Article

Vegetal Polyphenol Extracts as Antioxidants for the Stabilization of PLA: Toward Fully Biobased Polymer Formulation

Luna Valero, Mael Gainche, Cécile Esparcieux, Florence Delor-Jestin,* and Haroutioun Askanian*

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The use of natural antioxidants as substitutes for traditional synthetic stabilizers has been investigated for the stabilization of biobased and biodegradable polymers, with the aim of designing fully biobased plastic formulations. This study focused on the thermo- and photostabilization of poly(lactic acid) (PLA) using vegetal polyphenol extracts as biosourced antioxidants. The polyphenols were extracted by microwave-assisted extraction from the valorization of vegetal waste, and their potential as antioxidant additives was evaluated (e.g., polyphenol content, composition, and antioxidant activity). PLA was then formulated with 2 wt % of the extracts exhibiting the highest antioxidant activities: green tea residues, pomegranate peels, grape marc, bramble leaves, and yellow onion peel extracts. The efficiency of the natural additives as thermal stabilizers was evaluated and compared with a synthetic antioxidant using rheological and thermal analyses. The results demonstrated the capacity of grape marc extract and pomegranate peel extract to significantly improve PLA thermal stability during processing and thermo-oxidation. Finally, photorheology was conducted to evaluate the influence of the bioadditives on the biopolyester photodegradation. The different polyphenol extracts seemed to significantly hinder the photo-oxidation of PLA and constitute very promising natural UV stabilizers, combining UV absorbers and antioxidant functions.

1. INTRODUCTION

Nowadays, the plastic field increasingly develops sustainable solutions to meet environmental concerns such as plastic pollution and resource depletion. Bioplastics, i.e., biosourced and/or biodegradable polymers, constitute sustainable materials to face these challenges.[1,2] Biobased polymers, produced from renewable resources rather than fossil resources, are alternatives.[3] Additionally, the use of biodegradable polymers represents an approach to regulating the plastic waste by controlling the end-of-life of the materials.[1] A particular interest is given to promising materials such as biopolyester poly(lactic acid) (PLA).[4] Another perspective is to substitute synthetic additives with greener chemicals with the intent of developing environmentally friendly plastics. Environmental and health concerns regarding the additives (toxicity, migration...) are important issues that call into question the use of conventional additives in formulations.[5] The replacement of synthetic additives with biobased additives represents a major challenge in the plastic field.[6]

Stabilizers are essential additives to enhance polymer durability and stability, providing long-term performances of the material during the service life. Throughout their lifetime, polymers are exposed to environmental factors (heat, UV light, oxygen, humidity, etc.), leading to the deterioration of their properties.[7−9] For instance, PLA undergoes initial degradation during the melting process at high temperatures, typically around 200 °C, through thermal degradation, thermo-oxidative degradation, and thermo-mechanical degradation.[10] Some PLA-based materials can also be degraded by photo-oxidation caused by the exposure to UV radiation during their service life (e.g., outdoor applications exposed to sunlight, such as mulch

films in plasticulture, and packaging or medical products exposed to artificial lightning).[11,12] Thermo- and photo-oxidative degradation proceeds by radical chain reactions, leading to changes in the molecular structure of the polymer, resulting in physical, mechanical, and chemical modifications, affecting polymer properties.[7,9] Stabilizers are therefore used to prevent polymer aging by inhibiting or delaying the degradation mechanisms. To protect polymers from thermo-oxidative degradation, polymers are mainly stabilized with antioxidants, while photostabilization can be managed by the use of antioxidants as well as UV absorbers, lights screeners, or quenchers.[7,13] Studies demonstrating the migration and diffusion of antioxidants and light stabilizers from polymers have raised concerns,[5] as toxicity assessments reveal the risk of synthetic phenolic antioxidants.[14] To that extent, much research studies on polymer stabilization have focused on the use of natural stabilizers with the view of replacing conventional synthetic stabilizers.

In recent years, bioactive compounds with antioxidant properties have been considered as additives and have demonstrated promising results for the protection of polymers against degradation.[15,16] The main class of natural antioxidants used to stabilize polymers is the polyphenols, which regroup a large number of phenolic compounds classified as a function of

their structure (flavonoids, stilbenoids, phenolic acids, and phenolic polymers). The antioxidant activity of polyphenols involves mechanisms of radical scavenging—through a hydrogen atom transfer or a single-electron transfer from the phenolic hydroxyl—as well as chelation of transition metals.[17,18] Many publications have compared synthetic and natural antioxidants to achieve polymer stabilization. However, studies need to be conducted for each matrix–additive combination since the efficiency of polyphenols as antioxidants depends on different parameters, such as their chemical structure, their concentration (anti-/pro-oxidant effects), and the nature of the polymer. Among polyphenols, flavonoids have been particularly investigated as antioxidant agents for biopolyesters. Studies have shown that catechin protected PLA and PLA-polyhydroxybutyrate (PHB) from thermal oxidative degradation,[19] as did rutin and hesperidin with PLA and P(3,4HB) polymers.[20] Other research studies revealed the efficiency of quercetin as a photostabilizer for PLA and a starch-based polymer blended with biopolyesters[21,22] and its stabilizing effect on polyhydroxybutyrate-hydroxyvalerate thermo-mechanical degradation.[23] Among the phenolic acids, ferulic acid derivatives enhanced the stability of polybutylene succinate (PBS) to thermo-oxidative degradation,[24] while gallates improved the resistance to oxidation of PLA and PHA P(3,4HB).[25] Resveratrol, a polyphenol from the stilbenoid class, enhanced PLA stability under air for both thermo- and photo-oxidation.[26] Furthermore, other classes of polyphenolic molecules characterized by higher molecular weights have been examined as stabilizers. Within the tannins class, tannic acid procured an effective thermal stabilization of PHB, constituting a promising thermal and processing stabilizer.[27] Several researchers used lignin, a phenolic polymer, as a suitable and cheap natural antioxidant for polyesters with regard to the weathering of PLA[28] and the thermo-oxidation of polybutylene adipate terephthalate.[29]

An environment-friendly and cost-effective strategy for polymer stabilization is the use of vegetal extracts containing molecules of interest, such as polyphenol natural antioxidants. Investigations are conducted on the valorization and exploitation of biowaste and agri-food byproducts as a resource of high-value additives. The use of such products offers many advantages, such as a lower risk of migration and leaching of potentially toxic synthetic antioxidants and byproducts formed during the aging process of a polymer, as well as a broad spectrum of action for exerting their antioxidant activity.[30] Most of the time, those compounds can be extracted from their vegetal matrixes with simple water extractions, an eco-friendlier solvent for industry.[31] Wine byproduct extracts, rich in polyphenols, are studied for their stabilizing effect on polymers. The grape pomace extract and wine seed extracts demonstrated stabilizing effects by reducing the thermal degradation of PHB,[32,33] just as the wine seed tannin extract stabilized PBS with regard to thermo-mechanical degradation during reprocessing and thermo-oxidation during aging.[34] Other vegetal extracts have been studied for the stabilization of biopolyesters. Coffee, cocoa, and cinnamon extracts improved polymer stability relating to the weathering aging of PLA,[35] while citrus and green walnut husk extracts enhanced the thermal stability.[36]

The objective of this present work is to investigate the thermal and photostabilization of PLA using polyphenol extracts as biobased antioxidants. This study aims to provide new inputs on the biomass valorization for the replacement of synthetic additives in plastic formation, with a view of developing fully biobased materials. Eleven vegetal polyphenolic extracts were developed and characterized (polyphenol content, antioxidant activity, composition, etc.) to select potential natural antioxidants for polymers. The influence of five promising extracts on the processing stability and service-life durability of PLA was then evaluated using different characterization techniques to look at thermal degradation and photodegradation. We propose to identify suitable and relevant techniques for thermal degradation measurements [in situ thermal aging with melt rheology, oxidation induction time (OIT) with calorimetry, accelerated long-term thermal aging].

2. EXPERIMENTAL SECTION

2.1. Materials, Chemicals, and Reagents. The PLA Luminy L175, "PLA L175", was provided by Total Corbion PLA. According to the supplier, this grade of PLA is characterized by a glass transition temperature of 60 °C and a melting temperature of 175 °C.

The commercial synthetic antioxidant Irganox 1010 from BASF was used as an antioxidant reference for the study. This compound is a sterically hindered primary phenolic antioxidant, generally used as a processing stabilizer for polymers.

The vegetal biomasses used for the extraction were either collected in Clermont-Ferrand (France), provided by local producers, or bought in grocery stores. The screening was done with yellow onion peels (*Allium cepa*), pomegranate peels (*Punica granatum*), pineapple skin (*Ananas comosus*), olive leaves (*Olea europaea*), *Sequoia* needles, *Cedrus* needles, bramble leaves (*Rubus* sp.), wheat bran, sawdust, green tea residues (*Camellia sinensis*), and grape marc (*Vitis vinifera* var. *Gamay/Pinot Noir*).

Characterization tests were realized with the following reagents: Folin–Ciocalteu reagent was obtained from Sigma-Aldrich, sodium carbonate from Fluka, and DPPH (1,1-diphenyl-2-picrylhydrazyl free radical) from TCI chemicals.

2.2. Additive Development and Characterization. *2.2.1. Polyphenol Extraction—Microwave-Assisted Extraction.* Natural extracts containing a mixture of polyphenols have been extracted from vegetal biomass on a laboratory scale by microwave-assisted extraction (MAE). Extractions were realized with several vegetal matrices from biomass valorization (food peels, wild plant leaves, industrial residues, etc.) using a mixture of water/ethanol at 1:1 (v/v) as the solvent of extraction, with a proportion of 1 g of a grounded biomass sample in 40 mL of the solvent. MAE extractions were performed using the microwave-accelerated reaction system MARS 5 from CEM at 800 W and 105 °C for 30 min. After different steps of separation, rising, and filtration, the liquid extracts of polyphenols were stored at 5 °C in a fridge. Then, the solid extracts were obtained by the elimination of the solvent by vacuum distillation with a rotary evaporator, followed by lyophilization with a freeze-dryer. The freeze-dried extracts were stored in a freezer at −20 °C for further characterization and formulation with polymers.

