Mono and multilayer active films containing green tea to extend food shelf life

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Abstract

An active packaging film made of one and two-layers structure based on low-density polyethylene (LDPE) was produced with the incorporation of green tea extract (GTE) at different amounts by blown film extrusion. Film structure, optical, mechanical, antioxidant and barrier properties were characterized. The films revealed homogeneous film surface, the presence of GTE increases the tensile properties, improves friction coefficient and reduces LDPE films transparency. Moreover, the antioxidant capacity and barrier properties (water and oxygen) were enhanced, even at low concentrations. This study demonstrates the benefits of GTE incorporation into LDPE matrix, mainly in coextruded films, and its potential to develop an active and sustainable food packaging film at industrial scale.

Keywords

Active packaging; Blown film extrusion; Green tea extract; Antioxidant capacity; Barrier properties

1. Introduction

Beyond the preservation of food safety and quality during storage, packaging also extends food shelf-life, avoiding adverse elements, like deterioration by microorganisms, contamination by chemicals, oxygen and moisture, or by light and external forces, among others (Martins et al., 2018, Pereira de Abreu et al., 2012, Shin and Selke, 2014, Sung et al., 2013). The demand for packaged food has

risen due to population growth, encouraging the food industry to create solutions that protect food against internal and external factors, extending shelf life and prevent food spoilage (Ribeiro-Santos et al., 2018).

In the last years, with technological advances, active packaging has been developed with the incorporation of active agents into the polymer matrix. These active agents interact with the product aiming to extend its shelf life, preserving or enhancing it properties (European Commission, 2004, European Commission, 2009, Ribeiro-Santos et al., 2018). Comparing with traditional preservation systems, active packaging is a novel and great alternative on food packaging concepts due to the permanent changes in current consumer requirement and market trends. The controlled release of active agents, usually antioxidants, antimicrobial agents and/or nutrients to the surface or the internal part of the products can stop or postponement microbial, oxidative, and enzymatic spoilage, reduce weight loss and contaminations; ensuring the products quality during storage (Ahmed et al., 2017, Dong et al., 2018, Nerín et al., 2006). Therefore, due to both consumer health and environmental problems, current research has been highlighted on the application of natural components as active additives for food packaging (Carrizo et al., 2016, Nerín et al., 2006).

GTE's consumption its linked to lower incidences of various pathological conditions due to its reported anti-inflammatory, anti-tumor, antioxidative and antimicrobial properties. This is due to its constitution in polyphenols or flavanoids, among which catechins, amino acids, alkaloids like caffeine, volatiles, and mineral. Ambiental factors, such as, the climate and seasons of growth influence the active component concentration. Several reports have proved that the high GTE antioxidant effect is owing to the mixture catechins (Kim et al., 2006, López de Lacey et al., 2014, Muriel-Galet et al., 2015). Due to the bioactive properties and its classification as a food additive by the European Union, green tea extracts have been incorporated in several food packages to extend product shelf life (López de Dicastillo et al., 2013, Martins et al., 2018, Muriel-Galet et al., 2015, Rodrigues et al., 2022, Sadeghi et al., 2022).

Several approaches have been proposed, such as mixing (in solution or melt) or coating some active compounds, like GTE, curcumin, and cinnamon extract (Almeida et al., 2018, Ju et al., 2018, Luo et al., 2012, Panrong et al., 2019, Ribeiro-Santos et al., 2017, Silva de Sá et al., 2019) as active agents in polymer matrices. GTE was already used as active additive in combination with several polymers, such as ethylene-vinyl alcohol (López de Dicastillo et al., 2011), poly (*L*-lactic acid) (Martins et al., 2018), polypropylene (PP) (López de Dicastillo et al., 2013), oriented-polypropylene multilayer films (Carrizo et al., 2016), chitosan (Sabaghi et

al., 2015, Siripatrawan and Harte, 2010), gelatin (Jamróz et al., 2019), agar (López de Lacey et al., 2014), and soy protein (Kim et al., 2006).

Multilayer packaging film systems have been used to increase the shelf life and safety of food products, since these systems offer multiple benefits, for example, higher barrier to both water and gases and an increased mechanical strength. Moreover, the multilayer structure also allows to incorporate the essential oils (EOs)/extracts in the layer that is more appropriate to preserve the food. Hence, combining active compounds into multilayer polymers will be an effective approach to enhance product shelf life.

Low-density polyethylene (LDPE) is a polyolefin with low water vapor transmission rate (WVTR), medium gas permeability, good resistance to chemicals, good abrasion resistance, gloss and high transparency. Therefore, LDPE is one of the most used polymers in food packaging industry (Bumbudsanpharoke et al., 2022, Chatkitanan and Harnkarnsujarit, 2020, Chatkitanan and Harnkarnsujarit, 2021; Dong et al., 2018;).

Herein, the objective was to develop an active film for food packaging based on the incorporation of different amounts of GTE in LDPE in a twin screw extruder. After compounding, different films were prepared by blown film extrusion, varying the structure (one layer and multilayer). The produced films were characterized through mechanical, optical, microstructure, antioxidant properties and barrier.

2. Materials and methods

2.1. Materials

LDPE was kindly provided by Vizelpas, Lda. Commercial GTE was supplied from ESSÊNCIAD'UMSEGREDO, Lda (Portugal). Potassium Bromide (KBr) (CAS: 7758–02–3), Acros Organics, Belgium, spectroscopic standard) was used to prepare pellets for Fourier Transform Infrared Spectroscopy (FTIR). Extra pure calcium chloride ($CaCl_2$) (CAS: 10035–04–8, Riedel de Haën, Germany) was used for the water vapor transmission rate (WVTR) assays.

