From wine pomace and potato wastes to novel PHA-based bio-composites: examples of sustainable routes for full valorisation of the agro-wastes

ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

M. Vannini,[1] , P. Marchese[1], L. Sisti[1], A. Celli[1], M. Ferri[1,2], S. Monari[2], A. Tassoni[2], M. Ehrnell[3], L. Eliasson[3], E. Xanthakis[3], T. Mu[4], H. Sun[4]

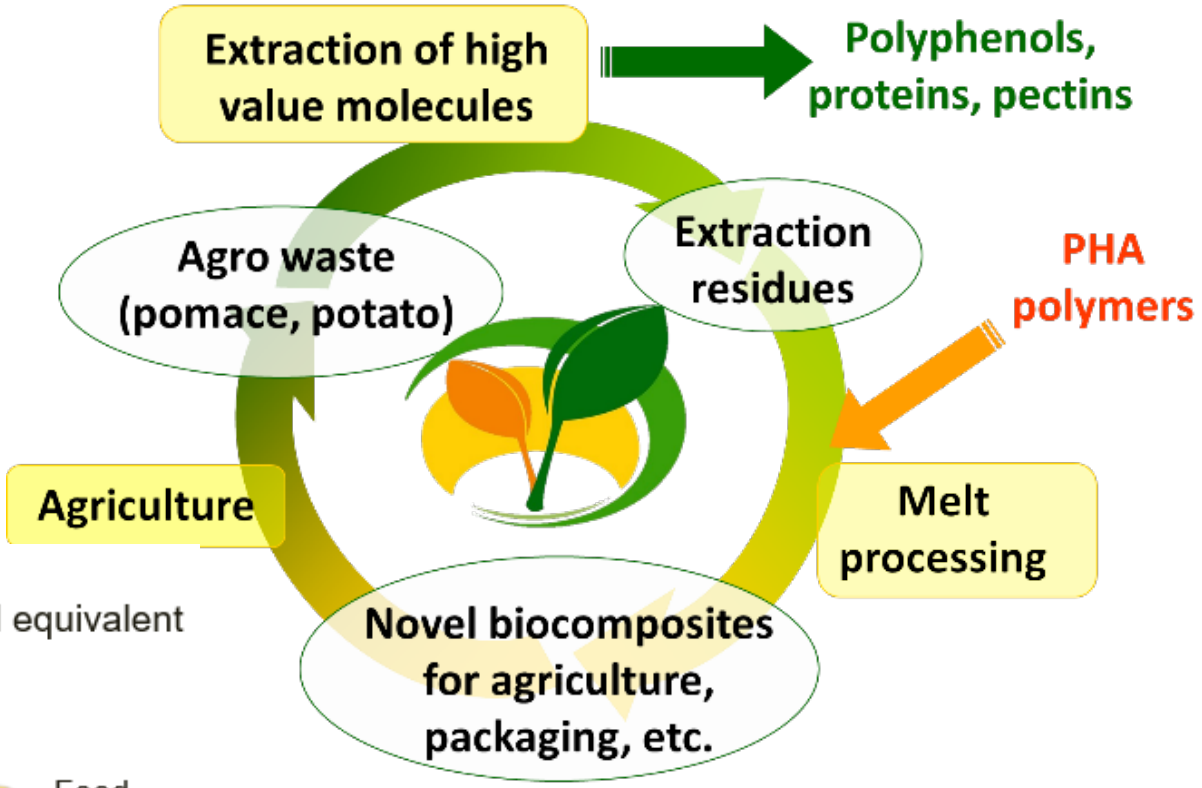
[1] Department of Civil, Chemical, Environmental, and Materials Engineering, University of Bologna, Italy; [2]Department of Biological, Geological, and Environmental Sciences, University of Bologna, Italy; [3]Agrifood & Bioscience Unit, RISE – Research Institutes of Sweden, Sweden; [4]Laboratory of Food Chemistry and Nutrition Science, Institute of Food Science and Technology, Chinese Academy of Agricultural Sciences; Key Laboratory of Agro-Products Processing, Ministry of Agriculture and Rural Affairs, China

	Now the situation	NoAW's ambitions
Available	86	25
Energy	450	420
	16	30
Fertlizer	3	6
	3	
Plastics	79	60
	1	20
Chemicals	79	60
	1	20

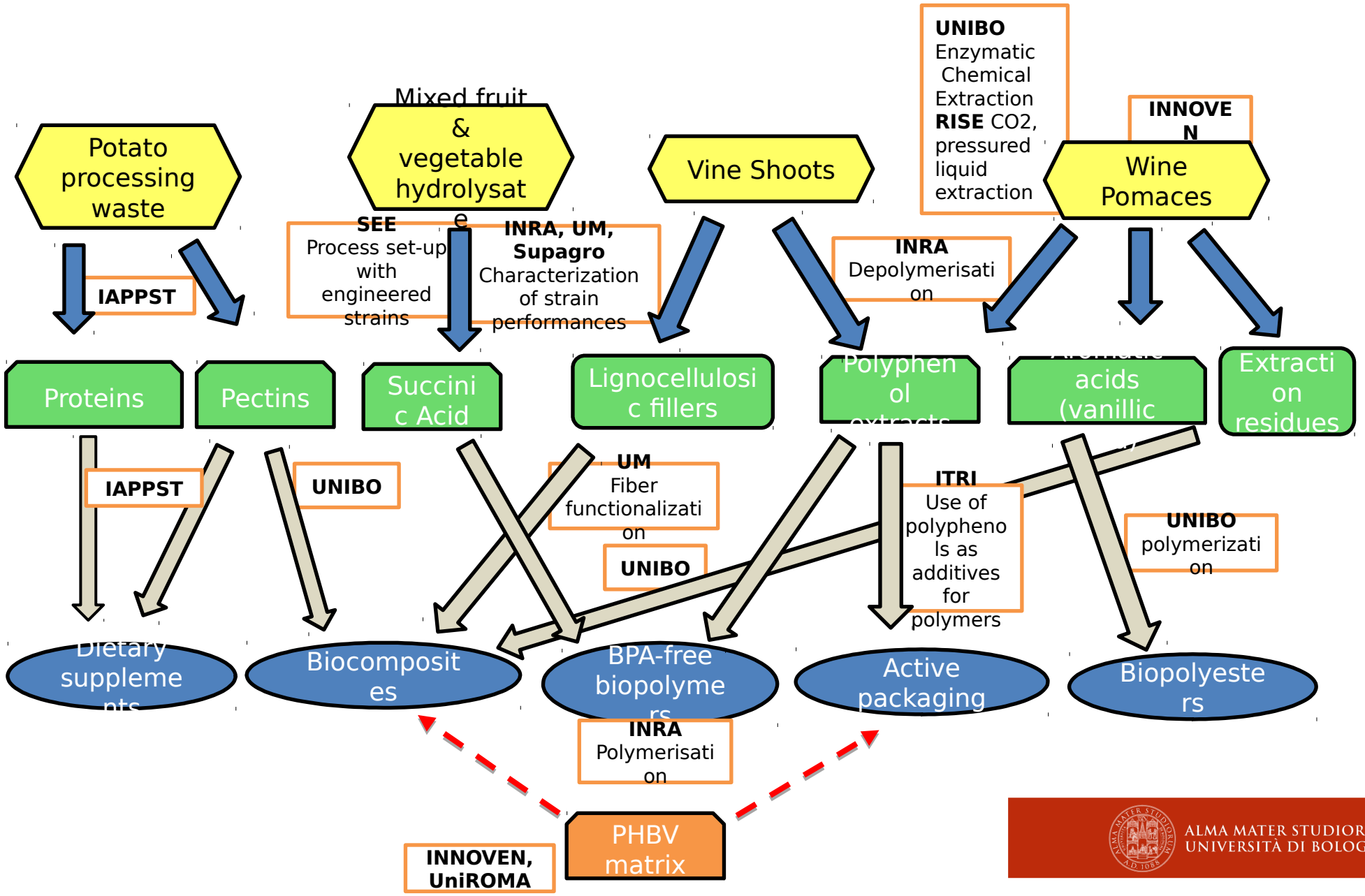
MTOE: million tons oil equivalent

Oil Vs. Food

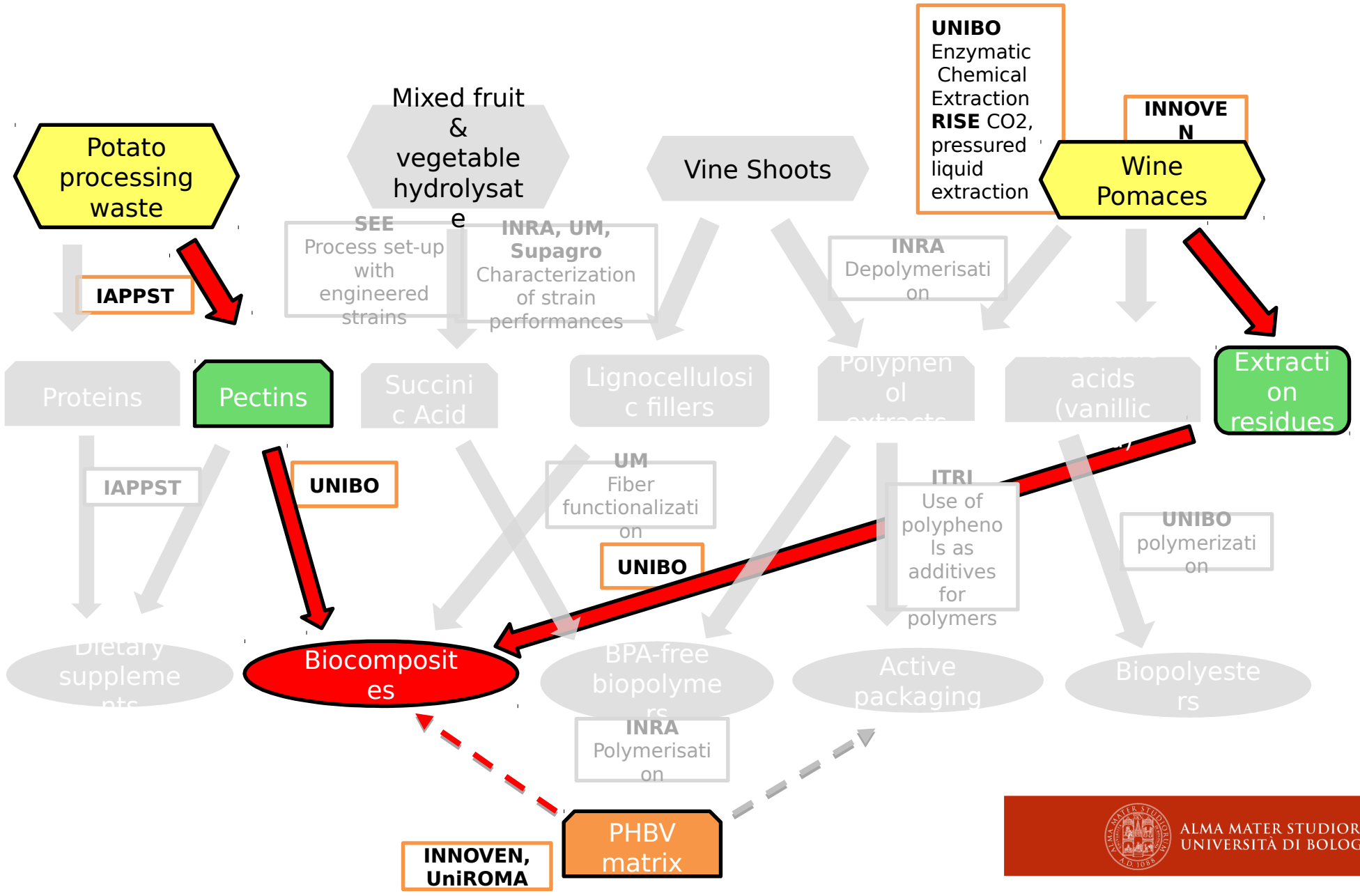
Vs. Agro-waste



WP4 Task 1


Potato processing waste
Mixed fruit & vegetable hydrolysate
Vine Shoots
Wine Pomaces
INNOVEN
UNIBO Enzymatic Chemical Extraction RISE CO2, pressured liquid extraction
IAPPST
SEE Process set-up with engineered strains
INRA, UM, Supagro Characterization of strain performances
INRA Depolymerisation
Proteins
Pectins
Succinic Acid
Lignocellulosic fillers
Polyphenol extracts
acids (vanillic
Extraction residues
IAPPST
UNIBO
UM Fiber functionalization
UNIBO
ITRI Use of polyphenols as additives for polymers
UNIBO polymerization
Dietary supplements
Biocomposites
BPA-free biopolymers
Active packaging
Biopolyesters
INRA Polymerisation
PHBV matrix
INNOVEN, UniROMA
ALMA MATER STUDIORUM UNIVERSITÀ DI BOLOGNA

