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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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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 (TGA), Oxidative Induction Time (OIT) and Oxidative Onset Temperature (OOT) measurements have been conducted to investigate the thermo-oxidative stability. Tensile tests, Dynamic Mechanical Analysis (DMA) and Different Scansion Calorimetry (DSC) have been conducted on the samples in order to evaluate the effect of the additives also on the thermal and mechanical proprieties. Scanning Electroscopic Microscopic (SEM) 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 proprieties 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 their environmentally and cost-effects advantages.

Keywords: winemaking by-products; thermal and processing stability; polypropylene; natural antioxidants; polyphenols

1. Introduction

In the last decade, the valorization 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 behavior, 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 pre-treatments 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 valorization 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 hemorrhoid products [19]), and in the food and beverage (to inhibit oxidation of oils during storage or frying, to inhibit lipid oxidation or to preserve color of some fresh meats [20-22]).

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.

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 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 (RA). 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 Sample preparation

Additives have been mixed 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 minutes of mixing, 180 °C and 32 rpm as rotors speed. The mixed materials have been used for thermal and stability measurements, processed in a hot plate hydraulic press (Carver) to obtain rectangular samples used for the SEM analysis and for DMA tests and processed by injection molding to obtain specimens for mechanical characterization of tensile proprieties.

2.4 Experimental techniques

2.4.1 Thermal proprieties

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 have been firstly heated from 25°C to 200 °C at 20 °C min⁻¹, to erase the previous thermal history. Therefore, after 2 minutes, samples have been cooled from 200°C to 25°C at 20 °C min⁻¹ and then, after 2 minutes, re-heated from 20°C to 200°C at 20°C/min. The crystallization temperature T_c and crystallization enthalpy T_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 proprieties

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 standard ISO527 (type 1BA) have been used. Tests have been performed at room temperature with a 10 mm min⁻¹ clamp separation rate. The reported data are the average values of at least six determinations.

TA DMA Q800 instrument in the single cantilever flexural configuration has been used to evaluate the dynamic mechanical behavior of the different samples. Sizes of the rectangular specimens have been 2×10×17 mm³. The tests have been run at a heating rate of 3 °C min⁻¹ from -40 °C to 80 °C. Oscillation frequency and strain have been 1 Hz and 0.1%, respectively. Glass transition temperatures (T_g) have been evaluated as the maximum value of the tan δ curves. The creep proprieties of the samples have been also measured on the same instrument with same size specimens. The creep tests have been carried out at temperature ranging from 20 °C to 80 °C at 20 °C temperature increments. At each temperature, samples have been firstly loaded for 10 min by 1 MPa stress and then followed by a 20 minutes relaxation. Master curves have been generated from the creep data using the William-Landel-Ferry (WLF) equations at a reference temperature of 20 °C.

2.4.3 Morphological proprieties

Morphology, adhesion, distribution and dispersion of the additives on the samples, have been observed with an environmental Scanning Electron Microscope, SEM (ESEM Quanta FEI 2000). Rectangular specimens, identical to the ones used for the DMA analysis, have been broken in liquid nitrogen. The cross section of the specimen has been covered by a 10 nm thickness gold layer (Gold Sputter Coater – Emitech K550). The obtained surfaces have been observed with the SEM operating in low-vacuum conditions.

2.4.4 Thermal stability behavior

The thermal stability of samples has been investigated by Oxidation Induction Time (OIT) and Oxidation Onset Temperature (OOT) tests performed with the TA DSC 2010 and by thermogravimetric analysis (TGA) performed with the TA TGA Q50.

OIT values have been measured in open Al pans, containing 4.8 ± 0.5 mg of sample. The material has been then heated under nitrogen flow (50 ml min⁻¹) with a rate of 15 °C min⁻¹, from room temperature to the set temperature (200 °C or 175 °C), and after 6 min of isothermal the purging gas have been switched to air. The heat flow has been recorded in isothermal conditions as function of the time. The beginning of oxidation has coincided with the sudden increase of the slope of the exothermal heat flow. The time interval elapsed between the gases switch and the exothermic degradative peak has been considered as the OIT, and it has been evaluated by the tangent method according to the ISO 11357-6.

OOT values have been also measured in open Al pans, containing 4.8 ± 0.5 mg of sample. After 5 min of room temperature isothermal under nitrogen flow (50 ml min⁻¹), heating has been started at 20 °C min⁻¹ and in the same moment, nitrogen has been switched to air. OOT has been evaluated as the temperature at which begin the increase of slope of the exothermal degradative peak.

Thermogravimetric analysis (TGA) have been conducted on 15 ± 5 mg of sample using a ramp temperature of 15 °C min⁻¹ from 50 °C to 650 °C. Tests have been conducted both in inert atmosphere (nitrogen, 50 ml min⁻¹) and in oxidative atmosphere (oxygen, 50 ml min⁻¹). Temperatures at 5 wt.% loss ($T_{5\%}$) and at 15 wt.% loss ($T_{15\%}$), residues at 650 °C (Res_{650}) and the peak temperatures of the degradation (T_{peak}) have been extrapolated from the graphs for both atmosphere conditions. T_{peak} is the temperature at which the maximum of the derivate of the weight in respect to temperature is observed.

3. Results and discussion

3.1 Additives' characterization

Table 2 reports the additives' mean size diameter, the total polyphenol content (TP), the moisture data (% w/w) and the TGA data of temperatures at 15 wt. % loss ($T_{15\%}$) and of percentage residue at 650 °C (Res_{650}) of wine by-products additives under nitrogen and oxygen atmosphere, respectively

