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ORIGINAL ARTICLE

Development of active LDPE packaging with antioxidants from agro-industrial wine waste

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Abstract

This study developed active low-density polyethylene (LDPE) packaging incorporating natural antioxidants from wine industry residues and compared them with synthetic antioxidant (BHT). The antioxidant extract (AE), obtained from wine residues, contained 15 phenolic compounds, with catechin (30.51 mg/100g) and epicatechin (22.40 mg/100g) as major flavonoids. Packaging films were produced via extrusion and characterized by FTIR, colorimetry and thermogravimetric analysis. The FE1 active packaging formulation with 12% AE, showed reduced light transmission and improved thermal stability. In peroxide index tests, FE1 preserved sunflower oil below the legal oxidation limit (10 mEq/kg) for up to 5 days, reduced oxidation by 67.90% compared to standard LDPE packaging and 67.71% compared to BHT packaging, maintaining peroxide levels below regulatory limits for a longer duration.The results indicate that incorporating natural antioxidant extracts into LDPE creates active packaging with promising antioxidant properties, with potential for developing innovative solutions through extrusion processes using residues from wine industry.

Keywords: *active packaging, agro-industrial waste, natural antioxidant, polyethylene.*

Data Availability: All data supporting the findings of this study are available from the corresponding author upon request.

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1. Introduction

Food spoilage is responsible for the loss of quality and food safety and can occur during production, transportation, processing or storage. Oxidation is a major cause, reducing shelf life by degrading essential nutrients, altering color and odor, and forming harmful compounds like trans isomers[1]. Packaging serves as a crucial barrier, protecting food from external factors like oxygen, moisture, light, and contamination[2].

The main raw material for food packaging is thermoplastic materials, and in this context, polyethylene (PE) stands out in packaging production[3]. New technologies in the packaging area aim to interact with the food product, in order to modify or maintain product quality parameters. Among the innovations are active packaging, which consists of incorporating functional components into the packaging that release or absorb substances into the packaged food or the environment, extending its useful life[4]. The concept of active packaging encompasses several technologies, such as oxygen and humidity absorbers, modified atmosphere, CO_2 emitters, ethylene absorbers, among others[5].

Among the most important active packaging are the antioxidant active packaging, which has a protective effect against oxidation of the packaged product, as it aims to remove any residual oxygen present in the packaging or improve barrier properties, acting as an active barrier[6]. Its use also allows the production of foods with less addition of synthetic antioxidants. Synthetic antioxidants are widely used to delay oxidation, but concerns over their toxicological effects have led to growing interest in natural alternatives, such as plant-based extracts[7].

Agro-industrial residues are of economic and environmental interest as sources of natural antioxidants, as many of them are rich in bioactive and antioxidant compounds. Although some are used as animal feed or field disposal, most are discarded untreated, contributing to environmental and economic issues in the production chain[8].

The wine industry generates significant by-products, including grape pomace, skins and seeds. In Brazil, wine production exceeded 800 million liters in 2023, resulting in approximately 200.000 tons of grape pomace as agro-

industrial waste[9]. These by-products, mainly seeds and peels, are rich in phenolic compounds (60% in seeds, followed by 30% in skin and 10% in pulp), responsible for their high antioxidant activity. Producers and wineries face the problem of disposing of residual biomass, which, although biodegradable, requires a minimum amount of time to be mineralized, becoming a source of pollutants. The possibility of obtaining phenolic compounds through a process of extracting these residues, and using them as natural antioxidant additives in polymeric films for active packaging, has attracted considerable attention[10].

Given the growing global emphasis on sustainability, current research in food packaging has increasingly focused on the development of materials that minimize environmental impact. The present study gains relevance by proposing the incorporation of antioxidants from agro-industrial wine waste—an abundant and underutilized by-product—into LDPE for active packaging. This approach aligns with sustainability goals by valorizing waste, reducing dependence on synthetic additives and advancing green technologies in polymer processing. Despite existing studies on chemical antioxidants used to protect polymers during processing, few have explored polyolefin films with natural antioxidants capable of interact with the food or product to be packaged, highlighting the novelty and potential of this research.

2. Materials and Methods

2.1 Chemicals

Standards of caffeic and galic acid, (+)-catechin, (-)-epicatechin, cianidin and quercetin were purchased from Sigma-Aldrich (St. Louis, MO). Acetonitrile and methanol both of HPLC grade were from Honeywell (Charlotte, North Carolina, USA). Formic acid was purchased from Merck (Darmstadt, Germany). Methanol (P.A.) was purchased from Neon Comercial (São Paulo, Brazil). Ethanol was purchased from Êxodo Cientifica (São Paulo, Brazil). Ultrapure water (Milli-Q) was generated by the Millipore System (Molsheim, FR). The synthetic antioxidant used was BHT [2,6-bis(1,1-dimethylethyl)-4-methylphenol] from Adicel (Belo Horizonte, Brazil). Maleic anhydride Polybond 3009, was purchased from SI Group (The Woodlands, USA).