WP4 Task 1



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

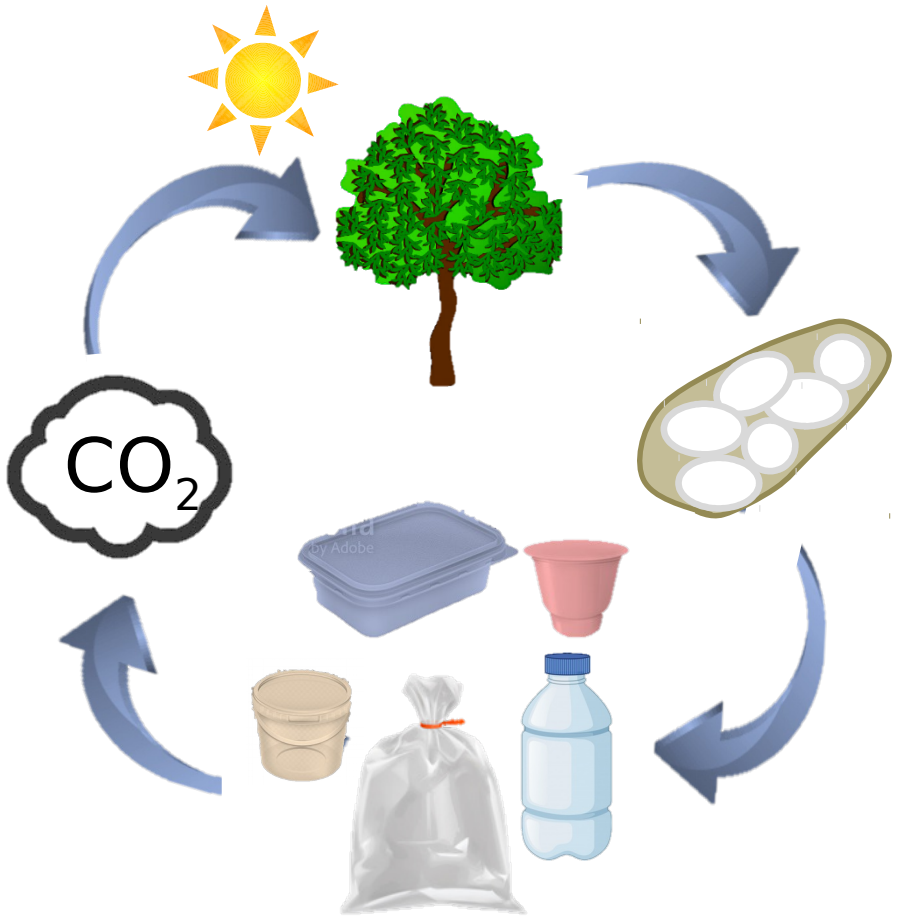
Choice of polymeric matrix

Poly(hydroxyalkanoate)s **(PHA)s** are a family of microbial biopolymers.

They have excellent biocompatible and biodegradable properties

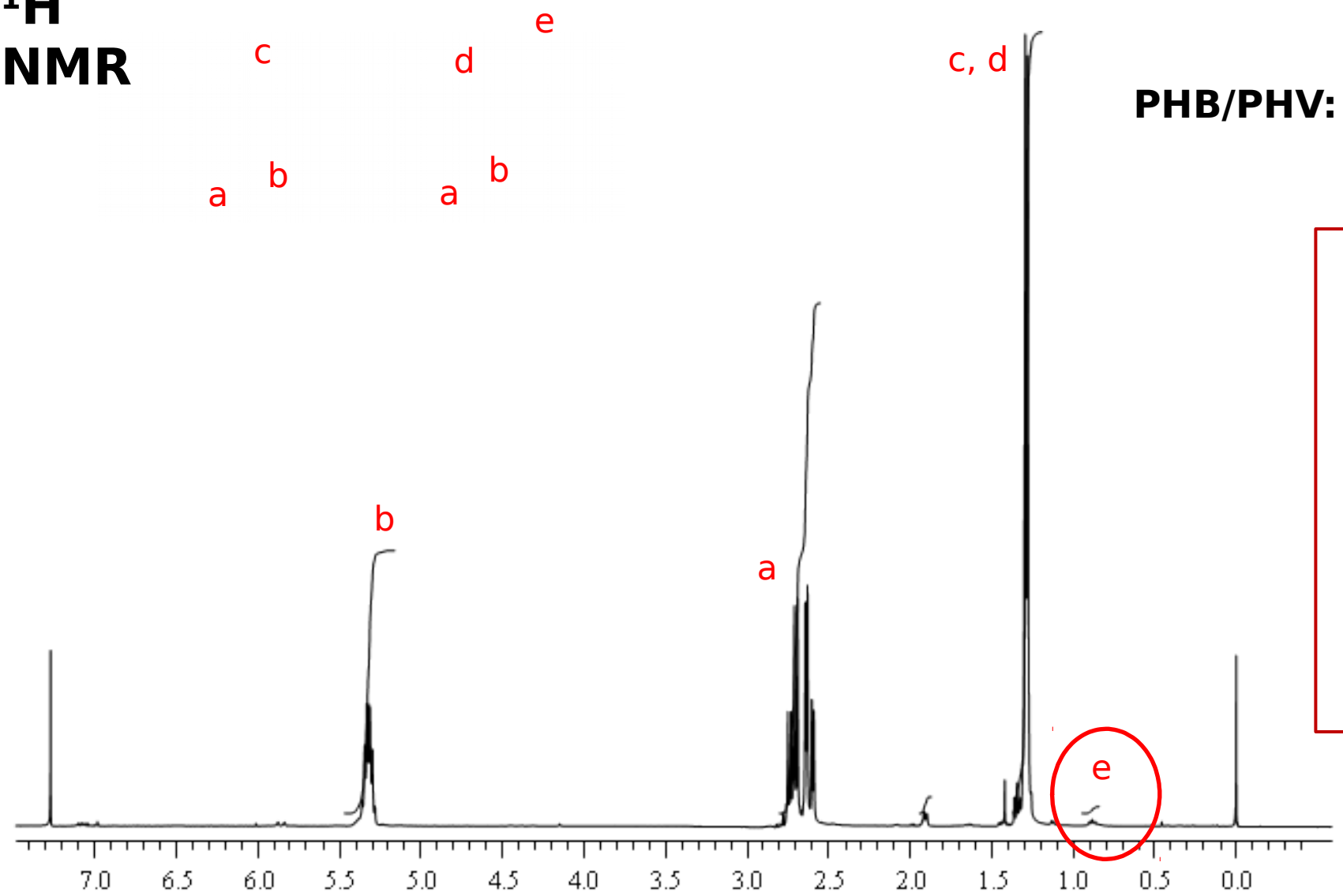
The PHAs are particularly **expensive**

and lack **mechanical properties**.



PHBV: poly(3-HydroxyButirate-*co*-Valerate)

^{1}H NMR



PHB/PHV: 98/2 (mol/mol)

PHBV thermal properties:

T_{onset}: 288°C

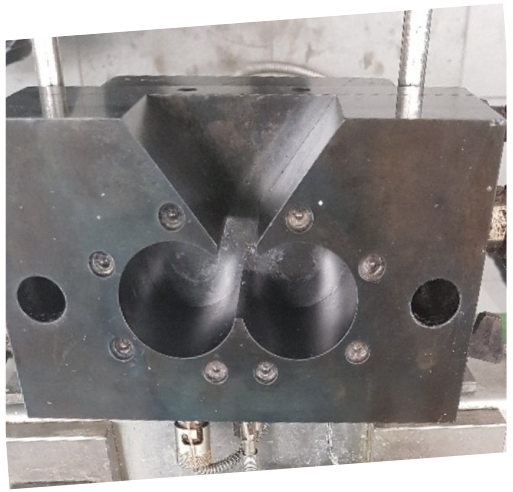
T_D: 302°C

T_m: 172°C, ΔH_m: 78 J/g

T_c: 114°C, ΔH_c: 73 J/g

Composites preparation

The composites are prepared by melt mixing in a **Brabender microcompounder**.



load: 45−50 g
screw speed: 50 rpm
temperature: 200 °C
mixing time: 5 min

For each fiber residue, different blends were prepared containing **5, 10** or **20 wt%** of residue.

Extractions of polyphenols from wine pomaces

INNOVEN
INNOVATION FOR THE ENVIRONMENT

Merlot

Garganega

Two methods:

Solvent-based extractions

Best conditions: Acetone/Water 75/25 (vol/vol)

Pressurized liquid extractions (only on red pomaces)

RI. SE

Best conditions: Ethanol/Water 50/5 (vol/vol)

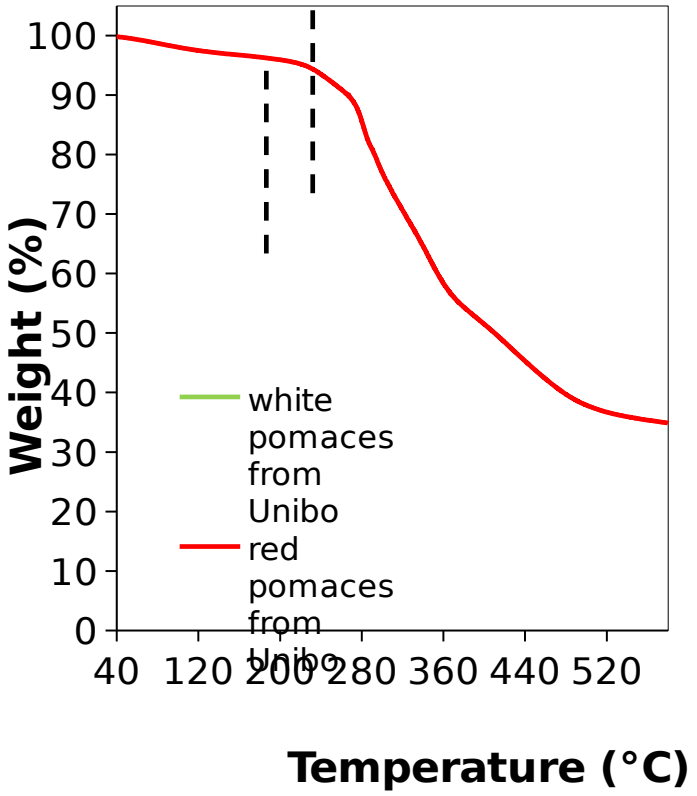
ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