2.2.2. Total Phenolic Content—Folin–Ciocalteu Assay. In order to quantify the concentration of polyphenols in the liquid extracts, the total phenolic content (TPC) was determined by the Folin–Ciocalteu method.[37] This colorimetric dosage is based on the reduction of the Folin–Ciocalteu reagent by the hydroxyl groups of phenols, forming tungsten and molybdenum blues, characterized by $\lambda_{max} = 765$ nm. Absorbance measurements at 765 nm allow quantification

of the phenolic compounds present in the extracts. A calibration curve with gallic acid (GA, the phenol of reference) permits the determination of the TPC of the extracts, expressed in milligrams of the gallic acid equivalent/g (GAE/g) sample. A modified version of the essay was used.[38] In a test tube, 0.5 mL of the extract solution is mixed with 2 mL of the Folin−Ciocalteu reagent solution (10% v/v in Milli-Q water). After 30 s, 2.5 mL of a sodium carbonate solution (7.5% w/v in Milli-Q water) is added. After mixing, the solution is incubated for 30 min in a thermostatic water bath at 25 °C in the dark. Then, absorbance at 765 nm is measured with the UV−visible spectrophotometer UV mini-1240 using Milli-Q water as a blank. The calibration curve obtained with GA (0−250 mg/L) allows the deduction of the GA equivalent concentration in the extract, enabling the TPC of the extracts to be calculated using

$$\text{TPC} = \frac{C_{\text{GAE}}}{C_{\text{extract}}}$$

where TPC is the total phenolic content (mg GAE/g biomass sample), C_{GAE} is the concentration determined from the GA calibration curve (mg/L), and C_{extract} is the concentration of biomass in the extract solution (g biomass/L).

2.2.3. Antioxidant Activity—DPPH Radical Scavenging Assay. The antioxidant activities of the natural extracts have been determined by the DPPH assay.[39,40] This colorimetric assay evaluates the ability of an antioxidant to scavenge the stable radical DPPH• (2,2-diphenyl-1-picrylhydrazyl) by a hydrogen or electron transfer. The reduction of DPPH• by antioxidants induces a color change from purple to pale yellow, followed by a measurement of the absorbance at 515 nm. The experiments provided access to the DPPH inhibition related to the antioxidant efficiency of the compounds. The antioxidant properties of the natural extracts studied were compared to those of a synthetic commercial antioxidant Irganox 1010.

A modified version of the DPPH assay was used.[41] The test was performed with antioxidant solutions in ethanol at different concentrations (0−1000 μg/mL). In a test tube, 100 μL of the antioxidant solution was mixed with 3.9 mL of a DPPH solution (60 μM in ethanol). After mixing, the covered test tube was incubated for 30 min at 25 °C in a thermostated water bath in the dark. The absorbance at 515 nm was measured with a UV−visible spectrophotometer UV mini-1240 using ethanol as a blank.

The absorbance values were used to calculate the inhibition of DPPH radical as a function of the antioxidant concentration according to the following equation and to graphically determine EC_{50} (the concentration of antioxidant reducing 50% of DPPH)

$$\text{DPPH inhibition} = \frac{A_{\text{control}} - A_{\text{antioxidant}}}{A_{\text{control}}} \times 100$$

where DPPH inhibition is the antioxidant activity (%), A_{control} is the absorbance at 515 nm of the DPPH solution/ethanol mixture, and $A_{\text{antioxidant}}$ is the absorbance at 515 nm of the DPPH solution/antioxidant solution mixture.

2.2.4. Composition—Liquid Chromatography−Mass Spectrometry (LC−MS). The chemical profiles of the extracts were determined by chromatographic analyses using the Gainche et al. method.[42] LC−MS analyses were carried out on an UHPLC Ultimate 3000 RSLC chain and an Orbitrap Q-Exactive (Thermo Scientific, Waltham, MA, USA) with an

Uptisphere C18-3 (250 × 4.6 mm, 5 μm) column from Interchim (Montluçon, France). Source operating conditions were as follows: 3 kV spray voltage; 320 °C heated capillary temperature; 400 °C auxiliary gas temperature; and sheath, sweep, and auxiliary gas (nitrogen) flow rates at 50, 10, and 2 arbitrary units, respectively; collision cell was used in stepped nCE mode, with an ionization voltage between 10 and 50 arbitrary units. The mobile phase was a mixture of formic acid in water (0.1% v/v) (phase A) and formic acid in acetonitrile (0.1% v/v) (phase B). The gradient of phase A was 100% (0 min), 80% (10 min), 73% (35 min), 0% (40−50 min), and 100% (51−60 min). The flow rate was 0.8 mL/min, and the injection volume was 5 μL. Full scan data were obtained at a resolution of 70,000, whereas MS data were obtained at a resolution of 17,500. Data were processed using Xcalibur software (Thermo Fisher Scientific Inc., Waltham, MA, USA). The identification of all compounds described was carried out using the negative ionization mode.

The analyses were conducted on solutions of extracts at 1 mg/mL in ultrapure water/ethanol absolute ratio at 1:1 (v/v) and filtered with a 0.45 μm PTFE filter.

2.2.5. UV Absorption—UV−Visible Spectroscopy. The capacity of the natural extracts to absorb UV radiation was measured by UV−visible spectroscopy with a Lambda 265 Double Beam UV−visible spectrophotometer from PerkinElmer. UV−visible spectra of the natural extracts were obtained from the absorbance measurements from 200 to 700 nm of solutions of polyphenol extracts at 6.25×10^{-2} mg/mL in water.

2.2.6. Thermal Stability—Thermogravimetric Analysis (TGA). TGA using the TGA 4000 instrument from PerkinElmer was carried out to evaluate the thermal stability of the additives at processing temperatures. Measurements of weight loss were performed with 10 ± 2 mg samples from 30 to 700 °C at 10 °C/min under N_2 at 20 mL/min.

2.3. Polymer Stabilization and Characterization. *2.3.1. Formulation and Compounding—Extrusion.* Compounding and processing were realized by extrusion using HAAKE Minilab II, a twin-screw micro compounder from Thermo Fisher Scientific, with PLA pellets and additives previously dried in a vacuum oven to eliminate residual moisture and prevent hydrolysis during processing. Additives were introduced at 0.5 or 2 wt % and mixed into the polymer matrix at 200 °C for 10 min at 100 rpm using the extruder to obtain extruded materials of 7 g. Neat PLA without additives was processed under the same conditions and referred to as "PLA (reference)".

2.3.2. Accelerated Thermal Aging—Oven. The thermal aging of PLA materials was simulated through the aging treatment under accelerated conditions in a Binder E53 standard incubator oven with natural convection. Sample films were prepared with a manual hydraulic hot press by pressing the extruded materials at 200 bar for 1 min at 190 °C to obtain 100 μm thick films. The polymer films were disposed in the heating chamber during 5 weeks at 100 ± 2 °C and taken for the rheological analysis after various exposure times.

2.3.3. Polymer Degradation—Melt Rheology. The degradation of the polymer was evaluated by melt rheology, which permitted the assessment of the evolution of the macromolecular structure. The rheological measurements were performed with an ARES Rheometric Scientific rheometer from TA Instruments, equipped with two parallel plates of 8 mm diameter and a dry air convection oven. Preliminary tests

were conducted to select suitable strain amplitude values, ensuring measurements within the linear viscoelastic region.

Frequency sweep tests (from 0.1 to 100 rad/s) were conducted at 200 °C and 10% strain amplitude on PLA materials to study the impact of processing and thermal aging exposure. The measurements provided, among others, the dynamic complex viscosity η^* and the determination of the zero-shear viscosity η_0 by using the Cole−Cole representation $\eta'' = f(\eta')$ and nonlinear regression that draws a half arc from the experimental values.

In situ thermal degradation of PLA materials was performed by time sweep tests to evaluate the thermo-oxidation of the polymers at high temperatures in the oven of the rheology tool. Analyses were carried out at 200 °C, 10 rad/s, and 20% strain amplitude for around 2 h. Normalized complex viscosity η^*/η^*_{t0} was used to evaluate the kinetics of thermo-oxidative degradation over time.

2.3.4. OIT—Differential Scanning Calorimetry (DSC). Oxidation of materials was investigated with OIT measurements[43] using the differential scanning calorimeter DSC 3+ device from Mettler-Toledo. The procedure was realized with 40 μL of open pan containing material samples of 10 ± 1 mg. The test consists of heating from 30 to 230 °C at 20 °C/min under an inert gas (nitrogen) at 50 mL/min, followed by a thermal stabilization at 230 °C for 10 min. Then, the gas was switched to oxygen at 50 mL/min and 230 °C, leading to an exothermic peak induced by the exothermic oxidation reaction.

2.3.5. Thermal Degradation—Thermogravimetric Analysis Coupled with DSC (TGA−DSC). Thermal analyses were conducted by the Simultaneous Thermal Analyzer TGA/DSC 3+ from Mettler-Toledo. The measurements were realized with 15 ± 1 mg samples from 30 to 600 °C at 10 °C/min under air (25 mL/min).

2.3.6. In Situ Photodegradation—Photorheology. The evaluation of UV stability was studied by means of photorheology.[44] This method combines viscoelastic analysis with UV exposition, giving an assessment of the kinetics and mechanisms of photodegradation. The device consists of two quartz plates, of which the upper plate has a mirror that directs the UV irradiation onto the sample. The measurements are performed with a rheometer ARES Rheometric Scientific (TA Instruments) and a mercury−xenon UV source LC6 (Hamamatsu) that irradiates between 250 and 600 nm with an intensity of 3500 mW/cm² at 365 nm.

Before analysis, the materials were dried in a vacuum oven for 16 h at 70 °C to remove water residues. The sample was heated to 200 °C for 5 min to melt the polymer and shape it between the rheometer plates with a gap of 1.2−1.5 mm. Then, the sample was cooled and stabilized for 15 min at 60 °C, during which a gap decrease occurred due to the shrinkage of PLA. A time sweep test was performed at a frequency of 1 rad/s and a strain of 0.01%. The UV source was switched on after 1120 s and activated for several hours to study the reactivity of PLA toward photo-oxidation at 60 °C. Normalized complex viscosity η^*/η^*_{t0} was used to evaluate the kinetics of photo-oxidative degradation over time.