2.2 Agro-industrial wine waste and antioxidant extract

The wine residue, consisting of skins and seeds from *Vitis labrusca* (Isabel grape), was supplied by a small winery in Bento Gonçalves-RS. To preserve phenolic compounds, the 5kg of residue was frozen at -80 °C, freeze-dried (Liobras model L101 equipment), milled, and vacuum-packed. To obtain the antioxidant-rich extract, 50 g of freeze-dried wine residue was subjected to exhaustive solid-liquid extraction using 250 mL of ethanol:water (80:20 v/v) acidified with 1.5% formic acid, in a centrifuge-compatible container.

The sample with solvent was stirred for 5 minutes using a vortex shaker (VELP ZX3), then centrifuged at 3000 g (10 min) in a refrigerated high-speed centrifuge (Hitachi CR 21GIII), as adapted from the methodology described by Selani et al.[11] and Lorrain et al.[12]. The supernatant at each stage of the exhaustive extraction process was collected in an amber bottle. The supernatant was concentrated in a rotary vacuum evaporator at 40 °C, until all the solvent was evaporated. The antioxidant extract (AE) was frozen at -18 °C, freeze-dried, and stored in amber bottles at -18 °C until use in active packaging preparation.

2.3 LC-DAD-ESI-MS/MS analysis

The analysis of phenolic compounds from the AE was carried out using HPLC (High Performance Liquid Chromatography) equipment, Shimadzu (Kyoto, Japan), which has a diode array detector (DAD) and is connected to the mass spectrometer (Bruker Daltonics, microOTOF-Q III model). The phenolic compounds separation was carried out using a Phenomex Synergi C18 (250 mm × 4.6 mm, 4 μm), with a flow rate of 0.7 L min^{-1}[12]. The mobile phase used in linear gradient consisted of water + 0.1% formic acid (mobile phase A) and acetonitrile + 0.1% formic acid (mobile phase B). The spectra were obtained at wavelengths of 280 nm, 320 nm, 360 nm and 520 nm.

After separating the phenolic compounds in the LC, the column eluate was divided using a "T" connection, in which 0.35 $mL.min^{-1}$ of the flow went to the MS. The ESI source was operated in negative and positive ionization modes, scan range from m/z 50 to 1000, capillary voltage of 3000 volts, drying gas (N_2) temperature and flow of 310 °C and 8 $L.min^{-1}$, nebulizer gas pressure of 4 bar. Phenolic compounds were identified by manual interpretation based on C18 column elution order, UV-VIS spectra, exact mass, and fragmentation patterns, compared with standards and literature data. Quantifications of phenolic compounds were carried out using the analytical curves of six phenolic standards (gallic acid, caffeic acid, catechin, epicatechin, cyanidin and quercetin).

2.4 Packaging production

The polymeric matrix selected for the production of antioxidant active packaging was Low Density Polyethylene (LDPE), commonly used for extrusion of tubular films for food packaging, with a melt flow index of 2.7g.$10min^{-1}$ at 190 °C/2.16kg and density of 0.923g/cm^3. To produce active packaging, masterbatches were prepared by incorporating the AE into LDPE using a Haake Rheomix OS – Thermo Scientific extruder.

Three formulations were developed: ME1-Masterbatch with LDPE and more concentrated AE masterbatch, ME2-Masterbatch with LDPE and less concentrated AE masterbatch, and MR1-Masterbatch with LDPE and Freeze-dried wine residue.

A HDPE grafted with maleic anhydride (PEgAm), Polybond 3009 from Addivant, was used as a compatibilizing agent in order to reduce the interfacial energy between the additives and the polymer matrix and improve their dispersion[13]. The LDPE and compatibilizing agent were first added to Haake, and processed for 4 minutes at 160 °C and then the antioxidants were added to mix until 5 minutes were completed. The formulations of masterbatches produced with a compatibilizing agent are described in Table 1.

The percentage of AE, Freeze-dried wine residue and PEgAm added to the LDPE in the masterbatch formulations, were based on preliminary tests did on Haake equipment and processing limitations. Based on the literature described by

Martins et al.[14], Chen et al.[15], Duran et al.[16], different mass percentages (w/w%) of antioxidant extracts can be added to polymeric materials in the production of active packaging, and the most common addition ranges are between 0.5% to 8%. For the production of active packaging, formulations were prepared with LDPE and 5% w/w of the previously produced masterbatches.

