



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

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

M. Vannini¹, P. Marchese¹, L. Sisti¹, A. Celli¹,
M. Ferri^{1,2}, S. Monari², A. Tassoni², M. Ehrnell³, L.
Eliasson³, E. Xanthakis³, T. Mu⁴, H. Sun⁴

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;

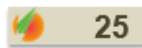
³ Agrifood & Bioscience Unit, RISE – Research Institutes of Sweden, Sweden; ⁴ Laboratory of Food Chemistry and Nutrition Science, Institute of Food Science and Technology, Chinese Academy of Agricultural Sciences; Key Laboratory of Agro-Products Processing, Ministry of Agriculture and Rural Affairs, China



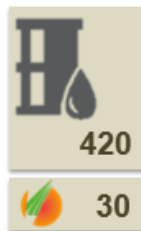
Now the situation

NoAW's ambitions

Available



Energy



Fertilizer



Plastics



Chemicals



MTOE: million tons oil equivalent



Vs. Food

Vs. Agro-waste

Extraction of high value molecules

Polyphenols, proteins, pectins

Agro waste (pomace, potato)

Extraction residues

PHA polymers

Agriculture

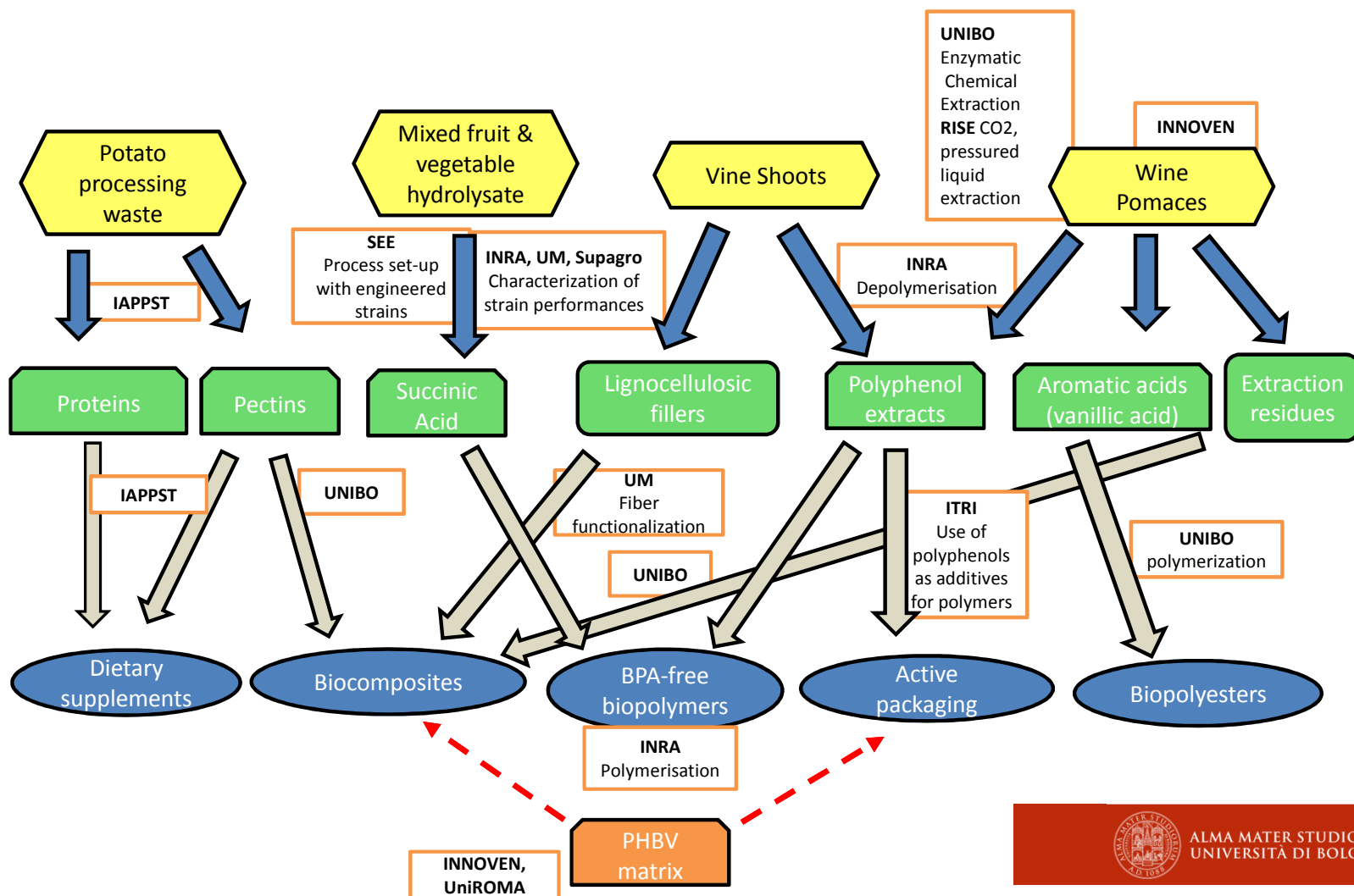
Melt processing

Novel biocomposites for agriculture, packaging, etc.

