Thermal and UV aging of polypropylene stabilized by wine seeds wastes and their extracts

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A commercial tannin wine seed extract powder (T), a seed polyphenol extract (Sext) and virgin wine seeds wastes (Se) have been mixed with polypropylene (PP) and tested as long-term stabilizers. Their stabilizing activity has been compared with that of a synthetic antioxidant commonly used within PP (Irganox 1010). Each sample has been subject to both UV and thermal aging. The PP-based films photo-oxidation has been followed through the C=O formation over the aging time by FT-IR. The PP-based tensile specimens have been oven aged and the mechanical properties loss have been investigated monitoring the variation of the elongation at break. Melt Flow Index (MFI) measures and Different Scanning Calorimetry analysis have been conducted on thermal aged samples. At the same time, wine derived additives have been characterized in terms of total polyphenol content, FT-IR and UV/VIS spectra meanwhile catechin and gallic acid have been quantified by LC-MS. Experimental results have evidenced the ability of all the wine derived additives to withstand both to thermal and UV long-term degradation. In particular, wine seeds extracts exhibit the best results in terms of stabilization (even better than Irganox 1010) without compromising the PP mechanical, thermal, morphological and rheological properties.

Keywords: winemaking by-products; thermal and UV aging; polypropylene; natural antioxidants; polyphenols; long-term stability

1. Introduction

In the last decade, the valorization of agro-industrial by-products or wastes 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. Because of both its dramatic and expanding pollution [1, 2] and the increasing crude oil price [3, 4], plastics industry is one of the sector that has started more to need new eco-friendly solutions able to replace the conventional petro-chemical products. Therefore, many attempts to utilize the agro-industrial wastes within the plastic world have been carried out in the recent past usually following three different valorization approaches. The first one has provided the use of natural by-products as new feedstocks for the synthesis of different biopolymers (biodegradable and not) as poly-lactic acid (PLA) [5-10] , polyhydroxyalkanoates (PHAs) [11-14], bio-polyethylene (bio-PE)[15, 16] and poly(butylene succinate) (PBS) [17, 18] or for new green building blocks further suitable also for bio-based polymers production [19-21]. The second approach has been focused on the effect of the natural crops, used as reinforcing or cost-effective filler in percentages ranging from 5 to 50% in weight, on the properties of bio and synthetic polymer [22-27]. Finally, with the third approach, many authors have recovered useful fractions from the green agro wastes in order to exploit them as new different natural polymer additives such as bio-plasticizers [28, 29], bio-coupling agents [30] and especially as bio-stabilizers. In fact, agro-industrial crops are rich in polyphenols (fruits like berries, grapes and cherries can contain up to 2-3 mg of polyphenols for gram of fresh fruit [31, 32]), a family of compounds originated directly by plants and fruits as secondary metabolites generally involved in defense against ultraviolet radiation and/or aggression by pathogens [33]. Because of their high

antioxidant capacity, polyphenols have gained attention in many different industrial fields including the plastic sectors. In fact, thanks to their structure characterized by several phenol rings and hydroxyl groups they can be used as natural stabilizers against the polymer degradation. In particular, polyphenols are able to work as radical scavengers antioxidant by hydrogen donation and resonance stabilization, interrupting the degradative radical reaction of the polymer chains [34]. Within polypropylene, these natural primal antioxidants can donate an hydrogen atom to a polypropylene (R•), or alkoxy (RO•) or peroxy (ROO•) free radical to form a polypropylene (RH), alcohol (ROH) or hydroperoxide (ROOH) product [35]. Therefore, polypropylene (PP) and high and low-density polyethylene (HDPE, LDPE) have been stabilized by extracts derived from wine pomace, tomato wastes, orange peels, hazelnut skins, cocoa wastes or coffee grounds [36-42]. Similarly, biopolymers like poly(3-hydroxybutyrate) (PHB) or Materi-Bi® have been stabilized using again antioxidants derived from the winery industry [43, 44]. In our previous work [37], for the first time, three virgin wine wastes (peels, stalks and seeds) were directly tested as PP short-term stabilizers. The obtained results showed the wine by-products ability to enhance the PP short-term stability pointing out the possibility to use them as processing antioxidant. Moreover, no significant differences were noticed using the virgin wine wastes and a commercial wine seed extract richer in polyphenols, assigning the stabilization key-role to the polyphenols quality and typology over their quantity and promoting the use of cost-effective virgin wine wastes instead of their expensive extracts. These mentioned positive results have encouraged this work which is aimed to deal with two important aspects untreated or emerged in the previous work. Firstly, the ability of virgin wine wastes and their extracts to protect the PP also during its expected life-cycle (long-term stabilization) has been tested in order to evaluate the concrete possibility to use wine derived stabilizers in large scale. The efficiency shown in short-term tests can not guarantee alone the long-term stabilization a priori [45, 46], because the many differences arising in the degradation pathway (Table 1). Moreover, antioxidants could be also completely consumed during the processing step

leading to a final manufacture destined to lose its mechanical properties earlier than expected. Therefore, in this work virgin wine seeds (Se) (selected from previous work as most promising virgin wine waste), a wine seed polyphenolic "lab" extract (Sext) and a commercial wine seeds tannin powder (T) have been tested as long-term stabilizers within PP, investigating the response of PP based samples to UV and thermal aging and comparing their results with Irganox 1010 ones. Secondly, wine wastes and their extracts have been deeply characterized in order to observe and propose possible empirical relation between the polyphenols structures and moieties and the PP stabilization results.

Table 1

Differences in short and long-term degradation pathways [45].

Parameter	Processing [Short-terms]	Use [long-terms]
Load typology	Temperature; Mechanical stress	Temperature; UV rays
Load intensity	High	Low
Load times	Short	Long
Physical state	Liquid (melt)	Solid
Oxygen	Oxygen-poor	Oxygen-saturation
R• concentration	[R•] >> [ROO•]	[R•] << [ROO•]
ROOH concentration	Low	High

2. Material and methods

2.1. Materials

Pure isotactic polypropylene (PP) (without any kind of additives and stabilizers and with a MFI 8 g/10 min; 2.16 kg, 235 °C) has been kindly supplied in the form of a reactor powder by

LyondellBasell. Wine wastes seeds (Se) have been obtained from the winery Cevico Group C.V.C, Lugo (RA), Italy, during the 2017 harvest and wine-making processes. They have been collected both from white grapes (Mostosa) and red grapes (Sangiovese) in the same weight ratio (1:1). Irganox 1010 (Irg), catechin and gallic acid (HPLC grade) have been supplied by Sigma-Aldrich and the commercial seed tannin extract powder (T) has been supplied by Cevico Group. Materials have been labelled as follow: "PP XY", where X is the number indicating the concentration (%wt) of the additive, and Y is the letter(s) indicating the additive typology. "PP proc" refers to the neat PP after twin-screw extrusion processing step. Table 2 resumes the name, and composition of the investigated materials. It is noteworthy underline that sample PP 01Irg, has been used as testing reference for the sample PP 6Se during the aging tests because of their similar content in effective antioxidant (see further paragraphs), meanwhile sample PP 1Irg, has been compared with PP 6T and PP 2Sext.

Table 2

Code, name and composition of the investigated materials.

