Strategies of valorization of food residues towards sustainable materials

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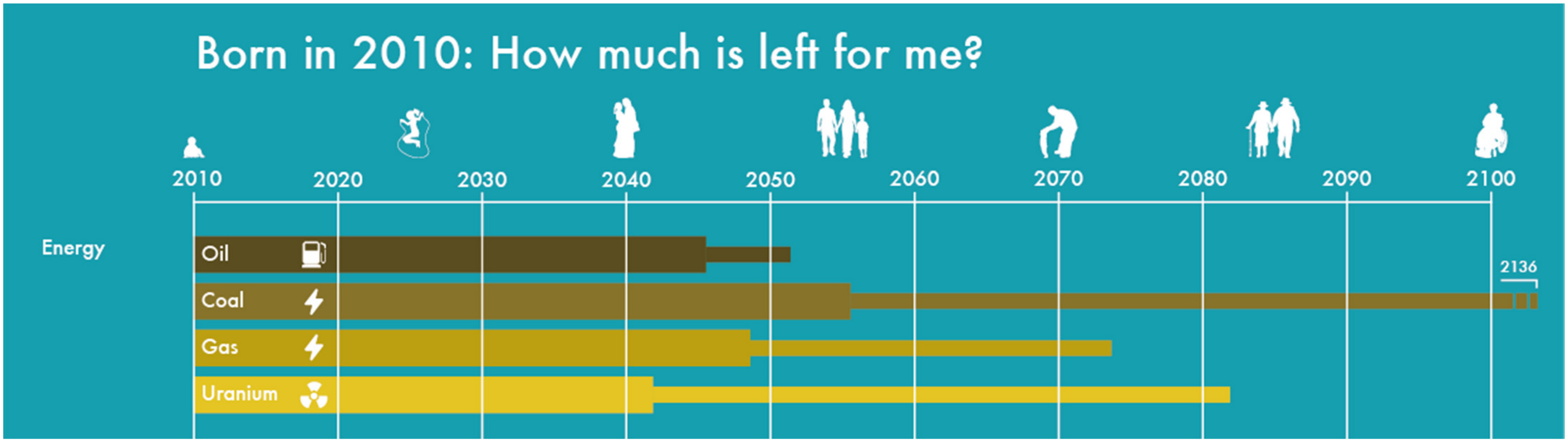
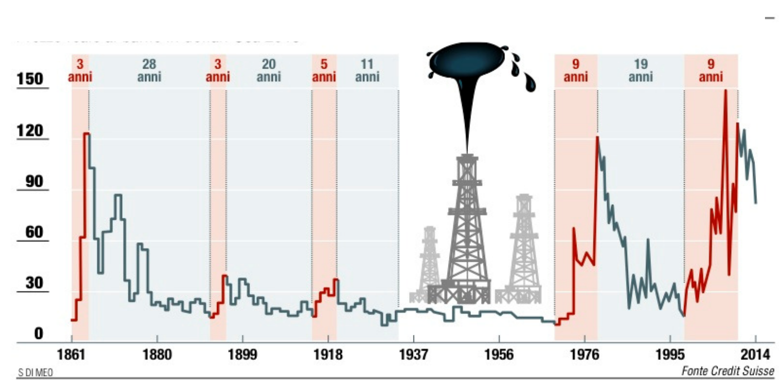
Fossil resources



Environmental and cost issues



European Union (EU) produced
55 million tonnes of vegetal wastes and
88 million tonnes of food wastes in 2016

Agro-waste: towards new bio-based materials

Biomass – agro-industrial residues – food residues

extraction

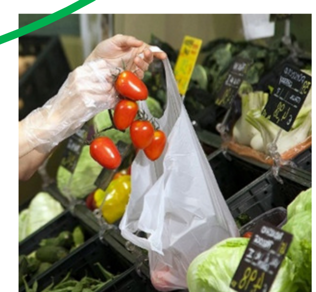
Biotech processes

Bio-based plastics

polyphenols
chitosan
cutin
cellulose
fibers
lipids
collagen
hydroxyacids
aminoacids
sugar
starch
pectins

additives
fillers
monomers
polymers
homopolymers
copolymers
composites
nanocomposites

Monomers
Bacterial polymers PHA
Materials by fungi



Polymer classification

Polymers derived from biomass

Not biodegradable polymers (but recyclable?)

Biodegradable polymers

Bio-polymers
Not biodegradable
and derived from biomass
e.g. bio-PET

Bio-polymers
Biodegradable
and derived from biomass
e.g. PLA, PHA

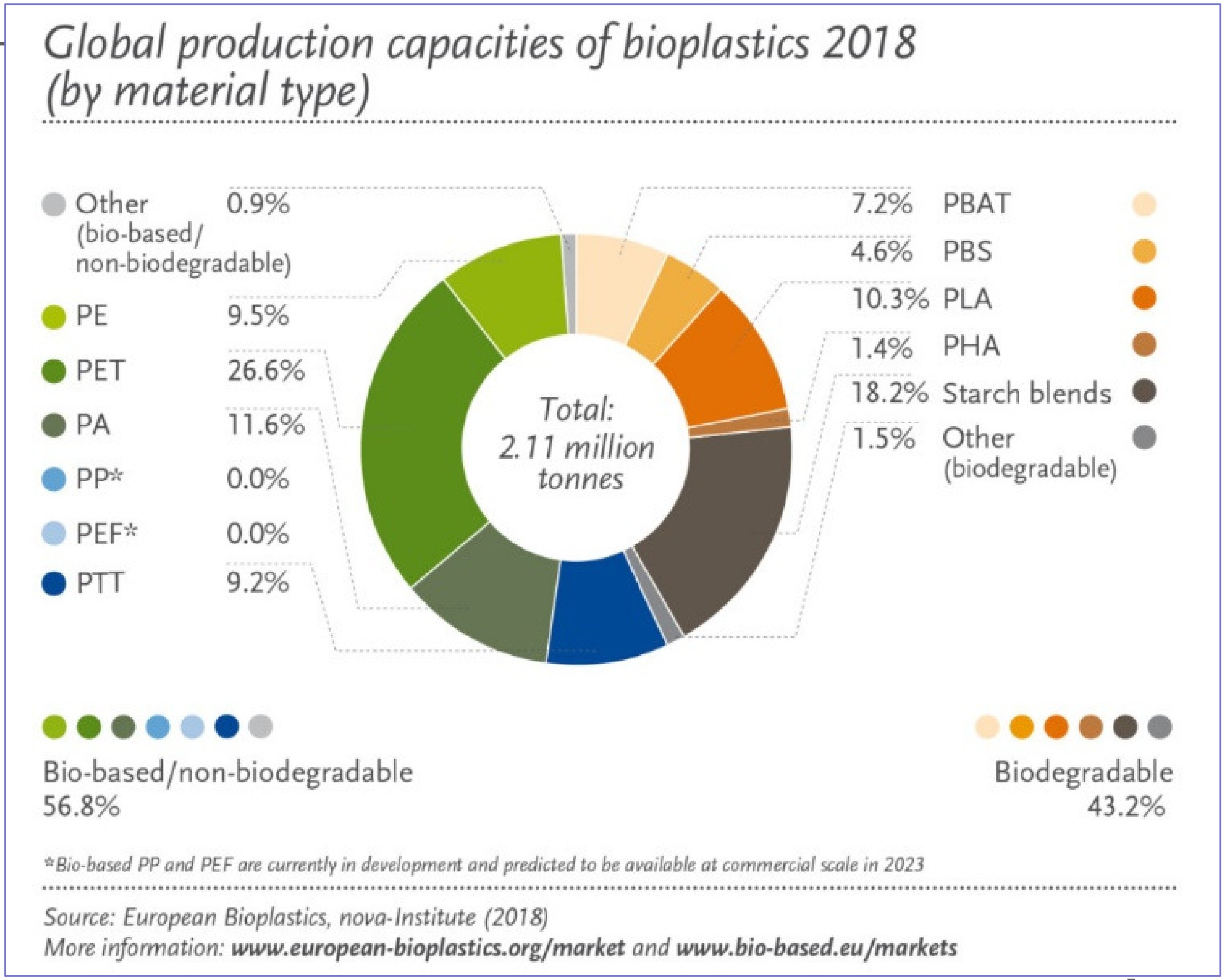
Traditional polymers
Not-biodegradable
and petro-derived
e.g. the maiority of commercial polymers

