Research Summary Sheet

Deliverable n°: 4.3

"Strategies for the production of performant 100% agro-wastes sourced polymers-based materials"

Context and Challenges

WP4 aims at developing eco-designed and innovative cascading agro-waste conversion into molecules and materials. Four value chains were considered (figure below), using winery waste, fruit/vegetable waste, anaerobic digestate and volatile fatty acids (VFAs) from anaerobic digestion as raw materials. The present deliverable addresses the production and structure/properties relationships of biopolymers (BPA-free thermosets from tannin building blocks, polyesters from aromatic derivatives, polyhydroxyalkanoates (PHAs) from photo-fermentation) polymer formulations with antioxidant and biocomposites (fiber-based composites) derived from molecules/fillers extracted from agrowastes. The objectives were to develop biomaterials using the intermediates previously developed as reported in D4.1 (polyphenols including tannin building blocks, lignocellulosic fillers, extraction residues, synthetic VFA, succinic acid).

Results and Applications

1/ Active packaging with addition of polyphenols (ITRI)

The experiments carried out aimed at the exploitation of the antioxidant and bioactive polyphenols extracted from grape pomace to produce an active packaging, able to increase the shelf life of fresh food.

2/ Biobased epoxy resins (INRAE)

In the perspective of manufacturing potentially recyclable thermosets, ester bonds have been considered to replace the ether bonds conventionally connecting the three-dimensional network of the epoxy resins. The two components selected to create the ester bonds were: one hand, depolymerized condensed tannin building blocks recovered from grape pomace seeds, and succinic acid produced by yeast fermentation of vegetable waste.

The project leading to this application has funding from European Union's Horizon 2020 research and innovation programme under grant agreement No 688338.

3/ Vanillic acid derived copolyesters (UNIBO)

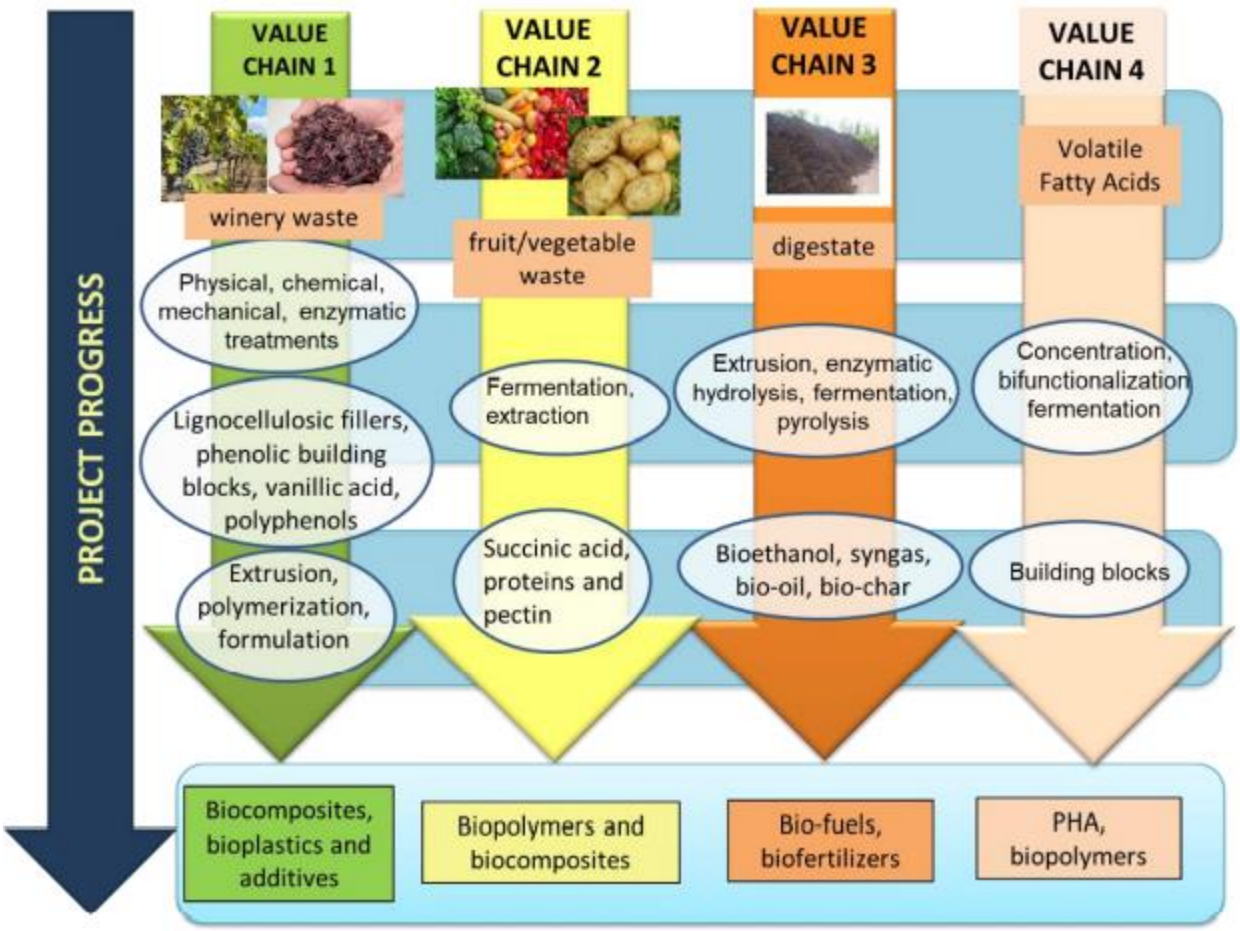
This research work aimed at valorizing vanillic acid, a natural monomer present in winery pomace (even if in small amount) and in other biomass, as building block for the preparation of new aromatic bio-based copolyesters.