2.2. Reagents for biological assays

For the antioxidant assays, absolute ethanol (CAS: 64–17–5), chloroform (CAS: 67–66–3), methanol (CAS: 67–56–1), sodium carbonate anhydrous (CAS: 497–19–8), sodium nitrite (CAS: 7632–00–0), sodium hydroxide (CAS: 1310–73–2), gallic acid (CAS: 149–91–7), 2,2-diphenyl-1-picrylhydrazyl (DPPH) (CAS: 1898–66–4), (±)-6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (CAS: 53188–07–1), epicatechin (CAS: 490–46–0), β-carotene (CAS: 7235–40–7), linoleic acid (CAS: 60–33–3), Tween®40 (CAS: 9005–66–7), and Folin-Ciocalteu reagent were acquired to Merck (Germany). Also, a rotary evaporator Büchi model R-210, a Thermo

Scientific Evolution 300 LC spectrophotometer and a Grant Instruments™ QB Series Dry Block Heating System were used.

2.3. Preparation of LDPE/GTE masterbatch

Previous to blown film extrusion, a LDPE/GTE masterbatch was prepared to guarantee better GTE dispersion into LDPE matrix. Initially, LDPE and GTE were dried in a vacuum oven at 60 ^{0}C, overnight. Then, a masterbatch with 10 wt% of GTE was compounded in a Leistritz AG LSM 34 6 L co-rotating twin-screw extruder at 170 ^{0}C, using a screw speed of 125 rpm and an output of 4 kg h^{-1}. In order to prevent the degradation of GTE, the extract was added downstream in the extruder *via* a secondary feed system. The extruded filaments were air cooled and granulated.

2.4. Blown film extrusion

Neat LDPE and LDPE/GTE masterbatch were dried in a vacuum oven at 60 ^{0}C, overnight prior to blown film extrusion. LDPE/GTE masterbatch was diluted into neat LDPE to produce films containing 1.5 and 3 wt% of GTE. Monolayer films of LDPE with GTE (LDPE_1.5GTE and LDPE_3GTE) and coextruded films LDPE/LDPE+GTE films (CO_LDPE_1.5GTE and CO_LDPE_3GTE) were prepared using a Periplast single screw extruder. The thickness of the films was in 48.7–54.0 μm range (Table S1 in Supplementary material). The processing conditions were constant, with a screw speed of 50 rpm, 170 ^{0}C on the first heating zone, 175 ^{0}C on the second zone and 180 ^{0}C on the remaining zones.

2.5. Scanning electron microscopy (SEM)

Morphological analysis was realized using a NOVA 200 Nano SEM (FEI Company). Samples were fractured in liquid nitrogen and coated with a gold thin film.

2.6. Fourier transform infrared (FTIR) analysis

FTIR spectra were obtained in a 4100 Jasco spectrometer apparatus in transmittance mode using as parameters: 32 scans.min^{-1}, 4 cm^{-1} resolution and a range of 4500–400 cm^{-1}. Thin films of all samples were prepared by compression molding in a hot press at 140 ^{0}C under a pressure of 10 tons. A sample pellet of GTE was used to obtain the FTIR spectrum.

2.7. Opacity and light transmission

The films' opacity was assessed using Eq. (1):(1)Opacity=Abs600Xwhere Abs_{600} correspond to the value of absorbance at 600 nm using UV–vis spectrophotometer (Shimadzu UV-2401 PC) and X is the average thickness of the film (mm). At least 5 samples of each film type were analyzed.

The films optical properties were assessed on dried conditions, amongst 200 and 800 nm, using a UV–vis spectrophotometer based on the procedure described by Han and Floros (1997). At least 5 samples of each film type were tested.

2.8. Mechanical properties

Tensile strength at break (TS), elongation at break (EB) and secant modulus (SM) of LDPE/GTE films were calculated according to the ASTM standard test method D882–02, using the INSTRON 3345 machine with a 500 N load cell and speed of 500 mm min^{-1}, temperature (23 ± 2 ºC) and relative humidity (50 ± 5%) controlled. The films were cut into rectangular strips (10 mm width), and their thickness was measured at 5 points. The samples were kept in parallel with 50 mm as the initial grip separation; repeating at least 5 times for each film, reporting the mean values. The calculated parameters (TS, EB and SM) were performed in the extrusion direction (MD) and transverse direction (TD) of the tubular film.

The coefficient of friction (COF) was determined according to ASTM D1894 using a RDM CF-800XS equipment. A sample with 130 × 320 mm was cut to cover the horizontal test plane. Another sample with dimensions of 110 × 170 mm was cut to cover the block, which allows to perform the test under the horizontal plane, a test speed of 150 ± 30 mm min^{-1} was used. Three specimens were cut (in the machine direction) for each side of the film, outer and inner for coextruded films. The analysis was performed at controlled temperature (23 ± 2 ºC) and relative humidity (50 ± 5%).

2.9. Antioxidant activity assays and determination of total phenolics content and total flavonoids content

Films with 6 cm^2 diameter were placed in contact with 10 mL of ethanol 95% (v/v), an alternative food simulant for fatty foods according to the Commission Regulation No. 10/2011 (Regulation, 2011), for 10 days at 40 ºC. Then the antioxidant activity was determined by the DPPH Radical Scavenging Assay and the β-carotene Bleaching method. Also, the total phenolics content (TPC) and total flavonoids content (TFC) were determined.