polymers
biodegradable
and petro-derived
e.g. PCL

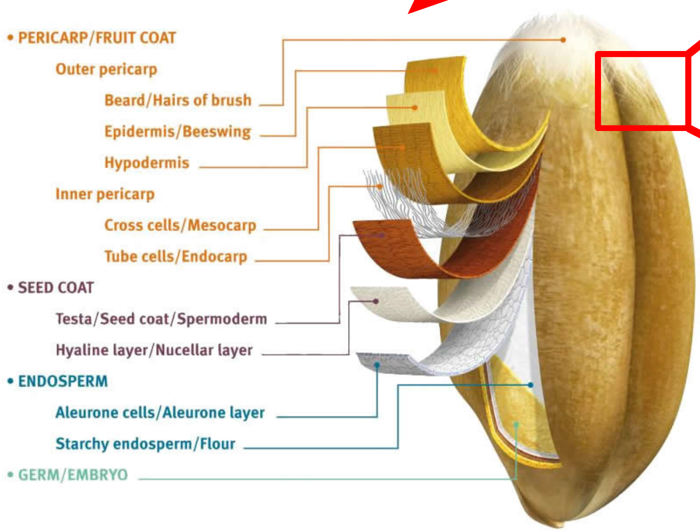
Polymers derived from oil

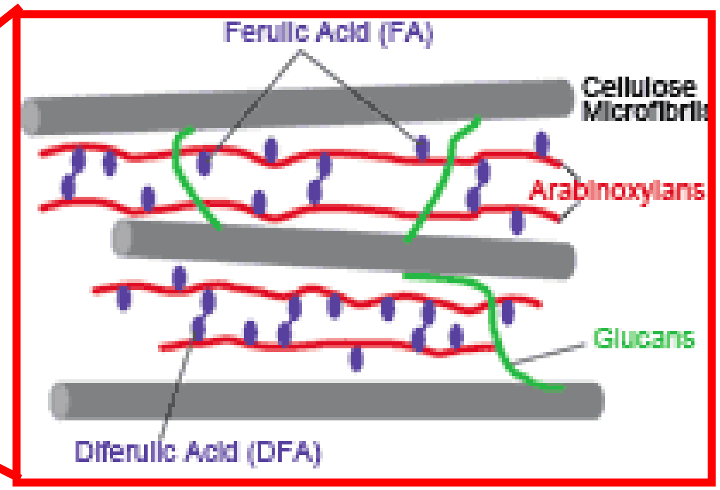
Bio-polymers: global production capacity

Currently, bioplastics represent roughly one percent of the 335 million tonnes of plastic produced annually

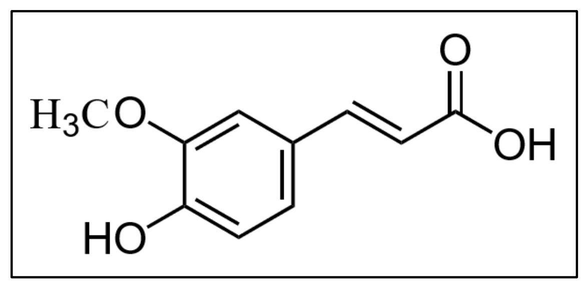


Wheat grain





Ferulic acid is the main phenolic component and it is mostly linked to cell wall polysaccharides



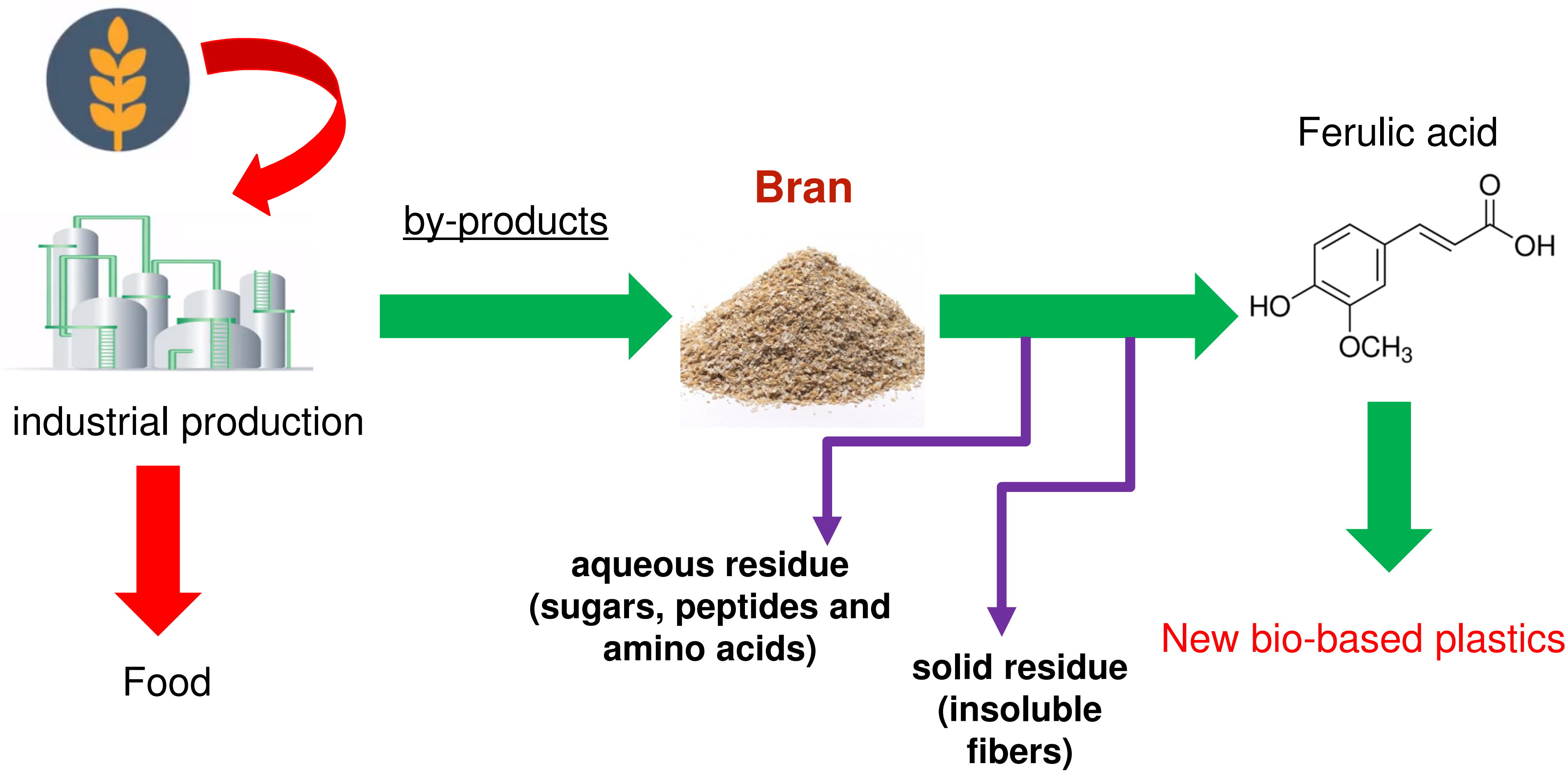
Wheat grain has a multi-layered structure: sequential milling led to different bran fractions

Horizon 2020 European Union funding for Research & Innovation

Bio-based Industries Consortium

This project has received funding from the Bio Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme under grant agreement No. **720719**.

Exploitation of wheat bran by-products



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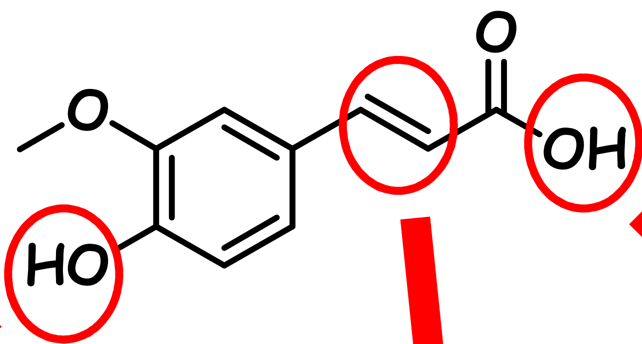
Ferulic acid



Phenol:
Poor reactivity toward polycondensation

Double bond:
Sources of degradation

Carboxylic acid:
Possible promoter of degradation

Solution: chemical modification!

