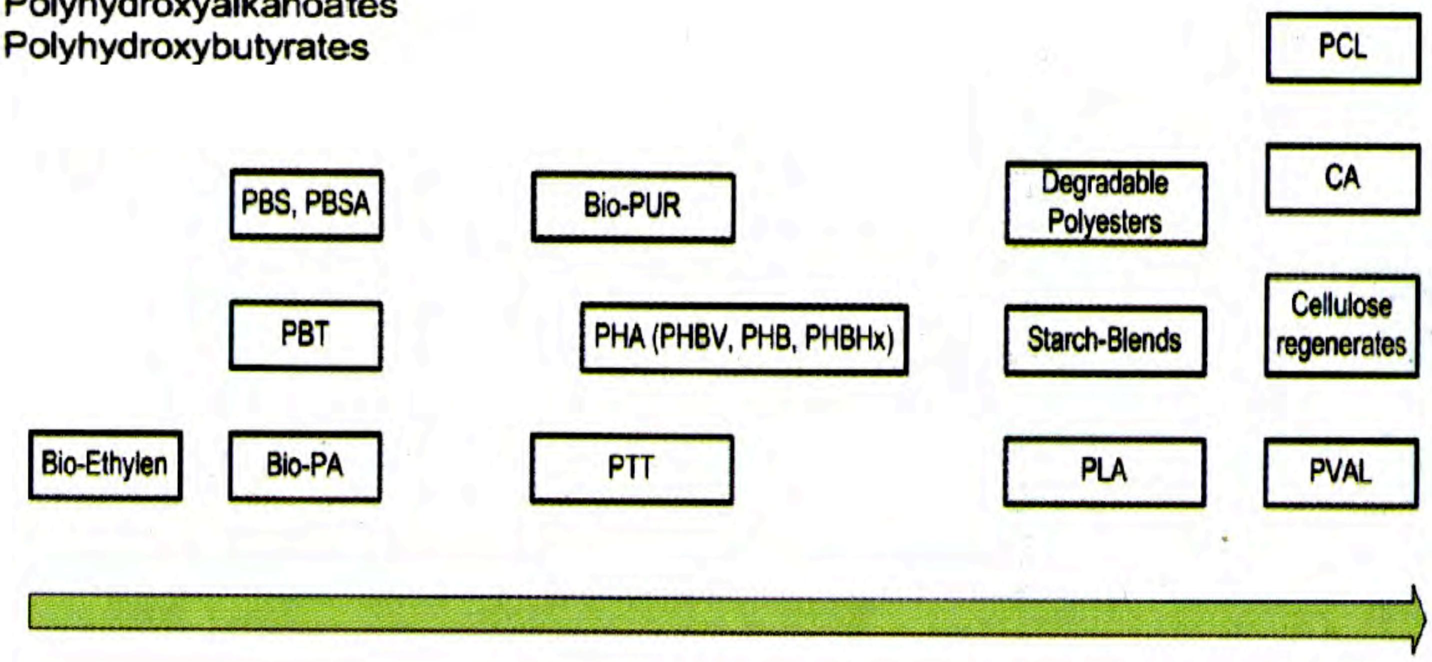
- Capacity 2009 400.000 t worldwide
- Small market, but high growth rates up to 10 %



Source: www.european-bioplastics.org 2010-02-17

State of development

CA: Cellulose acetates
PA: Polyamides
PBS: Polybutylensuccinates
PBT: Polybutyleneterephthalates
PCL: Polycaprolactones
PHA: Polyhydroxyalkanoates
PHB: Polyhydroxybutyrates
PHBV: Polyhydroxybutyrat-co-hydroxyalonates
PHBHx: Polyhydroxybutyrat-co-hydroxyhexanoates
PLA: Polylactides
PTT: Polytrimethyleneterephthalates
PUR: Polyurethanes



Research > Development > Pilot Plant > Commercialization > World-scale Plant > Industrial production

Source: bioplastics Magazine 03/2007

Biodegradable materials

- In general 4 materials commercially available
  - Starch-based polymers
  - Polylactic acid
  - Polyhydroxyalkanoates
  - Cellulose derivates

- Polymer blends and composites

Source: www.basf.com 2008-09-12
YU L. et al. 2006

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Starch-based polymers Mater-Bi®

- Maize and/or potatoe starch in blend with polycaprolactones and other biodegradable esters
- Europeas most common bioplastic

Source: www.novamont.com 2009-12-01

Starch-based polymers
Others

- Plantic®
  Starch from maize and hydroxypropyl, Plantic Technologies (AUS)
- Solanyl®
  Starch from potatoes, Rodenburg Biopolymers (NL)
- Bioplast®
  Starch blend, Biotec (DE)
- Biopar®
  Starch from potatoes and blends, Biop AG (D)

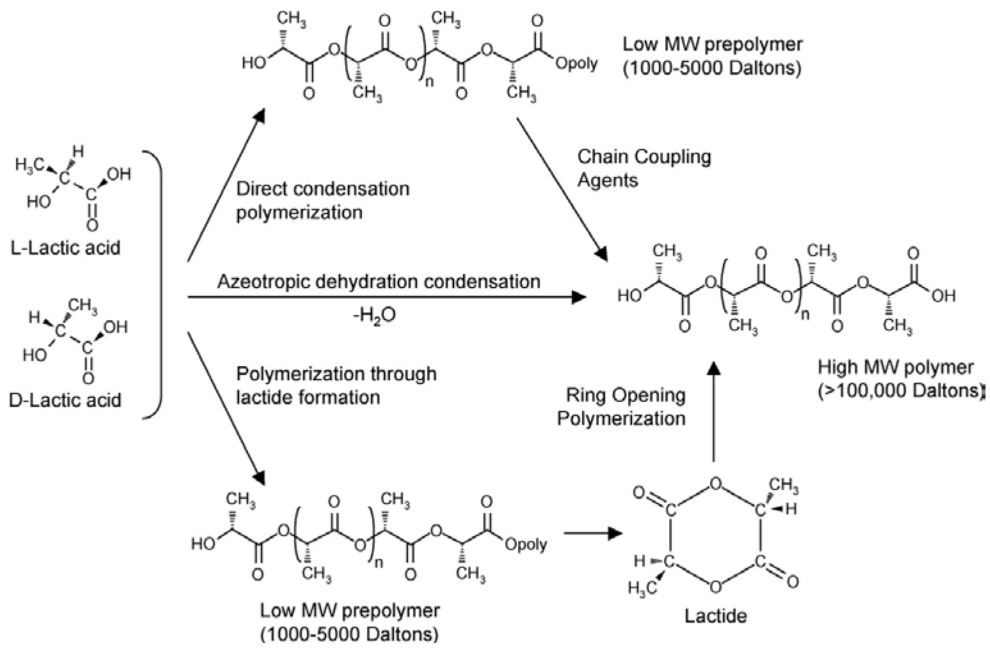
Similar to PE (converting)

Limited applications!

Source: www.plantic.com.au 2009-04-01

Polylactic acid

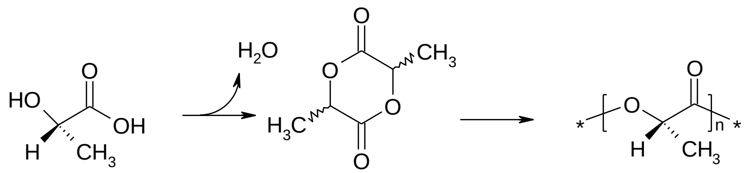
- Main producer: NatureWorks (US)
- Other Producers: Hycail (FI), Toyota (J) and Uhde Inventa (D)
- Glucose from maize or lactose from whey



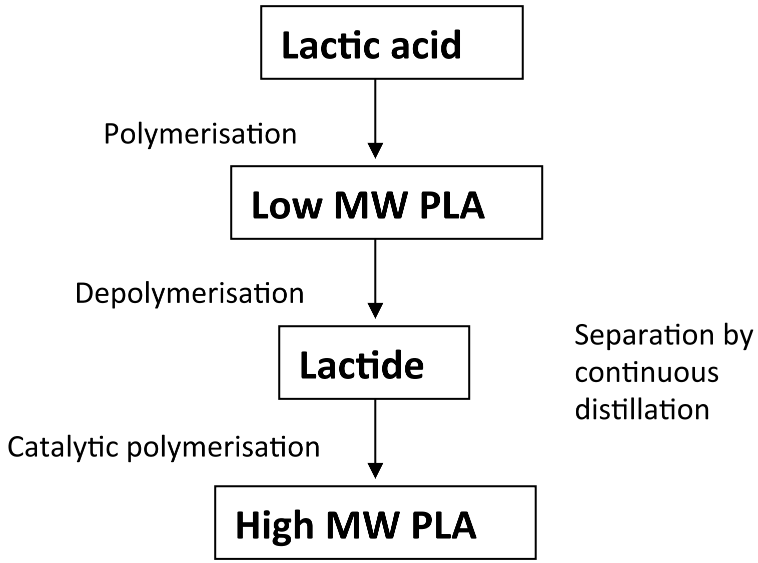
Source: LIM L.-T. et al. 2008

Polylactic acid

- Polylactic acid (PLA) is not a new polymer, it has been known since 1932.
- Producing low molecular weight PLA is a simple process, however, making high molecular weight PLA is a more complicated affair.
- Cargill-Dow has developed a novel process involving selective depolymerisation of low molecular weight PLA to a cyclic intermediate (lactide), which is purified by distillation.
- Catalytic ring opening of the lactide results in continuous controlled weight PLA preparation.



Lactic acid **Lactide** **poly(3,6-dimethyl-1,4-dioxan-2,5-dione)**



J. Lunt, Polymer Degradation and Stability, 59, (1998), 145-152

http://www.cargilldow.com/home.asp

Properties and uses of Polylactic acid (PLA)

- The PLA materials have mechanical properties that lie somewhere in between that of polystyrene and PET.

