Bio-plastics:
Properties and processing challenges

Dr. Gizela Mikova

Polymer Technology Group Eindhoven BV

Contents

1.1. Plastics

- Cheap source of monomers
- Established processing/production
- Low density (steel 7x higher)
- Large range of properties (Elastomers/Stiff materials)

- Source depletion
- Environmental impact – waste management

What are the alternatives?

Change the way of producing current plastics

Produce / use new plastics from new sources (renewable)

Different source
- Coal, Gas (methane)
- Gas To Liquid (GTL)
- CTL, **BTL**, ... via Fisher-Tropsch
- **Bio-ethanol**
- **Monomers from nature**

Bio-based plastics

Bio-based plastics

- Renewable source
- Environmentally friendly
- Low density
- Processing by techniques known from current plastics

- Processing/Production not fully established
- Higher (production) costs
- Limited properties (toughness/stiffness/durability)

Fossil vs. Bio-based plastics

- Not all Bio-based plastics are **compostable**
- Some of the fossil based plastics are **compostable**

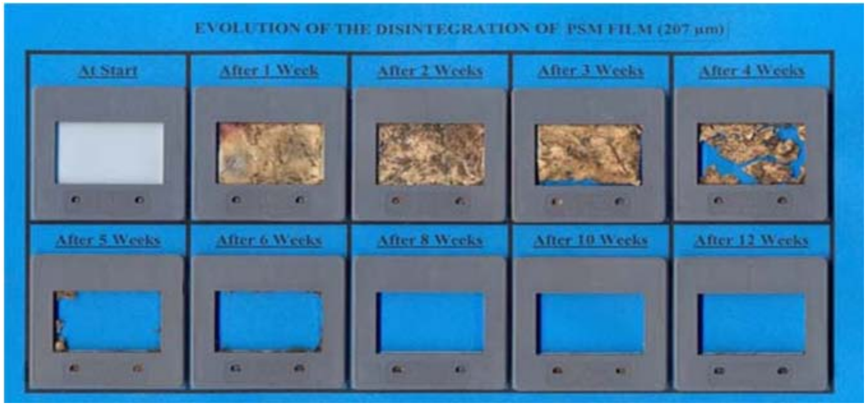
	Bio-based	Fossil based
Compostable materials **(Disposables Packaging)**	Poly(lactic acid) (PLA) Starch-based polymers Poly(hydroxy alkanoates) (PHA) **Poly Butylene Succinate (PBS)**	Aliphatic/Aromatic polyesters Polyamide esters Polyvinyl esters **Poly Butylene Succinate**
Not compostable Materials **(Engineering / Durable app.)**	**PE, PP (Bio-ethanol)……** Poly (trimethyl terephthalate) (PTT) Polyurethane (PU)	**Commodity polymers** **Polyethylene (PE),** polypropylene (PP), polystyrene (PS), Polyester (PET), acrylonitrile butadiene styrene (ABS)……

1.2. Compostable vs. Biodegradable plastics

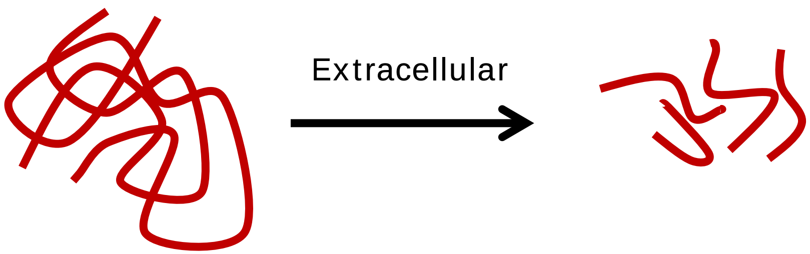
- Composting according to EN-13432, ASTM-D.6400-04, ISO-17088 and DIN-V-54900
- **Composting** consists of ***disintegration*** and ***biodegradation*** process

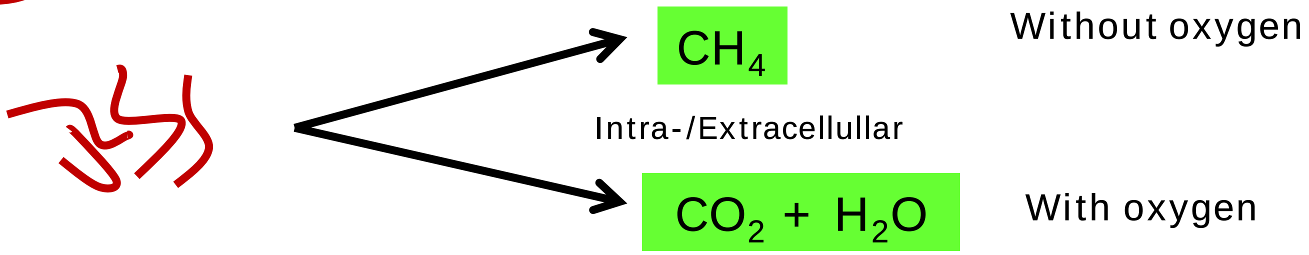
- ***Disintegration***

- ***Biodegradation***



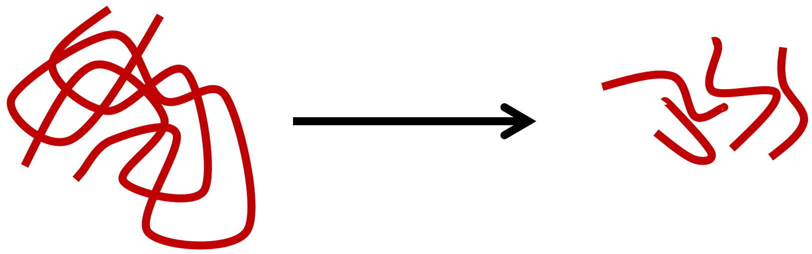
http://www.psm-hk.com/Eng/material.htm





Oxo-degradable plastics

- Oxo-degradable PE, PP
- Pro-degradation additives speed up the disintegration step
- Accumulation of heavy metals (catalysts) in soil
- Do not pass compostability tests



