Bio-sourced polymers
Etienne Grau

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Bio-sourced polymers

Dr Etienne Grau
egrau@enscbp.fr

There is no such thing as a stupid question, so please, do not hesitate to interrupt me
1- Why?

2- How?

3- Bio-based plastics from natural polymers

4- Drop-ins: Bio-based alternative to fossil-based polymers

5- Smart drop-ins: Bio-based derivative of “fossil” polymers

6- New polymers from biomass

7- Conclusions and perspectives
Hydrocarbons are running out and/or become much more expensive.
Petroleum is the starting materials of 99% « commodity » chemicals

- 33% polymers (PE, PVC, PET, PMMA, PS, nylon …)
- 30% organic molecules (acetone, toluene, petroleum ether…)
- 20% others (surfactants, pigment, carbon black, …)
- 12% Inorganic component (soda, acids, Cl₂, …)
- 6% Fertilizers (NH₃)

\[ \text{Petroleum} = C \] \[ \text{Petroleum} = J \]
20th century: A petroleum area

Synthetic polymers are based on petroleum

Platform molecules

C2
C3
C4
C6,7,8

Cracking

~350 million tons (annual global production)

Steel 1800 Mt (230 Mm³)

20th century:

A petroleum area

Gases >C1-4
Gasoline >C5-12
Kerosene >C12-16
Fuel oil >C15-18
Lubricating oil >C16-20
Residue (asphalt) >C20

Crude Oil
Furnace
From crude oil to platform molecules

1. Distillation
2. Steam cracking
3. Catalytic cracking ('hydrocracking')
4. Isomerisation
5. Reforming ('platforming')
6. Sulfur is removed
Oil refinery – example of the C3 platform

**Oil refinery**

- **H₂**: Hydrogen
- **C1**: Methane
- **C2**: Ethylene
- **C3**: Propene
- **C4**: Butane
- **C5**: Hexane
- **C6**: Benzene
- **Alkanes**: Ethanol, Propanediol, Butanediol
- **Aromatics**: Propane, Butadiene
- **Complex products**: Petrol, Diesel
- **Asphalt hydrocarbons**

**Naphtha**

1. **H₂O**
2. **Acid**
3. **Base**
4. **Isomerisation**

- **CO**
- **H₂**

- **gas phase oxidation**
- **ammoniation**
- **H₂O**

- **acrylic acid**
- **acrylonitrile**
- **acrylamide**

- **université de BORDEAUX**
Oil refinery – example of the BTX platform

Phthalate plasticizers

Nylon-6 and Nylon-66

Polyurethanes

Synthetic dyes

Kevlar™

Polycarbonate

BTX

Surfactants

Aspirin

Phenolic resins

Epoxies
World crude oil price vs. oil consumption

The data visualization is available at OurWorldinData.org. There you find research and more visualizations on this topic.

Licensed under CC-BY-SA by the authors Hannah Ritchie and Max Roser.
Peak oil?

Worldwide oil reserves

- Peak oil?
- Worldwide oil reserves
- 70s peak oil
- Shale oil
- Oil production
Fossil fuel reserves

Years of fossil fuel reserves left

- Oil: 50.7 years
- Natural Gas: 52.8 years
- Coal: 114 years

Carbon Budget for 2C

- Global Fossil Fuel Reserves: 746 Gt CO₂
- Unburnable Reserves: 471 Gt CO₂
- Carbon Budget for 2C: 275 Gt CO₂

Only 1/3 can be burned.
CO₂ cycle

Atmosphere (800)

Photosynthesis 120 + 3

Plant respiration 60

Fossil fuels, cement, and land-use change 9

Atmospheric Carbon Net Annual Increase 4

Net terrestrial uptake 3

Soil carbon

Plant biomass (550)

Microbial respiration and decomposition 60

Air-sea gas exchange 90 + 2

Surface ocean (1000)

Phytoplankton photosynthesis

Net ocean uptake 2

Deep ocean (37,000)

Reactive sediments (6000)

Soil (2300)

Fossil pool (10,000)

GtC/y: Gigatons of carbon/year
Numbers in parentheses refer to stored carbon pools. Red indicates carbon from human emissions.
Last time the CO₂ was that high the Human didn’t exist
4 ppm/year more CO₂ in the atmosphere

Reduce CO₂ emissions and trap it sustainably.

May 2019: 415ppm
Since Sept 2016 > 400ppm
1987 : 350ppm
Carbon neutral society

George A. Olah
1927-2017
Nobel Prize 1994
CO₂ emissions from cradle to factory gate

GWP (kg CO₂ eq./kg)

- Epoxy
- PA-6
- PA-6,6
- PC
- ABS
- PS
- PET
- PP
- PVC
- PE
### Impact category

<table>
<thead>
<tr>
<th>Impact category</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Climate change</td>
<td>kg CO₂ eq.</td>
</tr>
<tr>
<td>Ozone depletion</td>
<td>kg CFC-11 eq.</td>
</tr>
<tr>
<td>Human toxicity, cancer effects</td>
<td>CTUh</td>
</tr>
<tr>
<td>Human toxicity, non-cancer effects</td>
<td>CTUh</td>
</tr>
<tr>
<td>Respiratory inorganics</td>
<td>kg PM2.5 eq.</td>
</tr>
<tr>
<td>Respiratory organics</td>
<td>kg NMVOC eq</td>
</tr>
<tr>
<td>Ionizing radiation</td>
<td>kBq U235 eq.</td>
</tr>
<tr>
<td>Terrestrial acidification</td>
<td>mol H⁺ eq</td>
</tr>
<tr>
<td>Eutrophication terrestrial</td>
<td>mol N eq</td>
</tr>
<tr>
<td>Eutrophication freshwater</td>
<td>mol P eq</td>
</tr>
<tr>
<td>Eutrophication marine</td>
<td>mol N eq</td>
</tr>
<tr>
<td>Ecotoxicity freshwater</td>
<td>CTUe</td>
</tr>
<tr>
<td>Non-renewable energy</td>
<td>MJ</td>
</tr>
<tr>
<td>Depletion of abiotic ressources</td>
<td>kg Sb eq.</td>
</tr>
<tr>
<td>Water</td>
<td>L</td>
</tr>
</tbody>
</table>
LCA: Example of the grocery bags