- Packaging
  - Films
  - Packaging foam
  - Containers (biodegradable)
  - Coatings for papers and boards
- Fibres
  - Clothing
  - Carpet tiles (Interface Inc.)
  - Nappies
- Bottles
  - Biodegradable bottles

http://www.cargilldow.com

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Polylactic acid blends

- Ecovio®

  45 % PLA + Ecoflex®, BASF (D)

- Ecovio® L-Foam

  75 % PLA + Ecoflex®, BASF (D)

- Bio-Flex®

  PLA + Copolyester, FKuR (D)

Similar to PET and/or PS (converting)

Sensitive to temperature!

Source: www.basf.com 2008-09-12
YU L. et al. 2006

Cellulose derivates

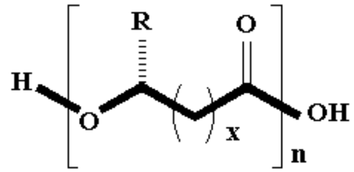
NatureFlex™ Innovia (UK)

Barrier coatings!

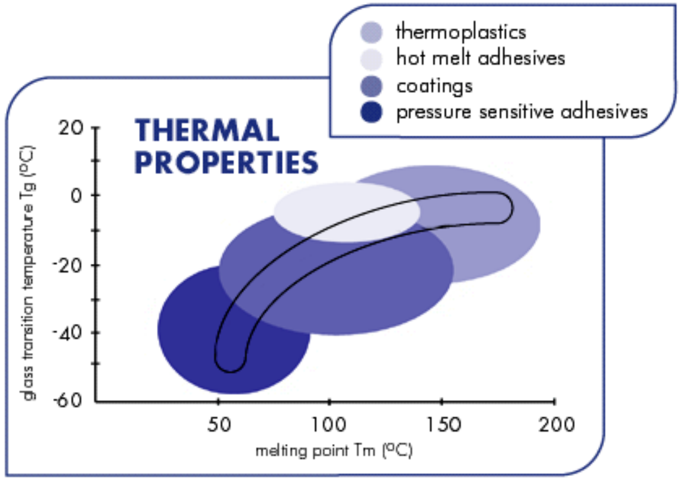
Polyhydroxyalkanoates

- Mirel™ Metabolix (US)
- Biomer™ Biomer (D)

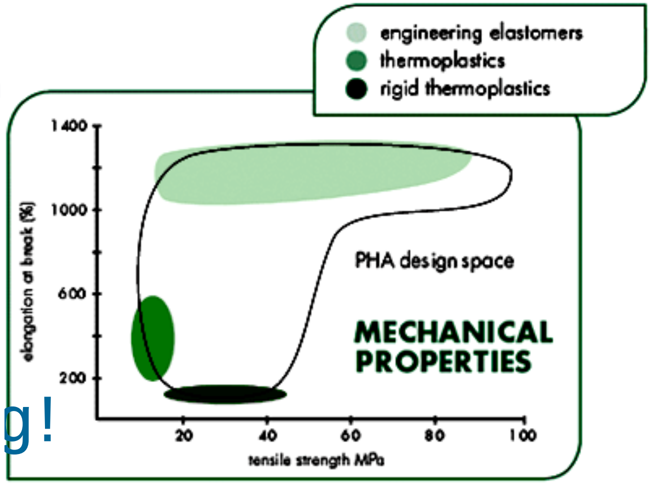
Fermentation of starch, rape, plant residues, etc.



PHB, PHV, PHBV, …



C g!

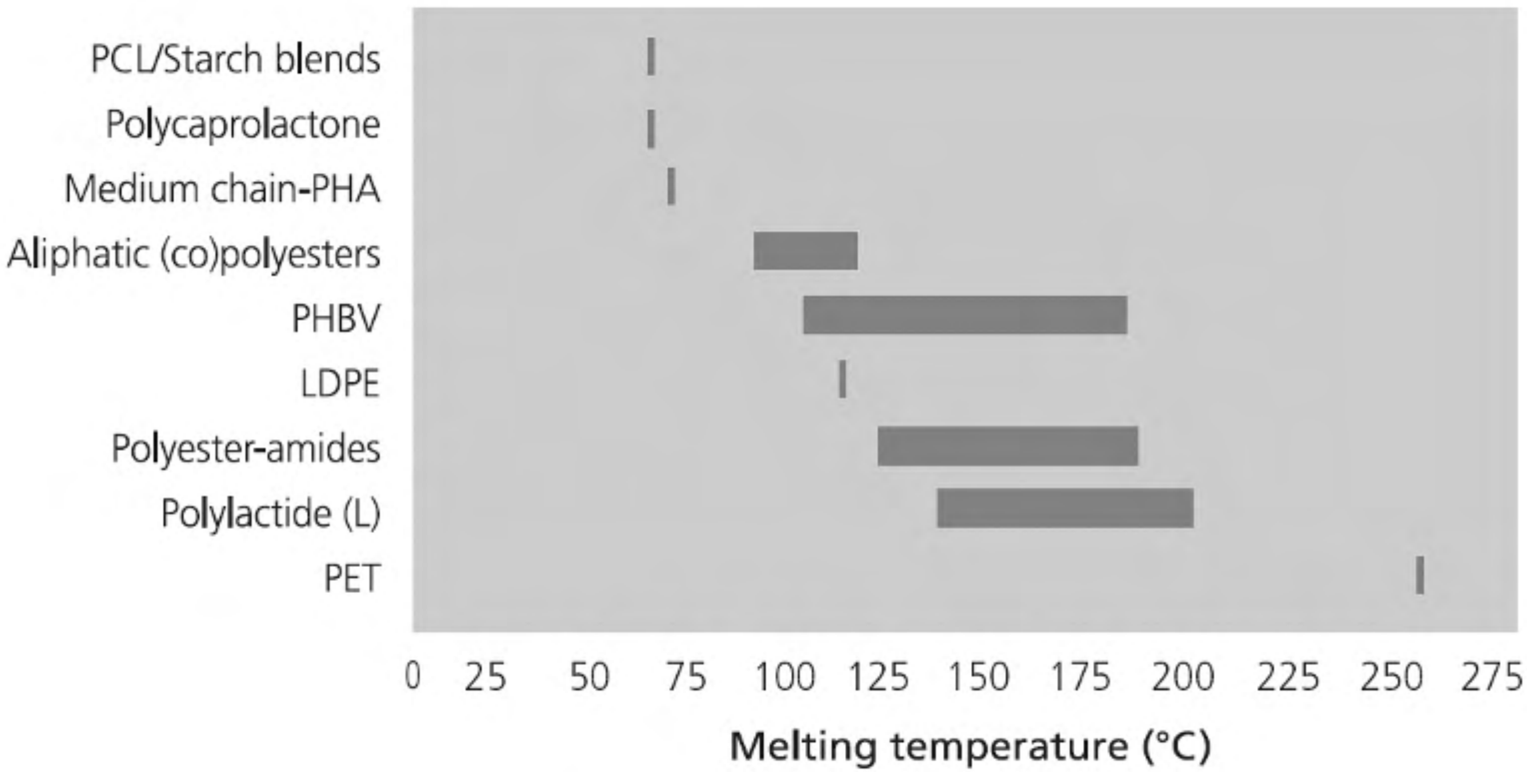


Source: www.metabolix.com 2008-09-12

Comparision

Thermal properties: Melting temperature

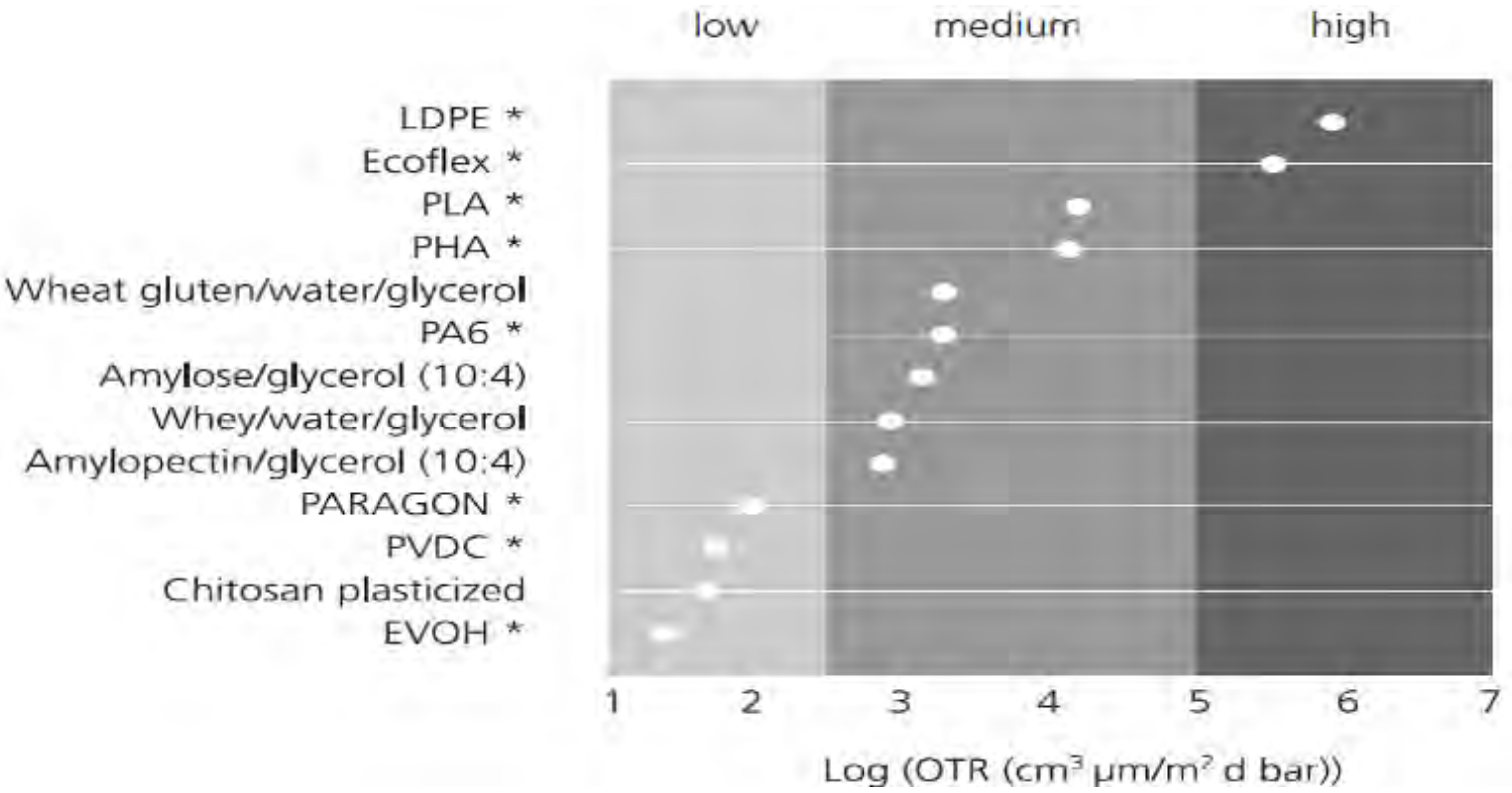
Biopolymers comparable with conventional plastics