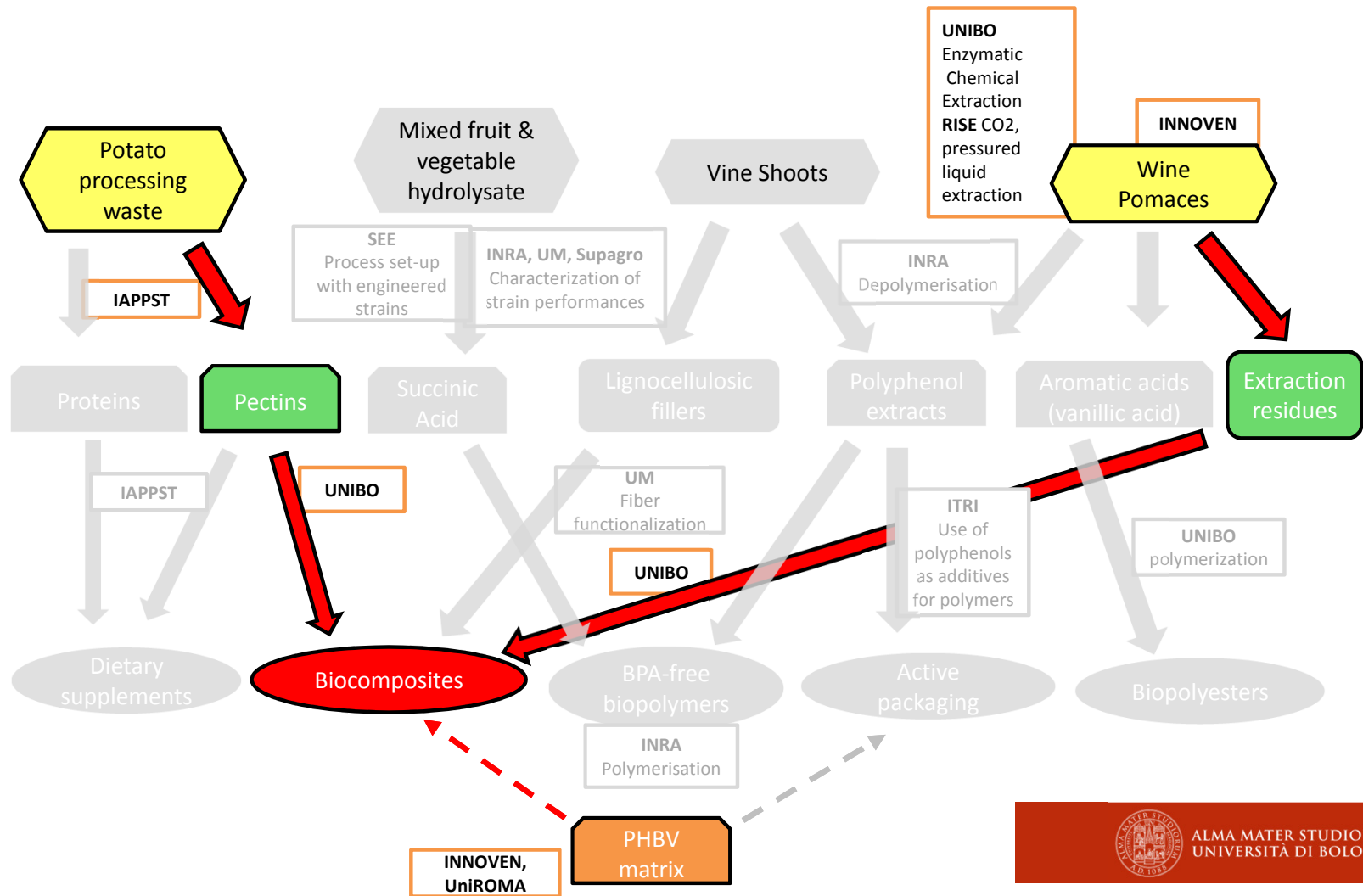


ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

WP4 Task 1



WP4 Task 1

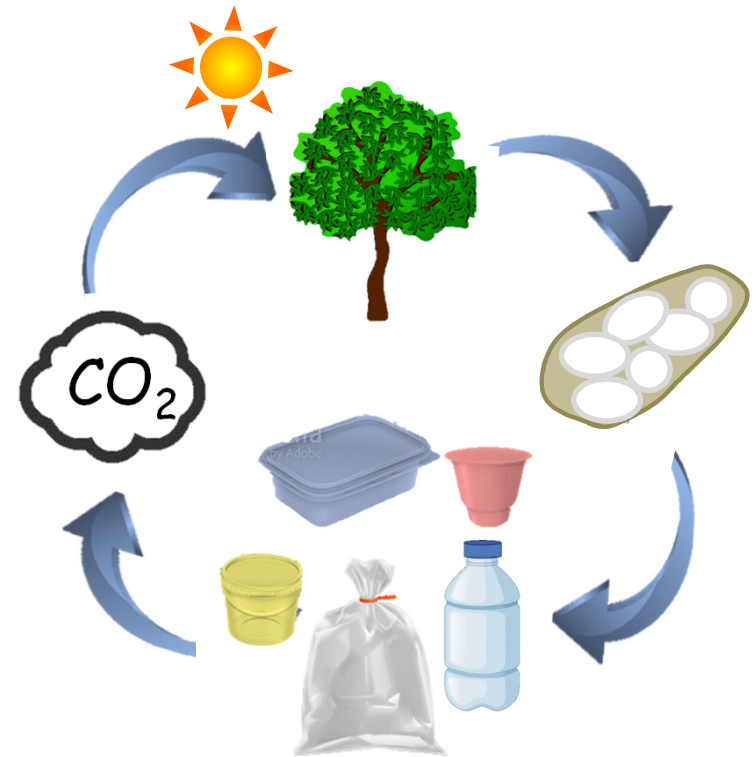


Choice of polymeric matrix

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

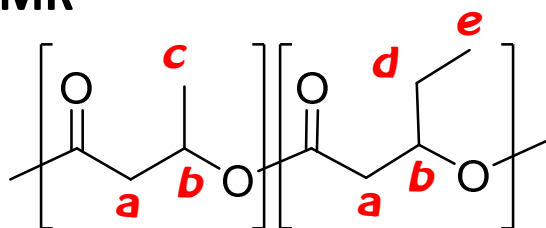
They have excellent biocompatible and biodegradable properties

The PHAs are particularly **expensive** and lack **mechanical properties**.

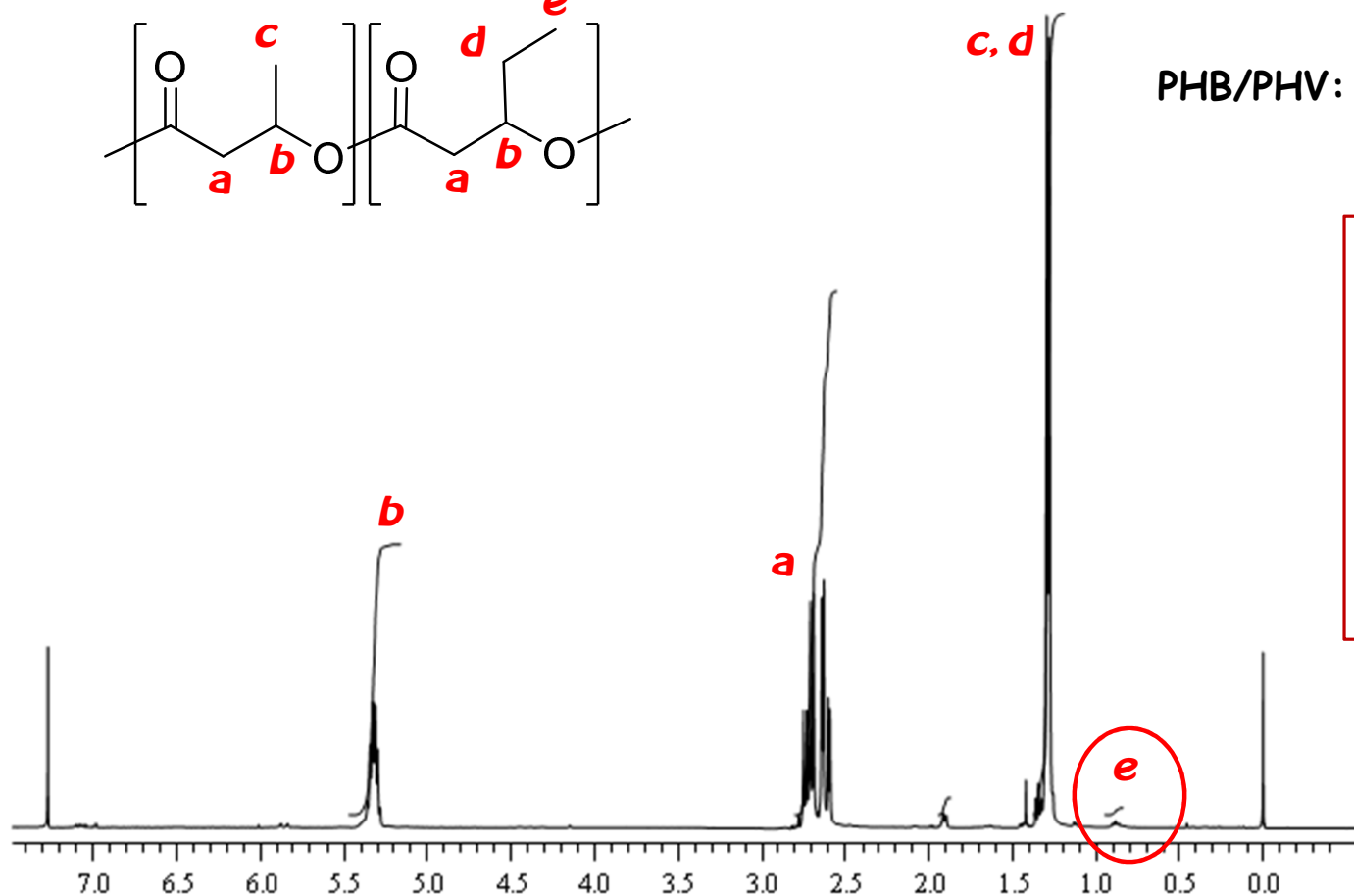


PHBV: poly(3-HydroxyButirate-co-Valerate)

