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A comparative study of different winemaking by-products derived additives on oxidation stability, mechanical and thermal proprieties of polypropylene

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ABSTRACT

Three different solid wine wastes (peels, seeds and stalks) have been mixed with polypropylene (PP) and tested as stabilizers. Their stabilizing activity has been compared with that of a commercial tannin extract powder, rich in polyphenol. Thermogravimetric analysis, Oxidation Induction Time and Oxidation Onset Temperature measurements have been conducted to investigate the thermo-oxidative stability. Tensile tests, Dynamic Mechanical Analysis and Differential Scanning Calorimetry have been conducted on the samples in order to evaluate the effect of the additives also on the thermal and mechanical properties. Scanning Electron Microscopy have been used to assess the adhesion and distribution of the wine-wastes additives within the PP matrix. Experimental results evidence that all three wine-wastes derived additives do not significantly change the mechanical and thermal properties of PP, meanwhile they enhance its thermal stability. Moreover, the expectation to obtain better results with the commercial tannin extract has not been achieved. The obtained results show how wine wastes can be effectively used as polymer stabilizers and represent a valid alternative because of theirs environmental and cost-effects advantages.

1. Introduction

In the last decade, the valorisation of agro-industrial by-products has gained a central role both in the scientific community and in the industry since it is able to solve simultaneously the problem of ecological and economical wastes disposal and the necessity to invest in new sustainable and environmentally friendly products and systems. Winemaking, especially in Europe, is one of the most developed primary sectors that generate millions of tons per years of solid wastes (Table 1). Despite their natural origin and intrinsic not hazardous behaviour, the management of these wastes in the last years have been modified according to new legal, economic and green political issues [1]. Conventional disposal operations such as waste-landfill or waste as animal feed have been reconsidered. Due to their low pH, high organic matter as well as high concentrations of macronutrients and polyphenols and low concentration of micronutrients and metals, wine wastes cannot always used as conditioner or fertilizer without pretreatments or conditioning steps [2]. The landfill of wine by-products or their use as amendments may inhibit or modify germination proprieties, affect the soil erosion and compaction and decrease the quality of groundwater because of the organic matter loss [3,4]. As animal feed, grape pomace can represent a problem because the high amount of polyphenols that bonding with proteins, lead them to be not suitable for nutritional goals [5,6]. These reasons and the scientific progresses have led to evaluate new cost-effective and sustainable environmental disposal alternatives. Today wine by-products can be treated in order to obtain adsorbent for the adsorption of heavy metals in aqueous solutions [7,8], for the production of pullulan [9,10], for the recovery of ethanol or organic acids as tartaric, malic, and citric [11,12] and for many others targets. Extraction and recovery of polyphenols has been one of the most investigated procedure for valorisation since the high abundance and high value of these secondary metabolites of plants. Due to their natural antioxidant capacity and their harmless [13], they can find space in many different fields. In the medical (as anti-carcinogenic and anti-inflammatory agents, for protection against cardiovascular diseases [14–18]), in the cosmetic and pharmaceutical (skin, hair, and haemorrhoid products [19]), and in the food and beverage (to inhibit oxidation of oils during storage or frying, to inhibit lipid oxidation or to preserve colour of some fresh meats [20–22]).

In the last years, many authors have started to investigate the effect of the antiradical activity of polyphenols on the stability and proprieties of polymer matrixes. Due to their structure (one or more aromatic rings with one or more hydroxyl group attached), polyphenols can interrupt, via electron donation and resonance stabilization, the degradative radical reaction of polymers [28,29]. Indeed, these stabilizers can actively work only with polymer mainly characterized by a radical degradation

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Table 1
Production data of winemaking wastes, polypropylene and synthetic antioxidants in Europe and in the world [23–27].

	Europe [Mtons/y]	World [Mtons/y]
Grape Skins	1.9	3.28
Grape Seeds	0.77	1.33
Stalks	0.95	1.64
Polypropylene	9.30	56.10
Synthetic Antioxidants	0.44[a]	1.25[b]

[a,b]: refers to Mtons of antioxidants in world used just for PP and for all the plastics respectively.

mechanism. In literature, the effect of wine by-products additives on the stability of some polymers has been already investigated. Grape seed additives have been tested with polyolefin films [30,31] and pomace extracts with poly(3-hydroxybutyrate) (PHB) [32] and with Mater-Bi® [33]. In these works, wine by-product additives have always shown an enhancement of the stability of the polymer matrixes without compromising or modifying significantly their thermal or mechanical proprieties. In the present work, three different solid wine by-products (peels, stalks and seeds) and a commercial seed extract powder, with a high polyphenol concentration, have been tested as additives on polypropylene (PP). The direct use of different wine by-products as antioxidant additives is investigated and compared with the commercial seed extract powder in order to estimate the effect of the polyphenol concentration on the efficiency of the stabilization, and therefore, to justify or not expensive extraction operations. PP has been chosen as polymer matrix because of its radical thermal and thermo-oxidative degradation mechanism [34], its huge production (Table 1), and the high cost of the synthetic stabilizers classically mixed with PP. Therefore, despite the high-efficiency of synthetic antioxidants (e.g. Irganox 1010) [31], natural antioxidants can represent a valid alternative because of their environmentally and cost-effects advantage.

