



ALMA MATER STUDIORUM  
UNIVERSITÀ DI BOLOGNA

# Full valorization of winery waste towards new materials inside the NoAW project

**Annamaria Celli**

Department of Civil, Chemical, Environmental, and Materials  
Engineering, University of Bologna, Italy



***“Innovative approaches to turn agricultural waste into ecological and economic assets” (NoAW) (2016-2020)***

---

**Grant Agreement Number 688338**

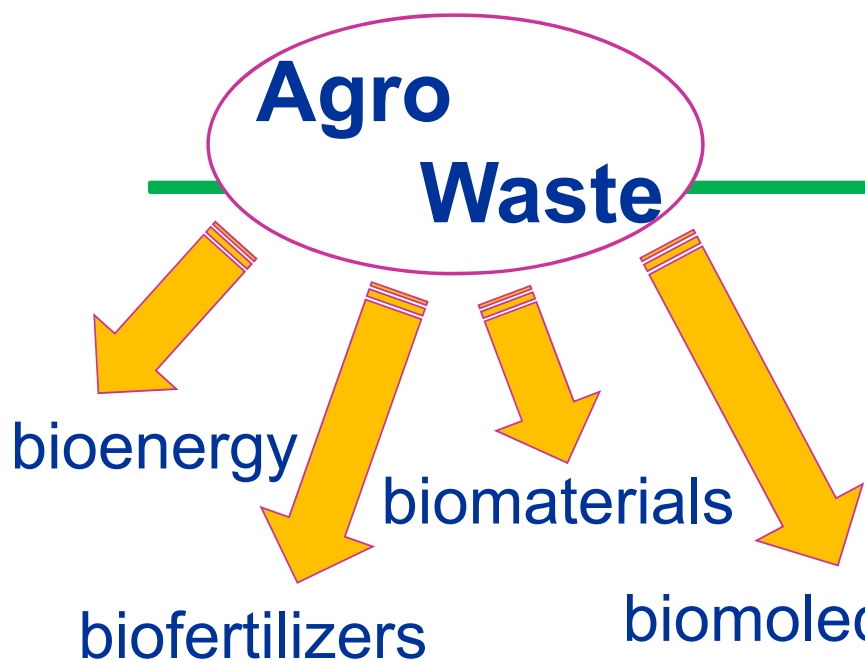
**Call H2020-WASTE-2015-two-stage**

**Topic:** WASTE-7-2015: Ensuring sustainable use of agricultural waste, co-products and by-products

**Coordinator:** INSTITUT NATIONAL DE LA RECHERCHE AGRONOMIQUE (INRA) France

NoAW aims to contribute to  
**a sustainable agro-waste bio-refinery concept**  
by developing innovative conversion processes of agro-waste into  
**high-value products.**



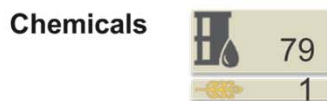
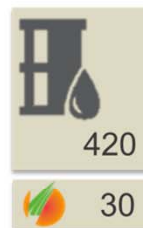


Now the situation

NoAW's ambitions



MTOE: million tons oil equivalent



✓ **NoAW aims to substitute** non renewable oil and noble food resources with agricultural waste that will be converted into energy, fertilizer, plastics and chemicals.

# List of Beneficiaries

**RISE** (Sweden)  
**DTU** (Denmark)  
**AAU** (Denmark)  
**WFBR** (Netherlands)  
**FRAUNHOFER** (Germany)  
**INRA – Coordinator** (France)  
**UM** (France)  
**UNIROMA** (Italy)  
**UNIBO** (Italy)  
**CBHU** (Hungary)  
**IAUS** (Serbia)  
**NTUA** (Greece)  
**ITRI** (Taiwan)  
**SEE** (Hong Kong)  
**IAPPST** (China)  
**SYSU** (China)



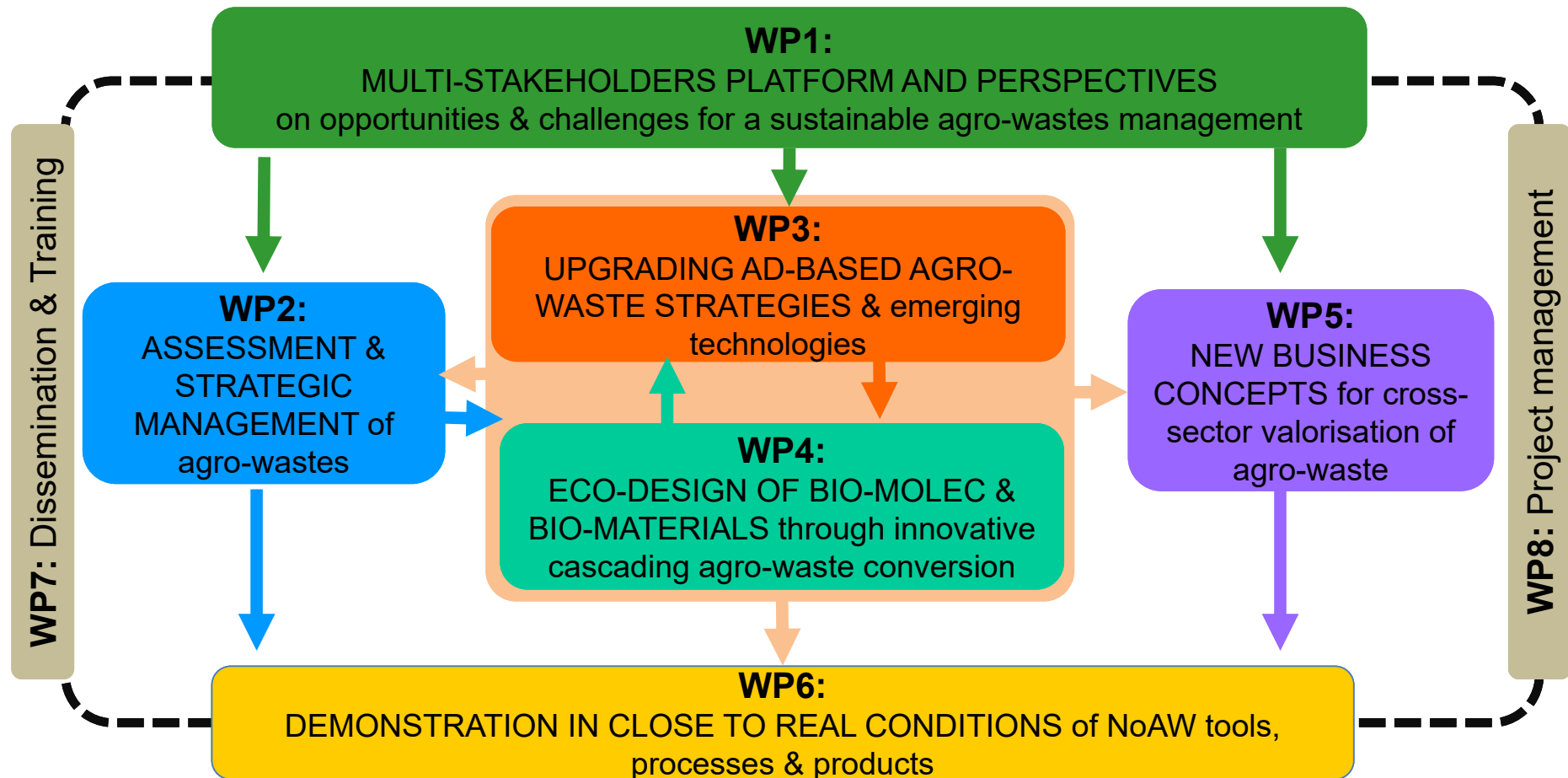
**BioVantage** Denmark  
**AGRIPORT** (Netherlands)  
**ECOZETP** (Germany)  
**IBBK** (Germany)  
**VERMI** (Germany)  
**SCHIESSL** (Germany)  
**SOFIES** (Switzerland)  
**IFV** (France)  
**GRAPSUD** (France)  
**APESA** (France)  
**IT** (France)  
**INNOVEN** (Italy)  
**GCIA** (Italy)  
**IBET** (Portugal)  
**VA** (Serbia)

## **NoAW's partners:**

NoAW is coordinated by **INRA (France)** and the consortium involves 31 partners from universities, public research organizations and other institutions from a dozen countries.