2.9.1. Determination of total phenolics content

TPC was evaluated by the procedure described by Erkan et al. (2008) using an Evolution™ 300 UV–Vis Spectrophotometer to measure the absorbance at 725 nm.

The content of phenolic compounds was assessed using the regression equation of the gallic acid calibration curve, y=0.0065x-0.1473, with a coefficient of determination of 0.998, expressed in gallic acid equivalents (GAE) milligrams per milliliter.

2.9.2. Determination of total flavonoids content

The method described by Yoo et al. (2008) was applied to determine the TFC with the absorbance measurement at 510 nm.

2.9.3. DPPH radical scavenging method

The DPPH radical assay evaluate the *in vitro* antioxidant activity of a given sample. Succinctly, 2 mL of a methanolic DPPH radical solution (14.2 μg/mL) was added to 50 μL of sample. The solutions were homogenized and protected from the light for 30 min; then the absorbance was measured at 515 nm. The Inhibition Percentage (IP) was measured through the Eq. (2).(2)IP%=AC-ASAC×100where, *AC* stands for the control' absorbance and *AS* stands for the sample' absorbance. The applied method was in accordance with the method described by Andrade et al. (2018).

2.9.4. β-carotene bleaching method

The applied method was initially described by Miller (1971) and adjusted by Andrade et al. (2018). First, it was prepared an emulsion of 20 mg of linoleic acid, 200 mg of Tween®40 and 1 mL of a chloroform solution of β-carotene (2 mg/mL). Afterward, 50 mL of ultrapure water was added. Once the emulsion was prepared, 5 mL were immediately added to 200 μL of sample and the samples were kept at 50 ºC for 120 min, in a Grant Instruments™ QB Series Dry Block Heating System. The Antioxidant Activity Coefficient (AAC) was calculated through the Eq. (3) using the absorbances values at 470 nm.(3)AAC=AS-AC2AC0-AC2×1000

In which, *AS* is the absorbance of the samples, *AC0* the absorbance of the control before heating and *AC2* the absorbance of the control after the heating.

2.10. Water vapor permeability

The WVTR of films was evaluated by the desiccant method based on the ASTM method E96/E96 M-05. Each film was placed in a circular metal test cup, with 69.5 mm of surface diameter, filled approximately with 25 g of $CaCl_2$, previously dried at 150 ^{0}C in a vacuum oven. The cups were sealed with paraffin wax to ensure that humidity migration occurred exclusively through the film. Then, the test cups were arranged in a desiccator and sustained at 20.78 ± 1.37 ^{0}C, 94.26 ± 4.33% RH and weighed daily for one month. The assessed WVTR was calculated using Eq. (4):(4)WVTRg water/(m2.hour)=Gt×Awhere G/t (g water/hour) is the slope (weight *versus* time plot) and A is effective film area (m2). WVTR was calculated using three replications and expressed in g/h.m^2.

2.11. Oxygen permeability (O_2P)

A gas permeability tester (DP-100A, Porous Materials, *Inc*.) was used to quantify oxygen transmission rates through the films at 21 ^{0}C and 55% RH according to standard method D1434–82. The various film samples were placed in

the testing area with 4 cm of diameter. Tests were realized in triplicate and mean values were expressed as mL.mm/MPa.min.cm^2.

2.12. Statistical analysis

Microsoft Windows Excel 365 and OriginPro software (Version 17) were used to analyze the resulting data using the analysis of variance (ANOVA) with a Tukey's test at 5% of significance ($p < 0.05$); and all the results were displayed as mean ± standard deviations in a minimum of three replicates.

3. Results and discussion

3.1. Structural properties

The visual aspect of produced films containing GTE presented a brownish color, which is dependents on its amount (Fig. S1 in Supplementary material).

The GTE dispersion into the LDPE matrix is demonstrated by SEM micrographs of the film surface and cross-section (Fig. S2 in Supplementary material). The surface and cross-section of LDPE film exhibited a smooth and homogeneous surface with low porosity, as the results obtained by Dong et al. (2018). GTE aggregates in LDPE were not detected at the surface, even when the amount of GTE increased from 1.5 to 3 wt%. Coextruded films demonstrate good adhesion between layers, showing that the addition of GTE did not affect adhesion. Micrographs with high magnification confirm a very good dispersion of GTE in all samples, suggesting a possible miscibility of the film components (Bumbudsanpharoke et al., 2022).

FTIR spectrum of LDPE/GTE masterbatch (Fig. 1A), indicates LDPE characteristic vibrational bands, mainly CH_2 asymmetric stretching, located at 2918 cm^{-1}, CH_2 symmetric stretching at 2851 cm^{-1}, bending deformation at 1465 cm^{-1}, CH_3 symmetric deformation at 1376 cm^{-1}, twisting deformation at 1303 cm^{-1} and rocking deformation at 722 cm^{-1}. The presence of GTE can be confirmed through its characteristic vibrational bands, such as the O-H stretching at 3349 cm^{-1}, the C-C stretching at 1614 cm^{-1}, a band shift of C-O bending for 1374 cm^{-1} and the C-O-C stretching at 1237 cm^{-1} and 1030 cm^{-1} typical of aromatic ether groups.