The mixtures were processed using an AX Plásticos extruder - Mini Extruder AX DR 16:40, double counter-rotating screw, diameter of 16mm L/D of 40, mass pressure of 59 bar, and the feeder and screw rotations were 12,6 rpm and 12,1 rpm, respectively. Extrusion was carried out with temperature ranges (Zone 1 – 140 °C, Zone 2 – 150 °C, Zone 3 – 160 °C, Zone 4 – 160 °C, Zone 5 – 165 °C, Zone 6 – 170 °C, Zone 7 – 180 °C, Zone 8 – 180 °C, Zone 9 – 185 °C), to produce films with ~40 µm thickness. For comparative purposes, a reference sample with only LDPE, a sample with BHT (FE3), samples with masterbatches of natural AE (FE1-high concentration and FE2-low concentration), and a sample with freeze-dried wine residue (FE4) were extruded under the same experimental conditions.

In Table 2 the identification and description of the active packaging samples produced are represented.

2.5 Colorimetry

To evaluate the colorimetric properties of active packaging films, color analysis was carried out using a Spectro-Guide portable spectrophotometer (BYK brand, Sphere Gloss model). The analyzes were carried out using the CIELAB color system, from the International Commission on Illumination. In the CIELab system, colors can be decomposed into 3 independent orthogonal parameters, L^*, a^* and b^*.

2.6 Infrared spectroscopy with fourier transform (FTIR)

Fourier transform infrared spectroscopy (FTIR) was used to investigate the surface species of the film samples. Spectra were collected in H-ATR (Horizontal Attenuated Total Reflectance Accessory) mode in accordance with ASTM E1252-2021[17]. Analyzes in transmission mode were performed on a Perkin Elmer FTIR spectrophotometer (model Spectrum 1000). Spectra were collected with 32 scans, 4 cm^{-1} resolution, over 4000-600 cm^{-1}.

2.7 Peroxide index and antioxidant activity of active packaging

The peroxide index analysis was carried out according to the IUPAC methodology[18], also referenced by the Analytical Standards of the Adolfo Lutz Institute[19]. The formulations selected were LDPE, FE1 and FE3, to carry out a comparison between the use of extract versus synthetic antioxidants in active packaging. A control sample of unpackaged sunflower oil in a Petri dish was also analyzed.

The film samples in the form of sachets containing 8 mL of antioxidant-free sunflower oil were sealed and exposed to UV radiation chamber (4000-5000 lux, 40 °C, 50% RH) under accelerated conditions. After preparing samples for 7 days monitoring and recording initial readings, the sachets were placed in the chamber.

For analysis, 5 g of oil from sachets was mixed with 30 mL acetic acid:chloroform (3:2), stirred until the sample dissolved and then 0.5 mL of a saturated solution of potassium iodide, 30 mL of distilled water and 1.0 mL of 1% aqueous starch solution were added. The mixture was titrated with 0.1 N sodium thiosulfate until colorless. Tests were done in triplicate. In parallel, a blank test was conducted, without the oil sample. Sachets were removed after 2, 5, 7, 10, 12, 17, and 20 days for peroxide index analysis. To calculate the peroxide index, reported in meq/1000g of sample, the Equation 1 was used.

$$\frac{m_{equivalent}}{1000g\ of\ sample} = (A - B)\ x\ N\ x\ f\ x\ \frac{1000}{P} \quad (1)$$

where: A = volume in mL of the $Na_2SO_2O_3$ solution used for the sample; B = volume in mL of the $Na_2SO_2O_3$ solution used for the blank; N = normality of the $Na_2SO_2O_3$ solution; f = correction factor for 0.1N sodium thiosulfate solution. P = weight in grams of the sample.

Table 1. Masterbatch formulations.

Formulation	LDPE (%)	AE (%)	Freeze-dried wine residue (%)	PEgAm (%)
ME1	83	12	0	5
ME2	90	5	0	5
MR1	90	0	5	5

ME1 = Masterbatch with LDPE and 12% w/w antioxidant extract; ME2 = Masterbatch with LDPE and 5% w/w antioxidant extract; MR1 = Masterbatch with LDPE and 5% w/w of Freeze-dried wine residue *in natura*.

Table 2. Active packaging formulations.

