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ORIGINAL PAPER

Ground lemon and stevia leaves as renewable functional fillers with antioxidant activity for high-density polyethylene composites

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Abstract

The development of new sustainable material solutions in the processing of thermoplastic polymers concerns both the application of biopolymers and the use of valorized plant derivatives as fillers and modifiers of petrochemical polymers. Herein, the possibility of using unprocessed raw parts of two commonly used in the food industry leaves, i.e., lemon (LL) and stevia (ST), as active and functional fillers for high-density polyethylene (HDPE) has been verified. The series of composites containing 1, 2, and 5 wt% of ground leaves produced in the melt-mixing process were analyzed for thermal properties (DSC and TGA), and the antioxidant potential of the fillers was evaluated. Verifying the active effect of the ground leaves on the resistance to oxidation in the molten state was carried out by oxygen induction time (OIT by DSC) analysis and oscillatory rheology under steady-state shear conditions combined with spectroscopic (FTIR) carbonyl index (CI) analysis. Studies have shown that the introduction of 5 wt% of both types of leaves allows for a significant increase in the melt oxidation resistance (above 2 times longer OIT concerning HDPE, ~ 35 min) of composites without substantial changes in their crystalline structure and thermal stability. Determined after the long-term rheological measurements in an oxidative atmosphere CI showed 70 and 82% lower values for 5 wt% LL and ST composites compared to unmodified polyethylene.

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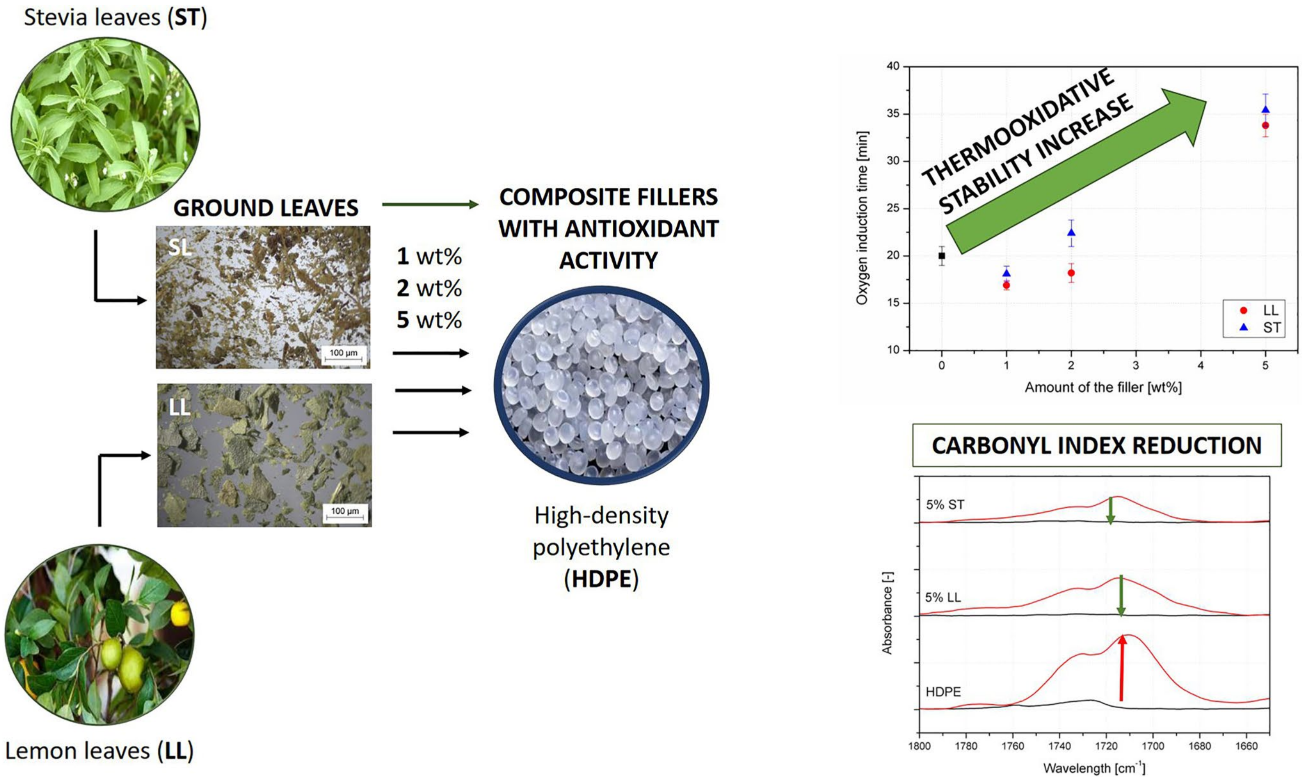
Graphical abstract



Keywords Polyethylene · Stevia · Lemon · Leaves · Functional filler · Composite

Introduction

The production of new sustainable materials is associated not only with the development of new generations of biodegradable polymers. The trend also plays a major role related to the possibility of producing bio-composites using valorized plant waste used as fillers (Jayaraman and Bhattacharyya 2004; Kruszelnicka et al. 2014; Awad 2021; Mohapatra et al. 2022; Ndukwe et al. 2022). Among them, we can distinguish fillers in the form of natural fibers, which in many cases compete with inorganic and synthetic fibers, low-cost particle-shaped fillers as shredded parts of the raw plants or food production waste (Bashir and Manusamy 2015; Zhang and Sablani 2021; Castellano et al. 2022).