# Structure of NoAW:



# From winery waste to new biomaterials



pomace

Vine shoots



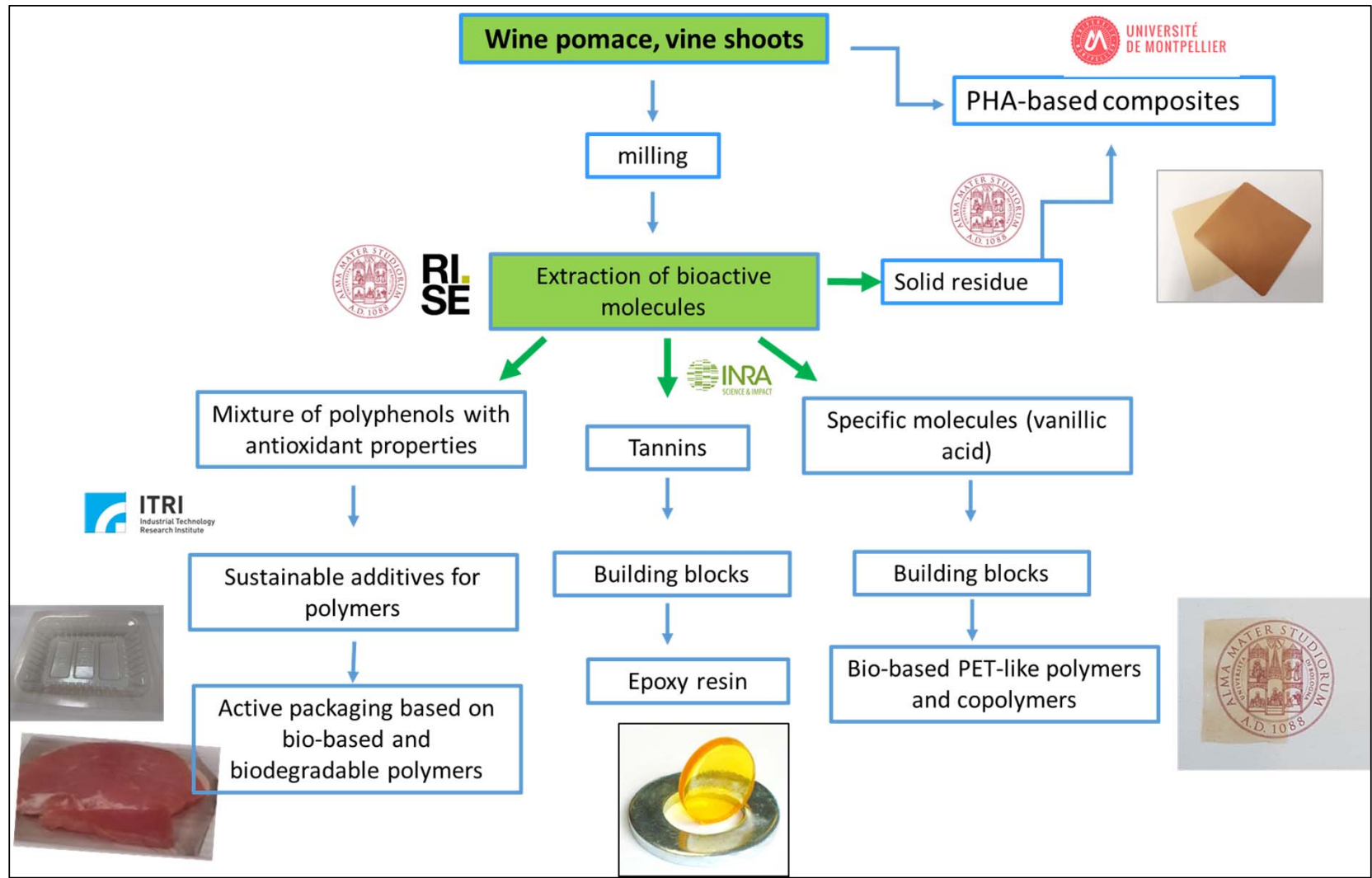
milling



Extraction of bio-active molecules



Preparation of composites



# Extractions of polyphenols from wine pomaces



Merlot

**RED POMACE:**  
Merlot cultivar,  
after wine fermentation and pressed



**WHITE POMACE:**  
Garganega cultivar,  
pressed



Garganega

Two extraction methods have been compared

**Solvent-based extractions**

**Pressurized liquid extractions**

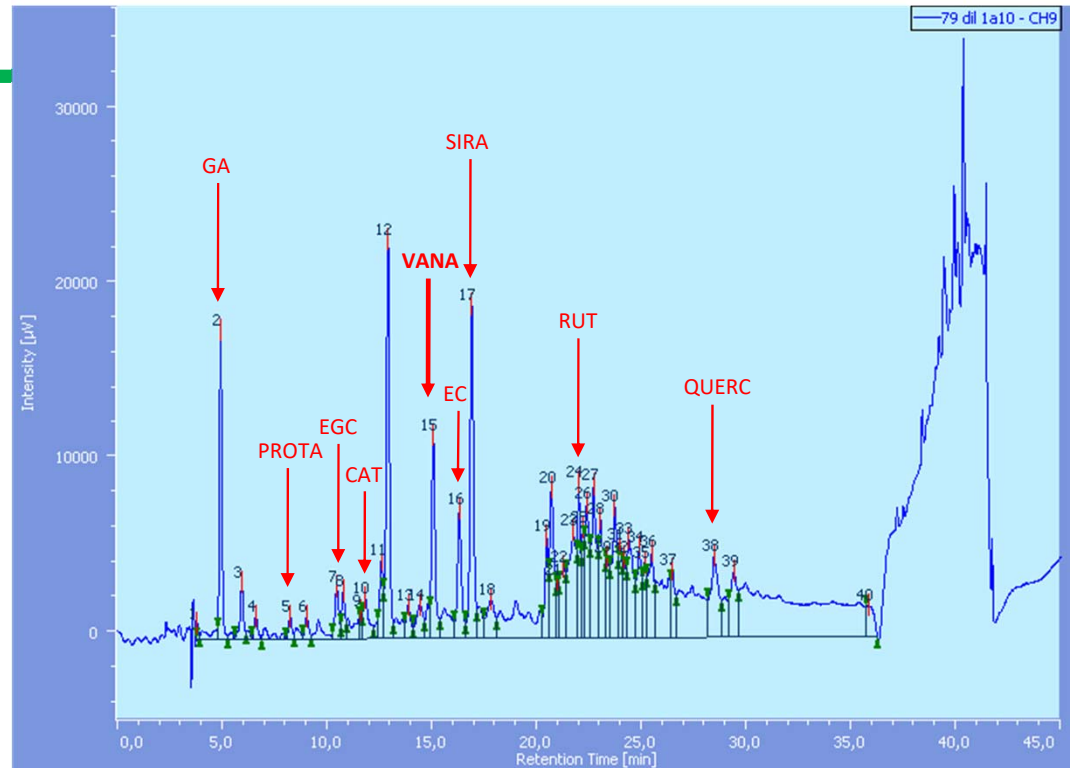
Optimised solvent-based extraction was selected as the best process for the recovery of bioactive molecules from both red and white grape pomace.