Simple LDPE

Non-woven PP

Rigid handle LDPE

Woven PP

biopolymer

paper

cotton

Recycled PET

polyester

composite
## LCA: Example of the grocery bags

<table>
<thead>
<tr>
<th>Impact category / bag</th>
<th>LDPE</th>
<th>PET</th>
<th>Bioplastique</th>
<th>Cotton</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Climate change</strong></td>
<td>1.1 $10^{-1}$</td>
<td>7.7 $10^{-1}$</td>
<td>9.0 $10^{-2}$</td>
<td>3.9</td>
<td>kg CO$_2$ eq.</td>
</tr>
<tr>
<td><strong>Ozone depletion</strong></td>
<td>1.2 $10^{-9}$</td>
<td>6.4 $10^{-8}$</td>
<td>1.5 $10^{-8}$</td>
<td>1.0 $10^{-5}$</td>
<td>kg CFC-11 eq.</td>
</tr>
<tr>
<td><strong>Human tox., cancer effects</strong></td>
<td>1.3 $10^{-9}$</td>
<td>7.0 $10^{-9}$</td>
<td>2.3 $10^{-9}$</td>
<td>1.7 $10^{-7}$</td>
<td>CTUh</td>
</tr>
<tr>
<td><strong>Human tox., non-cancer effects</strong></td>
<td>-1.1 $10^{-8}$</td>
<td>-1.6 $10^{-8}$</td>
<td>3.1 $10^{-8}$</td>
<td>5.6 $10^{-7}$</td>
<td>CTUh</td>
</tr>
<tr>
<td><strong>Respiratory inorganics</strong></td>
<td>1.6 $10^{-5}$</td>
<td>2.7 $10^{-5}$</td>
<td>1.2 $10^{-4}$</td>
<td>3.8 $10^{-3}$</td>
<td>kg PM2.5 eq.</td>
</tr>
<tr>
<td><strong>Respiratory organics</strong></td>
<td>2.0 $10^{-4}$</td>
<td>9.6 $10^{-4}$</td>
<td>3.4 $10^{-4}$</td>
<td>8.7 $10^{-3}$</td>
<td>kg NMVOC eq</td>
</tr>
<tr>
<td><strong>Ionizing radiation</strong></td>
<td>6.0 $10^{-4}$</td>
<td>1.4 $10^{-2}$</td>
<td>3.8 $10^{-3}$</td>
<td>1.3 $10^{-1}$</td>
<td>kBq U235 eq.</td>
</tr>
<tr>
<td><strong>Terrestrial acidification</strong></td>
<td>1.1 $10^{-4}$</td>
<td>1.1 $10^{-3}$</td>
<td>7.4 $10^{-4}$</td>
<td>2.0 $10^{-2}$</td>
<td>mol H$^+$ eq</td>
</tr>
<tr>
<td><strong>Eutrophication terrestrial</strong></td>
<td>8.7 $10^{-5}$</td>
<td>1.9 $10^{-4}$</td>
<td>1.4 $10^{-3}$</td>
<td>4.9 $10^{-2}$</td>
<td>mol N eq</td>
</tr>
<tr>
<td><strong>Eutrophication freshwater</strong></td>
<td>-5.6 $10^{-7}$</td>
<td>3.8 $10^{-5}$</td>
<td>1.6 $10^{-5}$</td>
<td>4.8 $10^{-4}$</td>
<td>mol P eq</td>
</tr>
<tr>
<td><strong>Eutrophication marine</strong></td>
<td>2.3 $10^{-5}$</td>
<td>2.2 $10^{-4}$</td>
<td>2.4 $10^{-4}$</td>
<td>3.4 $10^{-3}$</td>
<td>mol N eq</td>
</tr>
<tr>
<td><strong>Ecotoxicity freshwater</strong></td>
<td>7.2 $10^{-2}$</td>
<td>5.1 $10^{-1}$</td>
<td>1.3 $10^{-1}$</td>
<td>12</td>
<td>CTUe</td>
</tr>
<tr>
<td><strong>Non-renewable energy</strong></td>
<td>1.7</td>
<td>12</td>
<td>2.9</td>
<td>72</td>
<td>MJ</td>
</tr>
<tr>
<td><strong>Depletion of resources</strong></td>
<td>1.9 $10^{-6}$</td>
<td>2.1 $10^{-5}$</td>
<td>5.1 $10^{-6}$</td>
<td>1.6 $10^{-4}$</td>
<td>kg Sb eq.</td>
</tr>
<tr>
<td><strong>Water</strong></td>
<td>4.4 $10^{-2}$</td>
<td>1.4</td>
<td>2.4 $10^{-1}$</td>
<td>27</td>
<td>L</td>
</tr>
</tbody>
</table>
## LCA: Example of the grocery bags

### Production of carrier bag A (Primary use)

<table>
<thead>
<tr>
<th>Material</th>
<th>Climate Change</th>
<th>All indicators</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-woven PP, EOL = recycled</td>
<td>6</td>
<td>52</td>
</tr>
<tr>
<td>Woven PP, EOL = recycled</td>
<td>5</td>
<td>45</td>
</tr>
<tr>
<td>Recycled PET, EOL = recycled</td>
<td>8</td>
<td>84</td>
</tr>
<tr>
<td>Polyester, EOL = recycled</td>
<td>2</td>
<td>35</td>
</tr>
<tr>
<td>Biopolymer, EOL= waste bag or incinerated</td>
<td>0</td>
<td>42</td>
</tr>
<tr>
<td>Unbleached paper, , EOL= waste bag or incinerated</td>
<td>0</td>
<td>43</td>
</tr>
<tr>
<td>Bleached paper, EOL= waste bag or incinerated</td>
<td>1</td>
<td>43</td>
</tr>
<tr>
<td>Organic cotton, EOL= incinerated</td>
<td>149</td>
<td>20000</td>
</tr>
<tr>
<td>Conventional cotton, EOL= incinerated</td>
<td>52</td>
<td>7100</td>
</tr>
<tr>
<td>Composite, EOL= waste bag or incinerated</td>
<td>23</td>
<td>870</td>
</tr>
</tbody>
</table>

### Reuse X times (Primary reuse)

### End of Life

### Production of carrier bag LDPE (Primary use)

### End of Life

---

*Avoidance X times*
Global plastic production and its fate (1950-2015)

Balance of plastic production and fate (m = million tonnes)
8300m produced → 4900m discarded + 800m incinerated + 2600m still in use (100m of recycled plastic)
The route by which plastic enters the oceans

2% of the plastics enter the oceans → 160 Mt

Global primary plastic production: 270 million tonnes per year

Global plastic waste: 275 million tonnes per year
It can exceed primary production in a given year since it can incorporate production from previous years.

Coastal plastic waste: 99.5 million tonnes per year
This is the total of plastic waste generated by all populations within 50 kilometres of a coastline (therefore at risk of entering the ocean).

Mismanaged coastal plastic waste: 31.9 million tonnes per year
This is the annual sum of inadequately managed and littered plastic waste from coastal populations. Inadequately managed waste is that which is stored in open or insecure landfills (and therefore at risk of leakage or loss).

Plastic inputs to the oceans: 8 million tonnes per year

2 billion people living within 50km of coastline

Plastic in surface waters: 10,000s to 100,000s tonnes
There is a wide range of estimates of the quantity of plastics in surface waters. It remains unclear where the majority of plastic inputs end up — a large quantity might accumulate at greater depths or on the seafloor.

PRODUCTION

- PP
- LDPE
- PPA fibers
- HDPE
- PVC
- PET
- PU
- PS
- Other

WASTE

- 19%
- 20%
- 15%
- 14%
- 5%
- 11%
- 6%
- 6%
- 4%
- 19%
Share of plastic waste that is inadequately managed (2010)

260 kt in the ocean’s gires but 8 Mt/y of plastic enters the oceans.
Great Pacific Garbage Patch (GPGP) plastic sources

Ultraviolet light (UV) and mechanical wave forces break large pieces of plastic into smaller ones called microplastics.