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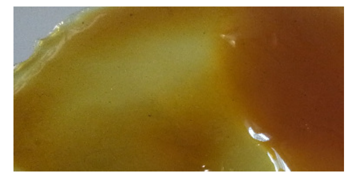
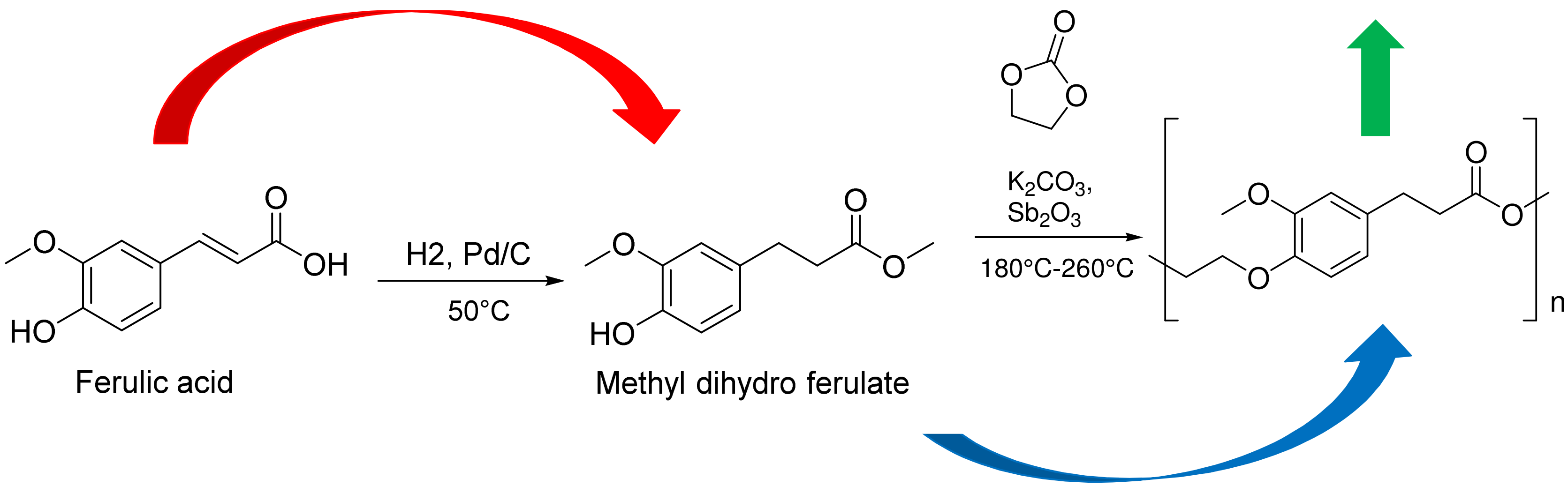
Modification and Polymerization

I Step: Hydrogenation + Esterification
- **Mild conditions**
- **Recyclable catalyst**
- **One pot**
- **No purification**

Poly (ethylene dihydro ferulate) PEHF





II Step: Etherification + Polymerization
- **One pot**
- **No purification**

100% bio-based polymer

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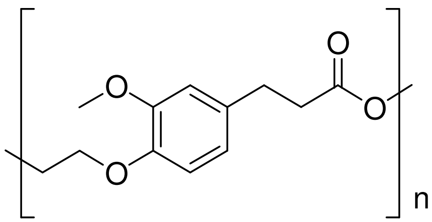
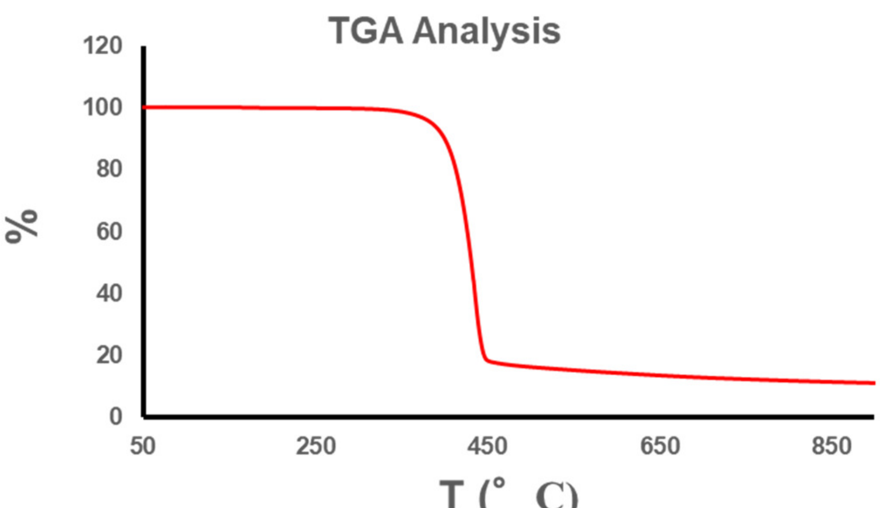
Poly (ethylene dihydro ferulate)
<u>PEHF</u>



Rigid and flexible packaging

Material for agricultural applications

Tg = 27°C
Mw = 12000



Horizon 2020
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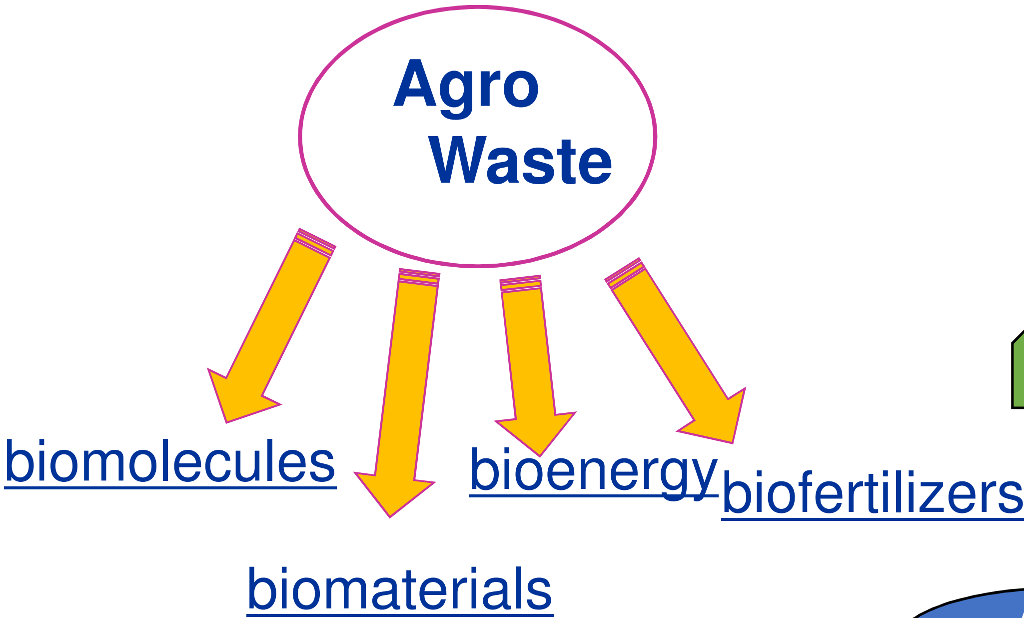
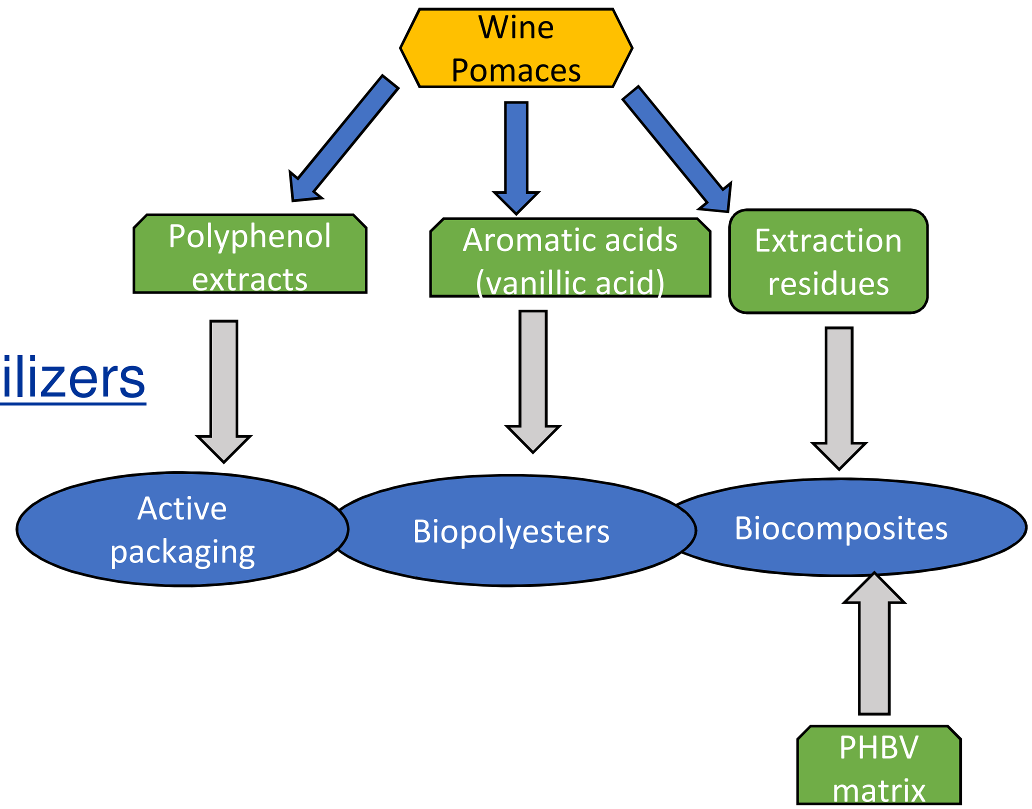
NoAW: Innovative approaches to turn agricultural waste into ecological and economic assets