In the research results published, many cases of using plant leaves as fillers have been reported. The most common practice is producing fibers from selected plant species leaves, such as banana or pineapple leaf fiber (George et al. 1998; Benítez et al. 2013; Ortega et al. 2016; Bhadane and Mishra 2022), that reinforce polymeric composites. In the case of tree leaves, which do not show much potential as a material for the production of long fibers, in most cases, they are treated as biomass and are utilized in the processes of burning, composting, or stored without finding applications solving the problem of their development in urbanized space. In work (Sałasińska et al. 2012), shredded tree leaves (linden, maple, walnut and cherry) were proposed as fillers for composites made of recycled high-density polyethylene. The presented results of the study showed that it is possible to introduce significant amounts of leaf-derived particle-shaped filler (up to 43 wt%), increasing the hardness and stiffness of HDPE composites without significantly compromising tensile strength. Kengkhetkit and Amornsakchai (Kengkhetkit and Amornsakchai 2014) analyzed the effect of three types of fillers obtained from pineapple leaf, mainly whole ground leaf, fibrous material, and non-fibrous material, on the mechanical properties of polypropylene composites produced with their participation. The research showed a beneficial effect of a fibrous filler and a gradual deterioration of tensile strength along with increasing powder filler or raw ground plant material not subjected to separation. The addition of non-fibrous parts was also characterized by lower water absorption due to the reduced tendency to exert mutual contact between better-dispersed filler particles in the polymer matrix. Considering the low reinforcing efficiency caused by the introduction of non-fibrous ground leaves and lignified plant parts, it is essential to pay attention to the additional modification effects resulting from the complex chemical composition of plants (Formela et al. 2022).

In addition to the widely used components of plant matter, such as lignin, cellulose, and hemicellulose, plant residues also contain significant amounts of different compounds, including waxes, essential oils, and other low-molecular substances that may have properties, including, in particular, antioxidant activity analyzed in recent years (Kirschweng et al. 2017; Mishra et al. 2018; Sukthavorn et al. 2021; Manikandan et al. 2022; Sienkiewicz and Członka 2022). Research has shown that many plant parts, which have not been used so far in polymer processing, are rich in phytochemicals such as polyphenols, flavonoids, or terpenes, introduced with fragmented plant fragments, migrate to the polymer matrix, modifying its ageing resistance (Iyer et al. 2016; Nanni et al. 2019). In addition, it has been shown that the introduction of fillers rich in active compounds may cause comparable effects, as in the case of the incorporation of plant extracts alone or petrochemical stabilizers (Iyer et al. 2016). It allows simultaneous utilization of post-production waste, obtaining other functional outcomes. These activities are part of the circular economy.

This work examined the effect of adding ground leaves of two plants commonly used in the food industry, i.e., lemon (*Citrus lemon*) and stevia (*Stevia rebaudiana Bertoni*). Lemon leaves (LL) are mainly used in the food, cosmetics, and pharmaceutical industries (Klimek-Szczykutowicz et al. 2020; Sania et al. 2020; Asker et al. 2020); however, it should be emphasized that the number of leaves harvested in these industries significantly exceeds their demand. Therefore, they are a valuable source of biomass whose alternative ways of development are sought. These leaves contain many phytochemicals, terpenoids, furanocoumarins, and coumarins that exhibit antimicrobial and antioxidant effects, including predominantly limonene, sabinene, citronellal, linalool β-ocimene, 3-carene, β-elemene, and citronellyl acetate (Klimek-Szczykutowicz et al. 2020; Chi et al. 2020; Asker et al. 2020).

Stevia (ST) is a perennial plant found in South and Central America and originated in Paraguay. Currently, its cultivation is widespread all over the world (Singh and Rao 2005; Periche et al. 2014). This plant is known mainly for its sweetening properties and use in the food industry. The glycosides in stevia, mainly stevioside, rebaudioside A and C, and dulside A, allow the production of sweeteners that are a healthy alternative to synthetic sweeteners or conventionally used sucrose (Singh and Rao 2005). In addition to glycosides, stevia leaf extracts contain phytochemicals such as phenols, which give the plant extracts antioxidant properties (Kim et al. 2011; Covarrubias-Cárdenas et al. 2018). The most antioxidant-effective phenolic compounds in stevia leaves are chlorogenic acid, caffeic acid, ellagic acid, rutin, ferulic acid, and diosmin (Covarrubias-Cárdenas et al. 2018). To sum up, both leaves of different plant species considered in this work are characterized by a complex chemical composition showing high potential as a filler of plant origin that can provide new functional properties to the composites produced with its participation.

In the literature studies published so far, one can find single cases of using lemon leaves as a filler to produce polymer composites. Faris M. AL-Oqla (AL-Oqla 2021) describes the effect of adding up to 40 wt% fibers made from lemon leaves as a reinforcement to composites with polyethylene and polypropylene matrix. The tests focused only on assessing mechanical properties; however, they show a favorable reinforcing effect against unmodified polymers, evaluated on the basis of flexural and compression tests. In the case of using stevia for modification and composites using low-processed parts of this plant, there is a report on the possibility of using leaf extracts. In more cases, extracts were used in the food industry (including packaging) and pharmacy. It has been shown (Hejabri kandeh et al. 2022), among others, that the modification with stevia extract nanofibers based on PVA and Fe-metal organic framework @Au nanoparticles allows for development of ecological materials that can be used in HPLC–UV analysis for the detection of pesticides.

Concluding, although the antioxidant potential contained in stevia and lemon leaves is used in various industries and its high antimicrobial antifungal and antioxidant effectiveness has been confirmed (Singh and Rao 2005; Kim et al. 2011; Periche et al. 2014; Covarrubias-Cárdenas et al. 2018; Klimek-Szczykutowicz et al. 2020; Sania et al. 2020; Chi et al. 2020; Asker et al. 2020; Hejabri kandeh et al. 2022), there has been no analysis of the impact of the addition of low-processed fragments of these plants, including leaves, on the possibility of modifying polymer composites and introducing new functional features through migration low molecular weight compounds directly from the filler to the polymer. This paper analyzed the effect of fillers obtained by grinding stevia and lemon leaves on the thermal properties and antioxidant resistance of high-density polyethylene (HDPE) composites produced from them. The presented study is a preliminary step focused on the proposal of composites for the rotational molding technology. From the view of the final use of the developed composites, it is necessary to simultaneously increase the resistance of thermo-oxidative stability in the molten state and possibly reduce the environmental impact of final products. Introducing low-processed plant fragments showing even partial antioxidant properties to polyethylene as extracts isolated from them may be a new alternative in producing and modifying polymers formed in this technology. Due to the targeted nature of the rotational molding technology, standard concentrations of fillers were used in the study, which potentially will not cause deterioration of process properties (max. 5 wt%).