Microplastic was up to four orders of magnitude more abundant (per unit volume) in deep-sea sediments than in surface waters.
Where does plastic accumulate in the ocean?

Macrolastics are greater than 0.5cm in diameter
Microplastics are smaller than 0.5cm

Two-thirds of buoyant macroplastic released into the marine environment since 1950 is stored close to the oceans’ shorelines.

A large part of the ‘missing plastic’ problem is explained by plastic accumulation, burial and resurfacing along shorelines.

125 Mt in the ocean’s gires but 8 Mt/y of plastic enters the oceans
• Each year, we use and throw away:
  - 3.7 billions of plastic cups,
  - 365 billions of plastics bottles,
  - 3650 billions of plastic bags,
  - by 2050 more plastics than fish
  - 10% of the plastics go to the sea

• Pacific ocean accumulations:
  o Plastic particles in suspension
  o Concentration: 5.1 kg/km²
  o More than 5 millions tons (?)

• Alliances of individuals, organizations and businesses working together to stop plastic pollution and its toxic impacts
350 Mt* plastics demand can be split into

- Thermoplastics: PE, PP, PS, PVC, PET, Engineering plastics (PA, PC, PEEK, TPE, …).
- Thermosets: PUR, UPR, Epoxy, Elastomers.

* Plastics Europe reports 299MT demand, but we included polyester, PA and acrylic fibers.

- Others include: engineering plastics, other thermosets and fibers, elastomers and blends & compounds

* TOP 5 polymers (PE, PP, PS/EPS, PVC & PET bottles/fibers) represent almost 75% of the market.
Huge market with continuous growth for more than 50 years (4% per year)
But still based on fossil raw materials (for more than 99%)
1- Why?

2- How?

3- Bio-based plastics from natural polymers

4- Drop-ins: Bio-based alternative to fossil-based polymers

5- Smart drop-ins: Bio-based derivative of “fossil” polymers

6- New polymers from biomass

7- Conclusions and perspectives
Plant photosynthesis uses sunlight energy to produce sugars (glucose ($C_6H_{12}O_6$)). This glucose is then condensed by the plant into natural polymers such as starch or cellulose.

This plant photosynthetic process allows the binding and storage of atmospheric carbon dioxide ($CO_2$) in the form of matter in plant tissues.

$$6 \text{ CO}_2 + 12 \text{ H}_2\text{O} + \text{light} \rightarrow C_6\text{H}_{12}\text{O}_6 + 6 \text{ O}_2 + 6 \text{ H}_2\text{O}$$

Plants, through this photosynthetic mechanism, thus produce renewable natural carbon-based molecules.

Annual plants such as wheat in the grains or potatoes in the tubers, synthesize starch that is renewed each year.
Emergence of biorefineries: use of biomass as raw materials instead of fossil resources

Biorefinery Concept

Fossil resources

BIOREFINERY

Biomass

1 to 50 years

Energy, chemical products, polymers, ...

1 to 50 years

>10^6 years

Food and Feed

Integrated Biorefinery

Bioenergy

Biomass Feedstocks
- Lignin
- Cellulose
- Starch
- Proteins
- Plant oils

Extraction

BioPlatform Molecules
- C2 (e.g. Ethanol)
- C3 (e.g. Lactic acid)
- C4 (e.g. Succinic acid)
- C5 (e.g. Furfural)
- C6 (e.g. Gluconic acid)
- Aromatic (e.g. Vanillin)

Fermentation

Sugars
- Glucose
- Fructose
- Arabinose
- Lactose
- Sucrose
- Xylose

Controlled Pyrolysis

Bio-based Polymers
- PET
- PE
- PLA
- PHAs
- PBS
- PA
- PU
- ...

Bordeaux

Chimie des Polymères Organiques
Example of a Biorefinery

- Ethanol
- Sugar
- Corn
The Innovation Promise of Bio-Based Materials

Offering a step change for growth

PHA
PLA
PBS(X)
NOP
PA
APC
UPR
PTT
Epoxy

Find new pathways to ‘old’ polymers....?

Ethylene
Propylene
Butadiene
Benzene
Toluene
Xylene
Methanol

PHA
PLA
PBS(X)
NOP
PA
APC
UPR
PTT
Epoxy

…..or Design novel polymers?

Propanediol
Succinic Acid
Lactic Acid
Vegetable oils
Hydroxy Alkanoates
Isosorbide
other
From biomass to polymers

- Natural Rubber
- Starch-based Polymers
- Lignin-based Polymers
- Cellulose-based Polymers

- Glucose
- Starch
- Saccharose
- Lignocellulose
- Natural Rubber
- Plant oils

- 1,3 Propanediol
- Isosorbide
- Methyl Metacrylate
- PMMA
- PET-like
- PET
- Polyethylene (PE)
- Polypropylene (PP)
- PVC
- Vinyl Chloride
- Ethylene
- Propylene
- MEG
- Teraphthalic acid
- p-Xylene
- Isobutanol
- THF
- 1,4 Butanediol
- Succinate
- 3-HP
- Acrylic acid
- FDCA
- HMF
- Other Furan-based polymers

- Lactic acid
- Adipic Acid
- HMDA
- PLA
- PLA
- PTT
- PA
- Caprolactam
- Epichlorohydrin
- Polyols
- Glycerol
- Fatty acids
- Disacids
- Epoxies
- PU
- PA
A comprehensive metabolic map for production of bio-based chemicals

Sang Yup Lee1,2,4, Hyun Uk Kim1,3,4, Tong Un Chae1,2, Jae Sung Cho1,2, Je Woong Kim1,2, Jae Ho Shin1,2, Dong In Kim1,2, Yoo Sung Ko1,2, Woo Dae Jang1,2,3 and Yu-Sin Jang1,2,4
Example of the glucose platform
Promising bio-based chemicals

Market analysis

Key characteristics:
- No. of carbon atoms
- No. of oxygen atoms
- No. of FGs
- Types of FGs

Promising (bio-based) replacement chemicals ($C_xH_yO_z$)

Flux balance analysis

Key indicator:
$$\frac{24 + 2(Y/X) + 32(Z/X)}{60 + 15(Y/X) - 30(Z/X)}$$

Demanded by market

Difficult to obtain through fossil-based production

Easy to obtain through bio-based production

*FG: functional group

Maravelias et coll. iScience, 2019, 15, 136
**Most promising bio-based building blocks: DOE 2004**

<table>
<thead>
<tr>
<th>Succinic acid</th>
<th>2,5-Furandicarboxylic acid</th>
<th>3-Hydroxypropionic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspartic acid</td>
<td>Glucaric acid</td>
<td>Glutamic acid</td>
</tr>
<tr>
<td>Itaconic acid</td>
<td>Levulinic acid</td>
<td>3-Hydroxybutyrolactone</td>
</tr>
<tr>
<td>Glycerol</td>
<td>Sorbitol</td>
<td>Xylitol</td>
</tr>
</tbody>
</table>
## Most promising bio-based building blocks: DOE 2016