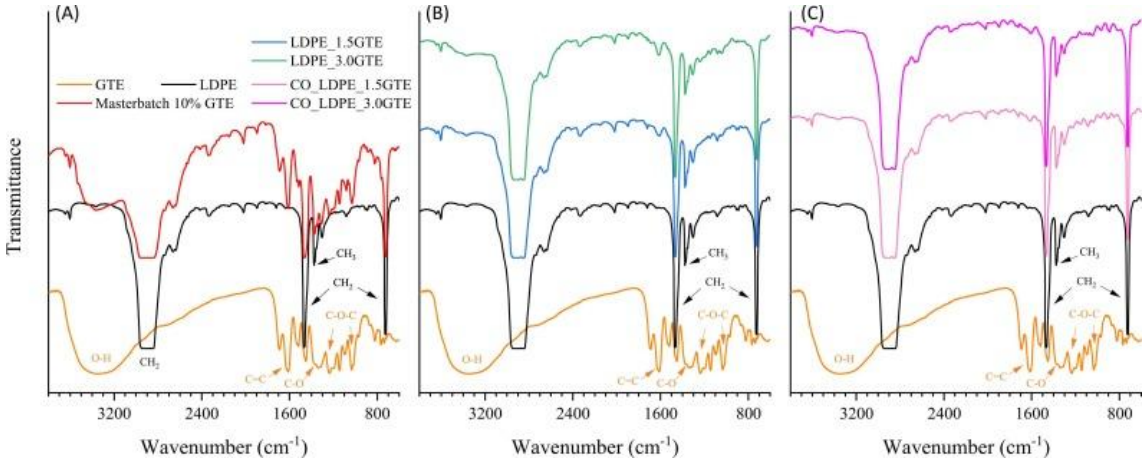

Fig. 1. FTIR spectrum of LDPE/GTE masterbatch (A), extruded films (B) and coextruded films (C).

FTIR analysis was also performed to confirm the presence of GTE in LDPE films (Fig. 1B and C). The FTIR spectra of extruded and coextruded films are similar to the one obtained for the masterbatch (Fig. 1A), evidencing the characteristic peaks of GTE related to the presence of polyphenols. Spectra exhibited in Fig. 1 do not show any significative difference between the two amounts of GTE used for both extruded and coextruded films, as no great difference in intensity of GTE characteristic bands was detected. The presence of both LDPE and GTE characteristic peaks at the same wavelength for all the films, reveals that no new chemical bonds were formed between GTE and LDPE species.

3.2. Optical properties

Optical properties are very important in the film appearance since they directly influence the consumer's willingness to buy a specific food product. Fig. 2 presents the parameters of light transmission (%) and opacity measured, which allows to compare the differences among the produced films.

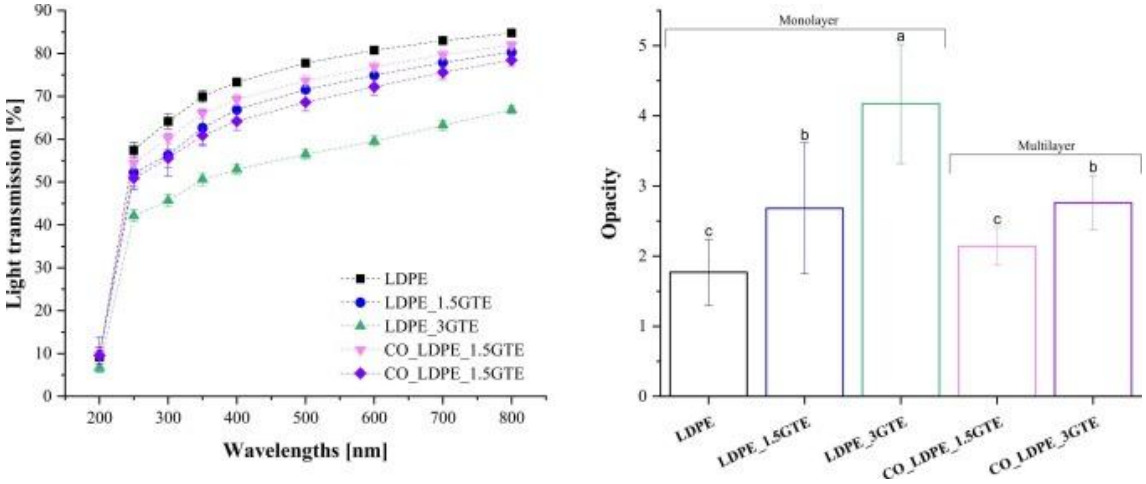

Fig. 2. Light transmission and opacity of LDPE monolayer and coextruded films containing GTE.

The UV transmittance of the LDPE film ranged from 9.13% to 73.32% in a wavelength range of 200–400 nm. However, the UV transmittance of the films containing GTE decreased as its content increased. While at 400 nm, LDPE_1.5GTE film exhibited 66.89% light transmission, LDPE_3GTE films presented 52.98%, indicating an increase in opacity. Nevertheless, the trade-off of this outcome was a decrease in the transparency of the films. In the visible light range (300–800 nm), the light transmission decreases with increasing GTE concentration. Film extruded with 3 wt% of GTE exhibited the highest block properties in the visible range, in fact, it is known that EOs/extracts influenced the light transmission. The results obtained for light transmission are similar to those reported by Lee et al. (2019), Mulla et al. (2017), Hosseini et al. (2015), and Ribeiro-Santos et al. (2018).

Opacity values demonstrated that GTE content significantly affect the transparency of the film (Fig. 2). The films containing GTE were darker than the control film (LDPE) and as GTE concentration increases, the tendency toward redness and yellowness is noticed. The increase in brown coloration can be explained by the brownish color of the GTE, which influences the light transmission. Similar findings were published for other polymer films by several authors, PVA (Alvarado et al., 2018, Chen et al., 2018), EVOH (López de Dicastillo et al., 2011), PLA (Martins et al., 2018) and chitosan (Peng et al., 2013, Siripatrawan and Harte, 2010, Wang et al., 2013). As expected, the results in the coextruded films are slightly different, and the effect of the increase of GTE concentration in the films is not so significant. Thus, for industrial application the amount of GTE incorporated into the LDPE matrix must be taken into account once it has influence on the color and opacity of the films, mainly in packages with high-level of transparency requests.