Name	Composition
PP Proc	Neat PP processed in the same conditions
PP 01Irg	PP + 0.1 %wt Irganox 1010 (Irg)
PP 6Se	PP + 6 %wt seeds (Se)
PP 6T	PP + 6 %wt commercial tannin extract (T)
PP 2Sext	PP + 2 %wt seed extract (Sext)
PP 1Irg	PP + 1 %wt Irganox 1010 (Irg)

2.2. Preparation and characterization of bio-additives

2.2.1. Seed Extraction

The wine wastes seeds have been firstly washed with distilled water and cleaned with a cloth in order to remove smug and other impurities. Then they have been oven-dried at 70 °C overnight and grounded by means a batch analytical mill. In this step, moisture content and mean diameter size have been determined monitoring the weight and sieving manually, respectively. Therefore, a part of grounded seeds has been stored at room temperature and another part has been used for the polyphenol extraction. Extraction has been carried out under magnetic stirring for 120 min at room temperature using a mixture of ethanol-water (7:3 v/v) as solvent (solvent/solid ratio of 5 ml g^{-1}). The solid residue has been separated by filtration under vacuum and the polyphenol fraction has been separated from the solvent by distillation in a rotary evaporator. The yield of collected polyphenol fraction has been 3 %wt with respect to the dried seeds.

2.2.2. Total polyphenol content

The total polyphenol content of seed extracts (Sext), as well as of pristine seeds (Se) and of commercial tannin seed extract powder (T) have been kindly measured by Cevico Group C.V.C., Lugo (RA). Firstly, each sample has been completely (Sext and T) or partially (Se) dissolved in the ethanol-water (7:3 v/v) solvent. Therefore, the solution has 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.

2.2.3 FT-IR and UV/VIS spectra

For each wine-derived additive, FT-IR spectra have been collected using a Perkin-Elmer Spectrum GX Infrared Spectrometer. Spectra have been recorded in ATR mode as an average of 64 scans in the range 4000-400 cm^{-1} and a 4 cm^{-1} resolution. UV/VIS spectra of commercial tannin extract “T”

and lab seed extract “Sext” have been collected using a UV/VIS Jasco V-650 Spectrophotometer using absorbance mode at 1nm intervals in 190-490 nm region.

2.2.4 Liquid Chromatography-Mass Spectrometry (LC-MS)

Catechin and gallic acid concentration within the commercial tannin extract “T” and the lab seed extract “Sext” have been carried out by Liquid Chromatography-Mass Spectrometry (LC-MS). LC-MS/MS system has been performed using an Agilent 1200 series HPLC and an Agilent 6410 Triplequdrupole mass spectrometer equipped with an electrospray ionization source (Agilent Technologies, USA). The chromatographic separation has been achieved on a Zorbaz SB-C_{18} (3.5 mm, 2.1 x 30 mm i.d., Agilent). All data have been acquired employing Agilent 6410 Quantitative Analysis version analyst data processing software. The initial mobile phase composition has been a mixture of 0.1% in volume of formic acid in water and acetonitrile (98:2 v/v). After the sample injection (5 mL), the initial mobile phase has been maintained under isocratic conditions for 1 min. A linear gradient has been then programmed to reach a mobile phase composition of 0.1% in volume of formic acid in water and acetonitrile (10:90, v/v) in 12 min, kept constant for further 5 minutes and then switched back to the initial composition in 0.1 min and allowed to re-equilibrate. The flow rate has been fixed at 0.3 mL/min during the whole chromatographic run and the temperature of the analytical column has been of 25° C. Total analysis run time has been of 25 min. “T” and “Sext” have been solubilized in HPLC grade water and injected in 10 ppb concentration. Mass spectrometric detection has been performed on a Series 6410 Triple Quad LC-MS (Agilent Technologies, USA) using multiple reaction monitoring. A turbo electrospray interface in positive ionization has been used.

2.3. Preparation of PP-based compounds

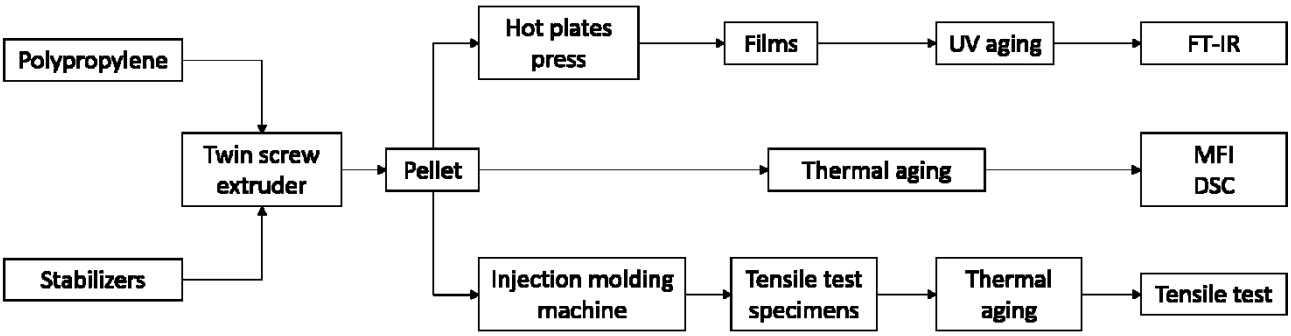

Fig.1 Working scheme.

Following the working scheme (Fig.1), PP has been firstly mixed with the stabilizers and bio-stabilizers through melt-compounding in a laboratory twin-screw extruder Rheomex 557 (Screw length: 300 mm, L/D screw ratio 10).

Table 2

Processing conditions resuming.

Extrusion Conditions		Injection molding conditions		Hot plates press conditions	
Feed zone Temp [°C]	180	Hopper Temp [°C]	185	Plate Temp [°C]	200
Barrel Temp [°C]	200	Screw-barrel Temp [°C]	205	Holding Pressure [MPa]	5
Die Temp [°C]	200	Die Temp [°C]	200	Holding time [min]	3
RPM [min^{-1}]	12±3	Injection Pressure [bar]	100	Cooling time [min]	5
Pressure [bar]	20±5	Holding Pressure [bar]	25		
		Holding time [s]	3		
		Cooling time [s]	4		

The compounded pellets obtained by twin-screw extrusion have been used for the preparation of suitable specimens for tensile test (type 1BA, according to technical standard ISO 527) by using a MegaTech Tecnica DueBi injection molding machine (see processing conditions in Table 2) and for

the preparation of suitable films ($20 \times 20 \times 0.5$ mm^3) for photo- and thermal-oxidation by using a Carver hot plate press operating at 200°C for 3 min under a pressure of 5 MPa.

2.4. Accelerated aging

UV aging of PP-based films has been carried out by irradiations in air in a SEPAP 12/24 unit (ATLAS) at a wavelength l > 300 nm and 60 °C. The apparatus was equipped with four medium-pressure mercury lamps with borosilicate envelope able to filter wavelengths below 300 nm and it was designed for accelerated artificial UV aging tests, in conditions comparable to natural outdoor weathering. Thermal aging has been carried out in a forced-air oven at 110°C for PP-based pellets and PP-based tensile specimens.