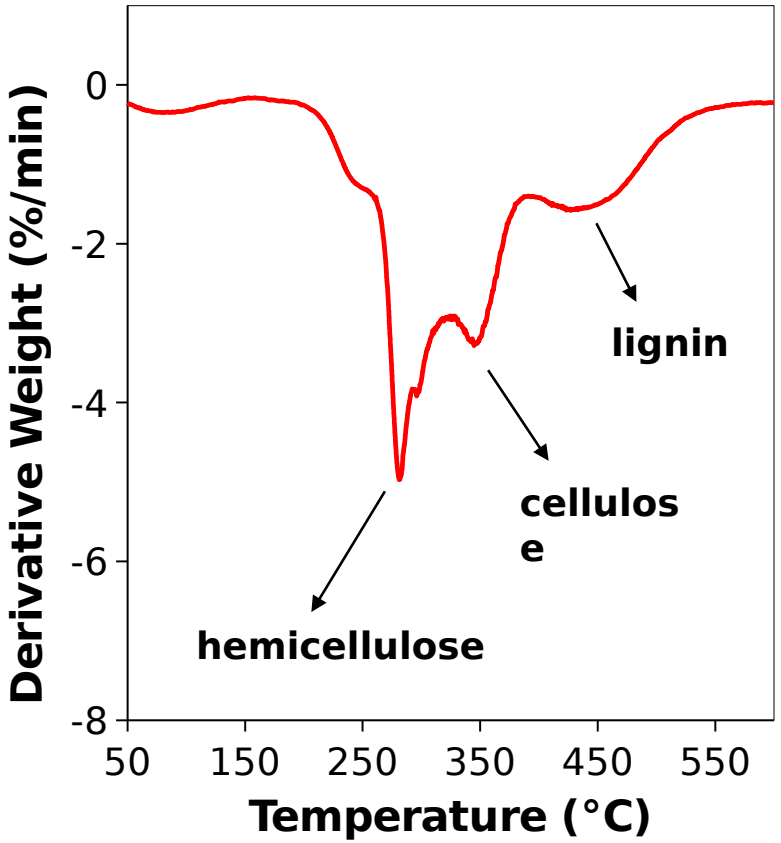
Characterization of chemically extracted resi (UNIBO)

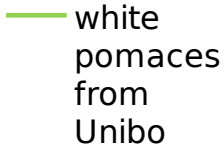
Gargane ga (WHITE) residue

Merlot (RED) residue

Thermogravimetric analyses

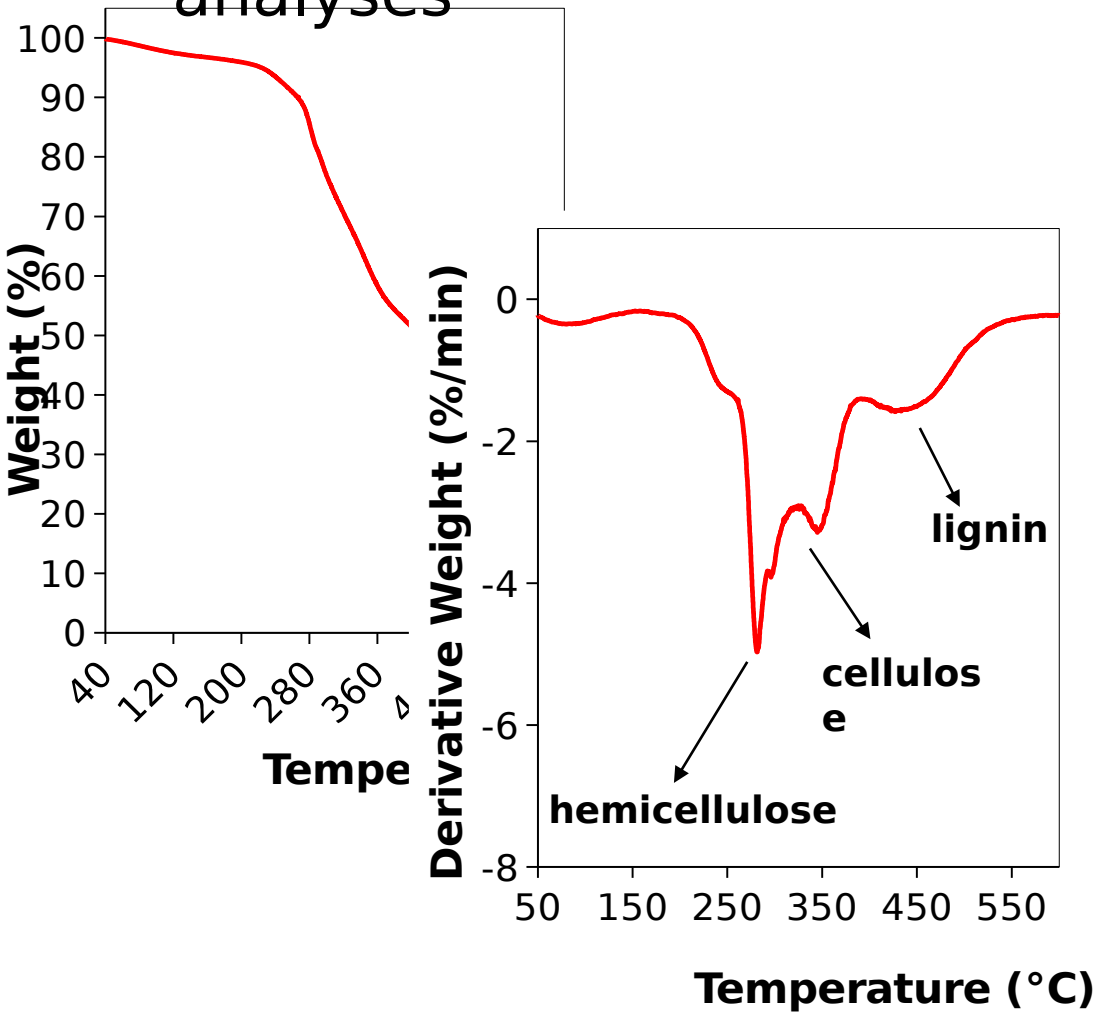




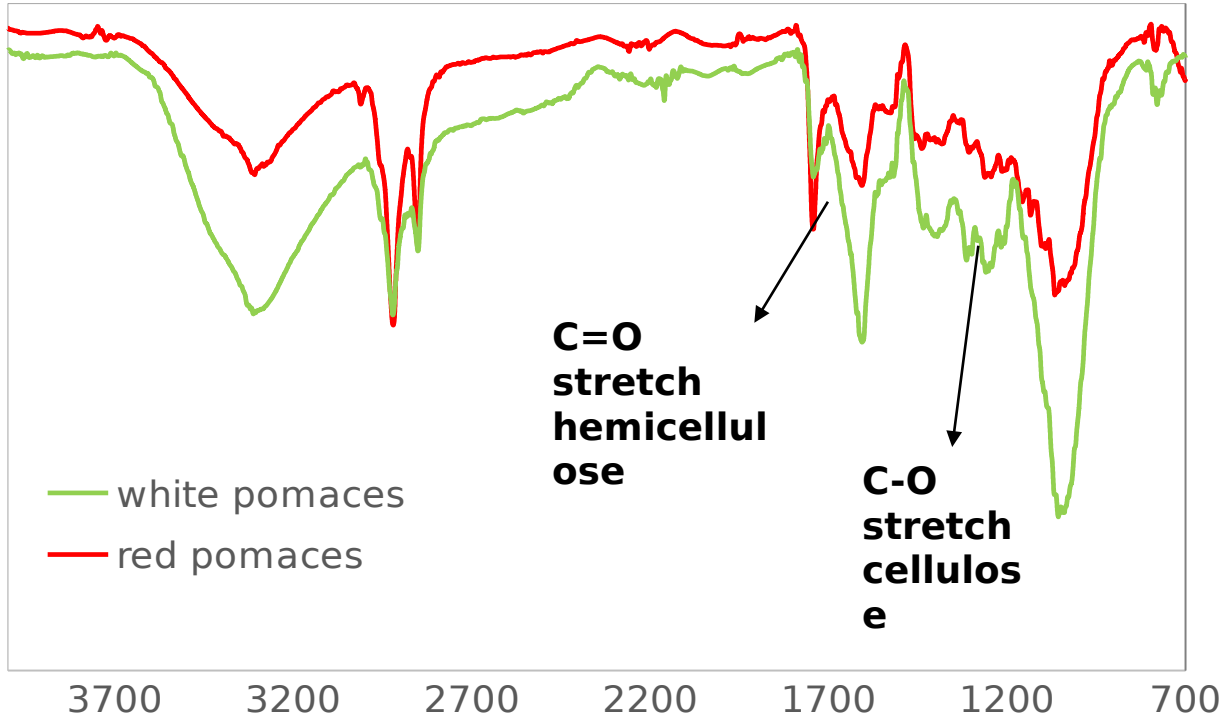


Characterization of chemically extracted residue

Thermogravimetric analyses



FT-IR spectra

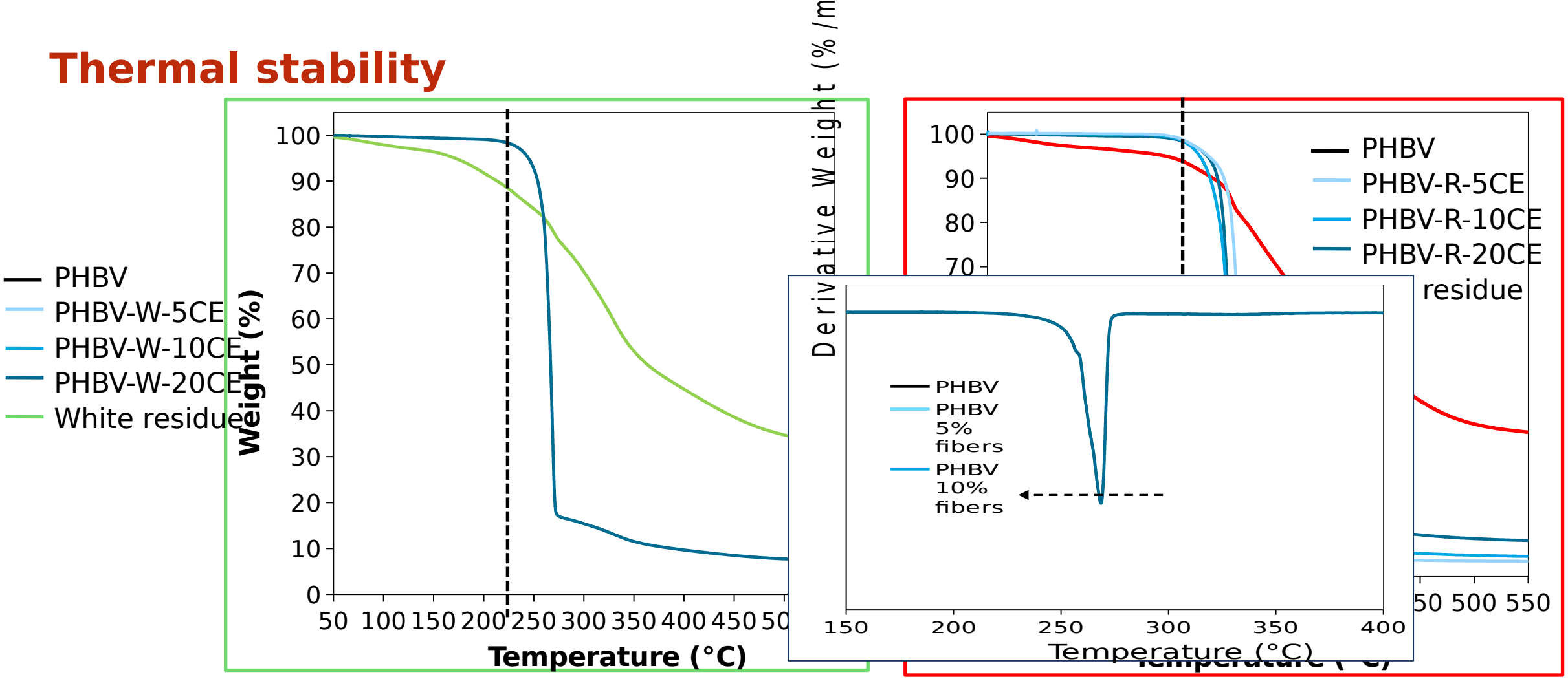


Bio-composites with residue from solvent extracted red and white pomaces

Sample code	1° heating scan		cooling scan		2° heating scan	
	T_m (°C) [b]	ΔH_m (J/g) [b]	T_c (°C) [c]	ΔH_c (J/g) [c]	T_m (°C) [d]	ΔH_m (J/g) [d]
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