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Type</th>
<th>Conversion Pathway</th>
<th>TRL Level based on commodity feedstocks</th>
<th>R&amp;D on-going for lignocellulosic feedstocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butadiene (1,3-)</td>
<td>Drop-in</td>
<td>BC – Biological</td>
<td>6</td>
<td>Y</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TC/BC – Gasification/Fermentation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butanediol (1,4-)</td>
<td>Drop-in</td>
<td>BC – Biological</td>
<td>8</td>
<td>Y</td>
</tr>
<tr>
<td>Ethyl Lactate</td>
<td>Functional</td>
<td>BC – Biological</td>
<td>9</td>
<td>Y</td>
</tr>
<tr>
<td>Fatty Alcohols</td>
<td>Drop-in</td>
<td>TC – Gasification, BC – Biological, Algae</td>
<td>9</td>
<td>Y</td>
</tr>
<tr>
<td>Furfural</td>
<td>Functional</td>
<td>TC – Pyrolysis, BC – Catalytic</td>
<td>9</td>
<td>Y</td>
</tr>
<tr>
<td>Glycerol</td>
<td>Functional</td>
<td>Algae</td>
<td>9</td>
<td>Y</td>
</tr>
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<td>Isoprene</td>
<td>Drop-in</td>
<td>BC – Biological</td>
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</tr>
<tr>
<td>Lactic Acid</td>
<td>Functional</td>
<td>BC – Biological</td>
<td>9</td>
<td>Y</td>
</tr>
<tr>
<td>Propanediol (1,3-)</td>
<td>Functional</td>
<td>BC – Biological</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Propylene Glycol</td>
<td>Functional</td>
<td>BC – Biological</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Succinic Acid</td>
<td>Functional</td>
<td>BC – Biological</td>
<td>9</td>
<td>Y</td>
</tr>
<tr>
<td>Xylene (para)</td>
<td>Drop-in</td>
<td>BC – Catalytic</td>
<td>6</td>
<td>Y</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TC – Pyrolysis</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Worldwide production of bio-based chemicals

- Adipic acid (AA)
- 11-Aminoundecanoic acid (11-AA)
- 1,4-Butanediol (1,4-BDO)
- Dodecanedioic acid (DDDA)
- Epichlorohydrin (ECH)
- Ethylene
- Furans
- Isosorbide
- D-lactic acid (D-LA)
- L-lactic acid (L-LA)
- Lactide
- Monoethylene glycol (MEG)
- Monopropylene glycol (MPG)
- 1,5-Pentametlyenediamine (DN5)
- 1,3-Propanediol (1,3-PDO)
- Sebacic acid
- Succinic acid (SA)
Ressources prize volatility

Extracted 9/10/2019 from https://markets.businessinsider.com
Refinery to Biorefinery

**Oxidation Chemistry**

- **Oil refinery cuts**
  - H2: methane, ethylene, propene, butane, hexane
  - C1: ethanol, propanediol, butanediol, benzene
  - C2: propene, propanediol, butanediol
  - C3: butane
  - C4: butanediol
  - C5: hexane
  - C6: benzene

- **Biorefinery cuts**
  - H2: Formic acid, acetic acid
  - C1: ethanol, acetic acid
  - C2: propanol, propanediol, propanoic acid, acetone, lactic acid, pyruvic acid, glycerol
  - C3: butanol, butanoic acid, butanediol, malic acid, succinic acid
  - C4: acetone, butanediol
  - C5: ethanol, butanediol
  - C6: succinic acid
  - C7: glucose, fructose, butanediol, glutamic acid
  - C8: butanol, butanediol, succinic acid

- **Materials**
  - Biopolymers: xanthan, dextran

- **Energy**
  - Fuels: petrol, diesel

- **Complex products**
  - Asphalt hydrocarbons

**Reduction Chemistry**

- **Agro resources**
  - Ethanoly, ethanol, propene, propanediol, butanediol
  - Glycolic acid, glycerol, succinic acid

- **Oxidation Chemistry**
  - Formic acid, acetic acid, butanediol, succinic acid

- **Biopolymers**
  - Xanthan, dextran

- **Dyes**
  - Butyl butyrate, phenylethanol

- **Surfactants**

- **Materials**
Bio-sourced chemicals and polymers

Market size ~ 50 million tones

- Chemical Derivatives
- Naval Stores
- Oleochemicals
- Biopolymers
- Alcohols
- Aliphatic acids
- Natural Products
- Amino Acids
- Other

Fermentation Products

- 54%
- 20%
- 17%
- 7%
- 1%

- 7%
- 5%
- 4%
- 1%
Schematic differentiation of pathways of drop-in, smart drop-in and dedicated bio-based chemicals
Worldwide production of bio-based polymers

Polymer applications vs bio-based polymer applications

Packaging

Building & Construction

Automotive

E & E

Others

2018

2023
Bio-based polymers: five drivers for development

Bio-based polymers development is driven by five main trends, combined or not:

- Societal demand for bio-based, lower environmental impact plastics drive development of drop-in bioplastics: PE, PP, ...

- Specific premium required on bio-plastics to compensate higher cost

-(perceived) Raw material supply constraint drive development of bio-based elastomers

- Chemical recycling the plastic waste

-Bioderived monomers and biodegradable polymers such as PLA or PHA

- Fermentation of (flared) natural gas to PHA, for use pure or in blend with PP

Bio-based plastic has no fossil-based equivalent. Its development is driven by new functionality: PLA, PHA, PEF,…

For some applications and in some countries (eg. FR, IT), the government imposes legislations obliging biodegradable packaging and maybe tomorrow tax incentives or obligations on bio-based plastics?

For a success story all 5 drivers are needed
Biomass production ≈ 120 billions tons/year vs. 350 millions tons/y of polymers (210 with algea)

10% of the biomass is used

Cellulose production ≈ 400 millions tons/year
Less 1% of the worldwide cellulose production ≈ 25% of the harvest wood
Food vs Fuel

- Can use crop wastes (traditionally use as soil fertilizer)
- Develop specific crops with high yield

Petroleum consumption in France 10 GL/y
100 kha of microalga needed
2 % of France surface
1- Why?

2- How? → Biomass transformation to platform chemicals

3- Bio-based plastics from natural polymers

4- Drop-ins: Bio-based alternative to fossil-based polymers

5- Smart drop-ins: Bio-based derivative of “fossil” polymers

6- New polymers from biomass

7- Conclusions and perspectives
Bio-based plastics from natural polymers

Natural rubber from latex

- Rubber products: polyisoprene 1,4-cis
  13.9 Mt (2018)

Production increase is too slow for the worldwide demands

→ Other sources

Synthetic polyisoprene: 15.6 Mt (2018)
Bio-based plastics from natural polymers

Natural rubber from latex

Biosynthesis pathway of natural rubber

Impossible to obtain by regular polymerization processes → Enzymatic pathway
Bio-based plastics from natural polymers

Starch based polymers

Starch blend with different polymers
400 Kt (1Mt for the blend)
- Starch in blends with polyesters
  - Polycaprolactone
  - Poly(butylene adipate-co-terephthalate) (PBAT)
  - Poly(butylene azelate) (PBAZ)
  - PLA, PHA, PBS, …
- Starch acetate in alloys with Polyolefins