# Extractions of polyphenols from wine pomaces

Complex mixture of polyphenols with antioxidant activity

Presence of a specific molecule: vanillic acid



Example of HPLC-DAD characterisation of solvent extracts derived from wine pomace (CAT, catechin; EC, epicatechin; EGC, epigallocatechin; GA, gallic acid; PROTA, protocatechuic acid; QUERC, quercetin; RUT, rutin; SIRA, syringic acid; VANA, vanillic acid).

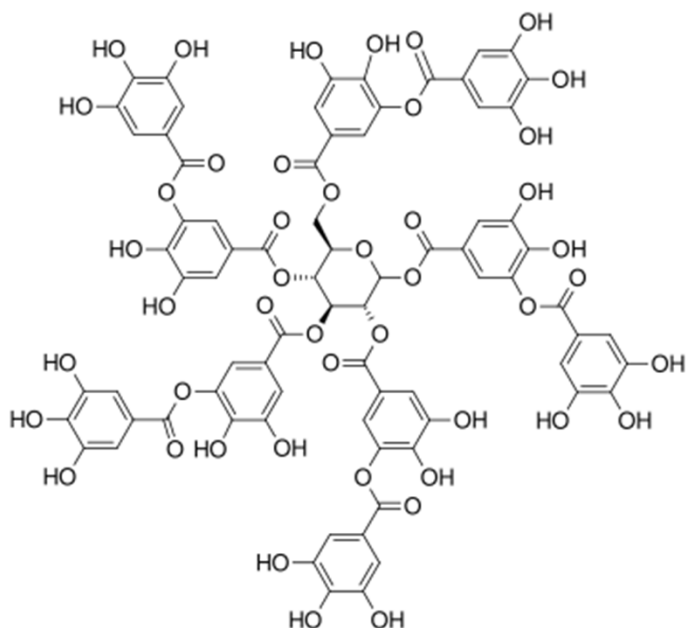
Solid residue of extraction

Merlot (RED) residue



Garganega (WHITE) residue

# Valorization of the mixture of polyphenols



## Polyphenols

They are characterized by antioxidant properties.

They can be used as additives for polymers.

They cannot be mixed to a polymeric matrix at the molten state because they don't have high thermal stability.

Therefore, they can be used in coating applications for food packaging: they can induce improvement in the shelf life of food and contribute to decrease the food waste.

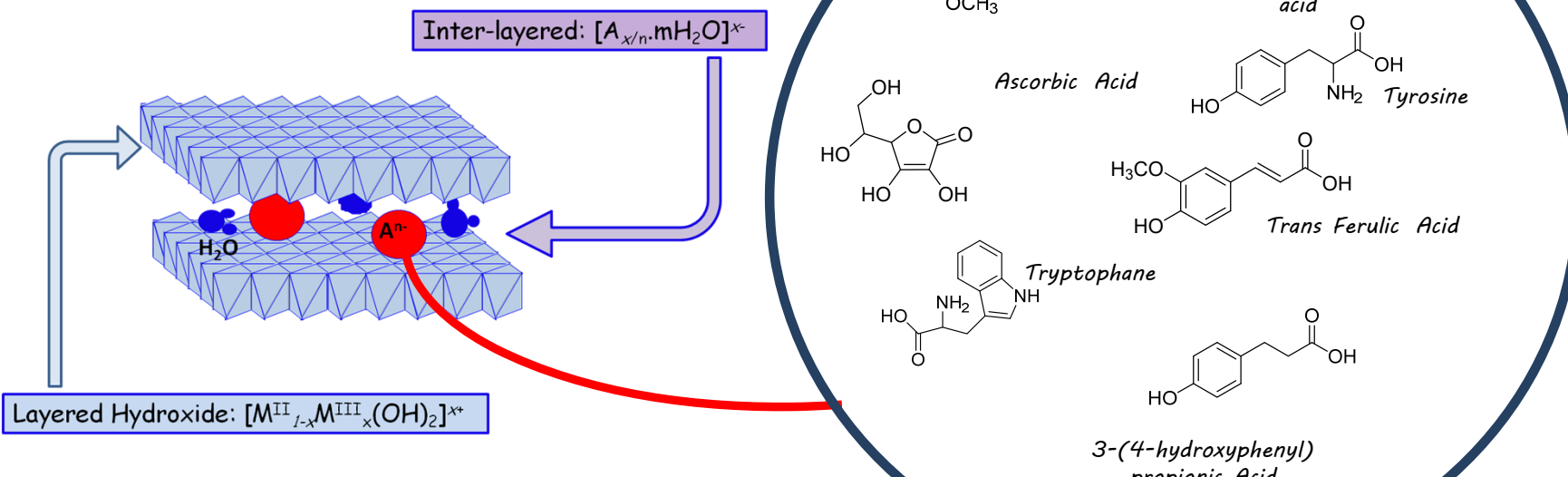
Otherwise, strategies of molecule protection can be developed.