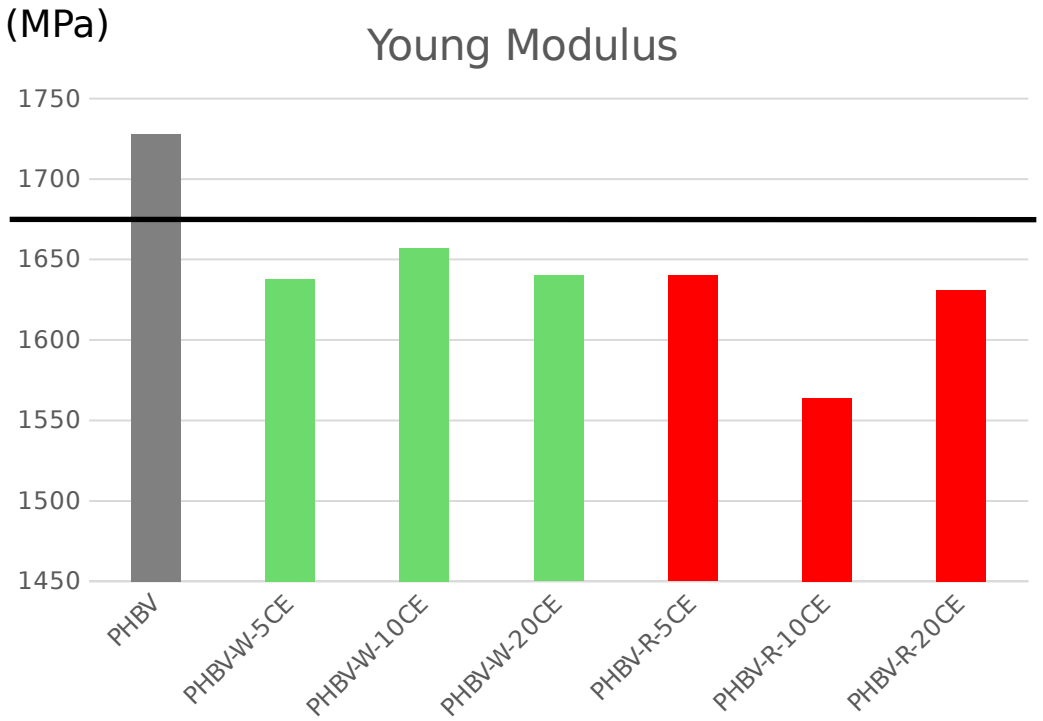
First scan, from 30 to 210°C at 20°C/min; 1 min at 210°C; cooling scan, from 210°C to 0°C at 20°C/min; 1 min at 0°C; second scan, from 0 to 210°C at 20°C/min.

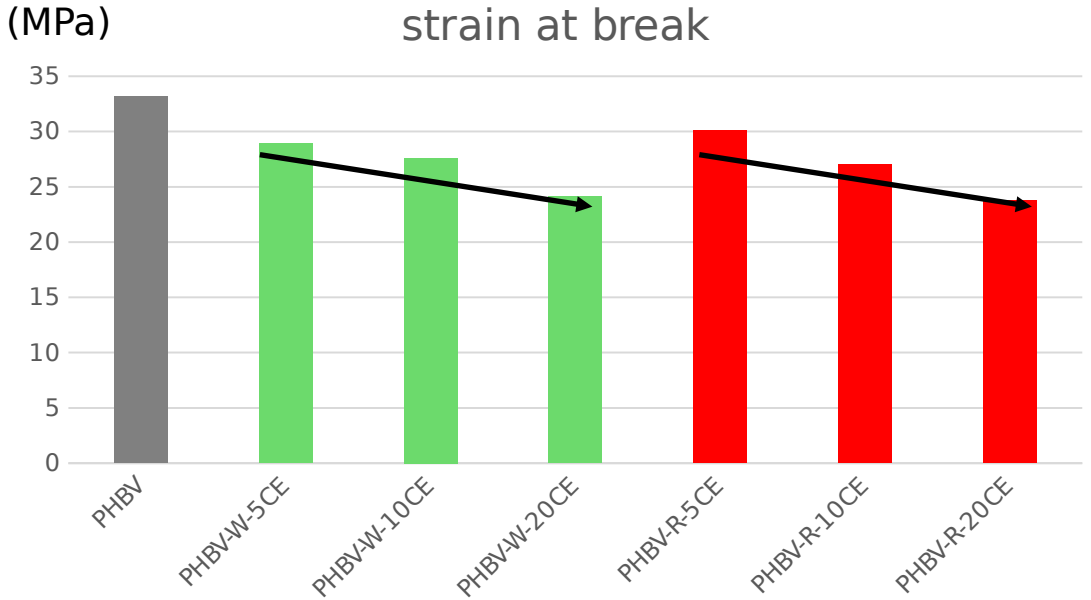
Thermal stability

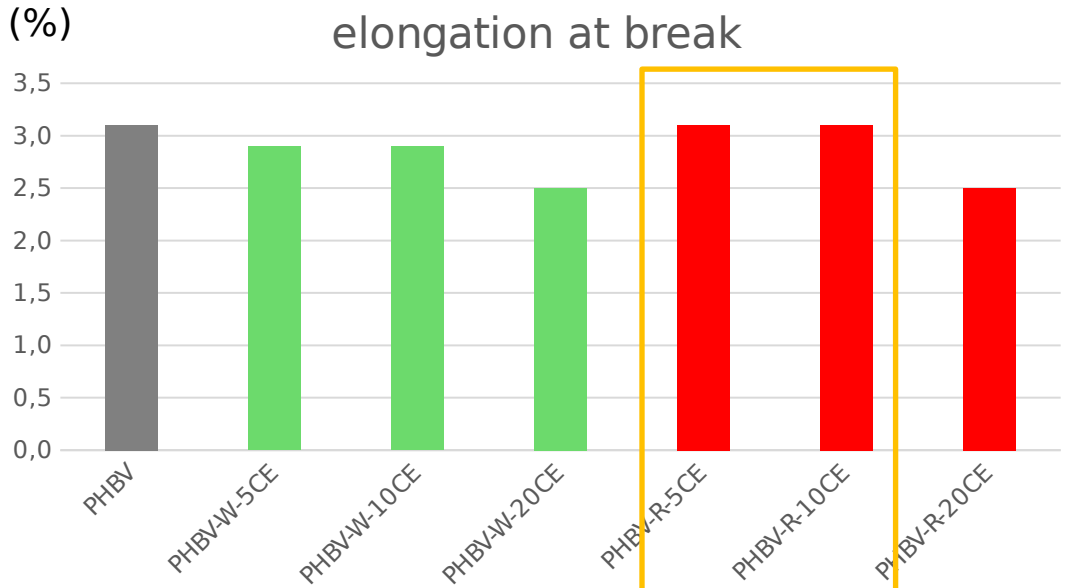


All the composites are stable over 230°C.
The thermal stability slightly decreases with the filler content.