Formulation	LDPE (%)	ME1 (%)	ME2 (%)	MR1 (%)	BHT (%)	Freeze-dried Waste (%)
LDPE	100	-	-	-	-	-
FE1	95	5	-	-	-	-
FE2	95	-	5	-	-	-
FE3	95	-	-	-	5	-
FE4	95	-	-	5	-	-

FE1 = Formulation 1 with LDPE and 5%w/w ME1 masterbatch; FE2 = Formulation 2 with LDPE and 5% w/w ME2 masterbatch; FE3 = Formulation 3 with LDPE and 5%w/w of BHT; FE4 = Formulation 4 with LDPE and 5%w/w MR1 masterbatch.

3. Results and Discussions

3.1 Antioxidant extract (AE) phenolic composition

A total of 15 phenolic compounds were identified in the ethanolic extract and 14 compounds in methanolic extract. The fifteen phenolic compounds found in the extract are shown in Table 3. Additional experimental data are provided in the Supplementary Material (Tables S1 and S2).

The AE is mainly formed by flavonoids, such as catechin and epicatechin. Anthocyanins represent the second most important class in terms of concentration in the AE. Eight anthocyanins were found, highlighting delphinidin 3-O-(6-O-p-coumaryl)glucoside, delphinidin 3-O-hexoside and petunidin 3-O-hexoside.

3.2 Characterization of masterbatches and wine residue

3.2.1 Thermogravimetric analysis (TGA)

The thermogravimetric curves (TGA) and derived thermogravimetric curves (DTG) are represented in Figure 1, in which results regarding the decomposition of the evaluated samples can be obtained.

Mass loss up to 100 °C indicates sample moisture. The freeze-dried waste showed peaks at 207 °C and 354 °C, which may be associated to hemicellulose and cellulose decomposition[20,21] respectively. Between 400-500 °C the LDPE, ME1, ME2, and MR1 samples exhibited mass losses typical of LDPE decomposition[22]. Above 900 °C, the freeze-dried residue presented a residue of 17.03%, suggesting inorganic fillers, possibly silica from grape skin fibers, similar to açaí fibers[23].

The samples that contain an AE (ME1 and ME2), showed greater thermal stability when compared to the LDPE reference sample, suggesting that the presence of these compounds provides greater resistance to degradation. The residual masses between ME1 and ME2 were similar up to 350 °C, however, from the degradation temperature of pure LDPE, approximately at 474 °C, a change in thermal stability was observed, where the ME1 sample contains a greater amount of AE than ME2, showed greater resistance to degradation.

Table 3. Determination of Phenolic Compounds by HPLC-DAD-ESI-MS/MS.

Compound	λmax (nm)	Concentration (mg 100 g^{-1} dry sample)
Gallic Acid	279	0.62 [a] ± 0.05
Galoyl-*O*-hexoside	277	1.85 [a] ± 0.12
Caftaric Acid	325	5.30 [b] ± 0.47
Delphinidin 3-*O*-hexoside	277/526	1.63 [c] ± 0.11
Catechin	277	30.51 [d] ± 4.88
Cyanidin 3-*O*-glucoside	279/527	0.53 [c] ± 0.03
Petunidin 3-*O*-hexozide	276/529	1.63 [c] ± 0.03
(epi)catechin isomer	275	4.54 [e] ± 0.43
Peonidin 3-*O*-hexozide	279/527	0.87 [c] ± 0.05
(-)-Epicatechin	277	22.40 [e] ± 1.13
Malvidin 3-*O*-glucoside	279/525	0.28 [c] ± 0.01
Quercetin 3-*O*-hexoside	280	3.35 [f] ± 0.12
Delphinidin 3-*O*-(6-*O*-p-coumaryl)glucoside	281/258	1.89 [c] ± 0.09
Cyanidin 3-(6-*O*-p-coumaryl)glucoside	281/523	0.52 [c] ± 0.03
Malvidin 3-*O*-(6-*O*-p-coumaryl)glucoside	278/529	1.39 [c] ± 0.06
Total phenolic compounds	-	**77.31**

[a]Quantified in gallic acid. [b]Quantified in caffeic acid. [c]Quantified in Cyanidine. [d]Quantified in Catechin. [e]Quantified in (-) Epicatechin. [f]Quantified in Quercetin.