Bio-based Carbon content: 25 to 100 %
Bio-based plastics from natural polymers

Cellulose-based polymers

Mature market with small growth (1.5Mt)

- Nitrocellulose 140 kT
- Viscose 150 kT
- Mercerised Celluloses 50 kT
- Microcrystalline Cellulose 85 kT
- Ethers 370 kT

Cellulose: \( R=H \)
Nitrocellulose: \( R=H \) & \( NO_2 \)
Cellulose acetate: \( R=CH_3CO \)
Cellulose acetate/butyrate: \( R=CH_3CH_2CH_2CO \)
Hydrophilic cellulose ethers: \( R=CH_2CH_2OH; CH_2CH(CH_3)OH; CH_2COOH \)

Not a thermoplastic
Bio-based plastics from natural polymers

Cellulose-based polymers
Emerging application

- Wood
- Wood cell walls
- Macrofibrils
- Microfibrils
- 50 μm

- Cellulose polymer
  - Non-reducing end
  - Reducing end
- Crystalline regions
- Disordered regions
- Strong acid hydrolysis
- Nanocrystals

CNC
- (100 nm)

CNF
- (200 μm)

BC

- High tensile strength
  - CNC
  - Glass
  - Steel
  - Kevlar

- High aspect ratio
  - CNC
  - Glass
  - Steel
  - Kevlar

Sources of CNC
- MECAI
- Bi-Gd Co-Pt
- Li-Pt-Ru-Pd-Al
- Nanopolymer

Lyotropic liquid crystalline behavior
- CNC Concentration (g/μl)
- Aramidic Volume Fraction
- CNC Concentration (vol %)

High thermal stability
Bio-based plastics from natural polymers

Other polymers
Bio-based plastics from natural polymers

Other polymers: Lignin
Extremely complex structure
500 kt

No plasticizer
Lignosulfonate, 0.4%
1- Why?

2- How? → Biomass transformation to platform chemicals

3- Bio-based plastics from natural polymers
   *Cellulose, lignin, Natural rubber*

4- Drop-ins: Bio-based alternative to fossil-based polymers

5- Smart drop-ins: Bio-based derivative of “fossil” polymers

6- New polymers from biomass

7- Conclusions and perspectives
Drop-ins: Bio-based alternative to fossil-based polymers

Polyethylene (PE)

200 Kt
• Industrial plant in Brazil (Braskem)
• Premium value on the market due to bio-origin
• Too expensive outside Brazil

-3.09 kgCO$_2$e/kg
(vs 1.96 kgCO$_2$e/kg)

27 Mha vs. 80 Mt of PE
¼ of the habitable land !!!
Polyethylene terephthalate (PET)

600 Kt

Most bio-based PET are only **30%** (20%) bio-based

Since 2015, Coca-Cola company produce **100%** bio-based
by 2020 all their PET bottles will be 100% bio-based

4 kgCO₂e/kg

(vs 2.73 kgCO₂e/kg)
Drop-ins: Bio-based alternative to fossil-based polymers

Polyethylene terephthalate (PET)

Other routes to terephthalic acid:

Other industrial routes
Polyethylene terephthalate (PET)

Other routes to terephthalic acid:

**Lignin**

![Lignin structure](image)

**Terpenes**

![Terpenes structure](image)
Drop-ins: Bio-based alternative to fossil-based polymers

Polyethylene terephthalate (PET)

Other routes to terephthalic acid:

**Sugars (C6)**

![Chemical diagram for the synthesis of terephthalic acid from sugars](image)
Drop-ins: Bio-based alternative to fossil-based polymers

Polyethylene terephthalate (PET)

Other routes to terephthalic acid:

**Sugars (C5)**

![Chemical reactions diagram showing the synthesis of terephthalic acid from sugars](image-url)
Drop-ins: Bio-based alternative to fossil-based polymers

Polypropylene (PP)

20 kt
Drop-ins: Bio-based alternative to fossil-based polymers

Super Absorbent polymers (SAP’s)

Pilot scale
Drop-ins: Bio-based alternative to fossil-based polymers

Poly(methyl methacrylate) (PMMA)

Pilot scale

Traditional route

Bio-based route

Toxic

Waste

PMMA

Greener

Safer

Bio-based
1- Why?

2- How? → Biomass transformation to platform chemicals

3- Bio-based plastics from natural polymers
   *Cellulose, Natural rubber*

4- Drop-ins: Bio-based alternative to fossil-based polymers
   *PE, PET*

5- Smart drop-ins: Bio-based derivative of “fossil” polymers

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7- Conclusions and perspectives
Polybutylene succinate (PBS)

100 kt

*Bio-based succinic acid cost ≈ fossil*

PBS polyethylene-like properties + biodegradable
Smart drop-ins: Bio-based derivative of “fossil” polymers

Polyester

PET, PPT, PBT, PBS, PBAz ... polyethylene mimick
Smart drop-ins: Bio-based derivative of “fossil” polymers

Polyamides (PA)

200 kt
Smart drop-ins: Bio-based derivative of “fossil” polymers

Polyamides (PA)

Stiffness

- PA 6
- PA 6-10
- PA 11
- PA 12

Hydrophobicity

Polycondensation

Polyether

- PEG
- PPG
- PTMO

Elasticity

TPO

- 2 transparent grades
- 7 biobased grades

PolyEther Block Esters (COPE)

Thermoplastic Polyurethane (TPU)

Polyamides

Rubber

Styrenics

Polycondensation of PA

PTMO
Smart drop-ins: Bio-based derivative of “fossil” polymers

Epichlorohydrin

1.5 Mt

Glycerol + 2HCl → 1,3-dichloro-2-propanol + 2,3-dichloro-1-propanol

Epichlorohydrin + NaOH → 1,3-dichloro-2-propanol + 2,3-dichloro-1-propanol

Propene + Cl₂ → Allyl chloride

Allyl chloride + HOCl → 1,3-dichloro-2-propanol + 2,3-dichloro-1-propanol
Smart drop-ins: Bio-based derivative of “fossil” polymers

Epoxy

- 75% of epoxy are derived from Bisphenol-A (BPA)

- Environnemental and economics concerns
  - Petrochemicals $\rightarrow$ fossil carbon
  - Price volatility

- High risk of obsolescence of BPA

- Toxicity of BPA $\rightarrow$ CMR $^{1B}$

- 40-25% bio-based if epichlorohydrine bio-sourced
Smart drop-ins: Bio-based derivative of “fossil” polymers

From Lignin to epoxy resins...

**Epoxy**

**Bisphenol A**

**DGEBA**

**Vanillin**

**Divanillyl Alcohol**

**Glycidyl Ether of Divanillyl Alcohol**

**Epoxidation**

**Dimerisation**
Laccase is an oxydative enzyme found in wood rotting fungi.

Laccase generates radicals which can undergo self coupling reactions yielding dimers.

