Effect of natural antioxidants on the stability of polypropylene films

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A B S T R A C T
A preliminary study on the efficiency of agri-food industry wastes as stabilizers for polypropylene (PP) films is reported. Several analytical techniques were employed to evaluate the stabilization effectiveness of the additives. DSC and CL analysis performed on unaged samples confirmed the antioxidant activity of natural additives, and provided the following order of efficiency: red grape seeds > white grape seeds > tomato extracts. The films were also artificially aged at 70 °C, and FTIR spectroscopy confirmed the stabilization trend obtained from the unaged films. Kinetic analysis of TG data alongside tensile tests indicated that the tomato extract is a good thermal and processing stabilizer, but it is sensitive to oxidation. In contrast, grape seeds provide long-term stabilization to PP under conditions of oxidative degradation. Our results show that tomato and wine processing by-products have good potential to be exploited as a low-cost source of value-added phytochemicals.

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1. Introduction

Waste material from industrial processing of some crops, nowadays a cost for agri-food companies, contains chemicals and raw materials which until now have been exploited only partially. Tomato solid waste is made up of processing residues, fibrous parts, seeds and peels. This material contains high amounts of polysaccharides and other chemicals, especially carotenoids, and recovering them from surplus biomass is highly cost-effective. Tomato processing by-products may contain up to 0.1% lycopene by weight, along with other carotenoids and tocopherols [1]. The antioxidant activity of tomato extracts is well known [2] and it was demonstrated that scavenging effects of carotenoids relate particularly to their abilities to donate electrons or hydrogen atoms and to their relative propensities to undergo oxidation. They may also act through forming radical adducts which can undergo bimolecular decay [3].

Antioxidant-rich fractions were also extracted from hazelnuts [4], chestnuts [5], and especially grape seeds [6,7]. It is notable that generally extracts of by-products (skin, hard shell) exhibited stronger activities than nut kernel [8]. The chemical components of these extracts are tannins and polyphenolic compounds, which represent the major family of both natural and synthetic antioxidants [9] and are chemical analogues of synthetic stabilizers widely used in plastic industry as well. Their antioxidant effect is related to the electron-donating nature and to the steric effect of the substituents. The electron-donating effect can enhance the electron density at the oxygen of the phenol, resulting in a high radical-trapping rate. The steric effect prevents phenoxy radicals from coupling, possibly leading to an increase in the number of trapped peroxyl radicals [10].

Until now, antioxidant activity of natural extracts was assessed almost solely based on free radical scavenging activity tests. As far as we are aware, few reports deal with the evaluation of the antioxidant activity of natural extracts dispersed in polymer matrices [10–12].

In this paper, by-products containing polyphenols and tannins deriving from grape processing for wine production, and carotenoid-containing waste from processing of tomatoes, were tested as potential antioxidants for polypropylene, to partially substitute synthetic, oil-based stabilizers. Several experimental techniques were used in order to investigate on the stability provided by the different additives, either by testing unaged films, or by subjecting them to thermal aging. Among the experimental techniques available to assess PP stabilization, oxidative induction time (OIT) by DSC, chemiluminescence (CL), FTIR spectroscopy and thermogravimetry (TG) were utilized.

2. Experimental part

Unstabilised isotactic PP (HP420M, MFI 8 g/10 min) was supplied in the form of a reactor powder by Basell, Italy. Phenolic
antioxidant Irganox 1010 was supplied by Ciba Specialty Chemicals, Pontecchio Marconi, Italy. Carotenoid solid fraction from tomato waste (skins and seeds) kindly supplied by a food packaging industry (Fontanella, Mercato San Severino, Italy), was extracted by solid-liquid extraction using diethyl ether at room temperature [13]. White and red grape seeds (Coda di Volpe and Aglianico varieties, respectively) from wine processing waste were obtained from a winery (Covino, S. Martino valle Caudina, Italy), and ground to a fine powder by means of a Retsch ZM1 blade mill, using liquid nitrogen. The powders so obtained were directly blended with the polymer.