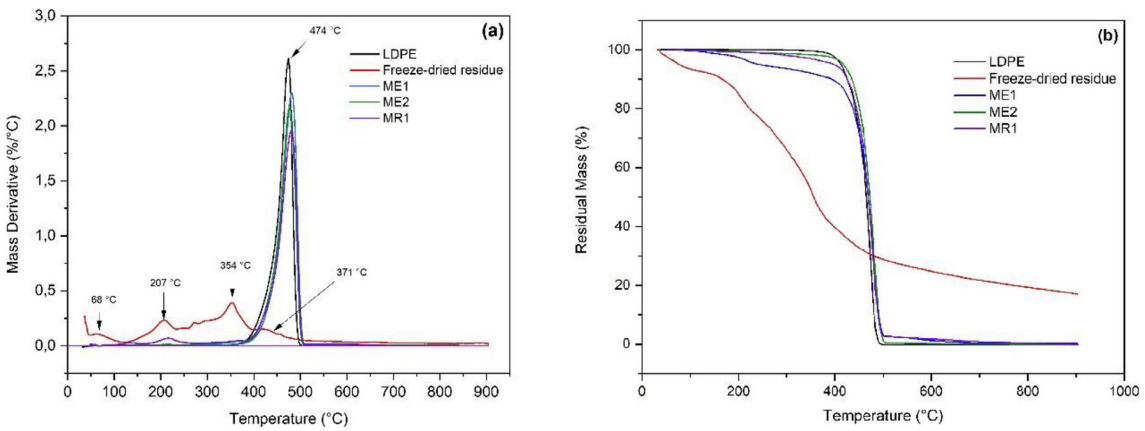

Figure 1. (a) Mass derivative × Temperature of the evaluated samples; (b) Residual Mass × Temperature of the evaluated samples.

Thermal degradation began at temperatures higher than those used during mixing and extrusion, indicating that conventional processing conditions are suitable and do not compromise material stability for active packaging production.

3.3 Characterization of active packaging

3.3.1 Colorimetric properties

The Figure 2 represents the films produced and their respective identifications.

In Table 4, the results related to the color parameters (L^*, a^* and b^*) of the formulations are presented.

The luminosity parameter L^* showed a decrease in the FE1 and FE2 formulations, when compared to the LDPE reference sample. These lower luminosity results are related to the addition of masterbatches with AE (anthocyanins compounds), which reduces the passage of UV/Vis light, a behavior also observed in the study with the addition of freeze-dried grape residue in the production of polymeric biocompounds[24].

The formulation with synthetic antioxidant, FE3, did not show significant differences when compared to the reference sample, because the BHT is colorless. The FE4 formulation did not have its luminosity affected by the incorporation of freeze-dried wine residue ($p > 0.05$). The change in color intensity in the FE1 and FE2 films, in parameters a^* and b^*, are related to the anthocyanins from the AE added to these formulations, so that the color of the films intensifies with the increase in the anthocyanin content.

The variation in the b^* parameter for the yellow scale in sample FE1 may be related to the shear stress that the sample suffered during the preparation of the masterbatch, as it was subjected to two passes through the Haake extruder to reach the final concentration, unlike the masterbatch of the FE2 formulation, which passed through the extruder only once. Thermo-mechanical processing results in degradation of the mixture and change in color (yellowish color). The superior result of the parameter b^* (yellow) in sample FE1 may also indicate the presence of pigments derived from the thermal degradation of grape skin constituents, mainly phenolic compounds and lignocellulosic material[25].

3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The characterization of films for active packaging and standard film was carried out using the Fourier Transform Infrared Spectroscopy (FTIR) technique, in transmission mode. The Figure 3 presents the FTIR spectra of the analyzed samples.

The FTIR spectra showed characteristic bands at of 2915 cm^{-1} and 2847 cm^{-1}, attributed to the vCsp3-H stretching, characteristic of aliphatic hydrocarbons originating from LDPE[26,27]. In Figure 4, the bands in the region of 1600 to 1200 cm^{-1} are presented with magnification, for better visualization.

The peaks observed at 1634 cm^{-1} in Figure 4 for samples containing wine residue FE1, FE2 and FE4, are related to the stretching of the aromatic ring (C=C and –OH) of the functional groups present in the phenolic compounds[21].

The intense band at 1465 cm^{-1} can be attributed to deformations of methylene δCH2, present in the polyolefin used to produce the films. The bands at 1375 cm^{-1} and 1300 cm^{-1} refer respectively to symmetric deformation of the methyl (terminal low-density methyl) and C-C vibrations.