3. RESULTS AND DISCUSSION

3.1. Additive Extraction and Characterization.

3.1.1. Extraction of Polyphenols. The extraction of polyphenols was performed by MAE as the most appropriate and practical method. Among the extraction techniques, MAE represents indeed an efficient and fast solid/liquid extraction

method, widely used for green extraction of polyphenols, allowing shorter extraction times and reduced solvent consumption.[31,45−47] A mixture of water and ethanol, commonly used to target polyphenols, was chosen as a suitable ecofriendly solvent to realize the screening of extractions from various biomass wastes (food peels, industrial residues, and wild plant leaves). The nature and proportion of polyphenols extracted from the vegetal extracts depend on both vegetal matrices and conditions of extraction. The Folin−Ciocalteu method was realized not only to quantify the polyphenols contained in the different liquid extracts, with a view to identify interesting vegetal matrices for further investigation, but also to ensure the extraction method's efficiency.

As observed in Figure 1, the TPC measurement allowed identification of vegetal matrices containing high amounts of
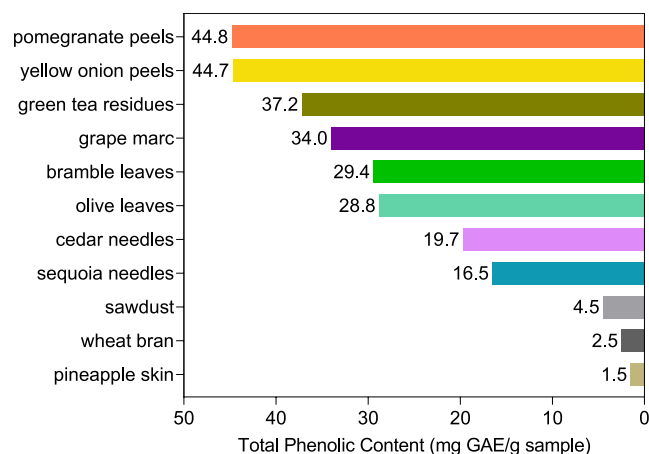
Figure 1. TPC of the natural extracts (in mg gallic acid equivalent/g sample of biomass) obtained with the Folin−Ciocalteu assay.

polyphenols. The best results were obtained with pomegranate peels and yellow onion skins, with 44.8 and 44.7 mg GAE/g sample, followed by green tea residues, grape marc, bramble leaves, and olive leaves, with TPC of 37.2, 34.0, 29.4, and 28.8 mg GAE/g sample, respectively. On the other hand, the cedar needle and sequoia needle extracts showed intermediate quantities of polyphenols, while sawdust, wheat bran, and pineapple skin extracts displayed low polyphenol contents. The TPC of the extracts is summarized in Table 1, along with the extraction yields obtained at a laboratory scale, ranging from 7.0 to 24.4% depending on the biomass. The MAE extraction using the water−ethanol solvent was suitable and efficient to extract phenolic compounds. The Folin−Ciocalteu assay was performed to quantify the concentration of polyphenols in the vegetal extracts, but it was also necessary to assess the polyphenolic composition and evaluate the antioxidant capacity of the extracts.
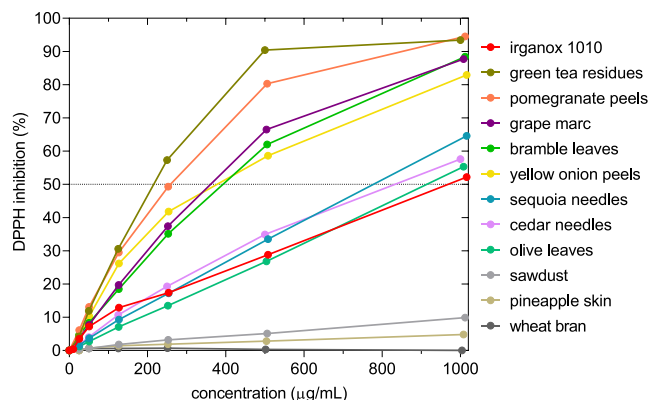
3.1.2. Antioxidant Activity of Additives. The antioxidant activities of the natural extracts were characterized by the DPPH assay and compared to those of the synthetic commercial antioxidant Irganox 1010. Figure 2 displays the capacity of the compounds to scavenge and inhibit the stable radical DPPH•, in function of the compound's concentration, and allows the determination of EC_{50}, the concentration of the antioxidant reducing 50% of DPPH•, informing on the efficiency of the antioxidants (Table 1).

Typical dose−response curves showing the antioxidant concentration dependency on the scavenging activity were

Table 1. TPC, Extraction Yield, and EC$_{50}$ Values of Additives

additive	TPC (mg GAE/g sample)	extraction yield (% w/w)	EC$_{50}$ (μg/mL)
Irganox 1010			968
pomegranate peel extract	44.8	21.1	259
yellow onion peel extract	44.7	10.3	378
green tea residue extract	37.2	11.9	216
grape marc extract	34.0	14.6	361
bramble leaf extract	29.4	11.9	393
olive leaf extract	28.8	24.4	914
cedar needle extract	19.7	16.2	832
sequoia needle extract	16.5	14.1	778
sawdust extract	4.5	7.0	N/A[a]
wheat bran extract	2.5	12.4	N/A
pineapple skin extract	1.5	11.3	N/A

[a]N/A: not applicable, too high to be determined.

Figure 2. Antioxidant activity of additives obtained with the DPPH assay.

obtained.[48] Sawdust, pineapple skin, and wheat bran extracts did not present important antioxidant properties, in compliance with TPC values, due to their very low concentration of phenolic compounds. The extracts from sequoia needles, cedar needles, and olive leaves displayed interesting antioxidant activities comparable to those of the synthetic antioxidant. The extracts of green tea residues, pomegranate peels, grape marc, bramble leaves, and yellow onion peels exhibited remarkable antioxidant capacities, even higher than Irganox 1010. The reaching of a plateau at high concentrations can be observed for the strongest antioxidants, attesting the total consumption of DPPH$^{\bullet}$. Inhibition of DPPH$^{\bullet}$ never reaches 100%, even with a stoichiometric excess of antioxidant, as discussed by de Menezes et al.,[49] explaining those limitations of the DPPH assay by the contribution of reaction byproducts to sample absorbance. The highest antioxidant activities were provided by the green tea residue extract (EC$_{50}$ of 216 μg/mL) and the pomegranate peel extract (EC$_{50}$ of 259 μg/mL). The extracts of grape marc, yellow onion peels, and bramble leaves exhibited significant antioxidant activities with EC$_{50}$ of 361, 378, and 393 μg/mL, respectively.

The results attested that the vegetal matrices are worth for their valorization and exploitation as renewable resources of powerful biobased antioxidants. In that way, the five natural

extracts exhibiting the highest antioxidant activities were selected for further characterization and incorporated as polymer stabilizers.

3.1.3. Composition of the Extracts. As pomegranate, yellow onion, green tea, grape marc, and bramble leaves showed higher phenolic contents, LC−MS was performed to identify the main polyphenols in these natural extracts. Chromatograms and detailed identification of all compounds with MS data are reported in Figures S1−S5 and Table S1. Identification was made according to standards or data available in the literature.[50−61]

The green tea extract contains many compounds derived from GA and catechin/epicatechin such as theogallin, epigallocatechin isomer (EGC), epigallocatechin gallate isomers (EGCG), or epicatechin methylgallate. It also contains many flavonoids derived from quercetin (rutin, isoquercitrin), kaempferol with several sugar moieties in position 3 (rutinose, galactose, glucose), apigenin-8-C-glucoside, and myricetin-3-O-glucoside. This chemical composition is supported by earlier studies.[50−52]

The grape marc contains mostly catechin and epicatechin, protocatechuic and GA, and traces of tannins, including procyanidins B1, B2, and B3. Finding procyanidin derivatives is not surprising as they are reported in grape.[53−55] Finally, the antioxidant activity of this extract seems to be correlated to its content in procyanidin derivatives, not its content in tartaric acid, as this compound plays a minor role in the global activity as reported in published study.[56]

Bramble leaves from *Rubus* sp. contain phenolic acids such as chlorogenic and neochlorogenic acids, quinic and citric acids, and gallic and ellagic acids. The presence of these two last compounds suggests the presence of ellagitannins which are represented in this plant mostly by sanguiin H-6. Traces of flavonoids can also be found with quercetin-3-O-glucuronide and kaempferol-3-O-glucuronide, as well as epicatechin. Those compounds are common compounds found in Rubus.[57] Among polyphenols, flavonoids are particularly studied as antioxidant agents in biopolyesters.[58]

A. cepa extract contains a few major compounds comprising protocatechuic acid derivatives and flavonoids such as kaempferol, isorhamnetin, quercetin, and quercetin-4′-O-glucoside (also known as spiraeoside).[59]

Finally, the analysis of the pomegranate peel extract showed the presence of gallic and ellagic acids, which suggests the presence of ellagitannins. We can find punicalagin isomers in the extract, a common tannin in this species.[60] We also found catechin and gallocatechin.