Kobayashi et al., Chem. Rev. 2009

Llevot et al., Polym. Chem. 2015, 6 (33)
Smart drop-ins: Bio-based derivative of “fossil” polymers

Synthesis of dimer from Vanillin

Epoxy

Self-sufficient process to synthesize dimers

Llevot et al., Polym. Chem. 2015, 6 (33) 6058-6066
Smart drop-ins: Bio-based derivative of “fossil” polymers

Epoxy

Aldehyde Reduction

1) NaBH4, NaOH (aq), 1h RT
2) HCl (aq)

Divanillin

Divanillyl Alcohol (DVA)

4 functional groups available to achieve high mechanical properties
Smart drop-ins: Bio-based derivative of “fossil” polymers

Synthesis of epoxy prepolymerms from DVA

<table>
<thead>
<tr>
<th>Properties</th>
<th>DGEBA</th>
<th>DiGEDVA</th>
<th>TriGEDVA</th>
<th>TetraGEDVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (°C)</td>
<td>45</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Glass transition (°C)</td>
<td>-18</td>
<td>16</td>
<td>-6</td>
<td>-15</td>
</tr>
<tr>
<td>Viscosity at 25 °C (Pa.s)</td>
<td>5</td>
<td>nd</td>
<td>975</td>
<td>14</td>
</tr>
<tr>
<td>Viscosity at 40 °C (Pa.s)</td>
<td>1</td>
<td>1300</td>
<td>60</td>
<td>2</td>
</tr>
<tr>
<td>EEW th.</td>
<td>170</td>
<td>209</td>
<td>158</td>
<td>132</td>
</tr>
<tr>
<td>EEW exp.</td>
<td>171</td>
<td>232</td>
<td>164</td>
<td>129</td>
</tr>
</tbody>
</table>
Smart drop-ins: Bio-based derivative of “fossil” polymers

Epoxy

Synthesis of polyepoxyde network

- Reactivity at lower temperature for biobased epoxy prepolymer.

<table>
<thead>
<tr>
<th>Epoxy prepolymer/IPDA</th>
<th>T\textsubscript{onset} (°C)</th>
<th>T\textsubscript{exotherm} (°C)</th>
<th>ΔH (J.g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA</td>
<td>73</td>
<td>111</td>
<td>430</td>
</tr>
<tr>
<td>DiGEDVA</td>
<td>47</td>
<td>107</td>
<td>(180)</td>
</tr>
<tr>
<td>TriGEDVA</td>
<td>48</td>
<td>113</td>
<td>(198)</td>
</tr>
<tr>
<td>TetraGEDVA</td>
<td>50</td>
<td>92</td>
<td>426</td>
</tr>
</tbody>
</table>
**Smart drop-ins: Bio-based derivative of “fossil” polymers**

**Dynamic Mechanical Analysis of epoxy resins cured with IPDA**

<table>
<thead>
<tr>
<th>Epoxy prepolymer/IPDA</th>
<th>$T_g^a$ (°C)</th>
<th>$T_α^b$ (°C)</th>
<th>$E'^b$ (Gpa)</th>
<th>$E'(T_α+30)^b$ (Gpa)</th>
<th>Network density $(10^3\text{mol.m}^{-3})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA</td>
<td>152</td>
<td>155</td>
<td>1.7</td>
<td>0.035</td>
<td>9.2</td>
</tr>
<tr>
<td>DiGEDVA*</td>
<td>138</td>
<td>140</td>
<td>1.9</td>
<td>0.035</td>
<td>9.5</td>
</tr>
<tr>
<td>TriGEDVA</td>
<td>163</td>
<td>177</td>
<td>1.3</td>
<td>0.084</td>
<td>21</td>
</tr>
<tr>
<td>TetraGEDVA</td>
<td>198</td>
<td>188</td>
<td>3.5</td>
<td>0.15</td>
<td>36.7</td>
</tr>
</tbody>
</table>

$a$ determined by DSC, $b$ by DMA, *80%DiGEDVA-20%TriGEDVA

---

**DiGEDVA**

**TetraGEDVA**
**Smart drop-ins: Bio-based derivative of “fossil” polymers**

**Epoxy**

*Thermal degradation of epoxy resins cured with IPDA*

<table>
<thead>
<tr>
<th>Epoxy prepolymer/IPDA</th>
<th>$T_d$ 5% (°C)</th>
<th>$T_d$ 30% (°C)</th>
<th>$T_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA</td>
<td>336</td>
<td>364</td>
<td>172</td>
</tr>
<tr>
<td>DiGEDVA</td>
<td>273</td>
<td>337</td>
<td>153</td>
</tr>
<tr>
<td>TriGEDVA</td>
<td>292</td>
<td>335</td>
<td>156</td>
</tr>
<tr>
<td>TetraGEDVA</td>
<td>275</td>
<td>316</td>
<td>147</td>
</tr>
</tbody>
</table>

- Slightly lower thermal heat resistance

<table>
<thead>
<tr>
<th>Epoxy prepolymer/IPDA</th>
<th>$T_d$ 5% (°C)</th>
<th>$T_d$ 30% (°C)</th>
<th>$T_s$</th>
<th>Char$_{600}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA</td>
<td>349</td>
<td>366</td>
<td>176</td>
<td>9</td>
</tr>
<tr>
<td>DiGEDVA</td>
<td>275</td>
<td>334</td>
<td>152</td>
<td>36</td>
</tr>
<tr>
<td>TriGEDVA</td>
<td>296</td>
<td>333</td>
<td>155</td>
<td>30</td>
</tr>
<tr>
<td>TetraGEDVA</td>
<td>276</td>
<td>313</td>
<td>146</td>
<td>28</td>
</tr>
</tbody>
</table>

- High char residue for biobased epoxy resins
Flaming test of epoxy resins cured with IPDA
Smart drop-ins: Bio-based derivative of "fossil" polymers

Polyurethanes

\[ \text{HO} - R - \text{OH} + \text{O} = \text{C} - \text{N} - R' - \text{N} = \text{C} - \text{O} \rightarrow \text{O} - \text{N} - R' - \text{N} - \text{O} - \text{R} \_ n \]
Smart drop-ins: Bio-based derivative of “fossil” polymers

Polyurethanes: polyol

Sugars (C6)

PU
Smart drop-ins: Bio-based derivative of “fossil” polymers

Polyurethanes: polyol

Acid catalyst

(Hydrogenation)/modification

PU
Smart drop-ins: Bio-based derivative of “fossil” polymers

Polyurethanes: isocyanate

Corynebacterium glutamicum
Smart drop-ins: Bio-based derivative of “fossil” polymers

Polyurethanes

Industrial process for the production of Polyurethanes:
The Isocyanate/alcohol route

Non Isocyanate PolyUrethane

Poly(HydroxyUrethane)

- Phosgene- and isocyanate-free
- Polyaddition: no by-product
- Less moisture sensitive

**Objective**: Design substituted fatty acid- and glycerol-based cyclic carbonates

**Glycerol platform**

- **Epichlorohydrin**
  - Alcohol
  - **Glycerol Carbonate**
  - Acyl chloride
- **Diglycerol**
  - DMC
  - **Thioglycerol**
  - Diene
  - Alcohol

Smart drop-ins: Bio-based derivative of “fossil” polymers

Polyurethanes: isocyanate

→ Tunable **heteroatom nature and position** nearby the CC by varying the glycerol derivative
→ **Ether, ester and thioether** functions inserted nearby the cyclic carbonate
Smart drop-ins: Bio-based derivative of “fossil” polymers