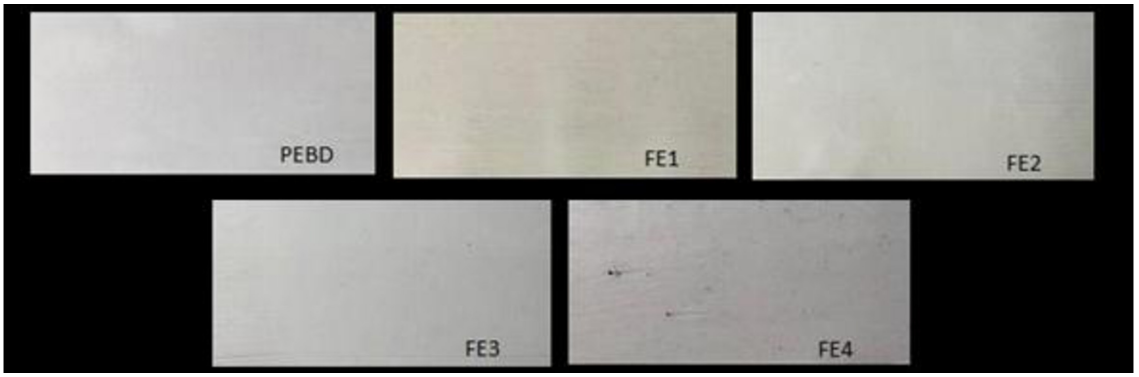

Figure 2. Films produced.

Table 4. Results of colorimetric properties for the different films produced.

Sample	L^*	a^*	b^*
LDPE	91.41 ± 0.16^{c}	0.25 ± 0.01^{ab}	-2.30 ± 0.04^{a}
FE1	88.90 ± 0.15^{a}	0.48 ± 0.08^{c}	3.12 ± 0.49^{c}
FE2	90.50 ± 0.33^{b}	0.33 ± 0.04^{b}	-0.03 ± 0.01^{b}
FE3	91.37 ± 0.07^{c}	0.25 ± 0.04^{a}	-2.26 ± 0.03^{a}
FE4	91.27 ± 0.14^{c}	0.28 ± 0.01^{ab}	-2.03 ± 0.05^{a}

Equal letters indicate that there is no significant difference with 95% confidence according to the Tukey test. LDPE = low-density polyethylene formulation; FE1 = Formulation 1 with LDPE and more concentrated AE masterbatch; FE2 = Formulation 2 with LDPE and less concentrated AE masterbatch; FE3 = Formulation 3 with LDPE and synthetic antioxidant BHT; FE4 = Formulation 4 with LDPE and masterbatch with freeze-dried residue.

3.3.3 Peroxide index and antioxidant activity of active packaging

The peroxide index was carried out to verify the effect of using polyethylene film and active packaging produced with AE and synthetic antioxidants on the oxidation of fresh sunflower oil. The results are presented in Table 5

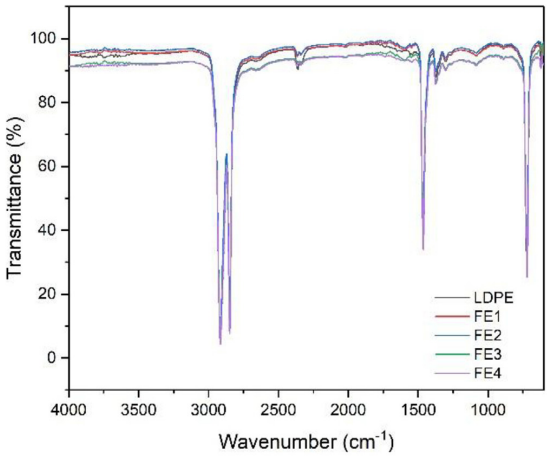

Figure 3. Overlaid FTIR spectra of the analyzed samples.

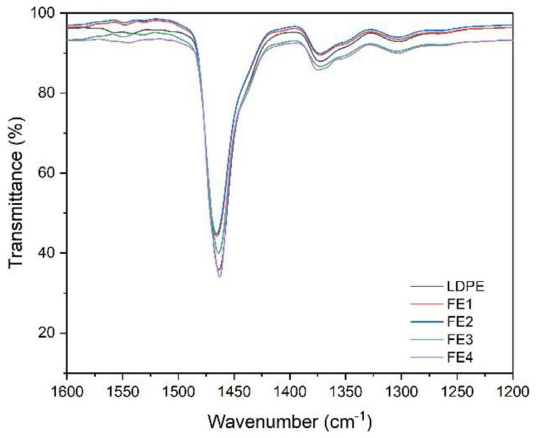

Figure 4. Magnification of overlapping spectra from the region 1600 to 1200 cm^{-1}.

The Figure 5 shows the stability of sunflower oil under oxidizing conditions, with a significant increase ($p < 0.05$) in the peroxide index after 20 days of storage in a UV chamber.