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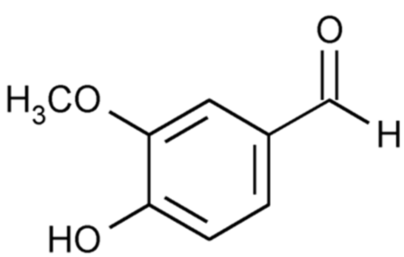
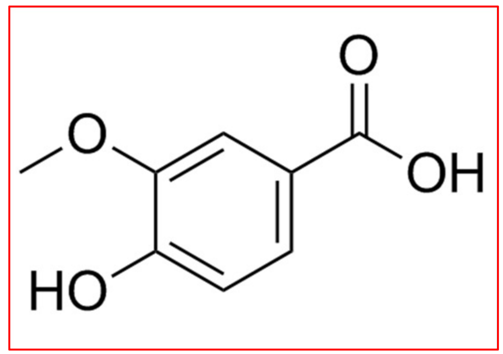
Vanillic acid

Availability of bio-based vanillic acid

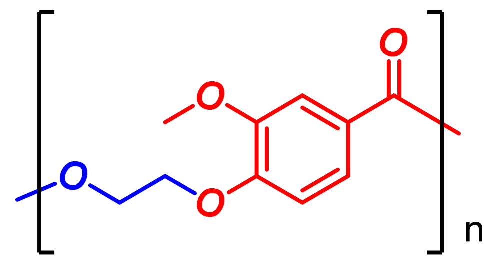
Feedstock	Amount (mg/100 g FW)
Sweet basil, dried	14.00
Oregano, dried	6.00
Thyme, dried	6.10
Dried fruits (date)	4.13
Red wine	0.32
Cereals (oat, rice)	0.28



vanillin



vanillic acid



Polyethylene vanillate (PEV)

PET-mimic polyesters

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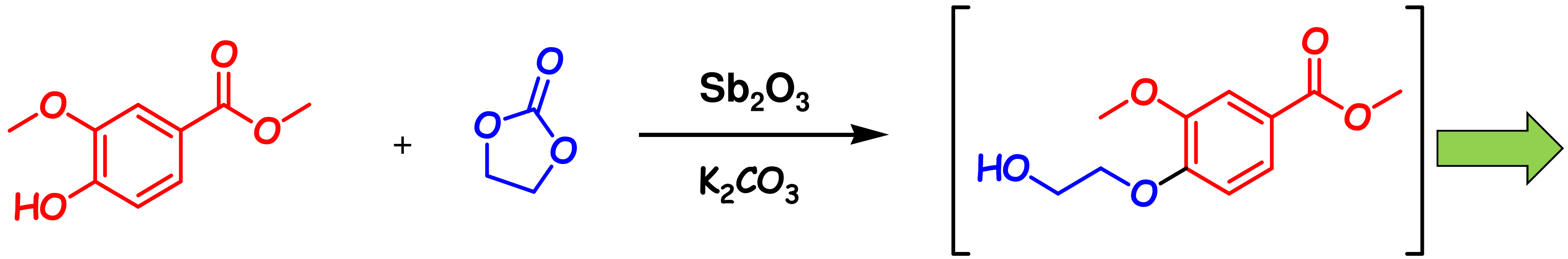
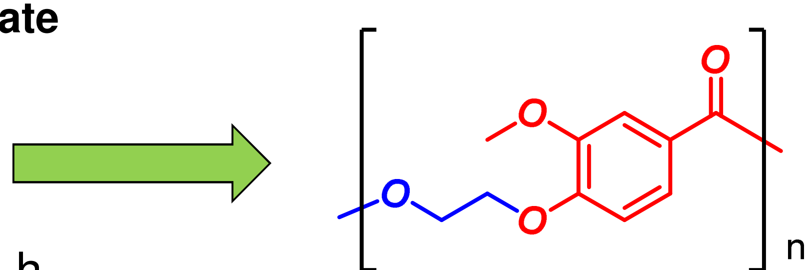
Vanillic acid as aromatic building block



methyl vanillate



100% bio-based PET-like polymer

$T_{first\ stage}$ = 180°C, t =3 h
$T_{second\ stage}$ = 240°C, t =3.5 h

<u>Polyethylene vanillate (PEV)</u>

ONE POT PROCEDURE
NO SOLVENT NEEDED
NO PURIFICATION STEP
100% POTENTIALLY BIOBASED PROCESS

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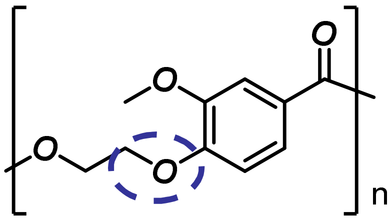
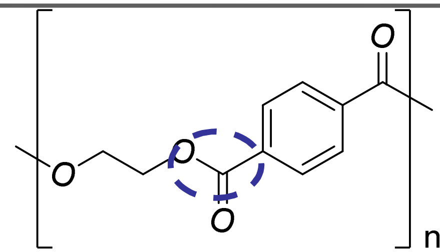
Comparison between PEV and PET



Polyethylene vanillate PEV



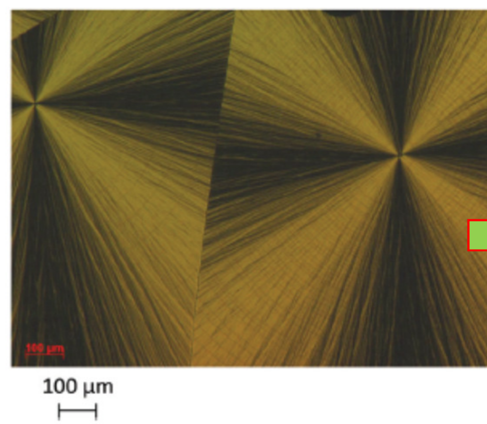
PET

Tm = 264°C
ΔHm = 77 J/g
Tg = 74°C
Molecular weight = 11000

Tm = 260°C
ΔHm = 42 J/g
Tg = 76°C

Cristallinity = about 26%

High level of crystallinity (about 58%)



brittleness

copolymers

Mobility of the chain around the rigid aromatic ring

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Processability

Copolymers are processable and filmable.

The brittleness of PEV has been overcome.

The colour is good.