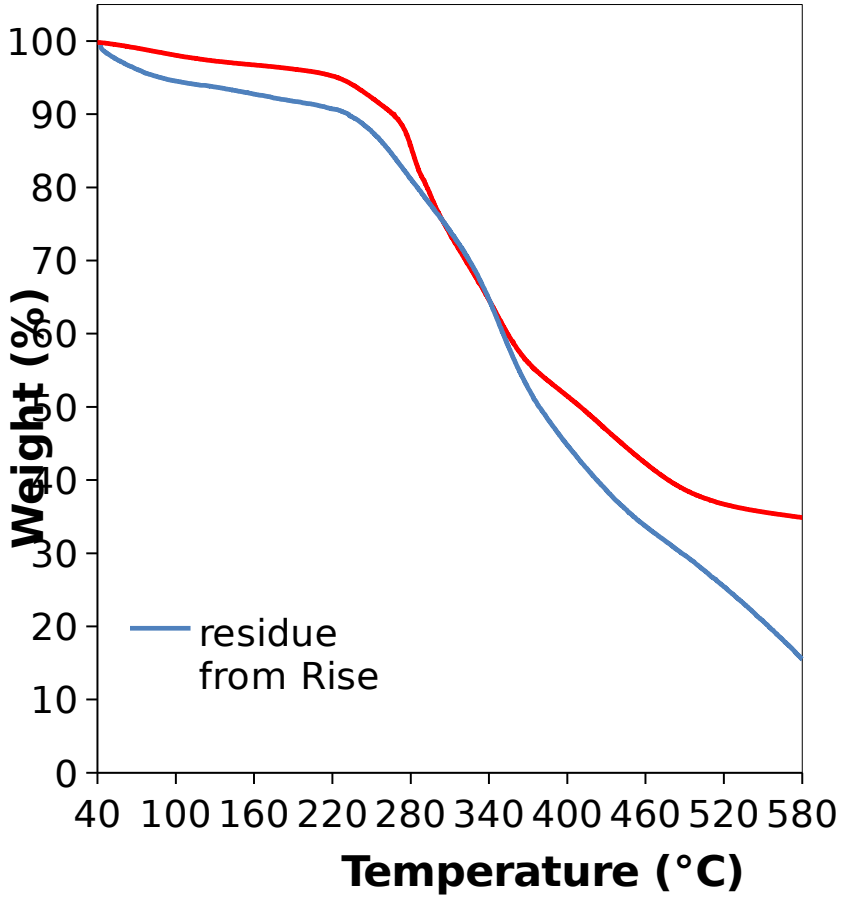
Tensile tests

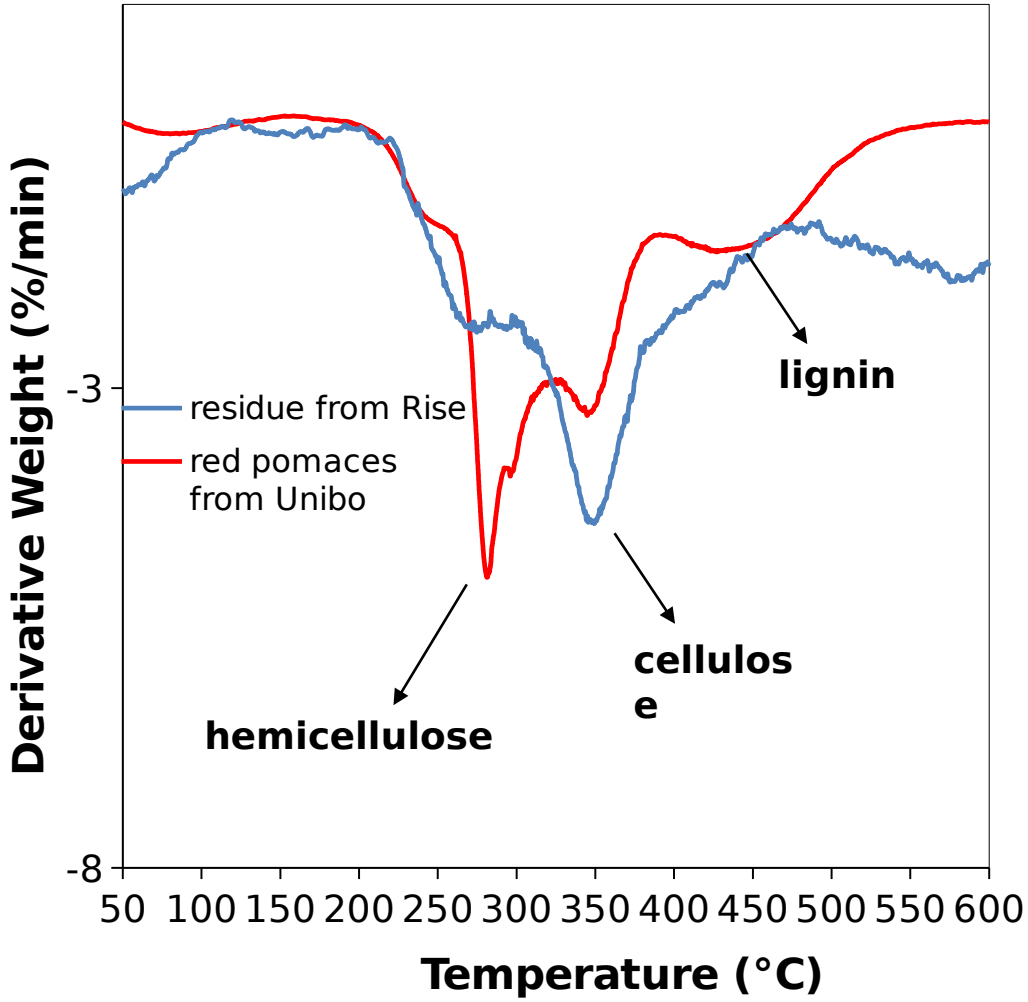






Characterization of pressurized extracted residue-comparison between the methods





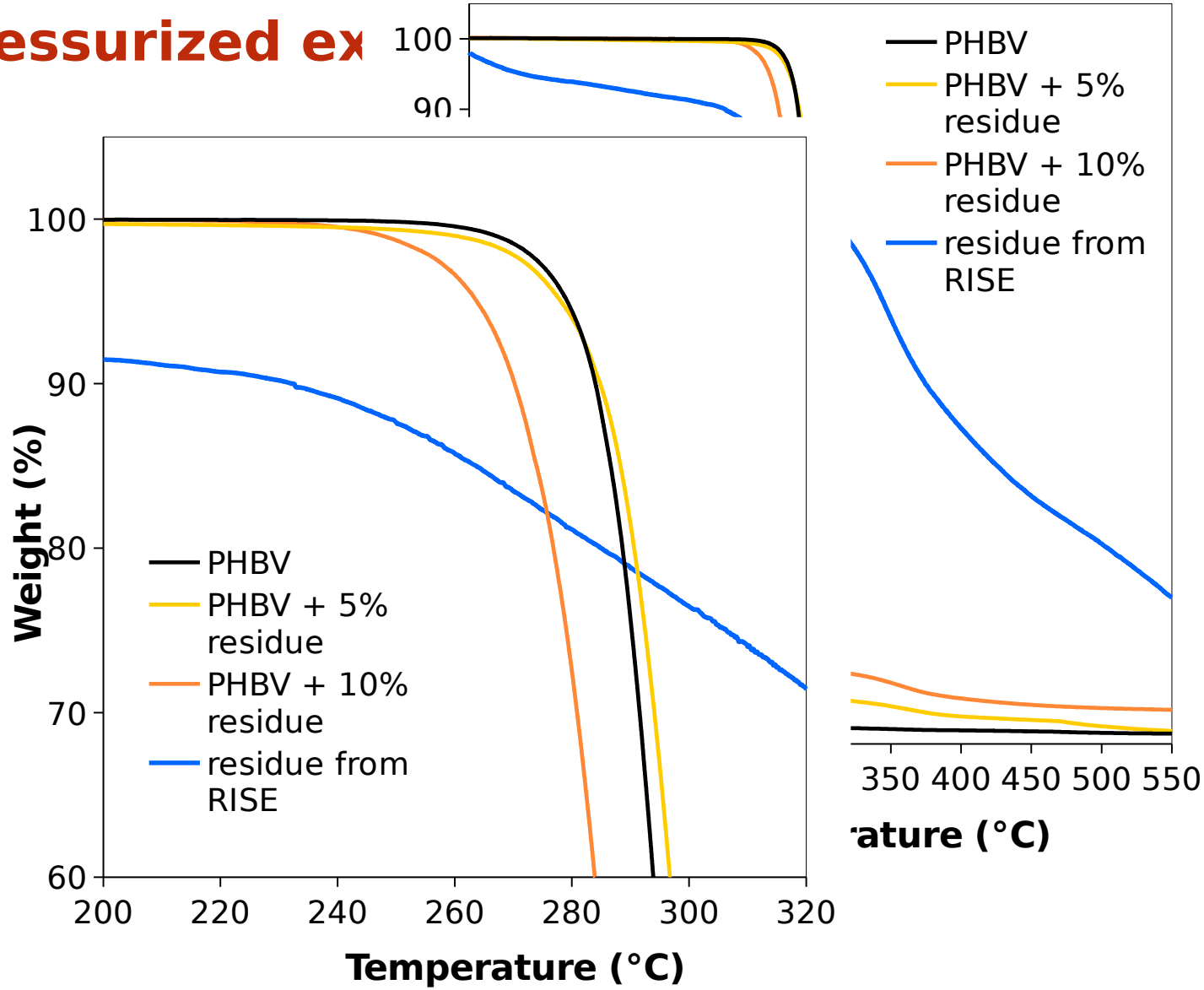
Bio-composites with red-pressurized ex

Thermal Properties

Sample code	1° heating scan T_m (°C) [b]	ΔH_m (J/g) [b]	cooling scan T_c (°C) [c]	ΔH_c (J/g) [c]
PHBV	172	78	114	73
PHBV-5PE	171	77	112	71
PHBV-10PE	171	73	110	66

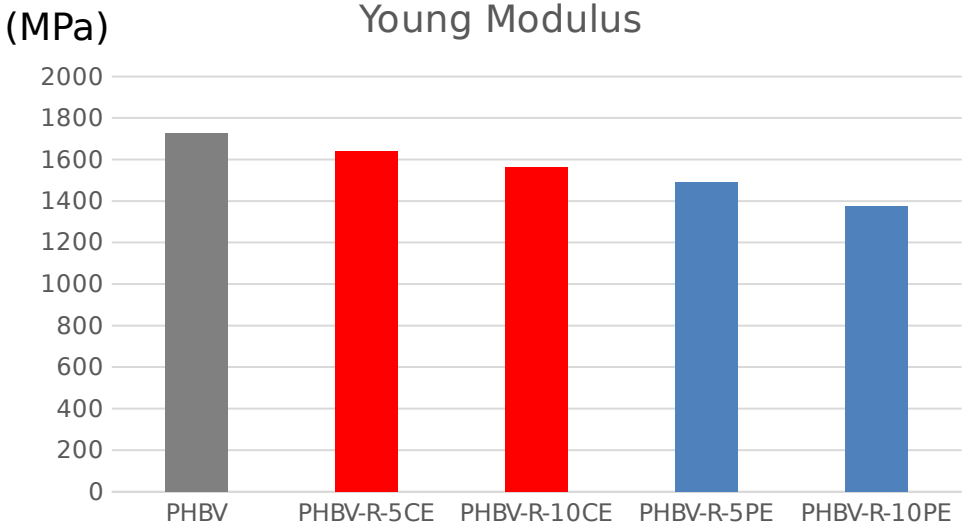
First scan, from 30 to 210°C at 20°C/min; 1 min at 210°C; 210°C to 0°C at 20°C/min; 1 min at 0°C; second scan, fr 20°C/min.

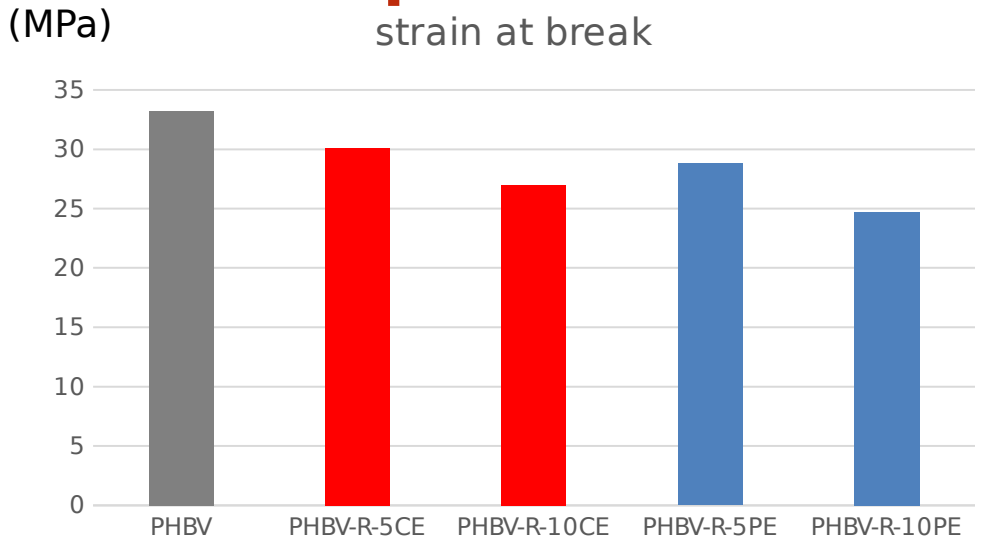
The thermal stability of PHBV and the composite containing 5 wt% of RISE extracts are comparable.

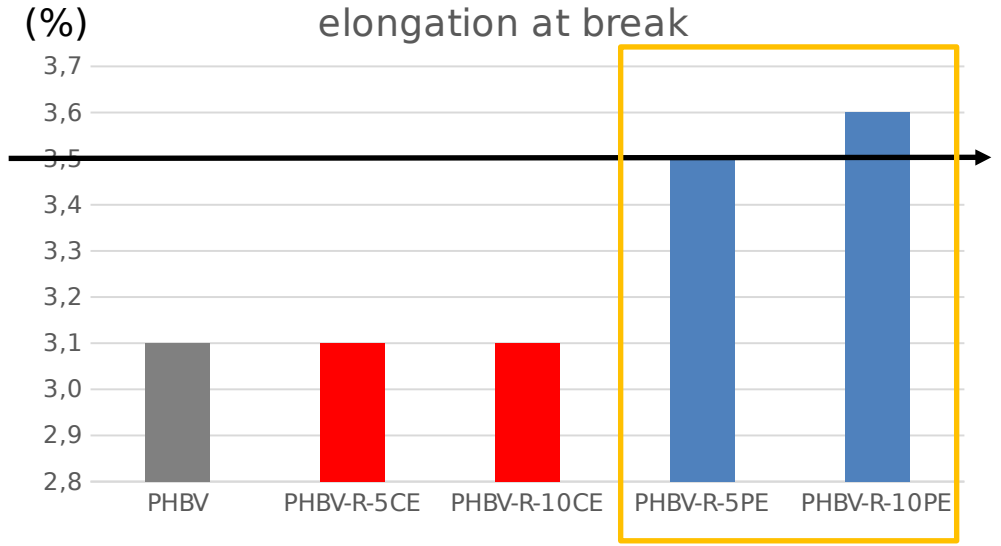


ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Tensile tests on bio-composites based on red pomaces residues