According to Codex Standard-1999[28] and Resolution-rdc nº 270 of the National Health Surveillance Agency[29], the maximum value of Peroxide index allowed for the commercialization of refined oils and fats is 10 mEq peroxides. kg^{-1} of sample. The control sample (sunflower oil without packaging), reached 14 mEq of peroxides.kg^{-1} of sample, after 2 days in direct contact with oxygen, temperature and absence of a light barrier. The control sample showed faster and greater oxidation compared to the LDPE, FE1 and FE3 formulations. This behavior for fresh sunflower oil was also reported in the study of biodegradable cellulose acetate packaging incorporated with norbixin, lycopene and zeaxanthin[30], and with starch-based antioxidant films with encapsulated eugenol[31].

From the 2nd day of testing, the unpackaged oil, LDPE and FE3 samples exceeded the limit of 10 mEq peroxides. kg^{-1} of sample. In relation to the peroxide index limit established in the legislation, only the oil sample protected with the active packaging formulation FE1 was suitable for consumption after 2 and 5 days of exposure.

The FE1 formulation had in its composition a natural AE consisting mainly of flavonoids of the flavan-3-ol type, highlighting catechin and (-)-epicatechin. The antioxidant effect of this active packaging may be associated with the primary mechanism of flavonoids to deactivate radicals formed during the propagation stage of lipid oxidation. Furthermore, flavonoids are able to chelate transition metals, which will decrease the rate of lipid oxidation. The flavonoids have chelating properties, which allow them to chelate, or bind to, metal ions to prevent them from being accessible for oxidation and the formation of free radicals[32].

The FE1 packaging showed lower luminosity (L) and higher color parameters (a^*, b^*), which reduced light transmission and therefore limited photooxidation of sunflower oil. This is due to the anthocyanins present in the extract (color filter) or their degradation products, which acted as filters for the passage of electromagnetic radiation.

On the 5th day of evaluation, the control sample showed higher peroxide index results than all other samples analyzed. These results may also be associated with the films having the property of oxygen permeability.

Table 5. Peroxide index results of selected samples over 20 days.

Day	Oil control (w/ packaging)	LDPE	FE1	FE3
0	2.51 ± 0.02^{a}	2.51 ± 0.02^{a}	2.51 ± 0.02^{a}	2.51 ± 0.02^{a}
2	14.34 ± 2.93^{c}	10.98 ± 1.47^{bc}	3.52 ± 1.69^{a}	8.41 ± 2.91^{b}
5	35.36 ± 0.06^{c}	23.49 ± 1.23^{b}	7.54 ± 0.02^{a}	23.35 ± 5.65^{b}
7	37.77 ± 4.04^{ab}	33.66 ± 1.42^{b}	22.41 ± 2.22^{a}	35.15 ± 0.35^{b}
10	58.25 ± 0.02^{b}	52.31 ± 6.92^{b}	40.44 ± 1.82^{a}	49.59 ± 1.80^{ab}
12	75.25 ± 5.78^{a}	68.81 ± 7.91^{a}	59.70 ± 0.62^{a}	68.27 ± 6.80^{a}
17	83.62 ± 0.13^{a}	80.70 ± 0.18^{a}	75.86 ± 2.58^{a}	80.39 ± 0.59^{a}
20	92.00 ± 3.75^{b}	87.04 ± 2.03^{b}	81.14 ± 2.64^{a}	86.41 ± 1.99^{ab}

Equal letters indicate that there is no significant difference with 95% confidence according to the Tukey test. Statistical analysis was performed comparing Day n *x* Samples.

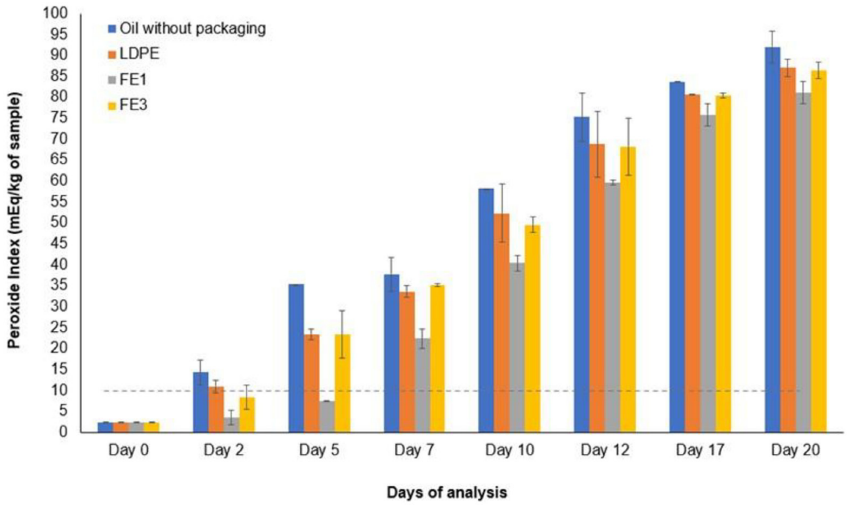

Figure 5. Peroxide Index as a function of the time of the samples evaluated.