With the DPPH assay, the highest antioxidant activities were obtained with extracts from green tea residues, pomegranate peels, grape marc, yellow onion peels, and bramble leaves. Those five plants contain mostly catechin derivatives (EGC, EGCG, tannins), ellagic acid derivatives (sanguiin H-6, punicalagin), and multiple flavonoids. All those compounds are well-known antioxidant compounds due to the presence of a phenolic group in their structure. The antioxidant activity in green tea and grape marc is strongly linked to their content of flavonoid and catechin derivatives.[61]

3.1.4. UV Absorbance of the Extracts. In addition to their antioxidant activity, polyphenolic compounds are molecules capable of absorbing UV radiation.[17] This characteristic could be interesting for the utilization of polyphenol extracts as light stabilizers to protect polymers from photodegradation caused by UV solar irradiation (290−400 nm). The UV absorbance of

the five selected extracts was evaluated through UV–visible spectroscopy. As observed in Figure 3, the natural extracts
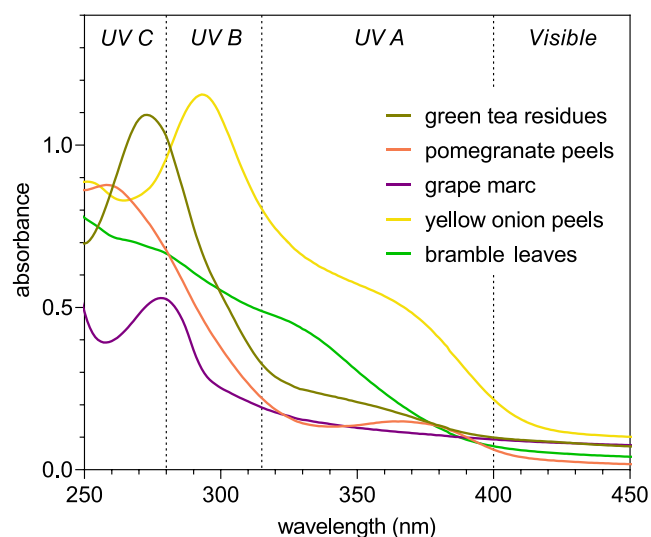
Figure 3. UV absorption of polyphenol extracts ($C = 6.25 \times 10^{-2}$ mg/mL in Milli-Q water).

absorb the UV radiation. The five extracts exhibited relatively widespread absorption in the range 250–400 nm, and the spectra showed maximum absorbance peaks at 273, 278, and 293 nm for green tea residue, grape marc, and yellow onion peel extracts, respectively. Thereby, the polyphenol extracts could provide the potential light stabilizer activity through UV absorption in parallel to the antioxidant activity.

3.1.5. Thermal Stability of Additives. Polyphenol extracts are reported to be particularly sensitive to high temperatures, undergoing degradation during thermal processing.[62] The thermal stability and structural integrity of the extracts were then characterized by TGA before their incorporation into the polymer, with the objective of verifying the match with PLA processing temperatures (Figures S6–S11). Figure 4 shows that the commercial synthetic antioxidant Irganox 1010 is thermally stable, whereas the polyphenol extracts display a
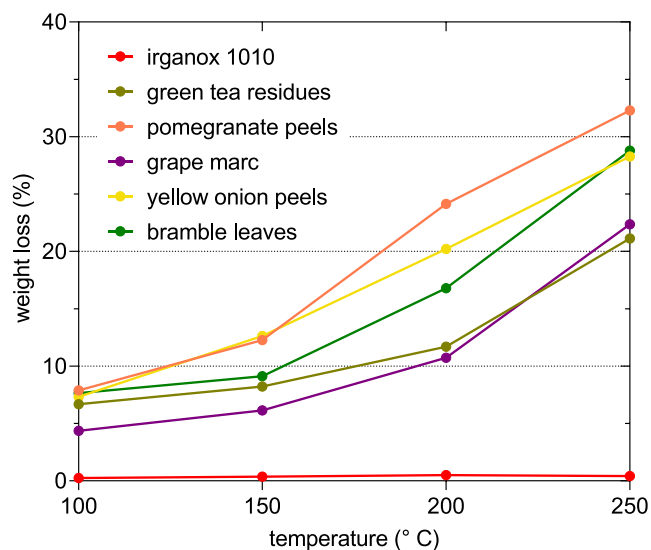
Figure 4. Thermal stability of additives obtained by TGA.

relatively marked weight loss at high temperatures. The compounding and processing of PLA formulations were realized at 200 °C. At this temperature, the synthetic antioxidant lost 0.5% of its weight, whereas the thermal decomposition of the vegetal extract resulted in weight loss between 11.7% (grape marc) and 24.1% (pomegranate peels). As observed in the TG/DTG curves of the additives (Figures S6–S11), the first stage of the weight loss for each extract indicates a removal of ethanol/water solvents and moisture, generally found in such extracts.[63,64] The weight loss of assumed residual solvents varies between 4.8% (grape marc) and 10.8% (yellow onion peels), representing, on average, half of the total weight loss at 200 °C due to both solvent evaporation and thermal degradation of the compounds present in the extracts. The results highlighted the need for a drying step for extracts before processing to avoid PLA hydrolysis and, above all, informed us that the stabilizing effect of the polyphenol extracts on the polymer could be affected by their thermal stability. It should be noted that natural polyphenolic extracts can be protected to enhance their thermal stability using protective strategies, such as encapsulation, to maintain their bioactivity and antioxidant activity.[65,66]

3.2. Polymer Stabilization and Characterization. Studies were conducted on PLA materials formulated with 2 wt % of the natural extract and 0.5 wt % of Irganox 1010. The quantity of the polyphenol extract was chosen on the basis of the average GA equivalent in the five extracts, equal to 0.29 $g_{GAE}/g_{extract}$, and the average thermal degradation at 200 °C, around 8.2%, requiring the addition of 2 wt % to obtain 0.5 wt % of GA equivalent from the extracts. The purpose was to analyze the efficiency of the selected polyphenol extracts as thermal and/or light stabilizers to improve PLA stability against degradation and aging (processing impact and thermo- and photo-oxidation during the service life).

3.2.1. Impact of Processing. Polymers undergo a first degradation during processing at high temperatures, during which they are exposed to thermo-mechanical degradation.[7] Thermal and processing stabilizers as antioxidants can be used to reduce the impact of processing.

The influence of the additives on PLA stability during processing was evaluated by melt rheology measurements before and after extrusion. This technique makes it possible to follow the evolution of the macromolecular structure, informing on the kinetics and mechanisms of degradation, including the competition between chain scission and recombination.[67] According to the power law $\eta_0 \propto M^{3,4}$ for linear polymers,[68–70] melt viscosity is proportional to polymer molecular weight, indicating the high sensitivity of a polymer's rheological properties to its molecular structure. When chain scission mechanisms predominate during degradation, a decrease in polymer molecular weight leads to greater chain mobility and a decrease in viscosity, while an increase in polymer viscosity is associated with an increase in polymer molecular weight due to chain recombination and/or cross-linking.[71] Moreover, the Cole–Cole plot of the melt rheology results allows calculation of the zero-shear viscosity η_0. In this study, the dynamic complex viscosity η^* and the zero-shear viscosity η_0 were used to monitor structural changes within the polymer during degradation and to evaluate the involved mechanisms.

The processing of PLA is known to lead to a decrease in Mw caused by thermal degradation, involving several phenomena

as hydrolysis, depolymerization, oxidation, random chain scission, and intra- and intermolecular transesterification.[11]

As illustrated by the reduction in the zero-shear viscosity (Figures 5 and 6) and the complex viscosity (Figure S12), PLA
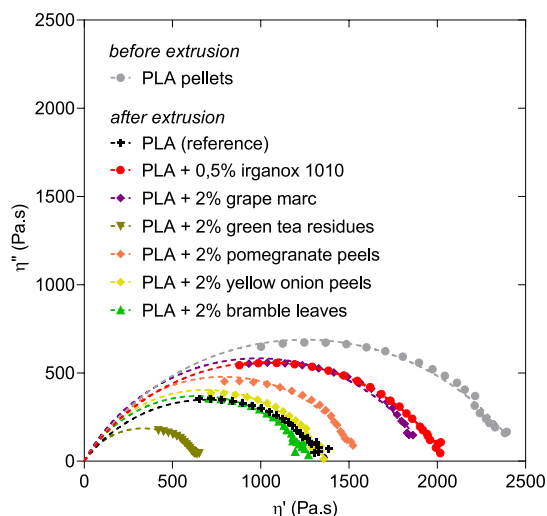
Figure 5. Impact of processing on PLA materials: the Cole−Cole plot (melt rheology: frequency sweep tests performed at T = 200 °C; γ = 10%).
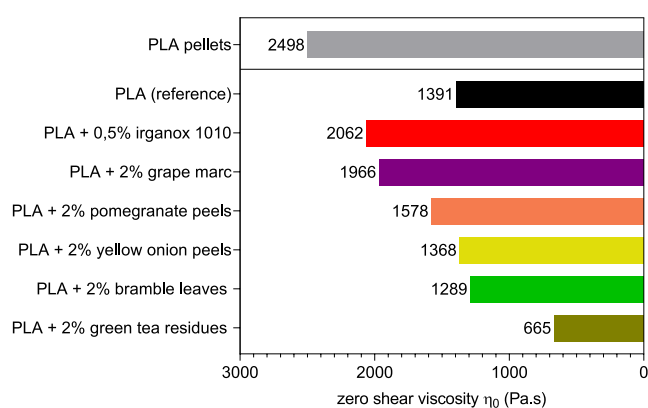

Figure 6. Impact of processing on PLA materials: the zero-shear viscosity determined by extrapolation of the Cole−Cole plot.

underwent thermo-mechanical degradation through mechanisms of chain scissions during the processing at 200 °C. D'Urso et al.[72] also observed a decrease in PLA complex viscosity after the extrusion at the same temperature, whose melt degradation by chain scissions was confirmed by a weight-average molecular weight decrease from 195 to 146 kDa, obtained by gel permeation chromatography. The evolution of zero-shear viscosity values, reported in Figure 6, reflects the impact of the additives on the thermo-mechanical degradation during extrusion. The zero-shear viscosity of neat PLA decreased significantly from 2498 to 1391 Pa·s, whereas an addition of 0.5 wt % of Irganox 1010 provides an efficient stabilization. In the case of natural extracts added at 2 wt %, the grape marc and pomegranate peel extracts exhibited stabilizing effects and protected PLA from the thermo-mechanical degradation during extrusion. The grape marc extract proved to be particularly effective as a processing stabilizer within the PLA formulation, offering an important antioxidant action comparable to that of Irganox 1010. The pomegranate peel

additive also protected PLA to a certain extent, permitting a decrease in viscosity less marked than the neat polymer. On the other hand, the addition of 2 wt % of yellow onion peels or bramble leaves did not impact the thermal stability of PLA during processing. Surprisingly, the extract of green tea residues demonstrated a pro-degradant effect that accelerated the chain scission mechanism. This phenomenon may be due to a concentration-dependent effect as this extract showed the highest antioxidant activity of all polyphenol extracts (Figure 2). In the literature, some natural polyphenols were reported to promote the oxidation of polymers due to the concentration-dependent anti-/pro-oxidant action. Polyphenols are H donors forming stable radicals, but at high concentration, they can extract H atoms from the polymer chains and create macroradicals accelerating the oxidation pathway.[73]

3.2.2. Thermo-stability. The intent was to explore different techniques to characterize polymer degradation and aging during service life. Usually, experiments are carried out at elevated temperatures to accelerate the thermo-oxidation mechanisms.[74] The thermo-oxidative stability of the different formulations was examined by melt rheology at 200 °C, OIT measurements with calorimetry, TGA and DSC analyses, and thermal aging under accelerated conditions at 100 °C. The thermal stabilization procured by the biobased antioxidant additives was compared to the Irganox 1010 formulation.