Source: WEBER C. J. 2000

Comparision

Oxygen transmission rate
Biopolymers in the midfield

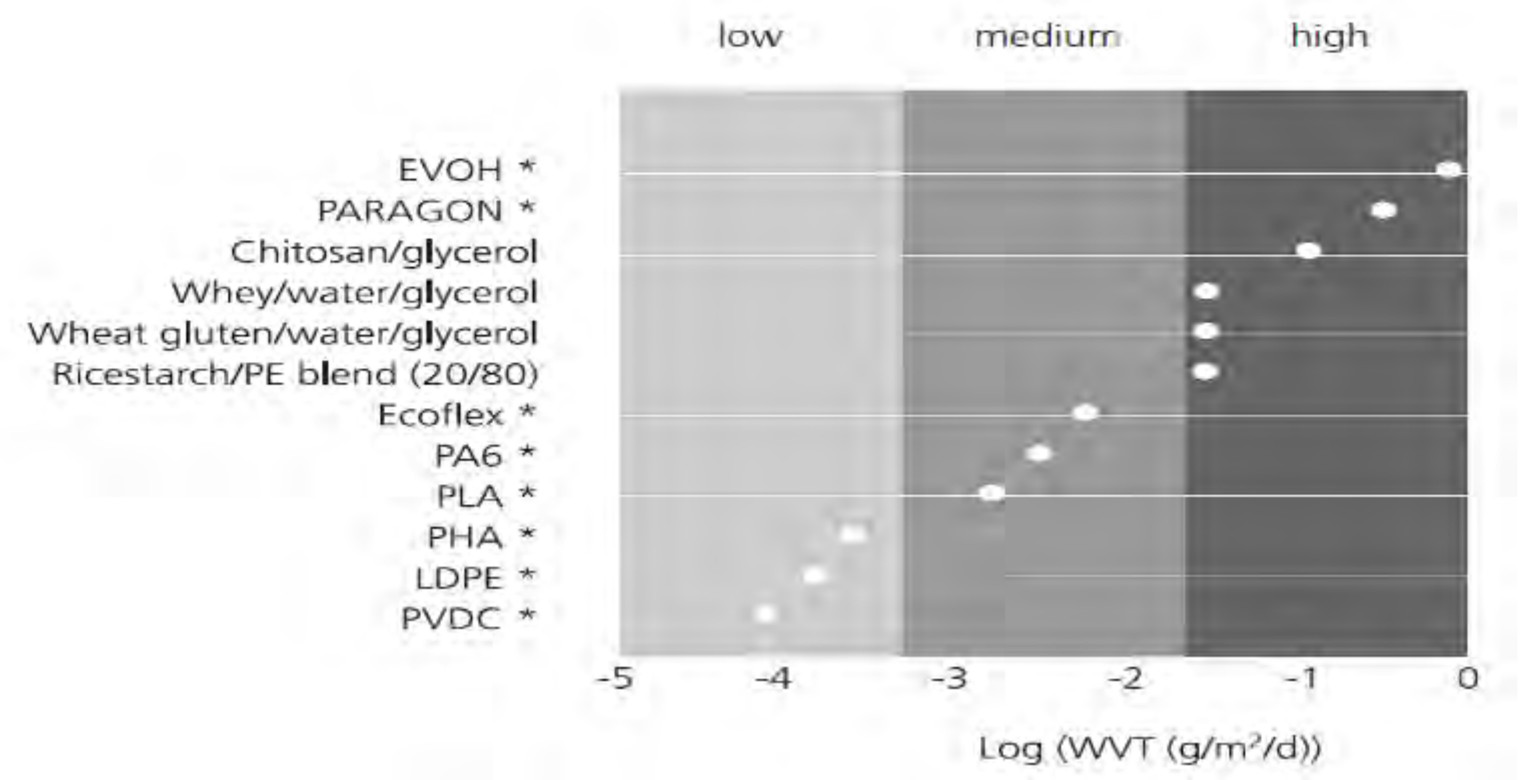


Source: WEBER C. J. 2000

Comparision

Water vapour transmission rate

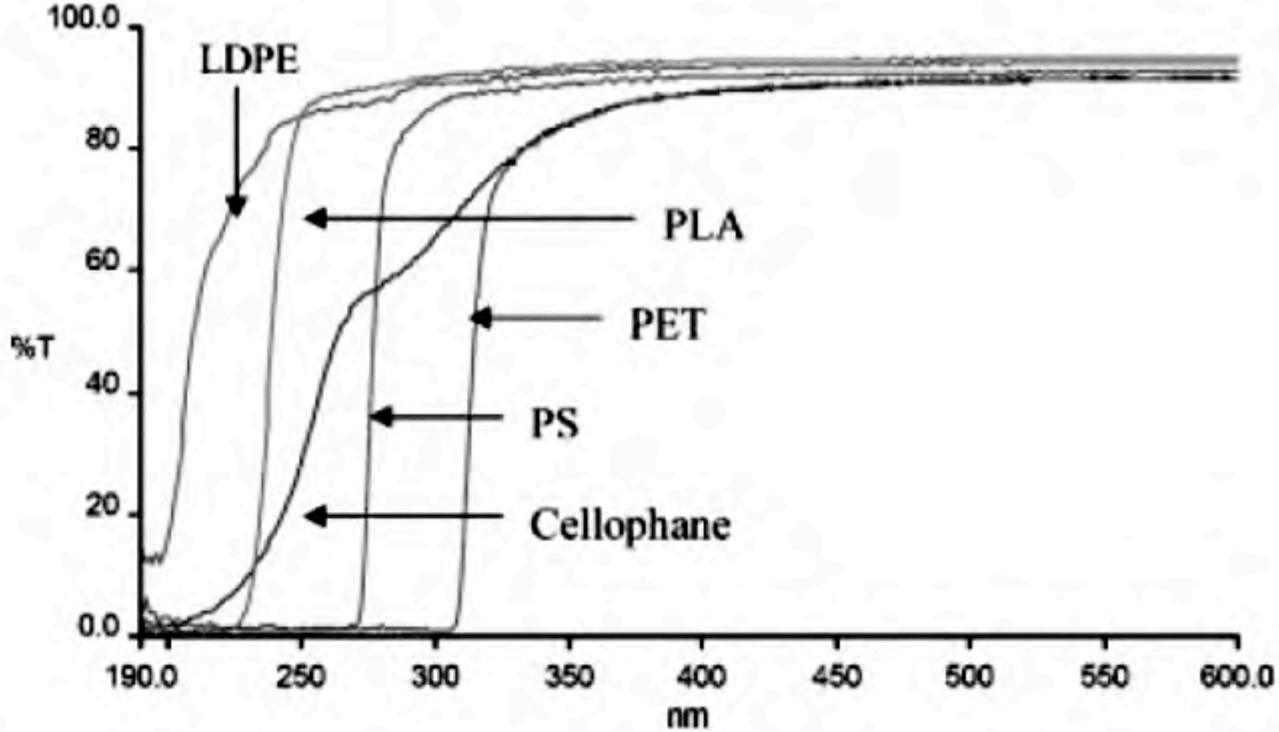
Biopolymers in the midfield



Source: WEBER C. J. 2000

Comparision

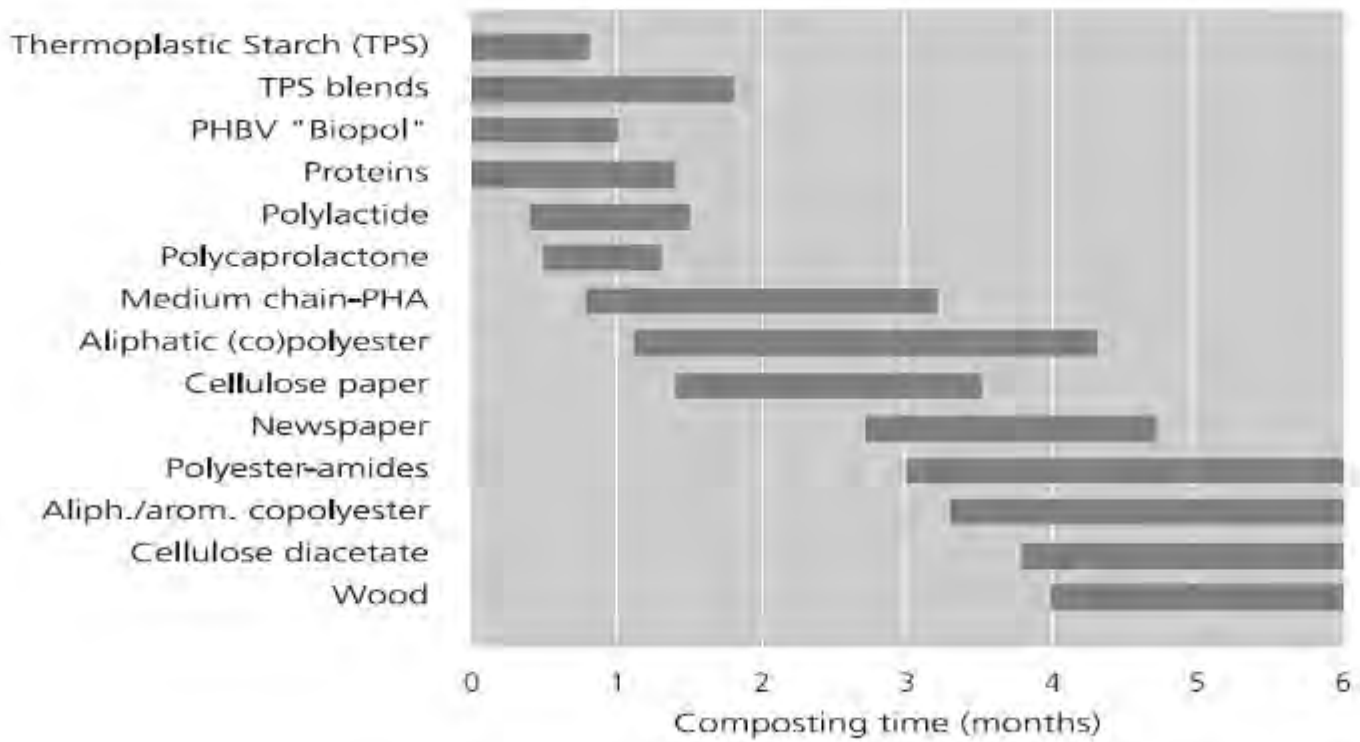
Transmission of UV-light



Quelle: Rafael Auras, R. et al.: An Overview of Polylactides as Packaging Materials. Macromolecular Bioscience. (2004), No. 4, p. 835–864