2.5. Characterization techniques

2.5.1. Oxidation induction time (OIT) by FT-IR

FTIR spectroscopy has been carried out on films subjected to accelerated aging by means of a Perkin-Elmer Spectrum GX Infrared Spectrometer. Spectra have been recorded in transmission mode as an average of 32 scans in the range 4000-400 cm^{-1} and a 4 cm^{-1} resolution. Both photo-oxidation and thermal-oxidation have been followed by monitoring the intensity of the maximum absorbance in the 1800-1690 cm^{-1} range (C=O vibration stretching band range) as a function of time. In order to avoid differences due to film thickness absorption, the degradation peak has been normalized to the absorption peak at 2723 cm^{-1} (C-H vibration stretching band of PP). Each film has been analyzed at a fixed time and then returned to the UV apparatus or to the oven to continue the aging treatment. The Oxidation Induction Time (OIT) have been calculated as the time at which the C=O peak start to increase linearly with time and the slope of that line has been indicated as the degradation rate (DR). The reported data are the average values of two determinations.

2.5.2. Tensile test

Tensile tests have been performed by means of the INSTRON 5567 dynamometer equipped with a 1 kN load cell and a 25 mm gauge length extensimeter. Tests have been performed at room temperature with a speed of testing of 10 mm min^{-1} . For each oven aging time, at least six specimens have been tested. Young's modulus (E), tensile strength (σ_M), and tensile strain at break (ε_b) have been measured as function of aging time.

2.5.3. Melt Flow Index

Melt flow index (MFI) of the oven aged PP-based pellets has been monitored according to ISO 1133 at a temperature of 235 °C, and load of 2.16 kg.

2.5.4 Differential Scanning Calorimetry

Thermal properties of oven aged PP based pellets have been evaluated by Differential Scanning Calorimetry (DSC). DSC measurements have been performed by a DSC TA 2010, using 7 ± 1 mg of sample and the chamber has been purged by nitrogen at 50 mL min^{-1}. Each sample has been firstly heated from 20 °C to 220 °C at 15 °C min^{-1} in order to erase the previous thermal history. Therefore, after a 2 min isothermal step at 220 °C, samples have been cooled at 15 °C min^{-1} to 20 °C and finally, re-heated to 220 °C at 15 °C min^{-1}. The crystallization temperature (T_C) has been evaluated as the peak maximum of the heat flow in the cooling cycle. The melting temperature (T_m), as well as the melting enthalpy (H_m) have been obtained from the second heating cycle as the peak maximum and as the integral of the area under the heat flow curve, in the 125 - 200 °C range, respectively. Melting enthalpy has been calculated considering the additives weight fraction. In order to evaluate the crystallinity percentage of the PP-based pellets, the value of 208 J g^{-1} [47] has been considered as reference for the 100% crystalline PP melting enthalpy.

2.5.5 Morphology

Morphology, adhesion, distribution and solution of the additives on the PP matrix have been observed with an Environmental Scanning Electron Microscope, SEM (ESEM Quanta FEI 2000). Tensile specimens have been broken in liquid nitrogen and the cross section 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.

3. Results and discussion

3.1. Bio-additives characterization

In Table 3, particle size, total polyphenol content, catechin and gallic acid concentrations are reported. It is useful to state that catechin and gallic acid have been chosen as targets among other many polyphenols because their usually abundancy in grape seeds and because they are the simplest molecules representative the two major polyphenol family, condensed tannins (catechin) and hydolyzable tannins (gallic acid). The reported wine wastes values can be affected by viticultural or environmental factors [48, 49] and by extraction techniques and analysis methods [50], but it is noteworthy to underline that they are still in accord with those carried out by different authors [51-53]. Despite these mentioned affecting factors, comparing "Sext" and "T" additives it can be surely said that "T" contains an higher level of total polyphenols and catechins meanwhile gallic acid seems to be more present in "Sext". This difference in gallic acid concentration could be a key point for the further presented results, suggesting that gallic acid could be better than catechin to withstand the PP degradation. The extreme antioxidant power of gallic acid has been reported numerously. R.Pulido et all. (2000) [54], through the ferric reducing ability of plasma (FRAP assay)

have measured the concentration of different dietary antioxidants having a ferric reducing ability equivalent to that of a 1 mmol/L of $FeSO_4,7H_20$ (CE), finding gallic acid almost two times more active than catechin (CE of gallic acid: 180 mmol/L; CE of catechin: 348 mmol/L). Brand-Williams et al. (1995) [55], using the DPPH radical scavenging method, found that gallic acid was the most effective polyphenol scavenging the DPPH• radical, and similar results have been carried out by other authors [56, 57]. By the way, these results can not state the antioxidant power superiority of gallic acid over catechin in PP stabilization because the antioxidant ability of polyphenols is strictly connected with the systems they are dealing, but nevertheless indicate a clue for the "Sext" additive's antioxidant power explanation.

In addition to (+)-catechin and gallic acid, other simple polyphenols typically present in wine seeds extracts are (-)-epicatechin, (-)-epigallocatechin, (-)-epicatechin gallate, (-)-epigallocatechin gallate (ECG), quercetin, resveratrol, ferulic and ellagic acid [58, 59]. Moreover, grape seeds result to be rich in procyanidins, a class of polpyhenols members of the condensed tannins family, which are olygomers formed by catechins and/or epicatechin as building blocks and a degree of polymerization ranging from 2.4 to 16.7 [60]. The chemical structure of the mentioned simple and polymerized polyphenols are reported in Fig.2.

