ORIGINAL PAPER

Grafting of functional oleuropein as a reactive antioxidant on polyethylene during reactive extrusion toward a durable thermally stable compound

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ABSTRACT

Growing interest in sustainable polymer additives has encouraged the replacement of synthetic phenolic antioxidants with naturally derived alternatives. In this study, oleuropein extracted from discarded olive leaves was chemically modified with vinyltrimethoxysilane (VTMS) and utilized as a reactive antioxidant for low-density polyethylene (LDPE), a polymer widely used in food packaging applications. Different amounts of the modified oleuropein were incorporated into LDPE through peroxide-initiated reactive melt blending. The successful incorporation of the modified antioxidant into the polymer matrix was supported by Fourier transform infrared spectroscopy, proton nuclear magnetic resonance analysis, extraction resistance, and overall migration results. The prepared materials were characterized by oxidative induction time (OIT), thermogravimetric analysis, tensile testing, scanning electron microscopy, differential scanning calorimetry, and rheological measurements. The incorporation of modified oleuropein significantly improved the thermo-oxidative stability of LDPE, increasing the OIT from approximately 6 min for neat LDPE to about 18 min for the modified samples. In addition, the modified antioxidant exhibited excellent resistance to extraction while maintaining overall migration values well below the regulatory limit. These findings demonstrate that VTMS-modified oleuropein is a promising naturally derived antioxidant for enhancing the thermo-oxidative performance of polyethylene through an industry-relevant reactive extrusion process.

Keywords: Low-density polyethylene (LDPE); modified oleuropein; reactive extrusion; thermo-oxidative stability; overall migration; food packaging.

Highlights

- VTMS-modified oleuropein was successfully grafted onto LDPE via peroxide-initiated reactive extrusion.
- Grafted oleuropein significantly enhanced the thermo-oxidative stability of LDPE.
- Covalent immobilization was supported by extraction resistance, retained OIT, and negligible overall migration.
- Grafting reduced polyethylene crystallinity while preserving the melting temperature.
- VTMS-modified oleuropein is a promising naturally derived antioxidant for polyethylene food-packaging applications.

INTRODUCTION

The growing demand for sustainable packaging materials has stimulated extensive research into replacing or improving conventional plastics with environmentally friendly alternatives [1,2]. However, many bio-based materials still suffer from inadequate thermal stability and mechanical performance, limiting their practical applications [3]. Incorporating natural antioxidants has emerged as an attractive strategy for enhancing the thermo-

oxidative stability of both conventional and bio-based polymers while reducing dependence on synthetic stabilizers [4–7]. Despite these advantages, the application of natural antioxidants is often restricted by their limited thermal stability, poor compatibility with non-polar polymer matrices, and their tendency to migrate during processing or service [8–10]. Among naturally occurring phenolic antioxidants, oleuropein, the major phenolic constituent of olive leaves, has attracted considerable attention because of its strong antioxidant activity [11–13]. Previous studies have demonstrated that olive leaf extracts can improve the antioxidant performance of polymeric packaging materials [14–16]. However, the complex composition of these extracts may result in variations in performance and processing behavior. Consequently, the use of chemically modified oleuropein offers a more controlled approach for improving compatibility with polymer matrices while enhancing the retention of antioxidant functionality [17–19].

This work explores the potential of modified oleuropein as a naturally derived antioxidant for low-density polyethylene (LDPE) used in food-packaging applications. Polyethylene is the most widely used commodity polymer owing to its versatility, low cost, ease of processing, and favorable barrier properties [20]. Among polyethylene grades, LDPE is extensively employed in food packaging because it combines good flexibility, low moisture permeability, chemical resistance, and suitability for direct food contact [21–23]. Packaging materials intended for food applications must satisfy multiple requirements, including adequate mechanical performance, cost-effectiveness, processability, recyclability, and food safety [2,21,22]. In addition, the inherently hydrophobic nature of LDPE generally limits its interaction with aqueous food systems, making it an attractive material for a wide range of packaging applications [24].

While LDPE possesses several desirable characteristics for food packaging, including flexibility, transparency, and excellent heat-sealing performance, it remains susceptible to thermo-oxidative degradation during melt processing and long-term service [25–27]. This degradation generates free radicals that initiate chain scission and structural deterioration, ultimately reducing the mechanical performance and durability of the material [28,29]. Phenolic antioxidants such as oleuropein can suppress these degradation reactions by scavenging free radicals and interrupting the oxidative chain reaction. Consequently, incorporating oleuropein into the polymer matrix has the potential to improve the thermo-oxidative stability of LDPE and enhance its long-term performance under processing and service conditions.

To address these challenges, the present study investigates the preparation and application of chemically modified oleuropein as a reactive antioxidant for LDPE intended for food-packaging applications. Among the available processing methods, reactive extrusion offers an attractive route for incorporating functional additives directly into the polymer melt. Under appropriate processing conditions, peroxide-initiated reactive extrusion can promote reactions between the modified antioxidant and polyethylene macroradicals, thereby improving the retention and effectiveness of the antioxidant within the polymer matrix [30–32].

The primary objective of chemically modifying oleuropein is to improve its compatibility with the non-polar LDPE matrix while reducing its tendency to migrate during processing and service. Such an approach is expected to provide a more uniform distribution of the antioxidant throughout the polymer and to enhance its long-term stabilization efficiency. The combination of reactive modification and melt processing therefore represents a promising strategy for developing more durable polymeric materials with improved thermo-oxidative stability [33–35].

Based on this concept, VTMS-modified oleuropein was prepared through reactive extrusion and evaluated as a reactive antioxidant for LDPE. The modified materials were comprehensively characterized using spectroscopic, thermal, rheological, mechanical, morphological, extraction stability, and overall migration analyses to evaluate their potential for food-packaging applications. This study provides a practical strategy for improving the thermo-

oxidative durability of polyethylene using a naturally derived antioxidant while addressing the compatibility and migration challenges commonly associated with natural stabilizers [35–38].

EXPERIMENTAL

Materials and Methods

Vinyltrimethoxysilane (VTMS) was purchased from Evonik Industries (Germany). Acetic acid (99.8%) and ethanol (≥99%) were obtained from Merck (Germany). 2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane (DHBP) was supplied by AkzoNobel (The Netherlands). Low-density polyethylene (LDPE0200) with a melt flow index (MFI) of 2 g/10 min and a density of 0.92 g/cm³ was obtained from Amirkabir Petrochemical Company (Iran). Reactive melt blending was carried out using a Haake internal mixer (Germany).

^{1}H NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer (Bruker BioSpin, Rheinstetten, Germany) using $CDCl_3$ as the solvent at room temperature. Thermogravimetric analysis (TGA) was performed using a TGA 1 instrument (Mettler-Toledo, USA) equipped with STARe software from room temperature to 600°C at a heating rate of 10°C/min under an air atmosphere. Differential scanning calorimetry (DSC) was carried out using a Mettler-Toledo DSC1 instrument (Switzerland) over the temperature range of 20–200°C at a heating and cooling rate of 20°C/min under a nitrogen atmosphere.

Oxidative induction time (OIT) was determined at 210°C using DSC according to ASTM D3895. Approximately 5–10 mg of each film sample was placed in an aluminum pan and heated under a nitrogen atmosphere. After reaching 210°C, the purge gas was switched to oxygen at a flow rate of 50 mL/min. The time elapsed until the onset of the exothermic oxidation peak was recorded as the OIT. Surface morphology was examined using a VEGA 3 scanning electron microscope (SEM) (TESCAN, Czech Republic). Prior to observation, the samples were sputter-coated with gold to improve electrical conductivity. The same instrument was equipped with an energy-dispersive X-ray spectroscopy (EDS) detector for elemental analysis.