# Protection of bioactive molecules

Matrix: PBS and PBSA

+ LDH containing active molecules

biocompatible  
food compatible  
tunable composition

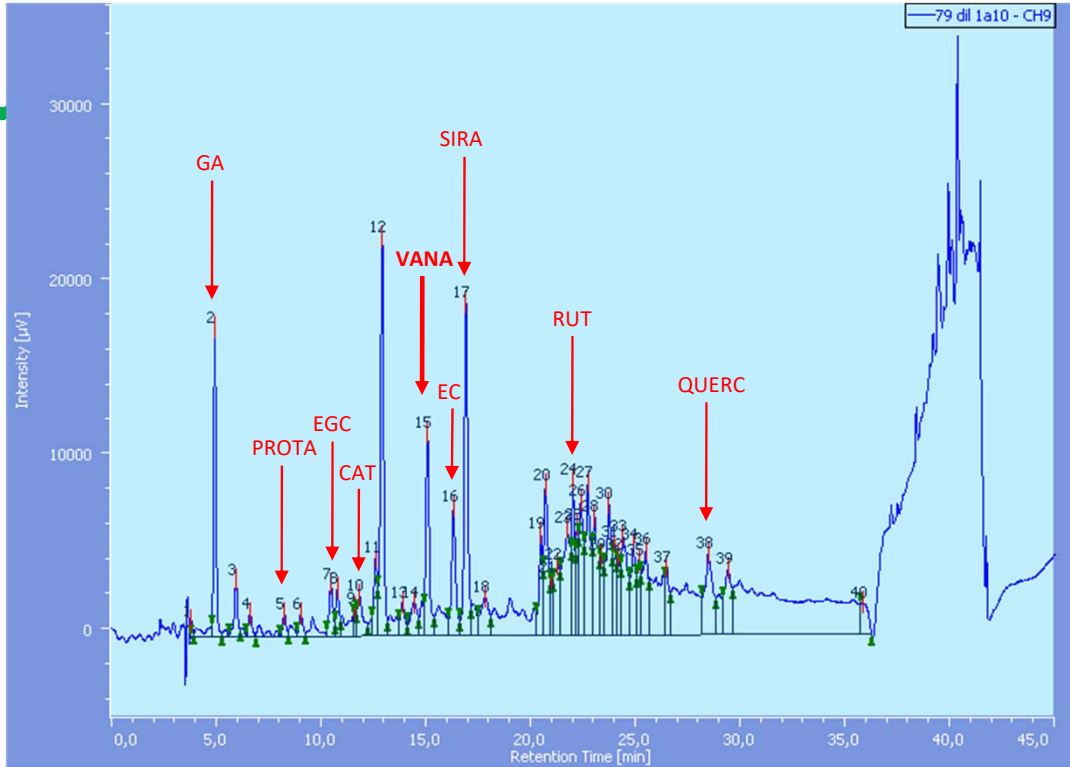


**MULTIFUNCTIONAL MATERIALS**

With antibacterial, antioxidant, barrier, mechanical properties

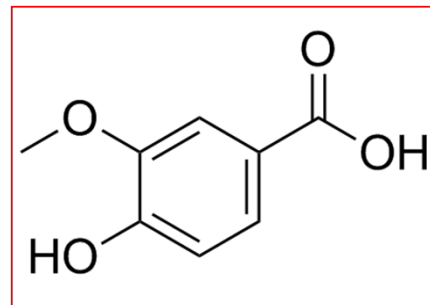
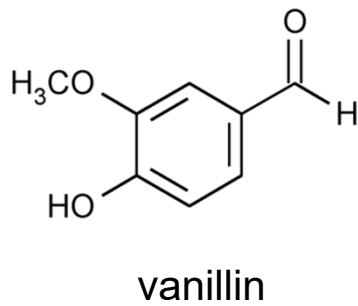


# Vanillic acid



## 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



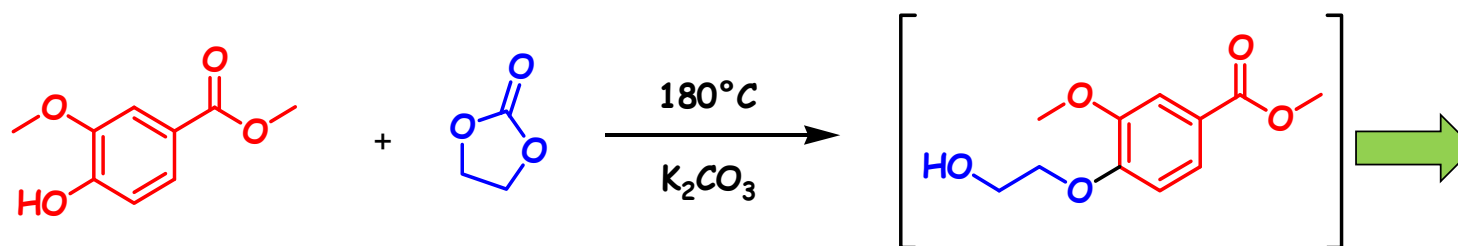
vanillic acid



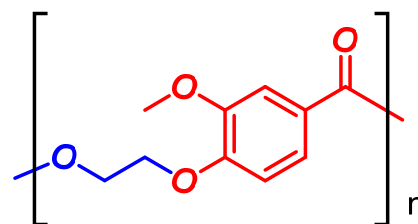
**PET-mimic polyesters**



# Vanillic acid as aromatic building block



methyl vanillate



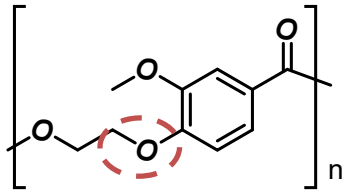
100% bio-based  
PET-like polymer

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

Polyethylene vanillate (PEV)

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

# Comparison between PEV and PET



**Polyethylene vanillate PEV**

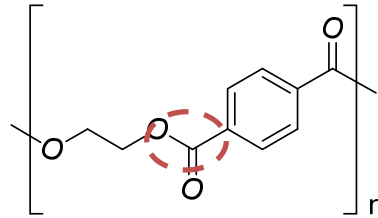
$T_m = 264^\circ\text{C}$   
 $\Delta H_m = 77 \text{ J/g}$   
 $T_g = 74^\circ\text{C}$   
Molecular weight = 11000



High level of crystallinity (about 58%)



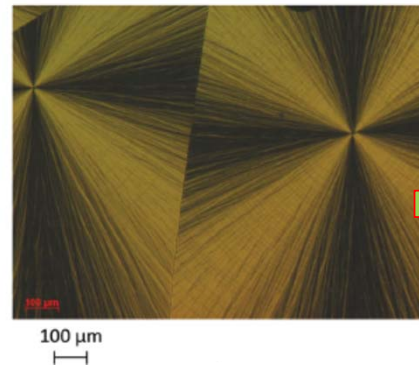
Mobility of the chain around the rigid aromatic ring



**PET**

$T_m = 260^\circ\text{C}$   
 $\Delta H_m = 42 \text{ J/g}$   
 $T_g = 76^\circ\text{C}$

Cristallinity = about 26%

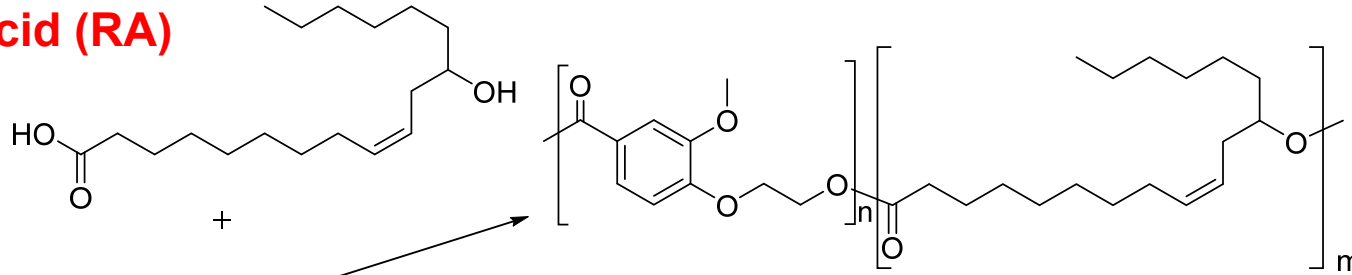


brittleness



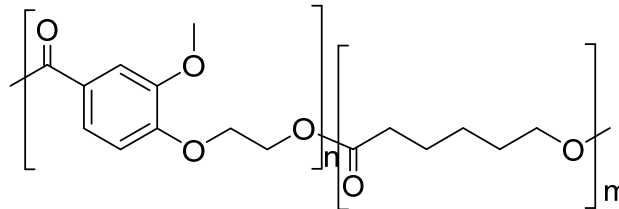
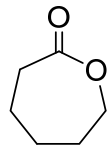
# New random copolymers based on PEV