Table 2

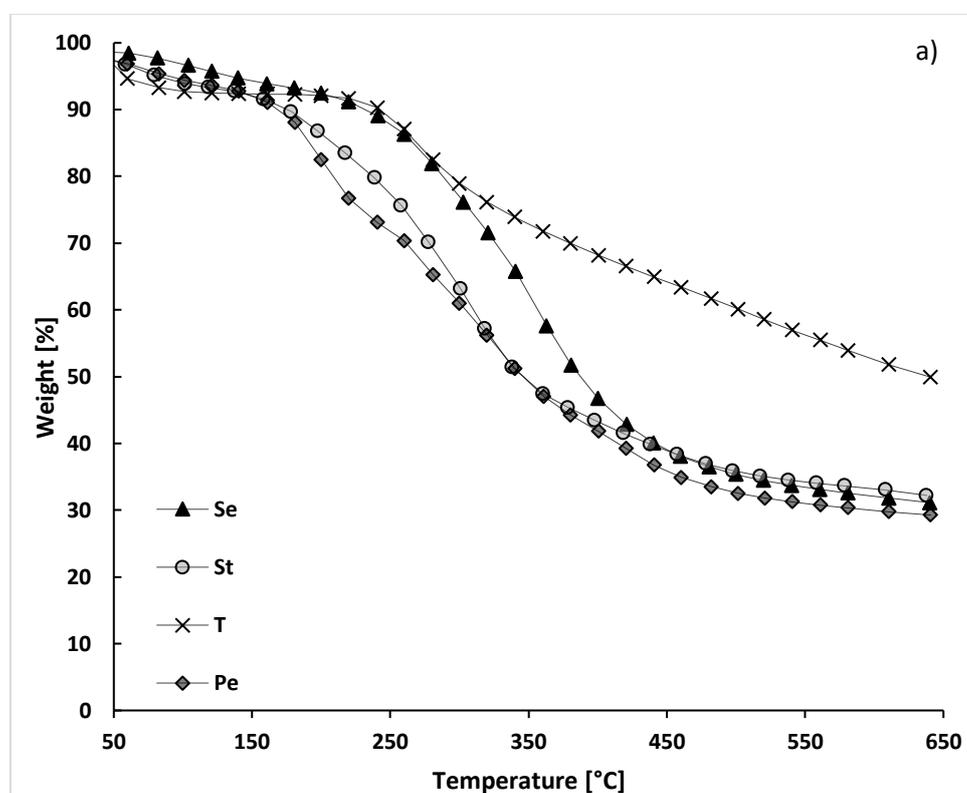
Additives' diameter, moisture content (%), total polyphenol content (TP) and TGA data

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

Additives show no differences regarding the mean size diameter except for the seed (Se) powder that exhibits the highest value, and this can be explained by the important presence of both oleic and linoleic acids [38] in the wine seeds that can aggregate the particles. The total polyphenol content of each wine by-product (Se, St, Pe) is approximately around at 1% wt, while the commercial seed tannin extract (T) has a concentration of polyphenols equal to 30% wt. Despite both extraction conditions and total polyphenol evaluation method can affect the result and be more or less suitable according to the investigated substance characteristics [4, 39], the deep gap evaluated between by-products and commercial powder does not leave room to doubts in this case. Table 3 shows the other constituents typically present in the wine wastes. Despite these data have not been obtained by the wine wastes used in this work, it is reasonable to believe that the eventual differences are not bigger than the ones that exist in the same wastes from one year to another. In Fig. 1, TGA curves under nitrogen and oxygen respectively are reported. It is possible to notice that seeds “Se” and tannin extract “T” start their weight loss at about 60-70 °C later than stalks “St” and peels “Pe”. $T_{15\%}$ of each additive is the same whatever the purging gas and always higher than the PP melt temperature. For this reason, wine additives are stable to thermal oxidation and are suitable to be mixed with the PP. The wine by-products additives residues at 650 °C under nitrogen are about 30-50 % in weight (Table 2), while residues of 1-8 % wt. are observed under oxygen. This gap is due by the combustion in presence of oxygen of the organic additives that leads to an instantaneous and huge loss of weight (Fig. 1b). Stalks “St” is the additive that suffer earlier this phenomena (at about 250 °C) because of its important composition of cellulose, hemicellulose and lignin [40].

Table 3
Main constituent present in the different solid wine wastes.

Peels [41, 42]		Seeds [42-44]		Stalks [40, 45]	
Constituent	[% w/w]	Constituent	[% w/w]	Constituent	[% w/w]
Ash	2-8	Carbohydrates	11.8	Ash	6-9
Carbohydrates	12.5	Complex phenolic compounds	7	Cellulose	20-30
Dietary fiber	60	Dietary fiber	40-50	Hemicellulose	3-20
Lipids	5	Lipids	15	Lignin	17-26
Protein	5-12	Protein	11	Protein	6
Soluble sugars	1-70			Tannin	16



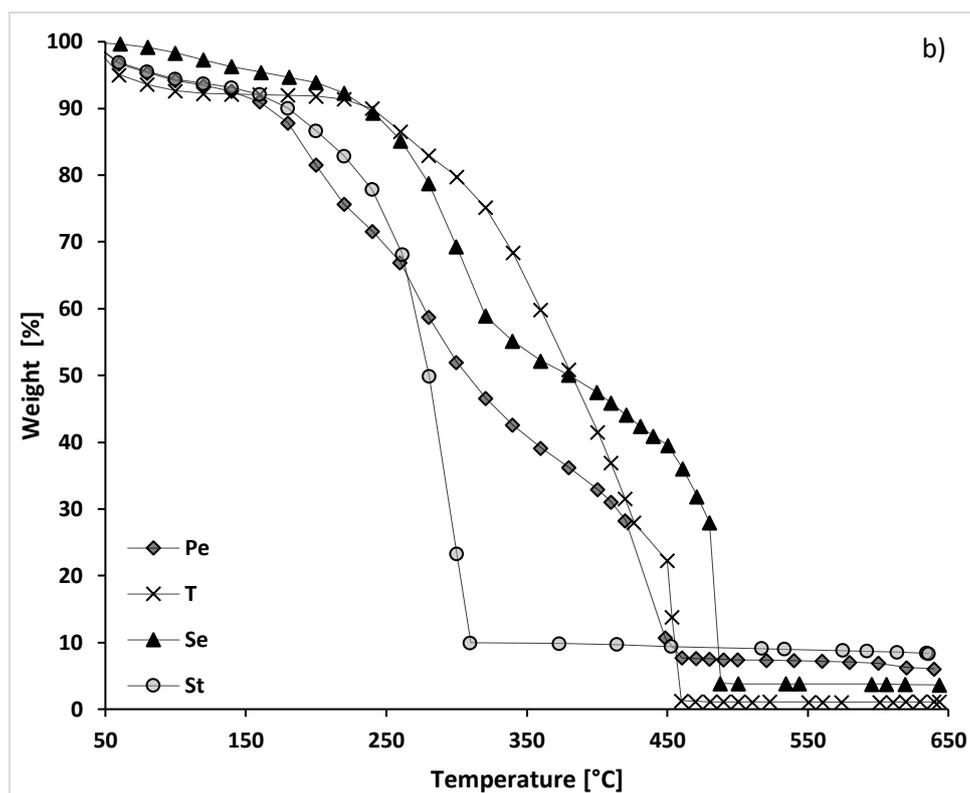


Fig.1 TGA curves of wine wastes derived additives: a) under nitrogen gas flow; b) under oxygen gas flow.

