Grape-wine chain biowaste tested as filler for biodegradable composites

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Grape stalks are lignocellulose biomass composed by three different bio-polymers: cellulose, hemicellulose, and lignin and represent a source of sugars, phenolic compounds, and fibre (Brandt *et al*, 2013). A possible use of grape stalk powder as filler for biodegradable composites (Seggiani *et al*, 2015; Cinelli *et al*, 2019; Nanni *et al*, 2019) is explored using poly-butylene succinate (PBS) as a base polymer. PBS is a thermoplastic polymer resin of the polyester family and degradable by some strains of Actinobacteria (Tokiwa *et al*, 2009).

Grape stalks, collected from local wine companies, were first cleaned to remove residues of grape skins and seeds and then oven-dried at 65 °C up to constant weight. Then, the dried grape stalks were subjected to milling in order to considerably reduce the dimensions of the material. A fine powder with a high surface area was obtained in order to facilitate the subsequent treatments of the material. The powder was then sieved to separate the finest fractions from the coarsest ones. The fraction of grape stalk powder with a particle size between 63 and 212 µm was selected and subjected to various derivatization reactions: acetylation, silylation, and silylation *in situ*.

The realization of biocomposites was carried out using 150 g of PBS, 1.5 g of paraffin oil, and 15 g (10% wt) of each sample of grape stalk powder. After thorough mixing, the biocomposites were formed through a twin-screw extruder (557 Rheomex, Haake S.r.l.). The extruded materials were collected in a coil, then granulated, and finally processed by injection moulding (MegaTech Tecnica DueBi injection moulding machine) in order to obtain specimens (Fig. 1) for mechanical and physicochemical characterizations. Mechanical tests on the specimens were carried out through a dynamometer (5567 Instron).

Figure 1: Biocomposites specimens.
From left to right: (A) PBS (blank), (B) 10% grape stalk PBS (control), (C) 10% acetylated grape stalk PBS, (D) 10% silylated grape stalk PBS, and (E) 10% silylated *in situ* grape stalk PBS.

The results of the mechanical analysis on the specimens are shown in table 1. The biocomposites obtained using grape stalks "as they are" (control), acetylated, and silylated grape stalk powder showed an increase by 14-15% of the stiffness (Young's modulus, E) in comparison with the pure PBS (blank). The same behavior was not shown by the sample silylated *in situ*, probably as a consequence of the poor derivatization of the substrate as also demonstrated by its FTIR spectrum. Tensile stress and elongation at break showed a marked reduction of values in grape stalks "as they are", and silylated one compared to PBS polymer, while acetylated sample maintained higher values.

Table 1. Mechanical measurements of biocomposites.
E: Young's modulus; σ_M: tensile stress; ε: elongation at break.
PBS: polybutylene succinate; 10 GS: 10% of grape stalk

	E [MPa]	σM [MPa]	ε [%]
PBS (blank)	623 ± 8	31 ± 2	399 ± 93
PBS + 10 GS (control)	712 ± 6	25 ± 1	98 ± 109
PBS + 10 GS acetylated	713 ± 15	26 ± 1	151 ± 125
PBS + 10 GS silylated	711 ± 9	26 ± 1	89 ± 94
PBS + 10 GS silylated *in situ*	635 ± 46	29 ± 2	267 ± 123

The use of fine grape stalk powder as filler to improve mechanical properties of biocomposites showed satisfactory results, in particular when grape stalk powder was subjected to acetylation. Aside from the improvement of the mechanical properties, the incorporation of grape stalk powder 10% into a biodegradable polymer as polybutylene succinate allows to reduce the rate of the polymer, the cost of the material, and provides various woody hues. This project could therefore have a strong impact in a circular economy perspective to obtain biomaterials from food chain solid waste.

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References

Brandt, A., Gräsvik, J., Hallett, J. P., & Welton, T. (2013). Deconstruction of lignocellulosic biomass with ionic liquids. *Green Chemistry*, 15(3), 550-583.

Cinelli, P., Mallegni, N., Gigante, V., Montanari, A., Seggiani, M., Coltelli, M. B., ... & Lazzeri, A. (2019). Biocomposites Based on Polyhydroxyalkanoates and Natural Fibres from Renewable Byproducts. *Applied Food Biotechnology*, 6(1), 35-43.

Nanni, A., Battegazzore, D., Frache, A., & Messori, M. (2019). Thermal and UV aging of polypropylene stabilized by wine seeds wastes and their extracts. *Polymer Degradation and Stability*, 165, 49-59.

Seggiani, M., Cinelli, P., Verstichel, S., Puccini, M., Vitolo, S., Anguillesi, I., & Lazzeri, A. (2015). Development of fibres-reinforced biodegradable composites. *Chemical Engineering Transaction*, 43, 1813-1818.

Tokiwa, Y., Calabia, B. P., Ugwu, C. U., & Aiba, S. (2009). Biodegradability of plastics. *International Journal of Molecular Sciences*, 10(9), 3722-3742.