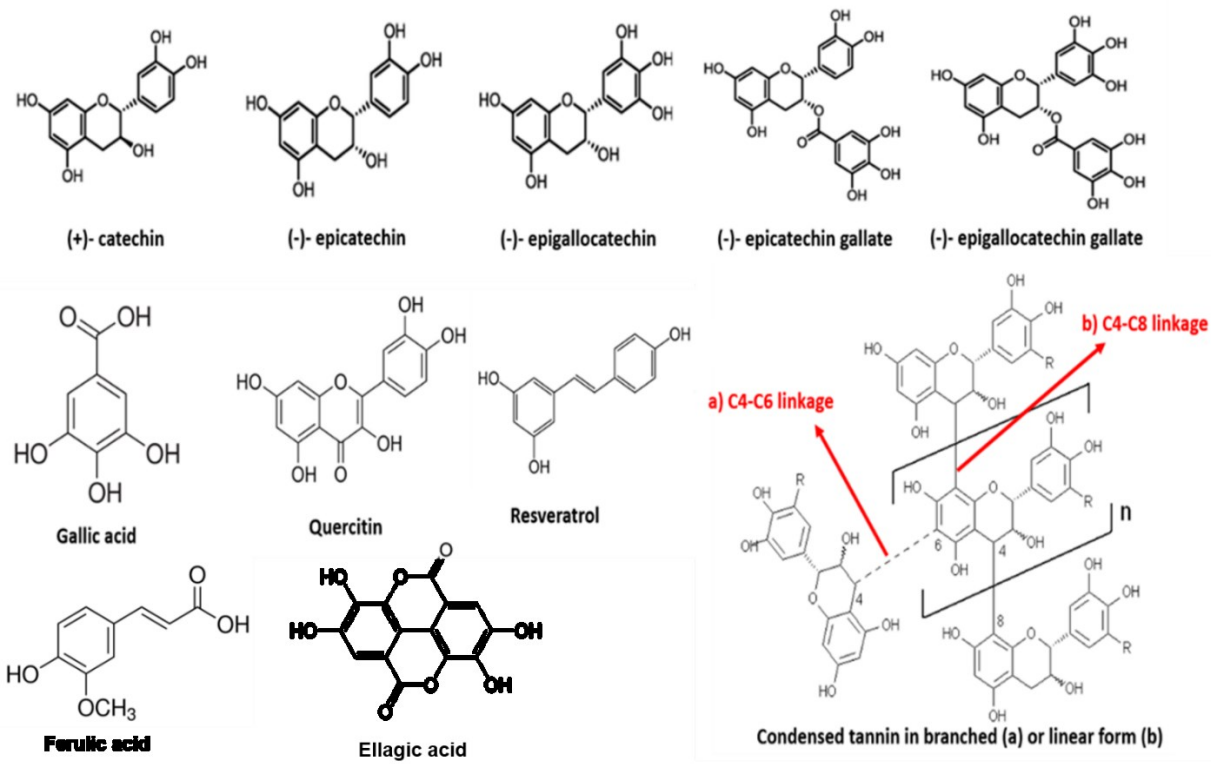

Fig.2 Wine seeds polyphenol extracts: chemical structure of the most important moieties.

FTIR has been used in order to collect and compare information on the chemical structure of the wine wastes seeds (Se), of their extract (Sext) and of the commercial seed tannin extract powder (T). Fig. 3 shows the acquired ATR spectra (normalized with respect to the most intense peak) and Table 4 lists the main bands.

Table 3

Particle size, total polyphenol content [% wt], catechin and gallic acid concentrations of bio-additives.

	Se	Sext	T
Mean particle size [mm]	0.30	0.17	0.17
Total polyphenol content [%wt]	1.4	15.7	38.2

Effective polyphenol content in PP-based sample [%wt]	0.084	0.31	2.29
(+)- Catechin [mg/g ext]		4.61	37.4
Gallic acid [mg/g ext]		3.75	0.67

From a qualitative point of view, it is possible to note that the spectrum of Se presents three sharp and intense peaks (**b**, **c** and **d)** in the 3000-2500 cm^{-1} range related to the stretching of aliphatic CH and CH_2 groups that confirm the relevant amount of unsaturated lipids in wine seeds (10-15 %wt) [61, 62]. Moreover, an intense peak at 1745 cm^{-1} (**e**) related to C=O stretching typical of galloylated compounds confirms the typical high content of procyanidins galloylation in grape seeds [60, 63]. Comparing the spectra of Se and T, it is observable how commercial extract T presents a cleaner signal presumably thanks to the industrial extraction method. By the way, the OH stretching band (3700-3000 cm^{-1}) has its maximum peak at the same frequency in both extracts and the breadth of the band results similar. Because the used solvent in the polyphenol and tannins extraction process affects the relative position of the maximum for the OH stretching [64], it is reasonable to believe that Sext and T have been obtained by solvent with similar polarity (maybe pure water has been used for T, being more suitable for large scale extractions). In the 3000-2850 cm^{-1} region, "Sext" spectrum presents two peaks (**c** and **d**) that could be assigned to the asymmetric stretching of aliphatic CH groups [65] or to a residual lipid fraction. The 1800-1680 cm^{-1} region is significant for qualitative analysis because shows a distinctive peak for carbonyl stretching of hydrolysable tannins [66, 67], whereas only a weak signal, if any, appears with condensed compounds [68]. The low intensity of the **e** peak (1740 cm^{-1}) shows the predominance of condensed tannins in both grape seed extracts confirming the grape seed tannin composition [60, 69]. In the 1150-900 cm^{-1} region it is remarkable a sharp peak (**h**) that results more intense in Sext spectra than in T one. This region is

characterized by the combination of different substituents in the phenolic rings. The bands appearing in this region are strongly affected by the number and position of substituents and provide a useful indication for the determination of tannin monomeric constituents [70]. Therefore, it is reasonable to conclude that Sext is characterized by tannins with a lower degree of polymerization [68] and many free phenolic hydroxyl groups. Thus, it could be explained the high intensity of **h** peak in Sext spectrum. This aspect is important for two reasons: firstly, the quantification of total polyphenols is highly affected by the extent of polymerization of tannins when using direct reading at 280 nm as reference method [71] and secondly, the free phenolic hydroxyl groups result to be more reactive than long chain tannins [72-74]. Despite the possible underestimation on the Sext polyphenol content, comparing PP 2Sext and PP 6T it is clear that an important gap concerning the effective polyphenol content within the PP samples still remains, because of the two different antioxidant percentages used (Table 3). In other words, the differences detected and discussed in **h** peak, testimonies again the role and the importance of the polyphenol structure and typology over the polyphenol content.

Table 4

ATR absorption signals and corresponding assignments.

Peak code	Wavenumber [cm^{-1}]	Assignment
a	3290	O-H and N-H stretching vibration of polysaccharides and proteins; O-H of polyphenols
b	3006	=CH stretching vibration of unsaturated lipids
c	2920	CH_2 asymmetric stretching vibration of lipids (mainly), proteins, polysaccharides and nucleic acid; CH_2 of catechins.
d	2852	CH_2 symmetric stretching vibration of lipids (mainly), proteins,

		polysaccharides and nucleic acids; CH_2 of polyphenols
e	1740	C=O stretching vibration of phospholipids and triglycerides; C=O of gallic acid
f	1615	C=O stretching vibration of amide (I) in proteins and nucleic acids; C=O of catechin
g	1458	CH_2 bending vibration of lipids and proteins; CH_2 of polyphenols
h	1160	C-C, C-O and C-N stretching vibrations

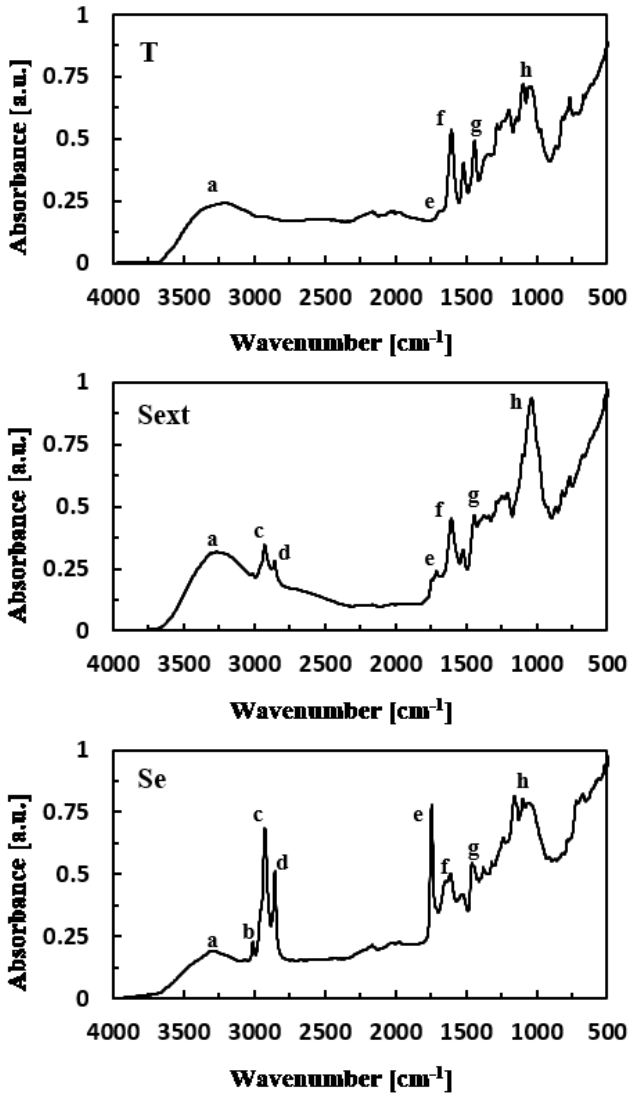

Fig.3 FT-IR ATR spectra of wine seeds (Se), wine seed extracts (Sext) and commercial tannin seed extract (T).