1.3. Routs to produce Bio-plastics

- **Direct extraction from biomass**

    e.g.: **starch**, cellulose

- **Extraction from microorganisms or genetically modified plants**

    e.g.: **PHAs**, bacterial cellulose

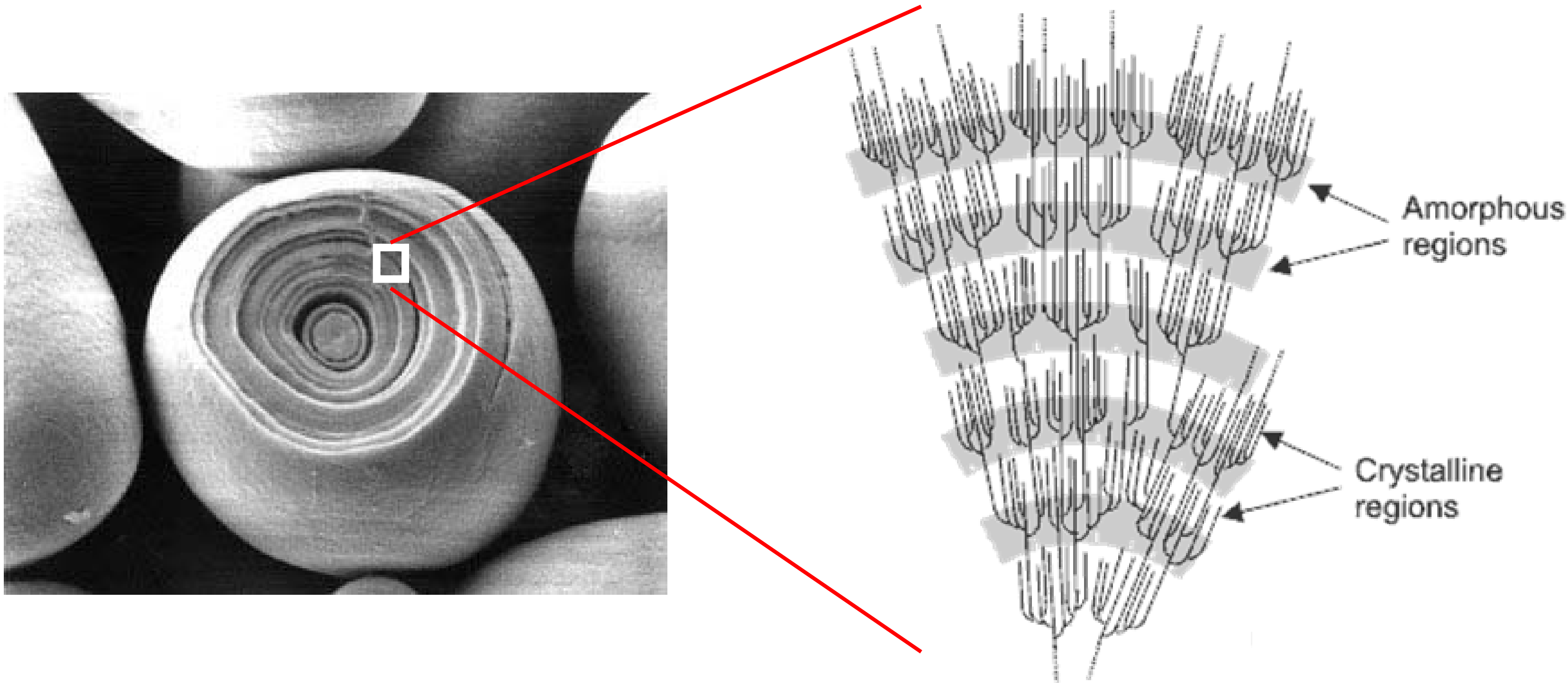
- **Conversion of biomass into bio-based monomers with subsequent polymerization**

    e.g.: **lactic acid**, succinic acid,
    furan-compounds, sorbitol...

Polymers: PLA, PBS, PBAT, PE, PP, PU, PA...

Contents

2.1. Starch

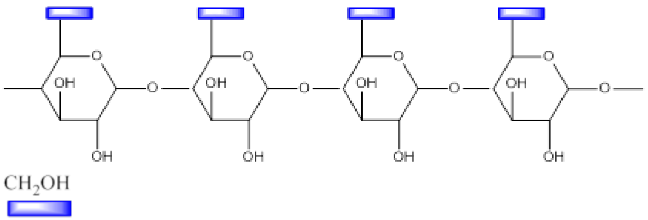


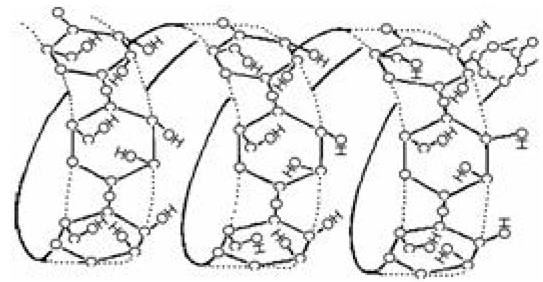
Granule size:
maize 2-30 μm
wheat 2-35 μm
potato 5-100 μm

Tester, R. F., Karkalas, J., Qi, X., Journal of Cereal Science, 2004, 29, 151-165

Starch structure & properties

Linear Amylose

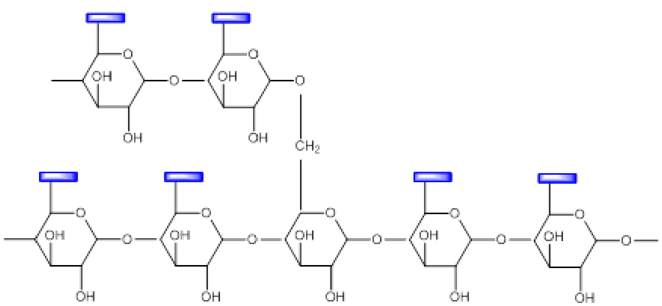


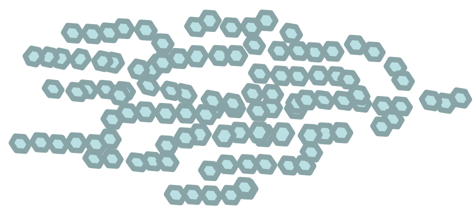


http://www.yxxb.com.cn:8080/yxxb_en/fileup/HTML/article_19250.htm

hydrophobic

Branched Amylopectin





hydrophilic

Amylopectin / Amylose ratio determines the properties

- More branched structure, more waxy starch
- Mole linear structure, more crystalline starch, less swelling (synthetic)