Reactivity of various CC towards aminolysis

In situ measurements
NMR Tube
24h, 50°C
DMSO-d6

→ CC conversion calculation

**Smart drop-ins: Bio-based derivative of “fossil” polymers**

**Scale of CC reactivity towards aminolysis**

$\rightarrow$ 2nd kinetic order law during the first hours - $k_{app}$

$$\frac{x}{1-x} = k_{app}C_0 \Delta t$$

$\text{CC conversion in function of time (50°C, DMSO-d6, 24h, ratio amine : CC = 1:1)}$
Smart drop-ins: Bio-based derivative of “fossil” polymers

> From DGDC & various DAs

CONVERSIONS (%) ............... 99% / 99%
Molar masses (g/mol). ......... up to 46800 / 50 000
T_g (°C). ..................... up to 18 / 17
T_m (°C). ............. -- / 100
T_d5% (°C). ............... up to 227 / 233

NMR spectra of DGDC monomer (up) and DGDC based PHU (down)

SEC analysis in DMF, with PS standards, at 50°C
DSC second heating cycle at 10°C/min
TGA traces at 10°C/min
Smart drop-ins: Bio-based derivative of “fossil” polymers

> Comparison with bulk polymerization in Schlenk tubes

Polymerization in Schlenk tubes:
- $80^\circ C$ - 4h / $130^\circ C$ - 4h

Reactive extrusion:
- $80^\circ C$ - 4h

SEC analysis in DMF, 50°C, 1g/L of Libr, conventional calibration column with PS standards

Conversions obtained by $^1$HNMR analysis in DMSO-d$_6$ at RT
1- Why?

2- How?  \(\rightarrow\) Biomass transformation to platform chemicals

3- Bio-based plastics from natural polymers
   *Cellulose, Natural rubber*

4- Drop-ins: Bio-based alternative to fossil-based polymers
   *PE, PET*

5- Smart drop-ins: Bio-based derivative of “fossil” polymers
   *PBS, Epoxy, PU*

6- New polymers from biomass

7- Conclusions and perspectives
New polymers from biomass: PLA

300 kt

Starchy Materials

L-lactic acid
D-lactic acid

Condensation and Depolymerization

L-lactide
Meso-lactide
D-lactide

Catalytic Ring-Opening Polymerization (ROP)

High Molecular Weight PolyLactide (PLA)

Physical properties

<table>
<thead>
<tr>
<th></th>
<th>PLLA (PDLA)</th>
<th>Atactic PDLLA</th>
<th>Syndiotactic PDLLA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tm (°C)</td>
<td>170-180</td>
<td>-</td>
<td>151</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>55-60</td>
<td>50-60</td>
<td>34</td>
</tr>
<tr>
<td>ΔHm (100%) (J.g⁻¹)</td>
<td>93</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Why PLA is not petro-sourced?

Petro-chemical resources

- Acetaldehyde
- HCN catalyst
- Lactonitrile

Hydrolysis by H₂SO₄

- Racemic DL-lactic acid

Plastic stereocomplex

\[ \text{PDLA content} = \begin{align*}
0 \text{ (0\%)} \\
10 \\
20 \\
30 \\
40 \\
50 \\
60 \\
70 \\
80 \\
90 \\
100
\end{align*} \]

Temperature (°C)
New polymers from biomass: PLA

Biobased, Compostable, Stiff

<table>
<thead>
<tr>
<th></th>
<th>PLLA</th>
<th>PS</th>
<th>PET</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg.m⁻³)</td>
<td>1.26</td>
<td>1.05</td>
<td>1.40</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>59</td>
<td>45</td>
<td>57</td>
</tr>
<tr>
<td>Elastic modulus (GPa)</td>
<td>3.8</td>
<td>3.2</td>
<td>2.8-4.1</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>4-7</td>
<td>3</td>
<td>300</td>
</tr>
<tr>
<td>Notched IZOD IS (J.m⁻¹)</td>
<td>26</td>
<td>21</td>
<td>59</td>
</tr>
<tr>
<td>Heat deflection (°C)</td>
<td>55</td>
<td>75</td>
<td>67</td>
</tr>
</tbody>
</table>

Heat stability, Low crystallization rate, Brittleness

PLA applications

Purac website

CO₂ absorption through photosynthesis

Composting, Energy recovery

Lactide & PLA resin

Recycle

PLA

Textiles

Packaging

Pharmaceuticals

Composites

Tissue engineering

Orthopaedics

Drug Delivery

Sutures
New polymers from biomass: PLA

PLA additive: Synthesis

\[
\text{Ti(iOPr)}_4
\]

<table>
<thead>
<tr>
<th>mol% DFA/total diacid$^a$ (feed)</th>
<th>$\bar{M}_n$ (kg.mol$^{-1}$)$^b$</th>
<th>$D^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFA0</td>
<td>0 (0)</td>
<td>59</td>
</tr>
<tr>
<td>DFA0.3</td>
<td>0.40 (0.3)</td>
<td>44</td>
</tr>
<tr>
<td>DFA0.7</td>
<td>0.78 (0.7)</td>
<td>64</td>
</tr>
<tr>
<td>DFA1</td>
<td>1 (1)</td>
<td>36</td>
</tr>
</tbody>
</table>

(a) $^1$H-NMR (b) SEC in THF, PS calibration
New polymers from biomass: PLA

PLA additive: Properties

<table>
<thead>
<tr>
<th>DFA</th>
<th>Tm (°C)(^a)</th>
<th>ΔHm (J.g(^-1))(^a)</th>
<th>Tg (°C)(^a)</th>
<th>T(_{5%}) (°C)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFA0</td>
<td>78.2</td>
<td>100.9</td>
<td>- 48.6</td>
<td>338</td>
</tr>
<tr>
<td>DFA0.3</td>
<td>55.2</td>
<td>57.7</td>
<td>- 45.9</td>
<td>389</td>
</tr>
<tr>
<td>DFA0.7</td>
<td>17.7</td>
<td>22.4</td>
<td>- 49.0</td>
<td>399</td>
</tr>
<tr>
<td>DFA1</td>
<td>- 5.8</td>
<td>16.2</td>
<td>- 50.0</td>
<td>394</td>
</tr>
</tbody>
</table>

\(a\) DSC - 10°C.min\(^{-1}\)

\(b\) TGA - 10°C.min\(^{-1}\)
**New polymers from biomass: PLA**

**PLA additive: Processing**

**Melt-blending:**
Twin-screw mini-extrusion
190°C for 5 min

**Sample preparation:**
Injection molding
200°C → 50°C

10%
New polymers from biomass: PLA

PLA additive: Mechanical Properties

**DMA**

**Heat stability**

- **Tensile test**
- **Impact strength test**

**Brittleness**
**New polymers from biomass: PLA**

**PLA additive: Thermal Properties**

**DSC**

**Isothermal crystalization**

**Avrami equation**: 
\[ \alpha_c = 1 - \exp(k \cdot t^n) \]

- \( \alpha_c \): the relative crystalline volume fraction
- \( k \): rate constant of crystallization
- \( n \): Avrami index