Differential scanning calorimetry (DSC) and thermogravimetry (TGA) analyzes were carried out to assess the effect of the filler additive on the melting and crystallization of composites and thermal stability. The antioxidant capacity was evaluated by determining the oxygen induction time (OIT) by DSC and supplemented with rheological analyzes carried out in an oxidizing atmosphere supplemented by a comparative methodology of carbonyl index (CI) by Fourier transform infrared spectroscopy (FTIR).

Experimental

Materials and sample preparation

High-density polyethylene (HDPE), type M300054, obtained from SABIC (The Netherlands), was applied as a matrix to prepare investigated composites. According to producer data, its density equaled 0.954 g/cm^3, and it was characterized by a melt flow rate (MFR) of 30 g/10 min (190 °C, 2.16 kg).

Lemon (LL) and stevia (ST) leaves were obtained from their own crops at the Poznan University of Technology. Before melt compounding, the filler was ground using Retsch GM 200 knife grinder and dried at 80 °C for 24 h.

The composites were prepared by mixing in a molten state. The HDPE pellets were pulverized into a fine powder using a Tria 25–16/TC-SL high-speed knife grinder to facilitate a more efficient physical mixing process with powdered organic filler. The polymeric powder was then preliminary mixed with 1, 2, and 5 wt% of fillers. Before mixing in the molten state, physical compositions were dried in laboratory cabined dryer Memmert ULE 500 for 12 h at 70 °C. The mixtures were processed using a ZAMAK EH16.2D co-rotating twin-screw extruder operating at 100 rpm with the maximum temperature of the process of 190 °C. The obtained materials were cooled in forced airflow and pelletized. The resulting composites were then compression molded at 170 °C and 4.9 MPa for 2 min and then kept under pressure at room temperature for another 5 min to solidify the material. The unfilled HDPE was processed along with its composites. The specimens were named in reference to their filler content, i.e., 1% LL, 2% LL, 5% LL.

Methods

The composite samples and filler particle size analysis were performed on the basis of the analysis of microscopic images obtained from the Opta-Tech MB200s optical microscope connected with the Meiji Techno HD2600T camera. The observations were made using 40× and 100× magnification. The presented results of particle size determination were made for at least 600 measurements.

The scanning electron microscope (SEM) from Hitachi model TM3000 was used to evaluate the microstructure of composites. The fillers and cryo-fractured surfaces of the composite samples were sputtered by gold and assessed with an accelerating voltage of 5–15 kV.

Fourier transform infrared spectroscopy (FTIR) was performed using the Jasco FT/IR-4600 apparatus in attenuated total reflectance (ATR) mode. FTIR analyses were carried out to investigate the structural changes in samples. 64 scans performed this measurement at a resolution of 4 cm^{-1} in the wavenumber range of 4000–400 cm^{-1}. The FTIR measurements for fillers before processing were realized for materials in form of powders. The second derivative method in the OriginPro software was used to deconvolute the carbonyl band at polyethylene and composites spectra. The curve fitting was also carried out in OriginPro software using the Gaussian profile, and the quality of obtained fitting was controlled by the coefficient of determination ($R^2 > 0.99$). For this evaluation, the FTIR measurement was performed in the wavenumber range 1800–1650 cm^{-1} by 64 scans, and the scanning resolution was 4 cm^{-1}. The carbonyl index (CI) on the basis of ATR-FTIR measurements was calculated according to the following equation (Carlsson and Wiles 1969; Gardette et al. 2013; Yagoubi et al. 2015):

$$\mathrm{CI} = \frac{A_{\mathrm{C=O}}}{A_{\mathrm{CH2}}} \tag{1}$$

where $A_{\mathrm{C=O}}$ is the absorbance of a carbonyl group (1800–1600 cm^{-1}) and A_{CH2} is the absorbance of the reference peak (1500–1420 cm^{-1}).

The PE samples' thermogravimetric analysis (TGA) was conducted on approximately 10 ± 0.1 mg samples in Al_2O_3 pans using a Netzsch TG 209 F1 Libra apparatus (Germany). The measurements were performed in a temperature range of 30–900 °C with a heating rate of 10 °C/min in a nitrogen atmosphere with a 60 ml/min gas flow.

Differential scanning calorimetry (DSC) measurements were carried out using a NETZSCH DSC204 F1 Phoenix apparatus (Germany) with aluminum crucibles and 5 ± 0.1 mg samples under nitrogen flow. Non-isothermal crystallization processes were performed at certain programmed temperatures. All samples were heated from 20 to 200 °C and held molten for five minutes. Then the samples were cooled to 20 °C with a constant cooling rate of 10 °C/min. The used temperature program was conducted twice to erase the thermal history of the samples. The crystallinity degree X_C of the samples was calculated using formula (2):

$$X_C = \frac{\Delta H_M}{(1-\theta)\cdot \Delta H_{M100\%}} \times 100\% \quad (2)$$

where ΔH_M melting enthalpy of a sample, $\Delta H_{M100\%}$ melting enthalpy of 100% crystalline polyethylene, $\Delta H_{M100\%} = 293$ J/g (Wunderlich 1990), θ filler weight fraction.

The oxidation induction time (OIT) of analyzed composites was determined by the differential scanning calorimetry (DSC) analysis, according to the procedure described in EN 728 standard and recommendations described in (Schmid and Affolter 2003). The 5 mg samples were placed in uncovered aluminum crucibles. They were heated from 20 to 190 °C with a heating rate of 20 °C/min in nitrogen and then kept at 190 °C for 5 min in nitrogen, and then gas was switched to oxygen, and the time required for sample oxidation was measured. The oxidation was recognized as an exothermal DSC signal and occurred after a defined time calculated relative to the gas switch point from nitrogen to oxygen (Schmid and Affolter 2003). The measurements were conducted using a Netzsch 204 F1 Phoenix apparatus. Three samples from each measurement series were analyzed.