Mechanical properties were evaluated using a universal testing machine (Santam, Iran) according to ASTM D882. Film specimens were tested at room temperature using a crosshead speed of 50 mm/min. Tensile strength and elongation at break were determined, and the reported values represent the mean ± standard deviation of three independent measurements. Fourier transform infrared (FT-IR) spectra of the extracted oleuropein and polymer films (thickness: 100 ± 5 μm) were recorded using a Bruker EQUINOX 55 spectrometer (Bruker Optik GmbH, Ettlingen, Germany).

Rheological measurements were performed using an MCR 300 rotational rheometer (Anton Paar, Graz, Austria) equipped with parallel-plate geometry. All experiments were conducted under a nitrogen atmosphere to minimize thermo-oxidative degradation. Frequency sweep measurements were carried out over the angular frequency range of 0.1–600 rad/s at 230°C. Temperature sweep measurements were performed from 25 to 200°C at an angular frequency of 0.01 rad/s. All measurements were conducted within the linear viscoelastic region using a strain amplitude of 4%. Overall migration tests were performed on the prepared films according to ASTM D4754 at 40°C for 10 days. Three measurements were carried out for each sample, and the reported values correspond to the mean of the three determinations.

Sample preparation method

For preparing the samples for this project, three steps were taken, as follows.

Extraction of oleuropein-rich extract from olive leaves

Olive leaves (500 g) were immersed in a 50% (v/v) ethanol–water solution at room temperature for 24 h. The resulting extract was filtered and concentrated by solvent evaporation at 50°C, followed by drying at the same temperature for an additional 24 h. Gravimetric analysis yielded approximately 0.1 wt.% extract based on the initial mass of olive leaves. Since olive leaves naturally contain a variety of phenolic compounds, the recovered material is referred to throughout this study as an oleuropein-rich extract, in which oleuropein is expected to be the predominant phenolic constituent rather than a chemically purified compound.

The extracted material was characterized by Fourier transform infrared (FT-IR) spectroscopy, and the corresponding spectrum is presented in Figure 1. A broad absorption band centered at approximately 3406 cm^{-1} was assigned to the O–H stretching vibration of phenolic hydroxyl groups. The absorption bands observed at 2919 and 2850 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of aliphatic C–H bonds, respectively. The band located at approximately 1626 cm^{-1} is attributed to aromatic C=C and conjugated carbonyl-related vibrations commonly associated with olive leaf phenolic compounds. Additional absorption bands at 1411 and 1097 cm^{-1} are assigned to C–H bending and C–O stretching vibrations, respectively, while the fingerprint region below 800 cm^{-1} agrees well with previously reported FT-IR spectra of oleuropein-rich olive leaf extracts [39,40]. Overall, the FT-IR spectrum is consistent with literature reports for oleuropein-rich olive leaf extracts and confirms the successful recovery of a phenolic extract suitable for subsequent chemical modification. Before incorporation into LDPE by reactive melt blending, the thermal oxidative stability of the oleuropein-rich extract was evaluated by the oxidative induction time (OIT) test at 210°C. No measurable oxidation exotherm was detected during 40 min of testing, indicating that the extract remained thermally stable under the selected processing conditions. This result suggests that the antioxidant could withstand the thermal conditions employed during reactive extrusion without significant oxidative degradation.

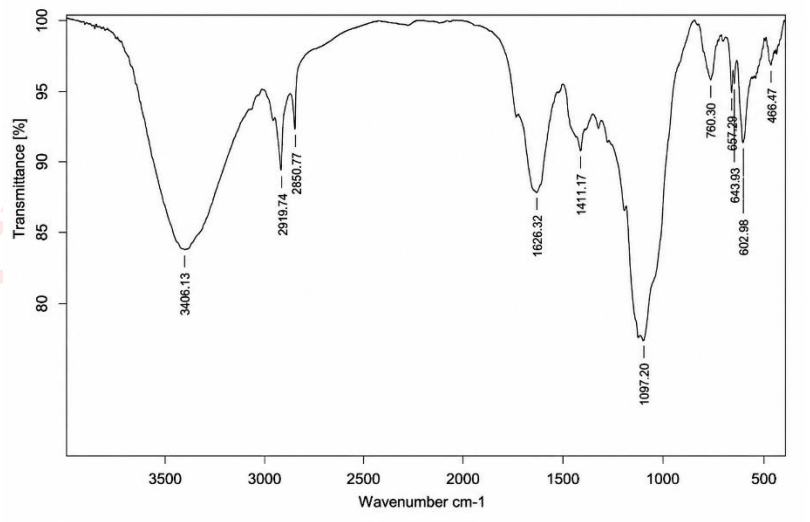

Figure 1. FT-IR spectrum of the oleuropein-rich olive leaf extract used in this study.

Modification of oleuropein with vinyltrimethoxysilane (VTMS)

Oleuropein was chemically modified with vinyltrimethoxysilane (VTMS) to introduce vinyl-functional silane groups that could subsequently participate in peroxide-initiated reactive extrusion with LDPE. Under mildly acidic conditions, VTMS undergoes hydrolysis to form reactive silanol species, which can condense with the hydroxyl groups present in oleuropein. These reactions are expected to generate Si–O–C linkages together with a limited degree of Si–O–Si condensation, producing a silane-modified oleuropein-rich extract suitable for subsequent reactive extrusion with LDPE. Similar reaction pathways have been widely reported for organosilane coupling agents used in polymer modification [41].

Briefly, 0.5 g of the oleuropein-rich extract was dispersed in 200 mL of ethanol and stirred at 60 rpm for 1 h at room temperature. Subsequently, 0.5 g of VTMS was added to the suspension, and stirring was continued for another hour under the same conditions. Acetic acid was then added dropwise until the pH reached 3.5 to promote the hydrolysis of VTMS and facilitate the subsequent condensation reactions (Figure 2). The reaction mixture was maintained under continuous stirring at room temperature for 24 h. Finally, the modified product was recovered by centrifugation and dried at 50°C for 24 h before being used in the reactive extrusion process.

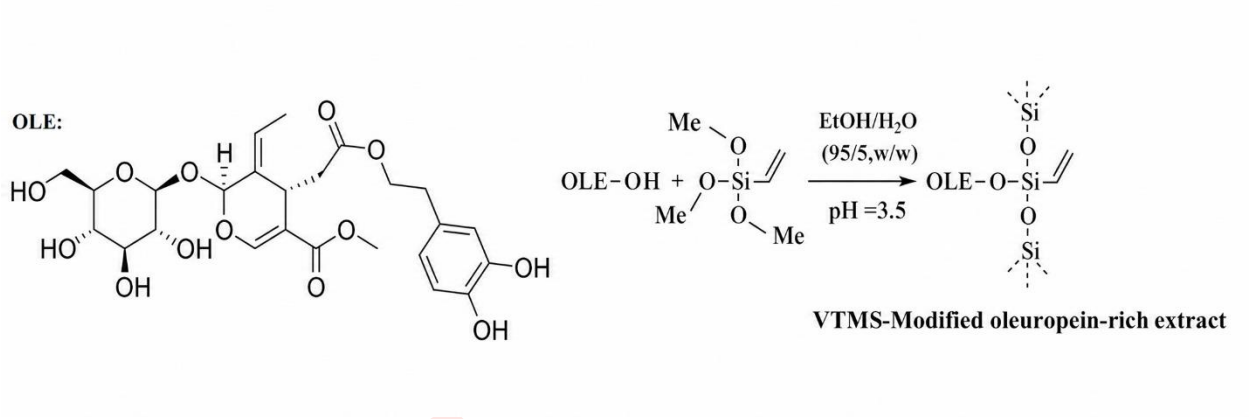

Figure 2. Schematic illustration of the modification of the oleuropein-rich extract with vinyltrimethoxysilane (VTMS).

Reactive grafting of modified oleuropein onto LDPE

The reactive grafting process was carried out according to the formulations listed in Table 1 using a Brabender PLASTI-CORDER internal mixer (Brabender GmbH, Duisburg, Germany). The mixing conditions were maintained at 140 °C, 100 rpm, and 6 min to ensure adequate melt mixing while minimizing undesired thermal degradation.