3.1 Thermal properties: DSC

Fig.2 reports the DSC curves of the cooling step after the thermal history reset and the second heating scan of the different compounded materials. Table 4 lists for each material the crystallization temperatures T_c and the melting temperatures T_m and melting enthalpies H_m and crystallization enthalpies H_c . Referring to curves of Fig.2, it is evident that the crystallization and melting phenomena are not significantly influenced by the presence of the additive. Moreover, also the typology of wine waste derived additive does not exhibit any particular behavior. Table 3 shows how the T_c s of compounded materials are lower than PP one, but the maximum deviation (“Se”) is limited to 2.1 °C. T_m s are always higher, but also in this case never more than 1.5 °C (“Pe”). These facts demonstrate how characteristics transition temperatures of PP are not affected by the natural additives in accordance to other similar work with PP [30]. Melting enthalpies of compounded materials are lower than the one of neat PP as well as the percentage of crystallinity that results 15% lower than neat PP. The decreasing of the crystallinity is in perfect accord with a similar study on PHB where crystallinity of compounded materials has been observed 10% lower of the neat polymer [32].

Table 4

DSC data comparison between neat PP and compounded PPs.

Material	T_c [°C]	H_c [J g ⁻¹]	T_m [°C]	H_m [J g ⁻¹]	% Crystallinity
PP powd	115.1	100.6	165.6	145.8	70
PP 6Se	113.0	94.0	166.7	106.4	55
PP 6St	113.4	93.7	167.6	109.4	56
PP 6Pe	113.7	104.3	167.1	115.0	59
PP 6T	114.7	100.7	165.7	112.6	58

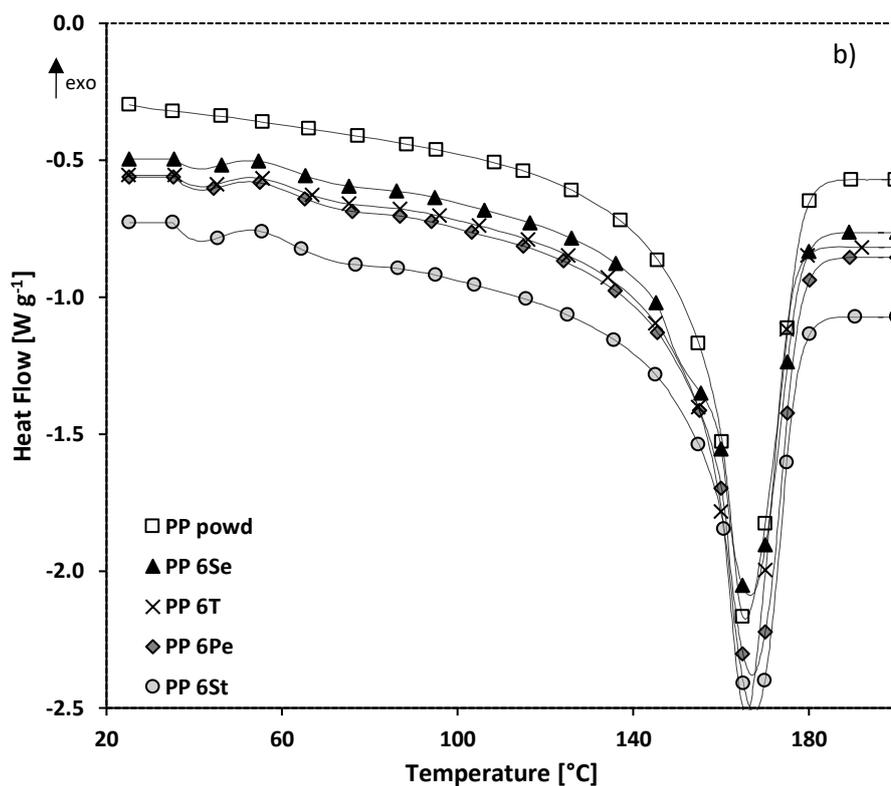
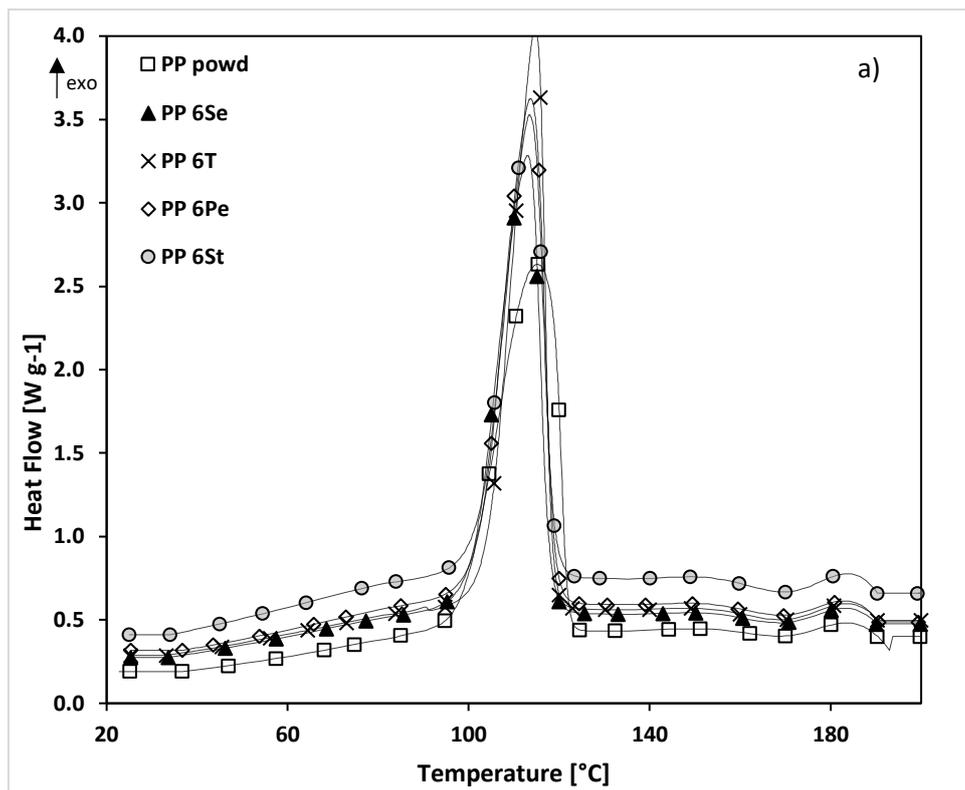


Fig.2 Cooling step (a) and second heating scan (b) of “PP powder” and PP based samples.