**Ricinoleic acid (RA)**



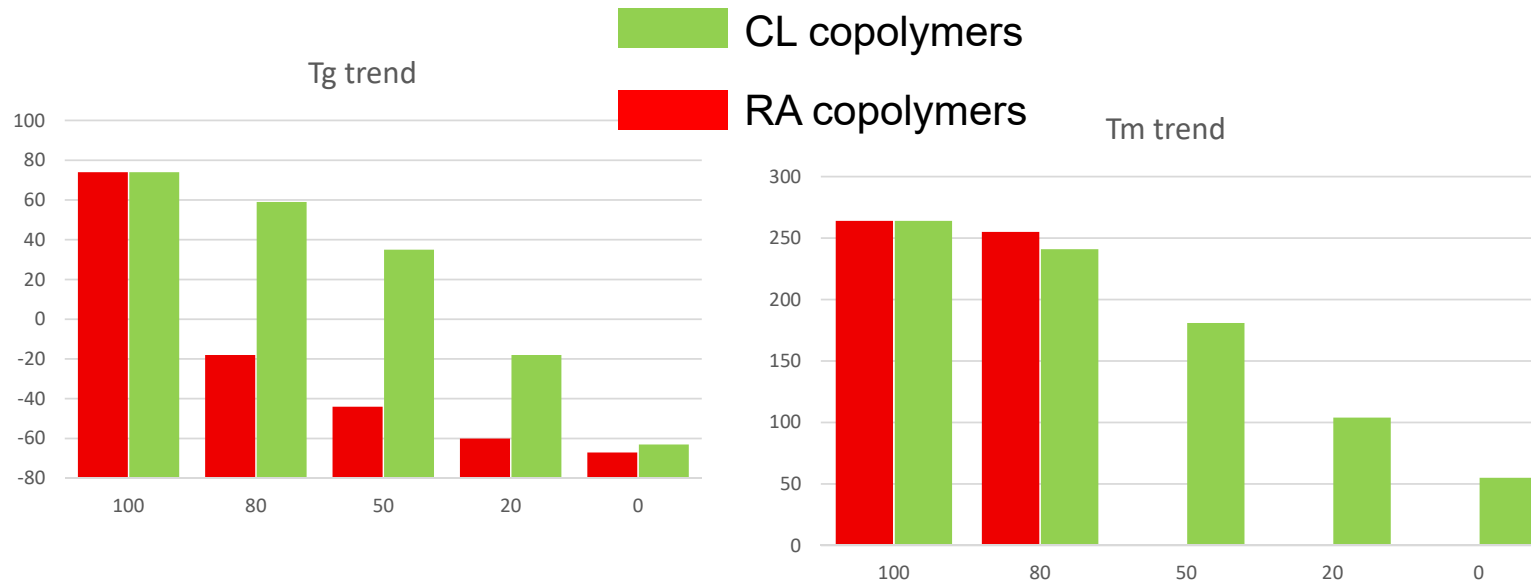
**PEV/PRA**

**Caprolactone (CL)**



**PEV/PCL**

# New random copolymers based on PEV



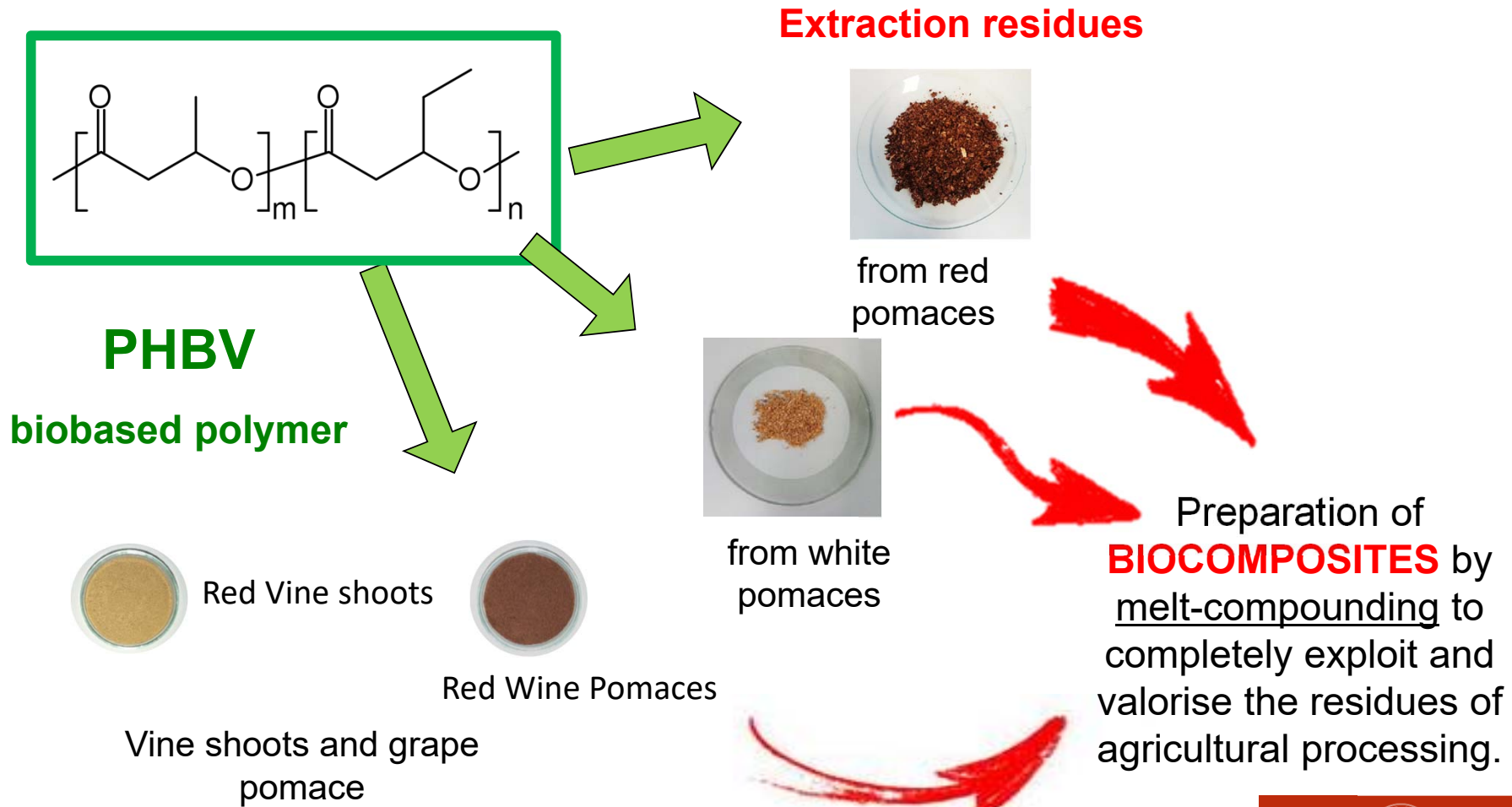
Increment of structure flexibility, reduction of crystallinity level.



Tuning of properties to simplify the material processing and to tailor the polymer for required application fields.