During reactive extrusion, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane (DHBP) thermally decomposes to generate highly reactive alkoxy radicals. These radicals abstract hydrogen atoms from the LDPE backbone, producing polyethylene macroradicals that serve as active grafting sites. The vinyl groups introduced onto oleuropein through VTMS modification subsequently react with these macroradicals, leading to the formation of stable carbon-carbon covalent bonds and the immobilization of the antioxidant onto the polyethylene chains. This peroxide-initiated free-radical grafting mechanism has been widely reported for the functionalization of polyethylene using vinyl-containing compounds and silane coupling agents [28,35,41,42].

Although competing reactions such as β-scission and peroxide-induced crosslinking may occur during reactive processing, these side reactions can be minimized by carefully controlling the peroxide concentration and processing conditions. In the present study, the DHBP concentration was selected based on previous studies together with preliminary optimization experiments to maximize grafting efficiency while preserving the processability and structural integrity of LDPE [35,43,44]. A schematic illustration of the proposed grafting mechanism is presented in Figure 3.

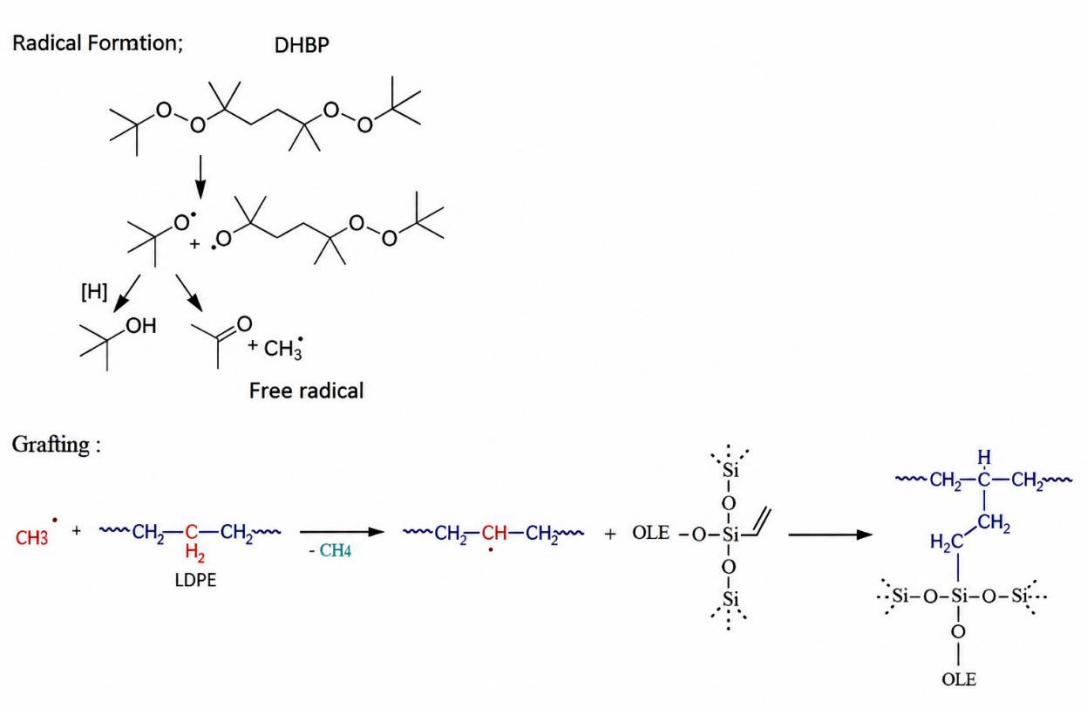

Figure 3. Proposed free-radical grafting mechanism of VTMS-modified oleuropein onto LDPE during peroxide-initiated reactive extrusion.

Table 1. Composition of samples.

Sample	LDPE (phr)	DHBP (phr)	Modified oleuropein (phr)
S_0	100	0	0
S_1	100	0.1	0
S_2	100	0.1	0.25
S_3	100	0.1	0.5
S_4	100	0.1	1

RESULTS AND DISCUSSION

Structural analysis

The FT-IR spectra of the prepared samples are presented in Figure 4. As expected, all samples exhibit the characteristic absorption bands of LDPE, including the asymmetric and symmetric stretching vibrations of methylene groups at approximately 2916 and 2848 cm^{-1}, the CH_2 bending vibration near 1464 cm^{-1}, and the rocking vibration at approximately 720 cm^{-1}. These bands remain essentially unchanged after reactive processing, indicating that the polyethylene backbone is preserved throughout the grafting process.

Compared with S0 and the peroxide-containing control sample (S1), the modified samples (S2–S4) exhibit a noticeable increase in absorption intensity within the 1000–1100 cm^{-1} region. This region is generally assigned to Si–O–Si and Si–O–C stretching vibrations originating from the hydrolysis and condensation products of vinyltrimethoxysilane (VTMS) and the formation of silane–oleuropein structures [45]. In addition, a weak absorption band is observed around 1730–1740 cm^{-1} corresponding to the ester carbonyl groups naturally present in oleuropein. The appearance and gradual increase of these characteristic bands with increasing modified oleuropein content strongly support the successful incorporation of the silane-modified antioxidant into the LDPE matrix. While FT-IR alone cannot unequivocally distinguish covalent grafting from strong physical interactions, the spectral changes are fully consistent with the proposed grafting mechanism.

The ^1H NMR spectra of S1 and S4 are shown in Figure 5. The resonance at 7.26 ppm corresponds to residual $CDCl_3$ solvent [46] whereas the broad signal centered around 1.33 ppm is assigned to the methylene backbone of LDPE. In contrast to the control sample (S1), the grafted sample (S4) exhibits additional resonances at approximately 6.12, 5.56–5.57, and 4.22–4.23 ppm, corresponding to the Ha, Hb, and Hc protons indicated in the proposed graft structure. The appearance of these new signals indicates the presence of the modified oleuropein moiety within the polymer matrix and provides strong evidence for its successful incorporation during reactive extrusion.

The relatively low intensity and broad line shape of these resonances are attributed to the limited solubility and restricted molecular mobility of LDPE in $CDCl_3$ at room temperature. Such peak broadening is commonly observed for polyolefins analyzed under conventional solution-state NMR conditions, whereas significantly sharper resonances generally require elevated-temperature solvent systems. Nevertheless, the emergence of characteristic oleuropein-derived signals in S4, while the LDPE backbone resonances remain essentially unchanged, is consistent with the proposed radical grafting mechanism rather than simple physical blending.

Taken together, the FT-IR (Figure 4) and ^1H NMR (Figure 5) results provide complementary evidence supporting the successful grafting of modified oleuropein onto LDPE. Whereas the grafting efficiency (GE%) was not quantified directly, several independent observations further support covalent immobilization rather than physical entrapment. These include the excellent resistance of the antioxidant to solvent extraction, the retention of oxidative induction time after extraction, and the absence of detectable overall migration. Collectively, these findings consistently indicate that the modified oleuropein was chemically anchored to the LDPE backbone through peroxide-initiated radical grafting, thereby providing stable and durable antioxidant functionality within the polymer matrix.

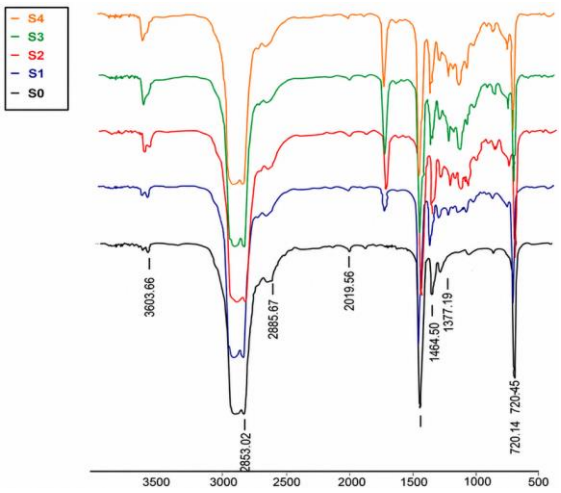

Figure 4. FT-IR spectra of pristine LDPE (S0), peroxide-treated LDPE (S1), and LDPE containing different contents of VTMS-modified oleuropein (S2–S4).

