ICPEES
Institut de Chimie et Procédés pour l'Énergie, l'Environnement et la Santé

ecpm

UNIVERSITÉ DE STRASBOURG

Training course on Bioplastics
Mecamat 2014
Aussois

INSTITUT CARNOT MICA

Pr. Luc Avérous
BioTeam
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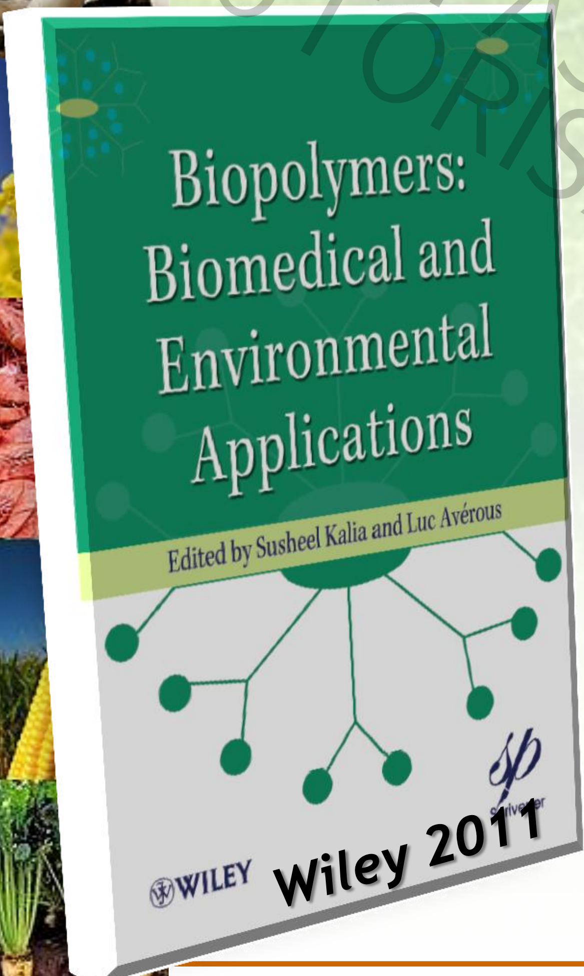
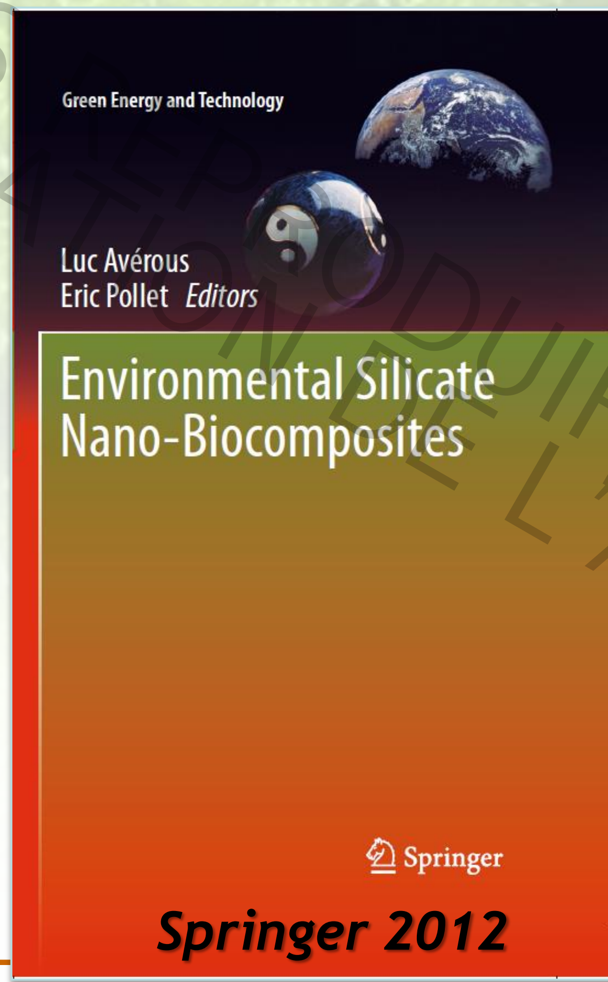
cnrs

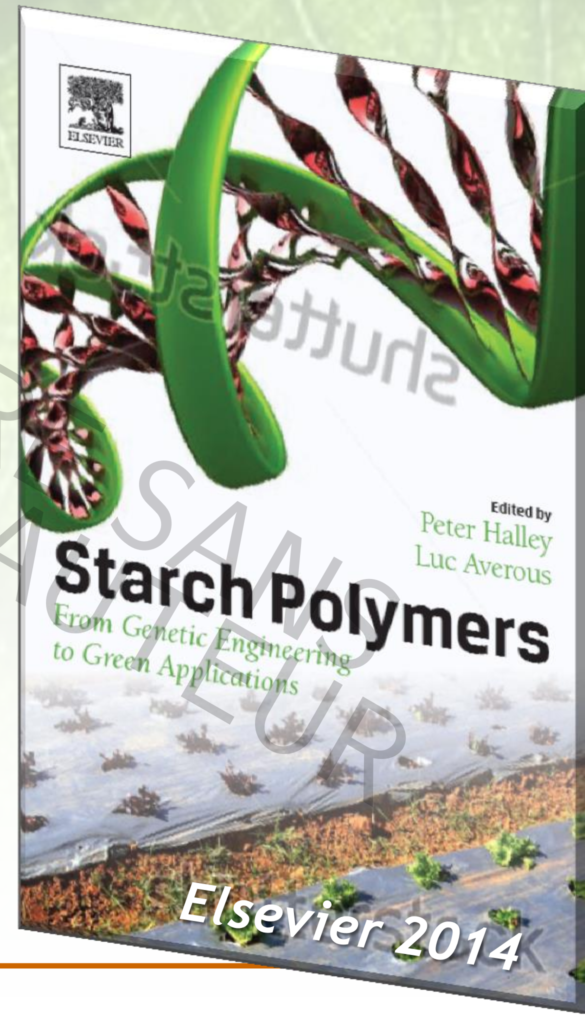
bio inside

General Topic (BioTeam):

► Biobased and/or Biodegradable Polymers, for Environmental and Biomedical Applications.







BioTeam Members (16) :

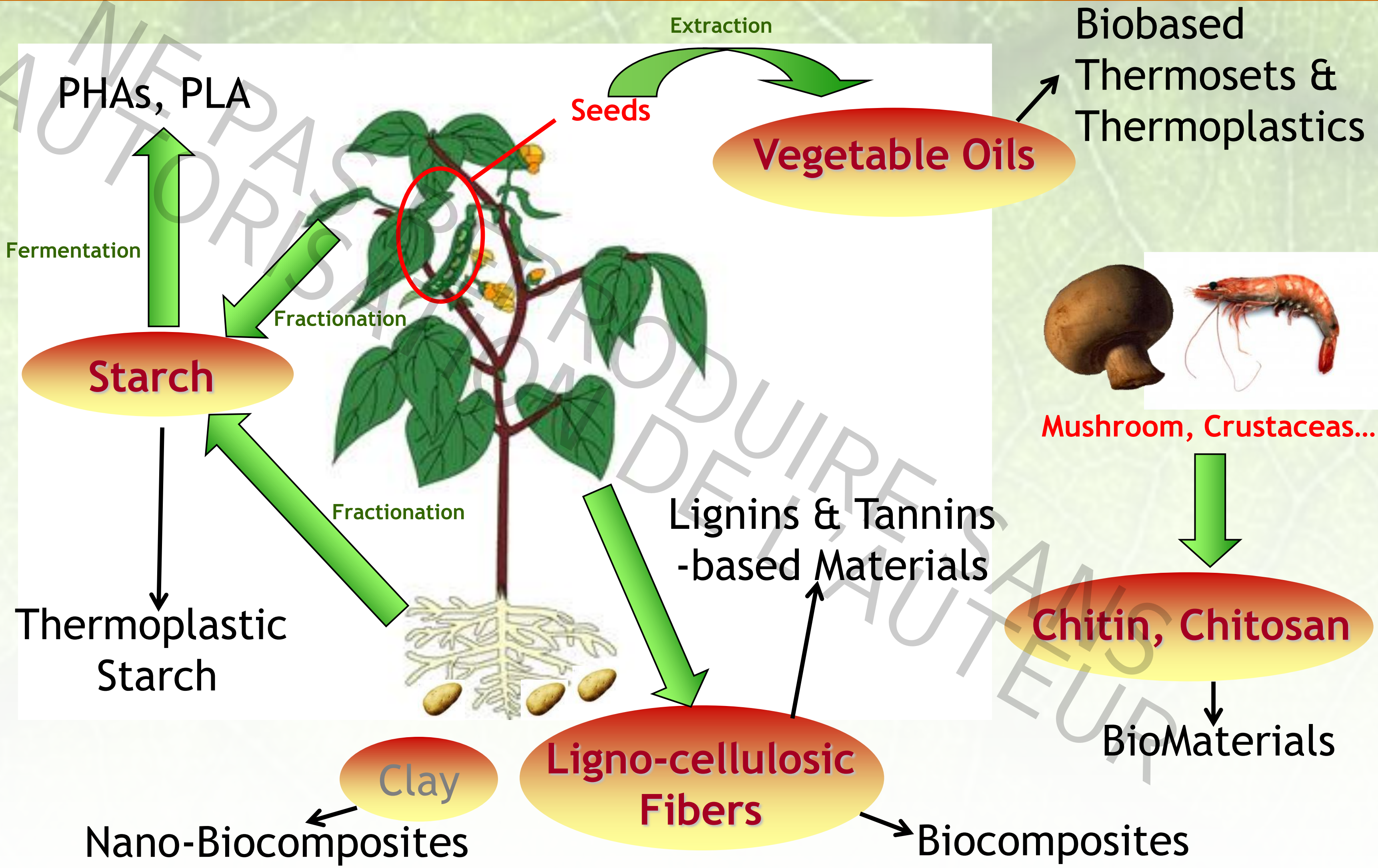
- **Staff(4):**
  - Pr. **Luc Avérous** (BioTeam leader)
  - Dr. **Eric Pollet** (A/Prof.)
  - Pr. **Jean Marc Jeltsch** (Vice-President UniStra)
  - Dr. **Vincent Phalip** (A/Prof.)

- **Researchers (9+2):**
  - **Post-Doct. (3):**
  - Dr. **Marina Magaton** (Funding Brazil, 2013-2014)
  - Dr. **Dhriti Khandal** (Europ. Project, 2013-2016)
  - **Dr. Alexandru Sarbu** (2014/15)

  - **PhD Students (9):**
  - **Flavie Prévot *(Government, 2011-2014)***
  - **Camille Carré *(Region + Company, 2011-2014)***
  - **Alice Arbenz *(CIFRE, 2011-2014)***
  - **Stéphane Duchiron *(Company, 2012-2015)***
  - **Marie Reulier *(CIFRE, 2012-2015)***
  - **Thibaud Debuissy *(European Project, 2013-2016)***
  - **Amparo Jimenez-Quero (Government, 2013-2016)**

  - **Rogerio Prataviera *(Co-Direction w/ Brazil – UFSCar)***

Biorefinery from Biomass



► Integration, from the biomass to final objects

BioTeam

Integration « Biochemistry/Chemistry & Process »

Bio-Production →	Chemical Synthesis →	Formulation Process
Characterization		

Biomass:
Triglycerides,
Ligno-cellulose,
Tannins, Starch,
Chitin, …

Final Objects:
For automotive,
Building, Textile,
Packaging,
Agriculture …

Academic international collaborations:

Outline

1. **Bioplastics: Some Definitions and the Market**
2. **Biodegradation-Compostability Biobased Content**
3. **Biotechnology / Biorefinery / Biocatalysis / Building blocks**
4. **Biobased and durable polymers / Biobased and biodegradable polymers**

1- Bioplastics: Some definitions and the Market

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Biodegradable polymers - Classification -

Biomass products From agro-resources => *Agro-polymers*

- **Polysaccharides**
  - **<u>Starches</u>: Wheat Potatoes maize**
  - Ligno-cellulosic: Wood, Straws
  - Others: Chitin,
- **Proteins, lipids …**
  - Animals: Casein Gelatine whey
  - Plant: Soya, Gluten

From microorganisms (obtained by extraction)

- **PolyHydroxy-Alkanoates (PHA)**
  - **- Polyhydroxy butyrate (PHB)**
  - **- Polyhydroxybutyrate co-valerate (PHBV), …**

From biotechnology (conventional synthesis from bio-derived monomers)

- **Polylactides**
  - **Poly(lactic acid) (PLA)**

From petrochemical products (conventional synthesis)

- **Polycaprolactones** (PCL)
- **Polyesteramides** (PEA)
- **Aliphatic co-polyesters** (e.g: PBSA)
- **Aromatic co-polyesters (e.g: PBAT)**

Please, Don't forget!

"Biobased plastic does not mean it is biodegradable and biodegradable plastic does not mean it is biobased!"

Some definitions (IUPAC):

- **Biomacromolecules** : Macromolecules, which are elaborated from living organisms (proteins, polysaccharides, bacterial polymers …) [Caracteristics]

- **Biopolymers** : substances based on biomacromolecules [Applications]

Nota: PLA is not a biopolymer!