Starch Challenges

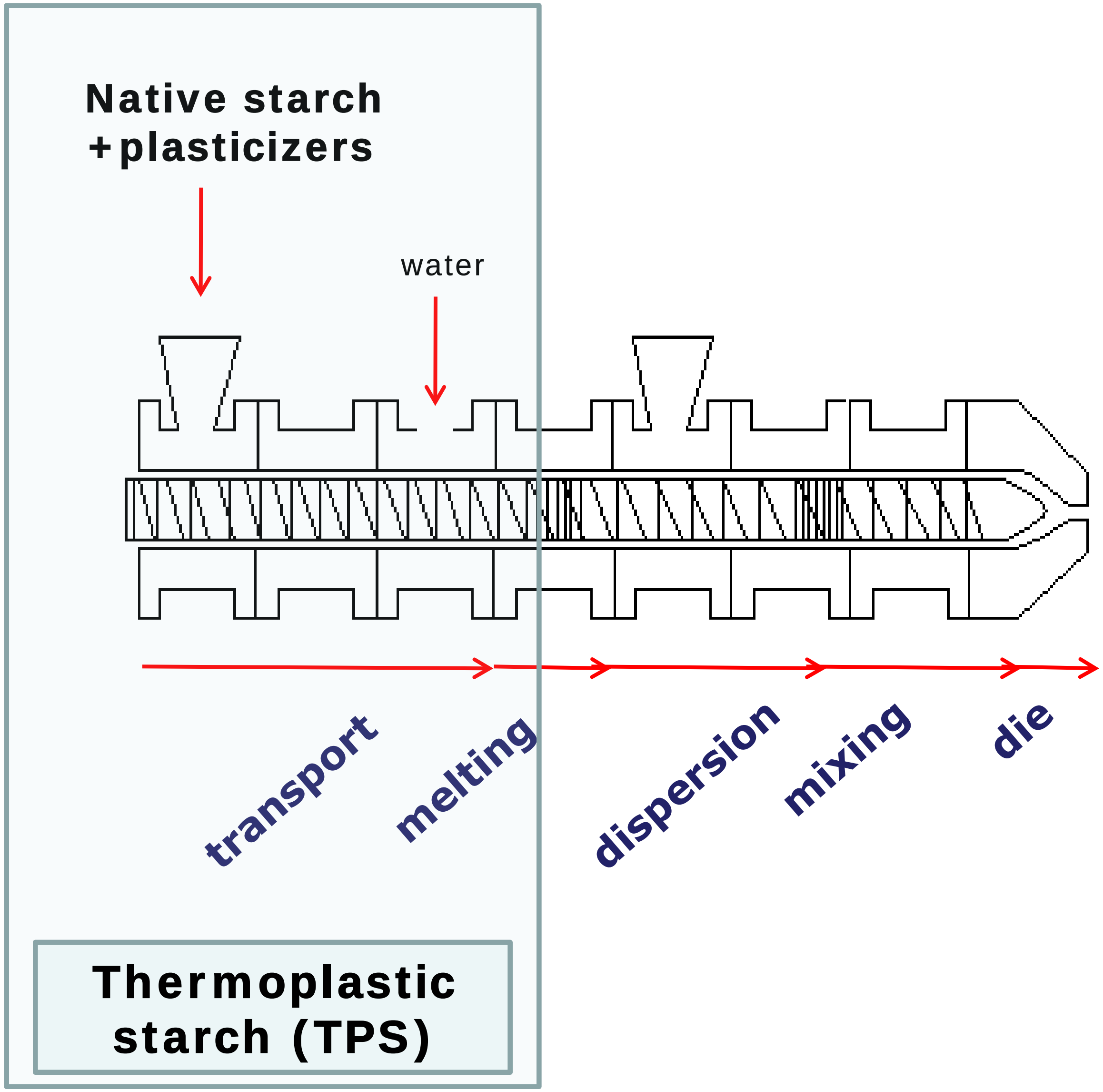
- Melting temperature is higher than degradation temperature – difficult to process!
- Brittle material

How to approach the challenges?

- Plasticization (water, glycerol, ethylene glycol, etc.)
- Blending with other Bio-plastics