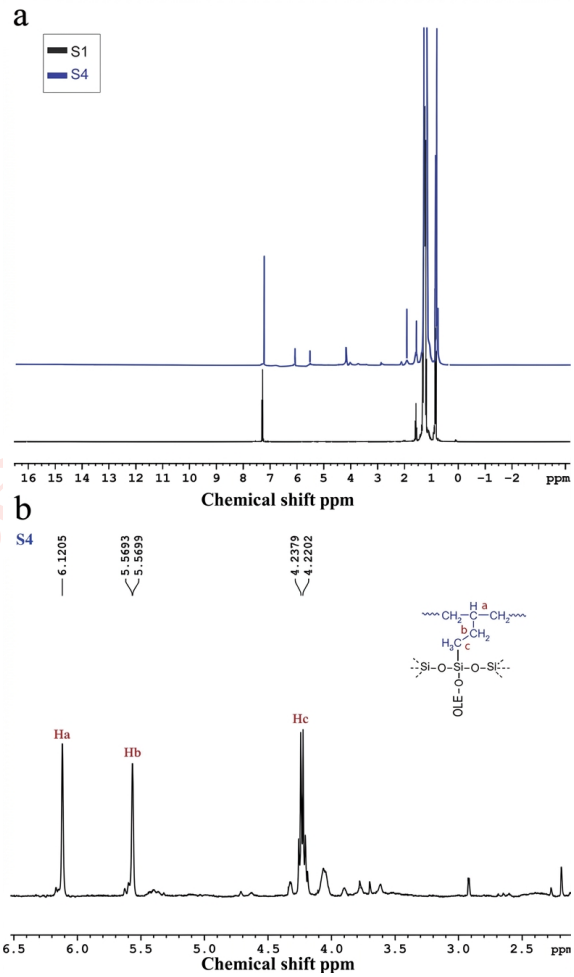

Figure 5. (a) Comparison of the ¹H NMR spectra of S1 and S4. (b) Expanded view of the characteristic proton signals assigned to the grafted VTMS-modified oleuropein structure.

Collectively, the FT-IR and ^{1}H NMR analyses provide complementary evidence supporting the successful grafting of modified oleuropein onto LDPE. Although the grafting efficiency (GE%) was not quantitatively determined, several independent observations support covalent immobilization of the modified oleuropein rather than simple physical entrapment. These include its resistance to solvent extraction, the retention of oxidative induction time after extraction, and the absence of detectable overall migration. Collectively, these findings provide strong evidence that the modified oleuropein was chemically anchored to the LDPE backbone through peroxide-initiated radical grafting, thereby providing stable and durable antioxidant functionality within the polymer matrix.

Thermal Oxidative Stability

To evaluate the antioxidant performance of modified oleuropein in LDPE, the oxidative induction time (OIT) test was selected instead of the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging assay. OIT directly measures the resistance of polymeric materials to thermo-oxidative degradation under elevated temperatures, making it particularly suitable for polyethylene-based food packaging applications where long-term thermal stability is essential [47]. In contrast, the DPPH assay primarily evaluates the radical-scavenging ability of antioxidants in solution and does not adequately represent their effectiveness after immobilization within a solid polymer matrix or under melt-processing conditions [48]. Therefore, OIT was considered the most appropriate method for evaluating the stabilization efficiency of modified oleuropein in the present study.

The OIT results are summarized in Table 2. Samples containing modified oleuropein (S2–S4) exhibited considerably higher OIT values than neat LDPE (S0), demonstrating the beneficial effect of the modified natural antioxidant on the thermo-oxidative stability of the polymer. In general, OIT increased progressively with increasing oleuropein content, indicating more efficient radical scavenging and improved stabilization at higher antioxidant loadings. Sample S1, which contained peroxide without oleuropein, exhibited the lowest OIT value owing to peroxide-induced radical formation in the absence of antioxidant protection.

The comparatively lower OIT value observed for sample S2 should not be attributed to peroxide concentration, since the DHBP content remained constant in all modified formulations. Instead, this behavior is more reasonably explained by the relatively low oleuropein concentration, which may have resulted in incomplete grafting together with competition between radical scavenging, chain scission, and grafting reactions during reactive processing. Consequently, a fraction of the generated macroradicals likely participated in degradation reactions rather than being efficiently stabilized, leading to a less pronounced improvement in oxidative stability. The thermo-oxidative degradation of LDPE proceeds through a free-radical chain mechanism initiated by heat, producing polymer radicals that rapidly react with oxygen to form peroxy radicals and hydroperoxides, thereby accelerating chain scission and oxidative degradation [43]. Antioxidants interrupt this process by donating hydrogen atoms to reactive radical species, terminating the oxidation cycle and delaying polymer degradation [49].

Previous studies have also demonstrated the effectiveness of natural antioxidants in improving the thermo-oxidative stability of polymeric materials. For example, incorporation of cannabidiol into an ethylene–norbornene copolymer increased the OIT from 5.09 to 8.49 min [50]. Similarly, incorporation of 1 wt.% water extract of French maritime pine bark into polypropylene increased the chemiluminescence onset time from 80 s to 570 s [51]. In another study, the addition of 1 wt.% *Silybum marianum* extract to LDPE increased the OIT measured at 210 °C from 0 to 21 min [52]. While the improvement in OIT observed in the present work cannot be directly compared with previous studies because of differences in antioxidant chemistry, grafting strategy, polymer grade, and testing conditions, the increase from 7 min for neat LDPE (S0) to more than 40 min for sample S4 demonstrates a substantial enhancement in thermo-oxidative stability. Collectively, these results indicate that the reactive

modification approach effectively improved the long-term oxidative stability of LDPE while maintaining the antioxidant within the polymer matrix, highlighting its potential for durable food-packaging applications.

Table 2. Oxidative induction time (OIT) values of LDPE samples measured at 210°C.

Sample	OIT(min)
S_0	7±0.1
S_1	3±0.1
S_2	15±0.1
S_3	30±0.1
S_4	Less than 40

Resistance to Antioxidant Extraction

One of the major advantages of covalently immobilized antioxidants is their improved resistance to solvent extraction compared with physically blended stabilizers. Reduced extractability contributes to improved long-term stabilization and is particularly desirable for polymeric materials intended for food-packaging applications, where minimizing additive migration is essential [42,53]. To evaluate the extraction resistance of the modified oleuropein, an accelerated solvent extraction test was performed. Films with a thickness of approximately 1 mm were immersed in ethanol and stored at 70 °C for 10, 20, and 30 days. After each extraction period, the residual antioxidant performance was evaluated by measuring the oxidative induction time (OIT). Three independent OIT measurements were carried out for each sample, and the average values are summarized in Table 3.

Only a slight decrease in OIT was observed after 10 days of extraction, corresponding to approximately 5% of the initial value. With increasing extraction time, the rate of OIT reduction gradually decreased and eventually reached a nearly constant level. The OIT values remained relatively high even after 30 days of extraction, particularly for samples containing higher concentrations of modified oleuropein (S3 and S4).

The extraction behavior is more clearly illustrated in Figure 6. The relatively small decrease in OIT suggests that most of the antioxidant functionality remained within the polymer matrix throughout the extraction period. The minor loss observed during the early stage of extraction is likely attributable to the removal of a limited amount of physically adsorbed or weakly associated antioxidant species located near the polymer surface. Once these species were removed, the remaining antioxidant exhibited excellent resistance to solvent extraction. Although the extraction experiment does not directly quantify grafting efficiency, the retention of antioxidant activity after prolonged solvent exposure, together with the spectroscopic characterization and migration results presented in this work, provides strong evidence that a substantial fraction of the modified oleuropein remained immobilized within the LDPE matrix. These observations are consistent with successful reactive incorporation of the modified antioxidant and demonstrate its suitability for long-term thermo-oxidative stabilization of polyethylene [54].