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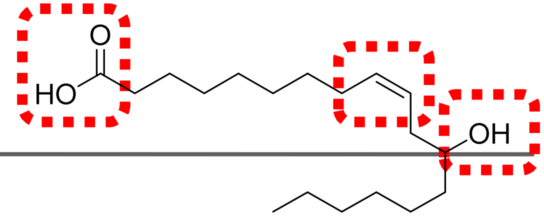
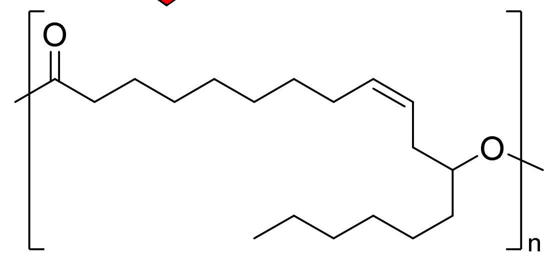
Castor Plant
Ricinus Communis

beans contain
castor oil

Ricinoleic acid

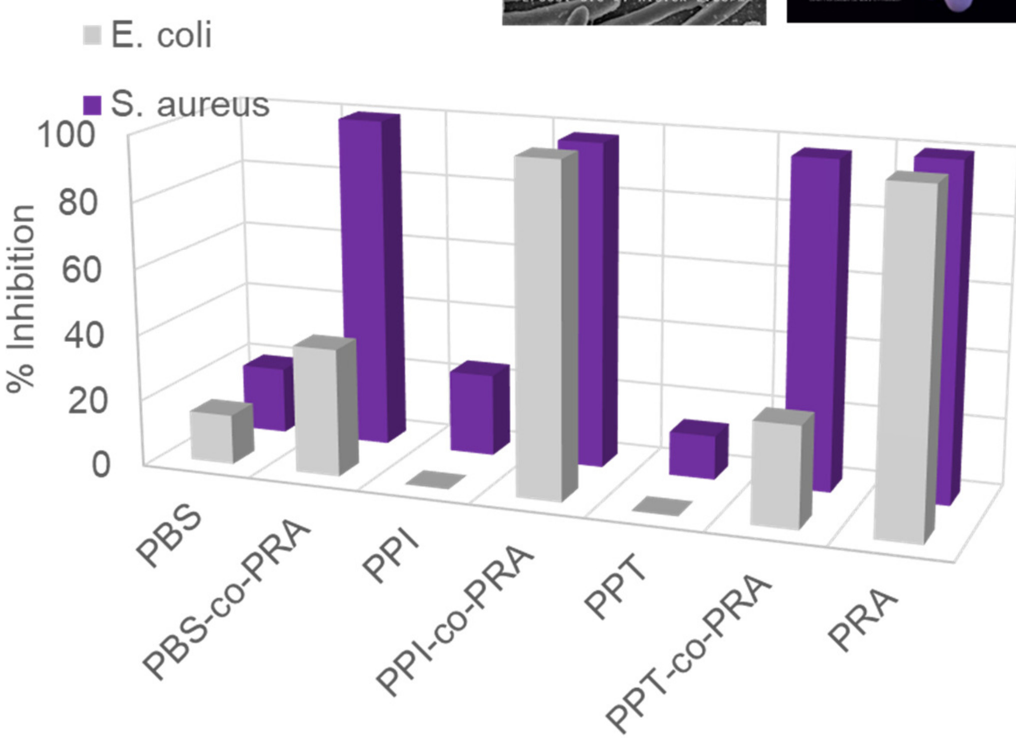


12-hydroxy-cis-9-octadecenoic acid



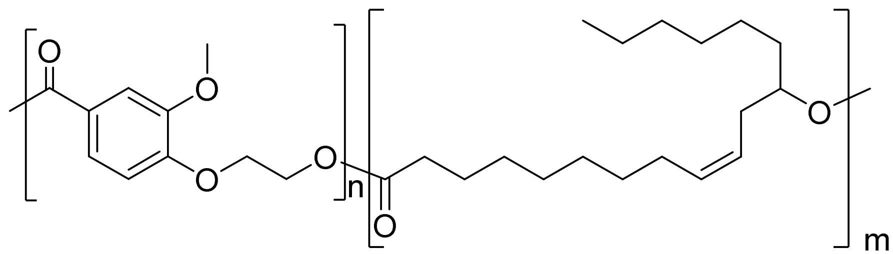
PRA

Antibacterial properties



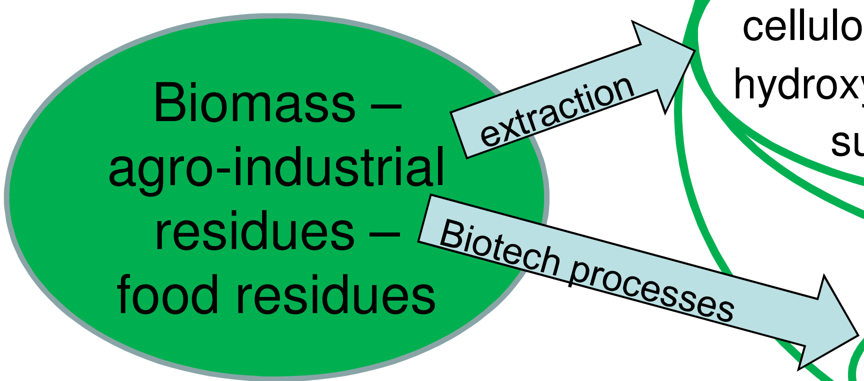
T_g = -67 °C
viscous liquid at RT
antibacterial properties

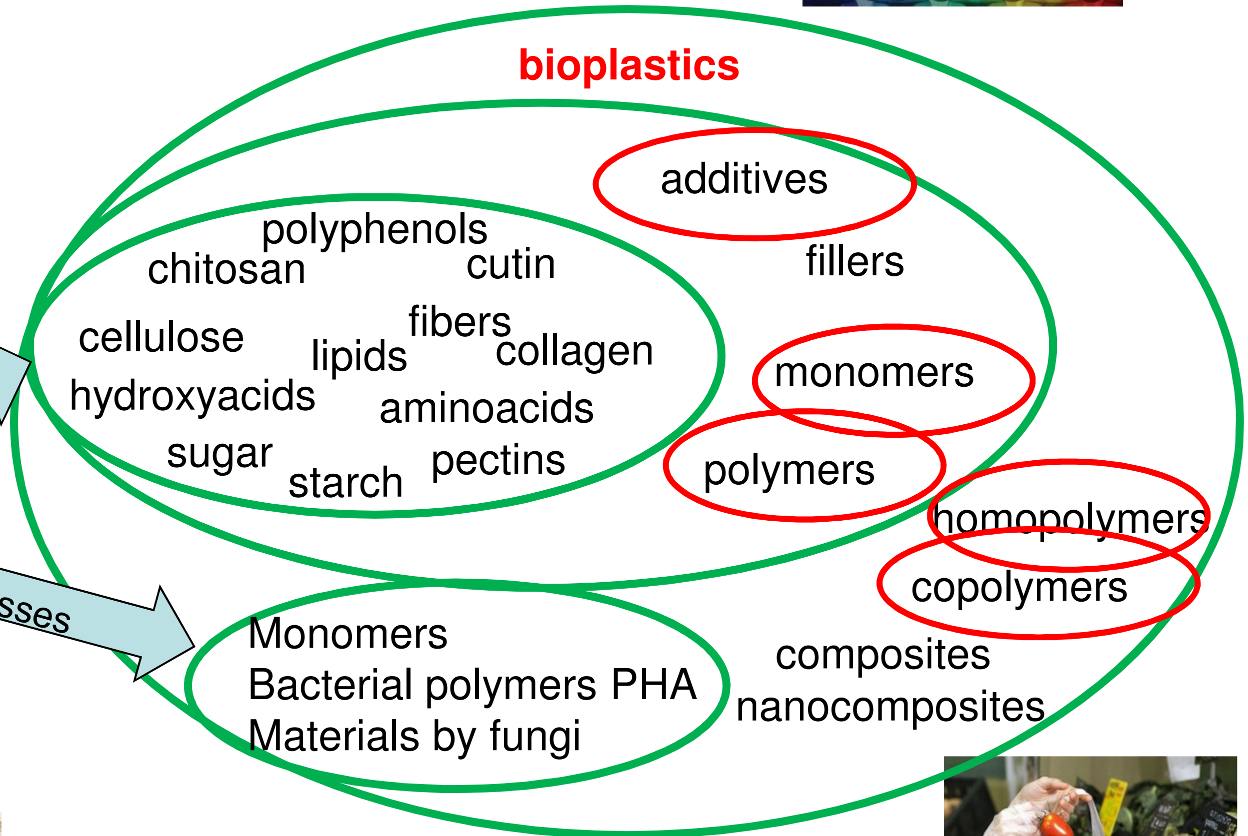
New materials based on vanillic acid



Copolymers based on vanillic acid and polyricinoleic acid for active packaging applications