^1H 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

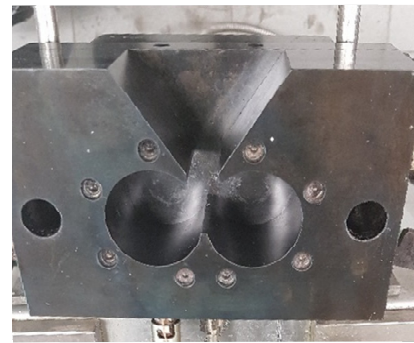
T_{c} : 114°C, ΔH_{c} : 73 J/g



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

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.



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Extractions of polyphenols from wine pomaces

Two methods:

Solvent-based extractions



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

INNOven
INNOVATION FOR
THE ENVIRONMENT



Merlot



Garganega

Pressurized liquid extractions (only on red pomaces)



**RI
SE**

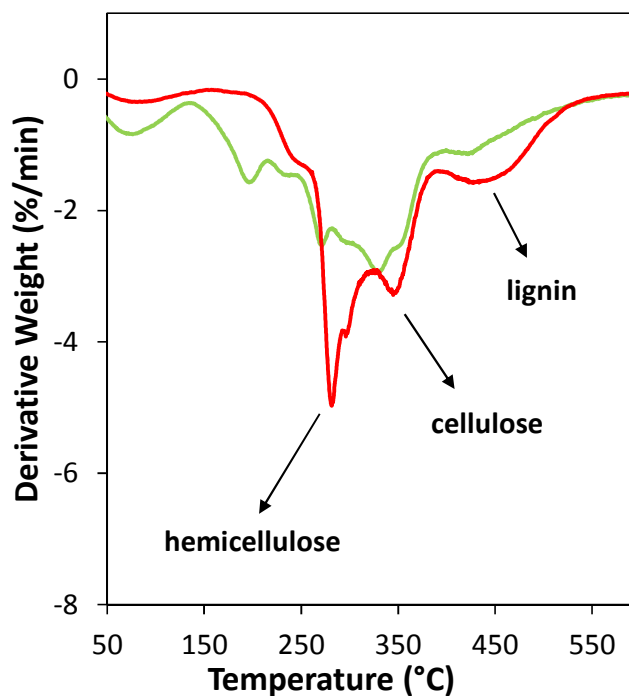
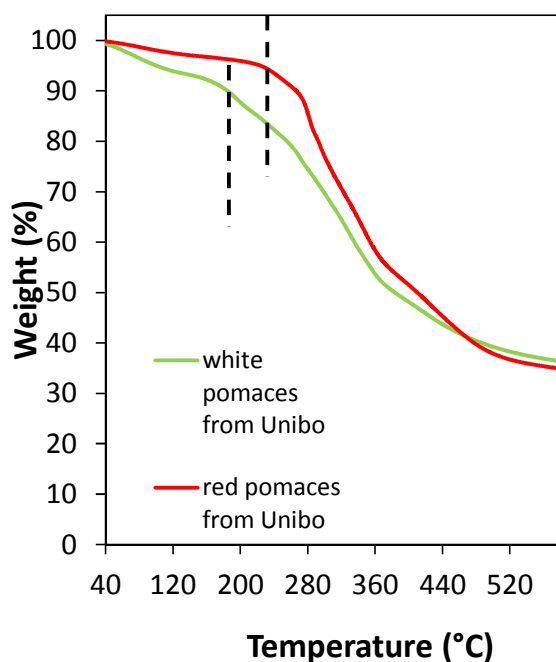
Best conditions:
Ethanol/Water 50/50
(vol/vol)



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Characterization of chemically extracted residue (UNIBO)

Thermogravimetric analyses



Garganega
(WHITE)
residue



Merlot
(RED)
residue

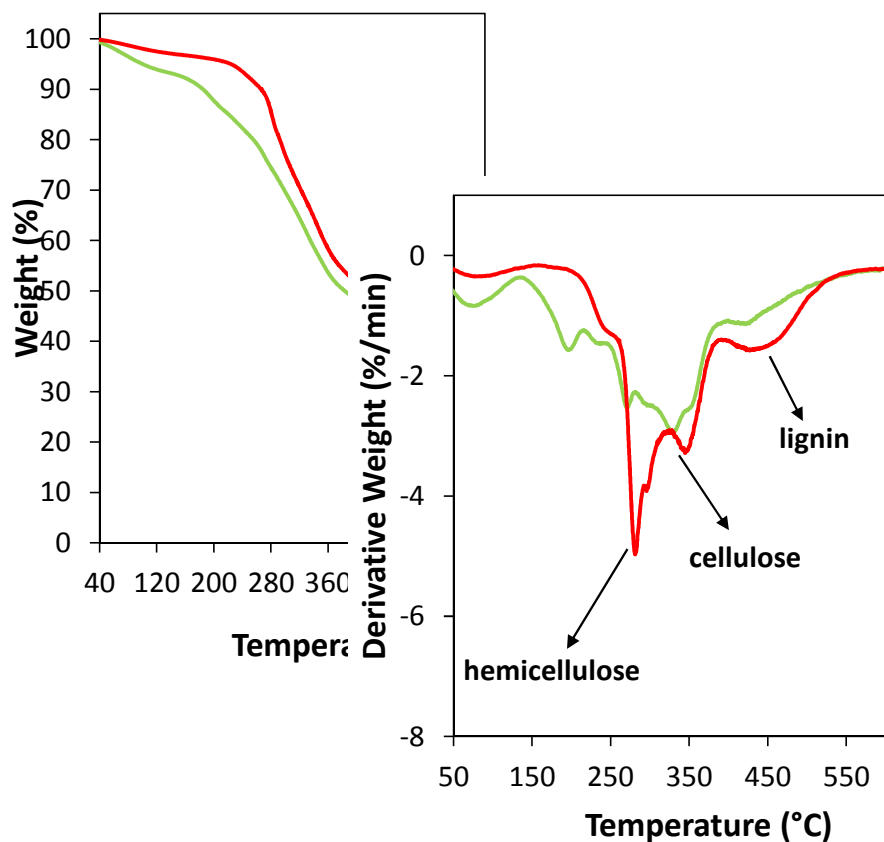
— white
pomaces from
Unibo
— red pomaces
from Unibo