# Preparation of new biocomposites

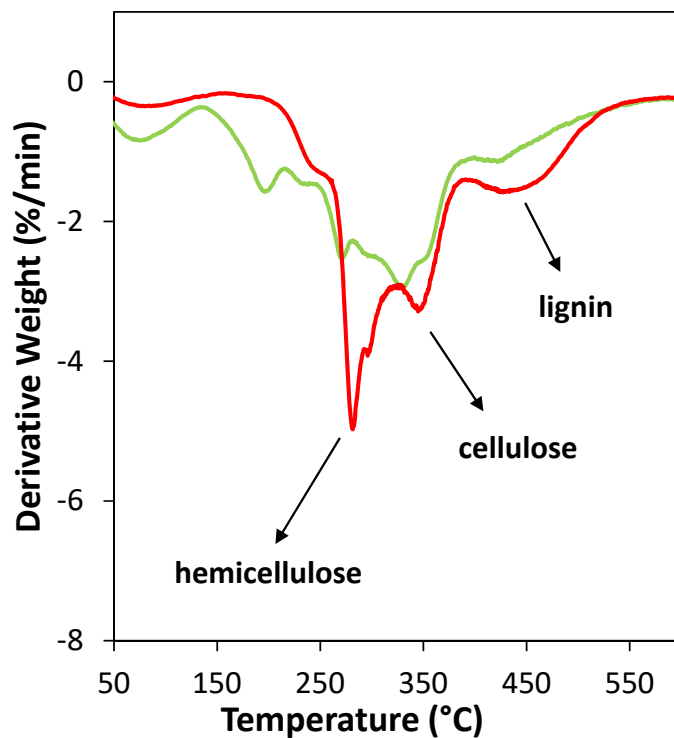
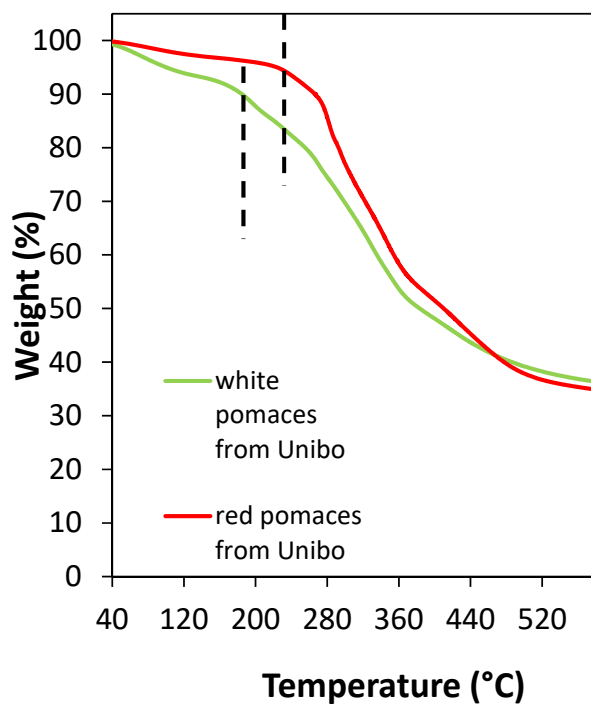




# Characterization of chemically extracted residue



## Thermogravimetric analyses



— white pomaces from Unibo

— red pomaces from Unibo



Merlot (RED) residue



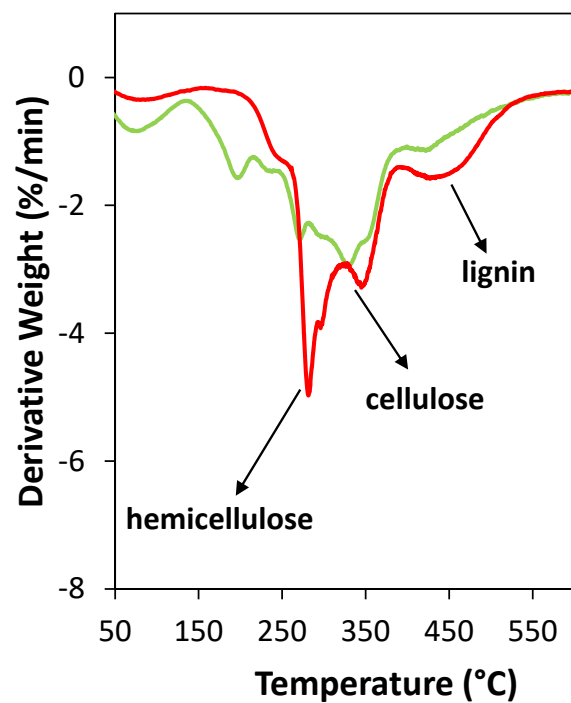
Garganega (WHITE) residue



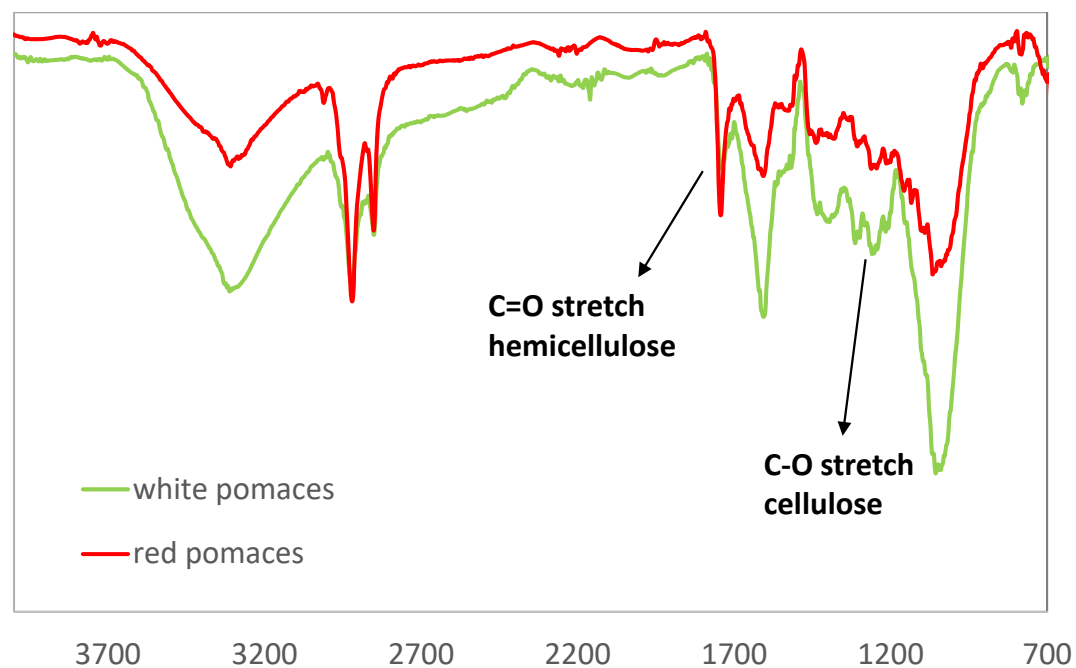
# Characterization of chemically extracted residue