Table 3. OIT values of extracted samples after accelerated ethanol extraction.

Sample	OIT after 10 Days(min)	OIT after 20 Days(min)	OITafter 30 Days(min)
S_2	14.3±0.1	14±0.1	13.8±0.1
S_3	28.5±0.1	27.5±0.1	27.2±0.1
S_4	38.5±0.1	37.6±0.1	37.1±0.1

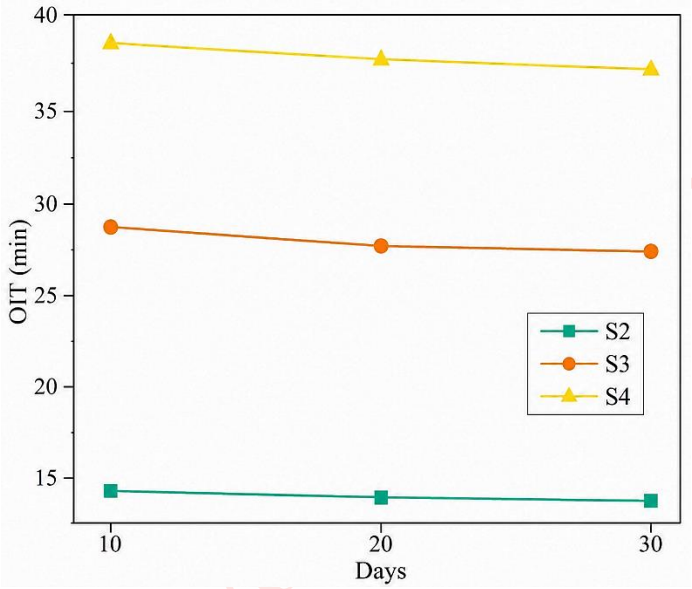

Figure 6. OIT values after 10, 20, and 30 days.

Mechanical properties

The tensile properties of the prepared LDPE films are summarized in Table 4. Tensile strength and elongation at break were evaluated to determine the influence of the grafted antioxidant on the mechanical performance of the films, since these properties are important indicators for food-packaging applications [55]. A slight increase in tensile strength was observed after reactive processing in the presence of peroxide. Sample S1 exhibited the highest tensile strength, increasing from 162 ± 1 to 173 ± 1 kg/cm (MD). Upon incorporation of modified oleuropein (S2–S4), the tensile strength decreased gradually with increasing antioxidant content but remained comparable to that of neat LDPE. Even at the highest loading (S4), the tensile strength was only slightly higher than that of the untreated sample, indicating that the grafting process did not adversely affect the load-bearing capability of the polymer.

In contrast, elongation at break decreased progressively from 590 ± 5% for S0 to 400 ± 5% for S4. This reduction indicates a gradual loss of ductility with increasing modified oleuropein content. The decrease can be attributed to the formation of covalent linkages between the modified antioxidant and the LDPE chains together with the limited branching reactions induced during peroxide-initiated reactive processing. These structural changes restrict polymer-chain mobility and reduce the ability of the material to undergo large plastic deformation before failure. Although flexibility decreased, all modified samples retained relatively high elongation values while maintaining tensile strength close to that of neat LDPE. This balance between mechanical strength and ductility is desirable for

flexible food-packaging materials, where sufficient toughness and dimensional stability are simultaneously required [55,56].

Table 4. Tensile strength and elongation at break of LDPE films.

Sample	Tensile Strength at break (kg/cm^2 MD)	Elongation at break (MD)
S_0	162±1	590± 5
S_1	173±1	510±3
S_2	171±2	480±3
S_3	168±2	430±5
S_4	165±2	400±5

Thermal stability

The thermal stability of the prepared LDPE samples was evaluated by thermogravimetric analysis (TGA) under an oxidative atmosphere. The TGA and derivative thermogravimetric (DTG) curves of samples S0, S1, and S4 are presented in Figure 7. To compare the onset of thermal degradation, the temperature corresponding to 5% weight loss (T_5%) was selected, as it is widely used as an indicator of the initial thermal stability of polymeric materials [56]. Neat LDPE (S0) exhibited the earliest onset of degradation, with a T_5% value of approximately 337 °C. The introduction of peroxide alone (S1) shifted the degradation onset to 345°C, while the sample containing grafted modified oleuropein (S4) exhibited the highest T_5% value of 357°C. These results indicate that both reactive processing and the incorporation of the modified antioxidant contributed to delaying the onset of thermo-oxidative degradation, with the greatest improvement observed for S4 [57].

The DTG curves further demonstrate that S4 exhibited the highest peak degradation temperature (T_peak), reaching approximately 471 °C. In addition, the degradation profile of S4 became broader than that of neat LDPE, indicating that thermal decomposition proceeded over a wider temperature interval. This behavior is consistent with enhanced resistance to thermo-oxidative degradation resulting from the presence of chemically immobilized antioxidant groups within the polymer matrix. The improved thermal stability of S4 agrees well with the OIT results discussed previously, where the same sample exhibited the longest oxidation induction time. The combined TGA and OIT results therefore suggest that grafting the modified oleuropein onto the LDPE backbone effectively enhanced the thermal oxidative stability of the polymer by delaying the initiation and propagation of oxidation reactions [58].

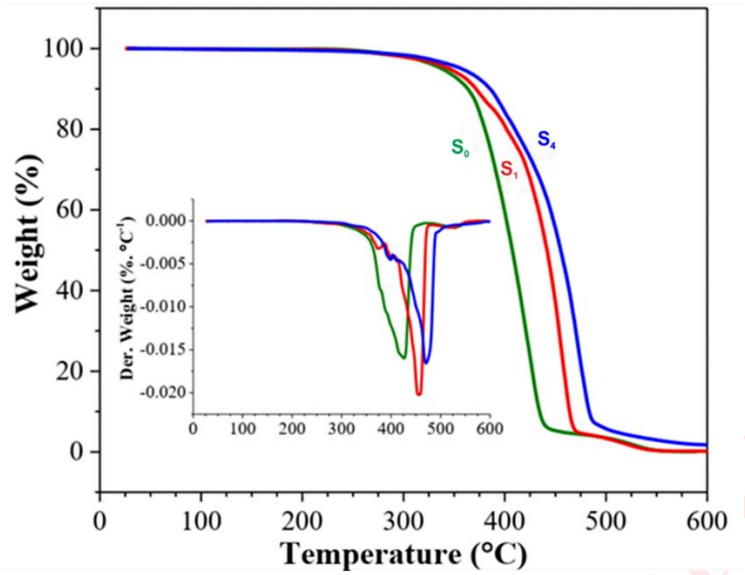

Figure 7. TGA and DTG curves of LDPE samples (S0, S1, and S4) under an oxidative atmosphere.

Differential scanning calorimetry (DSC)

Besides improving thermo-oxidative stability, the incorporation of modified antioxidants may also influence the crystallization behavior and thermal transitions of polyethylene by affecting chain packing and crystal growth [59]. The DSC heating and cooling thermograms of the prepared samples are presented in Figure 8.