In situ thermal degradation in the rheometer oven was performed to assess the influence of the additives on the thermo-oxidative degradation behavior of PLA. This method, combining melt rheological measurements with temperature exposure at 200 °C, allowed us to monitor changes in the normalized dynamic viscosity of the various formulations, as reported in Figure 7. The exposure of PLA to elevated
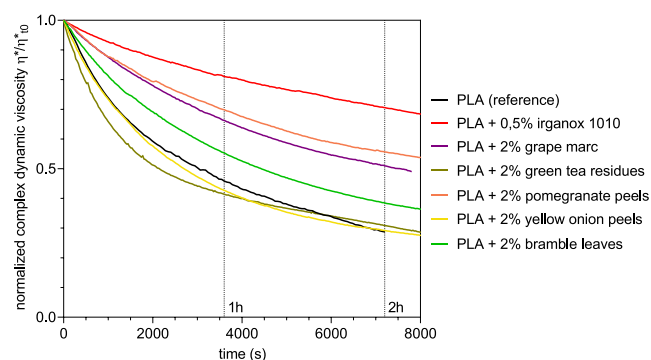

Figure 7. Thermal degradation in situ of PLA materials (melt rheology: time sweep tests performed at T = 200 °C; γ = 20%; ω = 10 rad/s).

temperatures in the presence of oxygen led to a mass reduction of the material over time, as illustrated by the viscosity decreasing over time. This phenomenon is the consequence of thermo-oxidative degradation of PLA, which is reported to occur predominantly by chain scission mechanisms, leading to a reduction of the polymer's chain length and resulting in a decrease in PLA's molecular weight and viscosity.[10,75] The presence of additives resulted in the same chain scission mechanisms but impacted the thermal degradation kinetics of PLA. The results demonstrated a significant thermal stabilization obtained by the synthetic antioxidant, followed by the pomegranate peel and grape marc extracts. For example, after 1 h at 200 °C, neat PLA lost 54% of its viscosity, while the

grape marc and pomegranate peel extracts attenuated the viscosity loss to 34 and 30%, respectively. The bramble leaf extract exhibited a moderate protection against PLA thermal degradation with a viscosity loss of 45% after 1 h. On the other side, the extract of green tea residues accelerated the thermal degradation of the material in the early stages, whereas the result of PLA containing the onion extract was comparable to the neat polymer. Finally, the two bioadditives providing the greater thermal stabilization (grape marc and pomegranate peel extracts) were the same vegetal extracts that ensured the best protection during processing.

The thermo-oxidative stability was then investigated by measuring the OIT measurement with the DSC. This method can indicate the efficiency of an antioxidant in inhibiting material oxidation. As observed in Figure 8, neat PLA was
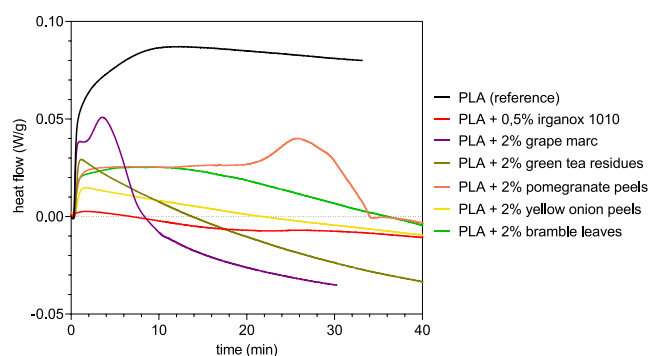
Figure 8. Thermo-oxidation of PLA materials monitored by OIT experiments performed at 230 °C.

directly oxidized when the gas switched from nitrogen to oxygen, with the apparition of an exothermic signal, while PLA with 0.5 wt % Irganox 1010 did not present oxidation reaction, suggesting an effective stabilization against thermo-oxidation. The use of polyphenol extracts allowed reducing oxidation, but the interpretation of the exothermic peaks was compromised by the nonstability of the polyphenol extracts at the experiment temperature. OIT assays were conducted at 230 °C to obtain an acceptable oxidation intensity of PLA, but this temperature involved degradative reactions of the vegetal extracts compared to the high thermal stability of Irganox 1010 as measured previously with TGA. Lastly, this technique was not suitable for our materials, as the results did not show an abrupt exothermic oxidation reaction after an induction time, enabling the OIT to be determined. PLA oxidation was characterized by a low energy reaction with an onset at the start of the experiment.[26]

Thermal analysis by TGA coupled with DSC under air was then realized to characterize the thermal decomposition and

thermo-oxidation of the materials. Results from TGA (Figure S13) and DSC (Figure S14) curves of PLA materials are reported in Table 2.

According to TGA results, the PLA thermal decomposition was shifted to a higher temperature by adding the pomegranate peel extract and Irganox 1010, which delayed Tonset by 14.5 and 7.0 °C and maintained comparable Tmax values to neat PLA. The four other polyphenol extracts showed lower Tmax values. The onsets of materials weight loss were similar to the neat polymer in the case of green tea, yellow onion, and bramble leaf additives, while the grape marc extract shifted the start of decomposition to 8.0 °C lower.

DSC results allowed observing the material's thermal degradation through the exothermic signal from thermo-oxidation and the following endothermic decomposition reactions (Figure S14). PLA oxidation and decomposition appeared to be retarded by the pomegranate extract, whereas the other extracts resulted in less energy released by oxidation but earlier decomposition. Besides, the differences in Tg of the formulations were not significant enough to inform the degradation mechanisms from processing, unlike rheology measurements.

Based on the thermal and rheological results, thermal stabilization of PLA at high temperatures was achieved by the pomegranate peel extract, which enhanced thermal stability regarding decomposition and structure, and by the grape marc extract, which provided great structural stability. However, the results of such high-temperature methods (melt rheology, OIT, TGA, and DSC) must be considered with precaution and confirmed with accelerated thermal aging to predict the long-term stability of the material. Thus, a thermal aging procedure under accelerated conditions in an aerated oven at 100 °C was then performed with two formulations and the references as a complementary method to study the durability. Melt rheology analysis was used to monitor the evolution of normalized complex dynamic viscosity over thermal aging, which is obtained by the ratio of the viscosity at t and at $t = 0$ of aging.

As illustrated in Figure 9, the thermal aging of PLA films at 100 °C is characterized by a decrease in viscosity, attributed to chain scission as the predominant mechanism during thermo-oxidation. This result was in line with the study of Rasselet et al. (2014) on the thermo-oxidative degradation of PLA at low temperatures, between 70 and 150 °C, leading to random chain scission causing mass reduction.[75] Furthermore, the presence of synthetic and biosourced additives in the polymer formulation also led to thermo-oxidation proceeding mainly by chain scission, as confirmed by the overall decreases in viscosity during aging. If Irganox 1010 managed to delay PLA thermo-oxidation, pomegranate peel and grape marc extracts exhibited stabilizing effects significantly higher at this low

Table 2. TGA and DSC Data of PLA Materials

| formulation PLA L175 | TGA | | DSC | | | | | | |
	T_{max} (°C)	$T_{onset5\%}$ (°C)	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	χ_c (%)	T_{dmax} (°C)
reference (without additive)	354.7	307.0	59.2	100.7	23.76	175.2	−37.69	15.0	365.0
0.5 wt % Irganox 1010	355.0	314.0	59.0	105.7	25.74	176.3	−33.42	8.3	367.0
2 wt % grape marc	339.2	299.0	56.5	105.5	22.45	176.5	−28.61	6.6	350.0
2 wt % green tea residues	349.5	305.0	54.2	107.5	28.61	175.5	−37.05	9.1	359.0
2 wt % pomegranate peels	355.2	321.5	55.7	103.0	25.64	175.7	−35.74	10.9	367.0
2 wt % yellow onion peels	349.0	307.0	55.3	104.2	24.17	175.8	−35.31	12.0	357.0
2 wt % bramble leaves	350.5	309.5	55.5	106.0	27.18	175.8	−35.27	8.7	360.0
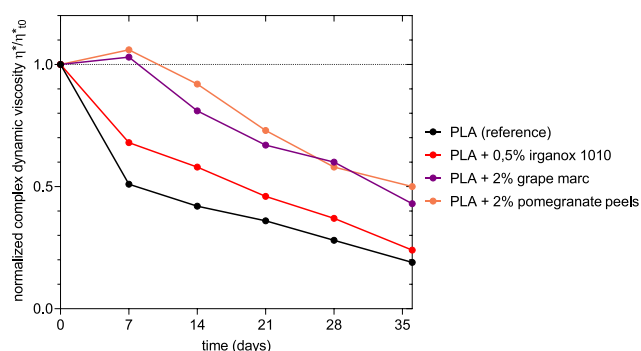
Figure 9. Thermal aging of PLA materials in accelerated conditions (oven at $T = 100\ °C$) (melt rheology: time sweep tests performed at $T = 200\ °C$; $\gamma = 10\%$; $\omega = 1$ rad/s).

temperature. It can be noticed that the addition of the two extracts caused an increase in the PLA viscosity in the early stages of thermal aging. This could be due to interactions or branching between the polymer chains and the polyphenols from grape marc and pomegranate peel extracts, acting as chain extenders.

3.2.3. Photostability. Given the antioxidant properties of polyphenol extracts, their effectiveness as light stabilizers was also well studied with a view to photostabilizing PLA and improving its long-term stability. The influence of the biosourced additives on the PLA photo-oxidation was evaluated by photorheology. This method enables in situ photodegradation while monitoring the evolution of the viscosity of the material under UV irradiation and air at 60 °C.