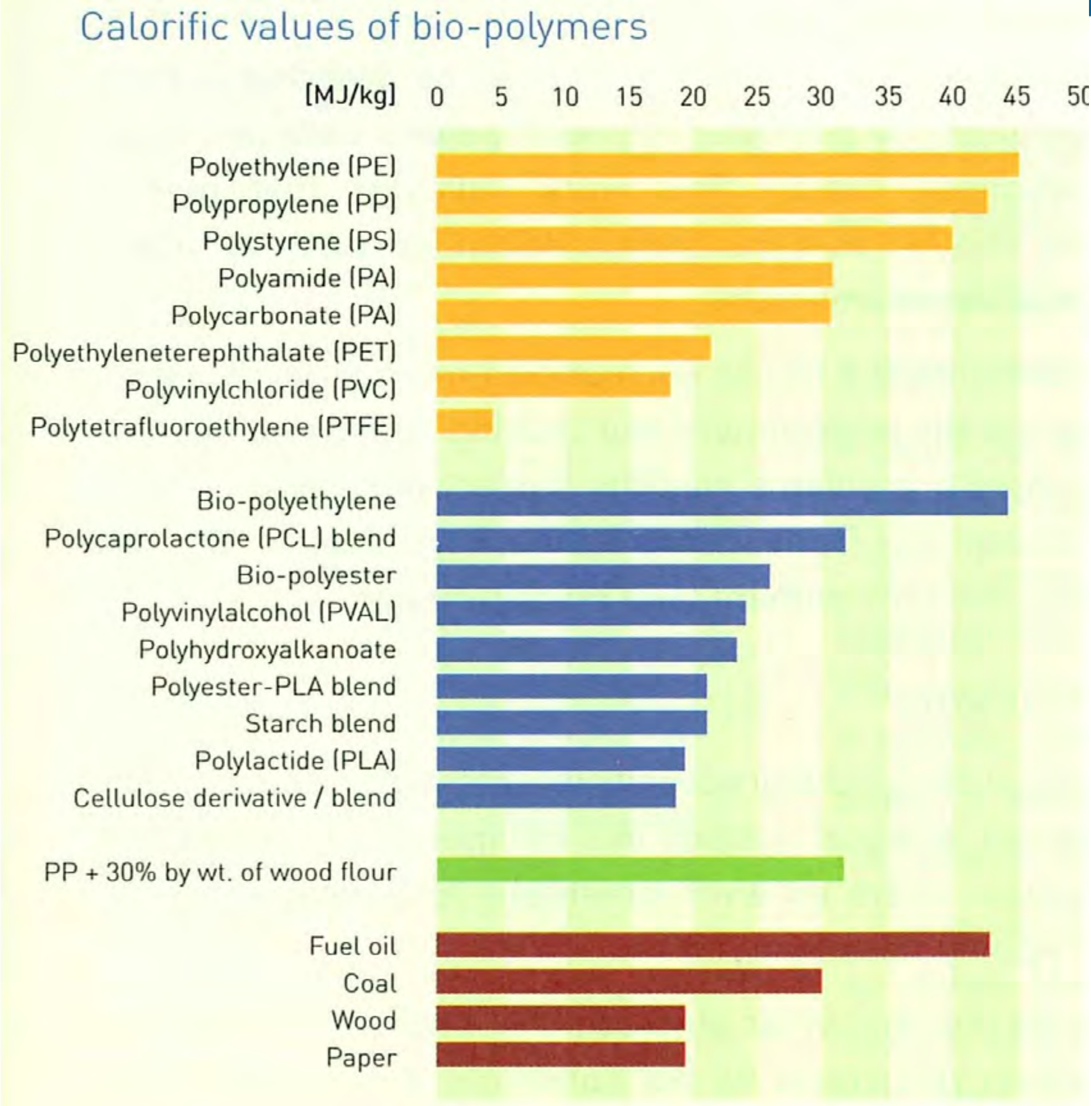
End of life

End of life
Composting?