4/ PHA from phototrophic fermentation (IBET)

The general objective was to further optimize the operational parameters that lead to the enrichment of a phototrophic mixed culture of phototrophic purple bacteria while outcompeting other non-PHA producing photo-synthetic organisms and attain high PHA accumulation.

5/ Composites with lignocellulosic fillers (UNIBO, UM)

The aim was the exploitation of final fibrous residues and lignocellulosic components deriving from vineyard cultivation (pruning wood), winemaking and starch-extraction processes to produce fillers and to introduce them into PHBV matrix, by means of melt blending, and to perform the complete characterization of the obtained biocomposites.



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Breakthroughs, benefits and added value

1/ Active packaging with addition of polyphenols (ITRI)

Modified polyphenol coatings on various plastic substrates (PHA, PLA, PS, PE and PP) were developed it results that polyphenol coatings on plastic substrates and absorbent pad inhibit bacterial growth on contact surface of fresh meat.

2/ Biobased epoxy resins (INRAE)

Grape seeds tannins extracted from pomace waste have been modified in order to prepare new bio-based building blocks for the production of bio-based epoxy resins, BPA free. Preliminary tests of formulations, involving either the mixed prepolymer of depolymerized condensed tannin building blocks with succinic acid, or bis-glycidyl succinate prepolymer with depolymerized condensed tannin building blocks were carried out. Succinic acid was not soluble in the tannin-based prepolymer, even at high temperature (160°C). The insolubility of succinic acid in the tannin-based prepolymer was overcome by using the anhydride form of succinic acid. The epoxy resin thus obtained showed the highest thermal stability and glass transition temperature. The second formulation based on bis-glycidyl succinate prepolymer allowed to produce a solid epoxy resin with lower thermal properties.

All the experiments were carried out at lab scale (TRL 3). The value chain for the industrial production of biobased alternatives to commercial petrochemical epoxy resins would require the establishment of new sectors that do not exist today to meet specific needs: production of condensed tannin extracts by others sectors than existing ones; fine chemistry for the transformation of tannin extracts into epoxy prepolymers (today industrial chemistry is carried out with petrochemical molecules, not biobased extracts) and formulation of the prepolymers by applicators. To overcome the barriers associated with this transition, strong support is needed at the political, legislative and economic levels.

3/ Vanillic acid derived copolyesters (UNIBO)

The syntheses of the new copolyesters were successful. The new materials showed good molecular weight, high thermal stability, crystallinity and crystallization rate that can be modulated according to the composition. The brittleness of the homopolymer based on vanillic acid (PEV) has been overcome and the copolymers are processable and filmable. Therefore, these new materials have properties that can be adapted to applications in the packaging sector and could be a potentially valid alternative to petro-based polymers, such as PET. The

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experiments have been carried out only at lab scale (TRL 3), even if the polymerization steps can be easily upscaled to an industrial process. The new copolymers have the advantage to be bio-based and processable, even if a complete characterization of them and a study of their possible applications are necessary.

4/ PHA from phototrophic fermentation (IBET)

As targeted, this phototrophic technology reached a TRL of 4 by the end of the project, presenting the unique feature of enabling PHA production without the need of aeration. The elimination of aeration and its replacement with free sunlight can lead to a substantial decrease of the operating costs. Future technological development will focus on external photo-bioreactor operation under direct sunlight illumination.

5/ Composites with lignocellulosic fillers (UNIBO, UM)

Lignocellulosic fillers were produced by dry fractionation of native vine shoots. Hydrophobizing the surfaces of vine shoot particles by gas-phase esterification was shown to not have a significant impact on the improvement of mechanical properties. Only the water permeability of the composites was reduced by 27% for a filler content of 30 wt%. Answering a biorefinery approach, the impact of a preliminary polyphenols extraction step using an acetone/water mixture on the reinforcing effect of fillers was assessed. It was shown that the removal of polyphenols did not modify the mechanical properties of the biocomposites, demonstrating an extraction process could be used to maximize their potential of valorization. It was demonstrated that PHBV-vine shoots biocomposites were fully biodegradable in soil.

Another family of composites was prepared by melt mixing 5-20% (w/w) pomace residues in PHBV at 200°C, using an eco-friendly approach not involving solvents and other additives. The thermal and mechanical properties of PHBV were only slightly modified by the presence of the pomace residues. However, PHBV crystallization temperature was favourably lowered from 114 to 108°C in the presence of 20% pomace, enlarging its processing window. Although the pomace residue does not act as a reinforcing agent, but as a filler, it does not present main problems in processing, is a low-cost component obtained from no-food competition biomass and biodegradable. The removal of polysaccharides and polyphenols by the extraction process makes the filler more hydrophobic and, therefore, more compatible with the polymeric matrix. The insertion of pomace residues led to an increment in water vapour permeability of composites, which could, therefore, find application in horticulture sector or the packaging area.

Potato residues, obtain after starch extraction, have been also used to prepare a new series of bio-composites. The thermal properties, crystallization and melting behaviour of PHBV were not affected by the presence of up to 40% potato extract filler. The negative impact on mechanical properties was quite limited, mainly for

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not too high amount of residues, when the PHBV matrix, without any other additives still presents properties suitable for practical applications.

As a conclusion, the use of both pomace and potato residues as fillers could therefore lower the cost of the final material by reducing the amount of PHBV required, and improvement of a few material properties, as well as to the full valorisation of agro-wastes

Further information on NoAW project: http://noaw2020.eu

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