Rheological properties of the polyethylene samples were tested using a rotational rheometer Anton Paar MCR 301 (Austria) equipped with a 25-mm parallel plate measuring system in oscillation shearing mode at a temperature of 190 °C and a gap of 0.8 mm. The preliminary strain sweep experiments were conducted before frequency sweep measurements to determine the linear viscoelastic region (LVE). Unmodified HDPE samples and composites containing 5 wt% filler were tested under constant shearing oscillatory conditions (2% and 10 rad/s) in an oxidizing atmosphere for 3600 s. Samples in the form of twin-screw extruded granulate, plastified directly in the rheometer system, were subjected to rheological analysis. Three samples from each measurement series were analyzed.

Phenolic compounds in samples were analyzed after alkaline and acidic hydrolysis (Stuper-Szablewska et al. 2017; Przybylska-Balcerek et al. 2021). Analysis was performed using an Aquity H class UPLC system equipped with a Waters Acquity PDA detector (USA). Chromatographic separation was performed on an Acquity UPLC® BEH C18 column (100×2.1 mm, particle size 1.7 µm) (Ireland). The elution was carried out using a gradient with the following mobile phase composition: A: acetonitrile with 0,1% formic acid, B: 1% aqueous formic acid mixture (pH = 2). The analyses were carried out at the wavelength $\lambda = 320$ nm and 280 nm. Compounds were identified based on comparing the retention time of the analyzed peak with the retention time of the standard and by adding a specific amount of the standard to the analyzed samples and repeated analysis.

The antioxidant properties of used fillers were measured using DPPH free radical scavenging assay. DPPH (A 2,2-diphenyl-1-picrylhydrazyl) is a stable organic nitrogen radical. The scavenging of free radicals by antioxidants causes fading of a DPPH solution in methanol. The UV–Vis spectrophotometer can be used to record the changes in color. To investigate the antioxidant activity of lemon and stevia leaves, the dried fillers were extracted using methanol in a proportion of 100 mg of material to 50 ml of methanol, which gives concentrations of 2 g/l. The extraction process was performed using a magnetic stirrer at ambient temperature with a rotation speed of 300 rpm for 30 min. The vacuum filtration station was equipped with quantitative medium filter papers to filter the extract. The prepared extracts were further diluted with methanol to obtain extracts in concentrations 2, 1, 0.5, 0.1, and 0.05 g/l. These extracts were then immediately added to the 63 µM DPPH solution in methanol (Rojas-Lema et al. 2020). To proceed with the DPPH assay, 0.15 ml of extracts and 2.85 ml of DPPH solution were added to the dark flask. They were kept closed in the dark for 30 min before measurement, which was performed using spectrophotometer UV–Vis Schott UviLine 9400 (Germany) at 517 nm (Moreira et al. 2013). The antioxidant activity of each extract is presented as an inhibition I (3):

$$I = \frac{A_{\mathrm{control}} - A_{\mathrm{sample}}}{A_{\mathrm{control}}} \quad (3)$$

where A_{control} absorbance of DPPH solution at 517 nm, A_{sample} absorbance of the sample at 517 nm. This helped to calculate the $IC_{50,}$ which is the 50% inhibitory concentration. This value expressed in a Trolox equivalent per gram of dry filler mass is called DRSC (DPPH radical scavenging activity). All of the other calculated inhibitions are also expressed in a Trolox equivalent.

Results and discussions

Structural characterization of fillers and composites

Figure 1 presents images from an optical microscope made for compression molded composite samples containing 1, 2, and 5% by weight of LL and ST fillers. The observations were performed to verify the dispersion of filler particles in the matrix. The proper particle dispersions in the matrix were achieved in the series containing above 2 wt% of the fillers. Moreover, in any case, no agglomeration of particles was noted.

The geometrical structure of ground plant-derived fillers (LL and ST) was depicted using SEM images compiled in Fig. 2. At the same time, the surfaces of brittle fractured

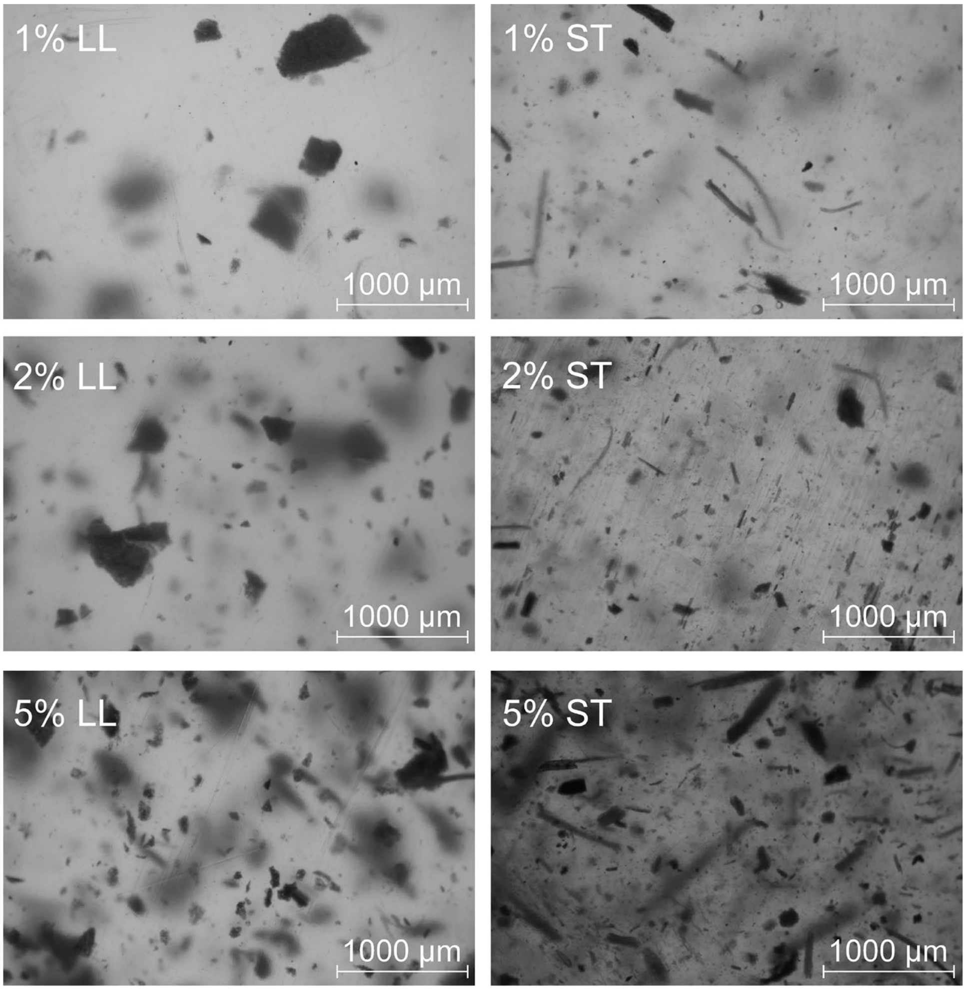


Fig. 1 Optical microscope images of composite samples, presenting filler dispersions in 1 mm thick compression molded samples