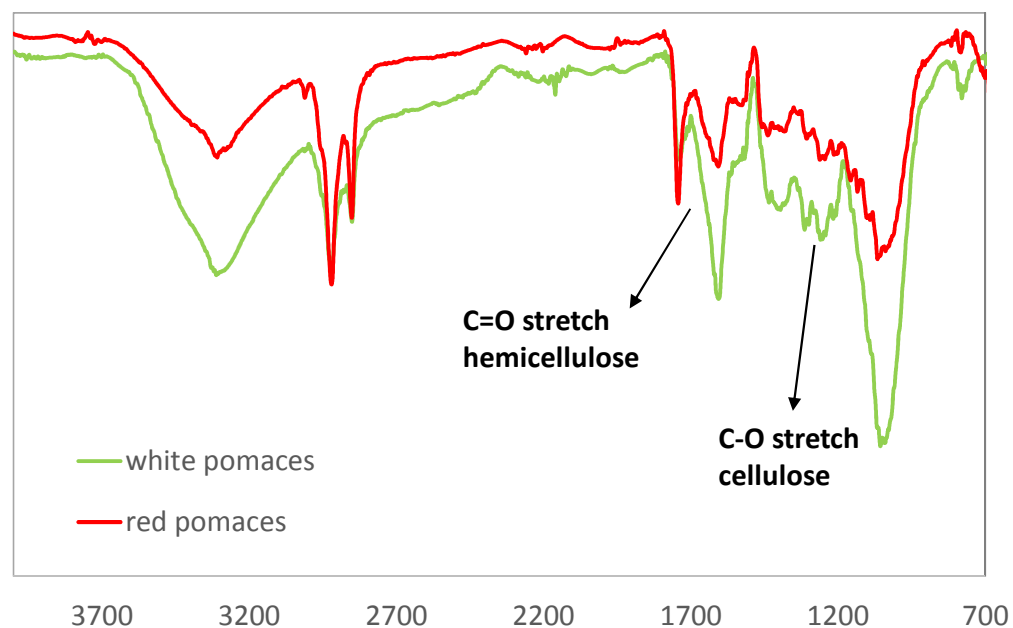
ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

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

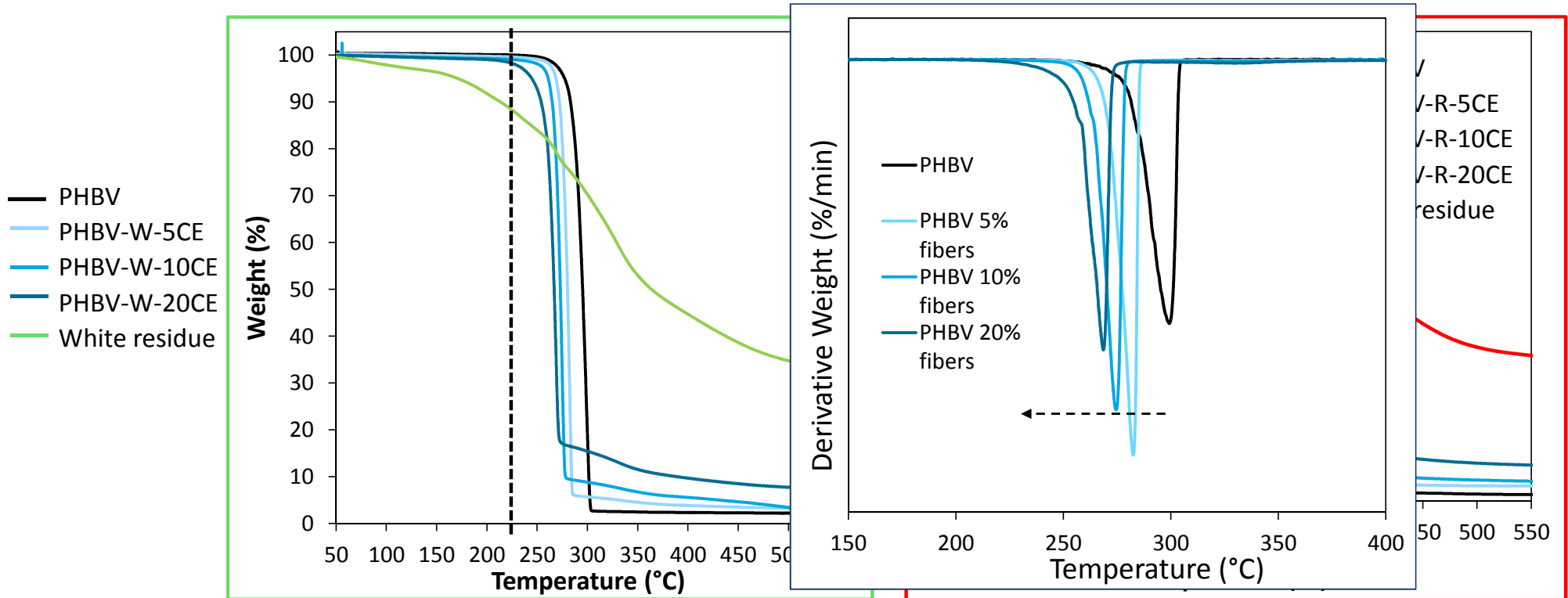


First scan, from 30 to 210°C at 20°C/min; 1 min at 210°C; cooling scan, from 210°C to 0°C at 20°C/min; 1 min at 0°C; second scan, from 0 to 210°C at 20°C/min.



