

From Nutraceuticals to Materials: Effect of Resveratrol on the Stability of Polylactide

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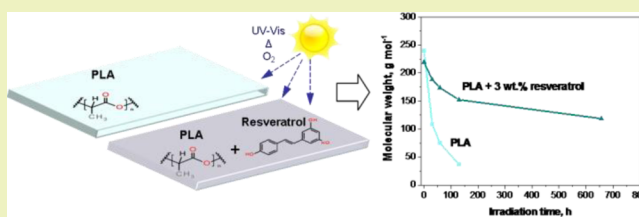
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S Supporting Information

ABSTRACT: Resveratrol is a naturally occurring polyphenol, well known as a nutritional supplement due to its strong antioxidant properties associated with anti-inflammatory activity and possible prevention of cardiovascular diseases. In this work, the effect of resveratrol on thermal, thermo-oxidative, and photo-oxidative degradation of polylactide is reported in the frame of developing fully biobased polymer formulations. Characterization of PLA films by thermal methods and photo-oxidative treatments demonstrated that resveratrol catalyzed high temperature transesterification reactions under inert atmosphere, whereas it efficiently inhibited the exothermal oxidative reactions of the polymer backbone. Low-temperature photochemical degradation experiments on PLA films allowed elucidating the stabilization mechanisms of the phenolic additive. Resveratrol is capable of slowing the oxidative chain reaction of PLA through a peroxy radicals scavenging mechanism, while it has little effect on the direct photolytical cleavage of the ester bonds. Moreover, direct resveratrol oxidation as well as the reaction between the phenol and photo-oxidized polymer species yield secondary photoproducts, which are also able to protect PLA against photo-oxidation likely due to the UV screening effect of the formed chromophores. Resveratrol is thus proposed as an eco-friendly and biocompatible additive for a sustainable approach to the stabilization of PLA films in packaging and other applications.

KEYWORDS: Polylactide, Biodegradable materials, Bioplastics, Resveratrol, Photochemical stability, Antioxidants



INTRODUCTION

Polylactide (PLA) is a biodegradable thermoplastic polymer that can be made from renewable resources such as beet sugar and corn starch.¹ Due to its high tensile strength, PLA is the most important biodegradable polymer in the market of fibers and medical devices and a potential substitute of polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET) in applications where high ductility is not a priority, such as packaging and agricultural uses.² To make this macromolecule suitable for a wider range of products, several polylactide modifications have been described, including copolymerization,^{3–5} blending,^{6,7} and preparation of hybrid systems.^{8,9} PLA physical properties are also strongly influenced by its stereochemistry and molecular weight, so that monitoring the structural changes occurring during polymer processing and service life is of prime importance, especially with regard to thermally and light-induced degradation.^{10–12} The activation energy of these reactions is often quite low, and a dramatic deterioration of properties can occur even at low temperatures. It has been shown that the mechanisms of thermal and photochemical degradation of PLA proceed with random chain excision. During thermal degradation, the polymer backbone

cleavage is mainly caused by nonradical intramolecular transesterification,^{13–15} while photochemical oxidation occurs through a radical mechanism, with hydroperoxide decomposition and formation of anhydride groups when the radiation source used is closer to a natural outdoor exposure.^{16–18} With wavelengths lower than 290 nm, the oxidation can be initiated by Norrish I and Norrish II chain cleavage reactions involving the carbonyl groups.^{12,19,20}

Recent studies have demonstrated that several naturally occurring phenolics are efficient stabilizers for polyolefins and polyester-based polymers.^{21–26} Natural phenols have been also used as additives for PLA to get active food packaging,^{27–29} however, these reports were mainly devoted to studying diffusion of the compounds through the plastic to the food, paying little attention on the stabilizing effect on the plastic itself. Resveratrol is a naturally occurring stilbenoid, which is commonly associated with the antioxidant potential of berries, peanuts, red wine, and grapes.³⁰ Resveratrol is well known as a

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nutritional supplement, as it is a strong inhibitor of the oxidation of lipids and lipoproteins and the aggregation of platelets. It plays a role in the prevention of human cardiovascular diseases and may also possess anti-inflammatory and anticancer properties.³¹ The photoprotective and antioxidant effects of resveratrol on the skin damage induced by UV radiation and cell ability to survive under stress conditions caused by UV-B light have been extensively reviewed.^{32,33} On the other hand, little information about the incorporation of resveratrol into polymer films has been reported in literature,^{29,34} and the effect of the addition of resveratrol on the UV-visible light stabilization of polymers has not been studied.

On the basis of the above, in this study, we investigate the influence of resveratrol on the degradation of PLA films, with the aim of generating completely renewable polymer formulations. Thermogravimetry measurements were carried out to determine the thermal and thermal oxidative stability of resveratrol and polymer formulations. Moreover, low-temperature UV-visible light irradiation of polymer films provided information on the mechanism and rate of photodegradation of resveratrol-doped PLA under service conditions.

EXPERIMENTAL SECTION

Materials. Poly(L-lactide) (PLA) grade 4042D (94% L-lactic acid) was obtained from NatureWorks LLC (U.S.A.); *trans*-resveratrol (99.4%) was obtained from Chroma-Dex (U.S.A.).