composite samples containing 5 wt% LL and ST were presented. Despite the use of the same grinding procedure, it can be seen that the filler particles differ significantly in geometry. In the case of LL, plate-shaped particles with an average particle size of about 800 µm are observed. In turn, stevia leaves revealed a higher degree of fragmentation with a more significant share of fine fractions and an increased content of fibrous inclusions with a high aspect ratio. The difference in the grinding process may result from the chemical structure of both fillers and different contents of the elementary components determining the structure of lignocellulosic materials and their cohesion, i.e., cellulose and lignin (Hernández et al. 1998; Segura-Campos et al. 2014). Furthermore, in the case of ST a much more developed filler surface is observed compared to LL. In addition, Fig. 3 shows the analysis of particle size distribution based on microscopic observations. The brittle fractures of the composite samples with the highest filler amount used in the study, shown in Fig. 2, allow concluding that in both cases, despite the lack of surface modification of the fillers and compatibilizers, the interfacial adhesion is proper. No distinct gaps were observed in the interfacial area for the 5% LL and 5% ST composites, which could indicate a loss of adhesion at the polymer–filler interface (Petinakis et al. 2009). Moreover, there were no pull-out holes after filler removal from the polymer matrix during the breaking of the sample cooled below the glass transition temperature.

Lemon and stevia leaves have been analyzed for chemical structure. Figure 4 shows the FTIR spectra for ground and dried fillers before the melt-mixing process with the polymer. The spectra differ slightly, and the differences result from the various amounts and types of extracts contained. The following bands may be distinguished for LL/ST, respectively: bending vibrations of hydrogen and phenolic bonds (3303/3297 cm^{-1}), asymmetric stretching vibrations of sp^3-CH (2918/2920 cm^{-1}), symmetric stretching vibrations of sp^3-CH (2851/2852 cm^{-1}), C=O stretching vibration from steviol glycosides (-/1727 cm^{-1}), amide I arisen from carbonyl stretch in proteins (1606/1600 cm^{-1}), vibrations of the phenyl ring ν(CdC) stretching of flavonoids (1515/1515 cm^{-1}), bending vibration of the CH bond (1315/1315 cm^{-1}), C–N stretching of amines

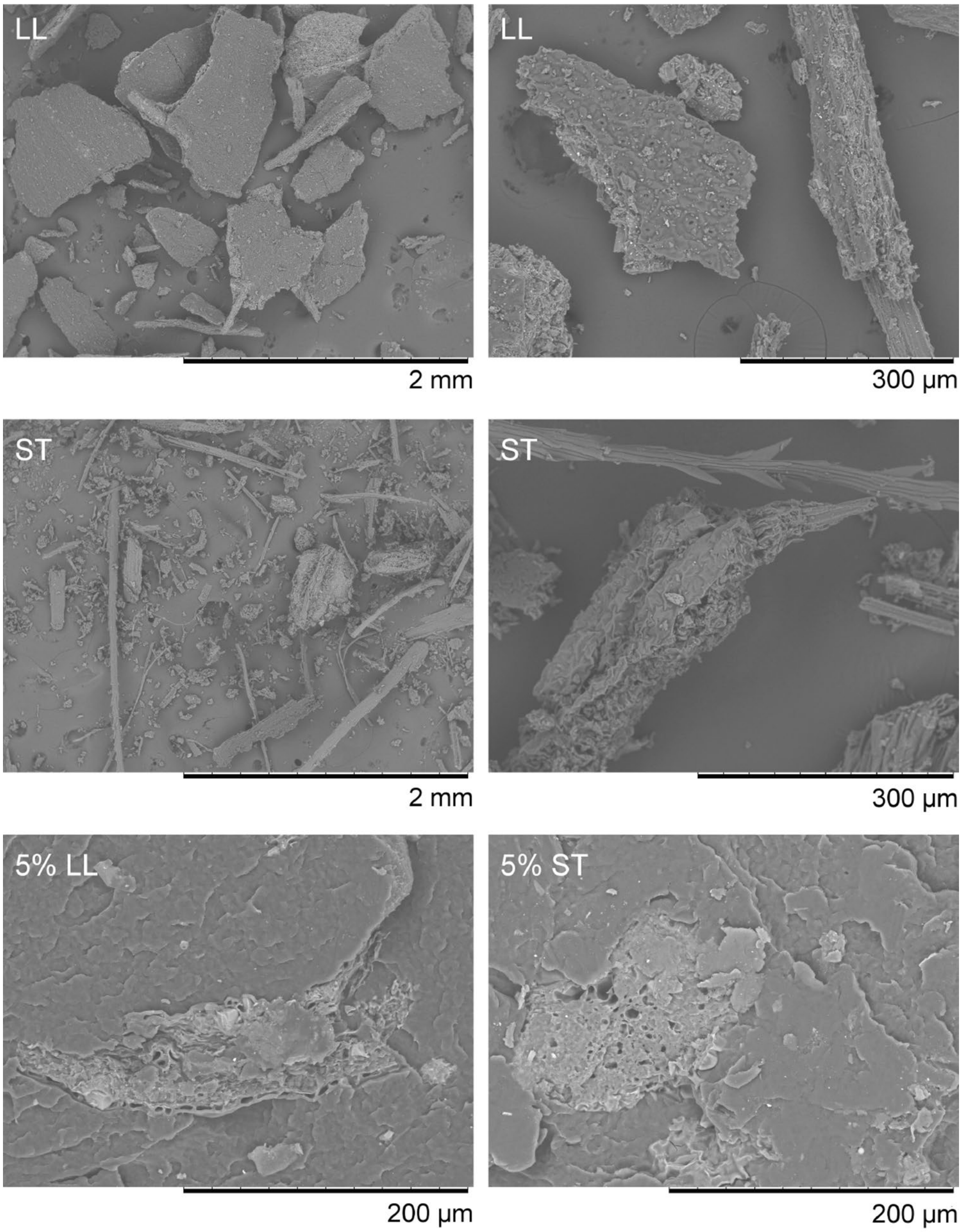


Fig. 2 SEM images of ground LL and ST used as a fillers and brittle fracture surfaces of 5% LL and 5% ST composites