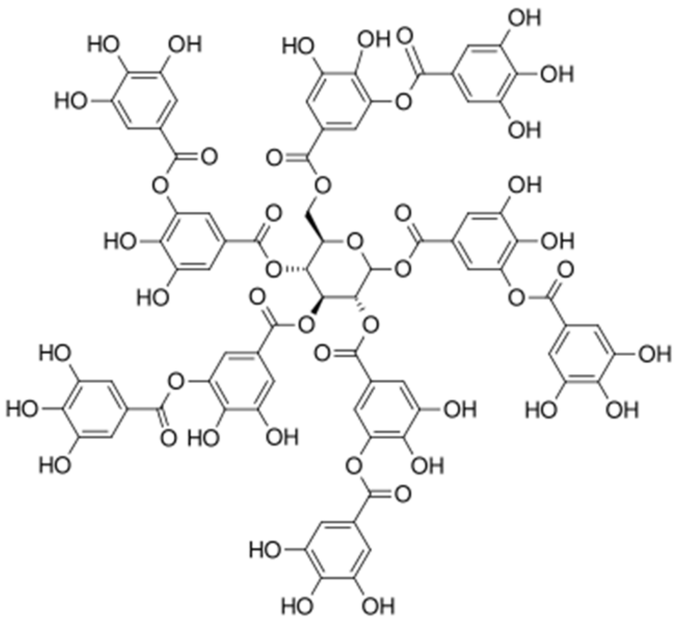
Agro-waste: towards new bio-based materials





High value compounds from food/agro waste

Polyphenols



They are characterized by antioxidant and antibacterial properties

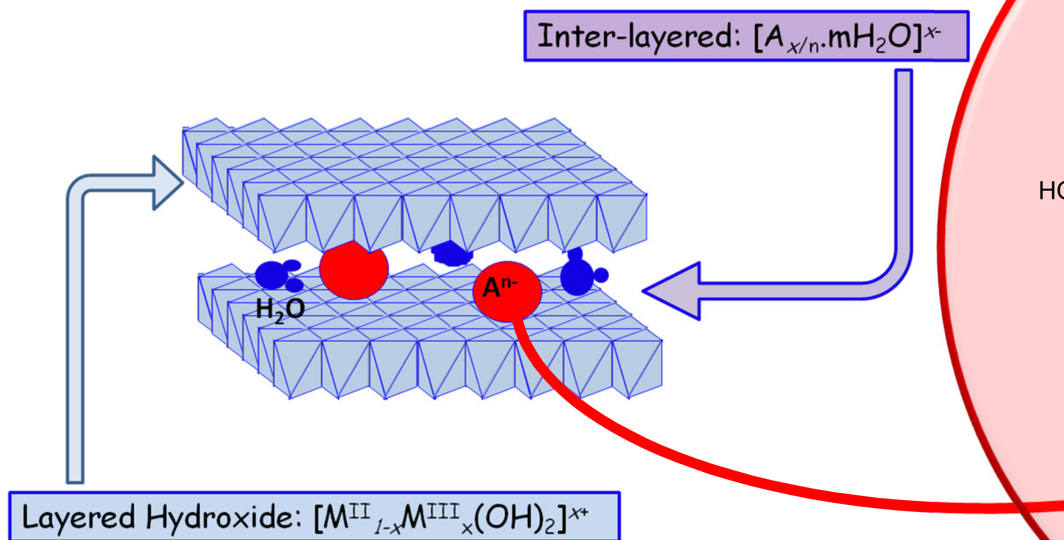
They can be used as additives for polymer formulation

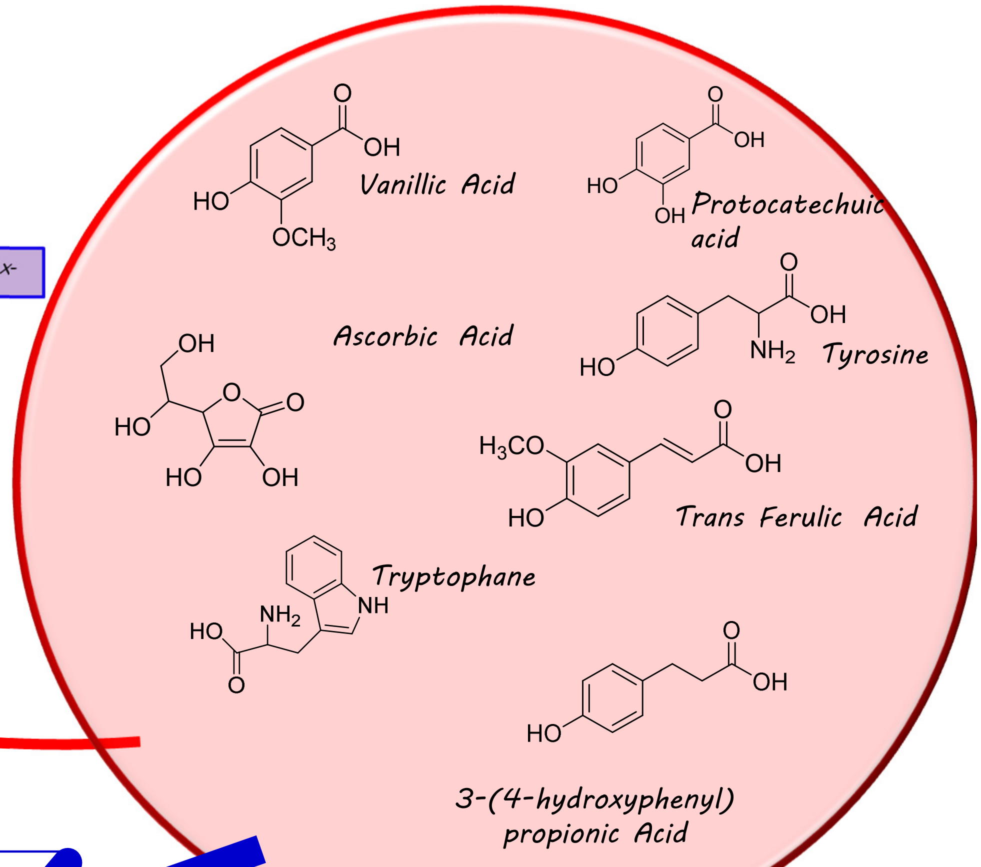
If mixed to a polymeric matrix at the molten state, they can confer these properties to the material.

Protection of bioactive molecules

Matrix: PBS and PBSA

+ LDH containg active molecules



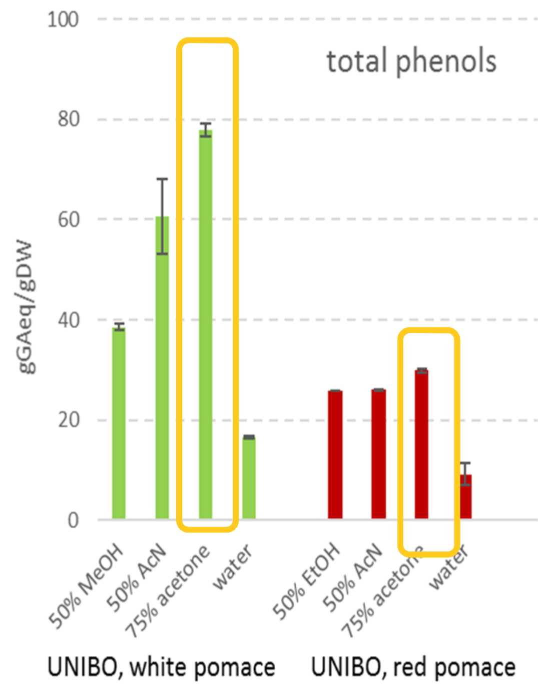


biocompatible
food compatible
tunable composition

MULTIFUNCTIONAL MATERIALS

With antibacterial, antioxidant, barrier, mechanical properties

Final extraction residue



Optimised solvent-based extraction with 75% (v/v) acetone was selected as the best process for the recovery of bioactive molecules from both red and white grape pomace.