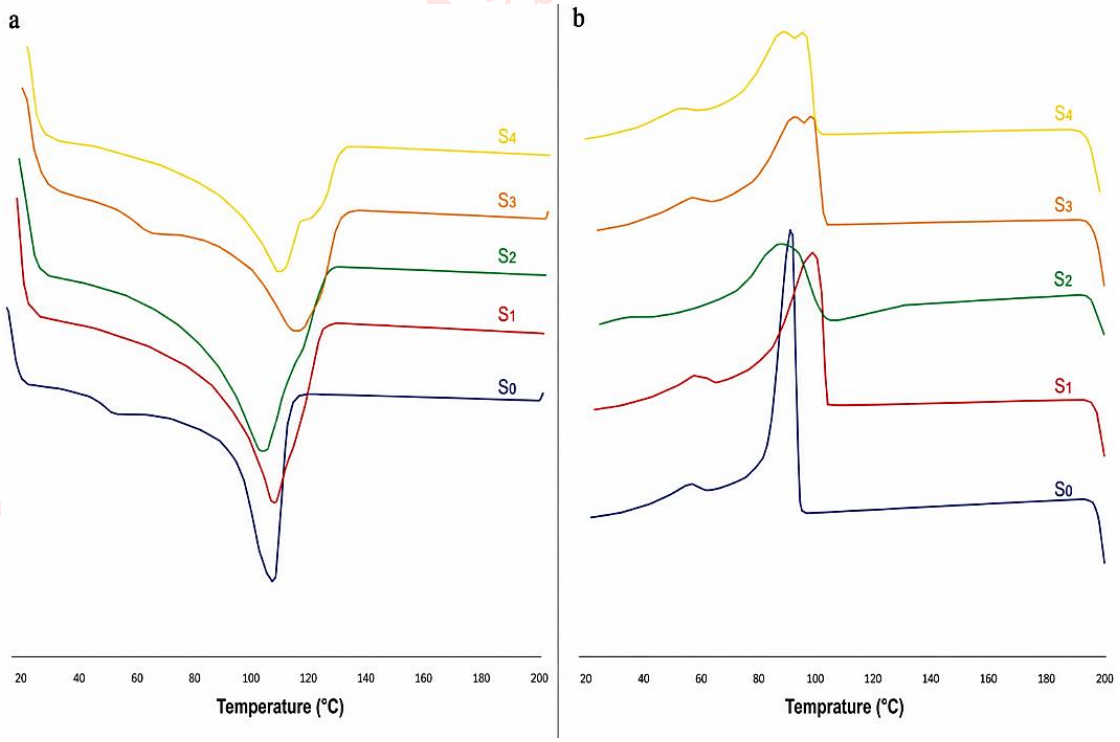

Figure 8. DSC thermograms of LDPE samples: (a) heating curves and (b) cooling curves.

As shown in Figure 8(a), the melting endotherms of samples containing modified oleuropein (S2–S4) exhibited a gradual reduction in peak intensity compared with those of S0 and S1, indicating a decrease in the degree of crystallinity after incorporation of the modified antioxidant. This reduction is attributed to the presence of grafted oleuropein moieties, whose bulky aromatic and phenolic structures partially disrupt the regular packing of polyethylene chains and hinder crystal growth [60,61]. Nevertheless, the melting peak temperature remained nearly unchanged, suggesting that the grafting process primarily influenced the degree of crystallinity rather than the stability of the crystalline phase.

A similar trend was observed in the cooling thermograms (Figure 8(b)). With increasing modified oleuropein content, the crystallization exotherms became broader and less intense, indicating a progressive reduction in crystallization ability. These observations suggest that reactive grafting introduced structural irregularities along the polyethylene chains, resulting in less ordered crystalline regions and a lower overall crystalline fraction [62]. Overall, the DSC results are in good agreement with the mechanical and rheological behaviors of the modified samples. Although the grafted films retained tensile strength comparable to that of neat LDPE, the reduction in elongation at break indicates restricted chain mobility, consistent with the observed decrease in crystallinity. Likewise, the reduced crystallization tendency agrees with the rheological results presented in the following section, where the grafted samples exhibited enhanced melt elasticity and increased resistance to chain relaxation [63].

Rheological analysis

The rheological behavior of the prepared LDPE films was investigated by small-amplitude oscillatory shear measurements within the linear viscoelastic region at a strain amplitude of 4%. Complex viscosity (η*), storage modulus (G′), and loss modulus (G″) were measured as a function of angular frequency to evaluate the influence of peroxide and modified oleuropein on the melt structure of LDPE. As shown in Figure 9, all samples exhibited typical shear-thinning behavior, where the complex viscosity gradually decreased with increasing angular frequency. Such behavior is characteristic of polymer melts, in which molecular chains progressively orient and disentangle under shear, resulting in lower flow resistance at higher deformation rates [64,65]. Compared with neat LDPE (S0), the peroxide-containing sample (S1) exhibited a slight increase in complex viscosity, while the modified samples (S2–S4) showed a much more pronounced increase throughout the entire frequency range. Moreover, the zero-shear viscosity increased continuously with increasing modified oleuropein content, following the order S4 > S3 > S2 > S1 > S0.

The increase in low-frequency viscosity and the extension of the zero-shear viscosity plateau suggest the formation of a more interconnected molecular architecture during reactive extrusion. This behavior is consistent with peroxide-induced radical reactions leading predominantly to long-chain branching (LCB), together with a limited contribution from short-chain branching (SCB), which increase molecular entanglement, melt elasticity, and resistance to flow [44,66]. The covalent incorporation of modified oleuropein further contributes to restricting chain mobility, resulting in higher melt viscosity. At higher angular frequencies, the viscosity values of all samples gradually converged because the applied shear became sufficient to overcome intermolecular interactions and molecular entanglements. Similar rheological responses have been widely reported for branched and functionalized polyolefin systems, where enhanced molecular connectivity increases low-frequency viscosity while preserving the characteristic shear-thinning behavior of polyethylene melts [67,68].

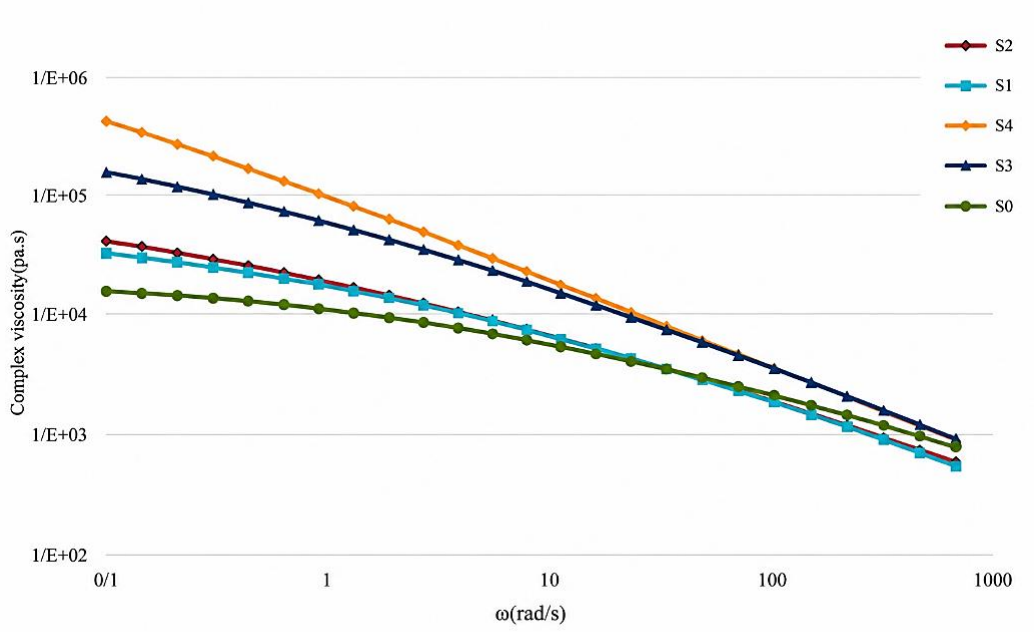

Figure 9. Complex viscosity as a function of frequency.

The storage modulus (G′) curves shown in Figure 10 reveal a noticeable upward shift for the peroxide-containing samples throughout the entire frequency range. This increase in G′ indicates peroxide-induced modifications in the LDPE molecular architecture, primarily through the formation of long-chain branching (LCB), which introduces longer relaxation times and enhances melt elasticity [44]. The higher G′ values observed in the low-frequency region further support the presence of branched molecular structures, since LCB is known to increase the elastic response of polymer melts at long relaxation times [64]. Furthermore, the progressive increase in G′ from S1 to S4 suggests that increasing the content of modified oleuropein further reinforces the branched network formed during reactive extrusion. This behavior is consistent with an increase in melt elasticity arising from long-chain branching and, to a limited extent, short-chain branching (SCB), rather than from improved compatibility or interfacial adhesion between LDPE and the antioxidant additive [65].