Film Preparation. PLA films, neat, and containing 1% and 3% w/w resveratrol (coded PR0, PR1, and PR3, respectively) were extruded through pilot plant-scale film-blowing equipment as previously reported,³⁴ with the following temperature profile (from hopper to die): 165, 170, 170, 170 °C. The films average thickness was 50.8 μm. The films were annealed between two glass plates in a vacuum oven at 60 °C for 24 h to prevent recrystallization and heat deformation during the photo-oxidation treatment.³⁵

Photo-Oxidative Aging. Irradiation of specimens was carried out in dry conditions (RH 0%) at 40 °C in an Angelantoni SU250 (Italy) forced air climatic chamber equipped with a mercury UV lamp ($\lambda > 250$ nm). Aged specimens were collected at different times to follow changes in crystallinity, molecular weight, functional groups formation, and mechanical properties. Figure S1 of the Supporting Information shows an irradiance map ($\mu\text{W cm}^{-2}$) and spectral distribution of the mercury UV lamp used in the chamber.

Differential Scanning Calorimetry (DSC). A differential scanning calorimeter (Mettler Toledo DSC 822, Switzerland) was used to determine glass transition temperature (T_g), melting temperature (T_m), and degree of crystallinity (X_c) of the materials. Film samples were heated from 10 to 250 °C at a heating rate of 10 °C min⁻¹ under nitrogen flow. Crystallinity was calculated using eq 1

$$X_c = 100 \frac{\Delta H_m - \Delta H_c}{f_p \Delta H_m^0} \quad (1)$$

where ΔH_c is the enthalpy of cold crystallization, ΔH_m is the enthalpy of fusion, f_p is the PLA weight fraction in the sample, and ΔH_m^0 is the enthalpy of fusion of crystalline PLA (91 J g⁻¹).³⁶

Thermogravimetry (TG). TG measurements were carried out under nitrogen or air atmosphere (flow rate 100 mL min⁻¹) using a PerkinElmer Pyris Diamond TG-DTA differential thermal analyzer (U.S.A.). Samples were heated at 10 °C min⁻¹ from 90 to 600 °C. To eliminate moisture, a 30 min isothermal treatment at 90 °C was carried out prior to the heating run.

Gel Permeation Chromatography (GPC). The average molecular weights (MW) of PLA films were determined at 30 °C using a Waters 150C (U.S.A.) gel permeation chromatograph equipped with an evaporative light scattering detector (Polymer Laboratories, U.K.). Two Polymer Laboratories (PLgel 5 μm MIXED-C) mixed columns in

series were used. An isocratic elution of chloroform at a flow rate of 1 mL min⁻¹ was applied. A MW calibration curve was constructed using 10 polystyrene standards with a MW range of 0.5–3000 kDa.

Fourier Transform Infrared (FTIR) Spectroscopy. FTIR spectra of the PLA-based films were acquired by means of a PerkinElmer Spectrum 100 spectrometer (U.S.A.) in transmission mode, as an average of 32 scans in the range of 4000–400 cm⁻¹ (resolution of 4 cm⁻¹). To avoid differences due to film thickness and inhomogeneity, for each formulation, a single film specimen mounted on a plastic sample holder was analyzed periodically and then returned to the oven for continued aging. The increase in functional groups content was measured by subtracting the area values of the absorbance peaks of unaged films from those of irradiated samples. Integration was performed in the following regions: 3300–3100 cm⁻¹ (O–H groups), 1865–1828 cm⁻¹ (anhydride groups), 1734–1716 cm⁻¹ (C=O groups), 1294–1273 cm⁻¹, (C–OH groups), and 956–924 cm⁻¹ (C=C groups).^{12,16}

Mechanical Properties. Tensile tests were performed using an Instron model 5564 dynamometer (U.S.A.) equipped with a 1 kN load cell at 23 ± 2 °C, 45 ± 5% RH with a 5 mm min⁻¹ clamp separation rate. Prior to mechanical testing, eight dumbbell-shaped specimens cut along the machine direction were conditioned in an environmental chamber at 25 °C and 50% RH for 48 h.

Experimental Design and Statistical Analysis. A randomized block design was used. Data were analyzed by Kruskal–Wallis one way analysis of variance on ranks using SigmaPlot (Systat Software, U.S.A.). Significant differences among the means were tested using Tukey's test ($P < 0.05$). The values are expressed as average ± standard deviation (SD).

RESULTS AND DISCUSSION

Thermal Stability of Resveratrol-Doped PLA Films.

Thermogravimetry measurements were carried out to determine the thermal and thermal oxidative stability of resveratrol and polymer formulations by means of a fast and direct method. Attempts to perform oxidative induction time measurements through DSC were unsuccessful, as the slow oxidation process of PLA proceeded constantly since the very beginning of the experiment, so that the calorimetric curves did not show a distinct onset of exothermic oxidation reaction. Moreover, because correlation between high-temperature methods, such as TG, and long-term stability in polymer/antioxidant systems could lead to inconsistent extrapolation of data to lower temperature, an accelerated photo-aging treatment at low temperature that can provide information on polymer durability under service conditions was also performed.

Figure 1 shows thermogravimetric and differential thermal analysis (DTA) curves related to the degradation of resveratrol under nitrogen and air. As shown, resveratrol was thermally stable until 300 °C under both atmospheres. From the DTA curve, a sharp melting endothermic peak was observed at 265 °C, followed by a broad endotherm with a maximum at 355 °C, which was connected with the single degradation step observed from the TG curve in nitrogen.

The weight loss onset was at 287 °C, a rather high temperature in comparison with other natural and even synthetic antioxidants.^{37,38} It is also noteworthy that resveratrol retained almost 50% of the initial weight even at 500 °C. A comparable behavior was observed under air until 350 °C, a temperature above which the oxidation of the phenol additive was detectable as an upward shift of the DTA curve. This exothermic process caused the weight loss rate in air to be slower than that in nitrogen due to the chemisorption of oxygen by the resveratrol molecules. A residual mass of 50% was measured also under oxidizing conditions.