3.2 Mechanical proprieties: DMA, creep tests, tensile tests.

Table 5

Glass transition temperatures (T_g), storage modulus at different temperatures (E'), Young modulus (E), tensile strength (σ_Y) and yield strain (e_Y).

Material	T_g [°C]	E' Storage Modulus [MPa]				E [MPa]	σ_Y [MPa]	e_Y [%]
		-20 °C	0 °C	25 °C	60 °C			
PP powder								
PP 6Se								
PP 6T								
PP 6Pe								
PP 6St								

PP proc	7.6	3460	2779	1749	1036	1544 ± 191	31.9 ± 0.9	8.6 ± 0.7
PP 6Se	8.1	4358	3568	2371	1355	1310 ± 320	27.3 ± 0.8	9.0 ± 0.7
PP 6St	12.1	3762	3218	2111	1224	1680 ± 249	30.8 ± 0.5	7.1 ± 0.5
PP 6Pe	8.7	3865	3113	2032	1134	1602 ± 280	28.6 ± 0.7	7.6 ± 0.9
PP 6T	14.8	3290	2899	1925	1201	1460 ± 149	29.7 ± 0.7	7.8 ± 0.3

In Table 5 the glass temperatures (T_g) and the storage modulus (E') at different temperatures (-20, 0, 25, 60 °C) obtained by DMA as well as the Young's Modulus (E), the yield strength (σ_Y) and yield deformation (ϵ_Y) values obtained by tensile tests are reported. From Table 4 is also possible to assert that additives slightly increase the T_g values leading to a stiffening of the amorphous phase of PP. Among all the additives, tannin extract powder "T" is the additive that more affects the glass transition temperature compared to "PP powd" (+ 7 °C), while seed and peel additives are the less influential. The improved stiffness of the material could be explained by the restriction of the chain mobility of the PP through the formation of hydrogen bonds between additive's hydroxyl and polymer's carbonyl groups formed by oxidation during the internal mixing and the press-molding steps [46, 47]. This fact is also confirmed by the storage modulus E' values that result always higher than the neat PP ones for each different temperature. The additive "Se" shows the highest storage modulus values and this could appear in contrast with data obtained by tensile tests, where additive Se exhibits the lowest yield strength value σ_Y (-14.4%). Nevertheless, the different processes used for the preparation of DMA and tensile test specimens (press molding and injection molding, respectively) do not allow justified comparisons. Concerning yield strength values σ_Y , compounded materials show practically the same values of the neat PP and the slight decrease can be probably explained by the reduced crystallinity of the filled samples. The Young Modulus E and elongation at yield ϵ_Y values are again not significantly altered and again additive "Se" lead to a slightly more ductile material, while others additives to a slightly stiffer material. Nevertheless, no important differences on mechanical proprieties and among additives are observed. Conversely, creep resistance is noteworthy enhanced by the natural wine derived additives. In Fig.3 the compliance values obtained after 10 minutes ($J_C, 10 \text{ min}$) creep tests at four different temperatures (20, 40, 60, 80 °C) are shown. As expected, an increase in temperature have been resulted in higher chain mobility and then in high creep deformations for all materials [48], but it is interesting to notice that from 60 °C the difference between neat PP and the others samples starts to increase. If no different behavior is observed at 20 °C and 40 °C, it is clear how wine-additives increase creep resistance of PP at higher temperature. In particular, seed additive "Se" implies the best creep resistance for any temperatures.

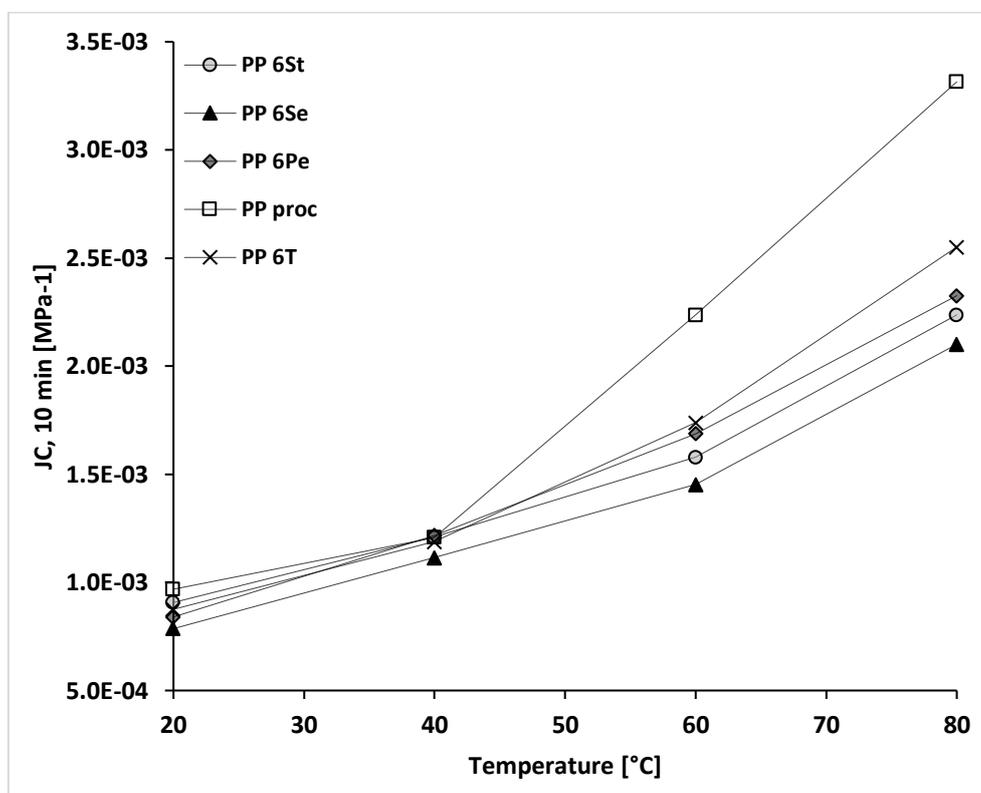


Fig.3. Values of compliance after 10 minutes as function of temperature for unfilled and filled PP samples.