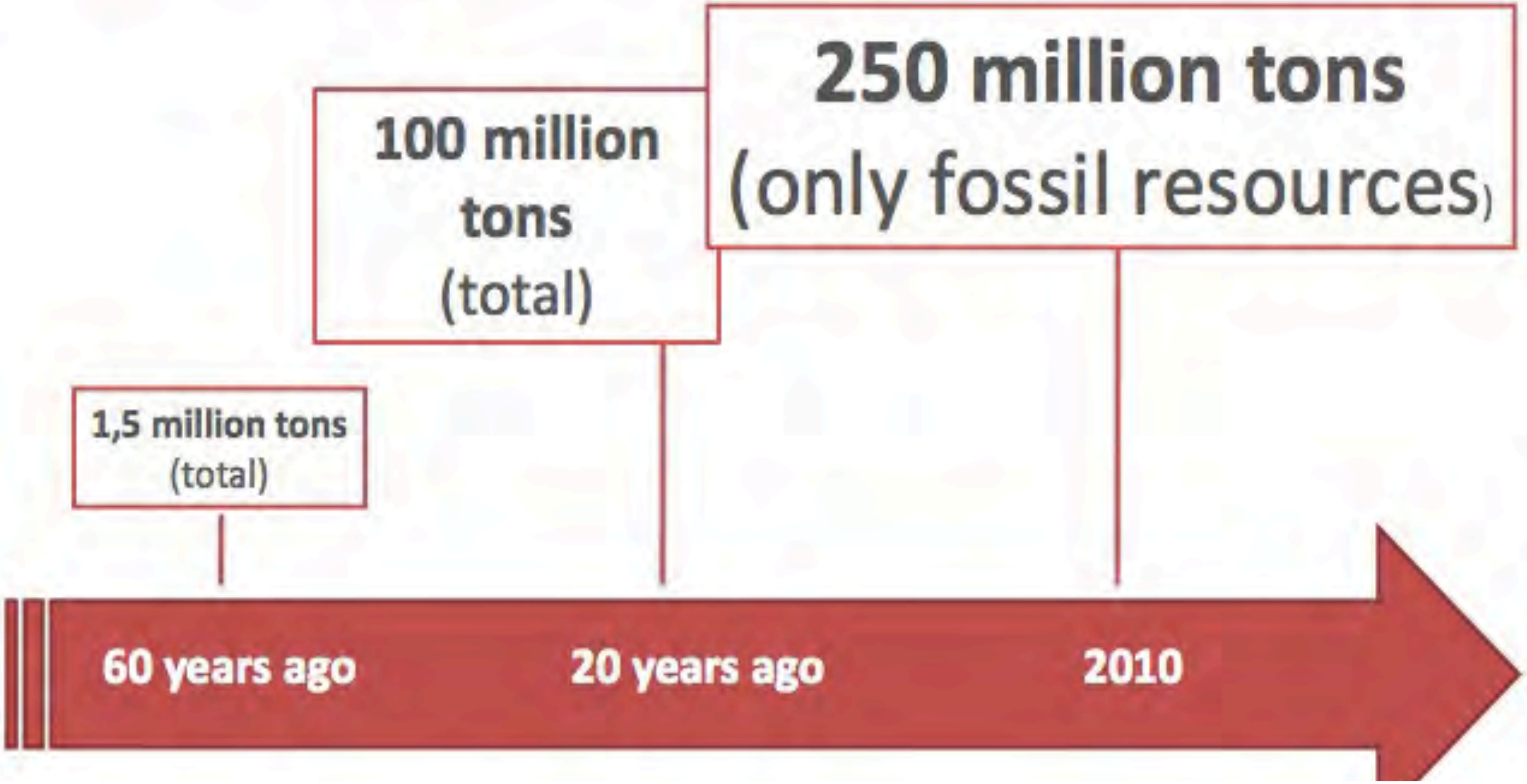
Source: WEBER C. J. 2000

End of life

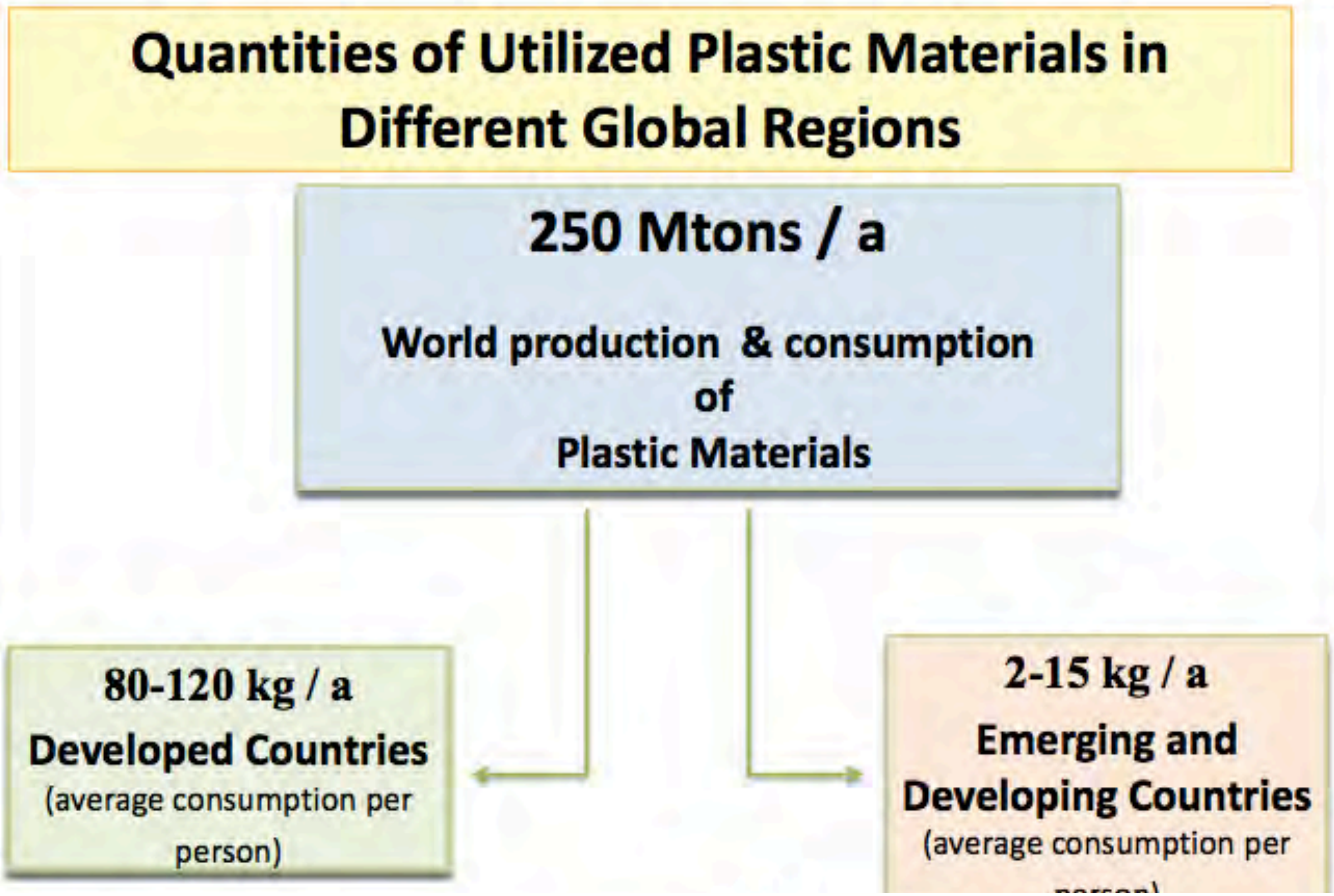


Source: ENDRES H.-J. 2009

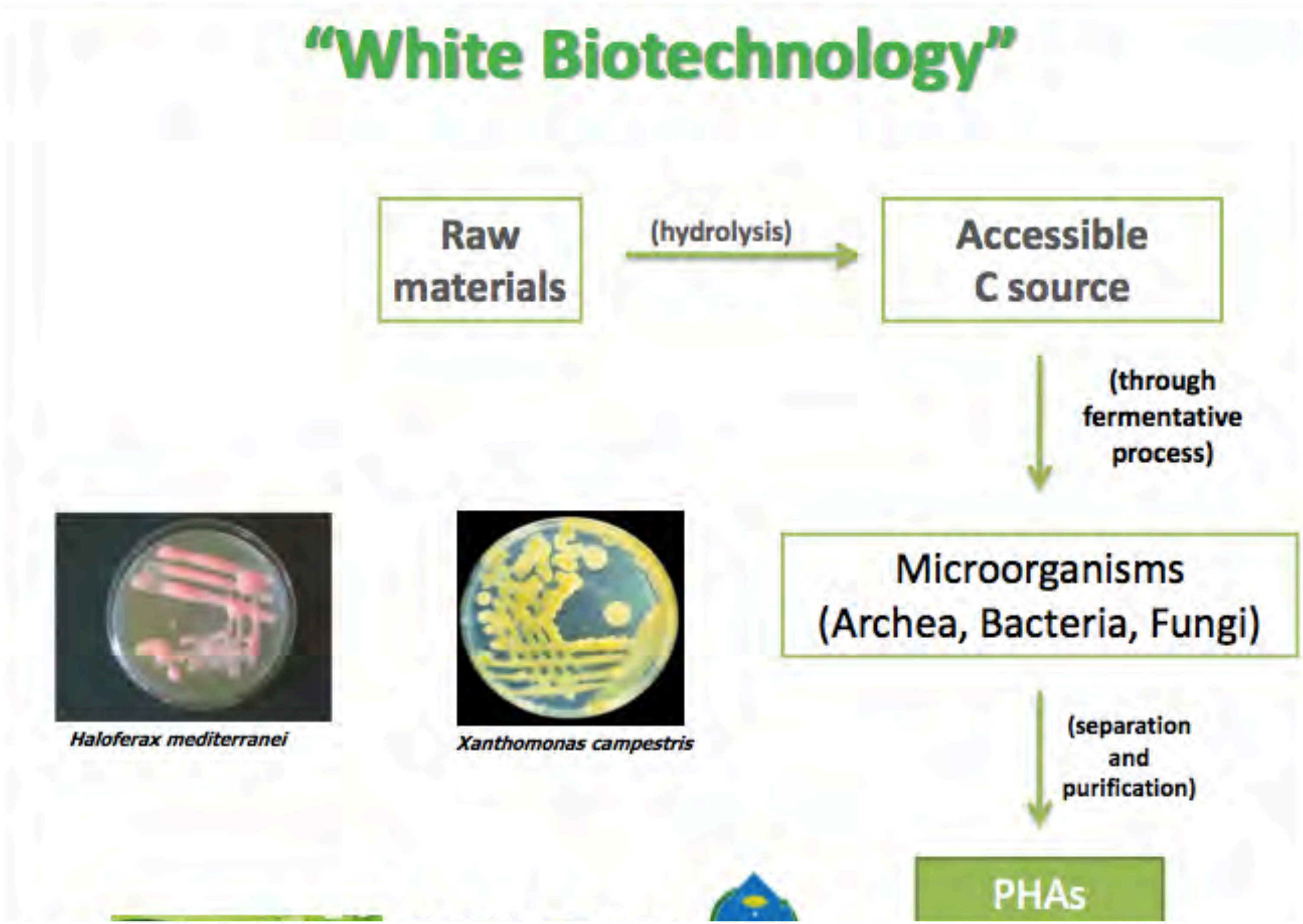
Nowadays, we live in the „Plastic Age"…



From ANIMPOL project, FP7



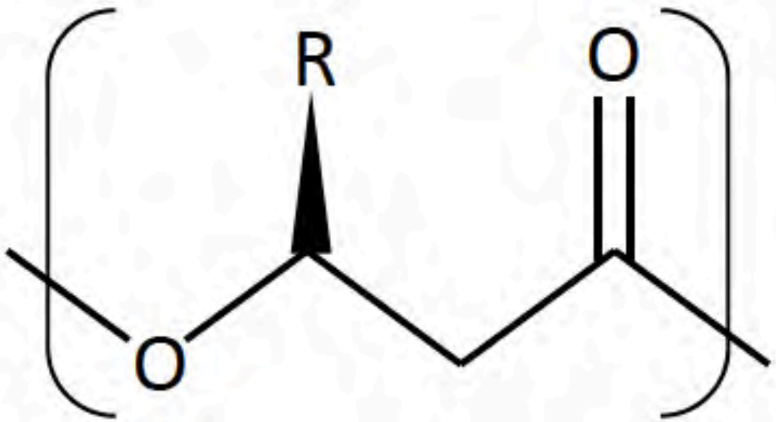
From ANIMPOL project, FP7



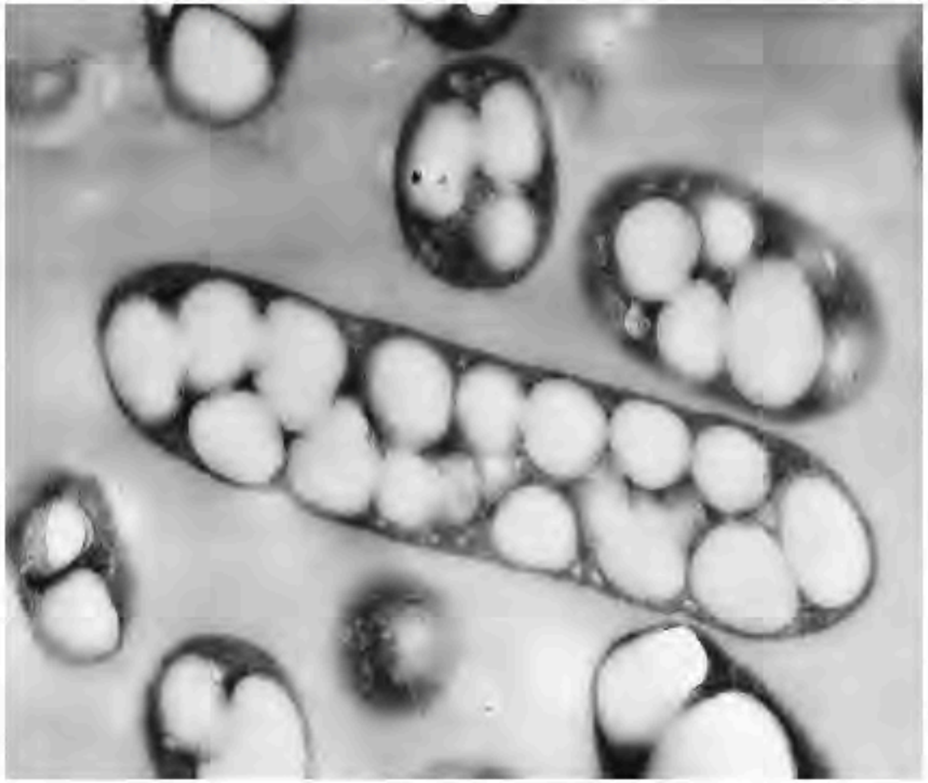
From ANIMPOL project, FP7

Polyhydroxyalakanoates (PHAs)