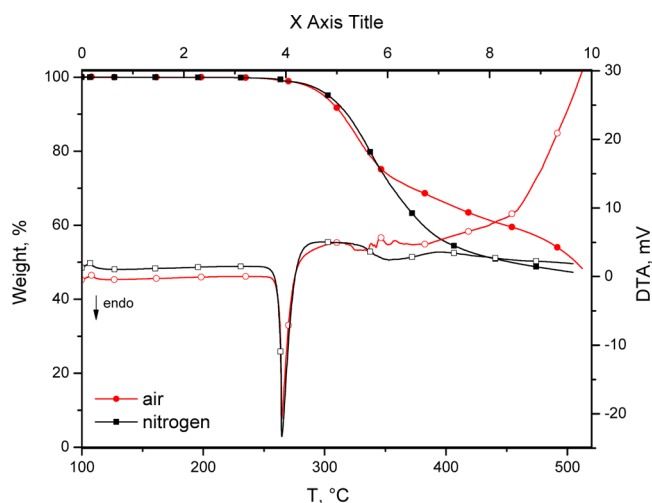


Figure 1. TG (full symbols) and DTA (empty symbols) curves of resveratrol under nitrogen and air atmospheres.

Figure 2 shows thermograms and DTA curves related to the degradation of resveratrol-doped PLA films under nitrogen (Figure 2a) and air (Figure 2b). The relevant thermal parameters are listed in Table S1 of the Supporting Information.

The thermograms recorded under inert atmosphere showed a single weight loss step for all samples related to an endothermic process peaked at about 350 °C. The presence of 1 wt % resveratrol (PR1) brought about an evident decrease in the degradation temperatures of PLA, which was even more pronounced at an additive content of 3 wt % (PR3). Resveratrol-containing formulations also displayed a residual char at 600 °C. Ortiz-Vazquez et al.³⁹ also observed a decrease in the degradation temperatures of PLA films added with BHT, attributed to the presence of degradation products formed during extrusion. The mechanism of thermal degradation of PLA has been addressed in other studies, which revealed that at temperatures below 230 °C the polymer backbone cleavage is mainly caused by nonradical intramolecular transesterification, leading to the formation of oligomeric rings, acetaldehyde, and carbon monoxide units as byproducts. The significant contribution of *cis*-elimination and radical reactions was also claimed even at such a low decomposition temperature.^{13–15} According to these findings, the observed decrease in PLA degradation temperatures in the presence of resveratrol can be attributed to the phenol hydroxyl-initiated ester interchange process giving oligomers and low molecular weight species,

which volatilize at lower temperatures. Transesterification can be accelerated in the presence of resveratrol due to the stronger nucleophilic character of the aromatic hydroxyls with respect to the aliphatic terminal groups of PLA.

Measurements carried out under air showed a second decomposition step due to the complete oxidation of the char produced during the first weight loss stage. Pure PLA was sensitive to the oxidative environment, as confirmed by degradation temperatures lower than in nitrogen. On the other hand, in the case of the additivated samples, the degradation temperatures in air were higher than those exhibited under inert atmosphere. This result was particularly evident for PR3 (Table S1, Supporting Information) and suggests that resveratrol was directly involved in the thermal oxidative process. This was confirmed by the DTA analysis, which showed that when going from PR0 to PR3 the main degradation step (approximately peaked at 320 °C) progressively changed from exothermic to endothermic. This observation indicated that resveratrol might inhibit oxidative reactions of the polymer backbone, which typically show an exothermic character. The possible mechanisms underlying resveratrol activity are addressed in the FTIR Spectroscopy Section.

Aging Behavior of Resveratrol-Doped PLA Films. Differential Scanning Calorimetry. The thermal parameters obtained from the DSC first heating runs of PR0, PR1, and PR3 are shown in Table 1. The respective thermograms are displayed in Figure S2 of the Supporting Information. Concerning the unaged samples, resveratrol did not significantly affect glass transition temperatures, whereas it brought about a reduction in PLA crystallinity and melting temperature.

UV irradiation treatment had minor effects on polymer crystallinity and glass transition and melting temperatures, which decreased to a small extent. A similar behavior was reported by Tsuji et al.,⁴⁰ who found no significant modification of the degree of crystallinity during PLA aging by photo-oxidation. In addition, Gardette et al.¹⁷ showed that the principal thermal parameters (T_g and T_m) remained at a similar level after the photo-oxidative degradation of pristine and calcium sulfate-doped PLA. Table 1 also shows that pure PLA exhibited increased cold crystallization enthalpy values after irradiation. This finding can be ascribed to chain scission due to oxidation reactions occurring upon photodegradation in the presence of oxygen. As a result, the entangled molecules were released, and their rearrangement was responsible for the observed increase in PLA crystallization enthalpy on heating.⁴¹ Resveratrol was likely able to reduce the rate of the oxidative

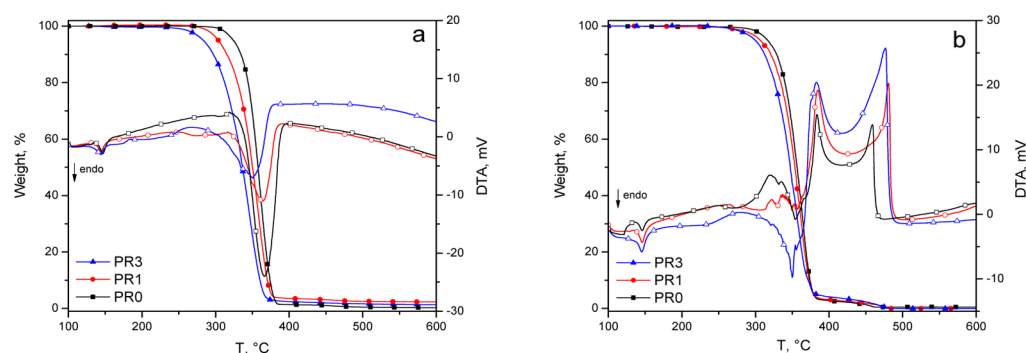


Figure 2. TG (full symbols) and DTA (empty symbols) curves of resveratrol-doped PLA films under (a) nitrogen and (b) air atmospheres.