Another definitions:

- **<u>BIOPLASTICS</u> : "Industrial" term used to qualify biobased <u>and/or</u> biodegradable (environment) polymers.**
  (e.g., PLA, PA11, PCL …)

Bioplastics : The market

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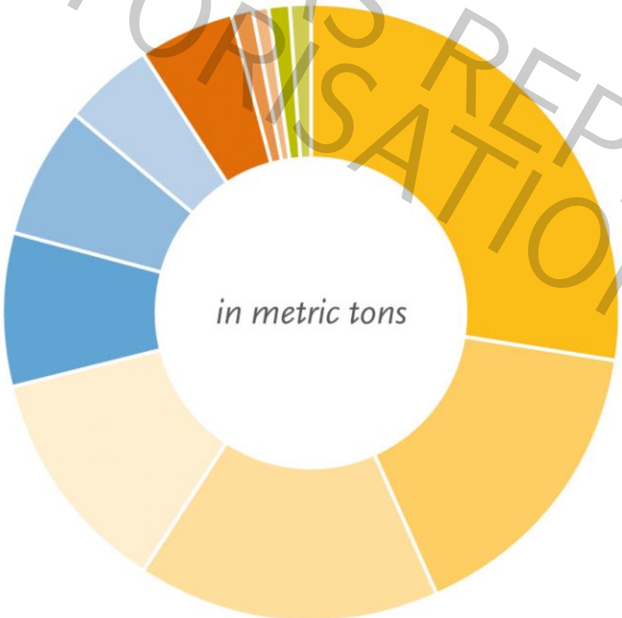
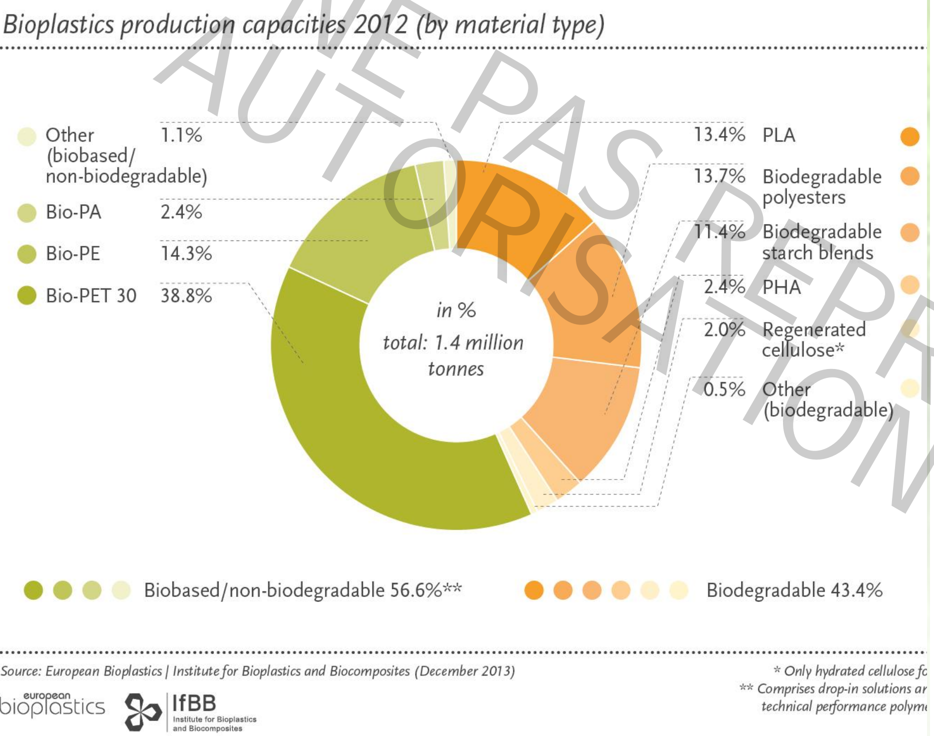
Worldwide Bioplastics Production
- Capacity in Tons (2010) -

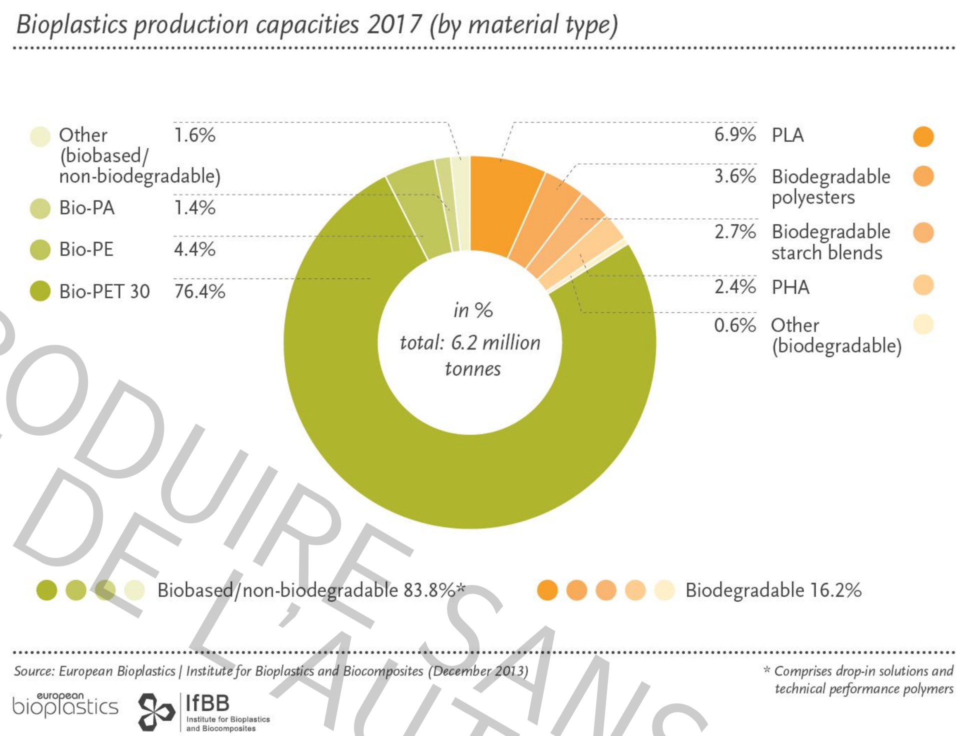


Bio-PE	200.000	28 %
Biodegradable Starch Blends	117.800	16 %
PLA	112.500	15 %
PHA	88.100	12 %
Biodegradable Polyesters	56.500	8 %
Bio-PET	50.000	7 %
Regenerated Cellulose[2]	36.000	5 %
Bio-PA	35.000	5 %
Cellulose Derivatives[1]	8.000	1 %
PLA-Blends	8.000	1 %
Durable Starch-Blends	5.100	1 %
Others	7.500	1 %
Total	**724.500**	100 %

[1] only cellulose ester | [2] only hydrated cellulose foils

Worldwide Bioplastics Projection
- Capacity in Tons (2012 vs. 2017) -





Land use for bioplastics

Land use for bioplastics 2012 and 2017

Source: European Bioplastics | Institute for Bioplastics and Biocomposites (December 2013) / FAO 2011

* In relation to global agricultural area
** Also includes approx. 1% fallow land

european bioplastics | IfBB Institute for Bioplastics and Biocomposites

Training course on Bioplastics

2- Biodegradation-Compostability Biobased Content

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Biobased Content

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Biodegradation

- **Biodegradable** means capable of undergoing decomposition into carbon dioxide (aerobic) and/or methane (anaerobic), water, inorganic compounds, and a new biomass.
- **Biodegradation:** <u>The predominant mechanism is the enzymatic action of micro-organisms</u> that can be measured by standard tests, over a specific period of time.
- There are different media (liquid, inert or compost medium) to analyze biodegradability.
- **Compostability** is material biodegradability using compost medium.

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2- Biodegradation-Compostability
Biobased Content

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OK Biobased & Biobased Content

Vinçotte launched the "OK biobased" (based on the **ASTM 6866 standard** and **C^{14} measurement method**) in September 2009 to provide companies an assessment of their product's renewability.
A system of 1 to 4 stars indicates the biobased content of the product tested:

- *(Only based on the Carbon ???)*

between 20 and 40 % Biobased	between 40 and 60 % Biobased	between 60 and 80 % Biobased	more than 80 % Biobased

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3- Biotechnology / Biorefinery / Biocatalysis / Building blocks

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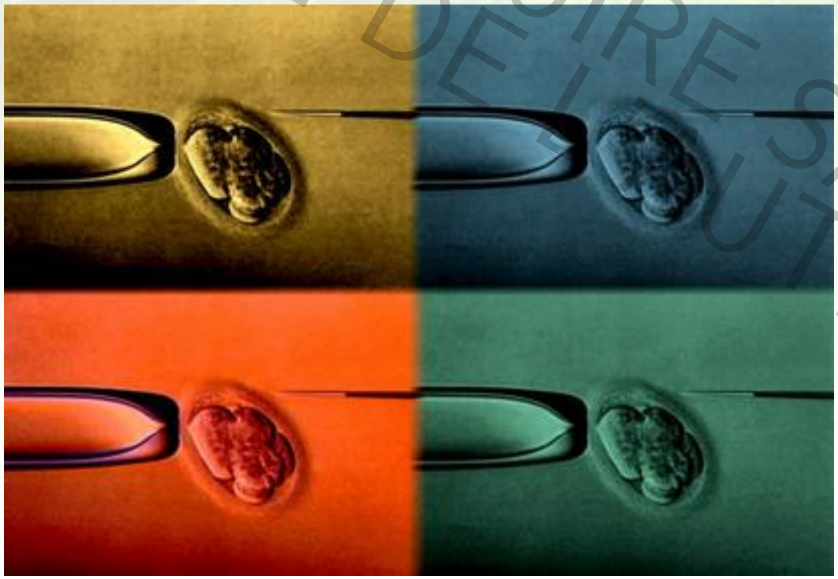
Biotechnology

White biotechnology, also known as industrial biotechnology, because applied to industrial processes.

Two examples:

- the designing of an organism to produce a useful chemical.
- the using of enzymes as industrial catalysts to produce valuable chemicals.

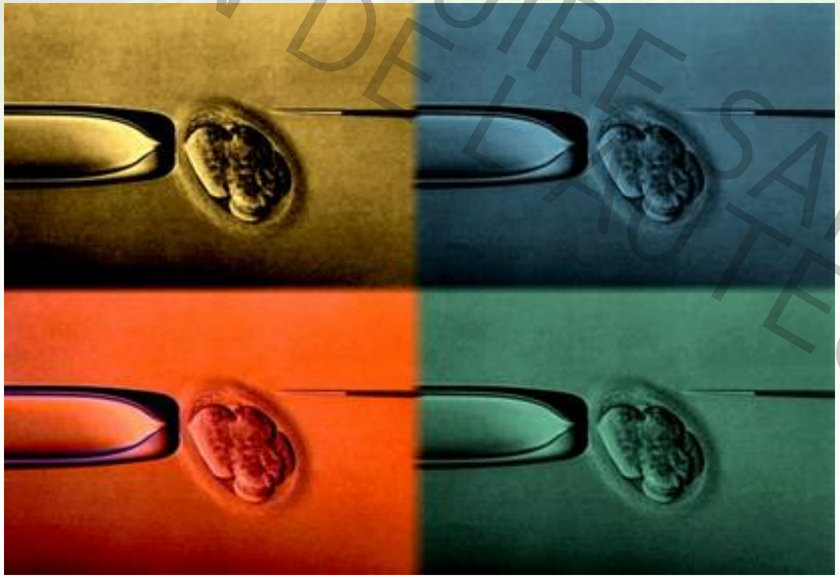
White biotechnology tends to consume less in resources (than traditional processes used to produce industrial goods).



Biotechnology

<u>**Green biotechnology**</u> is biotechnology applied to agricultural processes.

An example is the designing of transgenic plants to grow under specific environments in the presence (or absence) of chemicals.
e.g., the engineering of a plant to express a pesticide, ending the need of external application of pesticides (Bt corn …).



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Biocatalysis

Biocatalysis is the use of natural catalysts, such as protein enzymes, to perform chemical transformations on organic compounds.

- Enzymes display selectivities (Chemoselectivity, regioselectivity, enantioselectivity) => major reasons why chemists have become interested in biocatalysis.

Another important advantage of biocatalysts are that they are environmentally acceptable, being completely degraded in the environment.
The enzymes act under mild conditions, which minimizes problems of undesired side-reactions such as decomposition/degradation …

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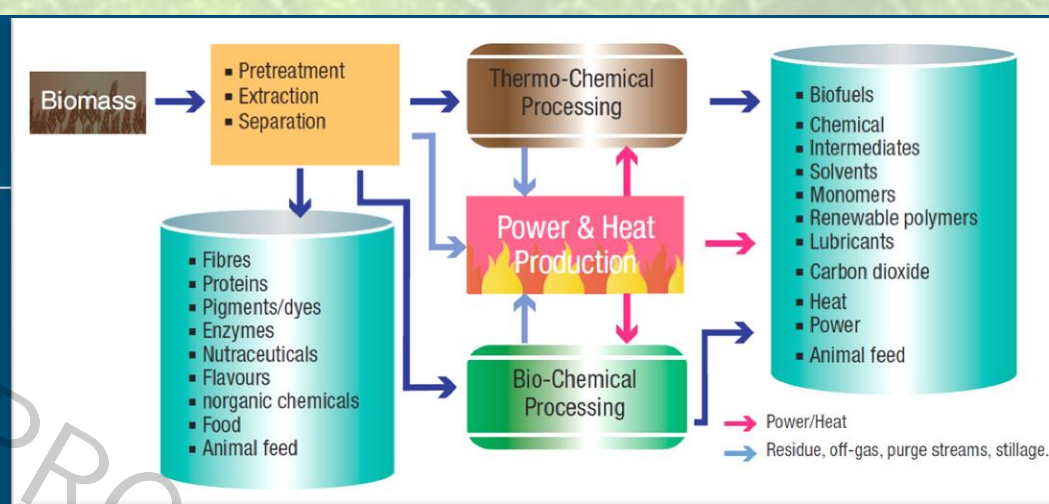
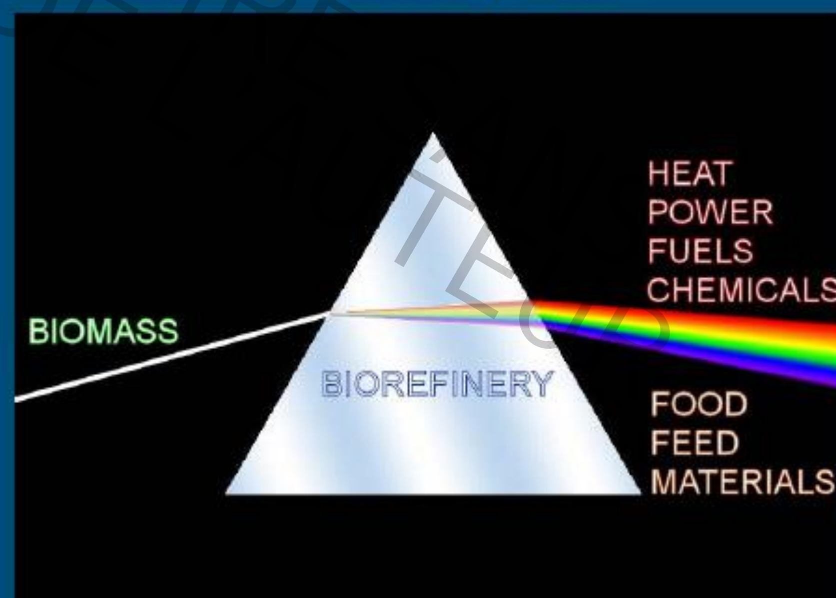
Introduction



- **What is a biorefinery?**

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass.