Blending of additives with polymer pellets was carried out under a nitrogen stream using a Haake Rheocord 9000 batch mixer operating at 180 °C, increasing the screw rate from 2 to 32 rpm for a total duration of 10 min. The concentration of additives was as follows: 0.2 wt.% for Irganox 1010 and the tomato extract, 2 wt.% in the case of powdered grape seeds. Compression-moulded films (average thickness 100 μm) were obtained by pressing the blended polymer chips at 200 °C and 50 MPa. Five samples were prepared: neat PP (PP0), PP blended and melted processed with Irganox 1010 (PP1), red grape seeds (PP2), white grape seeds (PP3), tomato waste extract (PP4), respectively.

The films were subjected to thermal-oxidative degradation at 70 °C in a forced air oven (Ghibli model Plus). Aged samples were collected at different times and subjected to chemical analysis by means of infrared spectroscopy and mechanical tests.

2.1. Experimental techniques

OITs were measured by a Mettler Toledo DSC 822 following ASTM D3895-02, at temperatures below and above the sample melting points. OIT values were measured in open Al pans, containing circular polymer samples (4 mm diameter, ca. 5 mg) punched out of the films. The material was then heated under nitrogen (50 mL min⁻¹) at a set temperature, and after 15 min the purging gas was turned to air. The heat flow was recorded in isothermal conditions as a function of time. The beginning of material oxidation was evident by a sudden increase of the slope of the exothermal heat flow. The time elapsed after switching to air for the slope increase to occur was taken as the OIT.

CL experiments were performed on unaged samples by means of a Lumipol 3 luminimeter manufactured by the Polymer Institute of Slovak Academy of Sciences, Bratislava, Slovakia. The measurements were carried out in an oxygen flow of 50 mL min⁻¹. The samples were circular cuts of polymer sheets weighing about 3 mg. Isothermal CL runs were performed at 150 °C. Non-isothermal runs were performed by the rate of heating 2.5 °C min⁻¹ from 40 to 220 °C. The intensity of luminescence was related to the sample mass, and expressed as counts s⁻¹mg⁻¹.

FTIR spectroscopy on films subjected to accelerated aging was carried out by means of a Nicolet Nexus spectrometer. Spectra were recorded in transmission mode as an average of 32 scans in the range 4000–400 cm⁻¹, with a resolution of 4 cm⁻¹. The carbonyl build-up during the thermal oxidation of the samples was measured as the carbonyl index (ACO), defined as the ratio of areas under the absorbance bands in the range 1650–1780 cm⁻¹ and the absorbance of the peak at 809 cm⁻¹ [14].

TG measurements were carried out at 2, 5, 10, and 20 °C min⁻¹ heating rates from 30 to 700 °C under nitrogen and air atmosphere (100 mL min⁻¹) by means of a Perkin Elmer Pyris Diamond TG-DTA. To calculate the activation energy, E_a, of the degradation process, kinetic analysis was conducted on TG data by using the Flynn-Wall-Ozawa method [15,16]. Tensile tests were performed using an Instron model 5564 dynamometer equipped with a 1 KN load cell. The results were evaluated by the Instron Merlin Series software.

The tests were performed at 23 ± 2 °C, 45 ± 5% RH, with a 10 mm min⁻¹ clamp separation rate.

3. Results and discussion

OIT is one of the most commonly used indicators of polymer stability both in academic and industrial environment [17], being the preferred test used by the industry to assess the oxidative stability of polyolefins. As the OIT is a relative measure of the degree or level of stabilization of the material tested, the longer the OIT, the more stable is the material tested.

Fig. 1 shows the plot of the OIT as measured by DSC at different temperatures. It has to be pointed out that OIT measurements were carried out both below and above melting temperature (approximately 165 °C). From the figure, it is evident that the natural additives tested improve PP oxidative stability. In particular, red grape seeds show the higher stabilization efficiency, especially at lower temperatures.