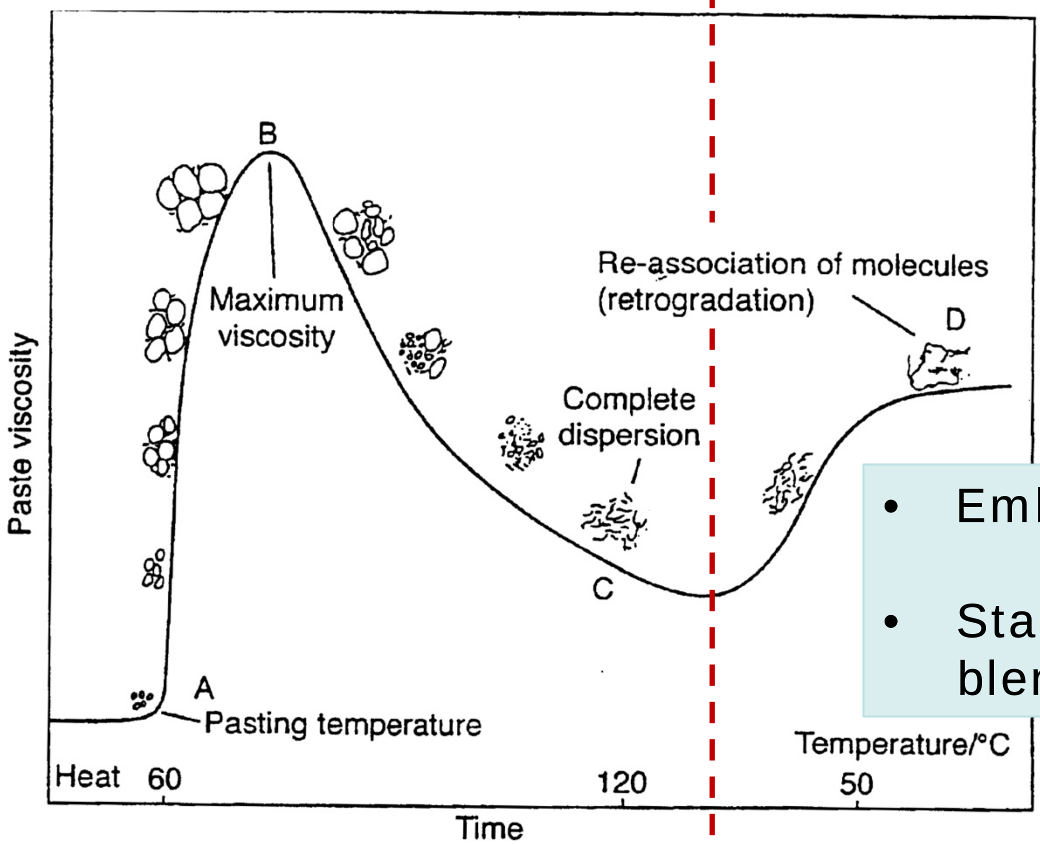
Starch processing

Step I



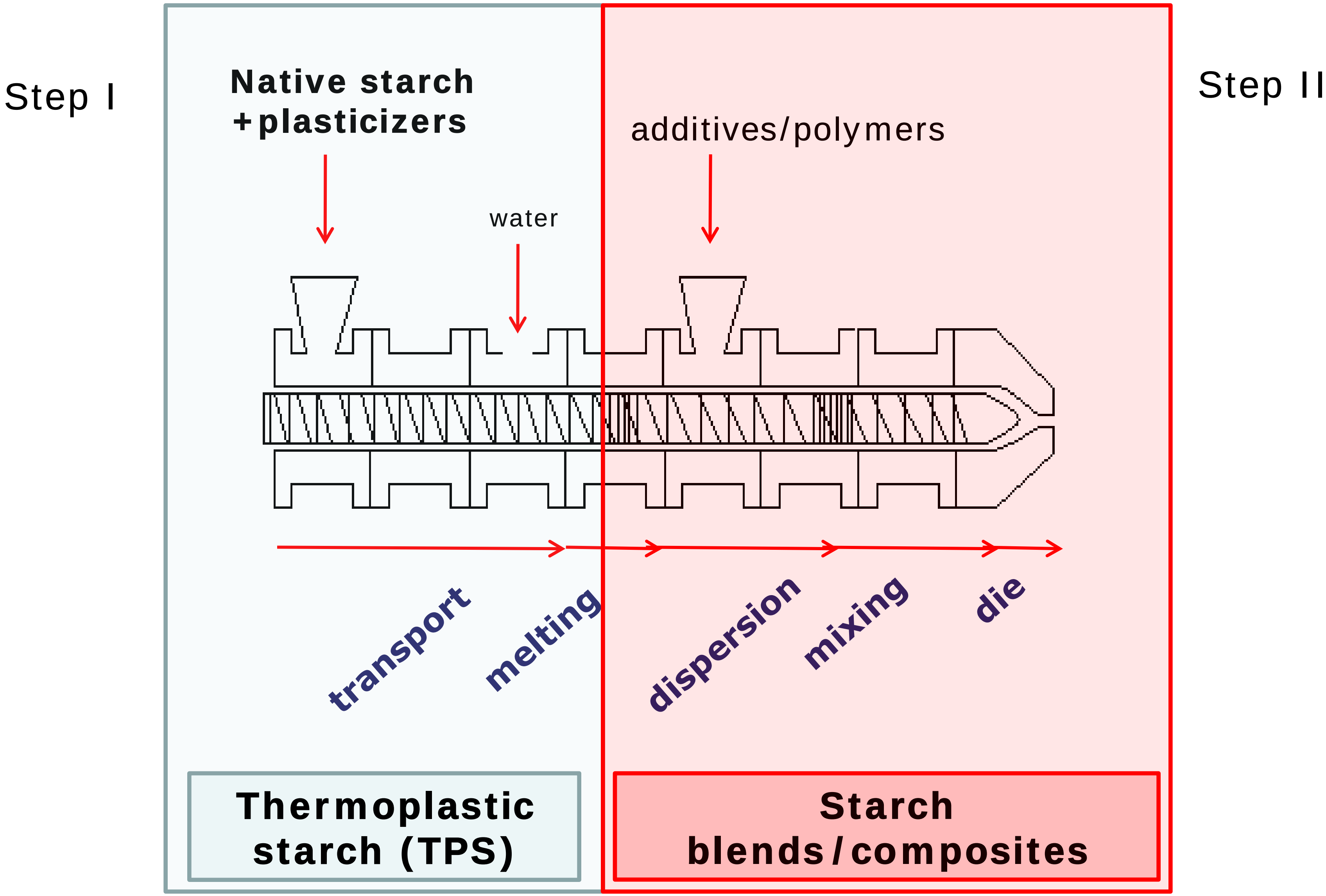
Gelatinization vs. Retrogradation

Gelatinization **Retrogradation**



- Embrittlement of TPS on storage
- Starch as a cheap component in blends/composites

Starch processing

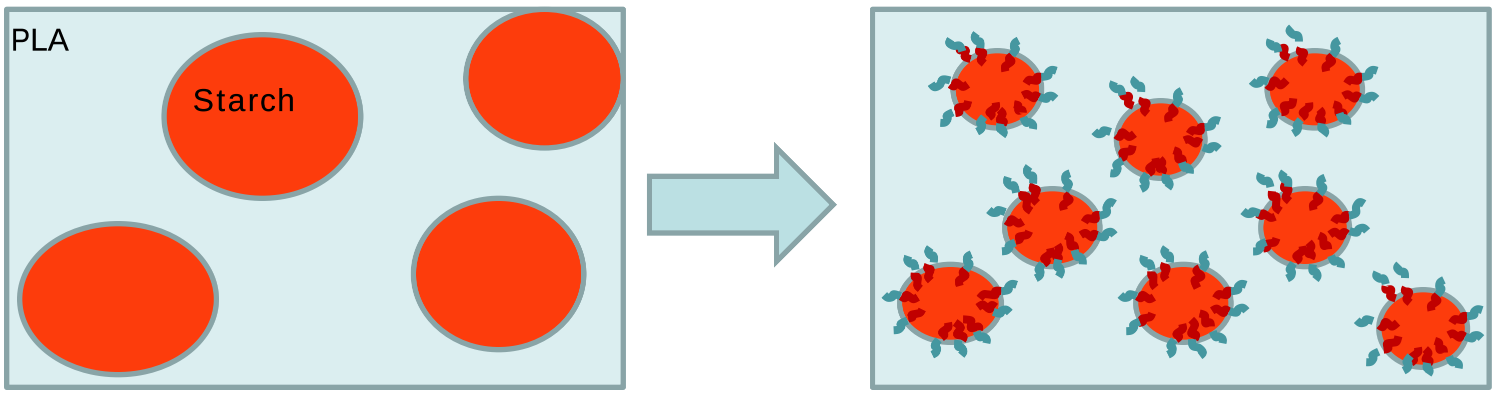


Blends: tuning the properties

e.g.: PLA/starch (55/45)