(1248/1254 cm^{-1}), characteristic absorption bands of steviol glycosides (-/1154 cm^{-1}), –O–C aromatic ring stretching of the polyols contained in flavones, terpenoids and polysaccharides (1100/- cm^{-1}), C–N stretching vibrations of amine from steviol glycosides (-/1024 cm^{-1}) (Manthey 2006; Vankar and Shukla 2012; Abbasi et al. 2021; Hidar et al. 2021).

Thermal and thermooxidative behavior of polyethylene-based composites

The results of the thermogravimetric analysis performed for the fillers, the unfilled HDPE, and its composites are presented in Fig. 5. The thermal parameters, such as the temperatures of 5, 10, and 50% mass loss ($T_{5\%}$, $T_{10\%,}$ and $T_{50\%}$, respectively), residual mass, and the dTG peak data, are presented in Table 1. It can be observed that both lemon and stevia leaves undergo thermal decomposition in like manner. The mass loss of the filler samples begins just at the beginning of the measurement, below 100 °C, which can be attributed to the evaporation of water and volatile compounds, including waxy substances and essential oils (Madhu et al. 2019). Most of the degradation occurs in the range of 200–400 °C. In the case of the LL filler, the dTG signal in this range is composed of two peaks, about 250 °C and 320 °C, related to the decomposition of hemicellulose and cellulose, respectively (Yoganandam et al. 2019). The stevia leaves present a slightly different

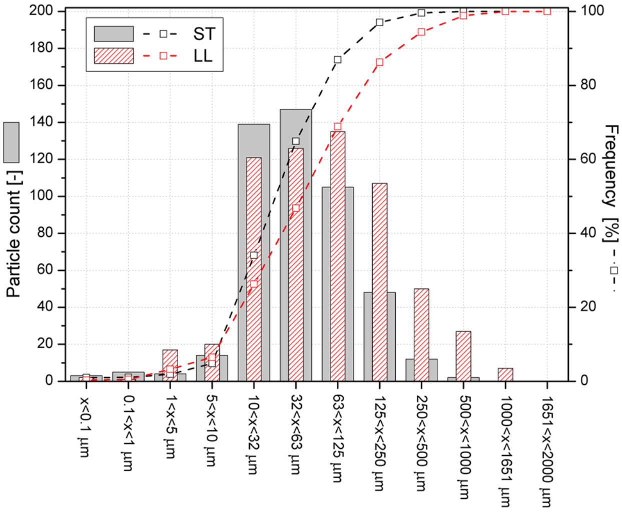


Fig. 3 Particle size distribution of ST and LL

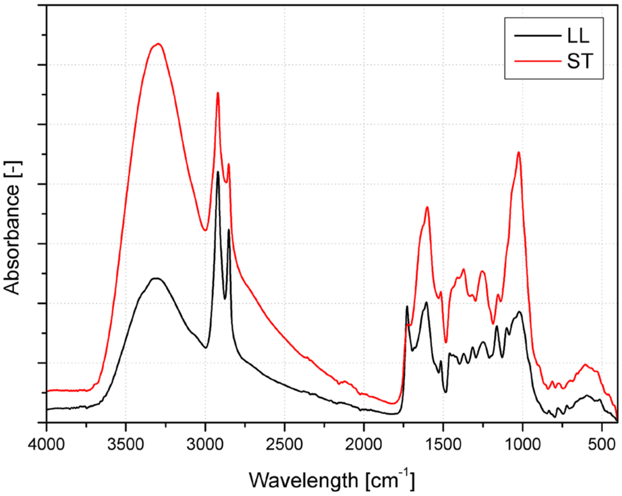


Fig. 4 FTIR spectra of the LL and ST fillers

behavior—no distinctive dTG peak resulting from the degradation of hemicellulose can be spotted, but rather a shoulder on the main peak at 320 °C. This behavior indicates differences in the chemical composition of the two fillers. The mass loss of the plant-based fillers does not end after the degradation of cellulose but slowly continues in the remaining part of the measurement. This behavior is caused by decomposition of lignin around 400–550 °C, as well as other non-lignocellulosic substances (Madhu et al. 2019). The stages of degradation in higher temperatures correspond to the decomposition of transient char. The residual mass after the test is about 25% for both fillers. Even though the commonly reported ash content of stevia does not exceed 13 wt% (Marcinek and Krejpcio 2015), the difference is presumably caused by the inert atmosphere during the measurement, which did not allow for the complete decomposition of the samples in the lack of oxygen.

The unfilled polyethylene samples undergo a one-step degradation, and its maximum intensity takes place at 483 °C, as indicated by the dTG peak, which is typical for this polymer (Chrissafis et al. 2009). The studied composites present similar behavior. Notably, no mass loss due to moisture evaporation can be observed, which indicates that the filler particles are well saturated by the polymeric matrix and cannot absorb water from the environment. The filler's content slightly influences the degradation's onset, defined here as the $T_{5\%}$ temperature, which decreases along with the percentage of stevia or lemon leaves. This results from the degradation of hemicellulose, which occurs before the depolymerization of HDPE (Avella et al. 2010). Therefore, the decrease of $T_{5\%}$ is more prominent in the LL-filled samples with the higher hemicellulose content in this filler, as indicated by the dTG results. It also needs to be stressed that even the lowest $T_{5\%}$, recorded for the 5% ST sample, is still approx. 310 °C higher than its melting temperature, so it will not influence the processing window of the studied materials. On the other hand, the dTG peak temperature of the composites is almost unchanged. Therefore, it can be stated that the presence of both lignocellulosic compounds does not influence the decomposition of HDPE.