As observed in Figure 10, the exposition of neat PLA to UV radiation led to a significant drop in viscosity over time, which
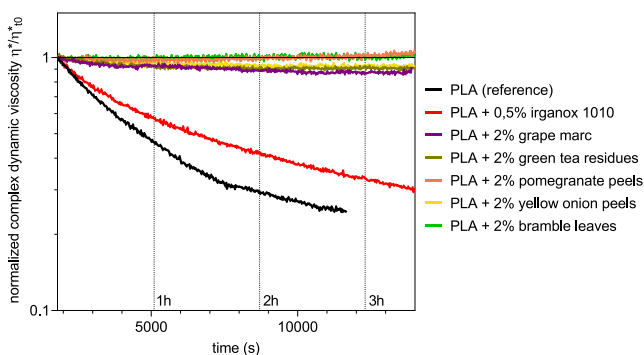
Figure 10. Photodegradation in situ of PLA materials (photorheology: time sweep tests performed at $T = 60\ °C$; $\gamma = 0.01\%$; $\omega = 1$ rad/s; Hg−Xe lamp).

is related to a molecular weight reduction caused by photodegradative mechanisms. The photochemical degradation of PLA is reported to proceed through carbonyl polyester cleavage via the Norrish II mechanism, leading to random chain scission with the formation of C═C and carboxylic end groups.[11,76] In addition, PLA undergoes radical photo-oxidation, leading to the formation of anhydride groups by β-Scission reactions of hydroperoxides intermediates.[77] Marek and Verney (2016) studied the photo-oxidation of PLA close to the glass transition region (50−70 °C) using the photorheology method and also observed a decrease in the PLA viscosity resulting from the degradation reactions under UV irradiation.[78]

In Figure 10, the PLA containing Irganox 1010 was also characterized by a chain scission mechanism during photodegradation. But, compared to the neat polymer, the synthetic (thermo) antioxidant slightly improved the photostability, attesting an oxidative pathway during photodegradation. On the other hand, the presence of 2 wt % of polyphenol extracts notably inhibited the drop in PLA molecular weight due to chain scission during photodegradation. The high stabilization of the natural extracts against UV radiation could result from synergistic effects between UV absorbance and antioxidant properties. Indeed, phenolic compounds have both UV filtering ability correlated to absorption in the UV region and antioxidant properties to scavenge UV-generated reactive oxygen species.[79] In addition, the use of natural extracts composed of different types of polyphenols can reinforce these phenomena. Such additives could provide preventive and curative effects for the photostabilization of the biopolyester.

From our results, the polyphenol extracts seemed to significantly hinder the photo-oxidation of PLA. In addition, the pomegranate peel and grape marc extracts were the biobased additives providing great thermal stabilization against processing and thermo-oxidation, representing promising natural photo stabilizer and thermal stabilizer for PLA.

To the best of our knowledge, the pomegranate extract has not yet been studied for the stabilization of biopolyesters. However, this extract has been shown to provide great processing stabilization to polyethylene (PE) by hindering oxidation and preventing the formation of long-chain branches.[80] Xia et al. (2020) demonstrated the good stabilizing effect on PE thermo-oxidative, UV, and processing stability provided by the pomegranate peel extract, which can be used as a multiple stabilizer for PE.[81] Regarding the grape marc extract, studies have been conducted on the stabilization of various biopolyesters, but not so far on PLA. Persico et al.[33] studied the effect of a grape pomace extract as a stabilizer additive for the biosourced and biodegradable PHB. Rheological tests, GPC analysis, and thermal analysis demonstrated the efficiency of the extract to improve the processing and thermal stabilities of PHB. The stabilizing effect of the biowaste additive was attributed to hydrogen-bonding interactions between the polyphenol hydroxyl groups and the carbonyl groups of PHB that could inhibit the PHB thermal degradation mechanism by random chain scission. Wine byproducts were also investigated as natural antioxidants for the stabilization of PBS.[34] The authors demonstrated the great stabilization of PBS by a commercial grape seed tannin extract, comparable to or even better than that of Irganox 1010, regarding thermo-mechanical degradation during reprocessing and thermo-oxidation during aging. The ability of the tannin extract to lower PHB degradation was explained by its composition of long-chain polyphenols, working as chain extenders not only by hydrogen bonding but also by the high radical scavenger activity of the extract. The grape marc extracts have demonstrated a photoprotective effect on polypropylene under accelerated photochemical conditions by slowing down the oxidation by the chain scission mechanism.[82]

While all five vegetal extracts introduced into PLA showed strong antioxidant activities to scavenge radicals and interrupt radical degradation reactions, only the pomegranate and grape marc extracts demonstrated efficient thermal stabilization of the polymer. In line with the stabilizing mechanisms proposed in the literature, the bioadditive extracts from pomegranate

peels and grape marc presented tannins in the polyphenols' composition, which could provide optimal hydrogen-bonding interactions with PLA chains, allowing a great stabilization by hindering degradation by chain scission.

4. CONCLUSIONS

In this study, the thermal stabilization and photostabilization of PLA were investigated using the vegetal polyphenol extracts as biobased antioxidants, with the aim of developing sustainable biobased materials. The exploitation and valorization of biomass as renewable resources for value-added phytochemicals such as antioxidants were proposed as solutions for the substitution of synthetic stabilizers.

Various vegetal extracts were extracted from different vegetal wastes. The extracts from green tea residues, pomegranate peels, grape marc, bramble leaves, and yellow onion peels exhibited particularly strong antioxidant activities in radical scavenging, high TPCs, and interesting UV absorbance properties. The stabilization of PLA against processing degradation and service-life aging was investigated with the five vegetal extracts previously mentioned and compared to that of Irganox 1010.

Rheological measurements revealed the efficiency of the grape marc and pomegranate peel extracts to hinder PLA thermo-mechanical degradation during extrusion at 200 °C by limiting the mass reduction of PLA caused by chain scission. TGA−DSC and in situ thermal degradation in the rheometer indicated protection of PLA at elevated temperatures by the pomegranate peel and grape marc extracts. Rheological analysis seemed to be the more appropriate technique to inform on materials thermo-oxidation, as the results were confirmed by accelerated thermal aging used to predict long-term stability. Thermal stabilization by the pomegranate peel and grape marc extracts, slowing down the degradation kinetics of PLA during processing and thermal aging, was attributed to hydrogen-bonding interactions between polymer chains and polyphenols—particularly tannins—hindering the molecular weight reduction of PLA caused by degradation mechanisms.

The photostabilization was attributed to synergistic effects between the UV absorbance and the strong antioxidant properties of the polyphenols in the extracts. The polyphenol extracts from pomegranate peels and grape marc seemed to represent promising thermal and light stabilizers and could be introduced in PLA formulations to enhance both thermal and photostability.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c07236.

> Data from LC−MS of vegetal extracts, TGA of vegetal extracts, TGA and DSC of PLA materials (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Florence Delor-Jestin − *Université Clermont Auvergne, Clermont Auvergne INP—Sigma Clermont, CNRS, ICCF, 63000 Clermont-Ferrand, France;* ⓞ orcid.org/0000-0002-4830-5108; Email: florence.delor_jestin@sigma-clermont.fr

Haroutioun Askanian − *Université Clermont Auvergne, Clermont Auvergne INP—Sigma Clermont, CNRS, ICCF,*
63000 Clermont-Ferrand, France;
Email: haroutioun.askanian@sigma-clermont.fr

Authors

Luna Valero − *Université Clermont Auvergne, Clermont Auvergne INP—Sigma Clermont, CNRS, ICCF, 63000 Clermont-Ferrand, France;* ⓞ orcid.org/0000-0001-7478-8767

Mael Gainche − *Université Clermont Auvergne, Clermont Auvergne INP—Sigma Clermont, CNRS, ICCF, 63000 Clermont-Ferrand, France;* ⓞ orcid.org/0000-0002-6823-3578

Cécile Esparcieux − *Université Clermont Auvergne, Clermont Auvergne INP—Sigma Clermont, CNRS, ICCF, 63000 Clermont-Ferrand, France*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.3c07236

Author Contributions

Luna Valero: conceptualization, methodology, investigation, formal analysis, and writing—original draft. Maël Gainche: methodology, formal analysis, and writing—original draft and review. Cécile Esparcieux: methodology. Haroutioun Askanian: conceptualization, methodology, validation, supervision, and writing—review and editing. Florence Delor-Jestin: validation, supervision, and writing—review and editing.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Nakajima, H.; Dijkstra, P.; Loos, K. The Recent Developments in Biobased Polymers toward General and Engineering Applications: Polymers That Are Upgraded from Biodegradable Polymers, Analogous to Petroleum-Derived Polymers, and Newly Developed. *Polymers* **2017**, *9* (12), 523.

(2) RameshKumar, S.; Shaiju, P.; O'Connor, K. E.; Ramesh Babu, P. Bio-Based and Biodegradable Polymers - State-of-the-Art, Challenges and Emerging Trends. *Curr. Opin. Green Sustainable Chem.* **2020**, *21*, 75−81.

(3) Shogren, R.; Wood, D.; Orts, W.; Glenn, G. Plant-Based Materials and Transitioning to a Circular Economy. *Sustain. Prod. Consum.* **2019**, *19*, 194−215.

(4) Farah, S.; Anderson, D. G.; Langer, R. Physical and Mechanical Properties of PLA, and Their Functions in Widespread Applications — A Comprehensive Review. *Adv. Drug Delivery Rev.* **2016**, *107*, 367−392.

(5) Hahladakis, J. N.; Velis, C. A.; Weber, R.; Iacovidou, E.; Purnell, P. An Overview of Chemical Additives Present in Plastics: Migration, Release, Fate and Environmental Impact during Their Use, Disposal and Recycling. *J. Hazard. Mater.* **2018**, *344*, 179−199.

(6) Dintcheva, N. T.; Infurna, G.; Baiamonte, M.; D'Anna, F. Natural Compounds as Sustainable Additives for Biopolymers. *Polymers* **2020**, *12* (4), 732.

(7) Zweifel, H. *Stabilization of Polymeric Materials*; Springer Berlin Heidelberg: Berlin, Heidelberg, 1998.

(8) White, J. R.; Turnbull, A. Weathering of Polymers: Mechanisms of Degradation and Stabilization, Testing Strategies and Modelling. *J. Mater. Sci.* **1994**, *29* (3), 584−613.