3.3. Mechanical properties

Mechanical properties of the extruded films (TS, EB, and SM) were measured both in machine direction (MD) and transversal direction (TD). The results depicted in Fig. 3 show that upon incorporation of 1.5 and 3 wt% GTE in LDPE (monolayer film), and 3 wt% GTE coextruded film, the TS reduced from 23.4 MPa to 18.5, 15.1 and 18.4 MPa, respectively, with the exception for 1.5% GTE coextruded film where the TS increase to 26.1 MPa. The decrease in TS might be ascribed to the presence of active compounds and its interactions with LDPE matrix, which can be associated to a possible disruption of the polymer chains connectivity due to the incorporation of GTE that reduced the strength against applied external force (Phothisarattana et al., 2021). In fact, similar results were already reported by Sung

et al. (2014), testing Allium sativum's effect on the TS of LDPE-based film and by Dong et al. (2018) who studied the impact of rosemary and cinnamon essential oils on the TS performance in new active bilayer structure based on LDPE films. Contrarily, the presence of GTE seems not to have an effect on EB for all the films. As expected, SM follows the same trend as TS.

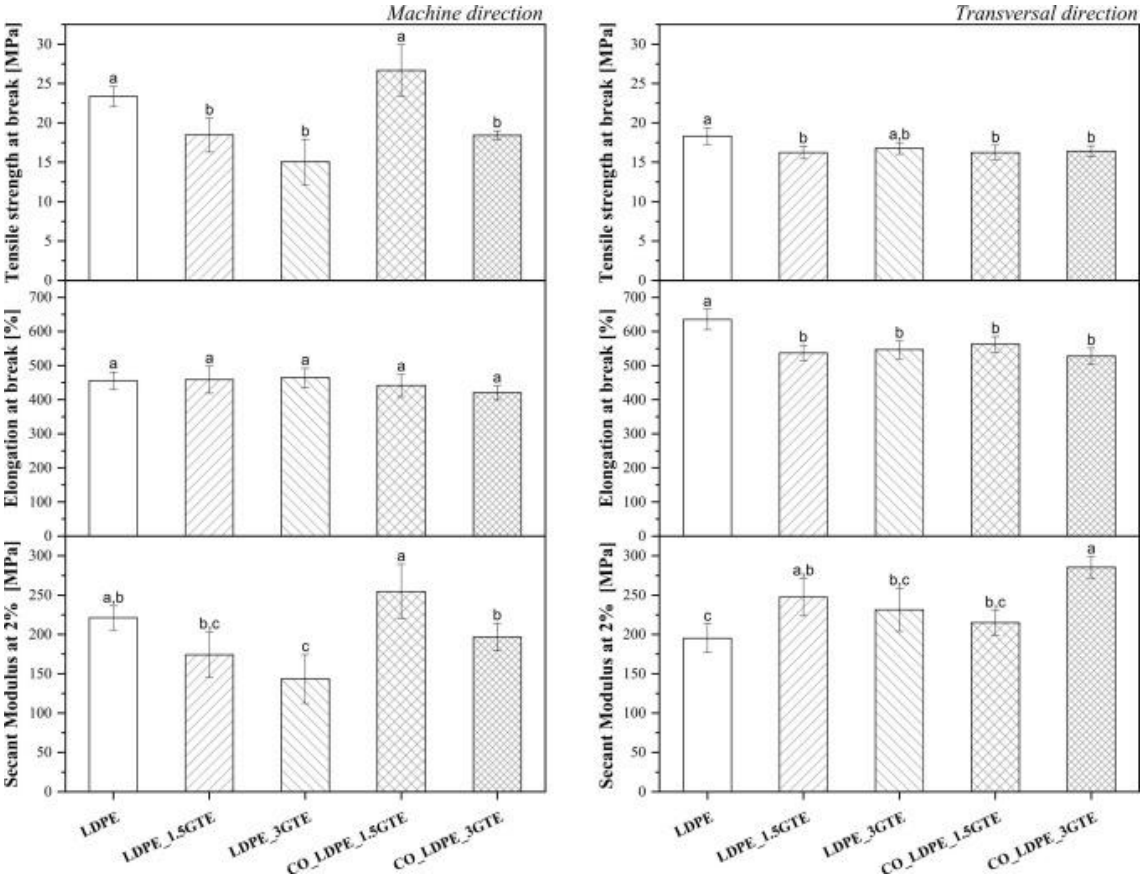

Fig. 3. Mechanical properties of LDPE/GTE films: tensile strength at break (TS), elongation at break (EB) and secant modulus at 2%, (A) in the machine direction (MD) and (B) transverse direction (TD).

TD results, represented in Fig. 3 indicate that TS value decrease by 8.6–11.4% compared to the control film, this means that the effect of GTE has minor than in the MD direction. The values obtained for EB decreased in comparison with the LDPE value (635.2%).

MD analysis demonstrate that SM value decreases as the amount of GTE increases, this can be associated to the poor distribution of GTE particles in the LDPE matrix. For multilayer films SM increased with the addition of GTE in the polymeric matrix. Even though the highest value is reached by 3% GTE coextruded film, a real correlation with the addition of GTE cannot be obtained.