On the other hand, at temperatures above PP melting point the oxidation rate is faster, and no differences can be observed between stabilized and unstabilised samples at 180 °C. It is noteworthy that the OIT experiments in the case of PP stabilized with Irganox 1010 were performed only at 180 °C, and a value of about 15 000 s was obtained. This implies that the synthetic antioxidant imparted far better stabilization to PP. However, it has to be pointed out that the exact amount of stabilizing compounds, either phenolics or carotenoids, in the natural additives was not quantified, and although it can be supposed that grape seeds contain approximately 10 wt.% of polyphenolic compounds [7], the effective content of active antioxidants may vary in the biomass. Furthermore, due to high temperatures, part of the stabilizer could possibly be lost during the processing step conducted at high temperatures. This can be particularly true when natural additives are used, as in nature they are synthesized to withstand much lower temperatures.

In Fig. 2 the CL emission at the oxidation of the samples in oxygen at 150 °C (Fig. 2a), and under non-isothermal conditions is reported (Fig. 2b). It’s known that in the case of polyolefins the antioxidant efficiency is related to the time needed for the CL signal to increase. Weathering of polymers is expected to cause an increase of carbonyl species, as the latter are the stable secondary products during thermal- and photo-oxidation of polymers. Several carbonyl compounds are produced during oxidative degradation of
polypropylene, namely ketones, esters, lactones, carboxylic acids [18], and the CL intensity is proportional to the accumulation of carbonyl species formed during oxidation [19].

CL isothermal experiments (Fig. 2a) confirmed the results obtained by DSC, although to a different quantitative extent. First, PP2 showed improved stabilization with respect to the other samples. Besides, the time to observe an increase in the CL trace (about 4000 s) was longer than that observed by DSC. However, when OITs are determined by DSC, the measuring time is supposed to start when purging gas is switched from nitrogen to air, so that the first isothermal equilibration segment is neglected.

Furthermore, the higher sensitivity of CL compared to DSC is witnessed by the behaviour of PP3, which at 150 °C is definitely more stable than PP4 and PP0. The behaviour of isothermal CL traces also suggests that the different chemical nature of tomato and grape constituents (carotenoids in the former case, phenols in the latter), greatly affects their temperature sensitivity. In fact, the sudden increase and high intensity (comparable with that of PP0) of the PP4 CL signal imply that the stabilizer is quickly degraded at 150 °C in oxygen, while phenols present in the grape seeds are more thermally resistant and also reduce the rate of PP oxidation. Similar results were obtained in the case of dynamic CL runs performed with a heating rate of 2.5 °C min⁻¹. In this case, it should be observed that CL emission of PP1 remains very low even at temperatures exceeding 180 °C.

To correlate the results of predictive experiments carried out on unaged samples with those obtained from samples subjected to accelerated aging, FTIR spectroscopy was performed on film samples aged at 70 °C in air. In Fig. 3 the carbonyl build-up as a function of the aging time is reported for each sample up to complete embrittlement.

As can be observed from the figure, in the case of neat PP, carbonyl index remains almost constant up to 165 h, which represents the induction time, but thereafter it increases at a very fast rate. This trend of the kinetic evolution of the carbonyls reveals the typical outlines of a thermooxidative reaction, i.e. an induction period followed by an autoacceleration [20]. On the other hand, the carbonyl index remains low and constant for very long times for PP1 and PP2. Even after 2000 h the induction step is still in progress, as the stabilizers are not completely consumed and they still protect polypropylene from oxidation. Failure of PP2 occurs at about 3000 h, while PP1 is still in the induction period up to 4500 h. The behaviour of the other antioxidants falls in between PP0 and PP2: the carotenoid extract does not change significantly the behaviour of PP, while PP3 shows to be stable up to 500 h, thereafter the carbonyl content increases. The marked difference between PP1 and PP2 could be ascribed to the lower amount of polyphenols contained in white grape compared to the red one [21,22].