(9) Gryn'ova, G.; Hodgson, J. L.; Coote, M. L. Revising the Mechanism of Polymer Autooxidation. *Org. Biomol. Chem.* **2011**, *9* (2), 480−490.

(10) Cuadri, A. A.; Martín-Alfonso, J. Thermal, Thermo-Oxidative and Thermomechanical Degradation of PLA: A Comparative Study Based on Rheological, Chemical and Thermal Properties. *Polym. Degrad. Stab.* **2018**, *150*, 37−45.

(11) Castro-Aguirre, E.; Iñiguez-Franco, F.; Samsudin, H.; Fang, X.; Auras, R. Poly(Lactic Acid)—Mass Production, Processing, Industrial Applications, and End of Life. *Adv. Drug Delivery Rev.* **2016**, *107*, 333−366.

(12) Copinet, A.; Bertrand, C.; Govindin, S.; Coma, V.; Couturier, Y. Effects of Ultraviolet Light (315 Nm), Temperature and Relative Humidity on the Degradation of Polylactic Acid Plastic Films. *Chemosphere* **2004**, *55* (5), 763−773.

(13) Yousif, E.; Haddad, R. Photodegradation and Photostabilization of Polymers, Especially Polystyrene: Review. *SpringerPlus* **2013**, *2* (1), 398.

(14) Liu, R.; Mabury, S. A. Synthetic Phenolic Antioxidants: A Review of Environmental Occurrence, Fate, Human Exposure, and Toxicity. *Environ. Sci. Technol.* **2020**, *54* (19), 11706−11719.

(15) Kirschweng, B.; Tátraaljai, D.; Földes, E.; Pukánszky, B. Natural Antioxidants as Stabilizers for Polymers. *Polym. Degrad. Stab.* **2017**, *145*, 25−40.

(16) Dintcheva, N. Tz.; D'Anna, F. Anti-/Pro-Oxidant Behavior of Naturally Occurring Molecules in Polymers and Biopolymers: A Brief Review. *ACS Sustainable Chem. Eng.* **2019**, *7* (15), 12656−12670.

(17) Belščak-Cvitanović, A.; Durgo, K.; Huđek, A.; Bačun-Družina, V.; Komes, D. Overview of Polyphenols and Their Properties. *Polyphenols: Properties, Recovery, and Applications*; Elsevier, 2018; pp 3−44.

(18) Francenia Santos-Sánchez, N.; Salas-Coronado, R.; Villanueva-Cañongo, C.; Hernández-Carlos, B. Antioxidant Compounds and Their Antioxidant Mechanism. In *Antioxidants*; Shalaby, E., Ed.; IntechOpen, 2019.

(19) Arrieta, M. P.; Castro-López, M. d. M.; Rayón, E.; Barral-Losada, L. F.; López-Vilariño, J. M.; López, J.; González-Rodríguez, M. V. Plasticized Poly(Lactic Acid)-Poly(Hydroxybutyrate) (PLA-PHB) Blends Incorporated with Catechin Intended for Active Food-Packaging Applications. *J. Agric. Food Chem.* **2014**, *62* (41), 10170−10180.

(20) Masek, A.; Latos-Brozio, M. The Effect of Substances of Plant Origin on the Thermal and Thermo-Oxidative Ageing of Aliphatic Polyesters (PLA, PHA). *Polymers* **2018**, *10* (11), 1252.

(21) Dintcheva, N.Tz.; La Mantia, F. P.; Arrigo, R. Natural Compounds as Light Stabilizer for a Starch-Based Biodegradable Polymer. *J. Polym. Eng.* **2014**, *34* (5), 441−449.

(22) Morici, E.; Arrigo, R.; Dintcheva, N. T. Quercetin as Natural Stabilizing Agent for Bio-Polymer. *AIP Conf. Proc.* **2014**, *1599*, 314−317.

(23) Bonnenfant, C.; Gontard, N.; Aouf, C. Biobased and Biodegradable Polymers in a Circular Economy Context: Understanding Quercetin and Gallic Acid Impacts on PHBV Thermal Properties. *Polym. Degrad. Stab.* **2022**, *201*, 109975.

(24) Reano, A. F.; Domenek, S.; Pernes, M.; Beaugrand, J.; Allais, F. Ferulic Acid-Based Bis/Trisphenols as Renewable Antioxidants for Polypropylene and Poly(Butylene Succinate). *ACS Sustainable Chem. Eng.* **2016**, *4* (12), 6562−6571.

(25) Latos-Brozio, M.; Masek, A. Biodegradable Polyester Materials Containing Gallates. *Polymers* **2020**, *12* (3), 677.

(26) Agustin-Salazar, S.; Gamez-Meza, N.; Medina-Juàrez, L. À.; Soto-Valdez, H.; Cerruti, P. From Nutraceutics to Materials: Effect of Resveratrol on the Stability of Polylactide. *ACS Sustainable Chem. Eng.* **2014**, *2* (6), 1534−1542.

(27) Auriemma, M.; Piscitelli, A.; Pasquino, R.; Cerruti, P.; Malinconico, M.; Grizzuti, N. Blending Poly(3-Hydroxybutyrate) with Tannic Acid: Influence of a Polyphenolic Natural Additive on the Rheological and Thermal Behavior. *Eur. Polym. J.* **2015**, *63*, 123−131.

(28) Spiridon, I.; Leluk, K.; Resmerita, A. M.; Darie, R. N. Evaluation of PLA-Lignin Bioplastics Properties before and after Accelerated Weathering. *Composites, Part B* **2015**, *69*, 342−349.

(29) Tavares, L. B.; Rosa, D. d. S. Stabilization Effect of Kraft Lignin into PBAT: Thermal Analyses Approach. *Rev. Mater.* **2019**, *24* (3), No. e-12405.

(30) Kirschweng, B.; Tátraaljai, D.; Földes, E.; Pukánszky, B. Natural Antioxidants as Stabilizers for Polymers. *Polym. Degrad. Stab.* **2017**, *145*, 25−40.

(31) Maroun, R. G.; Rajha, H. N.; El Darra, N.; El Kantar, S.; Chacar, S.; Debs, E.; Vorobiev, E.; Louka, N. Emerging Technologies for the Extraction of Polyphenols from Natural Sources. *Polyphenols: Properties, Recovery, and Applications*; Elsevier, 2018; pp 265−293.

(32) Nanni, A.; Messori, M. Effect of the Wine Wastes on the Thermal Stability, Mechanical Properties, and Biodegradation's Rate of Poly(3-hydroxybutyrate). *J. Appl. Polym. Sci.* **2021**, *138* (3), 49713.

(33) Persico, P.; Ambrogi, V.; Baroni, A.; Santagata, G.; Carfagna, C.; Malinconico, M.; Cerruti, P. Enhancement of Poly(3-Hydroxybutyrate) Thermal and Processing Stability Using a Bio-Waste Derived Additive. *Int. J. Biol. Macromol.* **2012**, *51* (5), 1151−1158.

(34) Nanni, A.; Ricci, A.; Versari, A.; Messori, M. Wine Derived Additives as Poly(Butylene Succinate) (PBS) Natural Stabilizers for Different Degradative Environments. *Polym. Degrad. Stab.* **2020**, *182*, 109381.

(35) Moraczewski, K.; Stepczyńska, M.; Malinowski, R.; Karasiewicz, T.; Jagodziński, B.; Rytlewski, P. The Effect of Accelerated Aging on Polylactide Containing Plant Extracts. *Polymers* **2019**, *11* (4), 575.

(36) Latos-Brozio, M.; Masek, A. Effect of Impregnation of Biodegradable Polyesters with Polyphenols from Cistus Linnaeus and Juglans Regia Linnaeus Walnut Green Husk. *Polymers* **2019**, *11* (4), 669.

(37) Singleton, V. L.; Rossi, J. A. Colorimetry of Total Phenolics with Phosphomolybdic-Phosphotungstic Acid Reagents. *Am. J. Enol. Vitic.* **1965**, *16* (3), 144−158.

(38) Bharti, R.; Singh, B. Green Tea (Camellia Assamica) Extract as an Antioxidant Additive to Enhance the Oxidation Stability of Biodiesel Synthesized from Waste Cooking Oil. *Fuel* **2020**, *262*, 116658.

(39) Blois, M. S. Antioxidant Determinations by the Use of a Stable Free Radical. *Nature* **1958**, *181* (4617), 1199−1200.

(40) Molyneux, P. The Use of the Stable Free Radical Diphenylpicrylhydrazyl (DPPH) for Estimating Antioxidant Activity. *Songklanakarin J. Sci. Technol.* **2004**, *26* (2), 211−219.

(41) de Oliveira, N. A.; Cornelio-Santiago, H. P.; Fukumasu, H.; de Oliveira, A. L. Green Coffee Extracts Rich in Diterpenes - Process Optimization of Pressurized Liquid Extraction Using Ethanol as Solvent. *J. Food Eng.* **2018**, *224*, 148−155.

(42) Gainche, M.; Ogeron, C.; Ripoche, I.; Senejoux, F.; Cholet, J.; Decombat, C.; Delort, L.; Berthon, J.-Y.; Saunier, E.; Caldefie Chezet, F.; Chalard, P. Xanthine Oxidase Inhibitors from Filipendula Ulmaria (L.) Maxim. and Their Efficient Detections by HPTLC and HPLC Analyses. *Molecules* **2021**, *26* (7), 1939.

(43) Schmid, M.; Affolter, S. Interlaboratory Tests on Polymers by Differential Scanning Calorimetry (DSC): Determination and Comparison of Oxidation Induction Time (OIT) and Oxidation Induction Temperature (OIT*). *Polym. Test.* **2003**, *22* (4), 419−428.

(44) Marek, A. A.; Verney, V. Influence of the Viscoelastic Regime onto the UV Reactivity of Poly(Lactic Acid). *Eur. Polym. J.* **2019**, *110*, 138−144.

(45) Chemat, F.; Abert-Vian, M.; Fabiano-Tixier, A. S.; Strube, J.; Uhlenbrock, L.; Gunjevic, V.; Cravotto, G. Green Extraction of Natural Products. Origins, Current Status, and Future Challenges. *TrAC, Trends Anal. Chem.* **2019**, *118*, 248−263.