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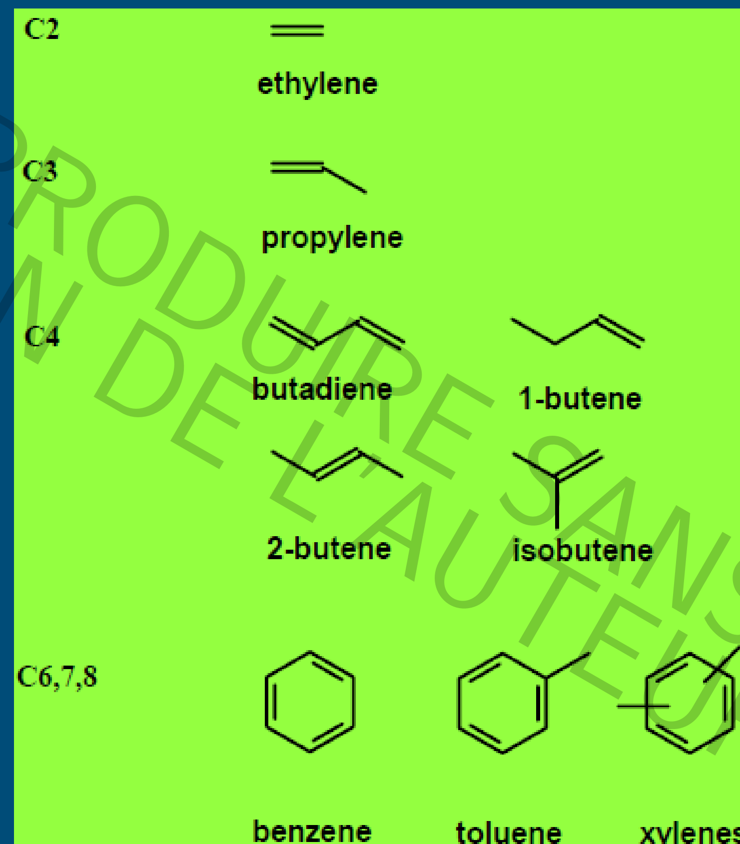
Building blocks

Current platform chemicals

- Chemical Industry: Platform chemicals from naphtha

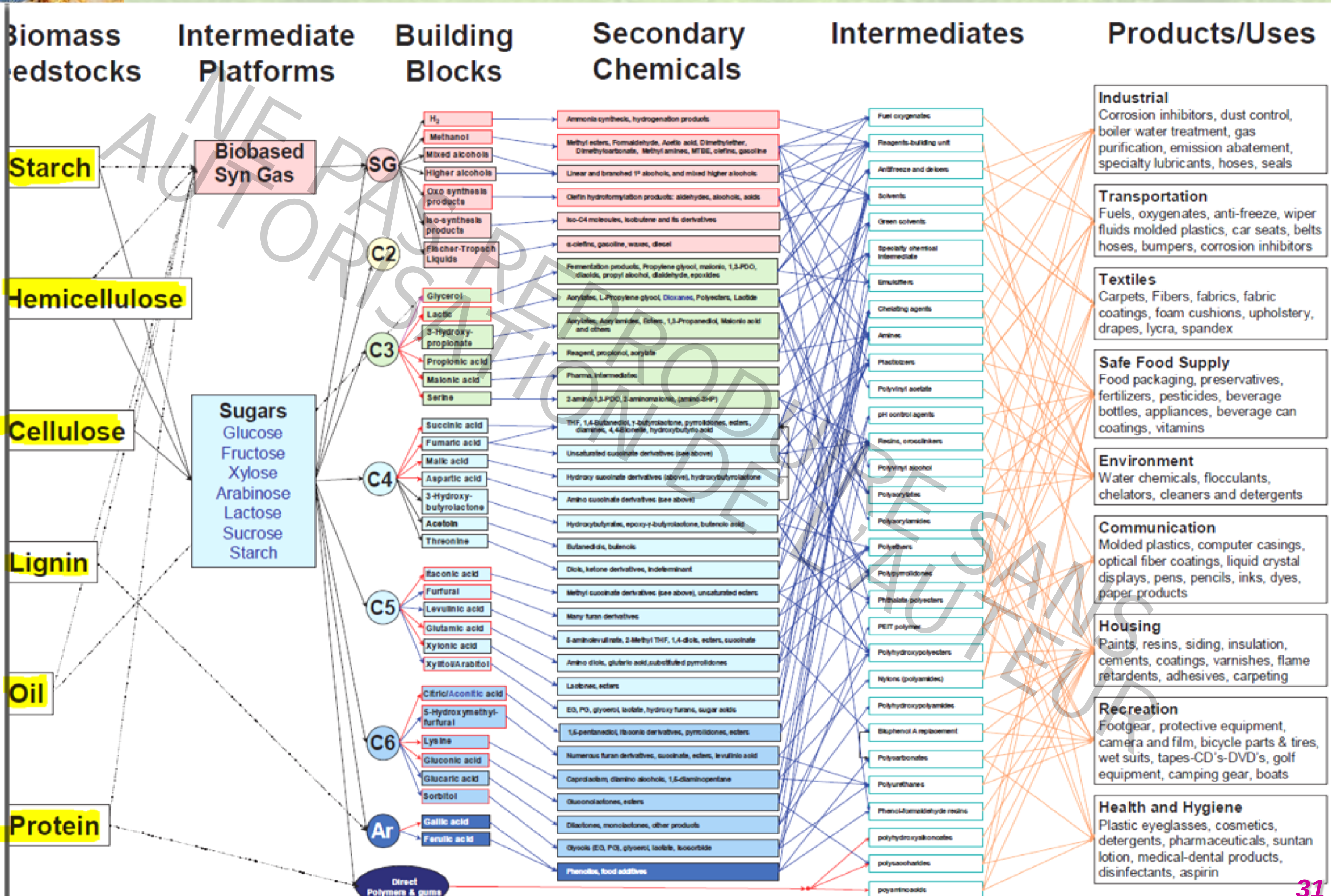
naphtha →



Shale gas? (C1-C4) with a lot of C1

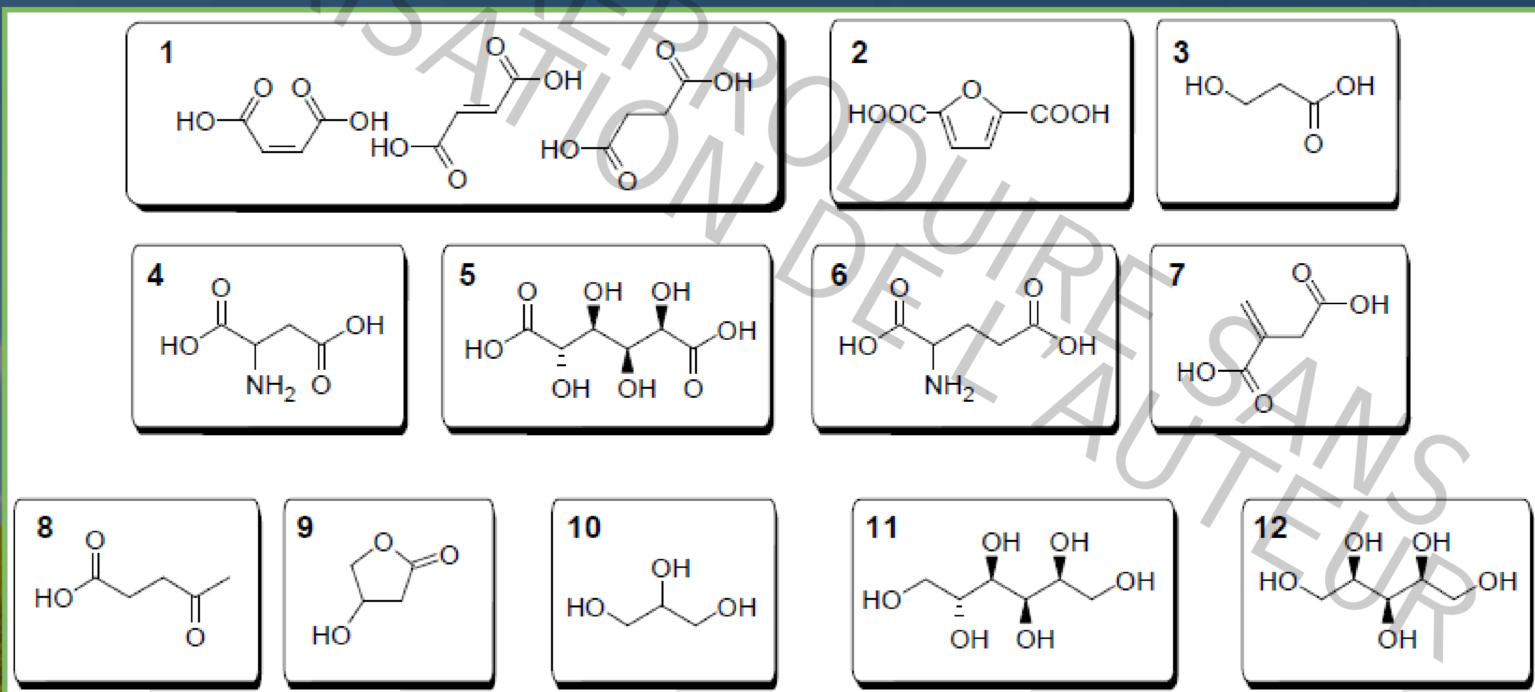
Building blocks

Source: USDA



Building blocks

- Top 12 chemicals from biomass (2004 US-DOE study)
  - Based on 2nd approach
  - Scientific fundamentals for certain choices are questionable



Training course on Bioplastics
4- Biobased and durable polymers / Biobased and biodegradable polymers

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Biobased polymers

- **Biobased polymers for Long term applications (Durable)** e.g., Automotive, Building …

- **Biobased and biodegradable polymers for Short term applications** e.g., Packaging, Agriculture, Hygiene …

Training course on Bioplastics
4- Biobased and durable polymers / Biobased and biodegradable polymers

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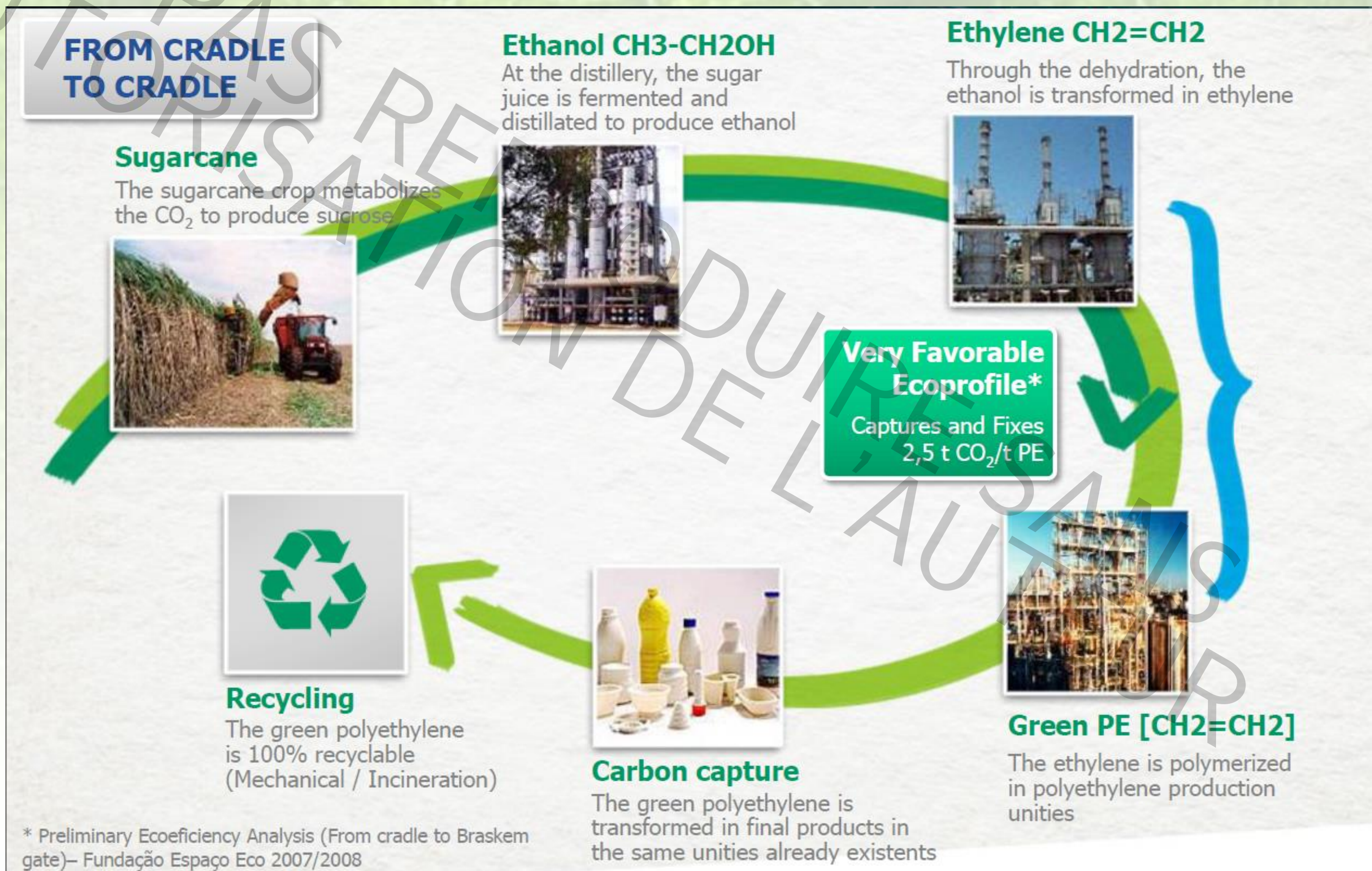
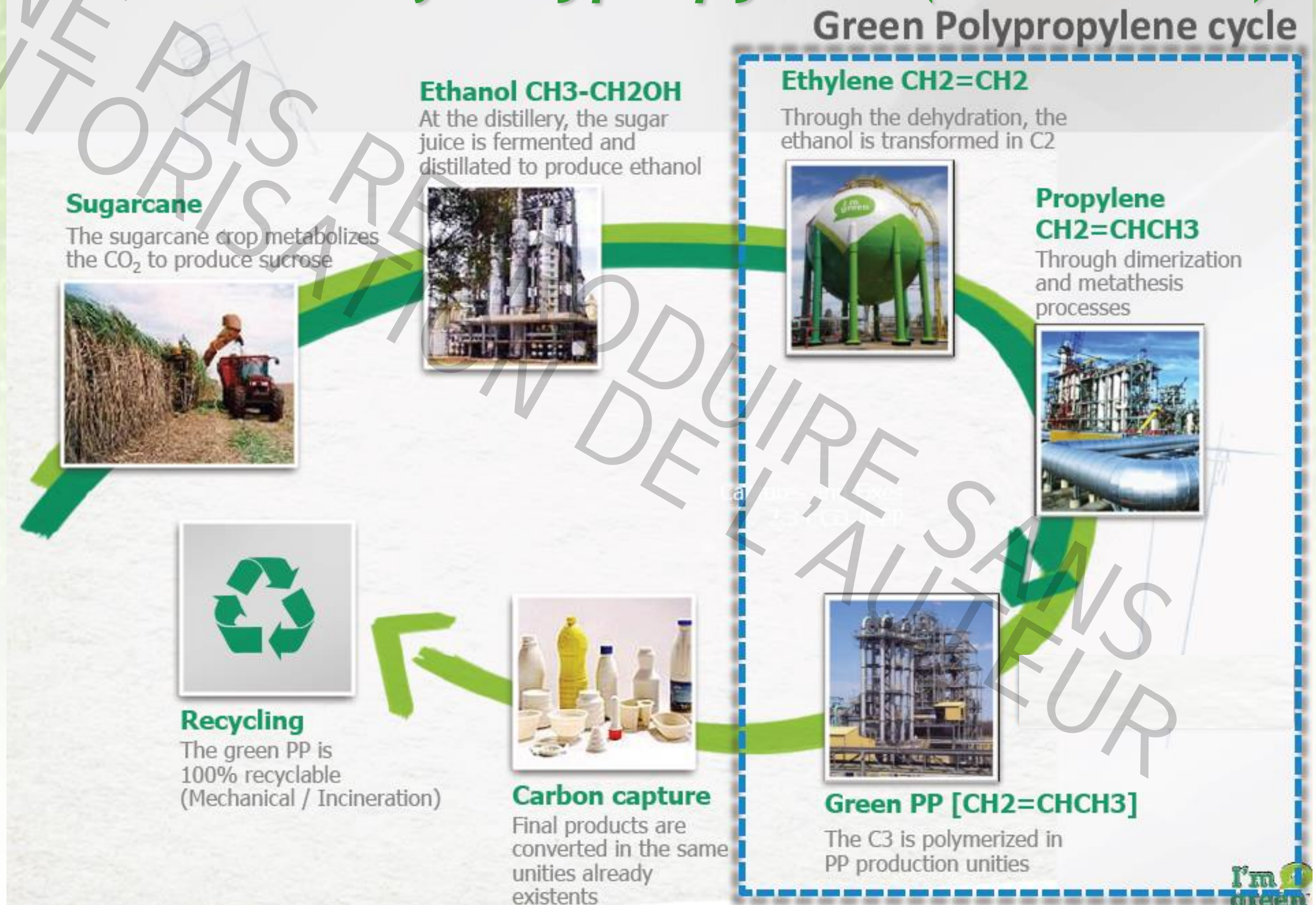
Biobased and Durable Polymers