The COF is a surface property that can be critical for good machinability and package transport, Fig. 4 presents the results that were measured in kinetic and

static mode. It can be noticed that films present a low COF (<0.25), indicating smaller resistance to friction, with the addition of GTE, the COF value decreases more than half. This behavior is visualized for both kinetic and static COF. The presence of GTE changes the surface properties, it seems that it acts as a "slipping agent".

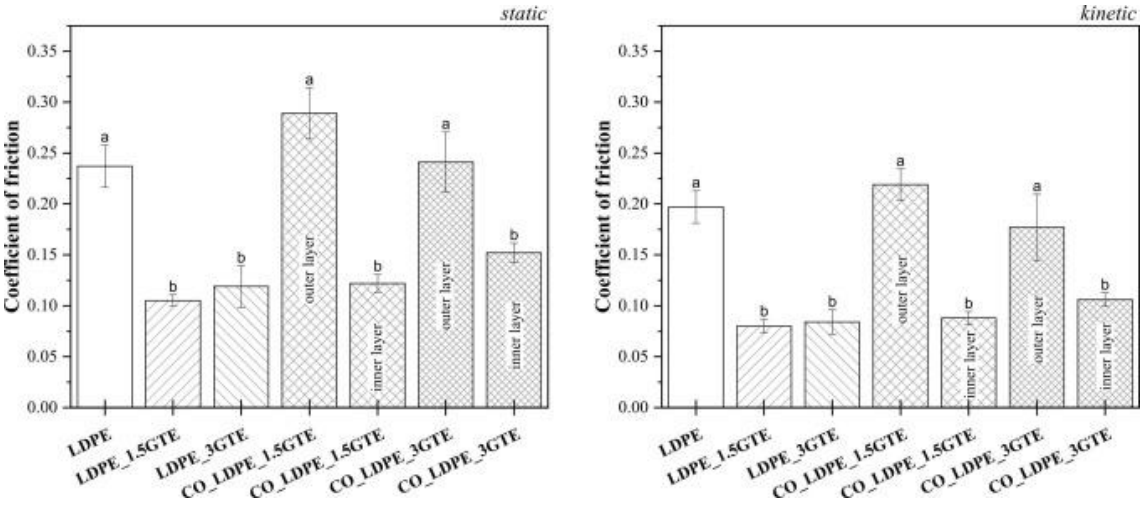

Fig. 4. Coefficient of friction, static and kinetic for LDPE/GTE films.

3.4. Determination of the total phenolics content and determination of antioxidant activity

The polyphenols present in the natural extracts are extremely effective as oxygen scavengers, reducing agents and hydrogen donors. Within polyphenols group, flavonoids (plant secondary metabolites) sub-group comprises some of the main chemical antioxidants with potential as metal chelators or inhibitors of lipoperoxidation; showing, consequently, antioxidant activity *in vitro* and *in vivo*. To construct the standard curve, it was used the natural compound epicatechin, with 9 calibration points in a range of 10–200 µg/mL; the results are expressed as µg epicatechin equivalents (ECE) per milliliter. The assays mentioned were carried out for all the prepared films (Table 1).

Table 1. Values of the total phenolic and total flavonoids compounds, DPPH radical inhibition results expressed in % inhibition, and the inhibition of β-carotene bleaching expressed by the coefficient of antioxidant activity (AAC), for the active films.

Film	Total phenolic compounds (mg GAE/mL)	Total flavonoids compounds (µg ECE/mL)	DPPH• method (% inhibition)	The β-carotene bleaching assay (AAC)
LDPE	18.01 ± 6.04^{b}	30.30 ± 0.15^{b}	0^{d}	94.5 ± 22.4^{a}

Film	Total phenolic compounds (mg GAE/mL)	Total flavonoids compounds (µg ECE/mL)	DPPH• method (% inhibition)	The β-carotene bleaching assay (AAC)
LDPE_1.5GTE	24.63 ± 0.03^{a,b}	32.23 ± 0.72^{a}	1.77 ± 0.74^{c}	99.6 ± 8.42^{a}
LDPE_3GTE	25.17 ± 0.09^{a,b}	31.25 ± 0.77^{a,b}	3.30 ± 0.31^{b}	130 ± 6.18^{a}
CO_LDPE_1.5GTE	25.04 ± 0.01^{a,b}	32.27 ± 0.20^{a}	2.39 ± 0.15^{b,c}	125 ± 14.2^{a}
CO_LDPE_3GTE	25.31 ± 0.25^{a}	30.50 ± 0.20^{b}	5.03 ± 0.77^{a}	128 ± 12.6^{a}

The results are expressed as mean ± standard deviation; distinct letters in the same column (a-d) indicate a significant difference (Tukey's test, $p < 0.05$) between means.

The results confirm that CO_LDPE_3GTE show a higher content of TPC (25.31 mg GAE /mL), whereas the CO_LDPE_1.5GTE presented a higher content of total flavonoids (32.27 µg ECE /mL). It can also be detected that all active films have a similar content of TPC, on 24.63–25.31 mg GAE /mL range, and analogous behavior was reached for the total flavonoids content.