Further insight on the possible stabilization mechanisms of the additives tested can be obtained by the kinetic analysis of the TG data recorded under air and nitrogen atmosphere, according to the Flynn-Wall-Ozawa method. The activation energy Ea was obtained from a linear fitting of log β versus 1000/T at different conversion degrees (x), where β is the experimental heating rate and T is the absolute temperature.

In Fig. 4 Ea values plotted vs. α up to a 50% conversion for the neat polymer and PP containing different stabilizers under nitrogen and air are reported. As far as experiments performed in nitrogen are concerned (Fig. 4a), Ea increases similarly with the conversion degree for all the samples, except PP4. The observed variation in Ea suggests that different processes govern the degradation phenomenon at the initial and final stages [23]. The initial lower value of Ea is associated with the initiation step that occurs at the polymer weak links. In particular, in the case of polypropylene, the initiation step involves the tertiary carbon atoms in the backbone, able to yield stable radicals. As the temperature increases, the limiting step of degradation shifts toward mechanism initiated by random scission characterized by higher activation energies [24]. It can be concluded that the presence of different additives does not change the mechanism of thermal decomposition of PP, however...
higher values are observed for PP stabilized with white grape seeds. In the case of PP4, the presence of carotenoid compounds causes a dramatic change in the curve, as a maximum can be observed at around 5% conversion values.

In air atmosphere (Fig. 4b), lower values of \( E_a \) can be observed, and slight changes in activation energies are recorded with respect to the additives used, since the thermal oxidation is the main degradative process. It is interesting to observe that under oxidizing conditions PP4 shows the lower values of \( E_a \), confirming that the carotenoid species are more sensitive to thermal oxidation. In contrast, higher values of \( E_a \) are associated with the presence of red grape seeds, which possess better stabilizing efficiency than those from white grape, as observed also by DSC, CL, and FTIR experiments discussed above. Once again the superior stability of the synthetic antioxidant is witnessed by the higher \( E_a \) values related to PP1, up to 10% conversion. However, once the phenolic stabilizer is decomposed and volatilizes, the activation energy values fall below those of PP2.

The peculiar behaviour observed for the additives either under nitrogen or air can be rationalized in terms of the different chemical structure of the components. Tomato extract contains over 80 wt.% lycopene, with small amounts of \( \alpha \)-tocopherol and carotenones [13]. These molecules possess extensively conjugated structures that are efficient in scavenging free radicals [25]. Carotenoids react efficiently with alkyl radicals to form radical adducts, while the rate constants of their reaction with alkylperoxy radicals is fairly low [26]. Furthermore, it was observed that \( \beta \)-carotene and carotenoids form relatively stable adducts with alkyl- and alkoxy-containing radicals [3], while per oxy radical addition yields an unstable intermediate radical adduct that collapses to an epoxide and releases an alkoxy radical. This result suggested that peroxo radical scavenging by initial radical addition is inherently inefficient, and peroxy addition contributes an antioxidant effect only to the extent that the released alkoxy radicals are subsequently scavenged. This entails that \( \beta \)-carotene shows greater antioxidant effectiveness at low oxygen tension [27].

The presence of multiple unsaturation on the hydrocarbon chain is an important factor to enhance trapping of alkyl radicals. Recently, Ohkatsu et al. designed new phenolic antioxidants that, due to the presence of allyl substituents, could trap both alkyl and peroxy radicals and increase the antioxidant activity [28].

Therefore, tomato extract can slow down thermal degradation of PP under nitrogen through alkyl radical scavenging, as confirmed by the larger values of activation energy showed during the initial stages of the process. Higher conversion extents, however, lead to its disappearance due to degradation and volatilization. On the other hand, in the presence of oxygen, carotenoids can degrade through free radical mediated auto-oxidation reactions, and it was shown that temperatures as high as 95 °C lead to their almost complete oxidative degradation in few hours [29,30]. Under these conditions the thermal oxidation of PP is even faster, as the number of free radicals able to initiate the oxidative chain reaction of the matrix increases, due to the formation of reactive carotenoid species. This is confirmed in Fig. 4b, where lower values of \( E_a \) are associated to the presence of the tomato extract.