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Thermal stability



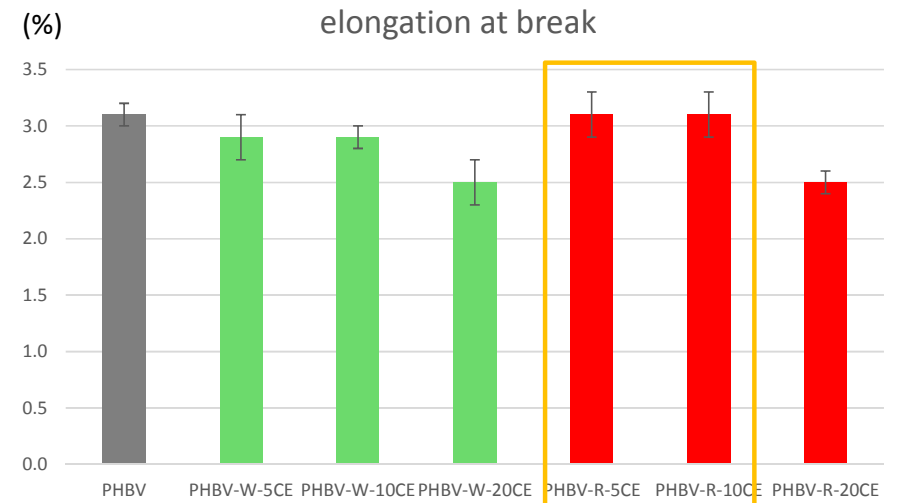
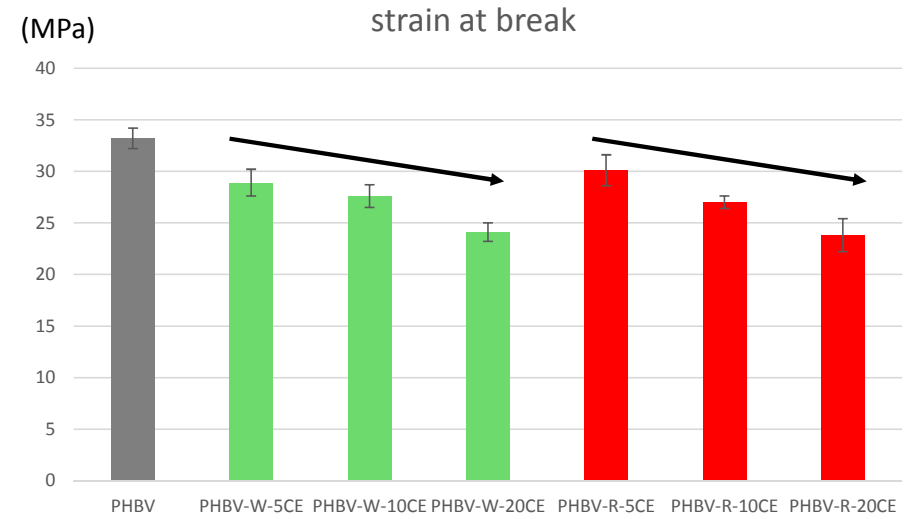
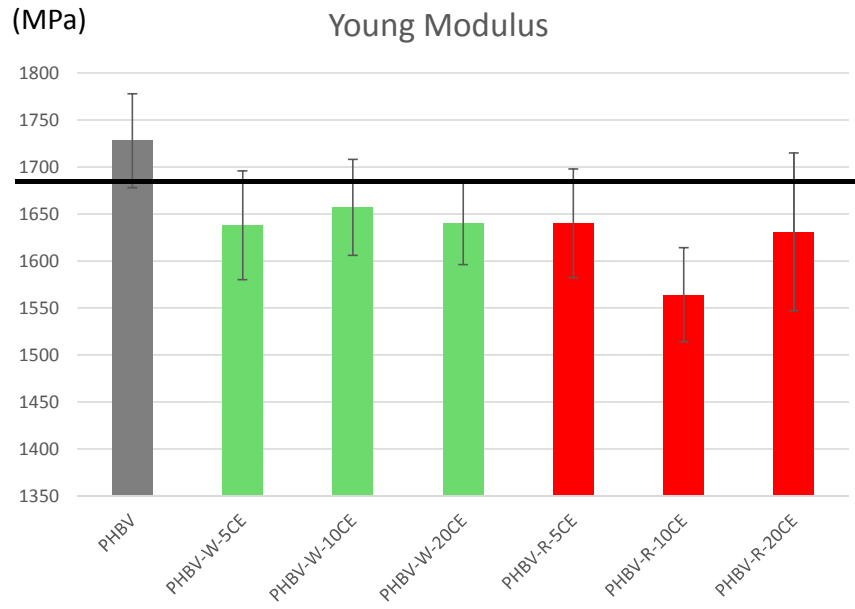
All the composites are stable over 230°C.

The thermal stability slightly decreases with the filler content.



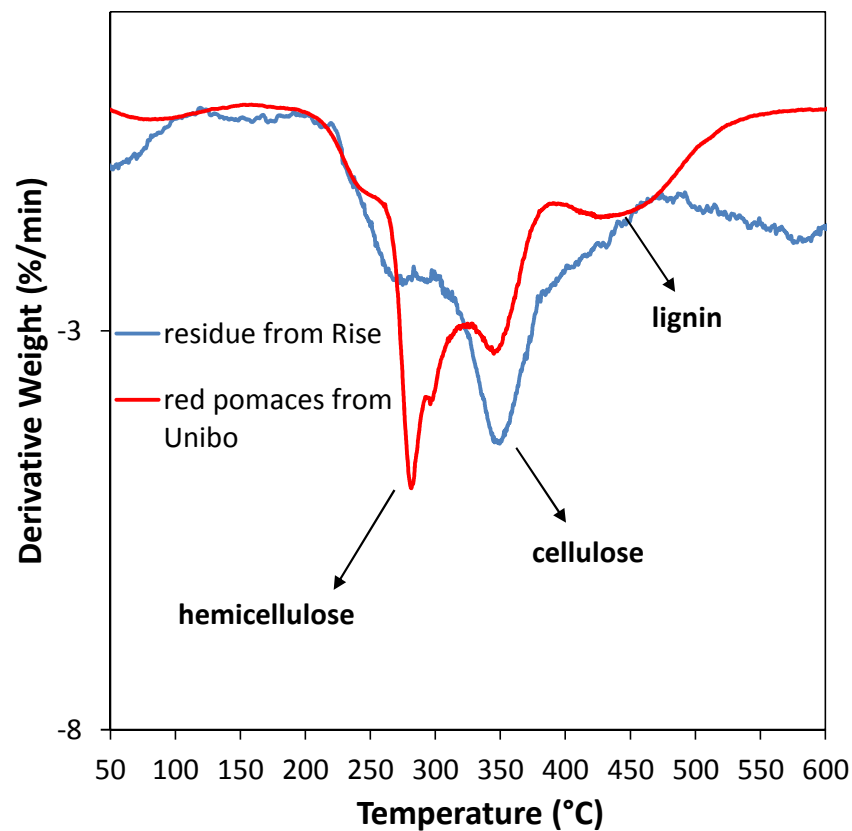
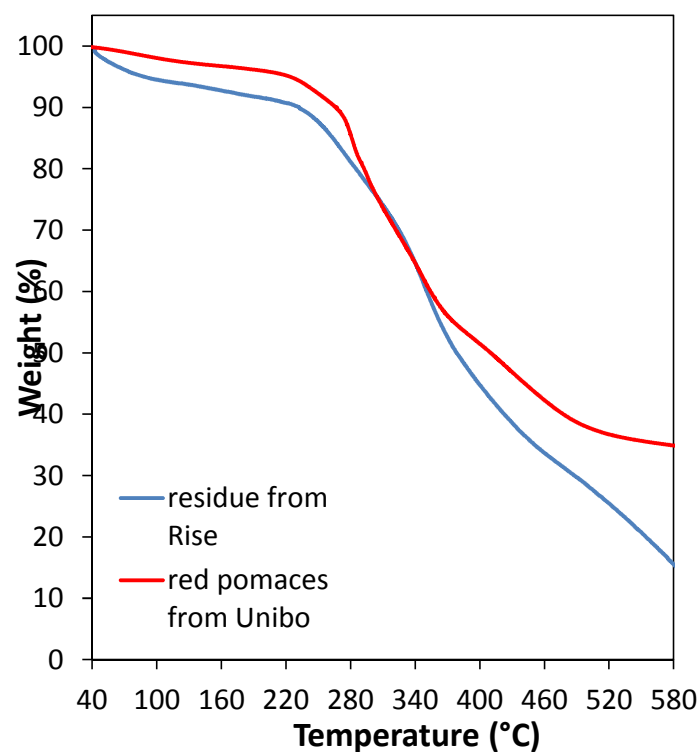
ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Tensile tests



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Characterization of pressurized extracted residue-comparison between the methods