The determination of the radical-scavenging activity of packaging films is very important because of the harmful effects of free radicals to food and biological systems. DPPH• assays depend on the reducing antioxidant ability (electron transfer) of the nitrogen radical, with a marginal radical reaction *via* hydrogen transfer mechanism (Panrong et al., 2019). This assay was established on the DPPH ability to be quenched and bleached in the presence of antioxidants causing a reduction on absorbance values (Jouki et al., 2014). The DPPH inhibition percentage values of the active film samples are shown in Table 1. As expected, all films presented antioxidant activity, with the exception of the film without GTE, which has a null result. The percentage inhibition values of DPPH radical-scavenging ability increased as the increased GTE concentration in the film. The antioxidant capacity of the active films coextruded containing 3 wt% GTE was higher than other film. This can be associated to the higher concentration of GTE that resulted in an increase of antioxidant capacity that is related with the total phenolics content, specifically catechin compounds, which is stated as the main responsible for the antioxidant ability of GTE. The increase in the amount of extract added in films is generally proportional to the total phenolic content and radical-scavenging activity (Nabilah et al., 2019).

Table 1 also exhibit the results of the β-carotene bleaching test. The active film with 3 wt% of GTE, presented similar antioxidant capacity among the evaluated

films. It is possible to notice that in DPPH inhibition, the active film containing 1.5 wt% GTE (LDPE_1.5GTE) showed the lowest inhibition % (1.77%), the same is confirmed in the β-carotene bleaching test (99.6 μg/mL).

3.5. Permeability

Barrier properties to oxygen of LDPE/GTE active films and LDPE are depicted in Fig. 5A. A decrease in O_2 permeability was noticed from $1.886E^{-4}$ mL.mm/MPa.min.cm^2 of control film to $1.365E^{-4}$, $1.601E^{-4}$ and $1.630E^{-4}$ mL.mm/MPa.min.cm^2, where LDPE_3GTE active film presents the smaller value. However, there was an exception for the LDPE_1.5GTE film, where the permeability increased to $2.304E^{-4}$ mL.mm/MPa.min.cm^2. Thus, the incorporation of GTE on LDPE matrix reduces LDPE permeability to oxygen, indicating that increasing concentration of GTE from 1.5 to 3 wt% for the monolayer films (LDPE_1.5GTE; LDPE_3GTE), improves the oxygen barrier property. This can be associated to the effective distribution of the extract into the LDPE matrix, where the interaction between GTE and polymer might form a closer polymer network resulting in denser pack of the matrix that reduces oxygen permeation, this is in agreement with previous findings (Dong et al., 2018, Yamamoto et al., 2009). This effect was not so significant for coextruded films. The active film with better O_2 permeability is the LDPE_3GTE, which demonstrated a decrease of 27.6% when compared with the control film. This fact may be explained mainly by the improvement of LDPE film hydrophobicity with the GTE incorporation. The oxygen diffusion in the active films becomes more difficult with the addition of GTE, where the interaction between LDPE-GTE hydrogen bonding may contributed to this phenomenon. Actually, similar results were found in literature concerning the GTE addition in different polymeric matrix (Chalob and Abdul-Rahman, 2018, López de Dicastillo et al., 2011, Vilarinho et al., 2021).

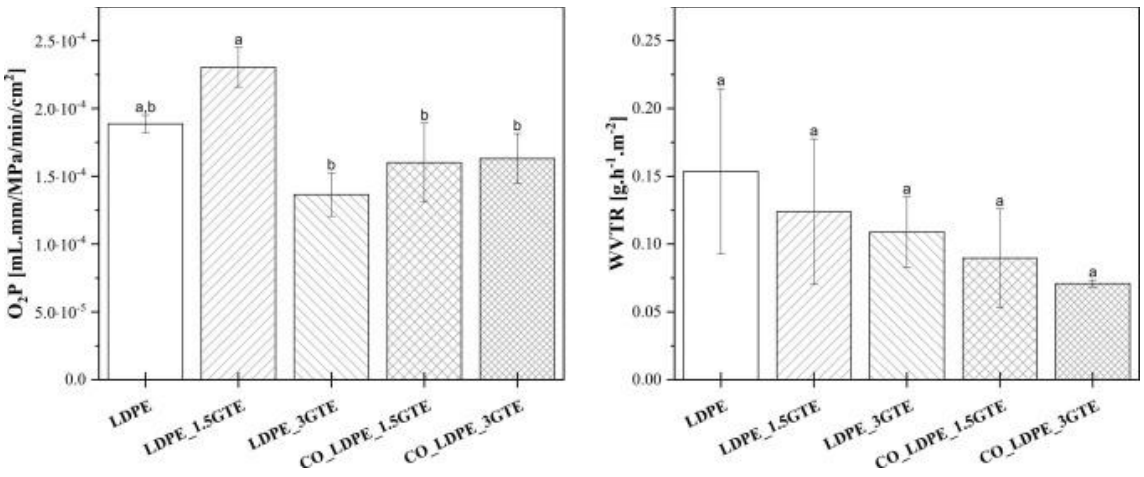

Fig. 5. Oxygen (O_2P) (A) and water (WVTR) (B) permeability of LDPE/GTE active films.

Good water vapor barrier property is crucial for packaging, which not only prevents excessive water loss from food products but also avoids moisture transfer from the atmosphere. This aspect is very important, since water can promote the growth of the microorganisms and decrease food shelf-life (Dong et al., 2018). It is known that WVTR is commonly dependent on hydrophilicity of the matrices *i.e.*, low hydrophilicity leads to lower WVTR (Chatkitanan & Harnkarnsujarit, 2021). Moreover, the hydrophobic nature of EOs/plant extracts might have an influence on the properties of polymer-based films developed with EOs/plant extracts due to decrease the water sorption capacity of the films (Ribeiro-Santos et al., 2018).