Garganega (WHITE) residue

Merlot (RED) residue

Dog-bones of PHBV (on the left) and the composites containing 5, 10 and 20 wt% of residues from the polyphenol extraction from white pomaces (from left to right)

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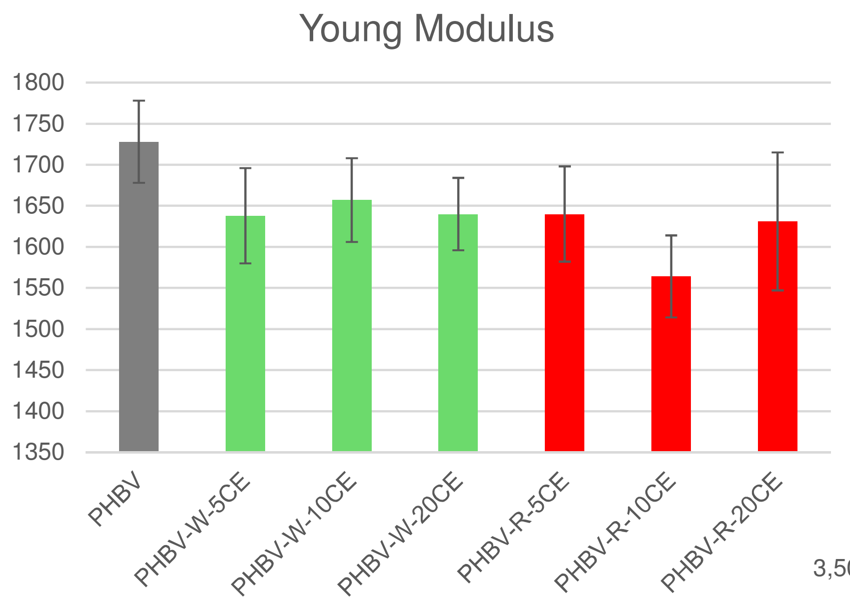
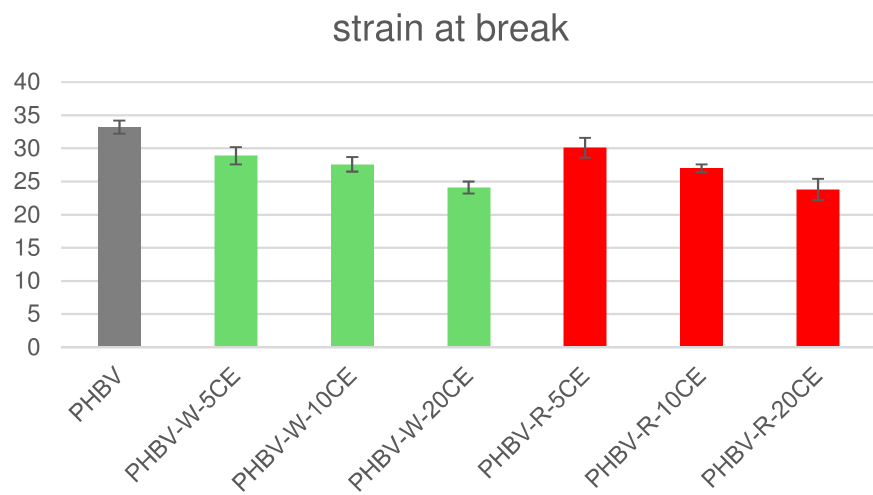
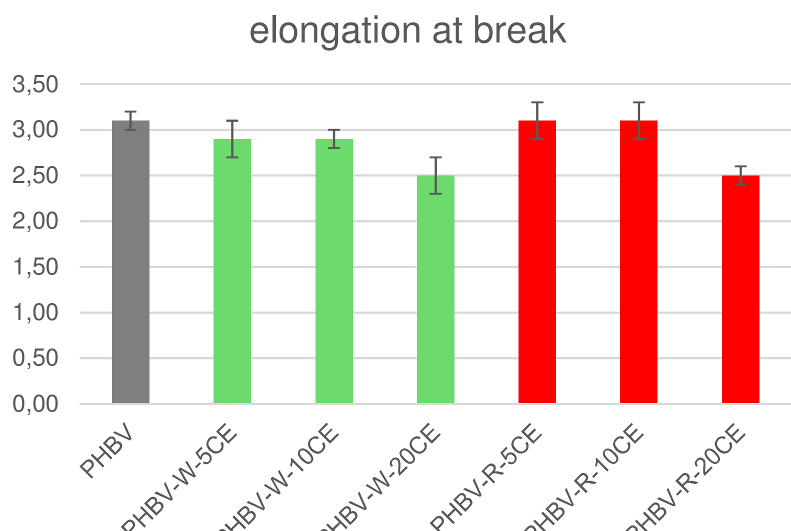
Tensile tests







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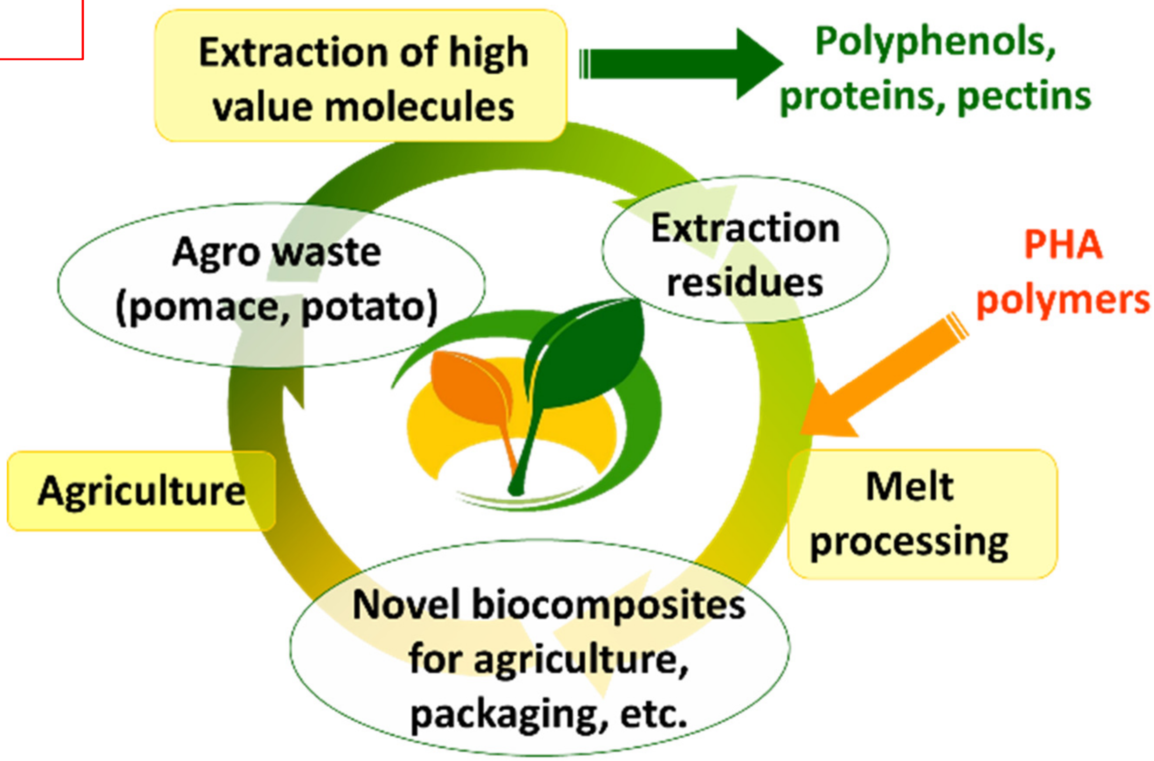
From final extraction residue to new materials

Circular economy principles



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Direct valorization of waste

Virgin
Olive Oil

Wastewater

83 - 94%

4-16% organic compounds:
2-15%: phenolic compounds

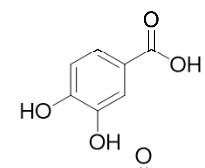
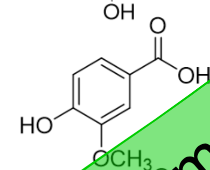
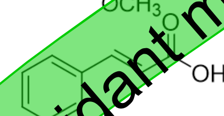
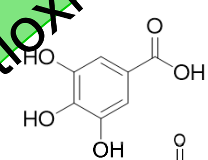
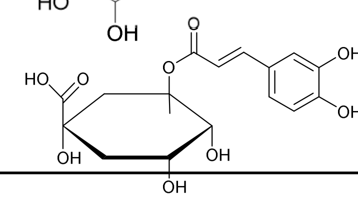
Olive Mill Wastewater (OMW)

- *Low pH (about 5)*
- *High electrical conductivity*
- *Dark-color (caused by lignin polymerized with phenolic compounds)*

0.4 - 2.5% mineral salts:
K^+, Ca^{2+}, Na^+....