In fig. 4, the UV/VIS spectra of neat powders “T”, “Sext”, “Se” and Irganox 1010 are shown. As expected, Irganox 1010 exhibits a maximum absorbance peak in the 280 nm region followed by a decreasing absorbance in the UV-A region (315-400 nm) and becoming totally transparent in the visible region (400-700 nm). The different wine seeds derived additives exhibit comparable spectra and, contrary to Irganox 1010, they are able to absorb in the whole UV and visible region. Thus, if mixed in polypropylene, they can act also as UV absorber screening the UV rays and discouraging the UV absorption by the PP chromophores groups. This prevention mechanism reminds both the one played by polyphenolic pigments when a UV barrier screen is needed by the plant or the fruit as sun protection and the effect of some zinc oxide nanoparticles used for UV shielding [75, 76]. By the way, absorbing also in the visible, the use of wine derived additives involve a change of color and opacity in PP matrix as main drawback.

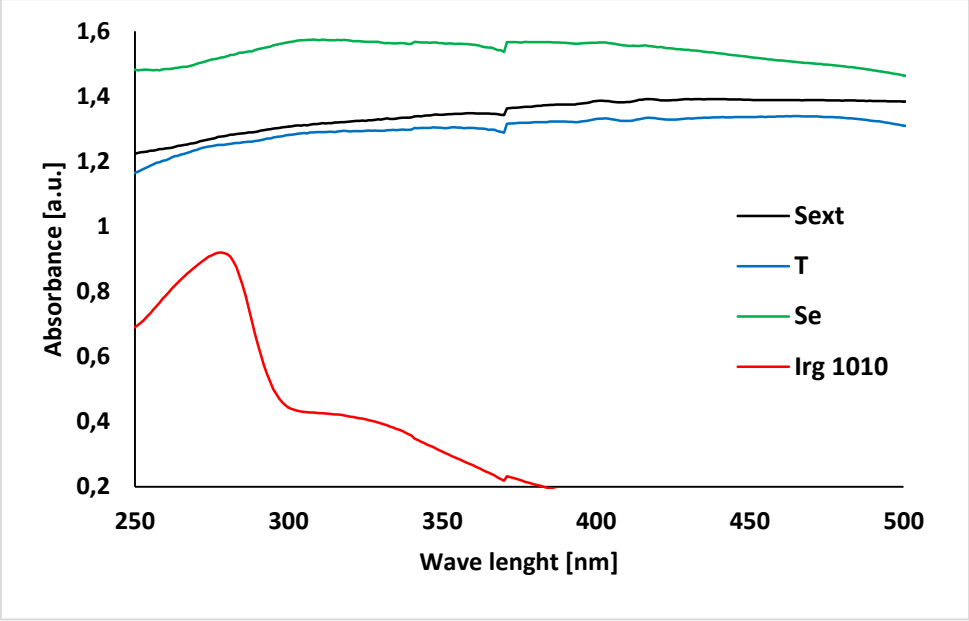

Fig.4 UV/Visible spectra of “Sext”, “T”, “Se” and Irganox 1010 additives.

3.2 UV aging of the PP-based films

The photo-oxidation mechanism of isotactic PP has been reported numerous times in literature [28, 77-80]. The main product of the combined action of UV-radiation and oxygen is the formation of the tertiary hydroperoxide. The oxidation continues up to the production of carboxylic acids, esters, peresters, lactones and other oxidized species. Therefore, the analytical detection of oxidation products has been performed by monitoring the intensity of C=O absorption in the 1800-1650 cm^{-1} IR-spectrum range. Fig.5 shows the FTIR absorption spectra, in particularly the carbonyl range, of the PP proc at different UV aging times. It is possible to notice (Fig.5b) that the carbonyl content remains constant up to approximately 10 hours which represents the induction time and then increases at a high rate up to 80 hours. The increasing of absorption intensity over time was caused by the accumulation of carbonyl groups in the polymer. In particular, three different peaks can be distinguished: ketons at 1725 cm^{-1}, isolated carboxylic acids at 1755 cm^{-1} and peresters or lactones at 1780 cm^{-1}. This kinetic behavior of the carbonyls reveals the typical outline of photo-oxidation reactions: an induction period followed by an auto-acceleration step. A similar trend of carbonyl evolution has been observed for all PP-based films, pointing out the fact that wine derived additives do not modify the photo-oxidation mechanism.

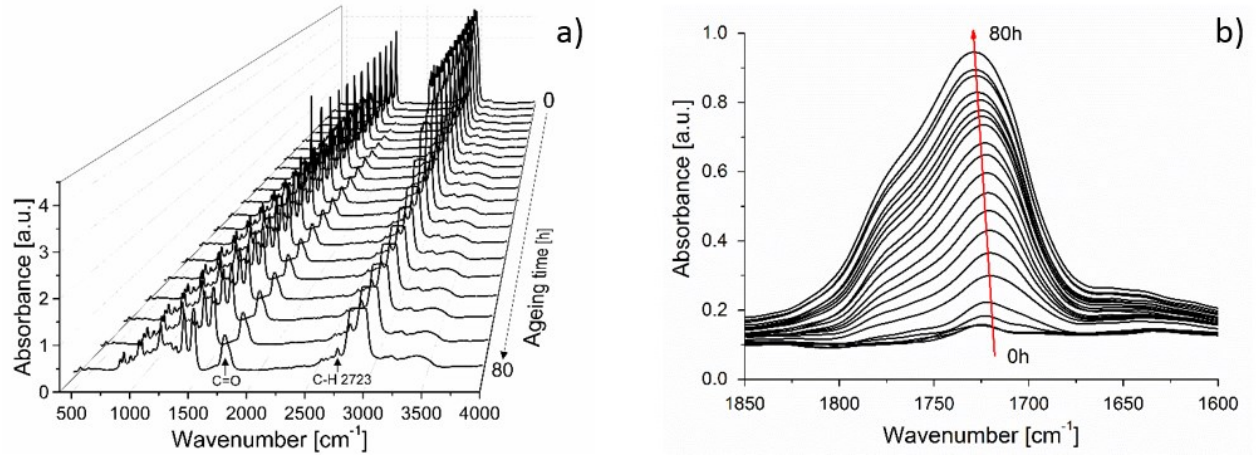

Fig.5 FTIR spectra of photo-oxidized "PP proc" film in 4000-400 cm^{-1} range (a) and in C=O 1850-1600 cm^{-1} zoom (b).