Table 1. Thermal Parameters Obtained by DSC Characterization of Resveratrol-Doped PLA Films after Different Irradiation Periods*

sample	irradiation time (h)	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	ΔH_c (J g^{-1})	ΔH_m (J g^{-1})	X_c (%)
PR0	0	61.8 ± 2.8^a	146.8 ± 1.6^b	4.4 ± 0.5^a	6.9 ± 0.6^b	2.8 ± 0.5^b
	200	61.2 ± 1.5^a	147.1 ± 1.2^b	11.5 ± 0.4^c	11.4 ± 0.4^d	nd
	420	59.2 ± 0.6^a	145.7 ± 0.6^{ab}	14.5 ± 0.6^d	14.5 ± 0.2^e	nd
PR1	0	62.1 ± 2.6^a	146.3 ± 1.3^{ab}	3.3 ± 0.6^a	2.7 ± 0.1^a	nd
	200	60.3 ± 2.9^a	146.9 ± 1.6^b	9.5 ± 0.7^b	8.8 ± 1.0^c	nd
	420	61.4 ± 1.4^a	144.5 ± 0.5^{ab}	8.4 ± 0.4^b	8.8 ± 0.2^c	0.3 ± 0.1^a
PR3	0	61.3 ± 2.5^a	144.2 ± 0.6^{ab}	3.9 ± 0.2^a	4.1 ± 0.4^a	nd
	200	60.5 ± 2.4^a	145.6 ± 0.5^{ab}	3.6 ± 0.6^a	3.6 ± 0.4^a	nd
	420	59.8 ± 1.5^a	143.7 ± 0.4^a	3.9 ± 0.4^a	3.3 ± 0.2^a	nd

*Values in the same column followed by the same letter are not significantly different ($p > 0.05$). Average of three determinations \pm standard deviation; nd: not detected.

Table 2. Number Average Molecular Weight (M_n) and Polydispersity Index (PDI) of PR0, PR1, and PR3 after Different Irradiation Periods

time (h)	PR0		PR1		PR3	
	M_n (g mol^{-1})	PDI	M_n (g mol^{-1})	PDI	M_n (g mol^{-1})	PDI
0	160,736	1.5	149,824	1.5	145,550	1.5
30	63,083	1.7	113,669	1.6	112,783	1.7
59	35,624	2.1	45,771	2.1	97,875	1.8
130	16,341	2.3	20,198	3.8	69,960	2.2
657	n.a.*	n.a.*	9297	3.9	31,848	3.7

*n.a. = not analyzed.

chain scission, as confirmed by the minor changes in crystallization enthalpy observed for PR3.

Changes in Molecular Weight and Polydispersity Index. In Table 2, the values of number average molecular weight (M_n) are reported as a function of the irradiation time. Weight average molecular weight (M_w) changes are reported in Figure S3 of the Supporting Information.

Prior to irradiation, M_n values of PR1 and PR3 were slightly lower than those of PR0. This can be due to transesterification reactions occurring during the extrusion process. Irradiation brought about a marked decrease of M_n for all samples as soon as the treatment started, indicating that chain scission occurred with no apparent induction period, as already described for thermally and photochemically oxidized PLA.^{18,42} Interestingly, the M_n decrease rate was higher for PR0 compared to PR1 and PR3. As an example, after 30 h of irradiation, M_n of PR0 was reduced by approximately 60%, while PR1 and PR3 retained about 75% of the initial molar mass. A catastrophic reduction in the chain length of PR0 occurred after 130 h of photo-oxidation, while for the doped samples, the decrease rate of M_n was proportional to the resveratrol concentration. The results were that after 130 h of irradiation, PR3 retained approximately 50% of the initial M_n . This behavior can be attributed to the effective antioxidant activity of resveratrol. Molar mass data for the photodegraded PLA-based samples as a function of time were satisfactorily fitted to a second-order kinetic law, as shown in Figure S4 of the Supporting Information. The calculated rate constants for PR0, PR1, and PR3 were 4.30×10^{-7} , 1.67×10^{-7} , and $3.61 \times 10^{-8} \text{ mol g}^{-1} \text{ h}^{-1}$, respectively, which confirm the stabilizing activity of resveratrol against the photo-oxidative degradation of PLA. A detailed comparison of these data with those available in the literature for photodegraded PLA is given in Supporting Information.^{13,17–19,43–45}

A slight increase in PDI was noticed for all the irradiated samples, suggesting that chain scissions occurred randomly

along the polymer backbone due to polymer oxidation, while hydrolytic degradation was negligible under the adopted dry conditions. On the other hand, PDI values increased significantly for PR1 and PR3 following the disappearance of resveratrol (Figure S5, Supporting Information). This suggests that massive irradiation may trigger the formation of PLA–resveratrol adducts that act as initiating sites at which degradation occurred preferentially rather than taking place at random places with equal probability. The possible reaction pathways between PLA and resveratrol are detailed in the next section.