Bio-composites with red-pressurized extracts

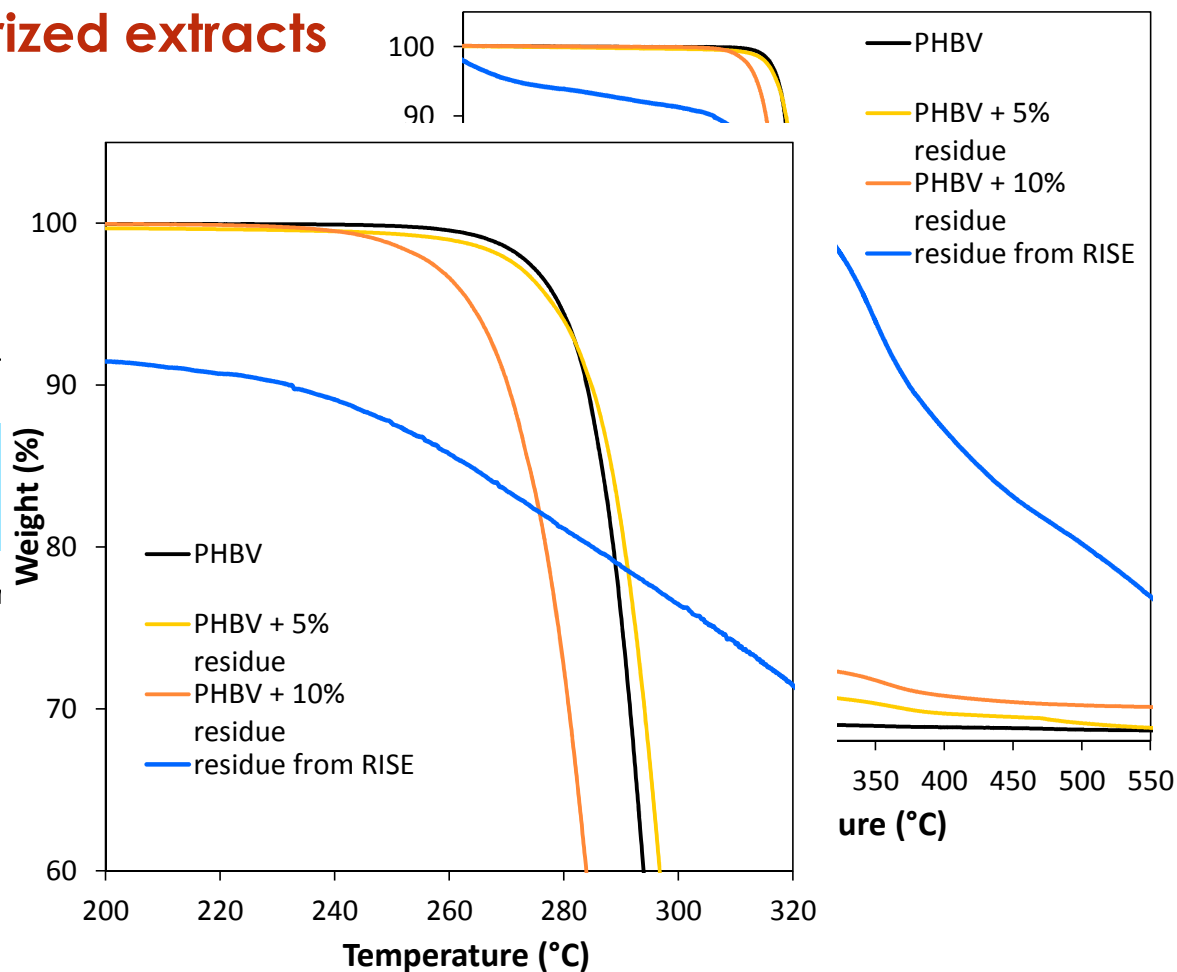
Thermal Properties

Sample code	1° heating scan		cooling scan	
	T_m (°C) ^b	ΔH_m (J/g) ^b	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; cooling scan 20°C/min; 1 min at 0°C; second scan, from 0 to 210°C at 20°C/min.

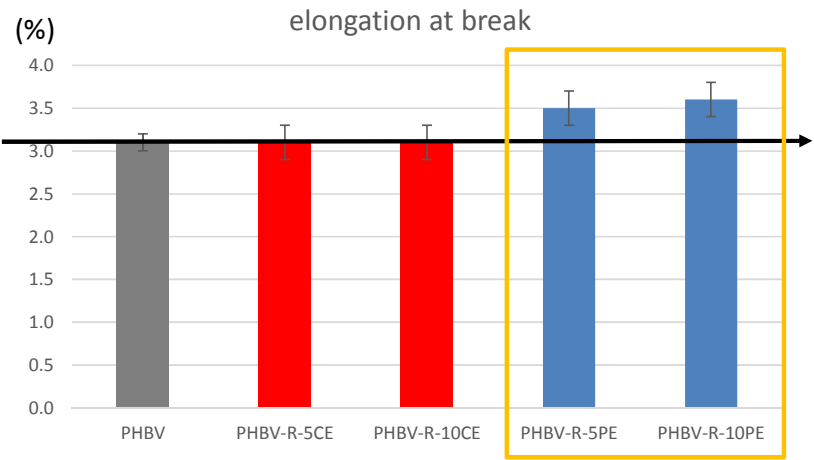
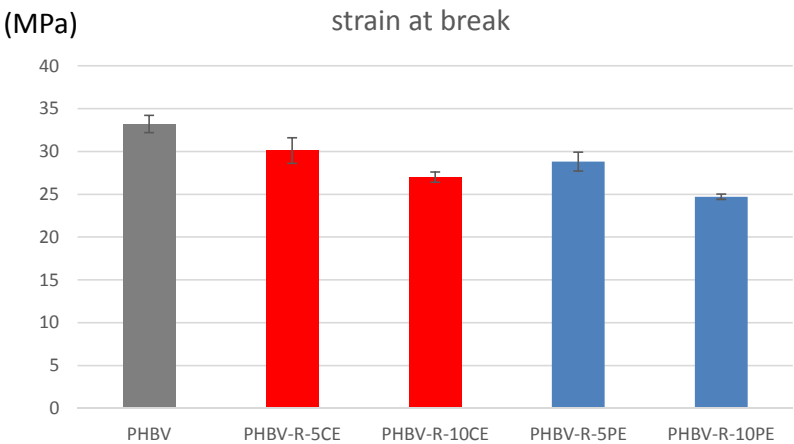
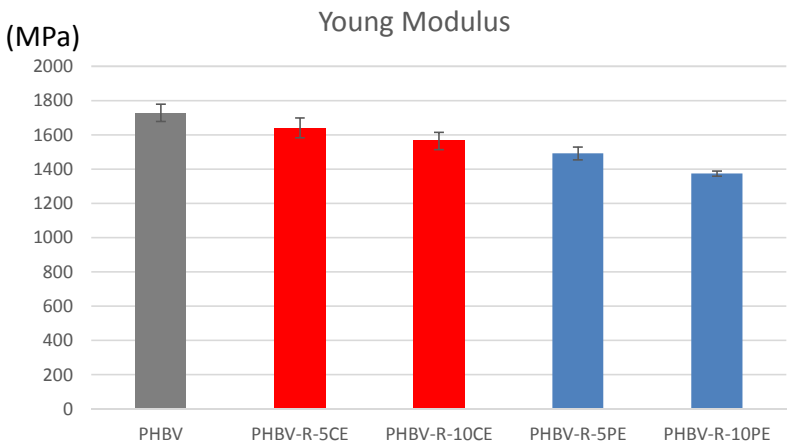


The thermal stability of PHBV and the composite containing 5 wt% of RISE extracts are comparable.