- Natural polyesters used for carbon and energy storage
- Renewable and biodegradable material



PHA chemical structure



Ralstonia eutropha H16 electron micrograph
Jiamin Tian

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RECOVERY OF PHAs

- PHA producing microorganisms stained with Sudan black or Nile blue
- Cells separated out by centrifugation or filtration
- PHA is recovered using solvents (chloroform) to break cell wall & extract polymer
- Purification of polymer

Eng. Life Sci. **2011**, *11*, No. 3, 222–237

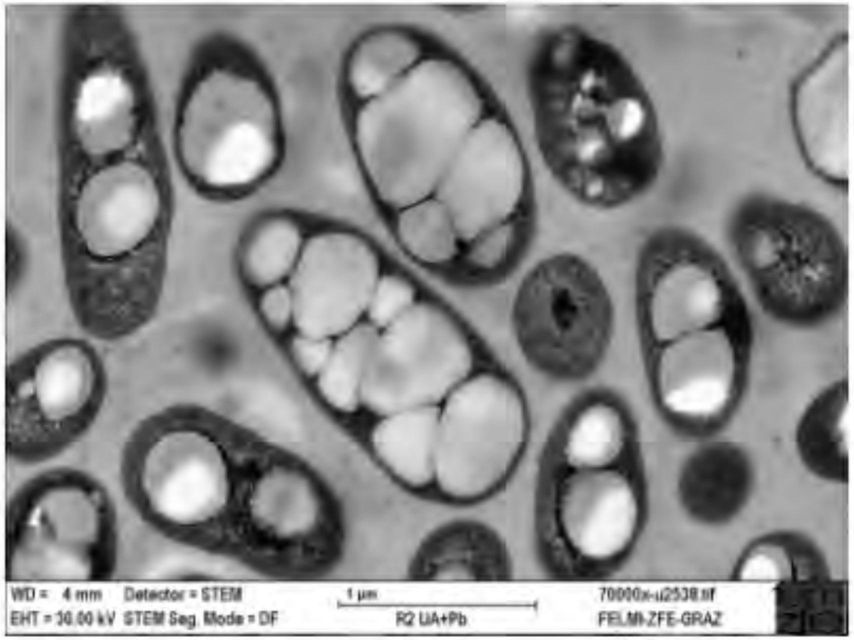

Figure 1. Electron microscopic pictures of PHA-rich *C. necator* DSM 545 cells cultivated in a continuous fermentation process on glucose. Magnification: 1/70 000; 48% of PHB in cell mass. The picture was kindly provided by Dr. Elisabeth Ingolić, FELMI-ZFE-Graz.

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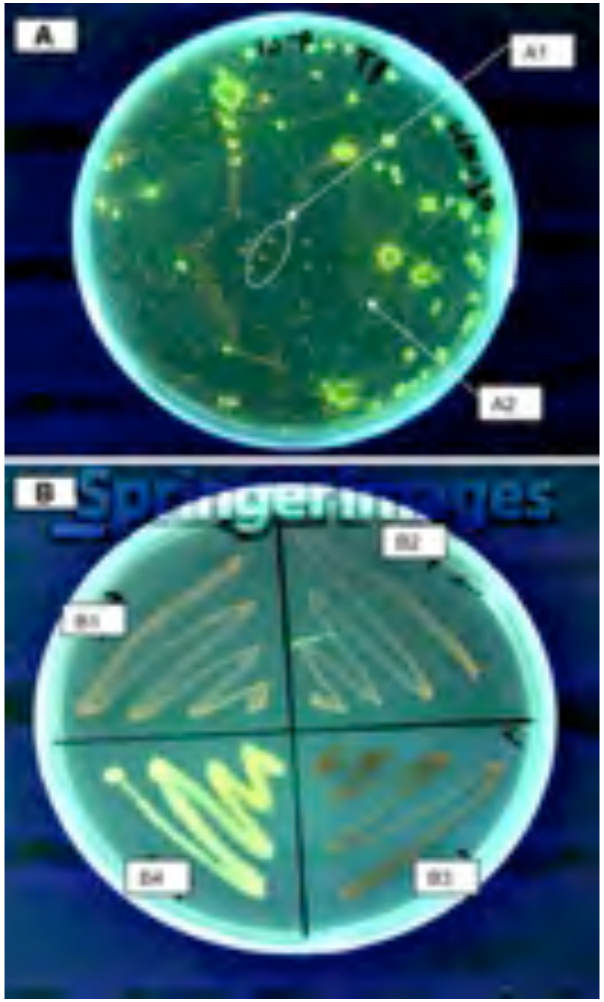
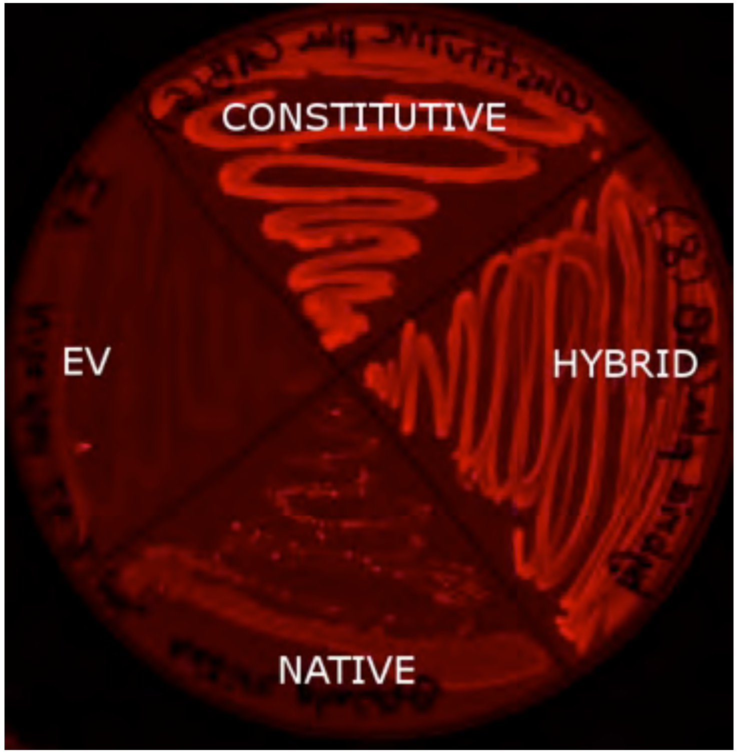
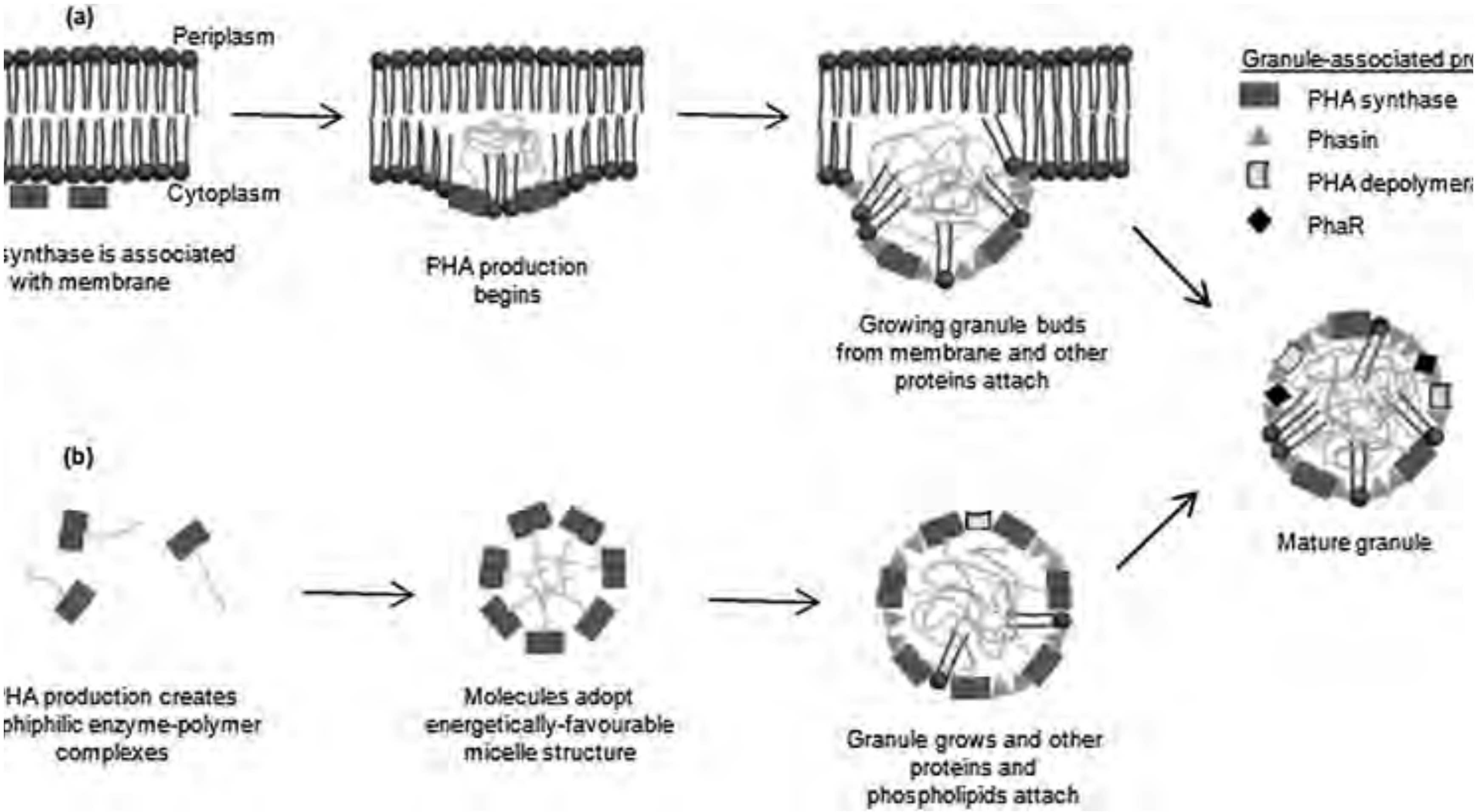
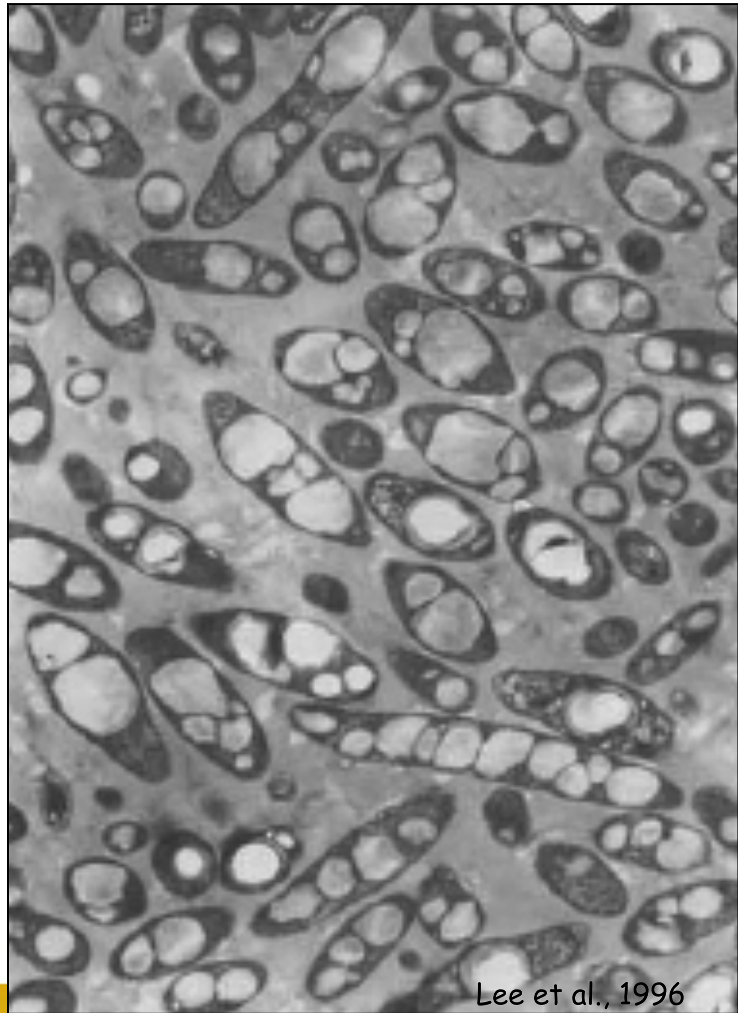