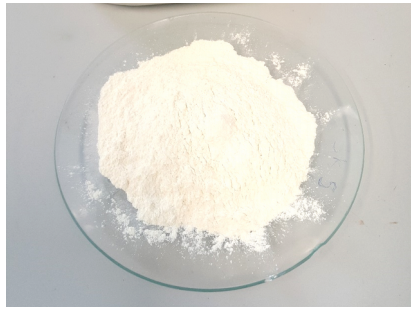




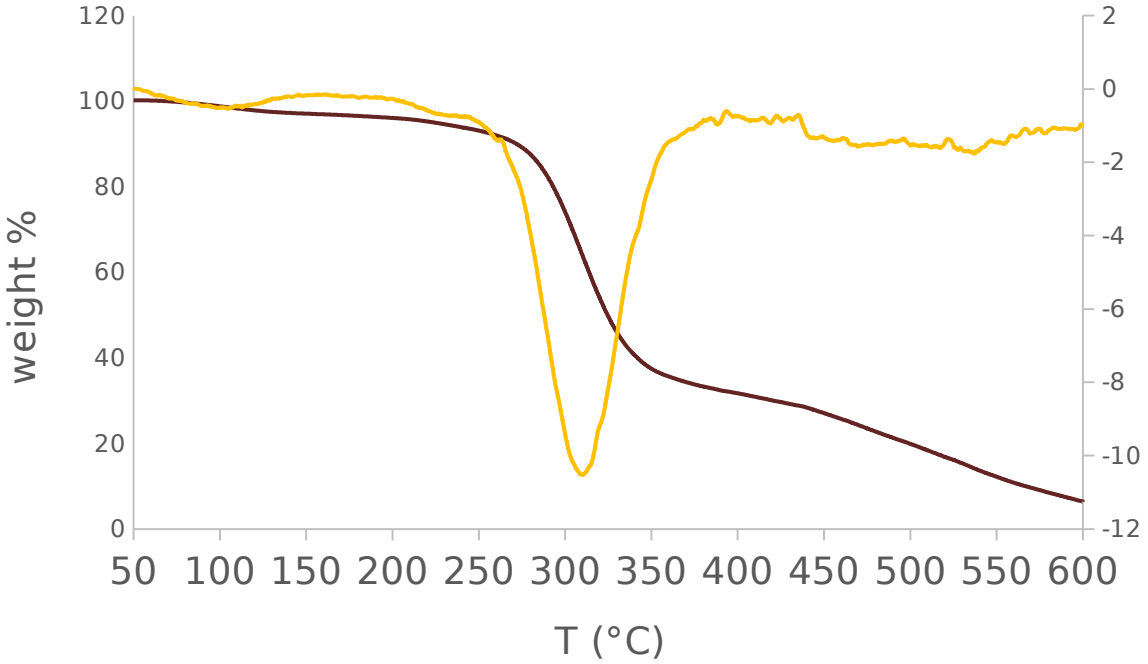


ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

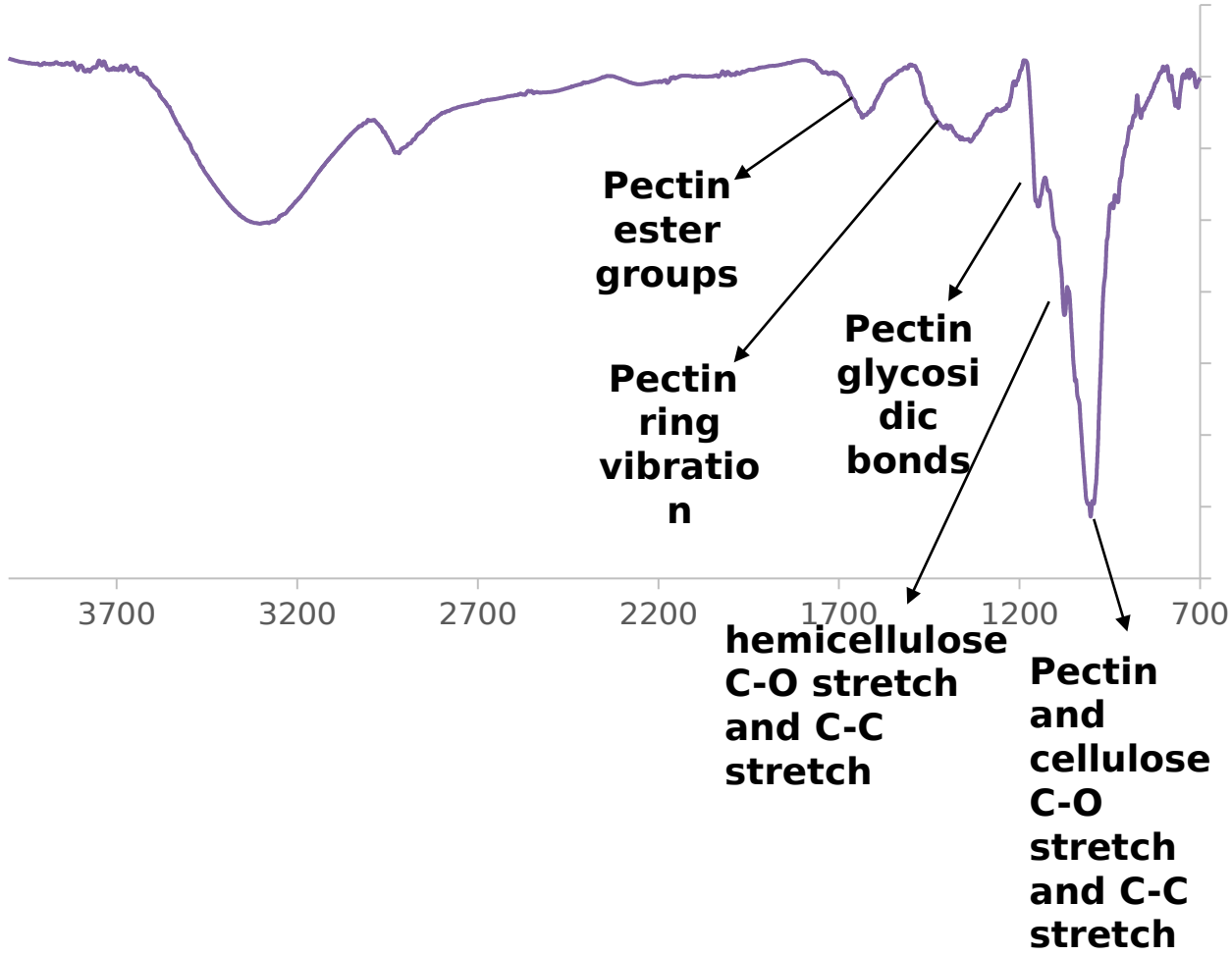
Characterization of potato’s residue



Thermogravimetric analysis



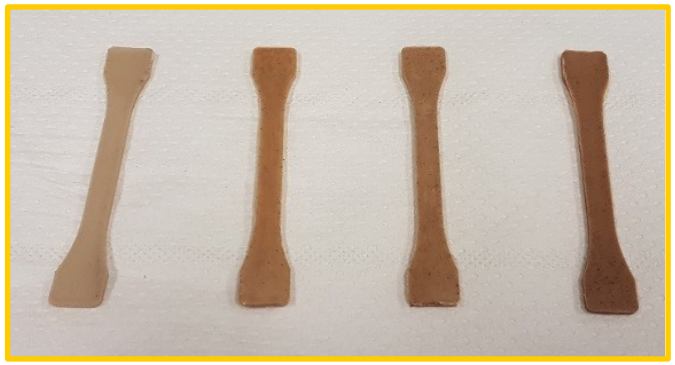
FT-IR spectrum



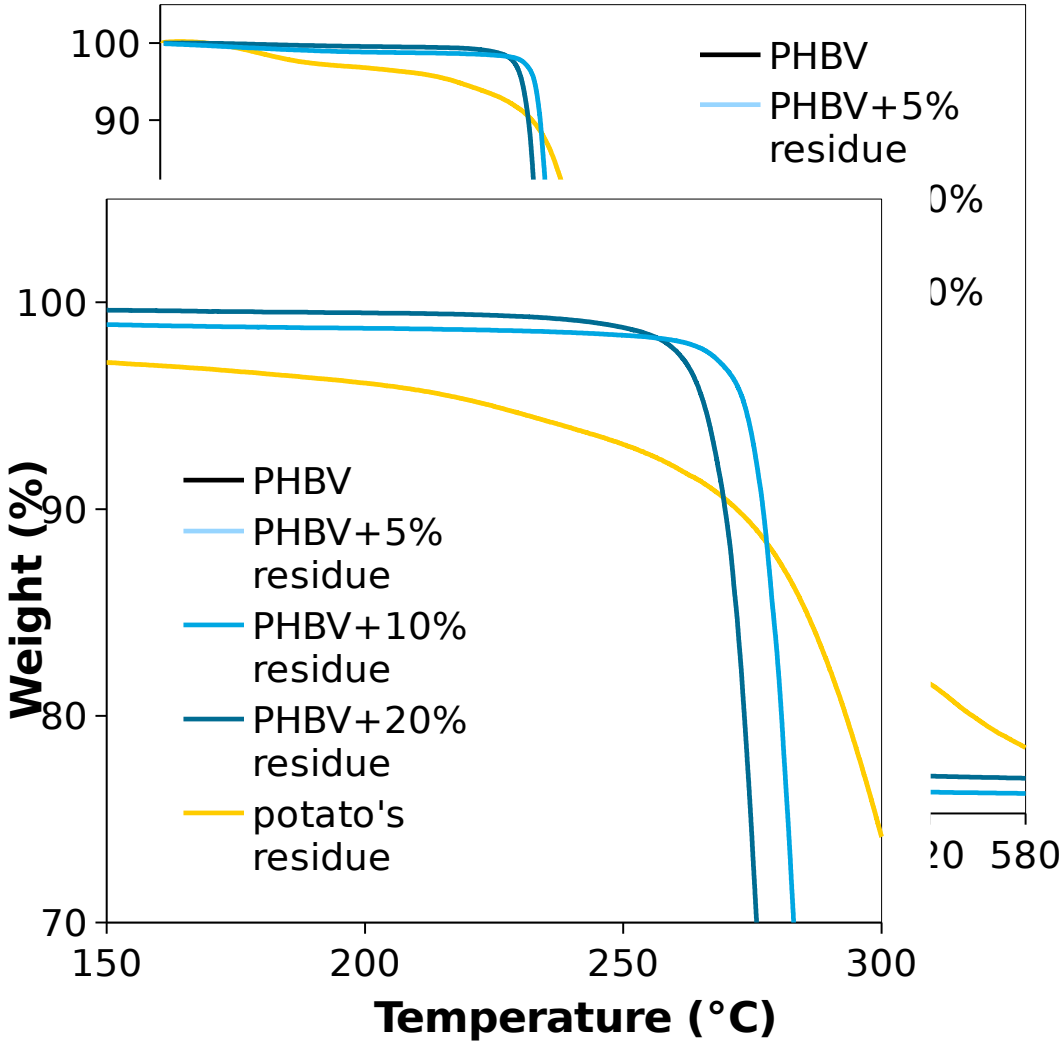
ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Bio-composites with potato's residue