Production of Polyethylene



Biobased and Durable Polymers

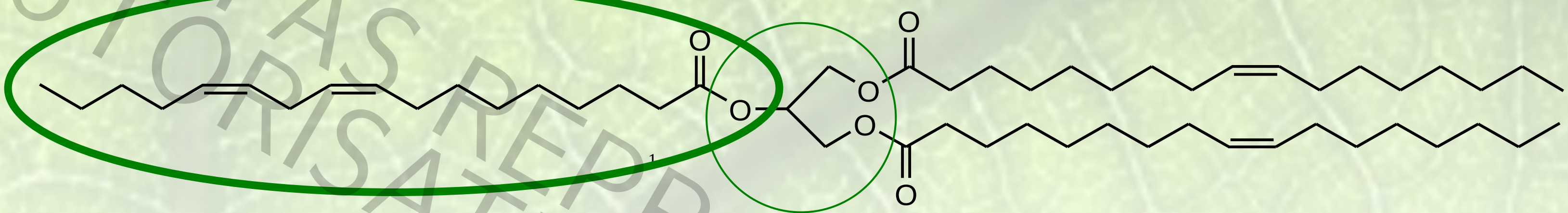
Production of Polypropylene (Metathesis)



Biobased and Durable Polymers

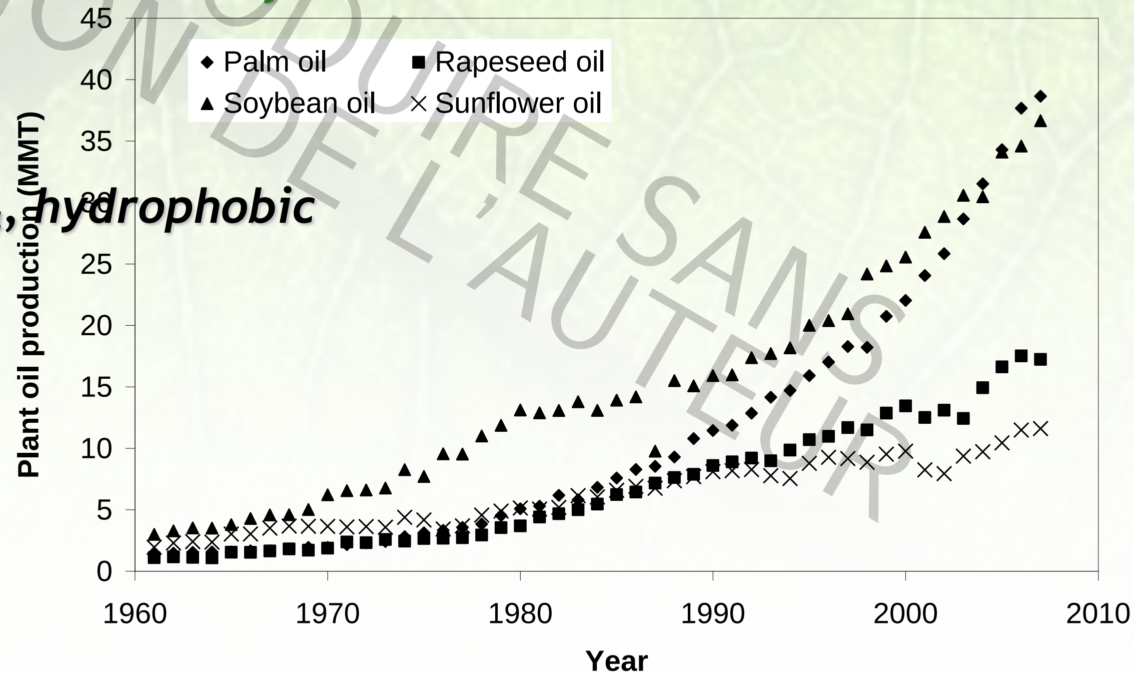
Vegetable oils

Vegetable oil = 95% of triglycerides (tri-ester of glycerol and fatty acids)



Fatty acid Glycerol

- *Chain length : C_6 à C_{24}, hydrophobic*
- *Low toxicity*
- *Low price*
- *Highly available*



Biobased and Durable Polymers

Production of polymers from vegetable oil:

Nothing New!

Production of polymers from vegetable oil:

Castor seed oil (composition):

Acid name	**Average % Range**		
Ricinoleic Acid	95	to	85%
Oleic acid	6	to	2%
Linoleic acid	5	to	1%
Linolenic acid	1	to	0.5%
Stearic acid	1	to	0.5%
Palmitic acid	1	to	0.5%
Dihydroxystearic acid	0.5	to	0.3%
Others	0.5	to	0.2%

Biobased and Durable Polymers

Materials from Vegetable Oils

- *Chemicals*
    - 1,3 propanediol
    - 1-nonanol
    - 1-hexanol
    - Specialized diesters, diacids, diisocyanates and diols
- *Polymers – plastics*
    - *Polyurethanes*
        - Automotive, Construction, Carpeting, Tubing, Coatings, etc.
    - *Polylactones*
        - Sutures, timed released drugs, stimuli-released drugs
    - *Copolymers of Polyurethane and "other"*
    - *Polyamides*
    - *Polyester-amides*

Training course on Bioplastics
4- Biobased and durable polymers / Biobased and biodegradable polymers

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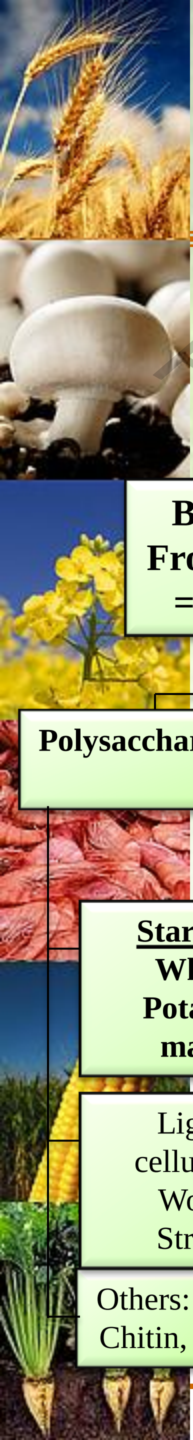


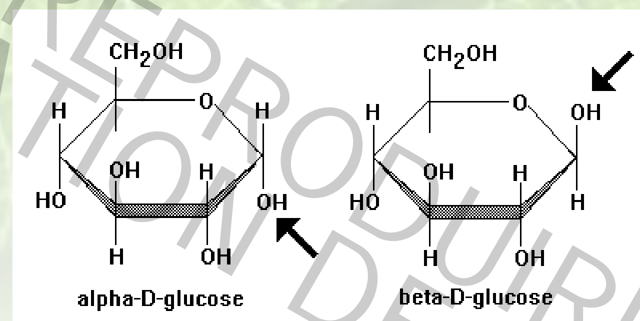
Biobased and Biodegradable Polymers

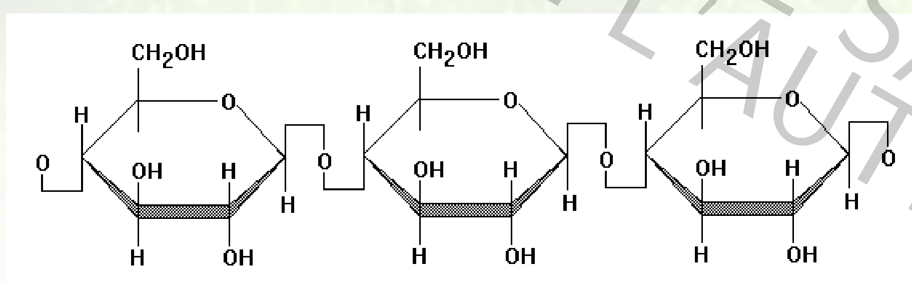
Biodegradable polymers - Classification -

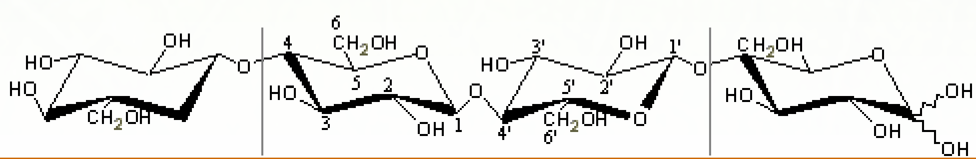
- **Biomass products From agro-resources => *Agro-polymers***
  - **Polysaccharides**
    - **<u>Starches</u>: Wheat, Potatoes, maize**
    - Ligno-cellulosic: Wood, Straws
    - Others: Chitin,
  - **Proteins, lipids …**
    - Animals: Casein, Gelatine, whey
    - Plant: Soya, Gluten
- **From microorganisms (obtained by extraction)**
  - **PolyHydroxy-Alkanoates (PHA)**
    - **- Polyhydroxy butyrate (PHB)**
    - **- Polyhydroxybutyrate co-valerate (PHBV), …**
- **From biotechnology (conventional synthesis from bio-derived monomers)**
  - **Polylactides**
    - **Poly(lactic acid) (PLA)**
- **From petrochemical products (conventional synthesis)**
  - **Polycaprolactones** (PCL)
  - **Polyesteramides** (PEA)
  - **Aliphatic co-polyesters** (e.g: PBSA)
  - **Aromatic co-polyesters (e.g: PBAT)**

Polysaccharide: Cellulose

Chemical structures:







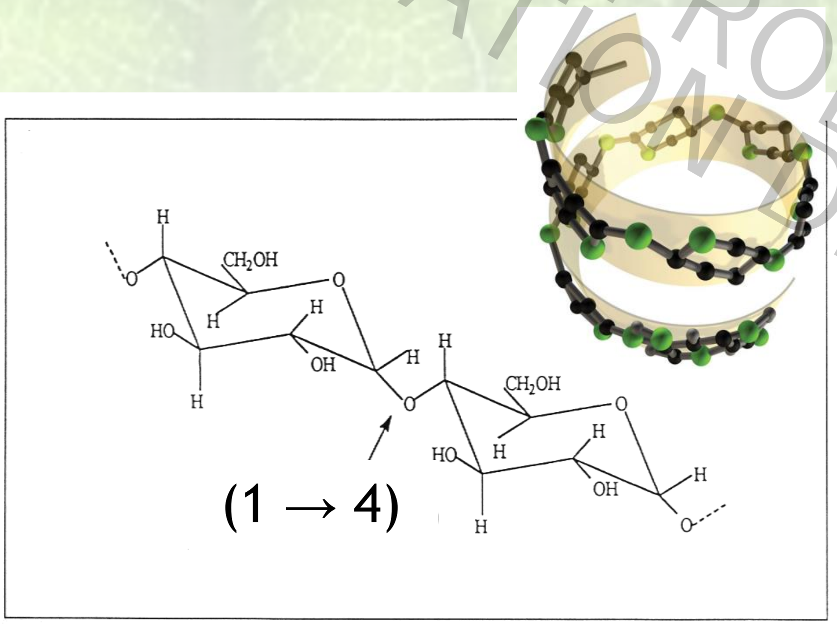
Biobased and Biodegradable Polymers

Polysaccharide: Starch

Polysaccharide: Starch

Starch is composed of two macromolecules: amylose & amylopectin

amylose: linear polymer (Mw=10^5-10^6)