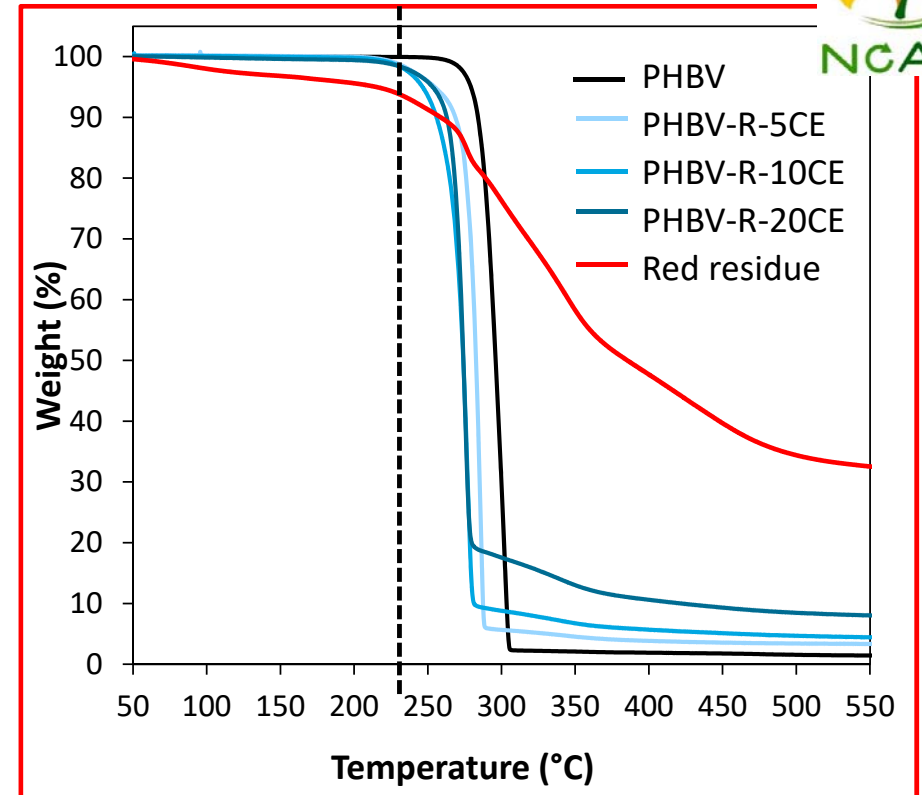
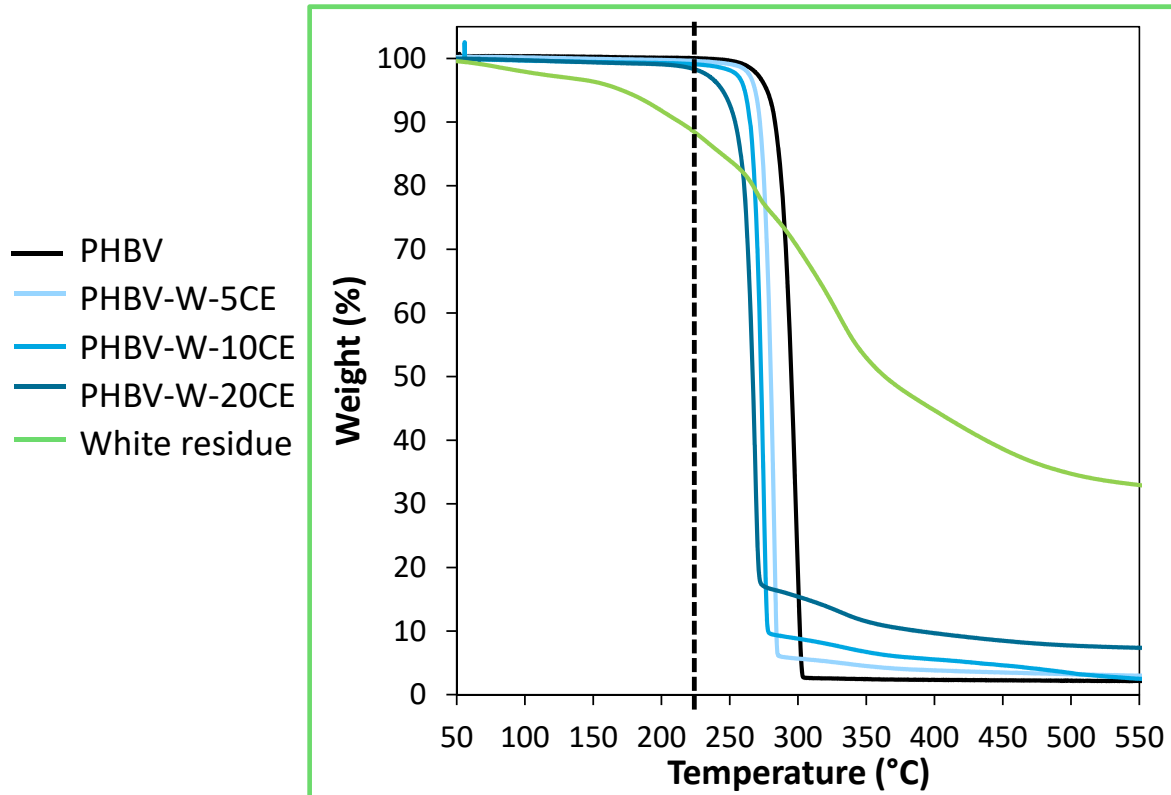
## Thermogravimetric analyses



## FT-IR spectra



# Thermal stability



All the composites are stable over 230°C.  
The thermal stability slightly decreases with the filler content.



# Bio-composites with residue from solvent extracted red and white pomace



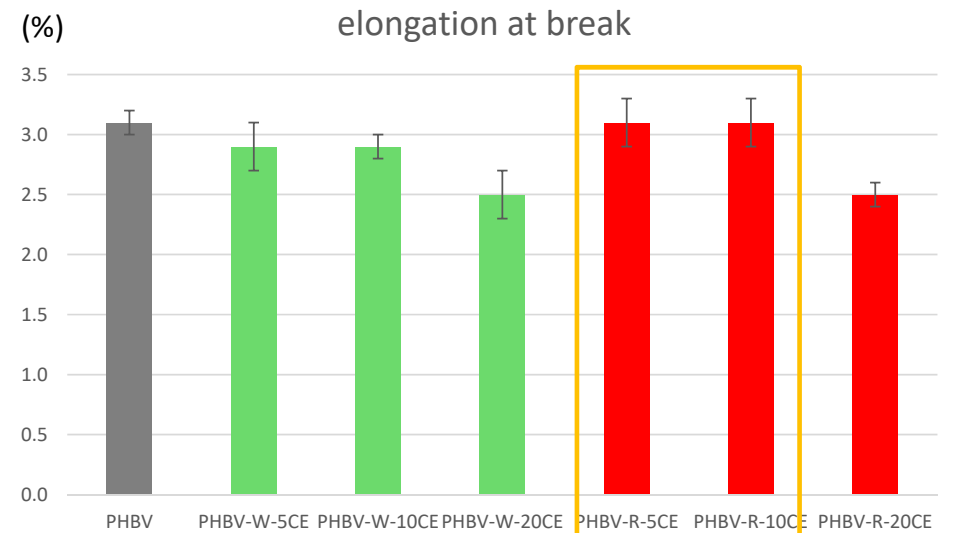
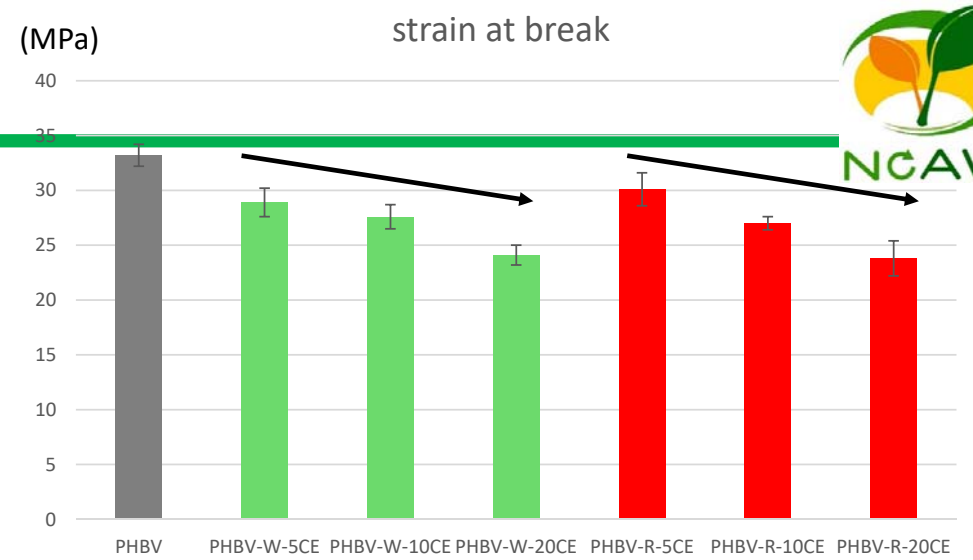
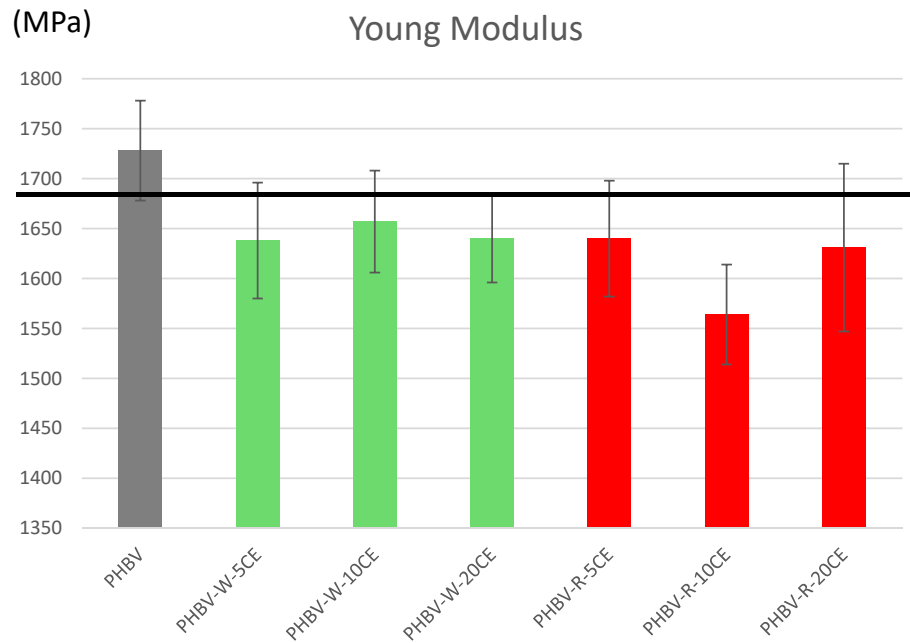
Sample code	1° heating scan		cooling scan		2° heating scan	
	$T_m$ (°C) <sup>b</sup>	$\Delta H_m$ (J/g) <sup>b</sup>	$T_c$ (°C) <sup>c</sup>	$\Delta H_c$ (J/g) <sup>c</sup>	$T_m$ (°C) <sup>d</sup>	$\Delta H_m$ (J/g) <sup>d</sup>
PHBV	172	78	114	73	168	82
PHBV-W-5CE	171	78	111	72	168	80
PHBV-W-10CE	170	71	111	67	168	78
PHBV-W-20CE	169	63	109	57	167	66
PHBV-R-5CE	170	72	112	68	168	77
PHBV-R-10CE	169	74	110	65	168	74
PHBV-R-20CE	170	64	108	57	168	66