Figure 6 shows the DSC curves of the first and second heating and the first cooling of HDPE and its composites. In addition, Table 2 lists thermal parameters such as crystallization temperature (T_C), melting temperature (T_M), melting enthalpy (ΔH_M), and crystallinity (X_C) determined according to Eq. (2). Polyethylene is a semi-crystalline polymer, which, due to the very high growth rate of crystallites, is slightly susceptible to the phenomena of heterogeneous nucleation caused by the introduction of nucleants and fillers (Seven et al. 2016; Mysiukiewicz et al. 2022). Adding both ground leaves caused minor changes in the crystallization temperature; LL caused a minimal increase in this value, while ST decreased it. This effect may be correlated with an increase in crystallinity, and in the case of composites containing LL the highest value was recorded (75.2%), while for ST the lowest was 68.9%. Crystallization values determined during the second cooling allow obtaining information only about the effect of fillers, without additional details and thermal effects caused by the processing of the samples and their thermal history. The introduction of both types of fillers resulted in a different impact on the HDPE matrix. The most reliable sample seems to be the series containing 5 wt% of the filler, which results from the large size of the filler particles and the homogeneity of its distribution in the polymer. The addition of fillers resulted in a slight improvement (LL) or a noticeable decrease (ST) in the degree of crystallinity, which is consistent with T_C. On the other hand, introducing

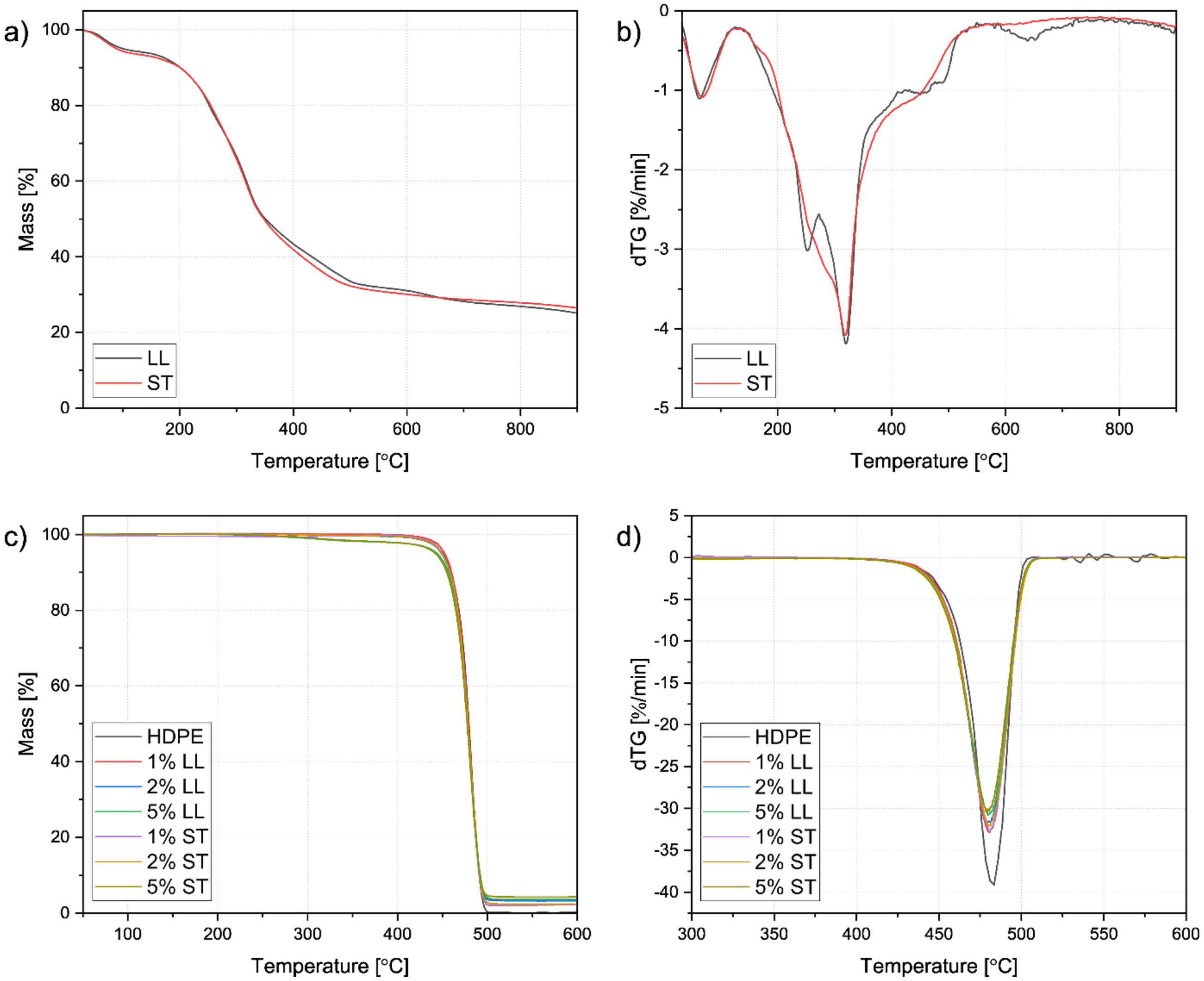


Fig. 5 TG and DTG curve of HDPE, the fillers and the composites with various amounts of LL and ST

Table 1 Thermal parameters obtained by TGA for HDPE, the fillers and the composites with various amounts of LL and ST

Material	$T_{5\%}$ (°C)	$T_{10\%}$	$T_{50\%}$	Residual mass (%)	DTG peak (°C; %/min)
HDPE	450	460	480	0.41	483; – 39.52
1% LL	452	460	479	3.47	481; – 32.95
2% LL	449	458	478	3.27	480; – 31.95
5% LL	444	456	478	3.60	480; – 30.87
1% ST	450	459	478	2.25	480; – 32.79
2% ST	449	458	479	2.43	481; – 32.09
5% ST	443	455	478	5.02	479; – 30.48
LL	101	201	351	25.14	63; – 1.10 252; – 3.02 320; – 4.19
ST	90	201	348	26.49	68; – 1.09 319; – 4.08

ground stevia leaves caused a noticeable decrease in X_C, which is also reflected in a reduction in the crystallization temperature. Considering the high content of glycosides in stevia, their increased migration to the polymer matrix and the plasticizing effects of HDPE cannot be excluded (Andreuccetti et al. 2010).