Table 5

UV aged PP-based samples: OIT, slope and R^2 of the experimental data interpolating lines and film breaking time.

PP based sample	OIT [h]	Slope [%]	R^2	Film breaking [h]
PP Proc	10.2 ± 0.4	2.23	0.9979	50 ± 2
PP 01Irg	16.5 ± 0.8	1.60	0.9931	62 ± 2
PP 6Se	14.4 ± 0.6	1.76	0.9950	56 ±8
PP 6T	32.8 ± 1.7	1.30	0.9863	Not occurred
PP 2Sext	43.5 ± 0.6	1.57	0.9971	Not occurred
PP 1Irg	23.2 ± 0.1	1.72	0.9939	60 ± 4

In Fig.6, it is reported the kinetic evolution of the maximum of the carbonyl bands (within the 1800-1650 cm^{-1} range) normalized to the peak at 2723 cm^{-1} (to compensate slight thickness differences) for each PP-based film. Three different behaviors are observable: one without any form of stabilization, the second one with good UV stabilizers and the last one characterized by excellent UV stabilization results. As predictable, unstabilized PP (PP proc) lies on the upper part of the graph: photo-oxidation starts just after 10 h and its rate is the highest among all the samples (Table 5). Subsequently, in the central part of the graph it is possible recognize three similar OIT lines which represent, in decreasing order of UV stabilization efficiency, the PP 1 Irg, PP 01 Irg and PP 6Se degradation responses. These samples are able to protect the PP matrix from 14.4 to 23.2 hours of UV aging (41% and 123% more than unstabilized PP) and the slopes of these lines are comparable and within the range of 1.6-1.76. It is noteworthy underline the fact that PP 6Se and PP 01Irg behaviors are comparable in agreement with their effective antioxidant content (0.084% wt and 0.1% wt, respectively) pointing out the seeds ability to work as long-term stabilizer in a way

proportional to their polyphenol content. This aspect indicates that the polyphenols released from the seeds during the extrusion process remain within the PP matrix without be absorbed again by the wine seed surfaces. In fact, fillers, absorbing stabilizers at their surface and therefore reducing their protective effect, may have a negative effect on the long-term properties of plastics [81]. Finally, as expected, PP 1 Irg exhibits the highest OIT value of this group being able to inhibit the photo-oxidation until 23 hours (+7 h than PP 01 Irg and +9 h than PP 6Se). As observable in the bottom right side of Fig.6, polyphenol extracts are the best PP bio-stabilizers against UV aging. This can be explained by the fact that polyphenols can work both as radical scavenger donating hydrogen from their hydroxyl groups (like Irganox 1010) and also as UV absorber as shown in 3.1 paragraph. The OIT values of PP 6T and PP 2Sext are here of around 33 and 44 hours, respectively (41% and 88% more than PP 01 Irg). The PP 6T samples exhibits the lowest interpolating line slope (1.30), and, especially in the beginning of the photo-oxidation, the degradation rate occurs slower than in the PP 2Sext, but then, towards the end, the PP 6T values seem to convert to the PP 2Sext ones. Therefore, it is possible to state that PP 2Sext, despite its lower effective polyphenol content, is able to delay the photo-oxidation of other 11 h, respect to PP 6T. Thus, as explained in the 3.1 paragraph, the polyphenol structure and quality have been proven to be the key role in long-term UV stabilization.

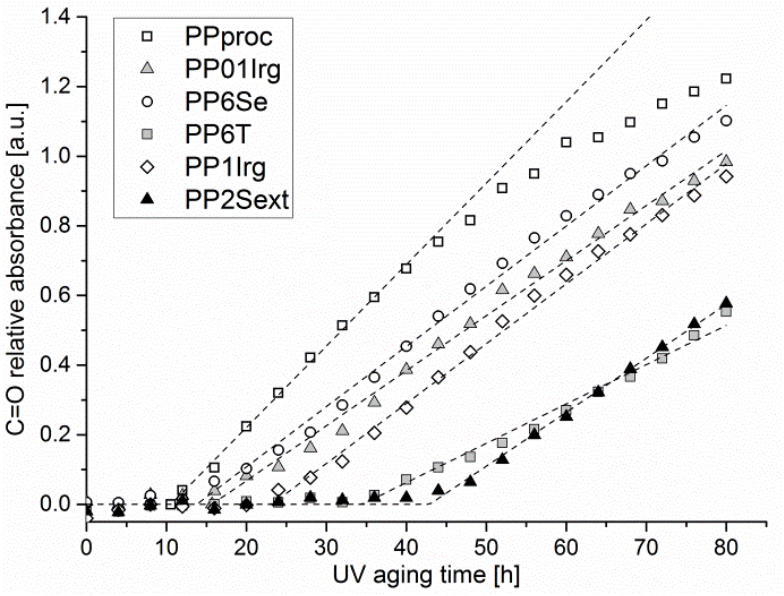

Fig.6 Relative absorbance of carbonyl bands versus UV aging time for PP-based films.

3.3 Thermal aging of PP-based tensile specimens and pellets.

Young's modulus (E), tensile strength (σ_M) and strain at break (ε_b) at different thermal aging times of each PP-based sample are reported in Table 6. Considering the unaged samples, no significant difference are notable except for PP 6Se and PP 6T samples that present very much lower elongation at break values and a higher elastic modulus (PP 6Se). This could be explained by the presence of micrometric solid inclusions in the polymer matrix, as already seen in a previous work [39], resulting in an embrittlement of the material and in the formation of defects able to accelerate the crack propagation. On the contrary, it is noteworthy underline that, despite the polarity difference between not polar PP and polar wine seeds extracts, PP 2Sext exhibit the same mechanical properties of PP proc (Fig.8). This can be explained because of the complete solubility of the natural additive within the PP matrix that gives to PP 2Sext the same morphology of the processed PP, as confirmed by the captured SEM images (Fig.7).

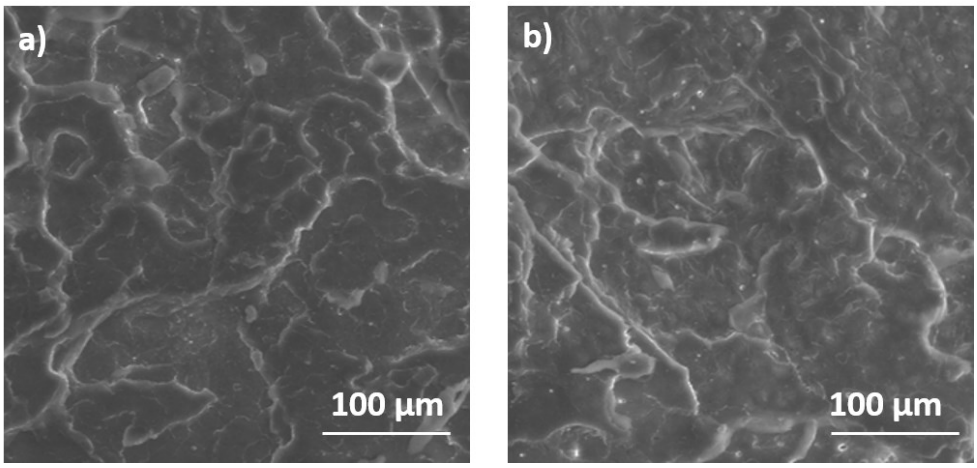

Fig. 7 Captured SEM images at 1000x magnitude of a) PP proc b) PP 2Sext.