In order to predict compliance behavior as longer times function time-temperature superposition principle has been applied to creep test data. In Fig.4, master curves of PP-based samples at 20 °C are reported. Observing the plot, is possible to notice two different zones: the first one, delimited from 0 to 4 abscissa's range, where PP mix values are slightly higher than compounded materials but the slopes of the lines are practically identical. This is concordant with the data plotted in Fig.3 where not relevant difference material behaviors were observed for short times and low temperatures. In the second zone (4-10 abscissa's range), the slope of the PP mix curve increases considerably and the compliance gap between unfilled PP and wine by-product additive filled PP become higher. As expected, seed additive "Se" is again the best additive that guarantees lowest compliance values. Creep tests show how wine by-products additives improve creep resistance of PP both in time and in temperatures and that the benefit become more and more important increasing temperatures or for longer times.

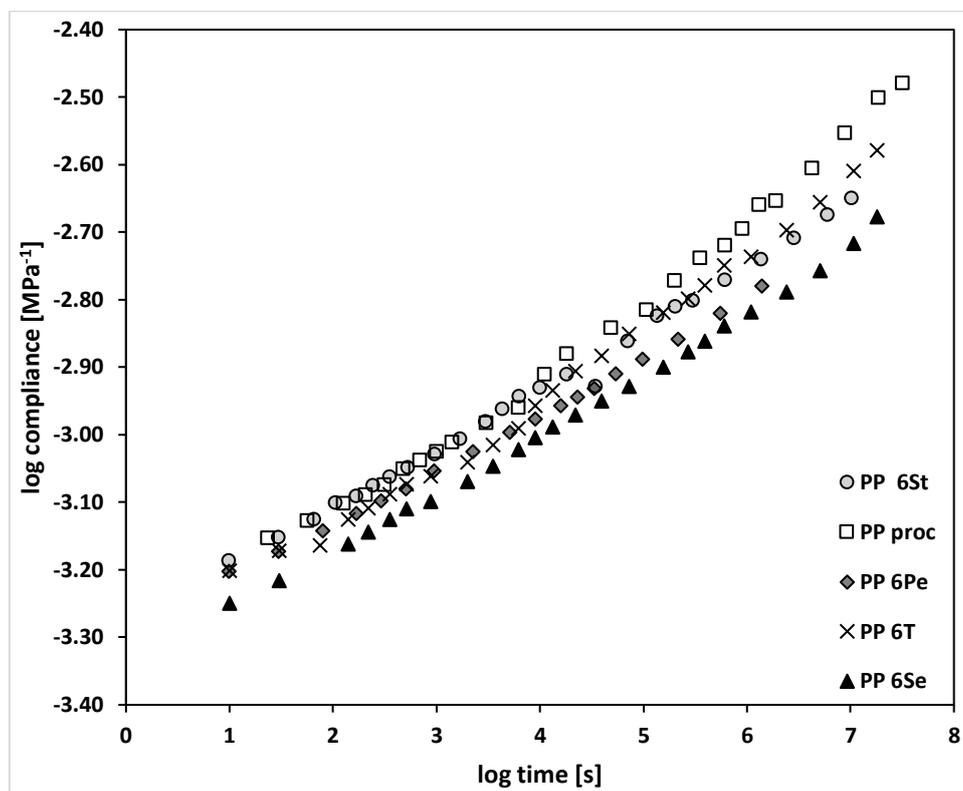


Fig.4 Creep behavior: master curves of filled and unfilled PP through time-temperature superposition principle at 20 °C.

3.3 Morphology: SEM

In Fig.5, scanning electron micrographs of the morphology of PP mix and PP with wine by-products additives are shown. The micrographs give important information about the distribution and dispersion of the additives and their adhesion to PP matrix. The images captured at lower magnifications (200×, 400×, upper row of Fig.5) show how the additive is dispersed in the PP matrix; they are not easily distinguishable and the morphology of the surface appears not modified and similar to the unfilled PP one. Moreover, they result uniformly distributed and aggregation or preferential additive's zones are not observed. Increasing the magnification (from 800× to 2000×, lower row of Fig.5), is possible to investigate the structure of the additive and the adhesion between the PP and additive surfaces. In each case, the additive is well connected with the PP matrix and no adhesion problems are remarked despite the polarity of the additives surface groups and the non-polarity of the PP chain [49]. Stalks additive "St" (Fig.5 B) and tannin extract additive "T" (Fig.5 D) show the best adhesion with the PP matrix, probably because of their minor particle's sizes. As expected from a natural source, the structures of additives are various and is not possible ascertain any typical shape both among different additives and the same additive typology.