Composition of OMW

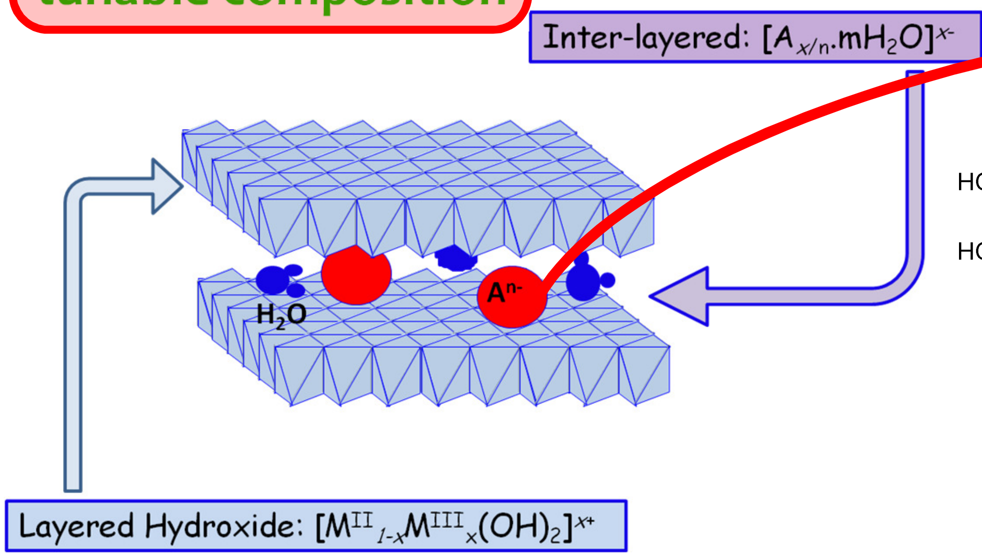
TOTAL PHENOLS CONCENTRATION: 4.51 ± 0.65 g GA eq / L

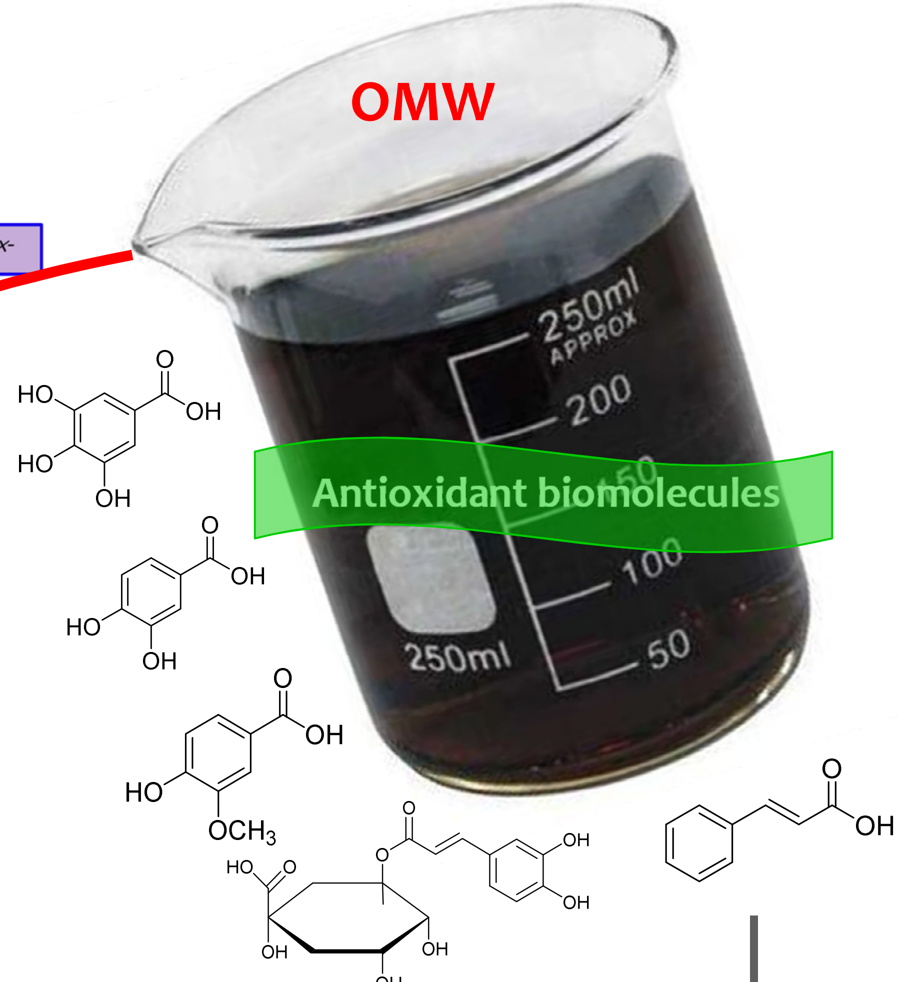
PHENOLIC COMPOUND	CONCENTRATION (μM)	FORMULA
3,4-Dihydroxybenzoic acid	249.3 ± 12.8	
Vanillic acid	70.1 ± 5.3	
trans-cinnamic acid	44.1 ± 8.0	
Gallic acid	17.3 ± 0.8	
Chlorogenic acid	12.1 ± 1.7	

Antioxidant molecules

Intercalation in Layered Double Hydroxides (LDHs)

biocompatible
food compatible
tunable composition



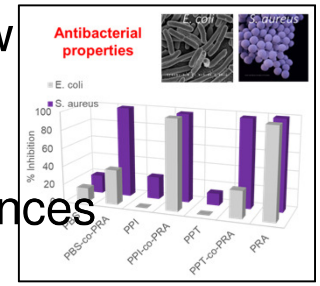


Intercalation in Layered Double Hydroxides (LDHs)

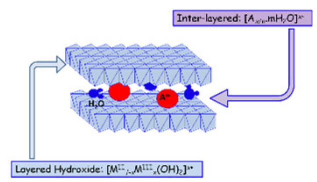
- *Olive mill wastewater was successfully exploited, WITHOUT ANY PRE-TREATMENT, through intercalation into a LDH;*
- *The dispersion of LDHs into the matrices was good;*
- *The LDHs protected the polymer matrices from oxidation;*
- *Olive mill wastewater improved the durability of some polymers such as PBS and PP.*

Final conclusions

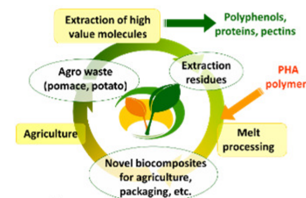
- Strategic routes to fully valorize agro-waste can be developed



- High value molecules can be exploited as monomers to prepare new polymeric materials (homopolymers and copolymers)
- Materials with tunable properties and intrinsic antibacterial performances can be prepared
- High value molecules can be exploited as additives to impart multifunctional properties
- LDH structures can stabilize the additives



- The final solid extration residues can be used as filler for polymeric matrix without deterioring mechanical performances and contributing to decrease the costs of the matrix



- In some cases agro-waste can be directly added to the polymeric matrix to prepare new composites.

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