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

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Introduction

Grape (*Vitis* sp.) is the world's largest fruit crop mostly used in winemaking, a process during which approximately 20-30% of the weight of processed grapes ends up as pomace, its primary by-product. These large amounts of by-products constitute a serious environmental and disposal problem for wineries. However, they also represent a rich but still underutilized source of valuable compounds. In particular, the extraction of polyphenols has some development at industrial level today, even if the solid residues of the extraction process are a by-product that has to be disposed of. Similarly, potato is commonly used in starch processing, which results in a large quantity of waste residues. In China, approximately 4.5 to 5 tonnes of fresh potato residues are generated for every tonne of starch produced, which means a large contribute to environmental pollution. Also in this case, high value molecules, such as proteins and pectins can be recovered from waste of potato processing, but the final extraction residue has not found a further valorization.

The aim of this work, within the NoAW H2020 European project, is to develop new routes for the valorization of the final industrial residues, obtained from the extraction processes of high value molecules from agro-wastes. The ambition is to close the loop in a zero waste perspective, as drawn in Figure 1.

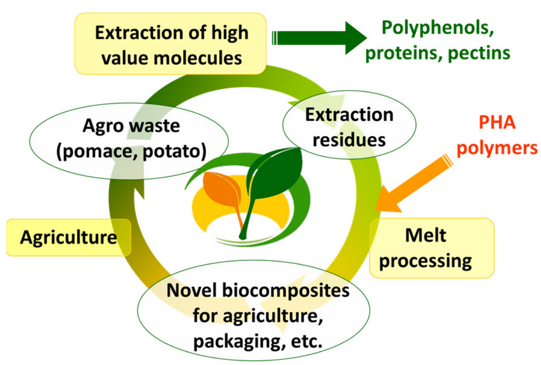

Figure 1: concept of the research activities on agro-waste

The described residues contain a certain fraction of fibers, which makes them suitable for composite preparation, with the advantages of biodegradability, lightness, low cost, and low energy consumption. Moreover, these fillers are not in competition with the food sector, but a real ultra-valorization of the wastes deriving from the food production.

The copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is the selected polymeric matrix, which finds applications in packaging, including films, boxes, coatings, fibers and foam materials with two main restricting factors: costs and limited performances (Rivera-Briso, 2018). Therefore, the preparation of biocomposites can fit two requests: fully exploiting agro-waste residues and improving the PHBV performances.

Experimental part

Commercial PHBV, containing 2 mol% of hydroxyvaleric units, was supplied from NaturePlast. Composites were prepared by mixing in a Brabender PHBV and four different kinds of fillers, as described in Table 1. The residues were first dried and milled, then mixed with the PHBV polymer matrix (in the form of pellets) at 200°C in amounts ranged from 5 to 20 wt%. The composites were characterized by NMR, DSC, TGA and Tensile tests.

Results

Table 1. Description of the samples.

Code	Amount of fillers (wt%)	Characteristics of the fillers
PHBV	-	-
WAc5	5	Residues obtained after extraction of polyphenols from white pomaces (Garganega cv) with aqueous acetone solution at 50°C
WAc10	10	
WAc20	20	
RAc5	5	Residues obtained after extraction of polyphenols from red pomaces (Merlot cv) with aqueous acetone solution at 50°C
RAc10	10	
RAc20	20	
REt5	5	Residues obtained after CO_2 pressurized aqueous ethanol extraction at 80°C of polyphenols from red pomaces (Merlot cv)
REt10	10	
P5	5	Final residues obtained from industrial potato by-products, after extraction of starch, and, then, after recovering of the proteins and pectins.
P10	10	
P20	20	

The novel composite materials are biosourced and potentially biodegradable. Their thermal properties do not change significantly with respect to the PHBV matrix. Indeed, the thermal stability is maintained well since the temperature of initial degradation is higher than 270°C, as reported in Table 2. The materials are semicrystalline, with melting temperatures *ca.* 170°C and melting enthalpies in the range of 70-80 J/g, depending on the composition.

Table 2. Thermogravimetric[a] and tensile[b] analyses on the prepared biocomposites.

Code	T_D (°C)	Young Modulus (MPa)	Tensile Strength (MPa)	Strain at break (%)
PHBV	302	1728 ± 50	33.2 ± 1.0	3.1 ± 0.1
WAc5	282	1638 ± 58	28.9 ± 1.3	2.9 ± 0.2
WAc10	274	1657 ± 51	27.6 ± 1.1	2.9 ± 0.1
WAc20	269	1640 ± 44	24.1 ± 0.9	2.5 ± 0.2
RAc5	286	1640 ± 58	30.1 ± 1.5	3.1 ± 0.2
RAc10	277	1564 ± 50	27.0 ± 0.6	3.1 ± 0.2
RAc20	276	1631 ± 84	23.8 ± 1.6	2.5 ± 0.1
REt5	302	1491 ± 38	28.8 ± 1.1	3.5 ± 0.2
REt10	290	1373 ± 15	24.7 ± 0.3	3.6 ± 0.2
P5	296	1417 ± 93	28.5 ± 2.2	4.1 ± 0.6
P10	289	1600 ± 104	29.2 ± 1.6	3.9 ± 0.3
P20	272	1553 ± 76	24.9 ± 1.5	3.1 ± 0.2

[a] determined by TGA in nitrogen at 10°C/min; [b]performed on dog bone specimens (technical standard ISO527, type 1BA) by an INSTRON 5966 series test apparatus equipped with a 10 kN load cell (test speed 5 mm/min, room temperature). The reported data are the average values of at least five determinations for each sample.

Regarding the mechanical tests, the data reported in Table 2 indicate that the composites based on pomaces treated with pressurized CO_2 aqueous ethanol solution and potato residues show an improvement in the elongation at break, making the materials less breakable. The composites containing pomaces treated with aqueous acetone solution do not display the same behavior. Probably, the higher amount of cellulose/starch fraction could be related with such results. Indeed, a higher content of glycosidic moieties may increase the polar interactions with the PHBV matrix, by favoring the compatibility between filler and polymer.

Conclusions

New biocomposites based on PHBV and fillers derived from agro-waste have been successfully prepared. The new materials are characterized by low cost and in some cases improved mechanical performances with respect the matrix. Potential applications could be within the sectors using composite materials (automotive, building, etc.) and within the fields requiring biodegradable and eventually biosourced materials, such as agriculture and packaging. These examples highlight the potentials for a complete valorisation of agricultural by-products.

References

A. L. Rivera-Briso, Á. Serrano-Aroca, Poly(3-Hydroxybutyrate-co-3-Hydroxyvalerate):Enhancement Strategies for Advanced Applications, *Polymers*, **2018**, *10*, 732; doi:10.3390/polym10070732.

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