Compatibilized blend

X. Sun, Biomacromolecules 2004, 5, *1446-1451*



Tensile strength: 35 MPa

Tensile strength: 50 MPa

- Addition of block or grafted copolymers (A-B)
- Functionalization of polymers (epoxy, maleate, succinate…)
- In situ compatibilization by a reactive blending (crosslinking/transesterification)

P. Ma, Tailoring the properties of bio-based and bio-compostable polymer blends, Doctoral thesis, TU/e Eindhoven, 2011

Starch Applications

Disposable

- Packaging, compostable bags
- Agriculture, mulch films, flower pots
- Blends with other compostable plastics, e.g.: Ecoflex, PCL, PLA...

Non – Disposable!!

- Blends with non compostable plastics, e.g.: PE, PP

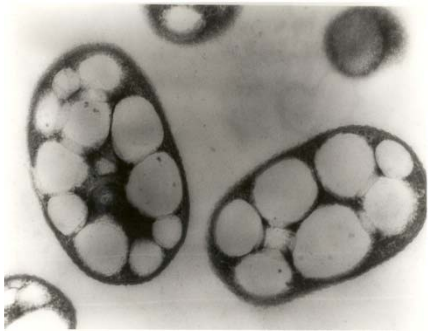
~~Durable~~

- Easy to degrade by temperature, moisture, bacteria...

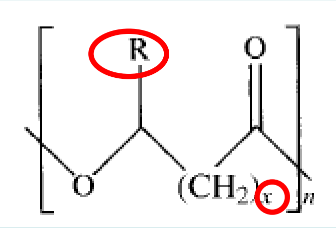
Producers

- Novamont – Mater-Bi® (IT), Biotec (GE), Cardia (CN), Rodenburg – Solanyl® (NL)
- Price of native starch 500 – 700 €/ton

2.2. Poly(hydroxy alkanoates) (PHAs)



- Produced by bacteria or in genetically modified plants
- Carbon/Energy storage material



Thermoplastic:

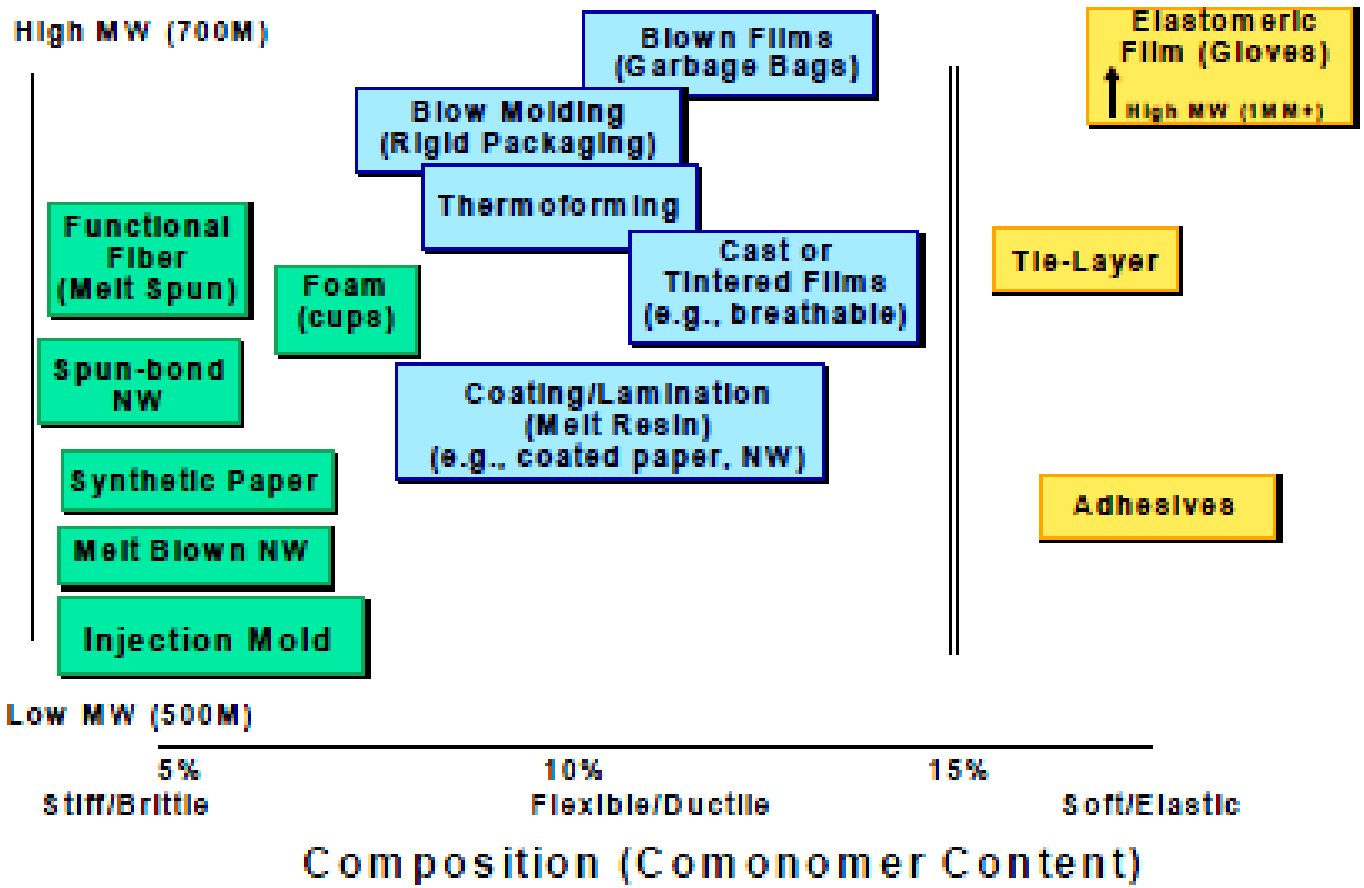
R: H, CH_3, C_2H_5
x: 1 – 3

Elastomeric:

R: C_3H_7 to $C_{13}H_{27}$
x: 1 – 4

Poly(3-hydroxy butyrate) (P3HB) is the most common PHA

PHA's properties vs. applications



PHAs mechanical properties

Commercialized PHAs:

P3HB, copolymer of P3HB with: hydroxyvalerate (**HV**), hydroxy hexanoate (**HHx**) and 4-hydroxybutyrate (**4HB**)

Polymer	Melting (°C)	Glass Transition (°C)	Tensile modulus (GPa)	Tensile strength (MPa)	Elong. at break (%)
P(3HB)	180	4	3.5	40	5
P(4HB)	53	-48	-	-	-
P(3HB-co-20 mol% 3HV)	145	-1	0.8	20	50
P(3HB-co-71 mol% 3HV)	83	-13	-	-	-
P(3HB-co-17 mol% 3HHx)	-	-	-	20	850
P(3HB-co-25 mol% 3HHx)	53	-4	-	-	-
i-PP	176	-10	1.7	38	400

PHB challenges and routes to approach

- Stiff but brittle material
- Crystallizes slowly
- Aging of PHB – embrittlement on storage
- Thermal degradation during melt processing (T>170 °C)

- Blends with other compostable plastics (impact, toughness, thermal stability, compatibility)
- Nucleation agents: no efficient NA yet.
  Conventional, e.g.: talc, BN; cyanuric acid compounds (patent); in house development
- Thermal stabilizers: no efficient thermal stabilizer yet.
  Conventional: T down, processing aids, plasticizers;
  in house development

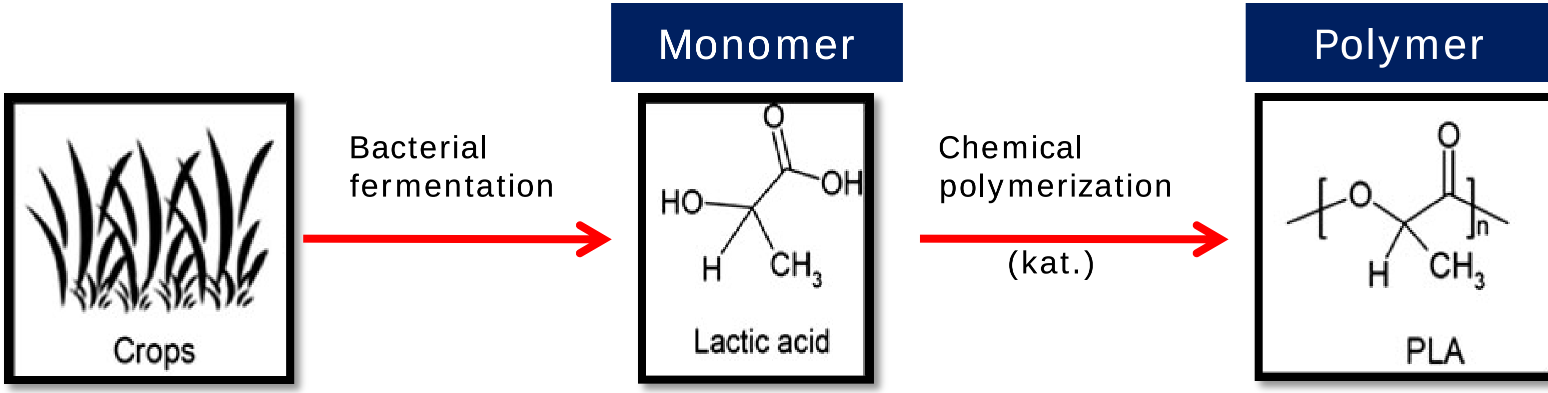
Producers

- PHAs: *Metabolix Inc.* (USA, Mirel®),
- P3HB + P(3HB-co-HV): *Tianan Biologic Materials Co. Ltd* (CN, Enmat®), *PHB industrial* (BR, Biocycle®)
- P(3HB-co-HHx): *Kaneka corporation* (JP, Aonilex®)
- P(3HB-co-4HB): *Tianjin Green Biosciences* (CN, Greenbio®)