Table 6

Young's modulus (E), tensile strength (σ_M) and strain at break (ε_b) of PP-based sample at different aging times.

PP proc			
Aging time [h]	E [MPa]	σ_M [MPa]	ε_b [%]
0	1574±113	28.7±1.6	1146±206
192	1727±130	28.5±0.7	27.8±3.6
271	1901±88	26.7±1.1	14.9±0.6
360	1774±102	27.9±1.4	16.0±1.3
PP 6Se			
Aging time [h]	E [MPa]	σ_M [MPa]	ε_b [%]
0	1938±232	29.2±1.2	12.6±3.5
192	1904±141	24.3±2.5	7.4±2.7
271	1997±58	27.0±2.7	11.1±1.5
360	1757±248	21.5±5.0	8.6±2.0
PP 6T			
Aging time [h]	E [MPa]	σ_M [MPa]	ε_b [%]

0	1656±214	27.3±0.7	44.2±4.2
192	1985±186	25.4±3.2	39.3±4.9
271	1762±178	27.9±0.9	28.9±4.1
360	2033±142	28.6±1.8	32.3±0.3

PP 1Irg

Aging time [h]	E [MPa]	σ_M [MPa]	ε_b [%]
0	1664±69	28.7±3.0	1060±140
192	1626±108	29.0±1.3	820±104
271	1714±73	26.7±2.2	795±77
360	1893±102	30.1±1.9	18.2±0.8

PP 2Sext

Aging time [h]	E [MPa]	σ_M [MPa]	ε_b [%]
0	1611±48	27.1±1.0	1138±200
192	1735±98	29.7±1.6	899±170
271	1714±121	28.8±2.6	890±99
360	1969±48	29.5±1.0	760±42
	2103±104	31.6±1.2	19.8±6.2

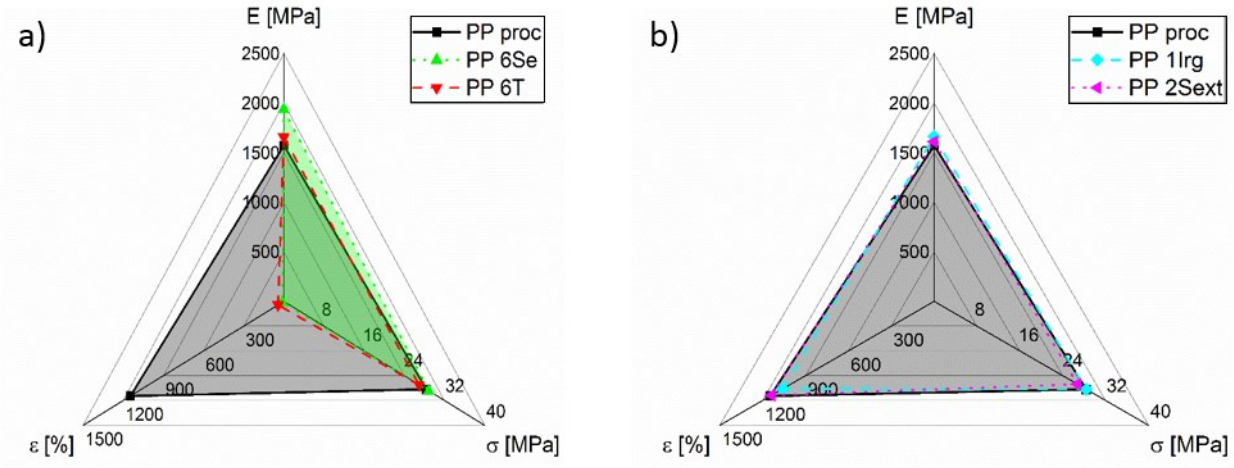

Fig. 8 Comparison of the mechanical properties between a) PP proc, PP 6Se and PP 6T; b) PP proc, PP 1Irg and PP 2Sext.

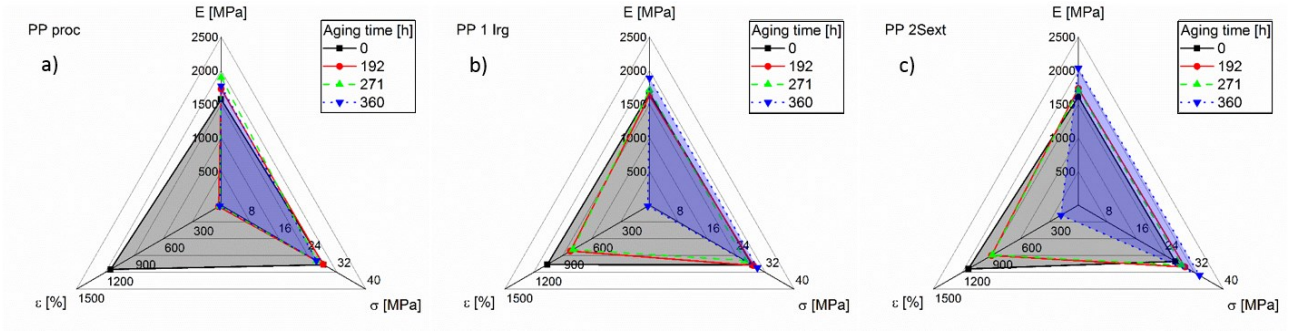

Fig. 9 Comparison of the mechanical properties between a) oven aged PP proc, b) oven aged PP 1 Irg and c) oven aged PP 2Sext.

The relative changes of deformation at break for PP-based specimens as a function of aging time is reported in Fig.10. A significant loss in deformation at break at 360 h and a not relevant difference in behavior between 192 h and 271 h of aging time can be observed for all the samples. From Fig.9, it also emerges the tendency of each sample, as expectable, to increase their Young Modulus and tensile strength during the aging time as embrittlement consequence of the thermal aging.

PP proc is not able to withstand the thermal treatment for long time, showing a dramatic loss in the strain at break already at 192 h. The significant loss of mechanical properties in the course of oven

aging can be explained by the decrease in the average molecular weight of the polymer due to the degradation phenomena. Therefore, PP 1 Irg and PP 2Sext are the samples that exhibit the best response to the thermal aging. They have an analogous behavior characterized by a slow loss of mechanical properties during the first 271 hours, followed by a fast loss of strain at break during the 271-360 h range. The only difference regard the final value of strain at break: in fact, at 360 h, PP 1 Irg shows a dramatic loss in deformation at break (-98% of its initial value) leaving no doubts on the occurred thermal degradation. Differently, in PP 2Sext it is possible to note two different groups of specimens at 360 h (Table 6): the 50% of the specimens have shown a total loss of the mechanical properties similarly to PP 1 Irg, meanwhile, the other 50% continue to exhibit significant strain at break values. This aspect could be explained by a not perfect distribution of the polyphenol seed extract within the PP matrix during the compounding processes, leading to specimens with less effective antioxidant content.