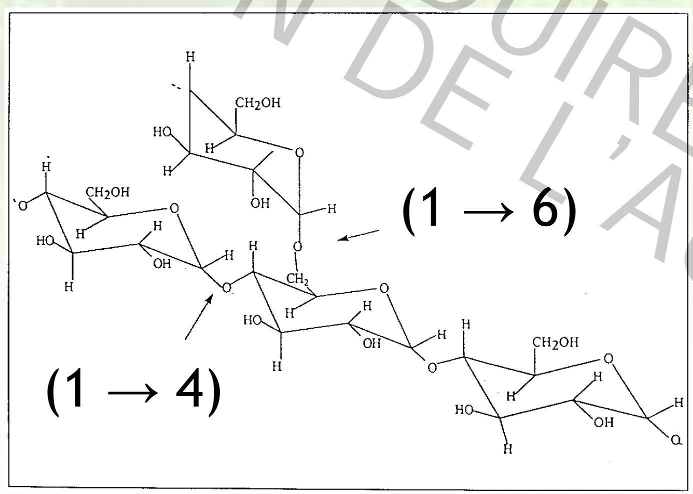


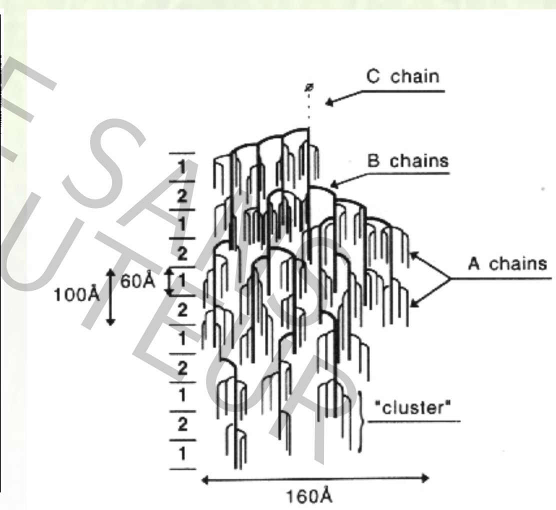
Amylose is a sparsely branched carbohydrate mainly based on alpha(1–4) bonds with a molecular weight of 10^5–10^6. The number of macromolecular config. based on alpha(1-6) links are directly proportional to the amylose molecular weight. The chains show spiral-shaped single or double helixes with a rotation on the alpha(1–4) link and with 6 glucoses per rotation.

Polysaccharide: Native Starch

Starch is composed of two macromolecules: amylose & amylopectin

Amylopectin is a highly multiple-branched biopolymer with a very high molecular weight (10^6–10^9). It is based on alpha(1–4) (around 95%) and alpha(1–6) links (around 5%), constituting branching points are localized every 22–70 glucose units, generating a kind of grape branched-like structure with pending chains.





amylopectin: highly branched polymer ($M_w=10^6$-10^9)

Polysaccharide: Native Starch

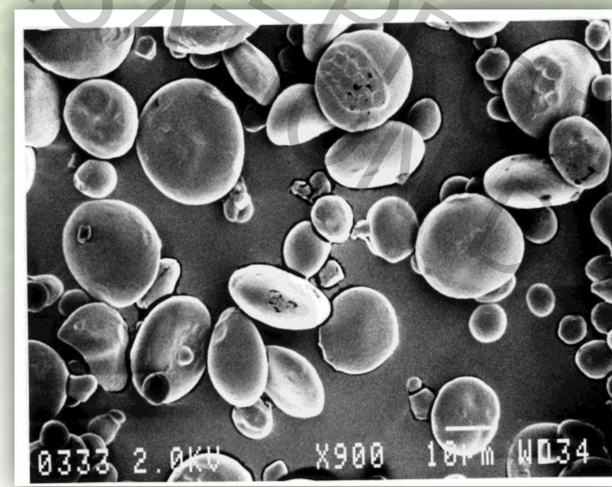
Starch	Amylose Content[a] (%)	Amylopectin Content[a] (%)	Lipid Content[a] (%)	Protein Content[a] (%)	Phosphorus Content[a] (%)	Moisture Content[b] (%)	Granule Diameter (μm)	Crystallinity (%)
Wheat	26–27	72–73	0.63	0.30	0.06	13	25	36
Maize	26–28	71–73	0.63	0.30	0.02	12–13	15	39
Waxy starch	<1	99	0.23	0.10	0.01	n.d.	15	39
Amylomaize	50–80	20–50	1.11	0.50	0.03	n.d.	10	19
Potato	20–25	79–74	0.03	0.05	0.08	18–19	40–100	25

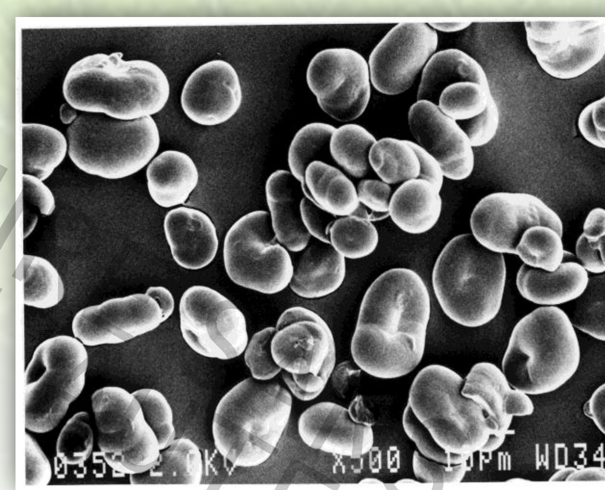
Protein = Maillard reactions

Source: L. Avérous

Polysaccharide: Native Starch

Native starch structure





e.g., wheat and pea

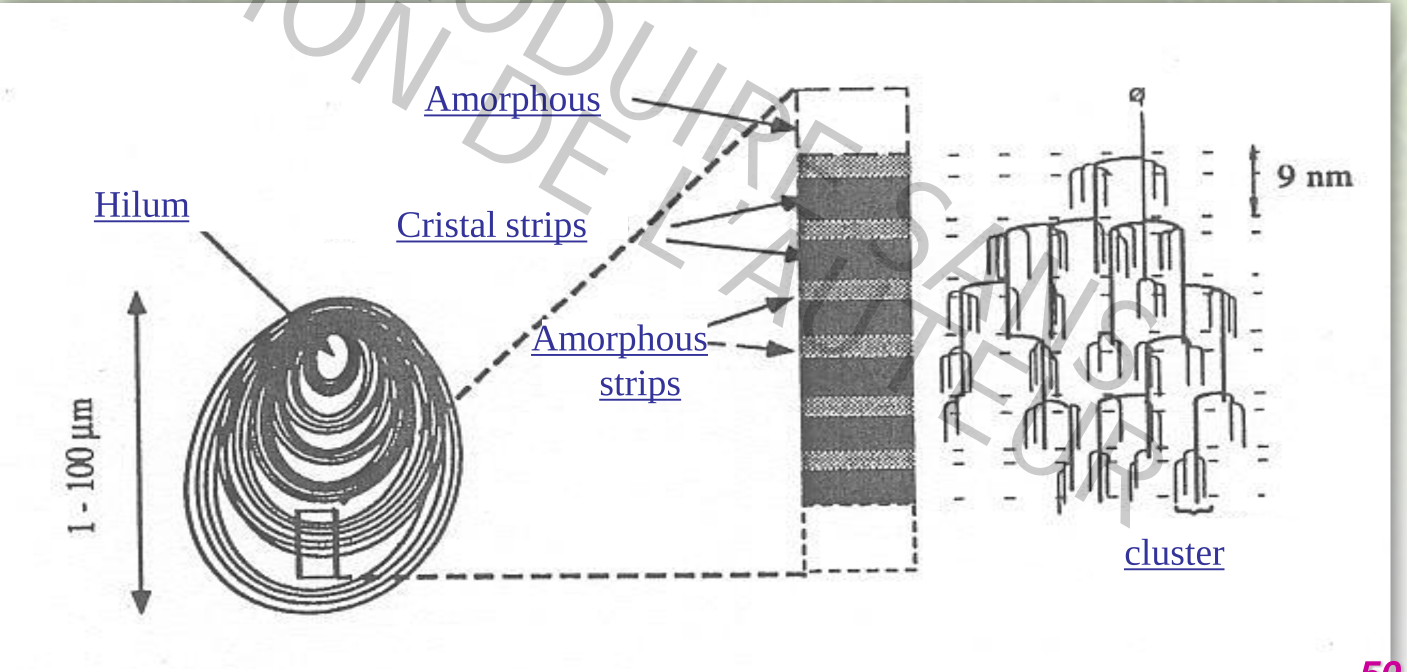
Variety of shape

Dimensions: 0.5 to 175 microns

Biobased and Biodegradable Polymers

Polysaccharide: Native Starch

- Radial organization from hilum
- Macromolecules are mainly oriented acc. radial axis
- Structure = inter-macro. links + water molecules
- Amylose + branching regions = amorphous zones



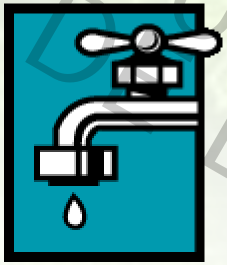
Source D.J. Gallant & B. Bouchet, *Food Microstr. 1986*

Polysaccharide: Destructured Starch

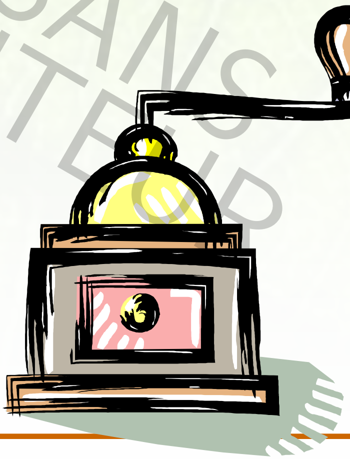
- From native starch, we obtain different processable materials,

According to

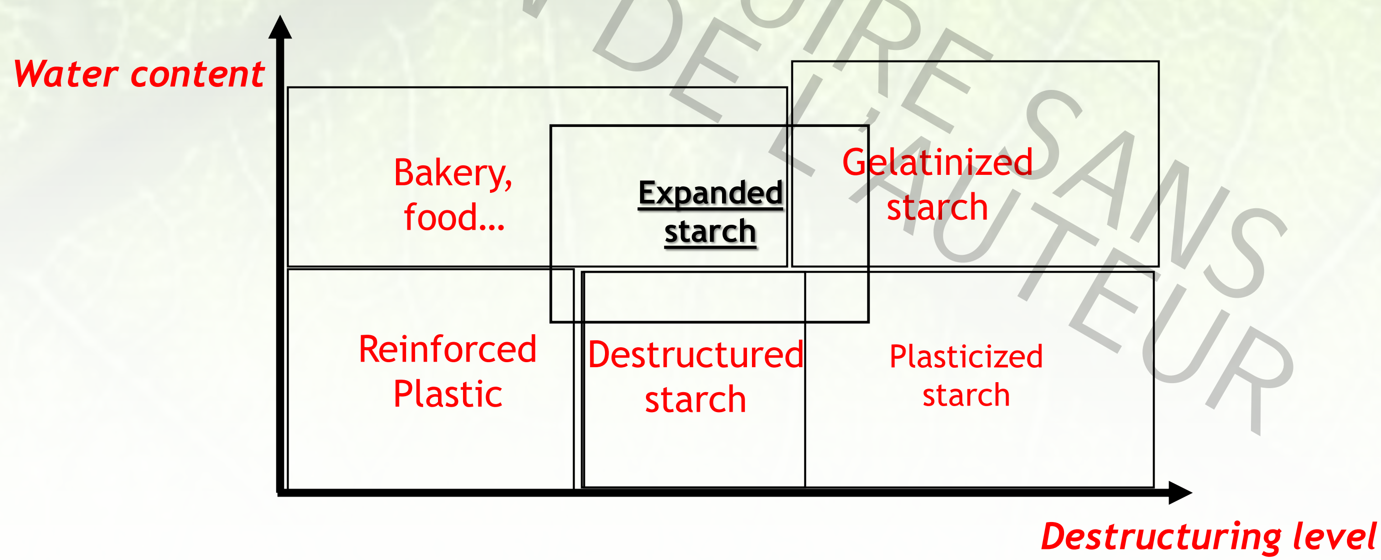
- the water content



- the thermo-mechanical input

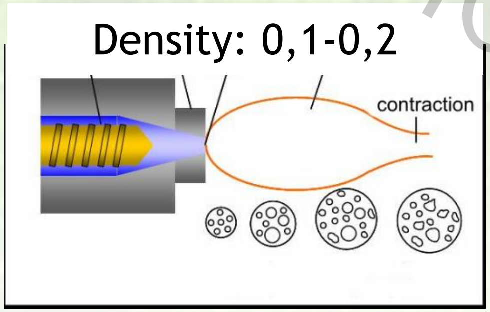


Polysaccharide: Expanded Starch



Polysaccharide: Expanded Starch

Extrusion:

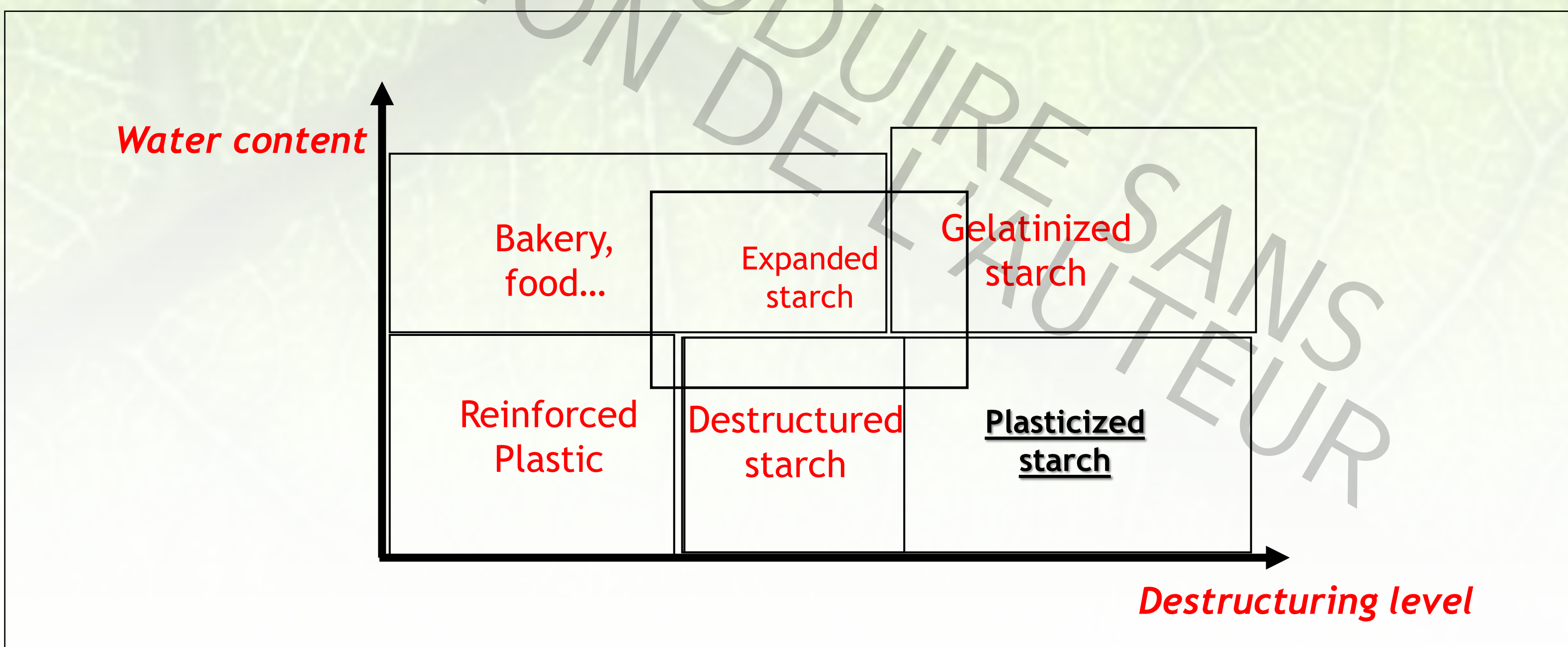


Packaging

Novamont, Storopack © Eco-Foam © (National Starch),

Loose fills

Polysaccharide: Plasticized Starch



Polysaccharide: Plasticized Starch

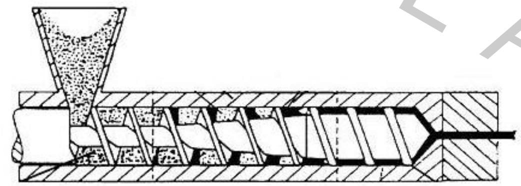
- The so-called “Thermoplastic Starch” or TPS
- The first patents and articles on these materials (plasticized starch or PLS) were published at the end of the eighties.

Biobased and Biodegradable Polymers

Polysaccharide: Plasticized Starch

Native starch
+ plasticizers = Dry-blend
(polyols, water)

Plasticized Starch



homogeneous molten phase

Shear + Heating (Thermo-mechanical)

Main parameters: Temperature (T) and Specific Mechanical Energy (SME)

Polysaccharide: Plasticized Starch

	Glycerol/Dry Starch Ratio [a] (w/w)	Water[a] (wt%)	Density[a]	T_g (by DSC) (°C)	α-Transition (by DMTA) (C°)	Modulus[a] (MPa)	Max. Tensile[a] Strength (MPa)	Elongation at Break[a] (%)
S74G10W10[b]	0.14	9	1.39	43	63	1144 (42)	21.4 (5.2)	3 (0)
S75G18W12[b]	0.25	9	1.37	8	31	116 (11)	4.0 (1.7)	104 (5)
S67G24W9[b]	0.35	12	1.35	−7	17	45 (5)	3.3 (0.1)	98 (5)
S65G35W0[b]	0.50	13	1.34	−20	1	11 (1)	1.4 (0.1)	60 (5)

Standard deviations are in brackets.

Source: Averous and Halley (2009).

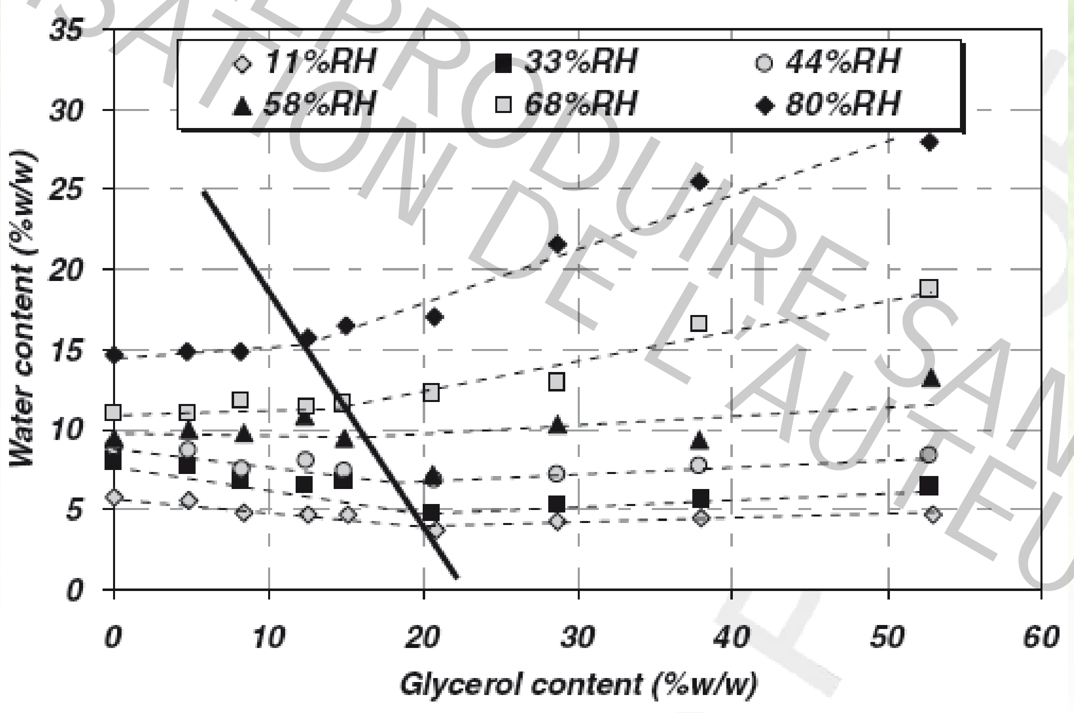
[a] Contents and properties after equilibrium at 23°C and 50% RH, 6 weeks.

[b] Initial formulation (SxGyWz): S = starch (*x* wt%), G = glycerol (*y* wt%), W = water (*z* wt%).

Source: L. Avérous

Polysaccharide: Plasticized Starch

Water content = f(Moisture, glycerol content)



Source: Godbillot et al. (2006).

Polysaccharide: Plasticized Starch

☺ **Attributes:**

- Tunable Properties
- Entirely biodegradable and from renewable resources
- Low cost material
- Transformed using conventional techniques

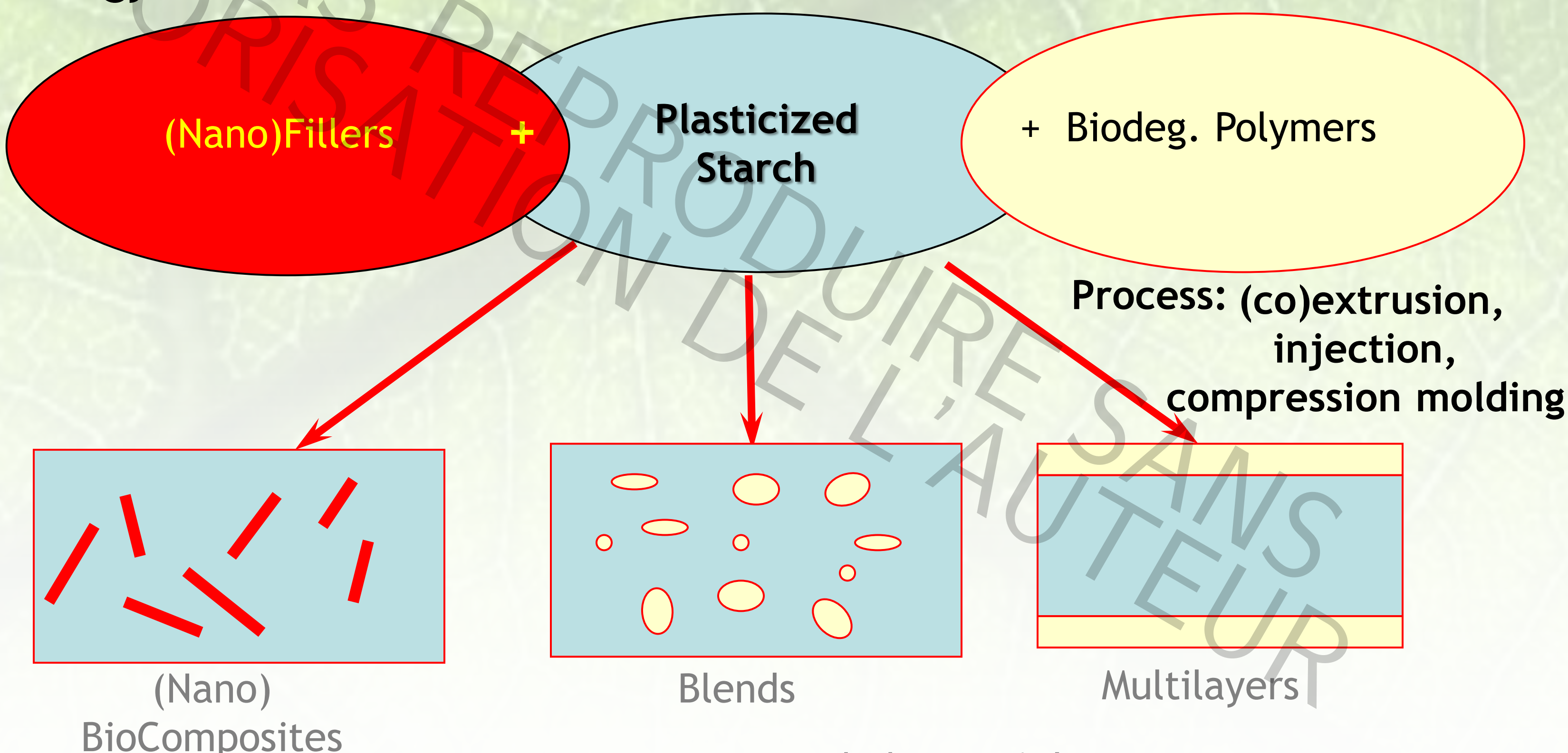
☹ **Issues:**

- Post-processing aging
- Weak mechanical properties
- Moisture sensitivity

Biobased and Biodegradable Polymers

Polysaccharide: Starch-based materials

Strategy: Association



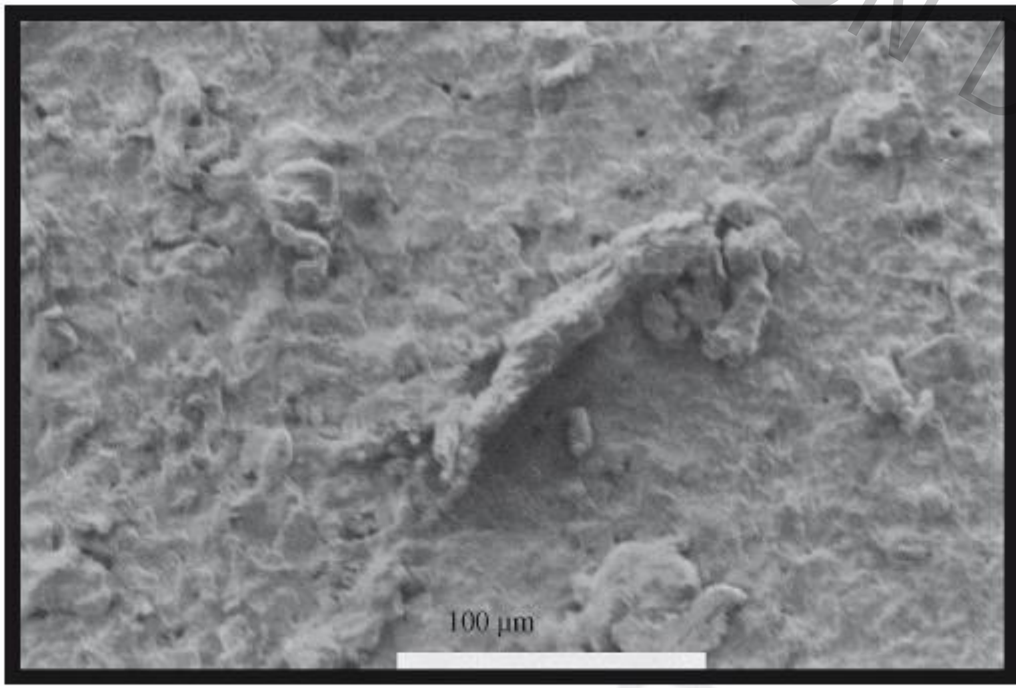
+ *Foam / Expanded material*

► **Elaboration of different structures**

Polysaccharide: Starch-based materials

Bio-Composites

Cryogenic fracture of composites -PLS - leafwood cellulose fibers- (white scale = 100 microns)

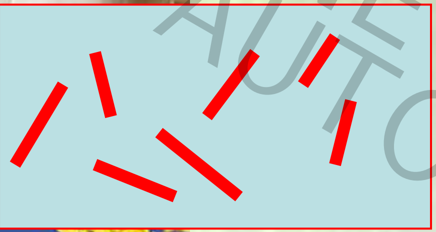


Improvements:

- higher mechanical properties linked to strong matrix/filler interactions,
- higher thermal resistance, due to the transition shift of Tg and increase in the rubber plateau,
- reduced water sensitivity due to fiber–matrix interactions and to the higher hydrophobic character of the cellulose (linked to its high crystallinity),
- reduced post-processing aging, due to the formation of a 3D network between the different matrix–filler carbohydrates based on hydrogen bonds

Source: Avérous et al. (2001)