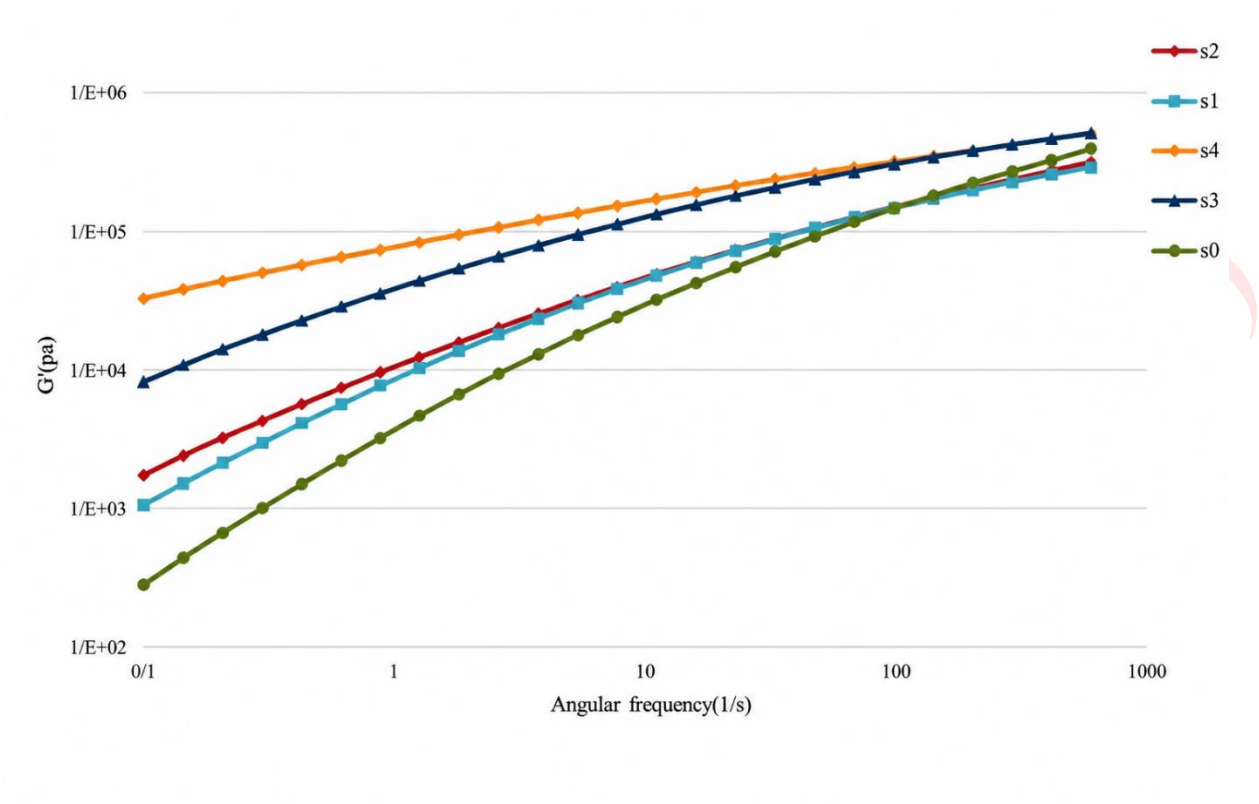

Figure 10. Storage modulus (G´) as a function of frequency.

Figure 11 presents the frequency-dependent behavior of the loss modulus (G″) for all samples. As expected, G″ increases with increasing angular frequency, reflecting the growing contribution of viscous relaxation mechanisms at shorter time scales. This behavior is typical of polymer melts, where segmental motions dominate the viscoelastic response in the high-frequency region. Compared with the control sample (S0), all peroxide-containing samples exhibit lower G″ values over most of the investigated frequency range. This reduction indicates a partial suppression of viscous flow resulting from peroxide-induced structural modifications in the LDPE matrix. The formation of long-chain branching and the grafting of modified oleuropein increase the elastic contribution of the melt while reducing energy dissipation through viscous flow. As a result, the viscoelastic response gradually shifts toward a more elastic behavior, which is consistent with the trends observed in the complex viscosity and storage modulus results. These findings further support the occurrence of branching and grafting reactions during reactive extrusion, leading to enhanced melt strength and improved structural stability [67].

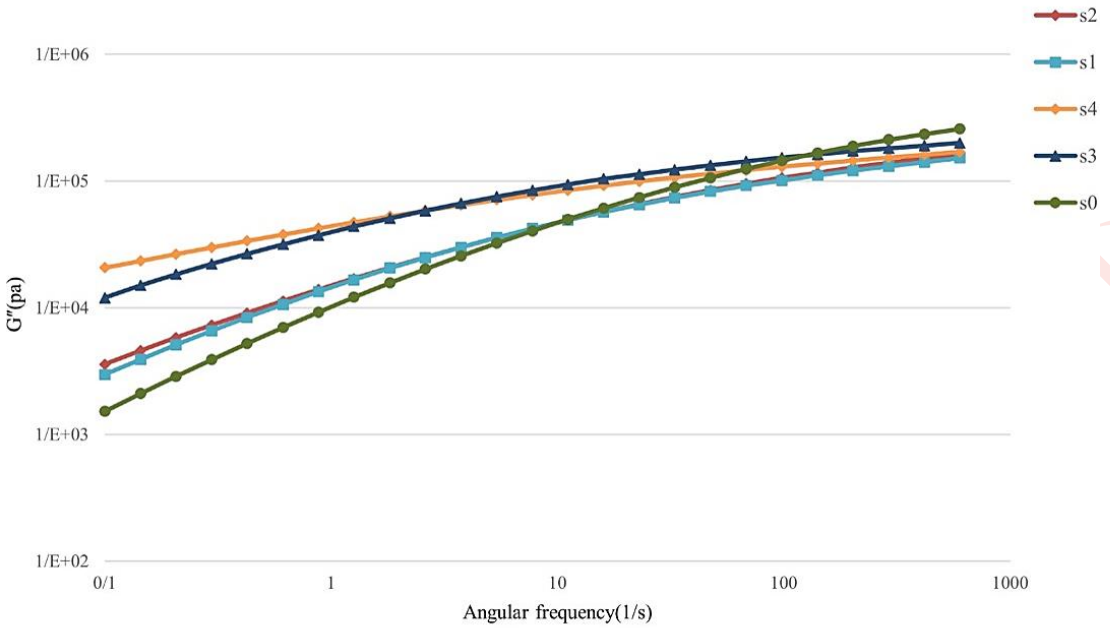

Figure 2. Loss modulus (G") as a function of frequency.

Figure 12 illustrates the G′–G″ crossover behavior of the investigated samples. For all materials, both moduli increase with increasing angular frequency, reflecting the characteristic viscoelastic response of LDPE-based systems, in which the balance between elastic and viscous contributions changes with deformation rate [67]. The crossover point, defined as the frequency at which G′ equals G″, provides valuable information regarding the melt structure and relaxation behavior of the polymer. A shift of the crossover toward lower frequencies, as observed for samples S2 and S3, indicates slower relaxation dynamics. Such behavior is commonly associated with peroxide-induced molecular architecture changes, particularly the formation of long-chain branching, which enhances melt elasticity and prolongs relaxation times without necessarily producing a crosslinked network [68,69]. In addition, the higher modulus values at the crossover point suggest a broader relaxation time distribution, further supporting the occurrence of branching reactions during reactive extrusion.

Among the modified samples, S3 exhibits the most pronounced shift of the crossover point, indicating a greater extent of molecular architecture modification and a more elastic melt response under small-amplitude oscillatory shear [70]. In contrast, no G′–G″ crossover is observed for sample S4 within the investigated frequency range. This result suggests that the relaxation processes of S4 occur at frequencies lower than the experimental window, consistent with a highly elastic melt containing extensive long-chain branching. This interpretation is further supported by the successful melt processing of the material and the absence of gel-like behavior during film formation, indicating that branching rather than extensive crosslinking is the dominant structural feature.