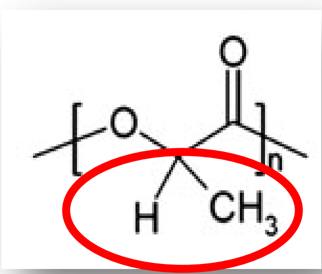
- Blends with Ecoflex, PLA, Starch…

- Price of PHAs: 3000 – 7000 €/ton

2.3. Polylactid acid (PLA)

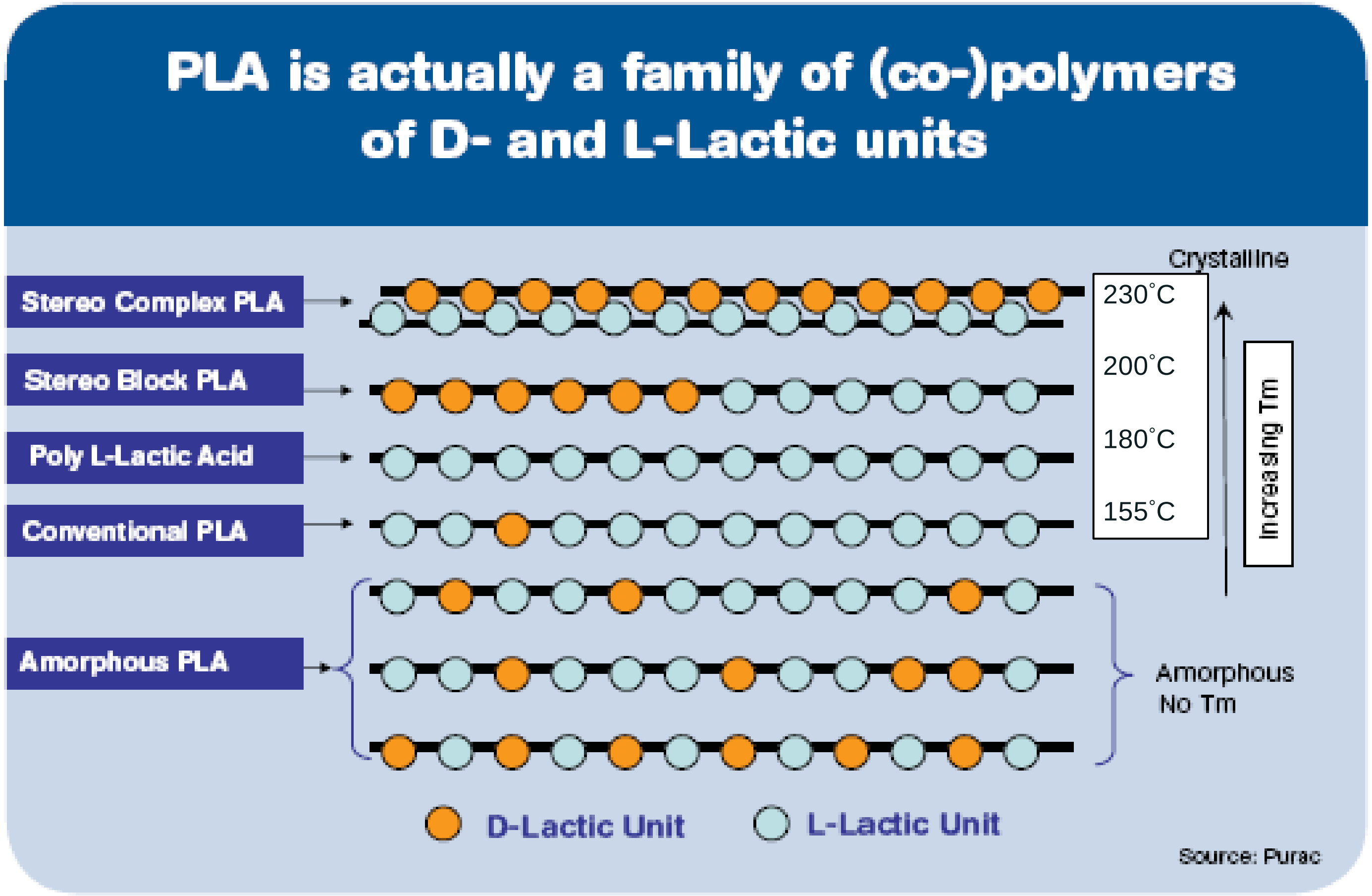


G.E. Luckachan, J. Polym. Environ, 19, (2011), 637



- Position of –H and –CH_3 group in space:
  (D) or (L) PLA
- Commercial PLA: PLLA with (D)LA inclusions

PLA structure vs. properties



PLA mechanical properties

Effect of PLA copolymer composition and processing…

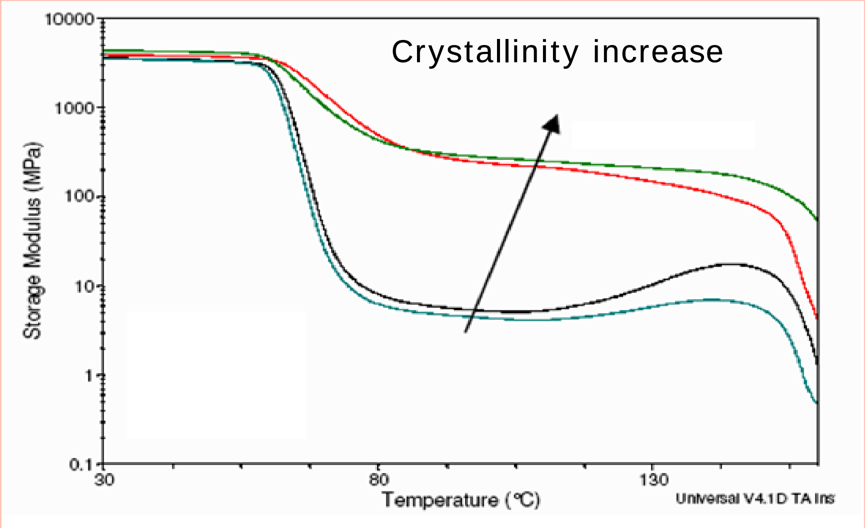
	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
PLA	4-6	60-1000	6
PLLA	9 -15	500–1200	
PET	3–4	50–80	80

K. Van de Velde, Polymer Testing 21 (2002) 433–442

PLA challenges and routes how to approach them

- Brittle
- Slow crystallization
- Low crystallinity polymer
- Low heat deflection temp. (HDT near Tg ~ 60°C)

Hot water →

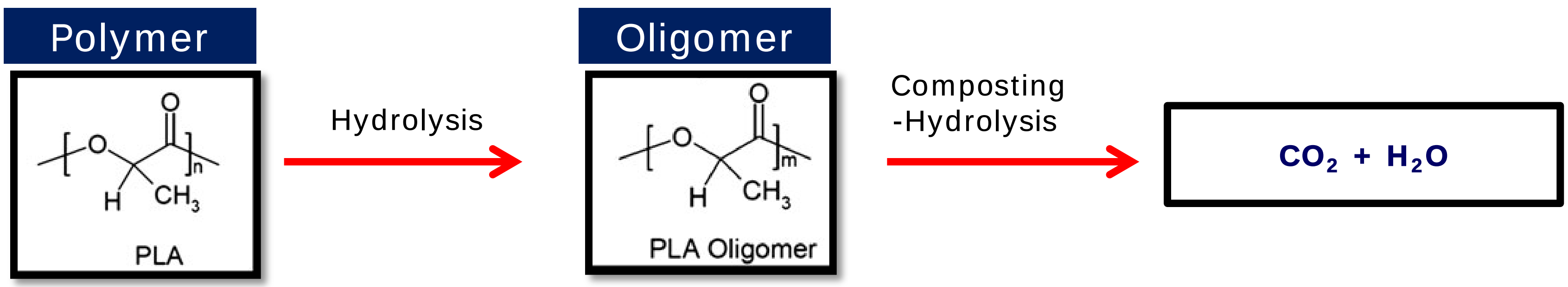


- Nucleation agents: Conventional: talc, BN, etc.
  Commercial: Sukano, Polyone, Polyvel Inc. etc.
- Block copolymer, Stereo complex (HDT)
- Blends (impact, toughness)

D. Hristova-Bogaerds, Eindhoven University of Technology, NL

Hydrolytic degradation of PLA

- Sensitive to hydrolytic degradation:
  Water, Temperature above 60 °C



- **Challenge for engineering application!**
  No efficient stabilizer yet
- **Desirable for disposable application!** Compostability