FTIR Spectroscopy. FTIR transmission spectra (Figure S6, Supporting Information) of films before irradiation showed the presence of the main resveratrol functionalities at 3500 cm^{-1} (phenol O–H stretching), 1608 cm^{-1} (resonance of the aromatic C=C), and 1515 cm^{-1} (in-plane bending of phenyl C–H bonds).⁴⁶

FTIR spectra were acquired at different times during sample photodegradation until the specimens became brittle and failed. The superposition of the spectra of irradiated samples shows several features accounting for the progress of photo-oxidation. As an example, Figure S7 of the Supporting Information shows the spectra of PR0 obtained after different irradiation times. In all instances, subtraction spectra give a more detailed picture of the spectral modifications occurring upon photo-oxidation (Figure 3).

The main changes were observed at 3450 , 1850 , 1730 , 1646 , 1285 , and 945 cm^{-1} due to the formation of O–H, C=O, and C=C functional groups in the oxidized photoproducts. Negative peaks were observed at 1456 , 1385 , and 1365 cm^{-1} because of the disappearance of C–H bonds due to oxidation.¹² It is worth noting that the samples containing resveratrol also showed decreasing peaks at 3500 , 1618 , and 1515 cm^{-1} owing to the reactions involving the phenol stabilizer (Figure S8, Supporting Information). In Figure 4, the changes in peak areas

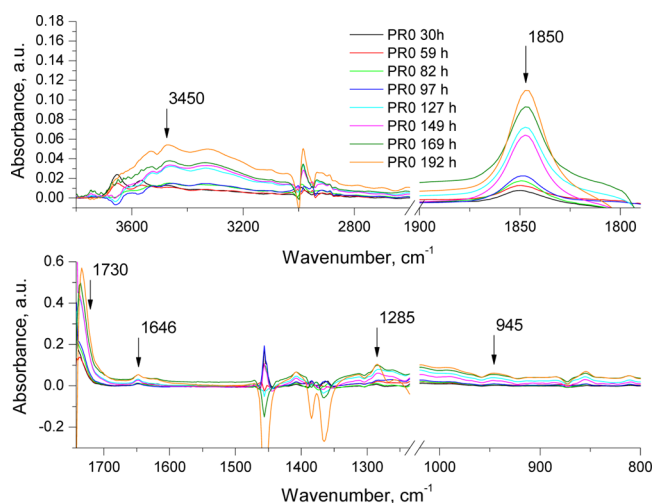


Figure 3. Subtracted FTIR transmission spectra recorded upon photo-oxidation of PR0. Arrows indicate major spectral changes.

at 3450 (a), 1730 (b), 1285 (c), and 945 (d) cm^{-1} are displayed for all samples as a function of the irradiation time.

The development of a broad band centered at about 3450 cm^{-1} upon photo-oxidation of PLA has been attributed to alcohol, hydroperoxide, and carboxylic acid group formation.^{16,18,47} However, none of these reports examined in detail the kinetic curve of the absorption increase in this spectral region. In the present work, peak integration was performed in the 3300–3100 cm^{-1} domain because the decreasing peak at 3500 cm^{-1} for PR1 and PR3 prevented performing the integration in a larger spectral area. In this region, a constant increase was measured for pristine PLA (Figure 4a), suggesting that this absorption was mainly due to the formation of stable photoproducts. A similar trend was displayed by the broad

band around 1730 cm^{-1} , attributed to the formation of aldehydes and carboxylic acids (Figure 4b). In particular, constant values of the O–H to C=O absorption ratio (3300 cm^{-1} /1730 cm^{-1}) versus irradiation time were found for pure PLA (Figure S9, Supporting Information), suggesting that the major photostable products are likely carboxylic acids. These spectral changes were accompanied by absorption increases at 1285 and 945 cm^{-1} , characteristic of C–OH bending of carboxylic acids and vinyl unsaturations resonance, respectively (Figure 4c,d). All these experimental findings allowed hypothesizing that under the adopted irradiation conditions, which included UV light at wavelengths below 300 nm, photolytical cleavage of ester carbonyl through Norrish type I and II mechanisms can be activated, yielding alcohol, carboxyl, and alkene compounds (Scheme S1, Supporting Information) as ultimate products.^{19,40,48}

Another characteristic pathway of the photodegradation mechanism of PLA, in particular when the polymer is irradiated at wavelengths above 300 nm, is the radical oxidation process, which leads to the formation of anhydrides.^{16,47} The detailed analysis of kinetic evolution of the anhydride groups at 1845 cm^{-1} and the anhydride to vinyl groups ratio (1845 to 945 cm^{-1}) are reported in Figure S10 of the Supporting Information, which also provides an estimation of the relative importance of the two reaction pathways during polymer irradiation. Summarizing, in the early stage of irradiation, direct photolysis through Norrish mechanisms was the major degradation route. As the photo-aging treatment proceeded, the contribution of the oxidative reactions became more important, and after 130 h, the value of the anhydride to vinyl ratio doubled that at the beginning of the exposure. Further irradiation did not bring about further changes, suggesting that for prolonged aging the respective contribution of the two degradation pathways was constant.