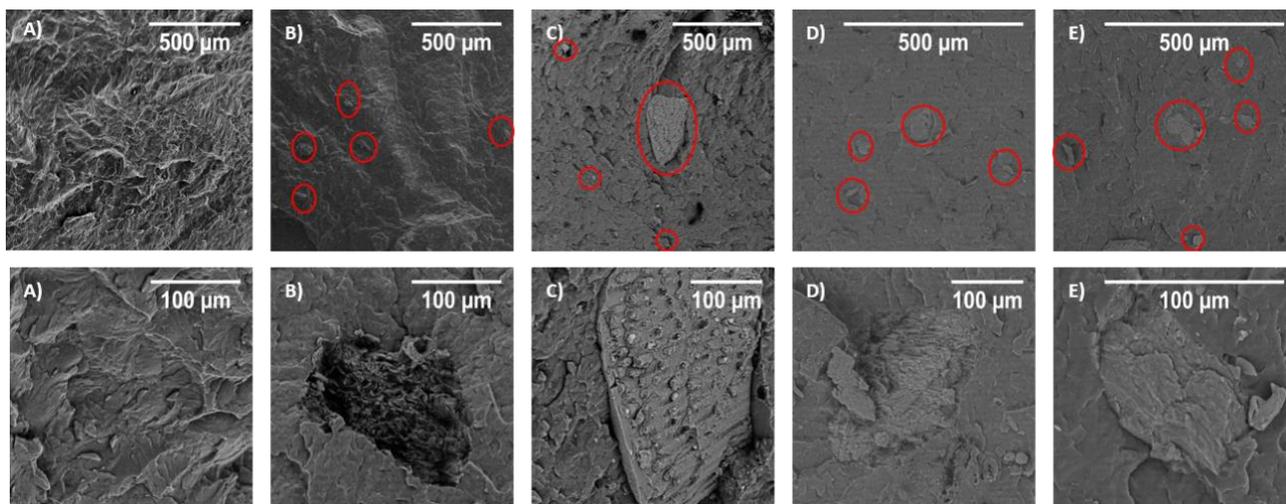


Fig.5 SEM images of: A) PP proc, B) PP 6St, C) PP 6Se, D) PP 6T, E) PP 6Pe. The upper row shows images captured at lower magnifications; the lower row at higher magnifications.

3.4 Thermal stability: OIT, OOT and TGA

OIT is one of the most reliable and commonly used test for the evaluation of polymer thermal stability, especially for polyolefins [50]. There is a direct correlation between OIT values and stability: higher OIT values involve more stable materials. In this work, OIT have been investigated at 175 °C and 200 °C, two temperatures higher than the PP melting temperature in order to verify the effect of the additives on the thermal stability during typical processing conditions of PP. For this reason, despite the fact that oxidation is a surface phenomenon, the shape of the sample has been not relevant: at the selected temperatures, materials were melt and so, identical surface have been supposed with criteria.

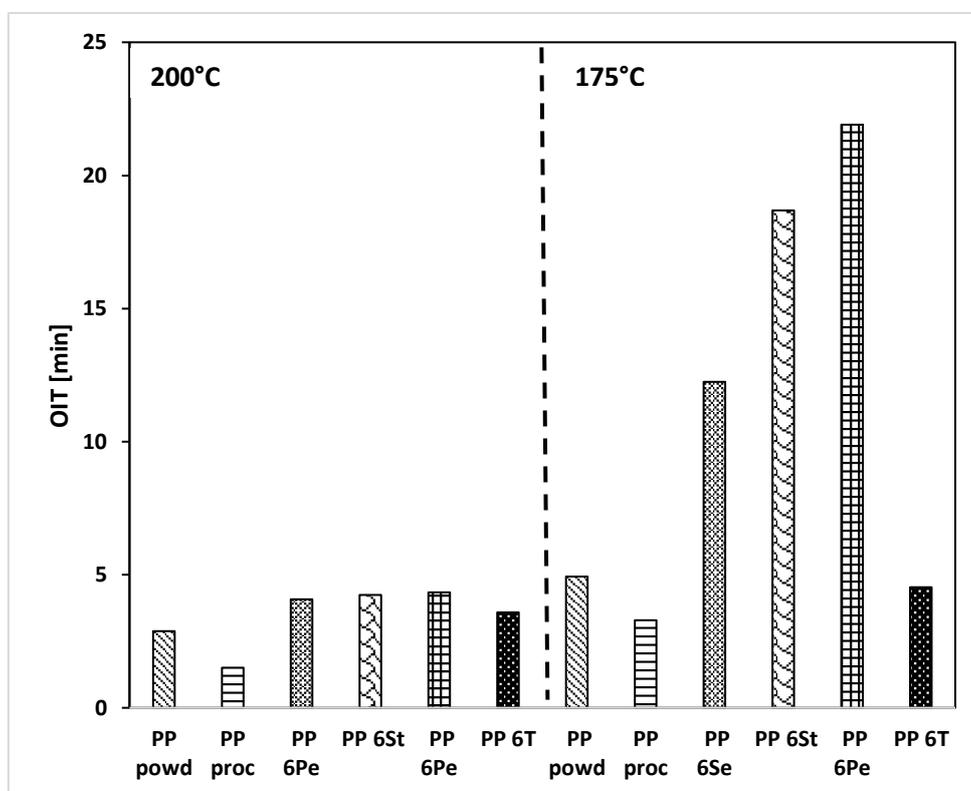


Fig.6 OIT values measured by DSC at 200 °C and 175 °C of PP powd, PP proc and the others PP-based materials under airflow.

Fig. 6 shows the OIT values of the different tested materials for the two temperatures. In this tests two different PP have been used: 'PP neat' intended here as virgin powder and 'PP mix' intended as PP processed in the same way of the others PP based materials. This distinction allows observing the degradation quota due to the material processing since 'PP mix' values are lower than the 'PP neat' ones, as expected. All the additives lead PP to a higher thermal stability as confirmed by the always

higher values at both temperatures. The gap between wine by-products based PP and ‘PP mix’ OIT values is not exceptional at 200 °C but considerably increases at 175 °C. At higher temperatures, in fact, the major heat generate more and faster free radicals that probably could be not contrasted by wine wastes additives. They are synthesized in nature to withstand with lower temperatures, and some part of the could have been lost due to the high temperatures [31]. Anyway, for the same reasons, is possible to affirm also the contrary which means that at lower temperatures (and at 175 °C is already noteworthy) the OIT values gap should increase as confirmed by other similar works [31]. Among all the additives, peels “Pe” is the best one, but also stalks “St” and seeds “Se” guarantee excellent results. It is interesting notice that seed tannin commercial extract “T” does not significantly improve the PP stability. This fact is unexpected because the great polyphenol concentration of “T” respect to the other additives. Therefore, the obtained results show how the polyphenol quantity does not ensure better results and how polyphenol structure plays a central role for the stability’s optimization. Anyway, this result could be of primary interest for industry, since not particular waste treatments or extractions are required to enhance the PP stability. Fig. 7 shows OOT values and again, the effect of additive on thermal stability is confirmed. Onset degradative temperature of “PP powd” is enhanced by 20-25 °C by all wine wastes additives and again is possible to see the effect of the melt processing on the PP stability comparing the “PP powd” OOT value with the “PP proc” one. As opposed to the OIT results, the gap between the efficiency of the additives is limited and “T” exhibits the best performance. Table 6 shows the comparison between the OIT and OOT values.