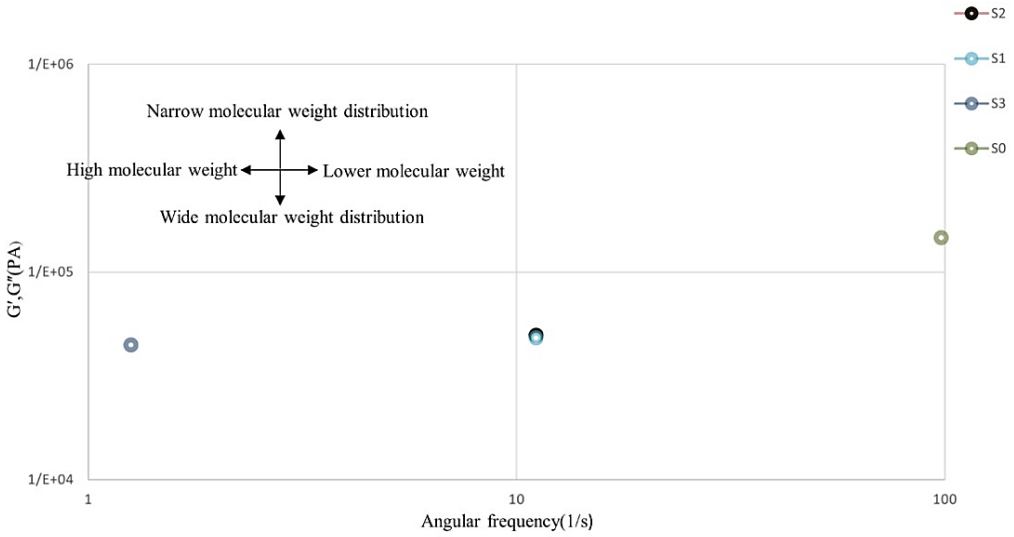

Figure 3. Intersection of loss and storage modulus curves vs. frequency.

The overall migration of the prepared films into the food

The overall migration test was performed for all prepared films in accordance with EC and FDA regulations using three food simulants following the ASTM D4754 method. The obtained results are summarized in Table 5. All samples exhibited overall migration values well below the regulatory limit of 10 mg/dm², indicating that the prepared films satisfy the migration requirements for food-contact applications. The incorporation of modified oleuropein did not produce any significant increase in overall migration compared with the control samples. Although samples S2–S4 showed slightly higher migration values in 3% acetic acid than in distilled water and 10% ethanol, all measured values remained substantially below the permitted limit. These findings indicate that the grafting strategy effectively retained the antioxidant within the LDPE matrix while maintaining low overall migration values [71].

Table 5. Overall migration results.

Sample	Overall migration (mg/dm²) (± 0.05)			
	In distilled water	In 10%ethanol	In 3% acetic acid	Limit
S_0	<1	<1	<1	10
S_1	<1	<1	<1	10
S_2	<1	<1	2<X<3	10
S_3	<1	<1	2<X<3	10
S_4	<1	<1	2<X<3	10

Microstructural analysis

The surface morphology of sample S4 was examined by scanning electron microscopy (SEM) to evaluate the effect of modified oleuropein grafting on the microstructure of the LDPE film. As shown in Figure 13a, the film exhibits a smooth, homogeneous, and defect-free surface without observable cracks, voids, phase separation, or particle agglomeration. This uniform morphology indicates that the grafting process did not adversely affect the structural integrity of the LDPE matrix and suggests that the modified oleuropein was well incorporated into the polymer.

To further verify the chemical incorporation of the grafted species, elemental mapping was performed using energy-dispersive X-ray spectroscopy (EDS). According to Figure 13b, oxygen and silicon are uniformly distributed throughout the analyzed region. Oxygen originates primarily from the functional groups of the modified oleuropein, whereas silicon is associated with the silane coupling agent introduced during the modification process. The homogeneous distribution of both elements, without localized silicon-rich or oxygen-rich regions, supports the successful incorporation of the modified oleuropein within the LDPE matrix and is consistent with the grafting mechanism proposed from the FT-IR and ^{1}H NMR analyses. Furthermore, the absence of silicon-rich domains suggests that no significant phase separation occurred during reactive extrusion, which is consistent with the formation of a homogeneous polymer matrix.

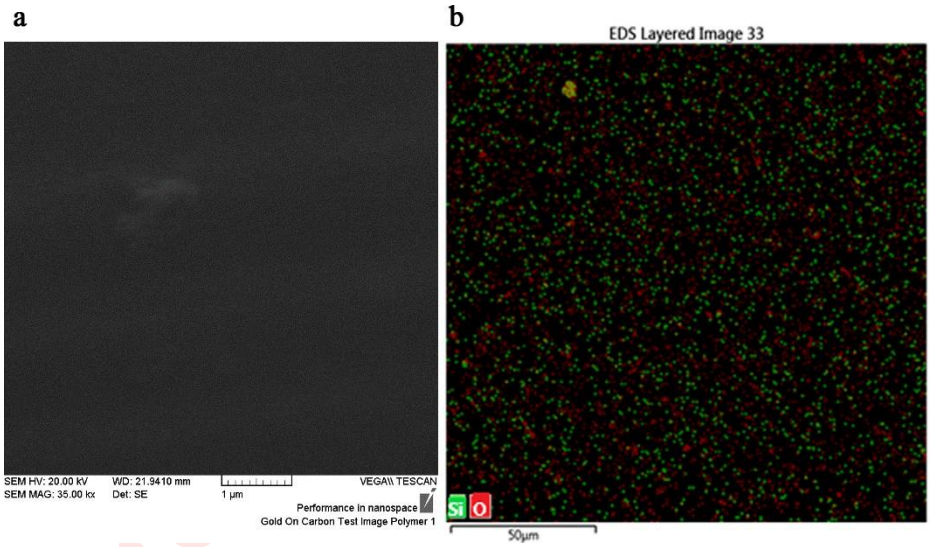

Figure 4. (a) SEM micrograph and (b) EDS mapping of S4 sample.

CONCLUSION

This study demonstrated that VTMS-modified oleuropein can serve as an effective reactive antioxidant for low-density polyethylene through peroxide-initiated reactive extrusion. Spectroscopic analyses (FT-IR and ^{1}H NMR) strongly support the successful modification of oleuropein-rich extract and its covalent incorporation into the LDPE matrix. The modified antioxidant significantly improved the thermo-oxidative stability of LDPE, as demonstrated by the OIT and TGA results, while maintaining good processability throughout melt processing.

Rheological measurements indicated peroxide-induced modifications in the molecular architecture of LDPE, characterized primarily by long-chain branching and enhanced melt elasticity. These structural changes were consistent with the DSC results, which showed reduced crystallization behavior due to restricted chain mobility

following grafting. Mechanical testing further demonstrated that the modified materials retained adequate tensile strength while exhibiting a gradual reduction in elongation at break, reflecting the expected trade-off between stiffness and ductility.

Extraction-resistance and overall migration analyses provide strong evidence fors the high stability of the immobilized antioxidant, with antioxidant performance largely retained after prolonged solvent extraction and migration values remaining well below the regulatory limit for food-contact materials. SEM and EDS analyses further demonstrated a homogeneous morphology together with the uniform distribution of silicon- and oxygen-containing species throughout the polymer matrix.

Overall, the proposed reactive modification strategy provides an effective approach for immobilizing a naturally derived antioxidant within polyethylene, thereby improving thermo-oxidative durability while minimizing antioxidant migration. These findings highlight the potential of VTMS-modified oleuropein as a sustainable alternative to conventional synthetic antioxidants for long-term food-packaging applications.

CONFLICT OF INTEREST

The authors declared that there is no conflict of interest.

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