(a)
Periplasm
Cytoplasm
synthase is associated with membrane
PHA production begins
Growing granule buds from membrane and other proteins attach
Granule-associated pr
PHA synthase
Phasin
PHA depolymer
PhaR
Mature granule
(b)
HA production creates phiphilic enzyme-polymer complexes
Molecules adopt energetically-favourable micelle structure
Granule grows and other proteins and phospholipids attach

Polyhydroxybutyrate (PHB)

- Example of short-chain-length PHA
- Produced in activated sludge
- Found in *Alcaligenes eutrophus*
- Accumulated intracellularly as granules (>80% cell dry weight)



Lee et al., 1996

PHA Biosynthesis

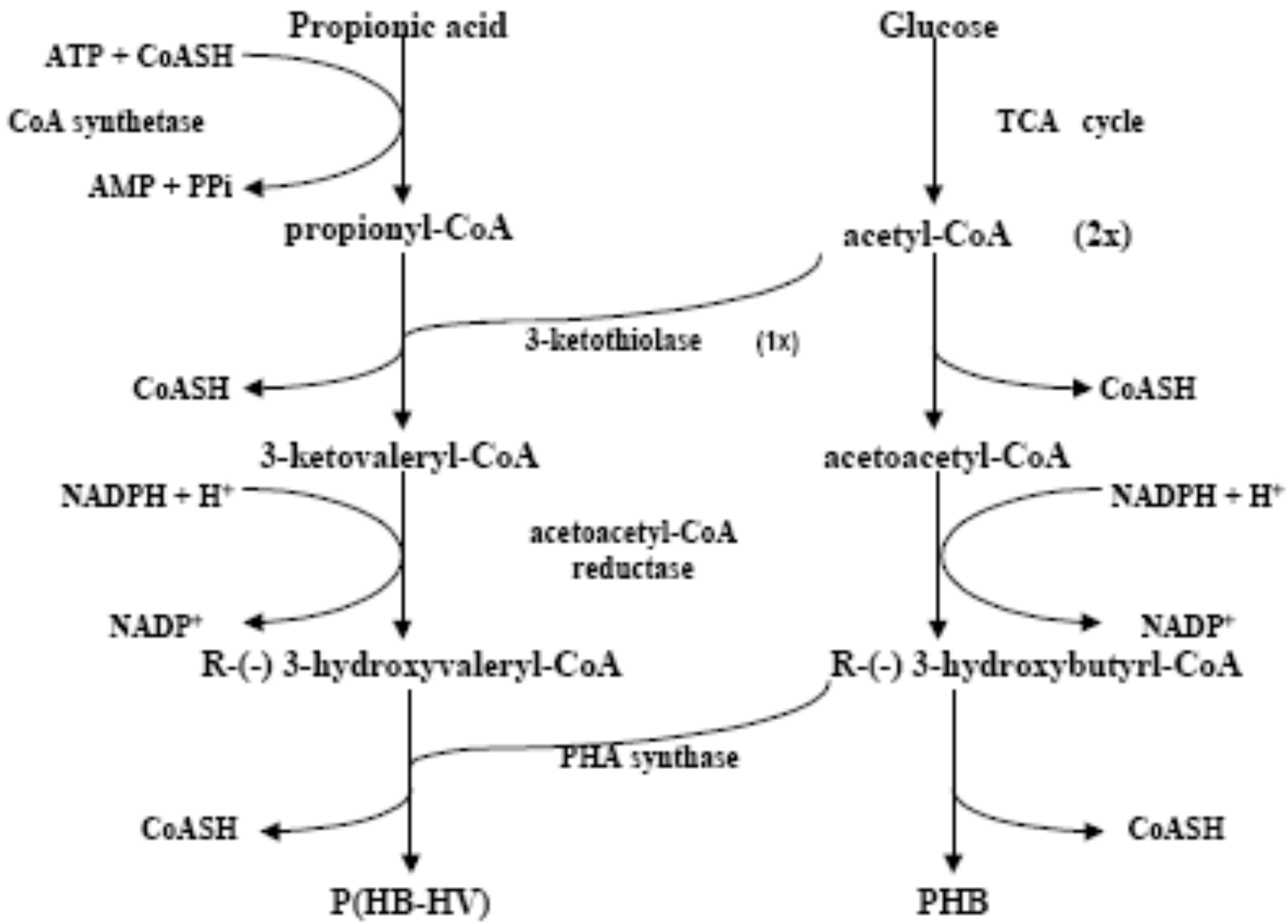


Figure 2. The biosynthetic pathway of PHB and P(HB-HV) in *Alcaligenes eutrophus*.

Ojumu et al., 2004

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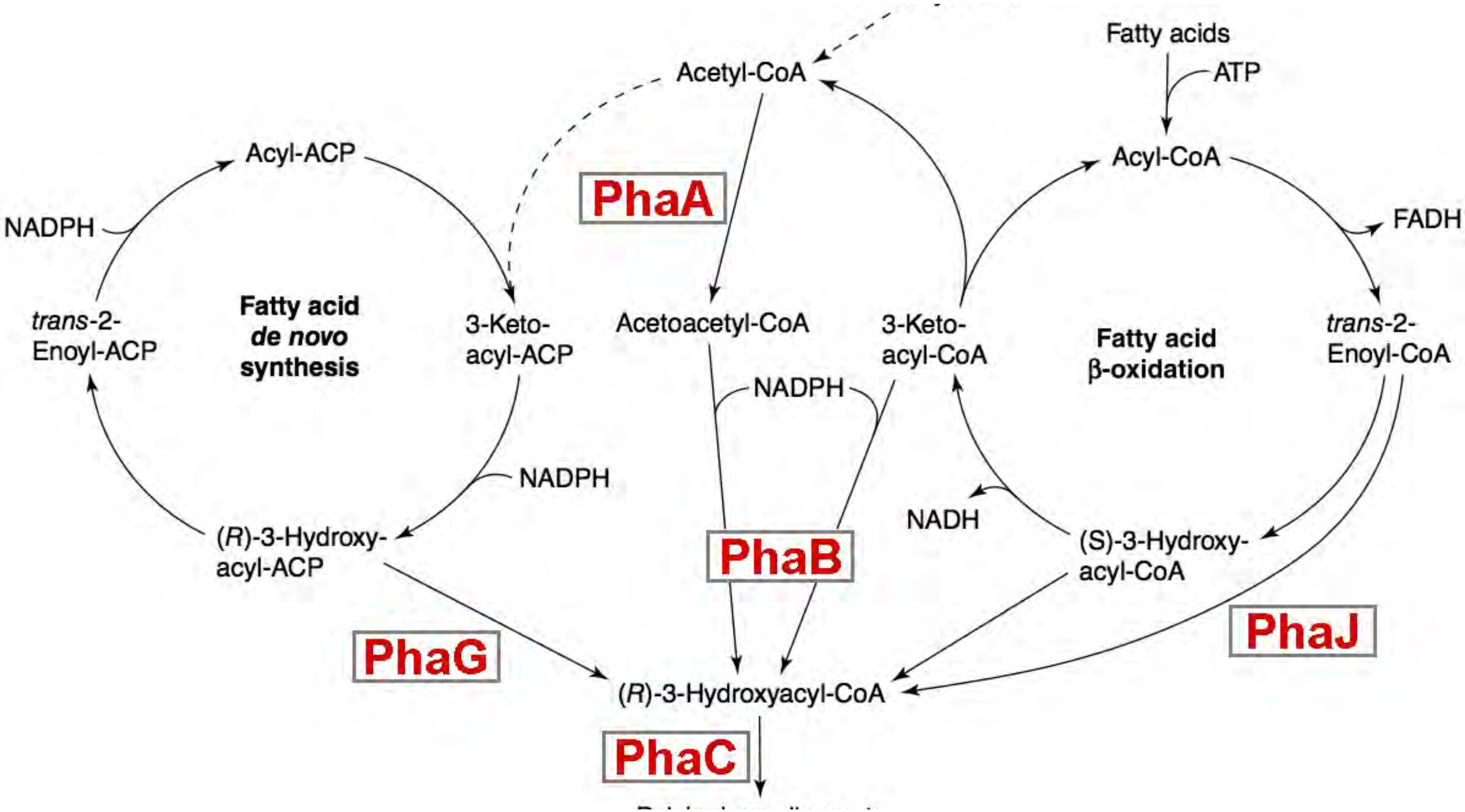
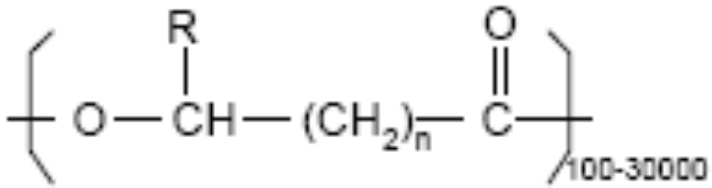