Thermal properties

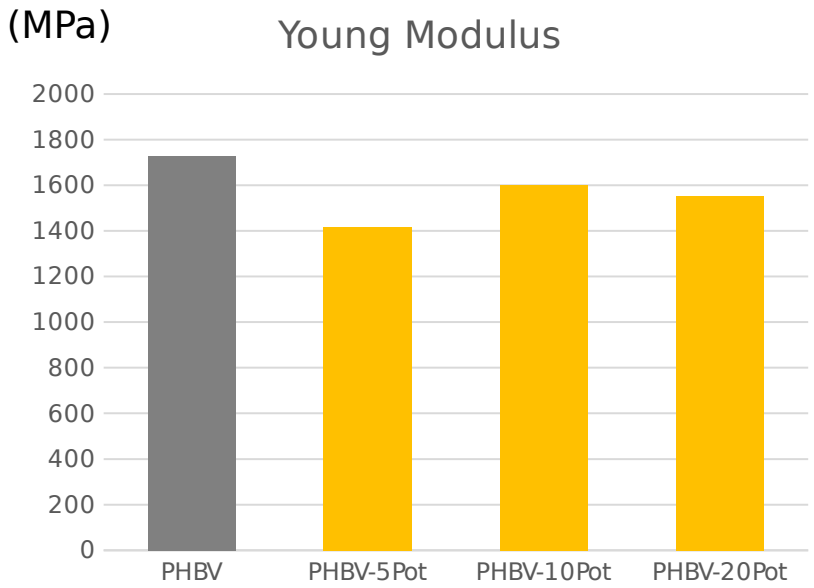


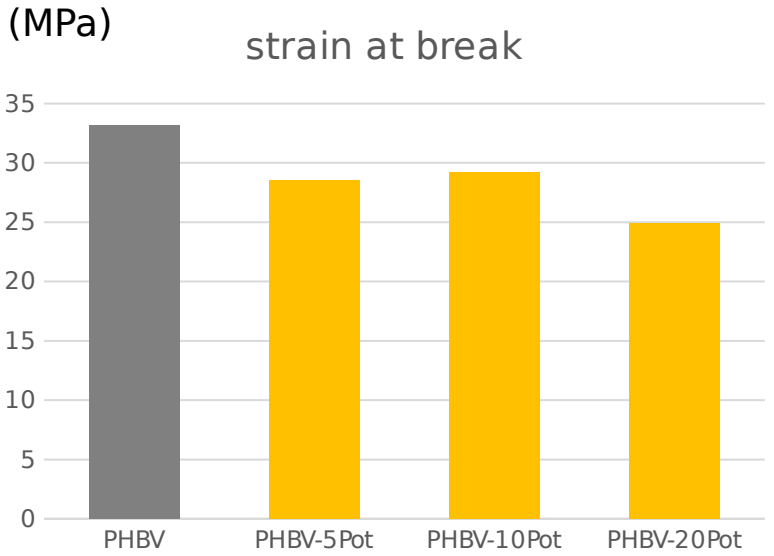
Sample code	1° heating scan T_m (°C) [b]	ΔH_m (J/g) [b]	cooling scan T_c (°C) [c]	ΔH_c (J/g) [c]	2° heating scan T_m (°C) [d]	ΔH_m (J/g) [d]
PHBV	172	78	114	73	168	82
PHBV-5Pot	170	75	114	71	169	81
PHBV-10Pot	172	73	114	66	169	76
PHBV-20Pot	171	63	113	59	169	68

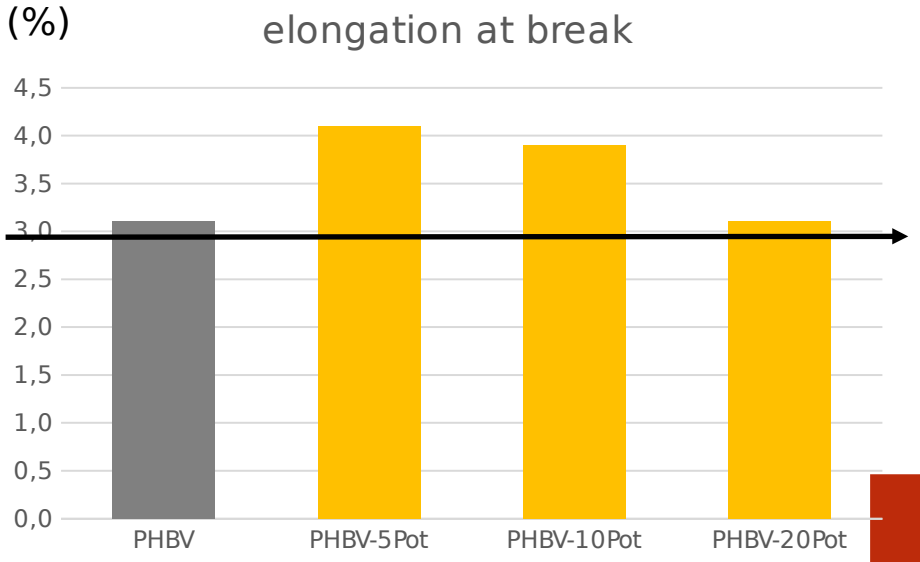


First scan, from 30 to 210°C at 20°C/min; 1 min at 210°C; cooling scan, from 210°C to 0°C at 20°C/min; 1 min at 0°C; second scan, from 0 to 210°C at 20°C/min.

Tensile tests on bio-composites based on potato residues

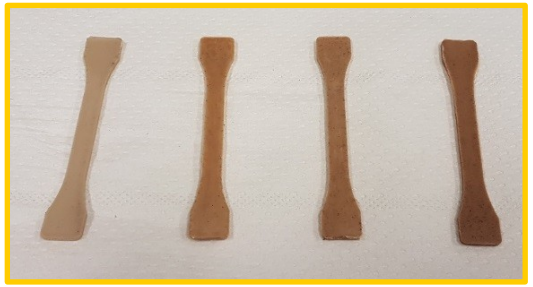






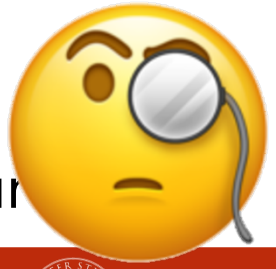
ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Conclusions

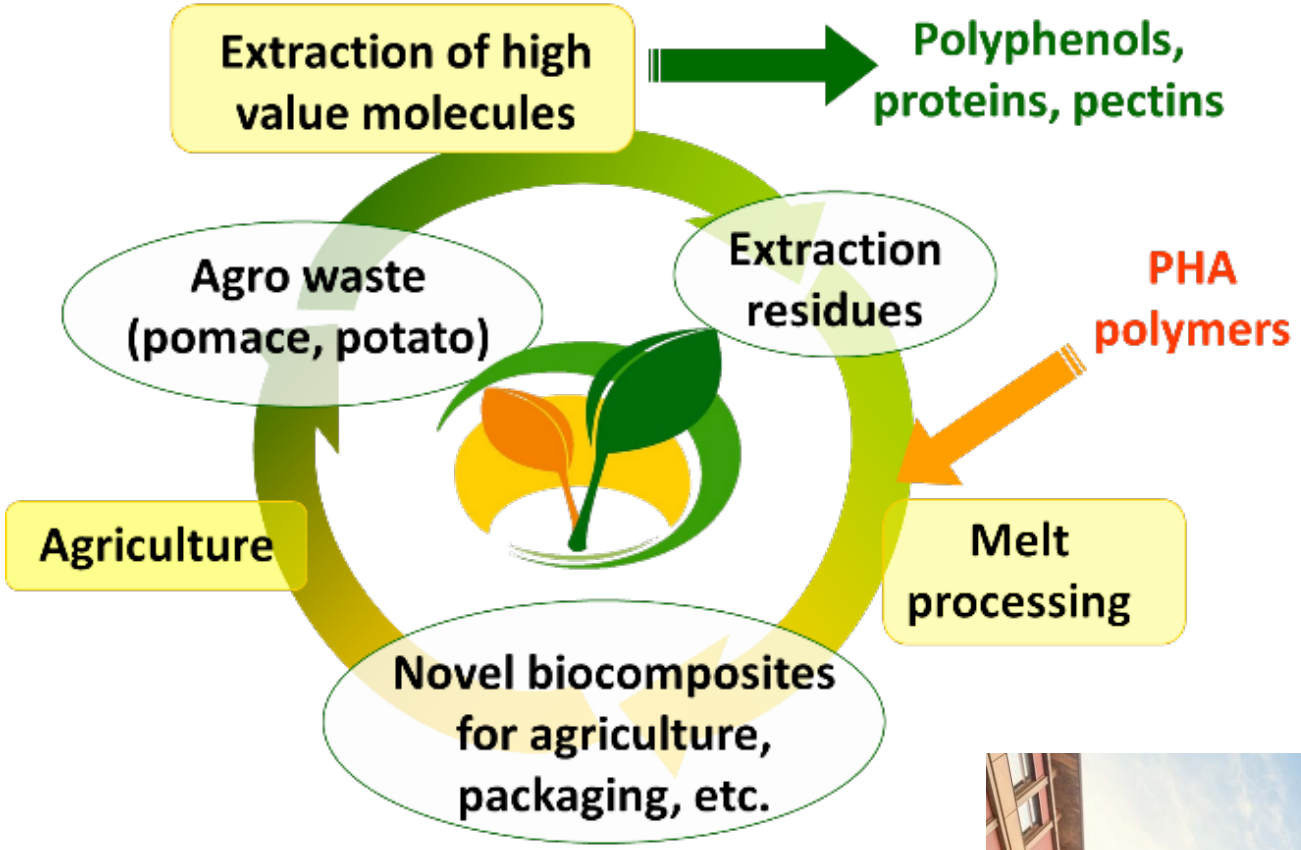


- New bio-composites based on PHBV have been prepared by compounding.
- The content of filler has been **5, 10** or **20** wt%.
- The filler is deriving from **potatoes** and **pomaces**. In particular, the filler is the residue after further valorization of wastes of potato and pomaces processing.
- The bio-composites are thermally stable and easily processable.
- The Young Modulus remains fairly constant whereas the strenghth and the elongation slightly decrease meanwhile the material cost decreases.

- In some cases, the elongation has been maintained (**red UNIBO pomaces**) or improved (**red RISE pomaces** and **potatoes**).
- The filler-matrix interface compatibility will be studied by SEM.



- The use of a compatibilizer will be evaluated and tested in the futur



***Bologna**: le 2 Torri and la fontana del Nettuno.*

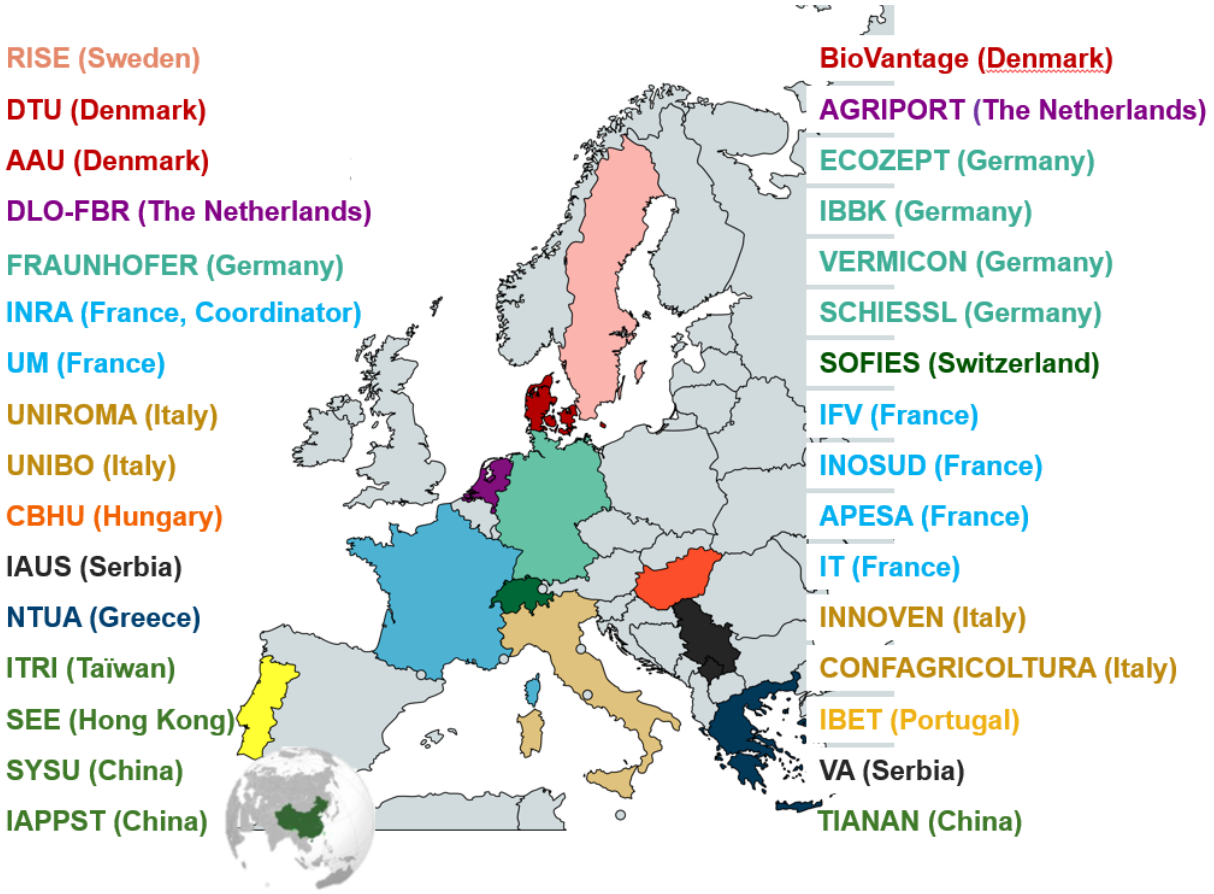
Thank you for your attention!

ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Micaela Vannini

Department of Civil, Chemical, Environmental, and Materials Engineering

micaela.vannini@unibo.it

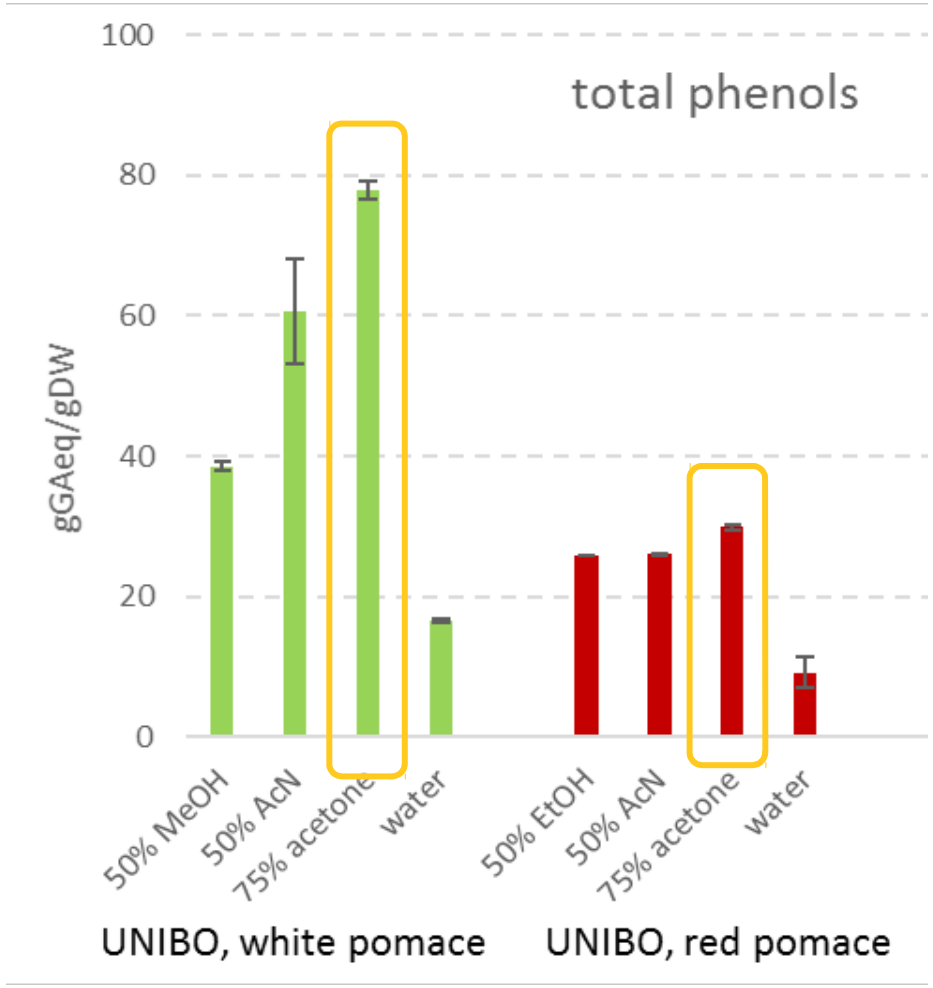


NoAW's partners:

NoAW is coordinated by **INRA (France)** and the consortium involves 32 partners from universities, public research organizations and other institutions from a dozen countries (**16 academics + 16 privates or associations**).

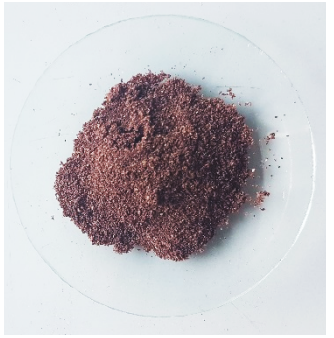
ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

1) Solvent-based extraction



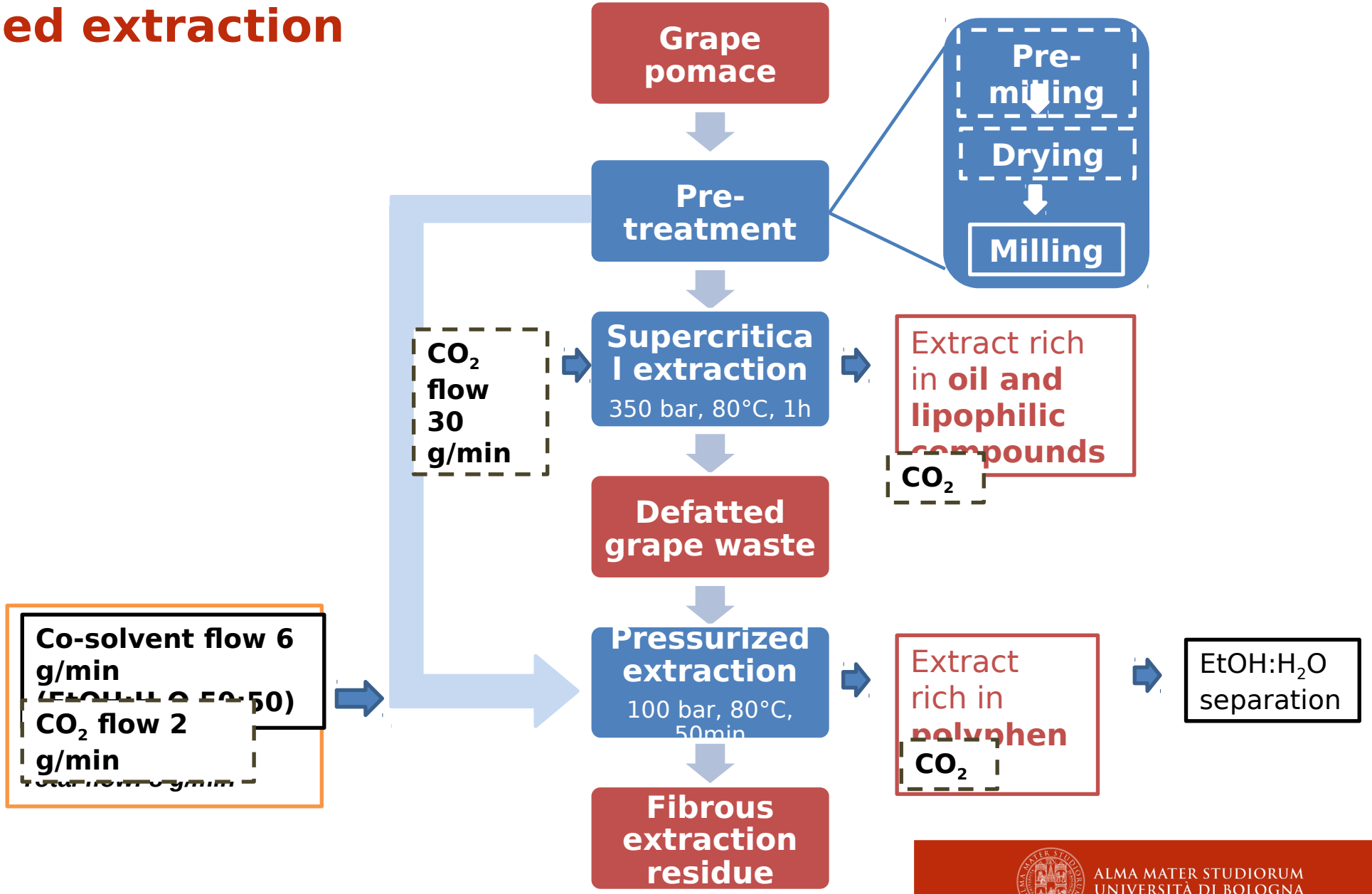
Optimised chemical extraction with 75% (v/v) acetone was selected as the best process for the recovery of bioactive molecules from both red and white grape pomace.

Gargane ga (WHITE) residue



Merlot (RED) residue

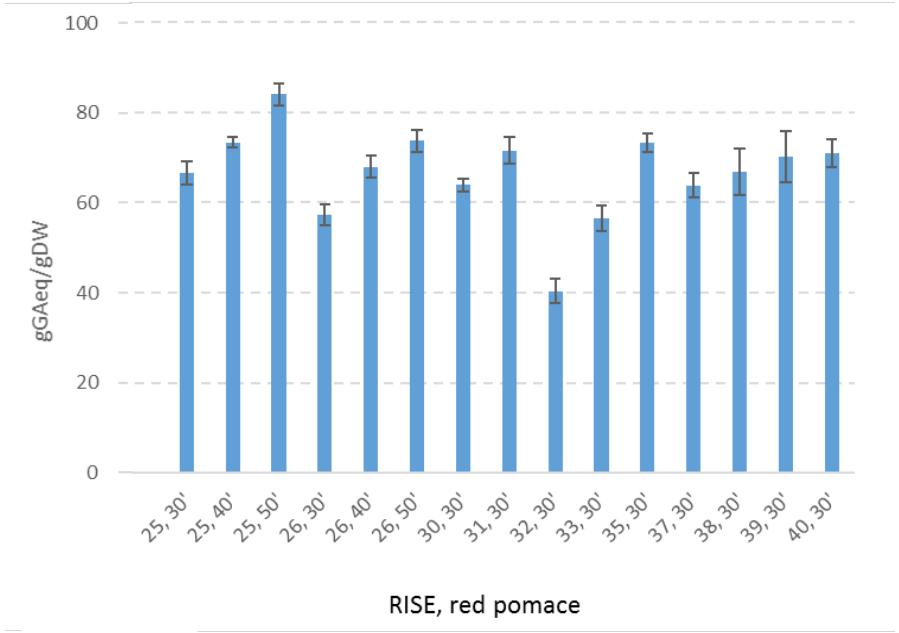
2) Pressurized extraction



RISE

ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

2) Pressurized extraction



Grape pomace

Pre-treatment

Pre-milling

Drying

Milling

CO_2 flow 30 g/min

Supercritical extraction

350 bar, 80°C, 1h

Extract rich in **oil and lipophilic compounds**

CO_2

Defatted grape waste

Co-solvent flow 6 g/min (EtOH:H2O 50:50)

CO_2 flow 2 g/min

Total flow 8 g/min

Pressurized extraction

100 bar, 80°C, 50min

Extract rich in **polyphen**

CO_2

EtOH:H_2O separation

Fibrous extraction residue

RISE

ALMA MATER STUDIORUM UNIVERSITÀ DI BOLOGNA

Potato residues from IAPPST (Institute of Agro-Products Processing Science & Technology, Chinese Academy of Agricultural Sciences)

Potatoes

Starch processing

Starch

Waste water

isoelectric or ammonium sulfate precipitation method

Residues

Protein

Thermostable α-amylase treatment

Dehydration

Acid extraction

Ethanol precipitation

Drying

Pectin product

ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Potato residues from IAPPST (Institute of Agro-Products Processing Science & Technology, Chinese Academy of Agricultural Sciences)

Potatoes

Starch processing

Starch

Waste water

isoelectric or ammonium sulfate precipitation method

Residues

Thermostable α-amylase treatment

Dehydration

Acid extraction

Ethanol precipitation

Drying

Pectin product

Protein

About 2 million tonnes (dry basis) of sweet potato residues are produced during starch processing every year

ALMA MATER STUDIORUM UNIVERSITÀ DI BOLOGNA