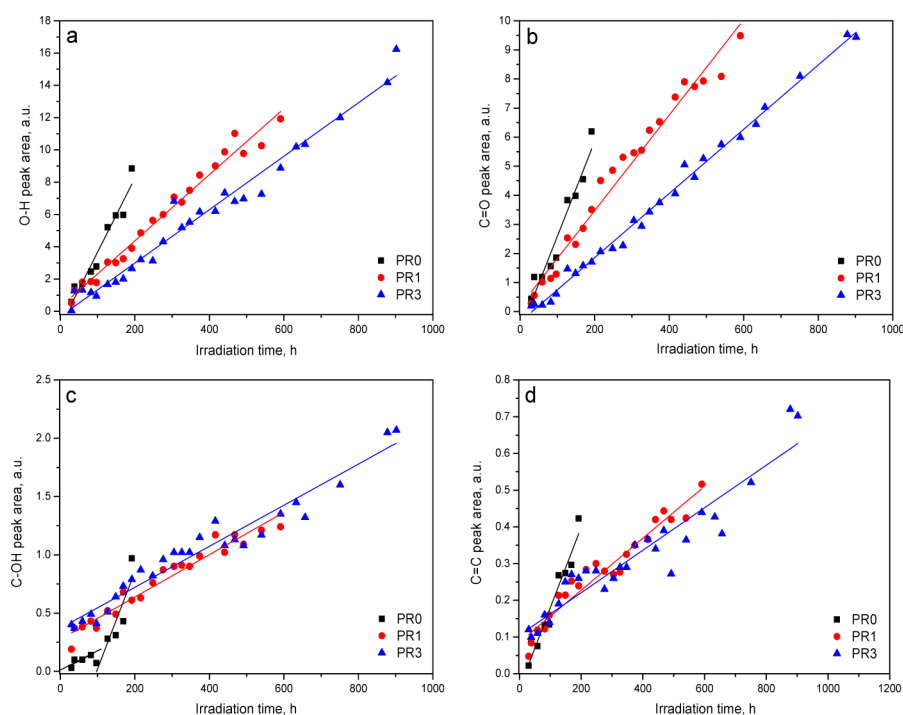
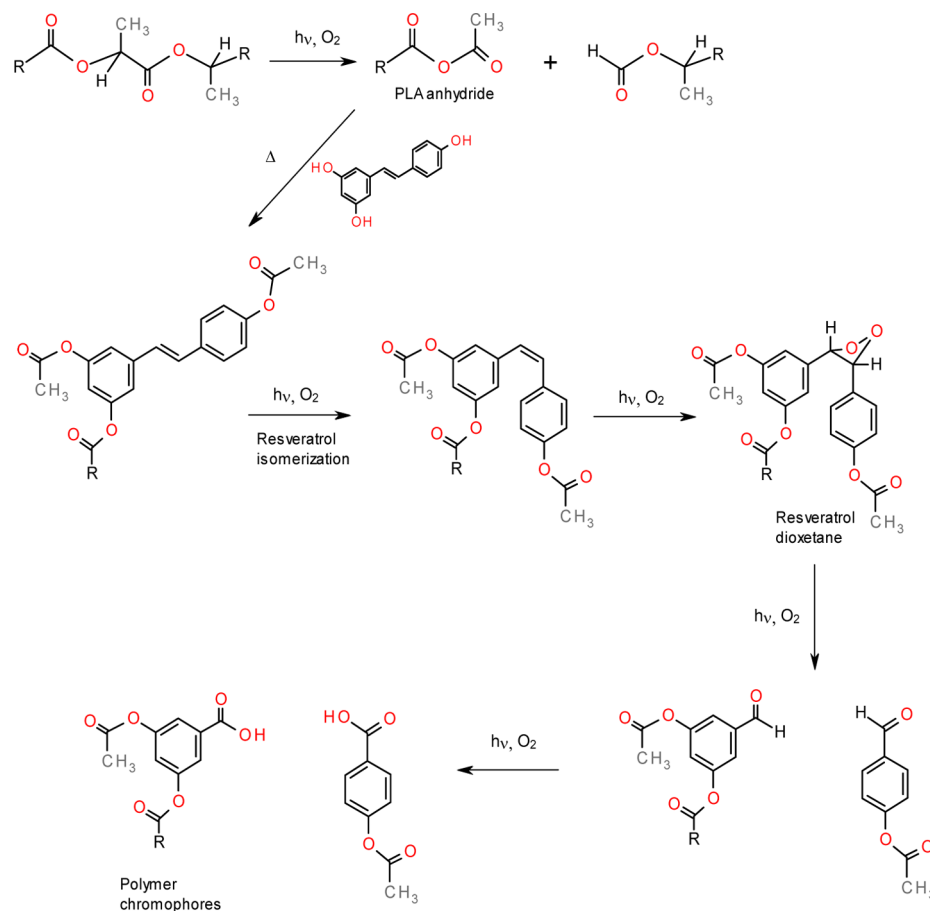


Figure 4. Kinetic evolution of (a) hydroxyl, (b) carbonyl, (c) carboxylic C–O single bond, and (d) vinyl groups upon photo-oxidation of PLA-based films. Fitting lines are guides for the eye.

Scheme 1. Possible Reaction Pathways Occurring upon UV Irradiation of Resveratrol-Doped PLA, Including Reaction between Resveratrol and PLA Anhydride Groups and Subsequent Formation of Resveratrol Dioxetane Derivative, Eventually Leading to the Formation of Carboxyl Groups and Bis-Acyloxy-Benzoic Acid Polymer Chromophores



The analysis of the time evolution of the FTIR peak area also provides insight into the PLA degradation mechanism in the presence of resveratrol. The phenol additive was effective in slowing down the accumulation rate of O–H and C=O groups, and the antioxidant activity was directly related to the stabilizer content (Figure 4a,b). Resveratrol also markedly reduced the buildup of anhydride groups, in particular at higher additive concentration (Figure S10a, Supporting Information). These results suggest that resveratrol is capable of slowing the oxidative chain reaction of PLA through a peroxy radicals scavenging mechanism (Scheme S2, Supporting Information), where the peroxy radical formally abstracts a H atom from one of the hydroxyl groups in resveratrol and forms a resonance-stabilized radical species.⁴⁹ On the other hand, the additive had no effect on the buildup of vinyl groups during the first 200 h of irradiation, while it induced a slight decrease in their accumulation rate afterward (Figure 4c). This finding indicates that resveratrol was not able to reduce the rate of Norrish II type photolytical cleavage.