- Polyesters accumulated inside microbial cells as carbon & energy source storage



n =1	R =	hydrogen	poly (-3-hydroxypropionate)
		methyl	poly (-3-hydroxybutyrate)
		ethyl	poly(3-horoxyvalerate)
		propyl	poly (-3-hydroxyhexanoate)
		pentyl	poly (-3-hydroxyoctanoate)
		nonyl	poly (-3-hydroxydodecanoate)
n = 2	R =	hydrogen	poly (-4-hydroxybutyrate)
n = 3	R =	hydrogen	poly (-5-hydroxyvalerate)

Ojumu et al., 2004

POLYHYDROXYALKANOATES

- Produced under conditions of:
  - Low limiting nutrients (P, S, N, O)
  - Excess carbon
- 2 different types:
  - Short-chain-length 3-5 Carbons
  - Medium-chain-length 6-14 Carbons
- ~250 different bacteria have been found to produce some form of PHAs

Potential Applications of PHAs

Agro-Industrial	• carriers and matrices for controlled release of nutrients, fertilizers and pesticides; mulch foils etc.
Therapeutic	• controlled release of active pharmaceutical ingredients
Use of Chiral building blocks	• as synthons for synthesis of organic fine chemicals
Packaging Materials	• compostable after utilization
Surgical	• implants

From ANIMPOL project, FP7

Applications for PHA Polymers

PHAs

Commodity

- Bulk polymer
- Sustainable
- Single use disposable items
- Solvents/Chemicals
- Paper coatings

Specialty

- PHA Latexes
- Film Forming
- Unique Properties
- Solvent Free

Medical

- Drug Delivery
- Orthopedic
- Hypoallergenic
- Nutrition
- Tissue Engineering

Commodity Plastic Applications

Pipette Tip Refill Base

Metabolix & VWR

Golf Tee

Metabolix

Gift Card

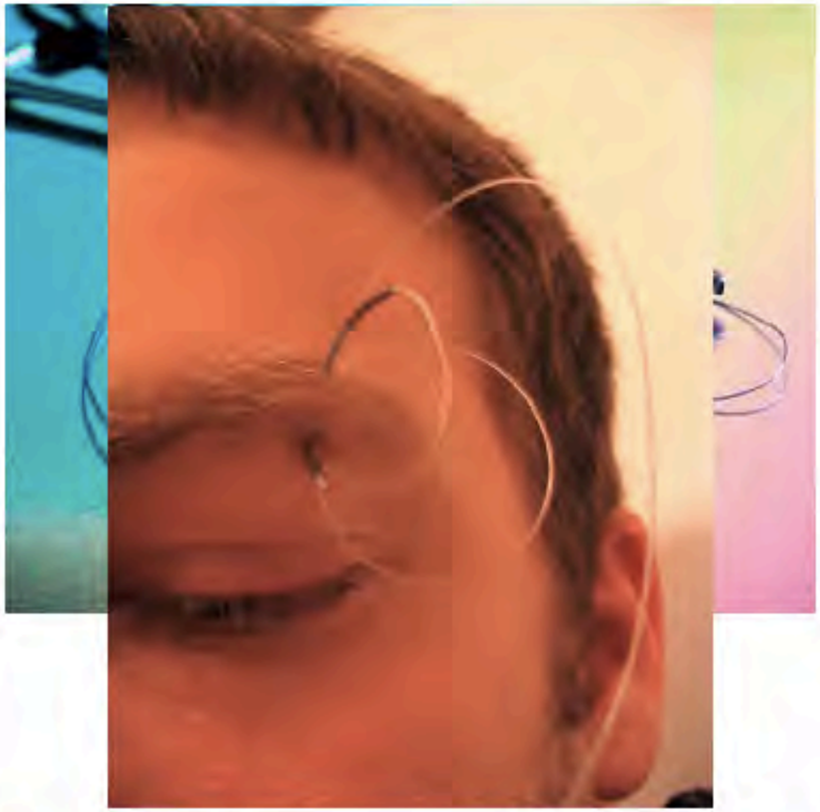
Metabolix & Target

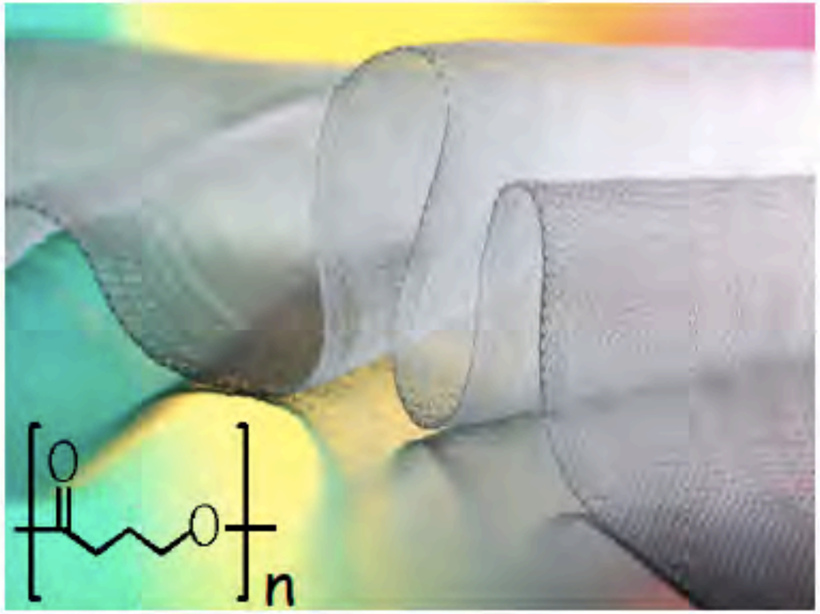
Other products: biodegradable compost bags, ground covers, etc.

APPLICATIONS

- Industry
  - Products, films, paper laminates & sheets, bags and containers
  - Automobiles
- Medical
  - Sutures, ligament replacements, controlled drug release mechanisms, arterial grafts…
- Household
  - Disposable razors, utensils, diapers, feminine hygiene products, containers…

Biocompatible medical supplies

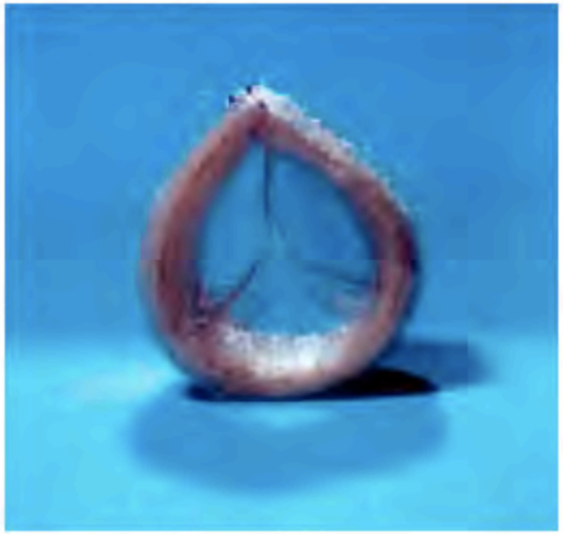


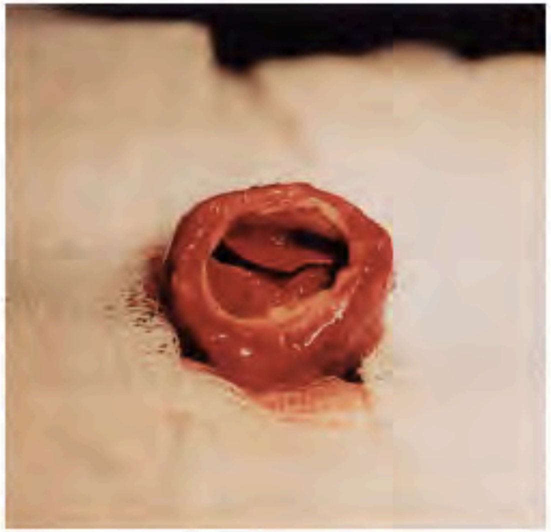


- Biodegradable PHA sutures are approved by the FDA via 510ks
- "TephaFLEX" biocompatible textiles are made from poly(4HB) and are available in sheets, braids, and tubes

Images: Tepha

PHA Heart Valve





- Tissue engineering: heart valve scaffold from PHA
- Valves are seeded with cells, implanted in sheep

Ralf Sodian, MD *et al*. *Circulation*. 2000. 102:III-22-III-29