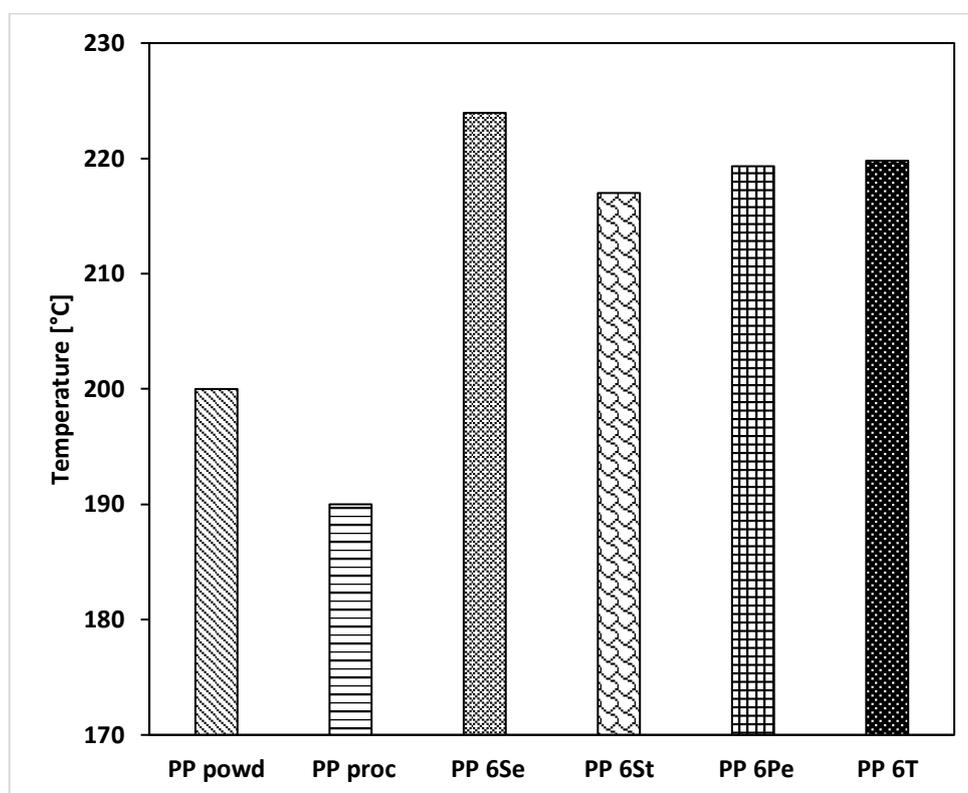


Fig.7 OOT values measured by DSC of PP neat (powder), PP mix (processed) and the others PP based materials under airflow.

Table 6

OIT and OOT data of PP based samples.

Material	OIT [min]		OOT [°C]
	175 °C	200 °C	
PP powd	4.93 ± 0.57	2.88 ± 0.22	200.4 ± 3.6
PP proc	3.29 ± 0.63	1.51 ± 0.16	190.3 ± 5.0
PP 6Se	12.25 ± 1.62	4.08 ± 0.25	223.7 ± 4.5
PP 6St	18.69 ± 1.74	4.24 ± 0.29	217.7 ± 2.1
PP 6Pe	21.91 ± 1.37	4.34 ± 0.47	219.3 ± 5.2
PP 6T	4.53 ± 0.72	3.59 ± 0.1	219.7 ± 3.8

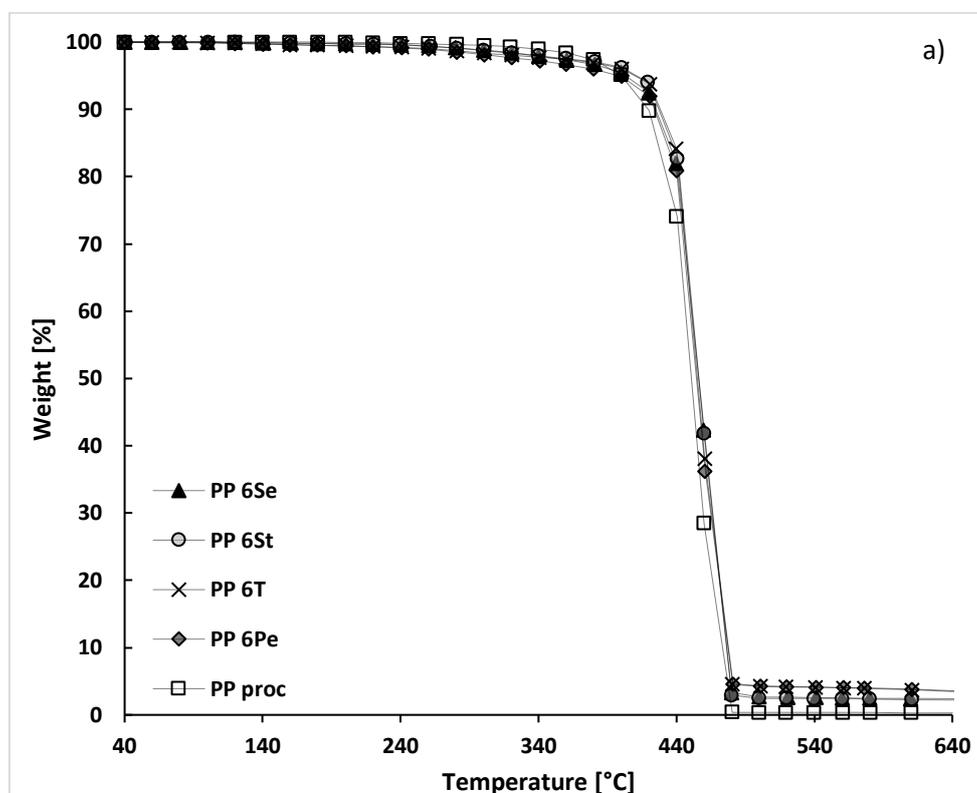
Table 7 shows the temperatures at 5 wt. % loss ($T_{5\%}$) and at 15 wt. % loss ($T_{15\%}$), residue at 650 °C (Res_{650}) and temperature of the degradation peak in the T-dW/DT curves (T_{peak}) of wine by-products additives and PP based samples under nitrogen and oxygen atmosphere.