A more detailed analysis of both subtracted spectra and curves of the functional group evolution during photo-oxidation of resveratrol-doped PLA provides evidence of more complex reaction pathways involving the phenolic antioxidant. From the examination of the subtracted spectra, it was observed that the already mentioned decrease in the hydroxyl band that peaked at 3500 cm^{-1} was also accompanied by a similar reduction of the peak at 1515 cm^{-1} , corresponding to the in-plane bending of

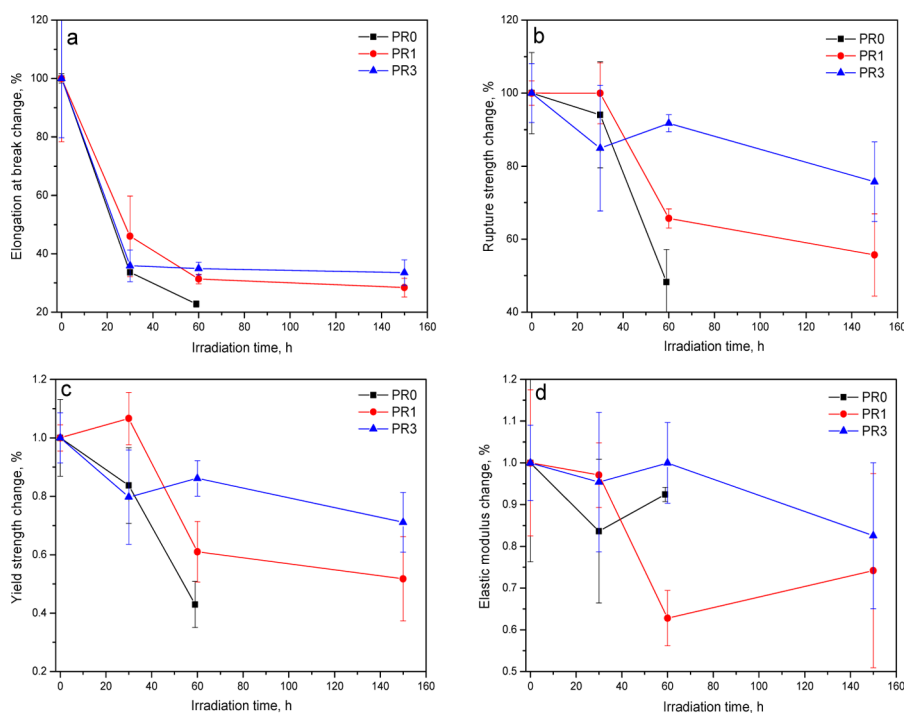
phenyl C–H bonds. The plot of the variation of the area of this peak vs time (Figure S5, Supporting Information) for PR3 showed that after only 100 h of aging about 50% of resveratrol was converted. It was also noticed that the anhydride kinetic curves of PR1 and PR3 showed a suppressive behavior (Figure S10a, Supporting Information), with absorbance plateau values inversely related to the resveratrol content. Moreover, the stabilized samples showed that the relative rate of formation of hydroxyls was much higher than that of carbonyls in the early 100 h of aging, in particular at higher resveratrol content (Figure S9, Supporting Information). This observation is consistent with the sudden increase in the 1285 cm^{-1} carboxyl absorption occurring in the presence of resveratrol in the first 100 h of irradiation (Figure 4c). All these findings can be related to the reaction between resveratrol and anhydride groups, which is reported to occur under mild conditions,⁵⁰ as well as to direct resveratrol photo-oxidation reactions, which also lead to the formation of carboxyl groups on the aromatic ring (Scheme 1).

Photochemical and radical-induced oxidation of resveratrol has been recently addressed, and it was described that under photochemical activation in the presence of oxygen, resveratrol undergoes rapid *cis-trans* isomerization. This can lead to the formation of phenanthrene derivatives via electrocyclic ring closure or to a dioxetane derivative that can spontaneously decompose, yielding two carbonyl species identified as hydroxybenzaldehydes.⁴⁹ The latter were also identified as

Table 3. Elongation at Break (ϵ), Tensile Modulus (E), Rupture Strength (σ_b), and Yield Strength (σ_y) for PLA Films Added with Resveratrol before and after Thermal Annealing*

sample	ϵ (%)		E (MPa)		σ_b (MPa)		σ_y (MPa)	
	not annealed	annealed	not annealed	annealed	not annealed	annealed	not annealed	annealed
PR0	30.0 ± 5.9 ^a	6.4 ± 3.1 ^b	2502 ± 339 ^a	2513 ± 595 ^a	35.7 ± 2.7 ^a	45.5 ± 5.1 ^a	42.6 ± 4.0 ^a	51.2 ± 6.7 ^a
PR1	34.9 ± 12.4 ^a	6.8 ± 1.5 ^b	2443 ± 280 ^a	2349 ± 411 ^a	29.8 ± 5.6 ^a	46.9 ± 1.6 ^a	38.0 ± 7.8 ^a	50.5 ± 2.3 ^a
PR3	23.7 ± 3.4 ^a	6.4 ± 2.3 ^b	2439 ± 338 ^a	2303 ± 208 ^a	42.2 ± 2.9 ^c	48.4 ± 3.9 ^a	46.8 ± 4.0 ^a	51.6 ± 4.4 ^a

*Values in the same column followed by the same letter are not significantly different ($p > 0.05$).