(46) Plaza, M.; Domínguez-Rodríguez, G.; Castro-Puyana, M.; Marina, M. L. Polyphenols Analysis and Related Challenges. *Polyphenols: Properties, Recovery, and Applications*; Elsevier, 2018; pp 177−232.

(47) Hernández-Carlos, B.; Francenia Santos-Sánchez, N.; Salas-Coronado, R.; Villanueva-Cañongo, C.; Cecilia Guadarrama-Mendoza, P. Antioxidant Compounds from Agro-Industrial Residue. In *Antioxidants*; Shalaby, E., Ed.; IntechOpen, 2019.

(48) Papetti, A.; Daglia, M.; Gazzani, G. Anti- and Pro-Oxidant Water Soluble Activity of Cichorium Genus Vegetables and Effect of Thermal Treatment. *J. Agric. Food Chem.* **2002**, *50* (16), 4696−4704.

(49) De Menezes, B. B.; Frescura, L. M.; Duarte, R.; Villetti, M. A.; Da Rosa, M. B. A Critical Examination of the DPPH Method: Mistakes and Inconsistencies in Stoichiometry and IC50 Determination by UV-Vis Spectroscopy. *Anal. Chim. Acta* **2021**, *1157*, 338398.

(50) Chacko, S. M.; Thambi, P. T.; Kuttan, R.; Nishigaki, I. Beneficial Effects of Green Tea: A Literature Review. *Chin. Med.* **2010**, *5* (1), 13.

(51) Maeda-Yamamoto, M.; Ema, K.; Monobe, M.; Tokuda, Y.; Tachibana, H. Epicatechin-3- O -(3″- O -Methyl)-Gallate Content in Various Tea Cultivars (Camellia Sinensis L.) and Its in Vitro Inhibitory Effect on Histamine Release. *J. Agric. Food Chem.* **2012**, *60* (9), 2165−2170.

(52) Reto, M.; Figueira, M. E.; Filipe, H. M.; Almeida, C. M. M. Chemical Composition of Green Tea (Camellia Sinensis) Infusions Commercialized in Portugal. *Plant Foods Hum. Nutr.* **2007**, *62* (4), 139−144.

(53) Fuleki, T.; Ricardo da Silva, J. M. Catechin and Procyanidin Composition of Seeds from Grape Cultivars Grown in Ontario. *J. Agric. Food Chem.* **1997**, *45* (4), 1156−1160.

(54) Rodríguez-Pérez, C.; García-Villanova, B.; Guerra-Hernández, E.; Verardo, V. Grape Seeds Proanthocyanidins: An Overview of In Vivo Bioactivity in Animal Models. *Nutrients* **2019**, *11* (10), 2435.

(55) Souquet, J.-M.; Cheynier, V.; Brossaud, F.; Moutounet, M. Polymeric Proanthocyanidins from Grape Skins. *Phytochemistry* **1996**, *43* (2), 509−512.

(56) Liu, Q.; Tang, G.-Y.; Zhao, C.-N.; Gan, R.-Y.; Li, H.-B. Antioxidant Activities, Phenolic Profiles, and Organic Acid Contents of Fruit Vinegars. *Antioxidants* **2019**, *8* (4), 78.

(57) Gasperotti, M.; Masuero, D.; Vrhovsek, U.; Guella, G.; Mattivi, F. Profiling and Accurate Quantification of Rubus Ellagitannins and Ellagic Acid Conjugates Using Direct UPLC-Q-TOF HDMS and HPLC-DAD Analysis. *J. Agric. Food Chem.* **2010**, *58* (8), 4602−4616.

(58) Sójka, M.; Macierzyński, J.; Zaweracz, W.; Buczek, M. Transfer and Mass Balance of Ellagitannins, Anthocyanins, Flavan-3-Ols, and Flavonols during the Processing of Red Raspberries (Rubus Idaeus L.) to Juice. *J. Agric. Food Chem.* **2016**, *64* (27), 5549−5563.

(59) Olsson, M. E.; Gustavsson, K.-E.; Vågen, I. M. Quercetin and Isorhamnetin in Sweet and Red Cultivars of Onion (Allium Cepa L.) at Harvest, after Field Curing, Heat Treatment, and Storage. *J. Agric. Food Chem.* **2010**, *58* (4), 2323−2330.

(60) Wu, S.; Tian, L. Diverse Phytochemicals and Bioactivities in the Ancient Fruit and Modern Functional Food Pomegranate (Punica Granatum). *Molecules* **2017**, *22* (10), 1606.

(61) Zanwar, A. A.; Badole, S. L.; Shende, P. S.; Hegde, M. V.; Bodhankar, S. L. Antioxidant Role of Catechin in Health and Disease. *Polyphenols in Human Health and Disease*; Elsevier, 2014; pp 267−271.

(62) Deng, J.; Yang, H.; Capanoglu, E.; Cao, H.; Xiao, J. Technological Aspects and Stability of Polyphenols. *Polyphenols: Properties, Recovery, and Applications*; Elsevier, 2018; pp 295−323.

(63) Olalere, O. A.; Gan, C.-Y. Microwave-Assisted Extraction of Phenolic Compounds from Euphorbia Hirta Leaf and Character-

ization of Its Morphology and Thermal Stability. *Sep. Sci. Technol.* **2021**, *56* (11), 1853−1865.

(64) Gullón, B.; Eibes, G.; Moreira, M. T.; Herrera, R.; Labidi, J.; Gullón, P. Yerba Mate Waste: A Sustainable Resource of Antioxidant Compounds. *Ind. Crops Prod.* **2018**, *113*, 398−405.

(65) Fang, Z.; Bhandari, B. Encapsulation of Polyphenols - a Review. *Trends Food Sci. Technol.* **2010**, *21* (10), 510−523.

(66) Hasbay, I.; Galanakis, C. M. Recovery Technologies and Encapsulation Techniques. *Polyphenols: Properties, Recovery, and Applications*; Elsevier, 2018; pp 233−264.

(67) Verney, V. Rhéologie, Oxydation et Vieillissement Des Polymères. *Rhéologie* **2011**, *20*, 6.

(68) Colby, R. H.; Fetters, L. J.; Graessley, W. W. The Melt Viscosity-Molecular Weight Relationship for Linear Polymers. *Macromolecules* **1987**, *20* (9), 2226−2237.

(69) Najafi, N.; Heuzey, M. C.; Carreau, P. J.; Wood-Adams, P. M. Control of Thermal Degradation of Polylactide (PLA)-Clay Nanocomposites Using Chain Extenders. *Polym. Degrad. Stab.* **2012**, *97* (4), 554−565.

(70) Dopico-García, S.; Ares-Pernas, A.; Otero-Canabal, J.; Castro-López, M.; López-Vilariño, J. M.; González-Rodríguez, V.; Abad-López, M. J. Insight into Industrial PLA Aging Process by Complementary Use of Rheology, HPLC, and MALDI. *Polym. Adv. Technol.* **2013**, *24* (8), 723−731.

(71) Commereuc, S.; Askanian, H.; Verney, V.; Celli, A.; Marchese, P. About Durability of Biodegradable Polymers: Structure/Degradability Relationships. *Macromol. Symp.* **2010**, *296* (1), 378−387.

(72) D'Urso, L.; Acocella, M.; Guerra, G.; Iozzino, V.; De Santis, F.; Pantani, R. PLA Melt Stabilization by High-Surface-Area Graphite and Carbon Black. *Polymers* **2018**, *10* (2), 139.

(73) Dintcheva, N. T.; Arrigo, R.; Baiamonte, M.; Rizzarelli, P.; Curcuruto, G. Concentration-Dependent Anti-/pro-Oxidant Activity of Natural Phenolic Compounds in Bio-Polyesters. *Polym. Degrad. Stab.* **2017**, *142*, 21−28.

(74) Celina, M. C. Review of Polymer Oxidation and Its Relationship with Materials Performance and Lifetime Prediction. *Polym. Degrad. Stab.* **2013**, *98* (12), 2419−2429.

(75) Rasselet, D.; Ruellan, A.; Guinault, A.; Miquelard-Garnier, G.; Sollogoub, C.; Fayolle, B. Oxidative Degradation of Polylactide (PLA) and Its Effects on Physical and Mechanical Properties. *Eur. Polym. J.* **2014**, *50*, 109−116.

(76) Tsuji, H.; Echizen, Y.; Nishimura, Y. Photodegradation of Biodegradable Polyesters: A Comprehensive Study on Poly(l-Lactide) and Poly(ε-Caprolactone). *Polym. Degrad. Stab.* **2006**, *91* (5), 1128−1137.

(77) Bocchini, S.; Fukushima, K.; Blasio, A. D.; Fina, A.; Frache, A.; Geobaldo, F. Polylactic Acid and Polylactic Acid-Based Nanocomposite Photooxidation. *Biomacromolecules* **2010**, *11* (11), 2919−2926.

(78) Marek, A. A.; Verney, V. Photochemical Reactivity of PLA at the Vicinity of Glass Transition Temperature. The Photo-Rheology Method. *Eur. Polym. J.* **2016**, *81*, 239−246.

(79) Stevanato, R.; Bertelle, M.; Fabris, S. Photoprotective Characteristics of Natural Antioxidant Polyphenols. *Regul. Toxicol. Pharmacol.* **2014**, *69* (1), 71−77.

(80) Tátraaljai, D.; Tang, Y.; Pregi, E.; Vági, E.; Pukánszky, B. Pomegranate Extract for the Processing Stabilization of Polyethylene. *Vinyl Addit. Technol.* **2022**, *28* (2), 321−330.

(81) Xia, H.; Sui, K.; Ge, T.; Wu, F.; Sun, Q.; Wang, Z.; Song, L.; Huang, X.; Yu, Q. Natural compounds from <i>Punica granatum</i> peel as multiple stabilizers for polyethyleneunica granatum Peel as Multiple Stabilizers for Polyethylene. *Polym. Eng. Sci.* **2020**, *60* (11), 2761−2769.

(82) Diouf-Lewis, A.; Commereuc, S.; Verney, V. Biowastes from Wine as Natural Additive of Polyolefins: Thermo- and Photo-Oxidation Efficiency. *J. Appl. Polym. Sci.* **2018**, *135* (34), 46607.