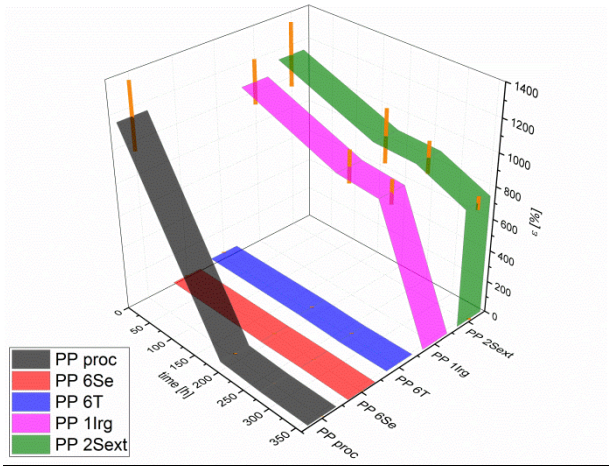

Fig.10 Strain at break as aging time function for PP-based tensile specimens.

The thermal degradation occurred by unzipping mechanism with related loss of molecular weight has been confirmed by the MFI test and by the DSC analysis. Fig.11 shows the MFR values of the oven aged PP-based pellets against the oven aging time. These data are in perfect accord with both the tensile test results and with the UV-aging OIT curves. In fact, is possible to notice how PP proc

exhibits a fast and dramatic increasing in MFR values after only 20 h of oven aging and after 50 h, it has been not possible measure the MFR value because of the too high melt fluidity (PP proc has been aged in this case only until 140 h). PP 01 Irg and PP 6Se, as well as for the UV aging, exhibit a comparable behavior being able to maintain their initial MFR value almost until 140-200 h. Despite PP 6Se and PP 6T have not been analyzed in terms of mechanical properties loss due to the thermal aging, because their already low initial elongation at break values, MFR confirms the ability of these bio-additives to work also as long-term thermal stabilizers. Finally, PP 1Irg and PP2Sext withstand the thermal aging for the longest times. In particular, PP 1Irg starts its degradation at around 300 h exhibiting a small increasing MFR value, meanwhile PP 2Sext seems to be undamaged even at 600 h. This last aspect gives rise to the possibility of optimize the polyphenol extract distribution in the compounding step, pointing out that tensile specimens could be able to maintain their properties longer than 360h. Finally, the similar MFR values of the unaged samples indicate that the wine additives do not affect in a significant way the PP rheological properties.

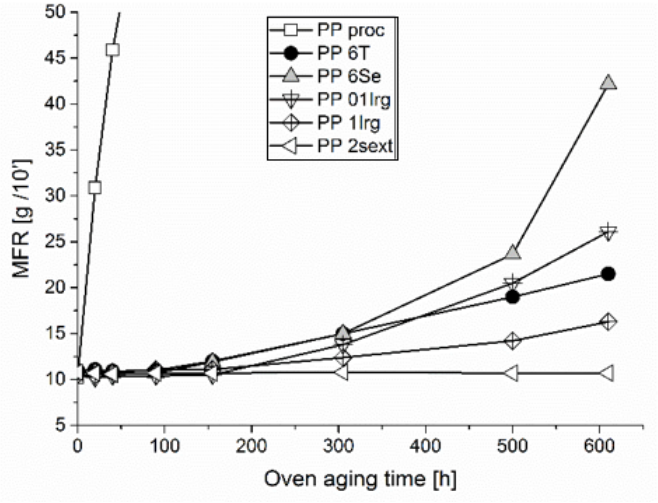

Fig.11 Melt Flow Rate values of PP-based pellets against oven aging time.

The degradative unzipping mechanism is confirmed also by the DSC data (Table 7) that shows the reduced molecular weight of the oven aged PP proc pellets both by the decreasing of the melting temperature (-26 °C) and by the increasing in crystallinity (+24%) testifying an occurred breakage of the PP molecular chains. These thermal properties differences between unaged and oven aged pellets have been not observed for the other PP-based pellets. By the way, referring to the unaged samples, it is noteworthy underline how polyphenol extracts as well as virgin wine seeds do not affect the PP thermal properties.

Table 7
Scanning Calorimetry data of the PP-based pellets.

Material	Oven aging [h]	T_c [°C]	T_m [°C]	H_m [J g^{-1}]	% Crystallinity
PP proc	0	117	167	85	41
	140	105	141	107	51
PP 6Se	0	116	167	79	41
	610	119	166	82	42
PP 1 Irg	0	114	167	88	43
	610	115	165	87	42
PP 6T	0	118	165	79	41
	610	116	166	79	41
PP 01 Irg	0	114	166	86	41
	610	113	164	87	42
PP 2Sext	0	114	167	87	43
	610	112	166	85	42

In conclusion, the thermal aging of tensile specimens has shown the polyphenol extracts (Sext) ability to interrupt the PP thermal radical degradation chain, guarantying remarkable mechanical properties even better than synthetic commercial antioxidant, Irganox 1010. In fact, despite Sext has been mixed with PP in percentages two times higher than Irg 1010 ones, the effective antioxidant content in the PP 2Sext is still less than in PP 1 Irg (0.31% wt against 1.0%wt). Moreover, the results exhibited at 360 h (both from tensile test and MFR) open a further possibility to improve the

thermal stability optimizing the polyphenol distribution through extrusion and injection molding processes.

4. Conclusion

The UV-oxidative stability as well as the thermo-stability of PP containing synthetic or natural antioxidants derived from wine seeds wastes has been studied. Long-term stability has been investigated through UV and thermal aging tests, monitoring the development of degradation products by FT-IR and the loss of mechanical properties. The main results obtained are summarized as follow:

- The polyphenol extract (Sext) is able to protect PP against UV aging and the OIT value of the PP 2Sext sample has been the highest among all the investigated samples. This has been due by the ability of Sext of working both as radical scavenging and UV absorber.
- The polyphenol extract (Sext) is able to protect PP against thermal aging and the mechanical properties of the PP 2Sext sample have not significantly changed until 360 h of thermal aging. Moreover, a better distribution of the additive within the PP could lead to a degradative resistance even for longer aging time as confirmed by MFR. In addition, despite the difference in polarity between polyphenol extracts and PP, the mechanical properties of the unaged specimens have been similar to the neat PP ones. Finally, also thermal and rheological properties have been not affected by the seed extract.
- Wine seeds (Se) are also able to protect PP from long-term UV and thermal aging in a way proportional to their effective antioxidant content as confirmed by the results similar to the PP 01Irg ones. The main drawback regards the necessity to mix high contents of wine seeds(6%wt) with PP to obtain an adequate polyphenol quantity, affecting in a dramatic way the PP mechanical properties (elongation at break values).

- The results obtained with Sext, if compared with the commercial tannin seeds extract T, show how the quality of the polyphenol compound plays a key-role in the PP stabilization. It is reasonable to believe that PP 2Sext has worked better than PP 6T, even with a lower content of antioxidants, because of the higher presence of free phenolic hydroxyl groups that result more reactive than long tannin chains. It is also possible to propose the superior antoxidant power of gallic acid (respect to catechin) in PP stabilization comparing the LC-MS data of Sext and T.
- The obtained results open new interesting works on the optimization of the PP stabilization using different percentages of the polyphenol extract (Sext) and/or combining their effect with synthetic antioxidants and/or virgin wine seeds.

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