The permeability of gases through polymers is influenced by factors like polymer type, film thickness, penetrant characteristics, pressure, and temperature. Inert gases such as oxygen interact minimally with polymers, resulting in low absorption and no structural changes. Their permeation is mainly determined by the polymer's structural features, including polarity, unsaturation, and side chains. The LDPE formulations in general present a lower barrier, and consequently higher oxygen permeability results, than formulations with HDPE. The presence of long branches in LDPE makes the packaging of macromolecules difficult, resulting in an increase in free volume and greater permeability[33]. The barrier created by LDPE films may have helped to reduce the oxygen permeability process for the food.

Among the films, on the 5th day of analysis, FE1 formulation showed lower peroxide index results, 78.67% lower than the Oil sample without packaging, 67.90% lower than LDPE and 67.71% lower than FE3.

On the 7th day of analysis, the FE1 sample continued to show lower peroxide index results, 40.66% lower than the Oil sample without packaging, 33.42% lower than LDPE and 36.42% lower than FE3. The LDPE and FE3 samples showed similar behavior, indicating that the addition of BHT as a synthetic antioxidant did not provide greater antioxidant action and oxidative stability. On the 12th and 17th day, the samples analyzed did not show significant differences between them ($p > 0.05$). Finally, on the 20th day of testing, the control sample without packaging reached a value of 92.00 ± 3.75 mEq of peroxides.kg-1 of sample, which represents a value much higher than the limit permitted by legislation[28,29].

4. Conclusions

The research demonstrates the feasibility of developing active LDPE packaging incorporating natural antioxidants extracted from agro-industrial wine residues. The integration of phenolic compounds, particularly flavan-3-ols and anthocyanins, into polymer matrices via extrusion enhanced thermal stability and light barrier properties, as evidenced by FTIR and colorimetric analyses.

The FE1 active packaging formulation, containing a higher concentration of antioxidant extract, exhibited superior performance in preserving sunflower oil under accelerated oxidative conditions. Notably, after 5 days of exposure, FE1 reduced oxidation by 67.90% compared to standard LDPE packaging and 67.71% compared to packaging with synthetic antioxidant BHT, maintaining peroxide levels below regulatory limits for a longer duration.

Based on the results obtained, it is possible to state that the addition of natural grape skin extract to a LDPE matrix resulted in an active packaging with promising results in antioxidant properties, indicating the potential and feasibility of these formulations for the development of new active packaging, obtained by extrusion processes.

5. Author's Contribution

- **Conceptualization** – Vanessa Machado Babinski Ramos; Ruth Marlene Santana; Eliseu Rodrigues
- **Data curation** – Vanessa Machado Babinski Ramos
- **Formal analysis** – Vanessa Machado Babinski Ramos; Ruth Marlene Santana; Eliseu Rodrigues
- **Funding acquisition** – NA.
- **Investigation** – Vanessa Machado Babinski Ramos; Ruth Marlene Santana; Eliseu Rodrigues
- **Methodology** – Vanessa Machado Babinski Ramos; Ruth Marlene Santana; Eliseu Rodrigues
- **Project administration** – Vanessa Machado Babinski Ramos; Ruth Marlene Santana; Eliseu Rodrigues
- **Resources** – Vanessa Machado Babinski Ramos; Ruth Marlene Santana; Eliseu Rodrigues
- **Software** – NA.
- **Supervision** – Vanessa Machado Babinski Ramos; Ruth Marlene Santana; Eliseu Rodrigues

- **Validation** – Vanessa Machado Babinski Ramos; Ruth Marlene Santana; Eliseu Rodrigues
- **Visualization** – Vanessa Machado Babinski Ramos
- **Writing – original draft** – Vanessa Machado Babinski Ramos
- **Writing – review & editing** – Vanessa Machado Babinski Ramos; Ruth Marlene Santana; Eliseu Rodrigues

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Supplementary Material

Supplementary material accompanies this paper.

Table S1. Chromatographic characteristics, UV-Vis absorption and mass spectral data of phenolic compounds from the ethanolic extract of wine residue analyzed by HPLC-DAD-MS

Table S2. Chromatographic characteristics, UV-Vis absorption and mass spectrum data of phenolic compounds from the methanolic extract of wine residue analyzed by HPLC-DAD-MS.

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