**Half-time of crystallization**: 
\[ t_{1/2} = \left( \frac{\ln 2}{k} \right)^{1/n} \]

<table>
<thead>
<tr>
<th></th>
<th>( n )</th>
<th>( k ) (min(^n))</th>
<th>( t_{1/2} ) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA</td>
<td>1.80</td>
<td>0.027</td>
<td>6.12</td>
</tr>
<tr>
<td>DFA0</td>
<td>3.53</td>
<td>0.021</td>
<td>2.70</td>
</tr>
<tr>
<td>DFA0.3</td>
<td>3.73</td>
<td>0.014</td>
<td>2.85</td>
</tr>
<tr>
<td>DFA0.7</td>
<td>3.81</td>
<td>0.116</td>
<td>1.60</td>
</tr>
<tr>
<td>DFA1</td>
<td>4.20</td>
<td>0.015</td>
<td>2.48</td>
</tr>
</tbody>
</table>
New polymers from biomass: PHA

40 kt

One-pot biosynthesis from biomass to polymer

Max prod. 3 g.L⁻¹.h⁻¹

Polyhydroxybutyrate (PHB)

Poly-3-hydroxyvalerate (PHV)

Poly(hydroxybutyrate-co-hydroxyalkanoates) (PHBV)

Inclusions (PHA Granula)
New polymers from biomass: PHA

PHA biosynthesis

- **Acetyl-CoA**
- **Chain elongation**
- **Fatty acid β-oxidation**
- **De novo fatty acid synthesis**
- **Ketoacyl-CoA reductase**
- **Enoyl-CoA hydratase**
- **3-Hydroxyacyl-CoA epimerase**
- **3-Hydroxyacyl-CoA-ACP transferase**
- **PHA synthase**
New polymers from biomass: PHA

**PHA properties**

<table>
<thead>
<tr>
<th></th>
<th>PHB</th>
<th>PHBV</th>
<th>PHBHx</th>
<th>MCL-PHA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tm (°C)</td>
<td>170 to 180</td>
<td>130 to 170</td>
<td>95 to 150</td>
<td>40 to 60</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>-5 to 5</td>
<td>-10 to 0</td>
<td>-3 to -1</td>
<td>-60 to -30</td>
</tr>
<tr>
<td>Mw x 10^3 (g mol⁻¹)</td>
<td>Up to 1500</td>
<td>Up to 1200</td>
<td>/</td>
<td>50 to 300</td>
</tr>
<tr>
<td>Density (g cm⁻³)</td>
<td>1.24</td>
<td>1.20</td>
<td>/</td>
<td>1.02</td>
</tr>
<tr>
<td>Crystallinity (%)</td>
<td>60 to 80</td>
<td>30 to 80</td>
<td>10 to 50</td>
<td>Up to 30</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>40</td>
<td>30 to 40</td>
<td>/</td>
<td>Up to 10</td>
</tr>
<tr>
<td>Young’s modulus (MPa)</td>
<td>3.5 to 4 x 10³</td>
<td>0.7 to 3 x 10³</td>
<td>500 (10%HHx)</td>
<td>Up to 15</td>
</tr>
<tr>
<td>Elongation to break (%)</td>
<td>3 to 8</td>
<td>Up to 100</td>
<td>Up to 400</td>
<td>Up to 450</td>
</tr>
</tbody>
</table>

- **P3HB**: Flexible, Good moisture and oxygen barriers, Ductile
- **PHV**: Flexible, Tough, Ductile
- **PHH**: Stiff, High operating temperature, Tough
- **PHO**: Strong, Stiff, High softening temperature
- **PH4HV**: Biocompatible, Resorbable, Strong
New polymers from biomass: PEF

Pilot scale 40 t → 90 kt by 2025
New polymers from biomass: PEF

FDCA synthesis
New polymers from biomass: PEF

Properties

- Sustainability: 100% biobased polymer
- FDCA
- GAS BARRIER PERFORMANCE
- Shelf Life improved transfer rates vs PET:
  - $O_2$ 10x
  - $CO_2$ 6-10x
  - $H_2O$ 3x
- BIOBASED
- MECHANICS
- RECYCLABILITY
- SUPERIOR HEAT RESISTANCE
- Lightweighting: 60% higher modulus vs PET
- Hot Filling: 12°C higher glass transition vs PET
- 100% recyclable
New polymers from biomass: PEF

PEF as a drop-in from PET bottles? No

1) PET is one of the best recycled plastic (30% worldwide)

1) 100% bio-based PET is competitive in term of price
New polymers from biomass: SAP’s

1. Fermentation
2. Polymerization

- Itaconic acid

1. Fermentation
2. Polymerization

- L-aspartic acid
New polymers from biomass: PIC

Isorbide: « regular » chemistry to transform sugar

Sucrose → acid + H₂O → Fructose → H₂ → D-Mannitol → acid - H₂O → Isomannide

Cellulose → acid + H₂O → Glucose → H₂ → D-Sorbitol → acid - H₂O → Isosorbide

Isosorbide (IS) + Dimethyl carbonate (DMC) → Reflux Basic Catalyst → Durabio™

Low Birefringence
Excellent Transparency
Superior UV resistance
High Impact Resistant (Multi-axial)
Heat Distance
Bio-based content
Flame retardance
Outlines

1- Why?

2- How? ➔ Biomass transformation to platform chemicals

3- Bio-based plastics from natural polymers
   Cellulose, Natural rubber

4- Drop-ins: Bio-based alternative to fossil-based polymers
   PE, PET

5- Smart drop-ins: Bio-based derivative of “fossil” polymers
   PBS, Epoxy, PU

6- New polymers from biomass
   PLA, PHA, PEF

7- Conclusions and perspectives
Conclusion and perspectives

Lignocellulose

Vegetable Oil

Carbohydrate

Terpens?
Terpenes as a source of various backbones

> 1000 of skeletons
What can we do with a little of Hop?

No! Polymers

Caryophyllene

Humulene

1 €/kg

Beer !!!
First direct ROMP of natural compounds

Caryophyllene

Humulene

Can be performed
• In bulk at RT
• In water dispersion
• In hop/clove oil

E. Grau, S. Mecking *Green Chem.*, 2013, 15, 1112-111
Conclusion and perspectives

Lignocellulose

Crossing the biomass !!!

Carbohydrate

Terpens

Sugarcane, corn, wheat, rice, guar

Clove, citrus

Eucalyptus, spruce, pine, coconut, palm, soybean, rapeseed, peanut, castor bean
Crossing the biomass

Wood

- Xylo-oligosaccharides

HYDROPHILIC

HYDROPHOBIC

Oil

- Fatty esters

Renewable feedstock
- Abundant
- High purity (up to 99%)
- Polymerizable

Cosmetics
- Emulsifiers
- Foaming agents
- Solubilizers
- Wetting agents

Detergents

Pharmaceutical
- Biocompatible, drug delivery

Food
- Use as emulsifier
Self-assembly by direct dissolution in H₂O

Bio-based polymers forecast vs. 350 Mt of polymer
Thank you all!

Questions ???

egrau@enscbp.fr