**Figure 5.** Percent relative changes of: (a) elongation at break, (b) rupture strength, (c) yield strength, and (d) elastic modulus for PLA-based films as a function of the irradiation time.

minor end products of the radical-induced oxidation of resveratrol through water gamma radiolysis, being dihydroxybenzoic acid prevailing.⁵¹ Because phenanthrene compounds are expected to be highly fluorescent, fluorescence emission was measured for unaged and UV-irradiated PLA films (Figure S12, Supporting Information). It was observed that unaged films containing resveratrol exhibited a fluorescence peak at 400 nm, which was completely quenched after photo-oxidation. This finding suggested that compounds with a decreased aromatic character with respect to the parent resveratrol were formed upon irradiation. Therefore, it can be hypothesized that upon photoaging, resveratrol was partially converted to benzaldehyde and benzoic acid derivatives, as depicted in Scheme 1. It is also worth noticing that the degradation products of resveratrol were still able to protect PLA against photo-oxidation, as demonstrated by the slower buildup of O–H and C=O groups in the case of PR1 and PR3 even after long-term UV irradiation. This result may be also related to the intense absorption observed in the UV domain up to 400 nm for the photodegraded samples containing the polyphenol (Figure S13, Supporting Information) due to the formation of polymer chromophores (Scheme 1) or to oligomeric condensation products between resveratrol radicals.⁵²

The strong screening effect of the degraded additive against active UV radiation could result in an effective UV protection of

the polymer through deactivation of the Norrish type photocleavage degradation pathways, as is confirmed by the slowing of the vinyl groups formation after 200 h of irradiation (Figure 4d). Similarly, Ortiz-Vazquez et al. found that under thermo-oxidative conditions butylated hydroxytoluene (BHT) forms colored oxidation byproducts that could be responsible for the color change of PLA-BHT films.³⁹

Mechanical Properties. Mechanical properties of the films were measured through tensile tests. Elongation at break (ϵ), rupture strength (σ_b), yield strength (σ_y), and elastic modulus (E) were measured for all film samples before and after thermal annealing (Table 3), as well as after different photo-oxidation periods (Figure 5).

Annealing significantly reduced the ductility of PLA, regardless of the presence of resveratrol. Elongation at break dropped down to about 20% of the initial values, while elastic moduli were unchanged. On the other hand, tensile strength increased by about 30% for all samples. These observations are in good agreement with the results described by Pan et al.,⁵³ who reported that fracture strain of PLA decreased from more than 300% to about 6% after only 1.5 h aging at 40 °C, while tensile strength and elastic modulus significantly increased upon prolonged annealing. Wide-angle X-ray diffraction measurements showed that no crystallization occurred during the aging process, and then the drop of ductility due to physical

aging was correlated to the rearrangement of polymer chains from disordered to more ordered morphology.

Figure 5 shows the changes in mechanical properties of PLA as a function of the photo-oxidation time. The reduction of the polymer molecular weight due to photo-oxidation caused a constant decrease in tensile properties with increasing irradiation times, as reported for PLA as well as for other thermoplastics.^{42,45,46,54,55} In spite of the large data scattering, the decreasing trend of the mechanical properties with irradiation time was higher for PR0. The elongation values dramatically decreased after only 30 h for all films, and afterward remained roughly constant in the case of PR1 and PR3 (Figure 5a). This behavior was reminiscent of that obtained for M_w as a function of time, which is attributable to the stabilizing effect of resveratrol in the PLA matrix. It is worth noticing that after 59 h of exposure it was not possible to test PR0 tensile specimens, as they were too brittle to be handled. The addition of resveratrol showed a positive effect on PLA rupture and yield strength (Figures 5b,c), as PR3 retained approximately 80% of the tensile strength after 160 h. The effect of the antioxidant was not so obvious when the elastic modulus was examined (Figure 5d); however, also in this case, PR3 showed higher values over the course of the process.

CONCLUSIONS

The addition of resveratrol significantly affected the thermal and photo-oxidative stability of polylactide. Under inert atmosphere, resveratrol catalyzed high-temperature transesterification reactions of PLA, while glass transition and melting temperatures of resveratrol-doped PLA were unchanged. On the other hand, the additive inhibited thermally and UV light-catalyzed oxidation of the polymer matrix. Resveratrol and its degradation products exerted potent inhibitory effects, most likely through trapping of highly reactive oxygen radicals, as well as by the UV screening effect of the formed chromophores. The protective effect was confirmed by the measurements of the polymer molar mass and changes during irradiation, and it was found that the photo-oxidation rate constants were dependent on the resveratrol content. Long-term mechanical properties of PLA were also improved, as the doped polymer retained its tensile strength also after long irradiation times. The results suggest that resveratrol can be proposed as an eco-friendly and biocompatible additive for a sustainable approach to the stabilization of PLA films in packaging and other applications.

ASSOCIATED CONTENT

Supporting Information

Irradiance map and spectral distribution of the UV lamp, M_w , and fitting of GPC data, FTIR spectra of PR3, analysis of photo-oxidation of PLA-based samples through FTIR, fluorescence, and UV-vis spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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