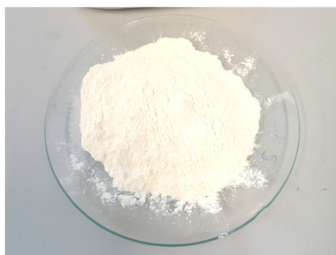


ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

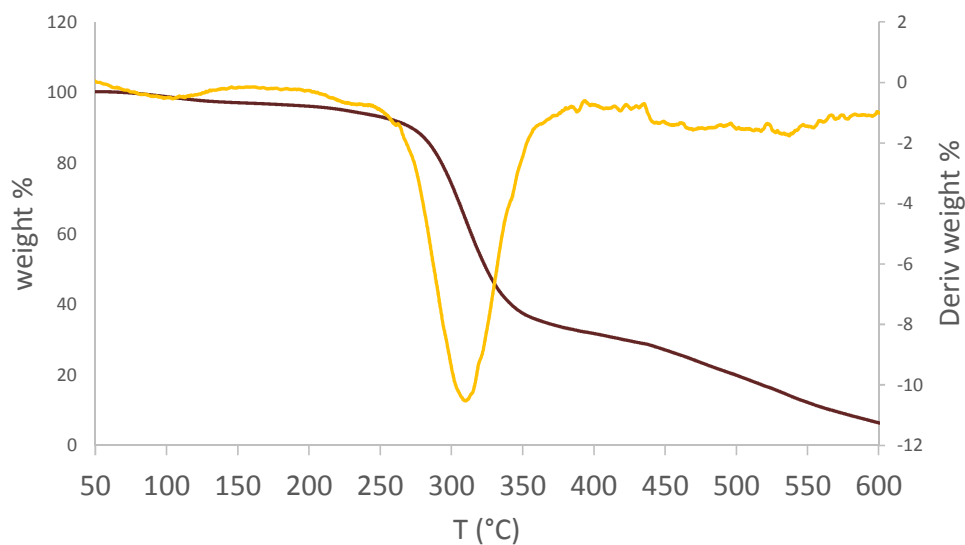
Tensile tests on bio-composites based on red pomaces residues