PLA Applications

Disposable & Durable

- (Food) packaging: compostable bags, cups, food containers, etc.
- Biomedical (bone fixation)
- Textiles: fibers, fabrics
- Electronics: computer keys (Fujistsu), Walkman (85% PLA, Sony)

- Blends with other compostable plastics e.g.: Ecoflex, PHAs…

Engineering

- **SC-PLA products**

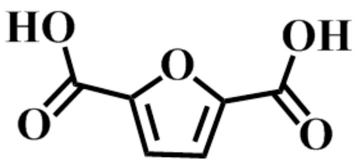
Producers

- Natureworks – Ingeo® (USA),
- Purac – Pharmaceutical grade Puralact®, PDLA for SC (NL)
- Galactic (BE)
- Tong Jie Liang Biosciences (CN)
- Synbra – Biofoam (NL)

- Price of PLA: 2000 – 4000 €/ton

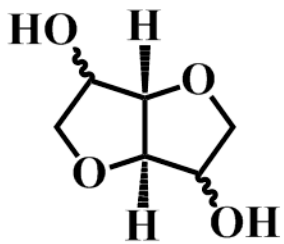
Other renewable monomers

R. Sablong



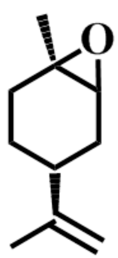
2,5-furandicarboxylic acid

⟹ Polyesters, polyamides



Dianhydrohexitols

⟹ Polyesters, polyurethanes, polycarbonates



Limonene oxide

+ CO_2

Succinic anhydride

⟹ Polycarbonates

Polyesters

In progress...

Producers

- ***Avantium*** (NL) – Furan Chemistry, polyesters
- **Solvay** (FR/TH) – Glycerin to Epichlorohydrin (Epicerol®)
- ***Braskem*** (BR) – PE, PP from bio-ethanol

- ***BASF*** (GE) – PBAT (Ecoflex®), PBS
- ***Showa High Polymers*** (JP) – PBS, PBSA (Bionolle®), PES
- ***Xinfu*** (CN) – PBS, PBSA, PBAT
- ***Mitsubishi Gas Chemicals/Bioamber*** (JP) – PBS (GSPla®)
- ***Novamont*** (IT) – Vegetable oil based polyester (Origo-Bi®)

- ***DuPont*** (US) – PBST/PET copolymer (Biomax®)
- ***Teijin*** (JP) – PETS (GreenEcoPet®)

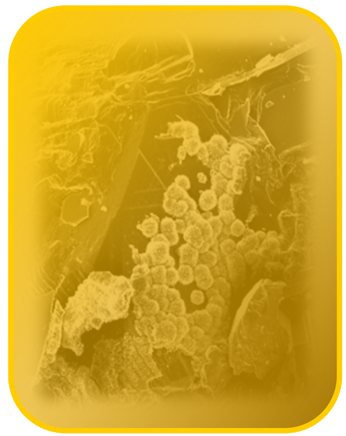
Contents

3. Polymer Technology Group Eindhoven BV

Polymer Chemistry

- Polymer synthesis
- Catalytic polymerization

Advanced Materials

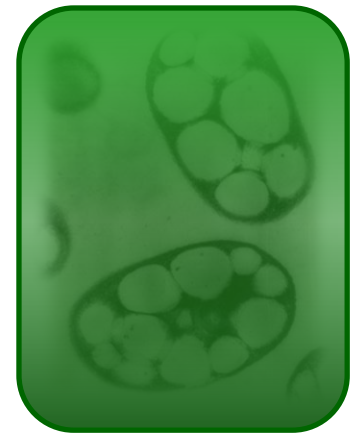


- Inorganic - Organic hybrid materials

Processing & Services

- Processing
- Analyses

Biobased Materials

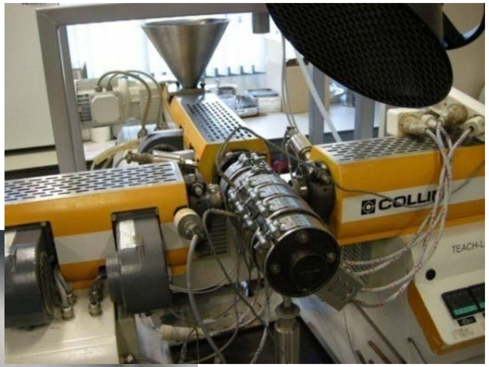


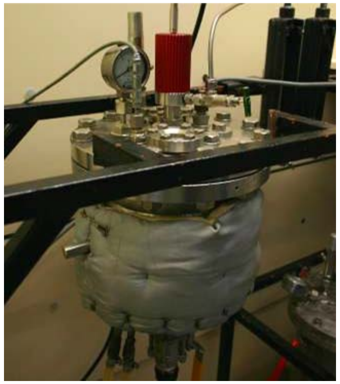
- Processing
- Polymer Modification
- Compatibilization
- Bio-based monomers polymerization

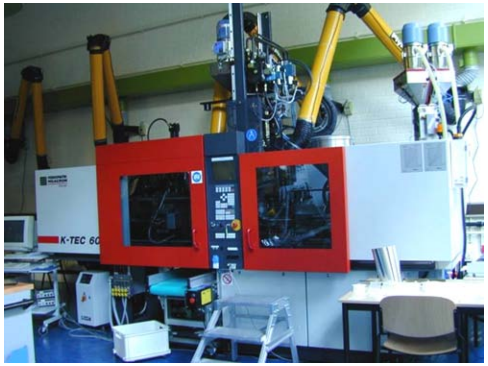
Processing/Modification of bio-plastics

Infrastructure

- Reaction vessels
- Injection molding
- Extrusion
- Film blowing
- Gel/melt spinning
- Capacity: 5 g – 5 kg scale







4. Conclusions – Trends

- **Short-term applications:** Compostable plastics (starch/ cellulose/PHAs/ PLA/PBS/PBAT/PCL)

- **Durable (Engineering) applications:** Bio-based plastics (PLA, PE, PP, polyesters, PU, PA, PC, etc.)

- **Bio-plastics are still in an early stage of development**

- **PTG/e has in house knowledge and infrastructure to approach the unsolved challenges!**

For further questions and discussions you are invited to our stand No # 61

www.ptgeindhoven.nl

gizela.mikova@ptgeindhoven.nl