First scan, from 30 to 210°C at 20°C/min; 1 min at 210°C; cooling scan, from 210°C to 0°C at 20°C/min; 1 min at 0°C; second scan, from 0 to 210°C at 20°C/min.



# Tensile tests



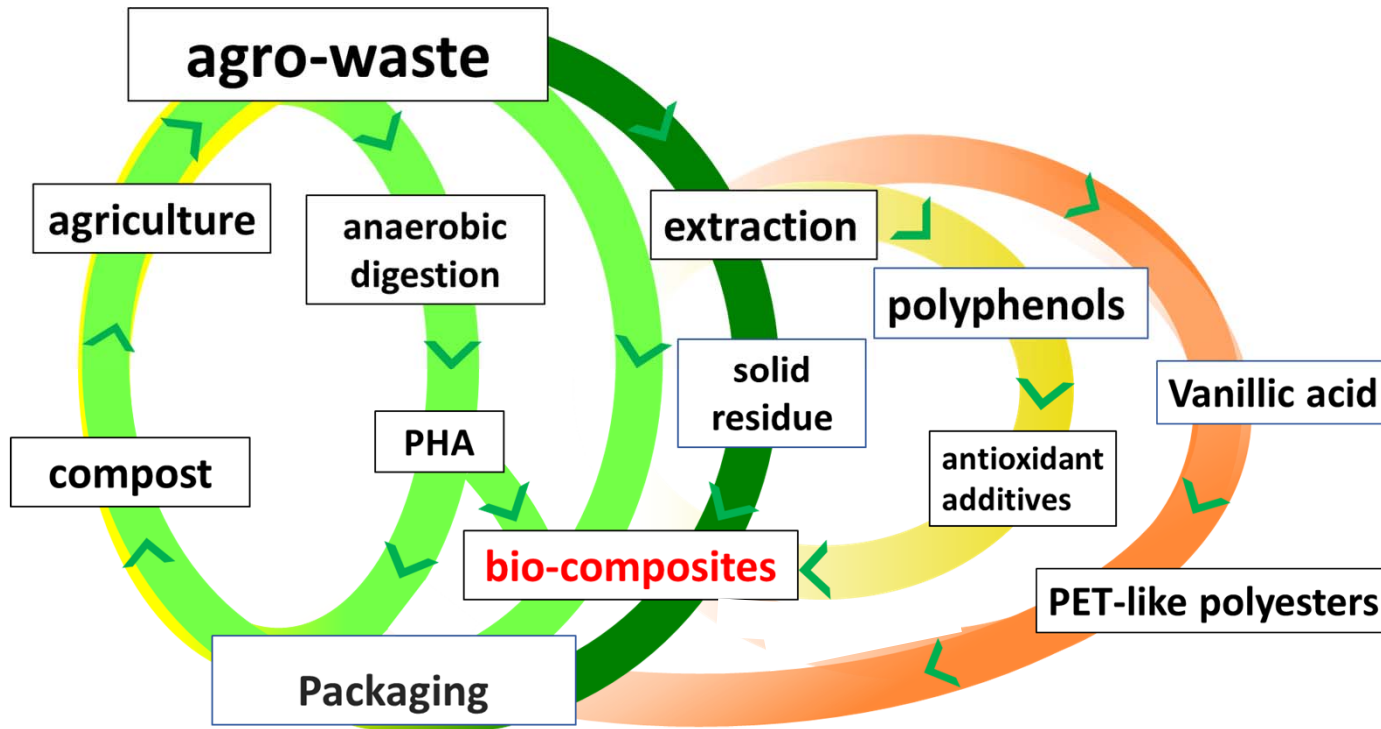
## Conclusions



- Winery waste can be fully exploited by a cascading approach
- A complex mixture of polyphenols can be extracted and used as antioxidant/antimicrobial additives for polymer formulation
- Specific molecules, such as vanillic acid can be identified and possibly extracted; new polymerization reactions allow one to obtain new families of bio-based polyesters
- New bio-composites based on PHBV can be prepared by melt compounding using the residues of the extractions or directly the lignocellulosic parts of the agro-waste
- The presence of a relatively high percentage of fillers does not impact on the thermal and mechanical properties of the matrix, whose price can be thus reduced



# Conclusions



An example of the application of the principles of the circular economy has been successfully developed and can be extended to other agro-wastes or agro-industry wastes.



ALMA MATER STUDIORUM  
UNIVERSITÀ DI BOLOGNA

**Annamaria Celli**

Department of Civil, Chemical, Environmental, and Materials Engineering

[annamaria.celli@unibo.it](mailto:annamaria.celli@unibo.it)

[www.unibo.it](http://www.unibo.it)