2. Materials and methods

2.1. Materials

Un-stabilized isotactic PP (MFI 12 g/10 min) has been kindly supplied in the form of a reactor powder by LyondellBasell. White and red grape peels (Pe), white grape stalks (St) and white and red seeds (Se) from wine processing wastes, and the commercial seed tannin extract powder (T) have been obtained from the winery Cevico Group S.R.L, Lugo (RA), Italy during the 2016 harvest and wine-making.

Materials have been labelled as follow: PP XY, where X is a number indicating the % in weight of the additive, and Y is the letter(s) indicating the additive typology. “PP powd” and” “PP proc” refer to the virgin PP powder and to the processed PP respectively.

2.2. Additive characterization

Solid wine wastes have been hand-washed with distilled water and a cloth in order to remove smug and other impurities. Then they have been dried in oven at 65 °C, monitoring at regular intervals the weight, until it has been constant (48h) and final moisture has been calculated in this phase. Despite the drying treatment can affect the composition and the structure of the wastes it is reasonable to suppose that at 65 °C no relevant chemical modification occurs, especially regarding the polyphenol content [35]. Finally, dried wine wastes have been grounded in a batch analytical mill with liquid nitrogen. The different powders have been manually sieved and different granulometry observed.

For each powder, solvent extraction has been conducted. The extraction has been carried out for 90 min at 55 °C; the solvent/solid ratio has been of 2 ml g^{-1} and the used solvent has been ethanol. The total polyphenol content of these extracts has been kindly evaluated by Cevico Group S.R.L, Lugo, Ravenna. Extracts have been properly diluted with distilled water and the absorbance has been directly read at 280 nm in a UV/VIS Jasco V-730 spectrophotometer. Total polyphenol content has been expressed as weight percentage referring to the dry matter, and as equivalent tannic acid. For this step, a calibration curve obtained with different concentration tannic acid solution has been used.

2.3. Samples preparation

Additives have been added at 6% by weight with PP in a Haake Polylab Rheomix internal mixer. Virgin PP powder has been processed in the same conditions to obtain the reference sample for comparisons. Operating conditions have been: 10 min of mixing, 180 °C and 32 rpm as rotors speed. The as obtained mixed materials have been used for DSC and stability measurements. Suitable specimens have been obtained by hot pressing (Carver hot plate hydraulic press) for the SEM and DMA analysis and by injection moulding (MegaTech Tecnica DueBi injection moulding machine) for determination of tensile proprieties.

2.4. Experimental techniques

2.4.1. Thermal properties

Thermal proprieties have been evaluated by Differential Scanning Calorimetry (DSC). DSC measurements have been performed by a DSC TA 2010, using 8 ± 1 mg of sample. The chamber has been purged by nitrogen at 50 ml min^{-1}. Each sample has been firstly heated from 25 °C to 200 °C at 20 °C min^{-1}, to erase the previous thermal history. Therefore, after 2 min, samples have been cooled from 200 °C to 25 °C at 20 °C min^{-1} and then, after 2 min, re-heated from 20 °C to 200 °C at 20 °C min^{-1}. The crystallization temperature T_c and crystallization enthalpy H_c have been measured in the cooling cycle, while melting temperature T_m and enthalpy of fusion H_m have been obtained in the second heating cycle. The enthalpy values have been calculated considering the weight fraction occupied by additives. Crystallinity percentage has been evaluated considering the value of 208 J g^{-1} (average of [36,37]) for the 100% crystalline PP melting enthalpy.

2.4.2. Mechanical properties

Tensile tests have been performed by means of the INSTRON 5567 dynamometer equipped with a 1 kN load cell and a 25 mm extensimeter. Dumbbell-shaped specimens according to technical

Table 2
Additives' diameter, moisture content (%), total polyphenol content (TP) and TGA data.

Material	Diameter [mm]	TP [% wt.]	Moisture (%)	Nitrogen atmosphere		Oxygen atmosphere	
				$T_{15\%}$ [°C]	Res_{650}[%wt]	$T_{15\%}$ [°C]	Res_{650}[%wt]
Se	0.75	0.95	24	267	31.0	261	3.6
Pe	0.35	0.64	47	192	29.2	190	6.0
St	0.20	1.40	22	208	32.0	209	8.3
T	0.15	30.0	–	269	49.8	268	1.1