The stabilization mechanism due to phenolics present in Lrganox 1010 and vinification waste involves scavenging of alkylperoxy radicals by donating a phenolic hydrogen atom, forming a polymer hydroperoxide and a resonance-stabilized antioxidant radical. The antioxidant radical is not reactive enough to propagate the chain of peroxyxidation, but decays by reaction with another radical, forming stable products, or may be recycled by another antioxidant [31]. However, phenols cannot scavenge alkyl radicals, as their radical-trapping rate is low, then alkyl radicals react faster with molecular oxygen.

The above reported results suggest that additives based on grape seeds could be suitable as long-term antioxidants, while carotenoid extracts seem to be effective as processing stabilizers, when oxygen partial pressure is relatively low.

To check this hypothesis we performed tensile tests on the polymer films at different aging periods (Fig. 5). First, it can be noticed that the high-temperature processing caused appreciable degradation of neat PP. This is shown by observing the values of strain at break before aging (Fig. 5a). The unstabilised sample retained only 10% residual strain at break, while the sample PP1 showed a value of about 300%. By the way, the samples containing grape seeds showed a behaviour very similar to that of neat PP, suggesting that natural phenols are not good processing stabilizers. Conversely, the lycopene extract stabilized the polypropylene during the processing step, as PP4 showed strain at break values around 100%, up to 24 h of aging. On increasing thermal aging time, unstabilized PP failed dramatically at about 400 h, and it turned out that also the mechanical performance of PP4 decayed faster, as the tomato extract is not effective as long-term stabilizer due to auto-oxidation. Interestingly, at very long times the curves related to the changes in stress at break (Fig. 5b) show that the PP4 film became very brittle due to extensive oxidation, while in the case of PP2 and PP3 the strength and the elongation at break did not change appreciably in the course of aging, analogously to the sample stabilized with the commercial antioxidant. Thus, the natural
phenols contained in the grape seeds examined in the present study are not good processing stabilizers but they are effective as antioxidants.

4. Conclusions

A preliminary investigation is reported on the antioxidant efficiency for PP films of waste products from tomato and wine processing. Several analytical techniques were employed in order to evaluate the stabilization due to the presence of additives. DSC and CL experiments performed on unaged materials confirmed that the additives provide polypropylene with stabilization against thermal-oxidative degradation, even though in a lower extent compared to the commercial stabilizer Irganox 1010. The order of efficiency of the natural additives is red grape seeds > white grape seeds > tomato extracts. The same efficiency sequence was obtained by investigating the build-up of carboxyls through FTIR characterization performed on samples artificially aged in air at 70 °C. The kinetic analysis of the TG data obtained both under air and nitrogen atmosphere was performed using the Flynn-Wall-Ozawa method. In nitrogen the activation energy, $E_a$, increased with the conversion degree for all the samples, showing the occurrence of a complex, multi-step decomposition process. Interestingly, the highest $E_a$ values were associated with the presence of tomato extracts, confirming that the carotenoids contained therein are very efficient in scavenging the alkyl radicals able to initiate the oxidative degradation. Under air, the thermal oxidation was the main degradative stage, and slight variations of $E_a$ were recorded with respect to the additives used. In these conditions, higher $E_a$ values associated with the presence of red grape seeds confirm the higher antioxidant efficiency of this additive. Tensile tests performed on aged samples definitively confirmed that carotenoid extracts are effective as processing stabilizers, while additives based on grape seeds could be suitable as long-term antioxidants. The results of the study point out the importance of performing further work aimed to evaluate the synergistic effect of tomato and grape seed derivatives on long-term stabilization of polypropylene.

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References