Table 7

Temperatures at 5wt.% (T5%) and at 15wt.% loss (T15%), residue at 650 °C (Res650) and temperature of the degradation peak in the T-dW/DT curves (T_{peak}) of wine by-products additives and PP based samples under nitrogen and oxygen atmosphere.

Material	Nitrogen atmosphere				Oxygen atmosphere			
	T _{5%} [°C]	T _{15%} [°C]	Res ₆₅₀ [% wt]	T _{peak} [°C]	T _{5%} [°C]	T _{15%} [°C]	Res ₆₅₀ [% wt]	T _{peak} [°C]
PP powd	424	442	1.0	468	240	260	1.0	283
PP proc	401	429	0.3	457	219	236	0.2	276
PP 6Se	405	436	2.4	462	238	255	0.7	290
PP 6St	413	438	2.2	461	237	253	1.2	286
PP 6Pe	399	435	3.5	460	241	257	0.9	301
PP 6T	413	439	3.4	460	240	265	0.8	327

In Fig.8 the TGA curves of PP based samples are reported. Both in nitrogen and in oxygen, samples degrade in a single weight loss step close to 460 °C (nitrogen) and 300 °C (oxygen). The thermogravimetric curves of the filled samples have a trend comparable and similar to that of the pure PP but it is noteworthy underline that the curves of PP based samples under oxygen are shifted to the right by about 20-40 °C presumably thanks to the electron donation of the wine by-products additives. In Table 5, it is also possible to observe the difference of values between “PP powd” and “PP proc” that indicates again the degradation process occurred to PP inside the internal mixer. Additives “T” and “Se” are the most efficient stabilizers. Anyway, the observed slight gap between them do not suggest expensive extraction procedures on the seeds. Comparing the OIT and OOT results with the TGA ones emerges a noteworthy consideration. Under the isothermal conditions (OIT tests) peels “Pe” and stalks “St” lead to the best results, while in non-isothermal conditions (OOT and TGA) seeds “Se” and tannin extract “T” result the best choice. It could be supposed that also the conditions of degradation affect the efficiency of these natural antioxidants and data would seem tell that “Pe” and “Re” are more suitable for lower temperatures and longer times, while “T” and “Se” for higher temperatures and shorter time. In conclusion, TGA data confirm that each wine waste derived additive enhances the PP stability against the thermo-oxidative degradation, and that not significant differences are relieved among the different wine additives used in this work.



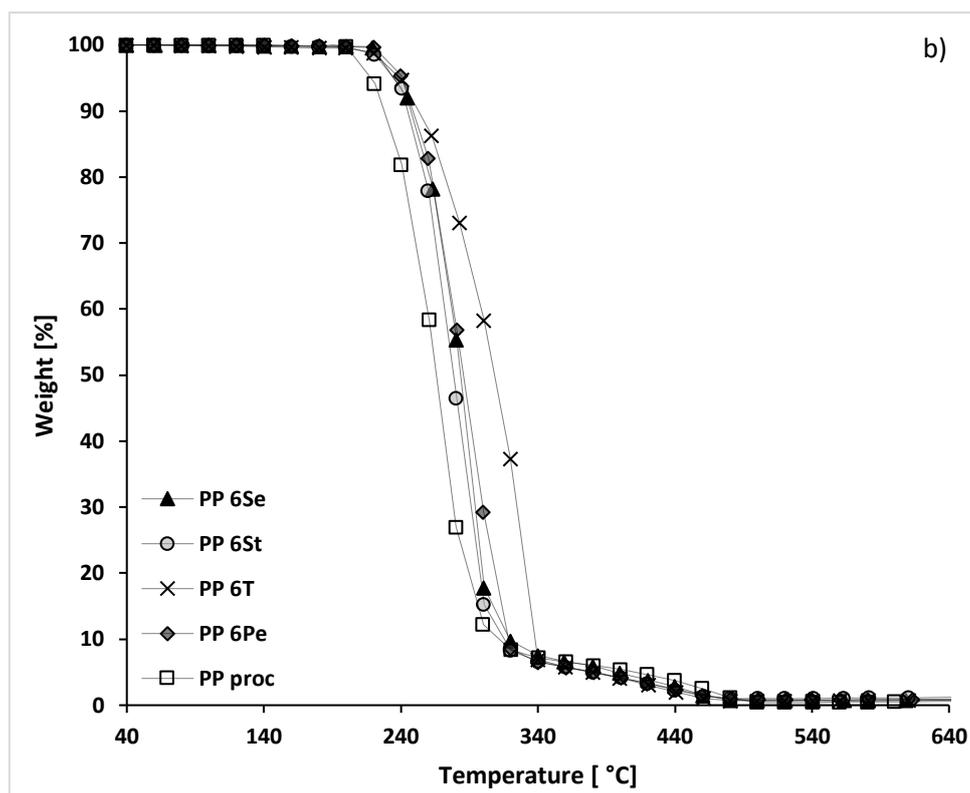


Fig.8 TGA curves of PP based samples: a) under nitrogen gas flow;b) under oxygen gas flow.

4. Conclusions

The use of wine-waste derived additives has been found to be very effective to improve the thermal stability of the PP, increasing its processing window. In fact, wine by-products additives have been able both to increase the OIT and OOT values of PP, typical parameters used for polyolefin stability determination, and to shift the TGA curve to higher temperatures, contrasting the random radical scission degradation behavior of the PP matrix. Among the additives, seed tannin extract “T” has been the less performant in the OIT tests, but the most performant in the TGA and OOT tests opening new interesting questions concerning both the role of natural polyphenol structure in stabilization and the degradative conditions affecting the natural stabilizers. Anyway, what has been gained in OOT and TGA by the use of the extract powder “T” is not enough to justify extraction procedures for large scale operations. No important differences on OIT and TGA values have been observed among others additives. This fact implies no need of waste separations and makes wine by-products additives low-cost stabilizers suitable for large-scale processes. The images captured by SEM have demonstrated the perfect adhesion and homogenization between additives and PP matrix despite their different polarity. This fact have emerged also in the mechanical proprieties characterization, where no significant differences between unfilled PP and filled PPs have been found. Overall, the reported results demonstrate the possibility to convert an agro-food by-product into a bio-additive able to improve the thermal stability of PP without compromising its mechanical and thermal proprieties, in an environmentally friendly and cost-effective way.

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