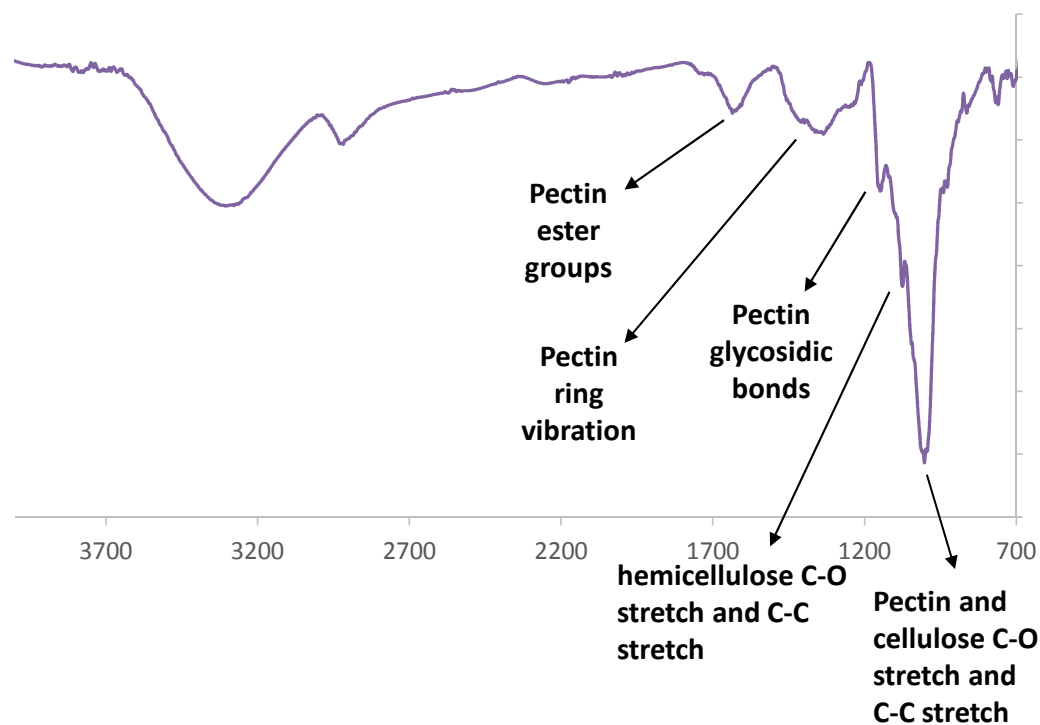
Characterization of potato's residue



Thermogravimetric analysis



FT-IR spectrum



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

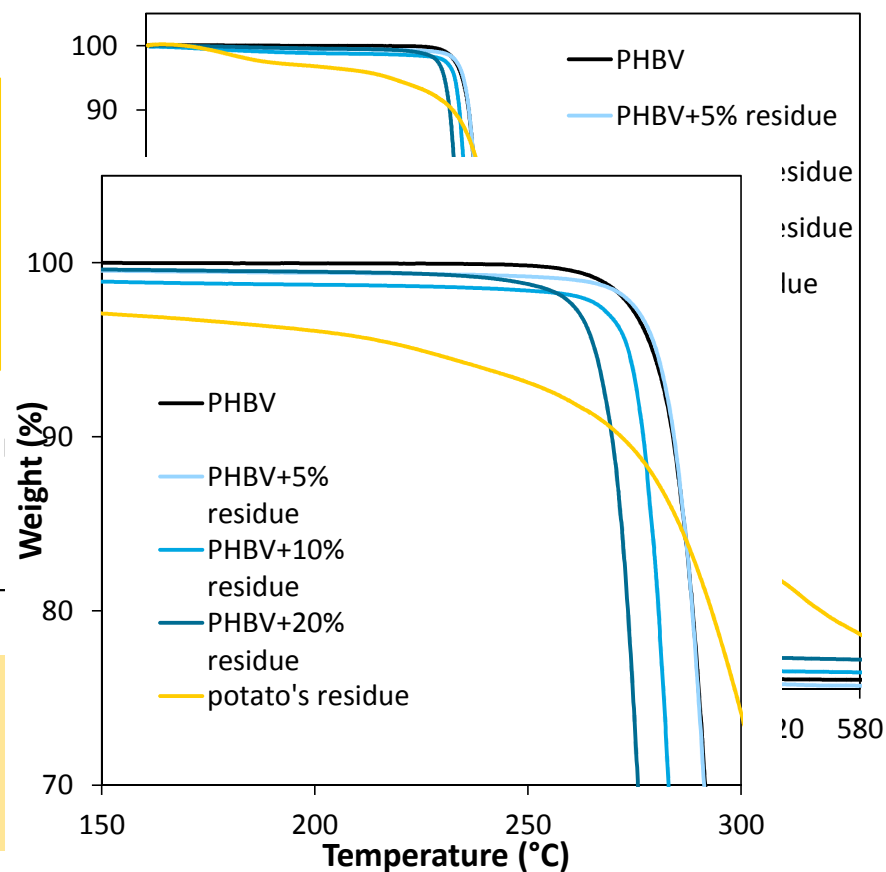
Bio-composites with potato's residue

Thermal properties



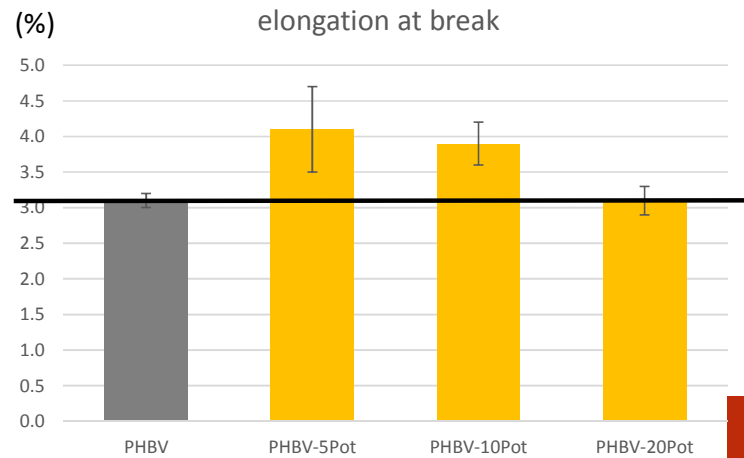
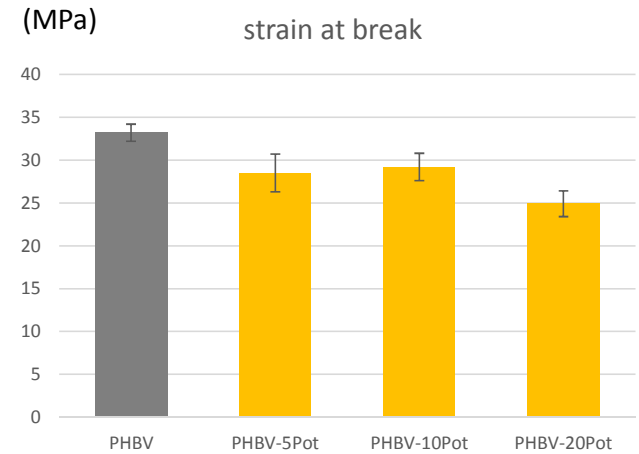
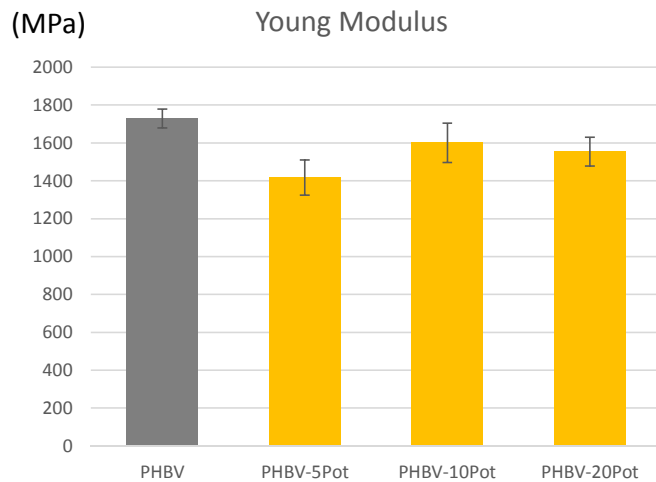
Sample code	1° heating scan		cooling scan		2° heating scan	
	T_m (°C) ^b	ΔH_m (J/g) ^b	T_c (°C) ^c	ΔH_c (J/g) ^c	T_m (°C) ^d	ΔH_m (J/g) ^d
PHBV	172	78	114	73	168	82
PHBV-5Pot	170	75	114	71	169	81
PHBV-10Pot	172	73	114	66	169	76
PHBV-20Pot	171	63	113	59	169	68

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.



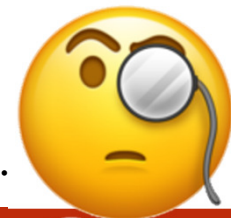
ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

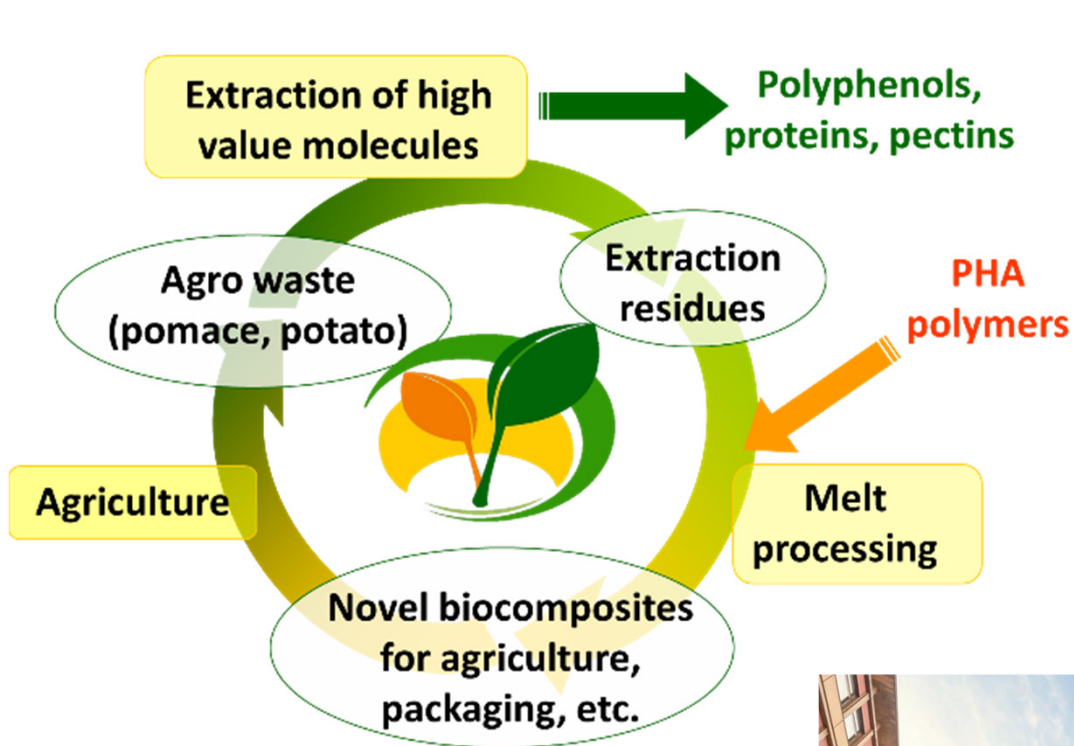
Tensile tests on bio-composites based on potato residues



Conclusions

- New bio-composites based on PHBV have been prepared by melt 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 strength 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 future.





Thank you for
your attention!



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



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Micaela Vannini

Department of Civil, Chemical, Environmental, and Materials Engineering

micaela.vannini@unibo.it

www.unibo.it