Polysaccharide: Starch-based materials



Nano-Biocomposites

Plasticized Starch
(BIOPOLYMER)

MMT …
(NANO-Objects)

↓

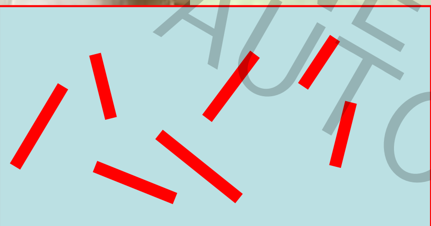
Processing

↓

NANO-BIOCOMPOSITE
Based on starch

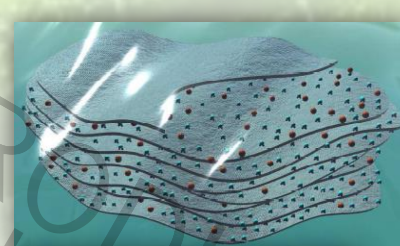
Chivrac et al., Materials Science & Engineering R, 2009

Polysaccharide: Starch-based materials



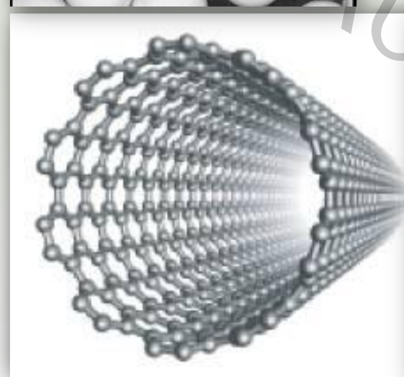
Nano-Biocomposites (Nanoparticles)

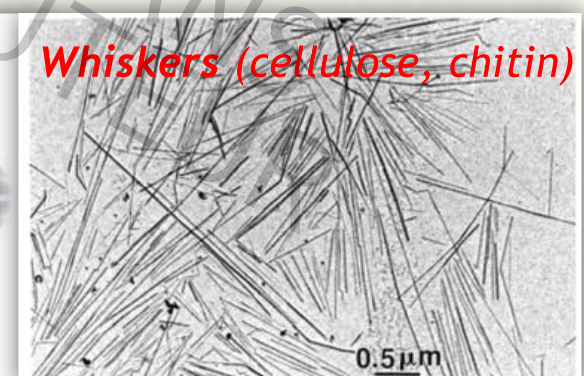
- ►*Lamellar*



- ►*Spherical Particles*

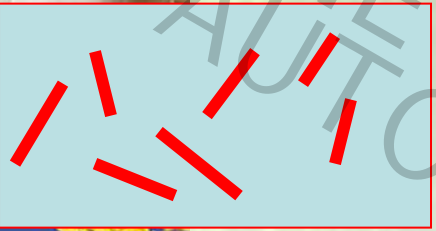
- ►*Fibres and Tubes*

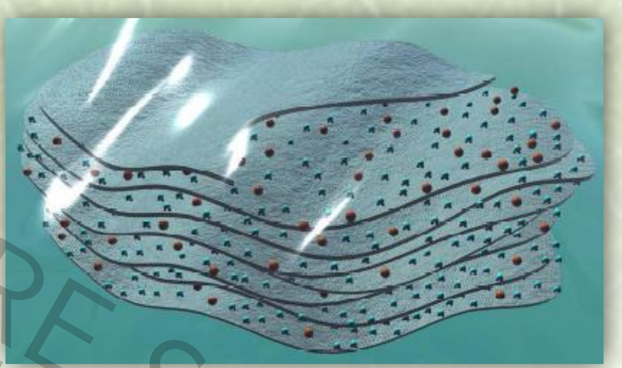




Polysaccharide: Starch-based materials

Nano-Biocomposites (MMT)





- *Clay lamellar structure*
- *Montmorillonite platelet:*
  - Thickness ~ 1nm
  - Length ~ 100-150nm

  High aspect ratio

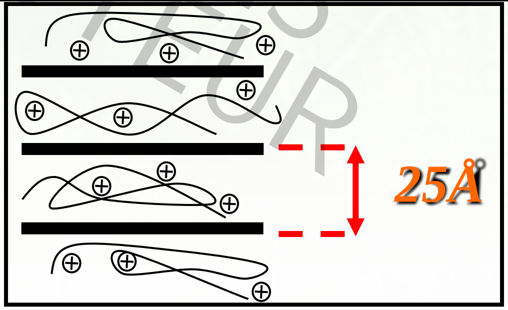
  - Specific surface ~ 700m²/g

Polysaccharide: Starch-based materials

Nano-Biocomposites (O-MMT/CS)

Clay organo-modifier content:

~ 40 wt% of cationic starch

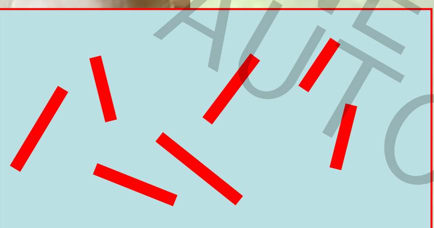


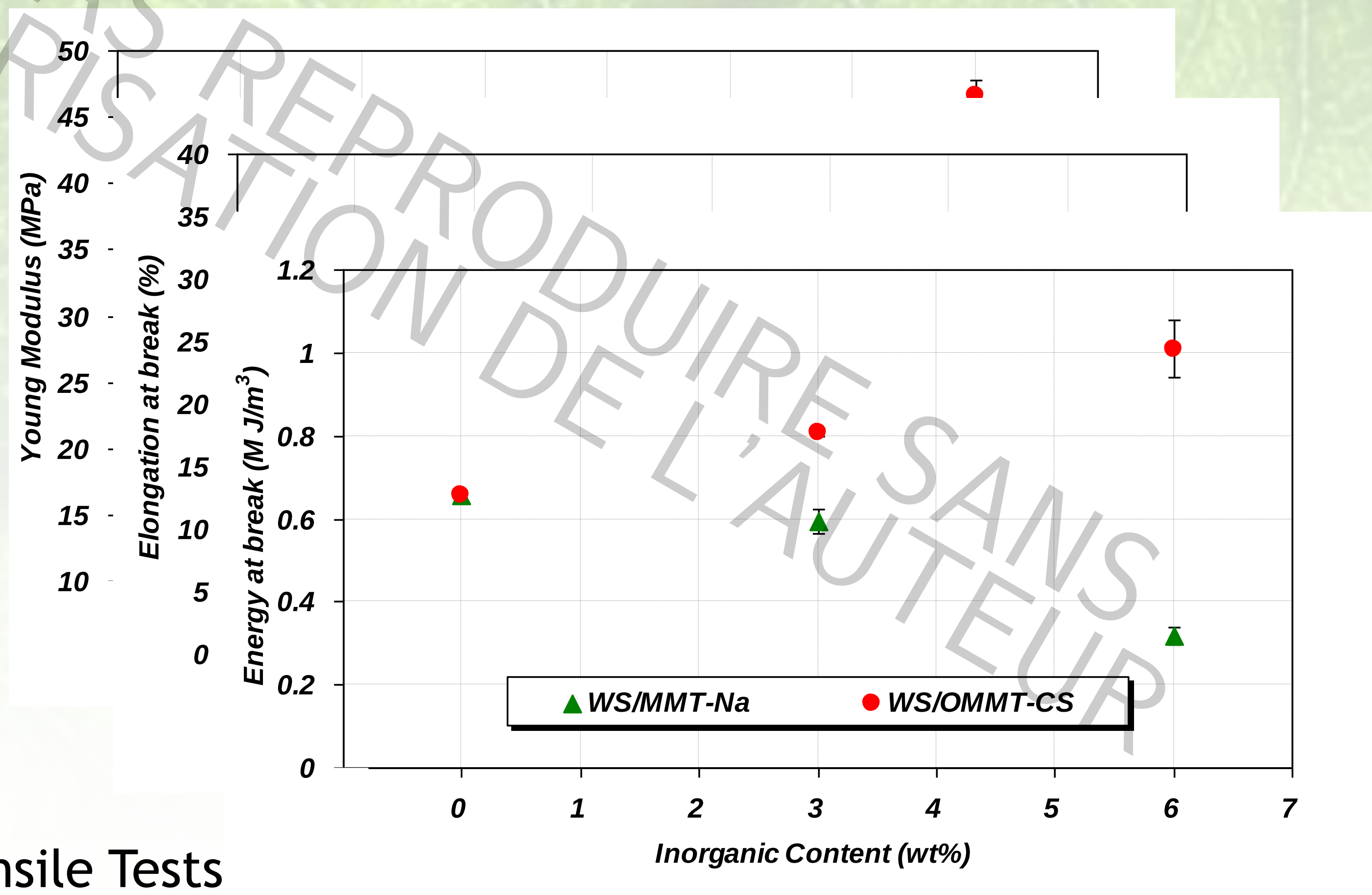
F. Chivrac et al., *Biomacromolecules*, 20

Biobased and Biodegradable Polymers

Polysaccharide: Starch-based materials

Nano-Biocomposites (OMMT/CS)

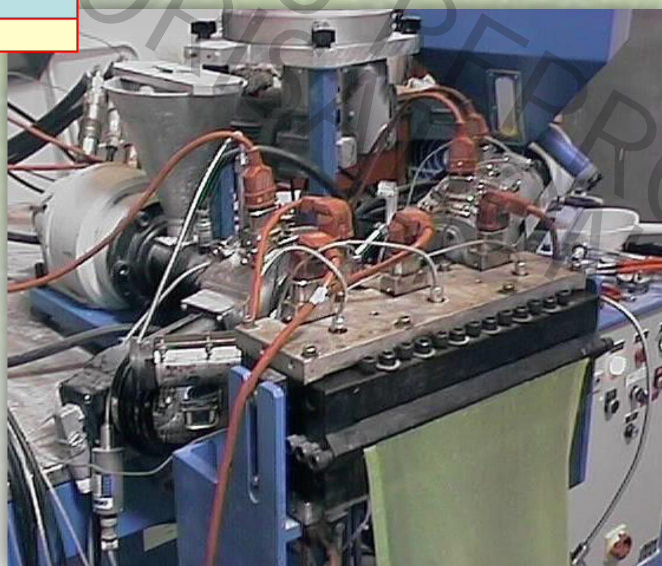




Uniaxial tensile Tests

Biobased and Biodegradable Polymers

Polysaccharide: Starch-based materials



Coextrusion system with flat die

Biodegradable Layer
Plasticized Starch
Biodegradable Layer

Thermoformed multilayer trays

(French Patent)

O. Martin et al. Starch/Starke 2001

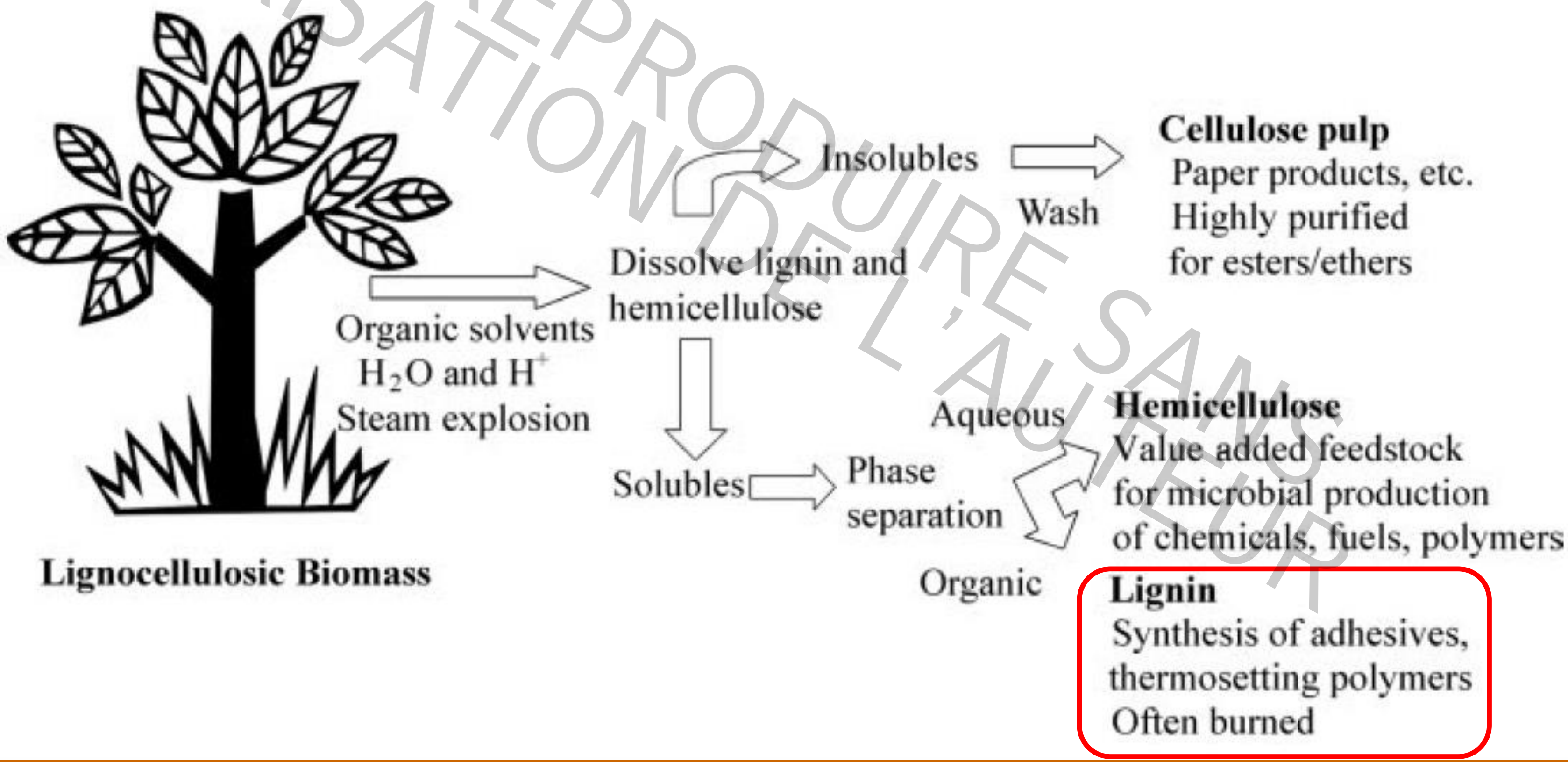
Biobased and Biodegradable Polymers

Polysaccharide: Starch-based materials

Applications: Packaging, Agriculture, Leisure, Hygiene, Catering, …

Biobased and Biodegradable Polymers

Lignins



Properties of dif. Biopolyesters

	PLA Dow–Cargill (NatureWorks)	PHBV Monsanto (Biopol D400G – HV = 7 mol%)	PCL Solvay (CAPA 680)	PEA Bayer (BAK 1095)	PBSA Showa (Bionolle 3000)	PBAT Eastman (Eastar bio 14766)
Density	1.25	1.25	1.11	1.07	1.23	1.21
Melting point (°C)[a]	152	153	65	112	114	110–115
Glass transition (°C)[a]	58	5	−61	−29	−45	−30
Crystallinity[b] (in %)	0–1	51	67	33	41	20–35
Modulus (MPa) (NFT 51-035)	2050	900	190	262	249	52
Elongation at break (%) (NFT 51-035)	9	15	>500	420	>500	>500
Tensile stress at break or max. (MPa) (NFT 51-035)	–	–	14	17	19	9
Biodegradation[c] (mineralization in %)	100	100	100	100	90	100
Water permeability WVTR at 25 °C ($g/m^2/day$)	172	21	177	680	330	550
Surface tension (γ) (mN/m)	50	–	51	59	56	53
γ_d (dispersive component)	37	–	41	37	43	43
γ_p (polar component)	13	–	11	22	14	11

[a] Measured by DSC.
[b] Determined on granules, before processing.
[c] After 60 days in controlled composting according to ASTM 5336.