The WVTR of LDPE-based films was evaluated, the results of Fig. 5B show that the addition of GTE in the LDPE matrix decreased the WVTR of the active films from 0.15 ± 0.06 g/h.m^2 (control film) to 0.12 ± 0.05; 0.11 ± 0.03; 0.09 ± 0.04, and 0.07 ± 0.003 g/h.m^2 corresponding to the LDPE_1.5GTE, LDPE_3GTE, CO_LDPE_1.5GTE, and CO_LDPE_3GTE film, respectively. The results indicate that the addition of higher amounts of GTE improves the LDPE-based film's water vapor barrier properties, which are in agreement with studies in the literature (Chalob and Abdul-Rahman, 2018, López de Dicastillo et al., 2011, Vilarinho et al., 2021).

Water vapor barrier property of LDPE-based active films is enhanced by the addition of GTE due to the polyphenolic compounds that contain hydrophobic groups, which consequently improve the hydrophobic property. SEM results indicates a good and homogeneous dispersion these hydrophobic components in the polymer matrix, which can explain the decrease of water vapor transmission (Wongphan et al., 2022). Moreover, the interaction between LDPE and GTE through hydrogen bonds is another possible reason for the hydrophobic character of the film, which led to the film structure become more compact, these aspects were also reported by Chen et al. (2018).

4. Conclusion

LDPE active films with different concentrations of GTE (1.5 and 3 wt%) and different layer structure (monolayer and coextruded) has been successful developed as a packaging material for food applications. For monolayer films, while the tensile properties were similar when compared to LDPE film, the incorporation of GTE improves COF, decreases the transparency of LDPE films and improves both the LDPE barrier properties and the antioxidant capacity, giving to this active film a great potential for food packaging industry. Comparing the results obtained for the two film structures, it is possible to conclude that coextruded films exhibit better properties. However, additional studies have to be made to assess the specific migration of main components of GTE from the polymer matrix into food simulants or model foods in order to establish the effective concentration of GTE to be incorporated in the polymeric matrix and to stablish

safety guidelines. GTE at low concentrations (1.5–3 wt%) has a good potential to be employed as a natural antioxidant to produce active films to preserve food, promoting consumer health by the reduction or substitution of synthetic additives. This study also demonstrates that LDPE/GTE films with different structures can be produced in commercial blown-film extrusion lines, as a promising alternative to conventional multimaterial systems for food packing industry.

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Table S1 – Description of blown extruded films based on LDPE/GTE.

Code	Film description	Film structure	Thickness (µm)
LDPE	Neat LDPE film	Monolayer	48.70 ± 0.01
LDPE_1.5GTE	LDPE film with 1.5 wt.% GTE	Monolayer	50.00 ± 0.01
LDPE_3GTE	LDPE film with 3.0 wt.% GTE	Monolayer	54.00 ± 0.01
CO_LDPE_1.5GTE	Coextruded LDPE and LDPE_1.5GTE	Two layers	49.30 ± 0.01
CO_LDPE_3GTE	Coextruded LDPE and LDPE_3GTE	Two layers	50.70 ± 0.01

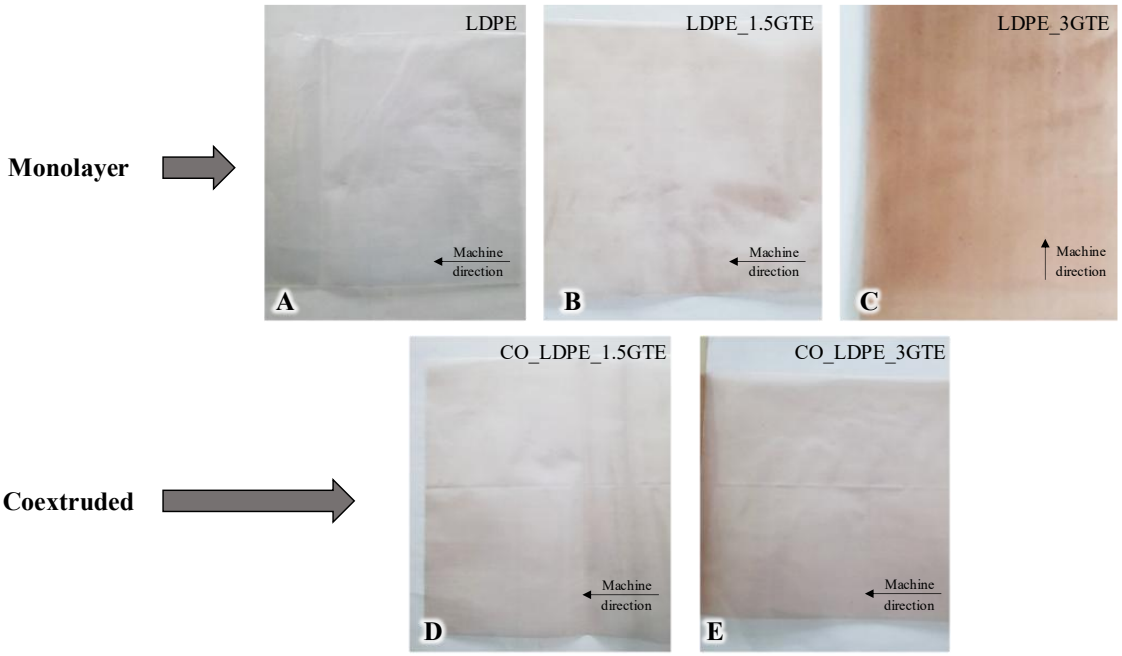

Figure S*1*

Figure S1 - Visual appearance of the films: LDPE (A); LDPE_1.5GTE (B); LDPE_3GTE (C); CO_LDPE_1.5GTE (D) and CO_LDPE_3GTE (E).