Source: P. Bordes et al. / Progress in Polymer Science 34 (2009) 125–155

Biobased and Biodegradable Polymers

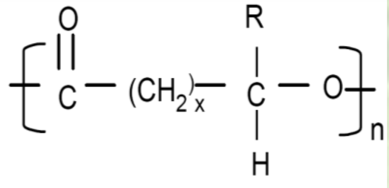
Polyhydroxyalkanoates (PHA)

Biodegradable polymers - Classification -

- **Biomass products From agro-resources => *Agro-polymers***
  - **Polysaccharides**
    - **Starches:** Wheat, Potatoes, maize
    - Ligno-cellulosic: Wood, Straws
    - Others: Chitin,
  - **Proteins, lipids …**
    - Animals: Casein, Gelatine, whey
    - Plant: Soya, Gluten
- **From microorganisms (obtained by extraction)**
  - **PolyHydroxy-Alkanoates (PHA)**
    - **- Polyhydroxy butyrate (PHB)**
    - **- Polyhydroxybutyrate co-valerate (PHBV), …**
- **From biotechnology (conventional synthesis from bio-derived monomers)**
  - **Polylactides**
    - **Poly(lactic acid) (PLA)**
- **From petrochemical products (conventional synthesis)**
  - **Polycaprolactones** (PCL)
  - **Polyesteramides** (PEA)
  - **Aliphatic co-polyesters** (e.g: PBSA)
  - **Aromatic co-polyesters (e.g: PBAT)**

Polyhydroxyalkanoates (PHA)

Homopolymers:



Chemical Name	Abbreviation	x	R
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)	1	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

Polyhydroxyalkanoates (PHA)

Main homo and co-polymers:

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

Polyhydroxyalkanoates (PHA Properties)

A comparison of the physical properties of PHBV with those of other biodegradable plastic

Polymer	PHBV	PLA	PCL	PEA	PBSA	PBAT
Density	1.25	1.25	1.11	107	1.23	1.21
Melting temperature (°C)	153	152	65	112	114	110–115
Tg (°C)	5	58	−61	−29	−45	−30
Crystallinity (%)	51	0–1	67	33	41	20–35
Modulus (MPa)	900	2000	190	260	250	52
Elongation at break (%)	15	9	>500	420	>500	>500
Water permeability $g\ m^{-2}$ per day	21	172	177	680	330	550

PHBV – poly-(3-hydroxybutyrate-*co*-3-valerate), Monsanto (Biopol D400G, HV 7%); PLA – poly(lactic acid), Dow-Cargill (Nature Works); PCL – polycaprolactone, Solvay (CAPA 680); PEA – polyesteramide, Bayer (BAK 1095); PBSA – poly(butylene succinate-*co*-adipate), Showa (Bionolle 3000); PBAT – aromatic copolyester, Eastman (Eastar bio 14766).

Source: L. Avérous

Biobased and Biodegradable Polymers

Polylactic acid (PLA)

Biodegradable polymers - Classification -

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  - **Polysaccharides**
    - **Starches:** **Wheat, Potatoes, maize**
    - Ligno-cellulosic: Wood, Straws
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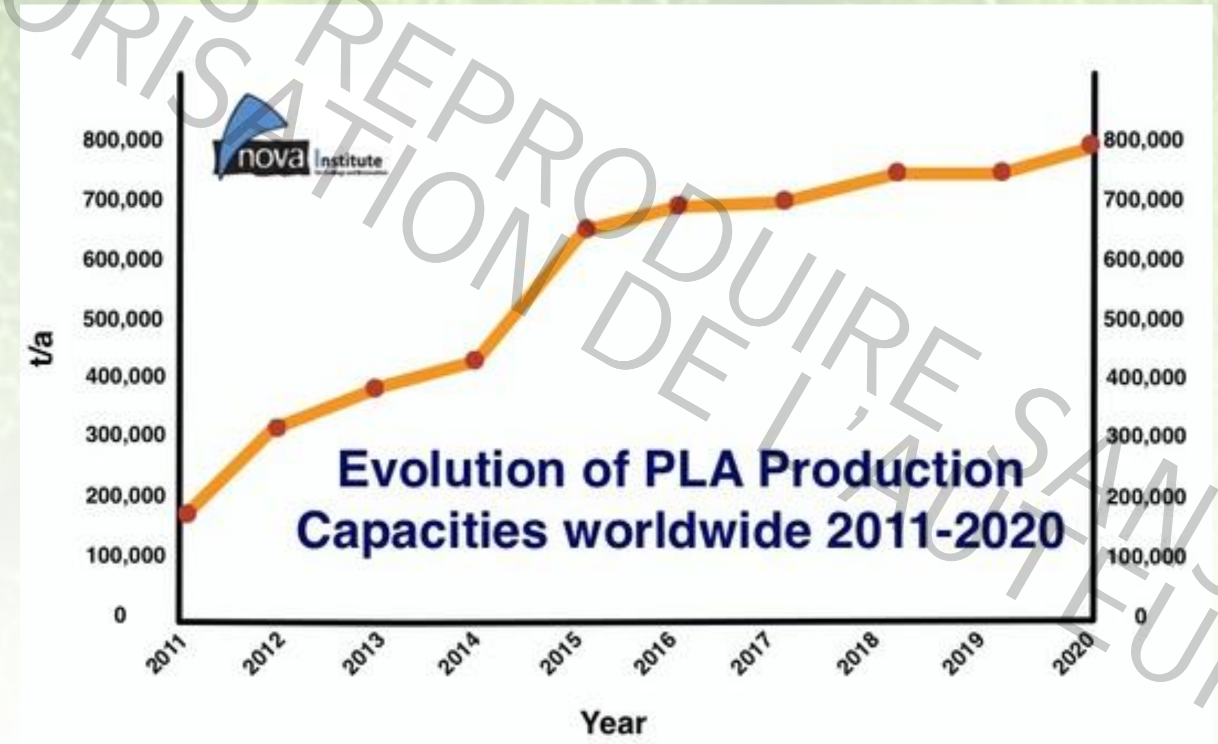
  - **Aromatic co-polyesters (e.g: PBAT)**

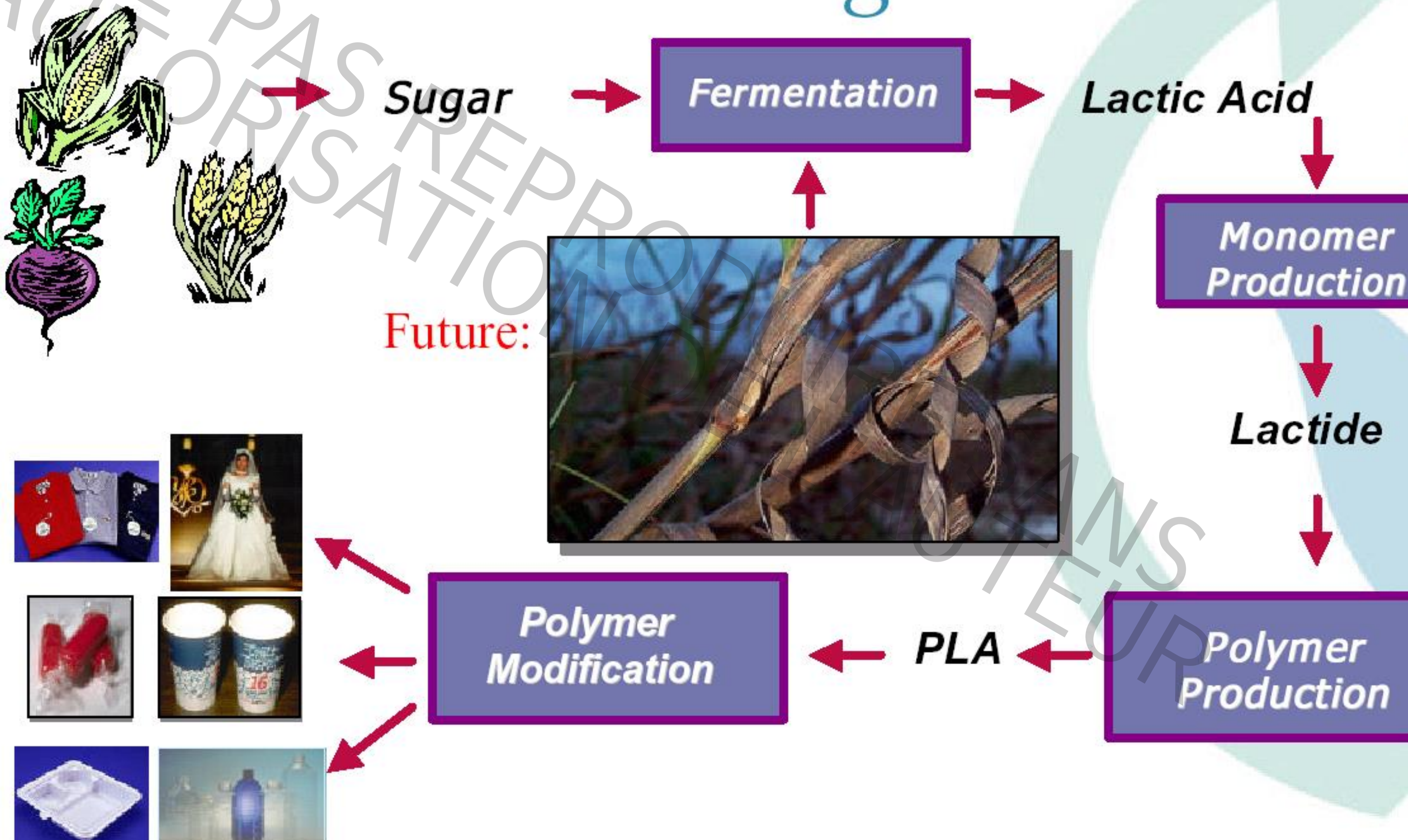
The PLA Production: A trend



Main PLA Applications

- Packaging (trays, bags, cups…)
- Textile,
- Agricultural products (mulch film, planting pots, clips)
- Automotive,
- Building …
- Catering (forks, knifes, plates, …),
- Leisure,
- Hygiene,
- Biomedical, …

PLA Manufacturing Overview



PLA Properties

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[a] Measured by DSC.
[b] Determined on granules, before processing.
[c] After 60 days in controlled composting according to ASTM 5336.

Source: P. Bordes et al. / Progress in Polymer Science 34 (2009) 125–155

Biobased and Biodegradable Polymers

Interest of the Stereo-complexed PLA

Physical properties	Stereo-complexed PLA	PLLA	PDLLA	Syndiotactic PLA	PCL	Poly[(*R*)-3-hydroxybutyrate] (R-PHB)
T_m(°C)	220–230	170–190	–	151	60	180
T_m^0(°C)	279	205, 212, 215	–	–	71, 79	188, 197
T_g(°C)	65–72	50–65	50–60	34	−60	5
ΔH_m(100%)[a] (J g^{-1})	142, 146	93, 135, 142, 203	–	–	142	146
ΔE_{td}[b] (kJ · mol^{-1})	205–297	87–104	–	–	–	–
Density (g · cm^{-3})	–	1.25–1.29	1.27	–	1.06–1.13	1.177–1.260
Solubility parameter (δ_p) (25 °C) (J$^{0.5}$ · cm$^{-1.5}$)	–	19–20.5, 22.7	21.1	–	20.8	20.6
$[\alpha]_{589}^{25}$ in chloroform(deg · dm^{-1} · g^{-1} · cm^3)	–	−155 ± 1	0	–	0	+44[c]
WVTR[d] (g · m^{-2} · d^{-1})	–	82–172	–	–	177	13[e]
Tensile strength (GPa)	0.88[f]	0.12–2.3[f]	0.04–0.05[g]	–	0.1–0.8[f]	0.18–0.20[f]
Young's modulus (GPa)	8.6[f]	7–10[f]	1.5–1.9[g]	–	–	5–6[f]
Elongation at break (%)	30[f]	12–26[f]	5–10[g]	–	20–120[f]	50–70[f]

[a] Enthalpy of melting of crystal having infinite size.
[b] Activation energy for thermal degradation estimated by thermogravimetry at a constant temperature (250–270 °C).
[c] 300 nm, 23 °C.
[d] Water vapor transmission rate at 25 °C.
[e] Poly[(*R*)-3-hydroxybutyrate-*co*-3-hydroxyvalerate] (94/6).
[f] Oriented fiber.
[g] Non-oriented films.

Source: Hideto Tsuji, Macromol. Biosci. 2005, 5, 569-597

Biobased polymers

The future ?

- *GMO (e.g., Starch)*
- *↓ Some fossil resources with ↗ price of some fractions (???$)*
- *Evolution of the « society » (« Grenelle de l'environnement », sustainability ?)*
- *Evolution of the governmental policy Eco-tax ?*

Europe?

Merci !

Strasbourg (Alsace)

Some Questions ?

Luc.averous@unistra.fr

www.biodeg.NET