Figure 7 shows the OIT values for HDPE and composites containing various concentrations of plant-based fillers (a) and the example DSC thermograms taken in an oxidizing atmosphere (b), based on which the oxidation resistance at elevated temperature was determined. Based on the obtained OIT values for the tested composite series, it can be stated that the adequate amount of filler allowing for a significant increase in the resistance to oxidation of polyethylene is 5 wt%. At the same time, the ground stevia leaves were characterized by increased effectiveness compared to lemon leaves. It should be emphasized that referring to earlier research

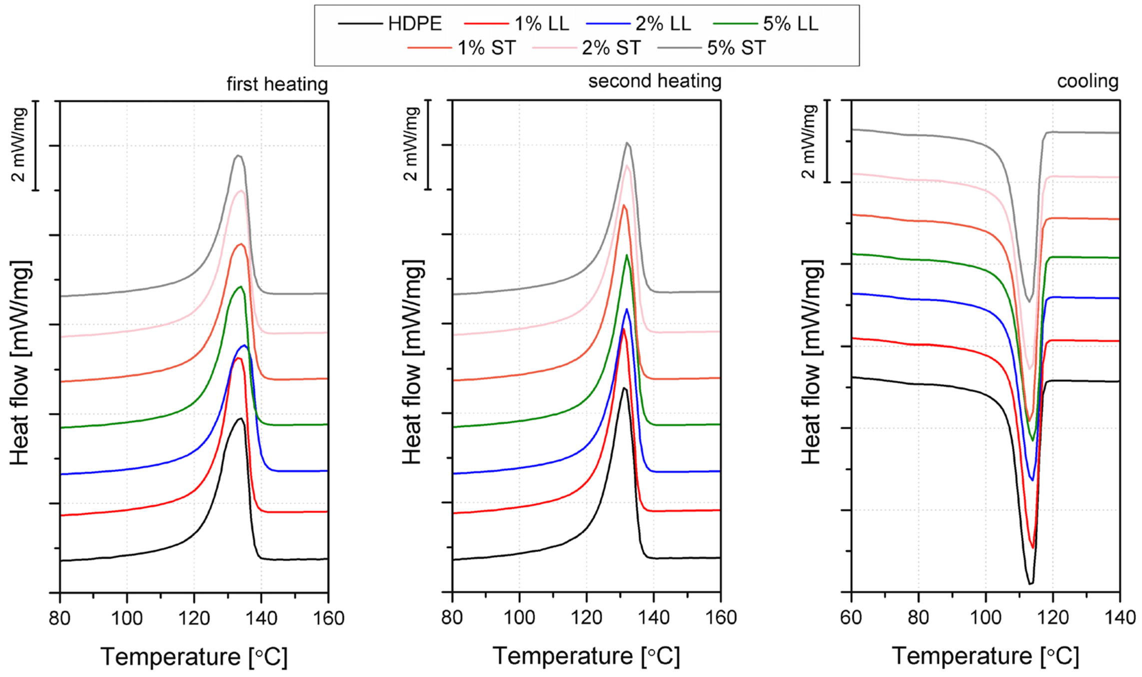


Fig. 6 DSC curves of HDPE and its composites with various amounts of LL and ST, endo up

Table 2 Thermal parameters obtained by DSC for HDPE and its composites with various amounts of LL and ST; 1 and 2 indexes refer to the heating/cooling cycle; exo down

Material	T_C (°C)	T_{M1}	T_{M2}	ΔH_{M1} (J/g)	ΔH_{M1}	X_{C1} (%)	X_{C2}
HDPE	113.5	133.8	131.5	215.8	219.2	73.6	74.9
1% LL	113.8	133.5	131.1	213.5	213.4	73.6	73.6
2% LL	113.8	134.9	132.1	209.9	205.6	73.1	71.6
5% LL	114.0	133.9	132.1	207.4	209.3	74.5	75.2
1% ST	113.2	133.9	131.3	212.5	210.6	73.3	72.6
2% ST	113.3	134.1	132.3	214.6	214.2	74.7	74.6
5% ST	113.1	133.1	132.4	199.9	200.0	68.9	68.9

results for composites filled with coffee spent grains, and cocoa husk (Hejna et al. 2023), the registered OIT values for HDPE-LL/ST composites are significantly higher. This behavior indicates a higher content of antioxidants in the fillers or increased migration to the polymer. The lack of a noticeable antioxidant effect of composites containing 1 and 2 wt% of the fillers may be due to the relatively big fractions of the introduced filler. Large filler particles with a small surface area resulted in a limited polymer-filler interfacial surface through which low molecular compounds migrated to the polymer. Moreover, the size of the filler particles also translates into their antioxidant activity and the number of compounds released (Castiglioni et al. 2015; Qiu et al. 2022).

In order to confirm the possibility of obtaining increased resistance to oxidation of polyethylene composites by introducing fillers in the form of ground lemon leaves and stevia, in addition to determining the OIT value, a rheological analysis was carried out supplemented with FTIR measurements. Figure 8a shows the complex modulus changes assessed under constant conditions of oscillation, temperature, and oxidizing atmosphere as a function of time. Concerning previously published works (Wiles and Carlsson 1980; Iring et al. 1986; Chabira et al. 2011), the expected effect caused by the oxidation of high-density polyethylene in the molten state is to increase its molecular weight and the associated viscosity. In the work of Iring et al. (Iring et al. 1986), an increase in torque in a dynamic chamber during long-term mixing at 200 °C for 20 min was correlated with an increase in gel content in the polymer of over 15%. The mechanism of dynamic melt degradation is associated with chain scission and crosslinking of the polyethylene structure, which in the case of HDPE is possible due to the high possibility of intermolecular recombination caused by small distances

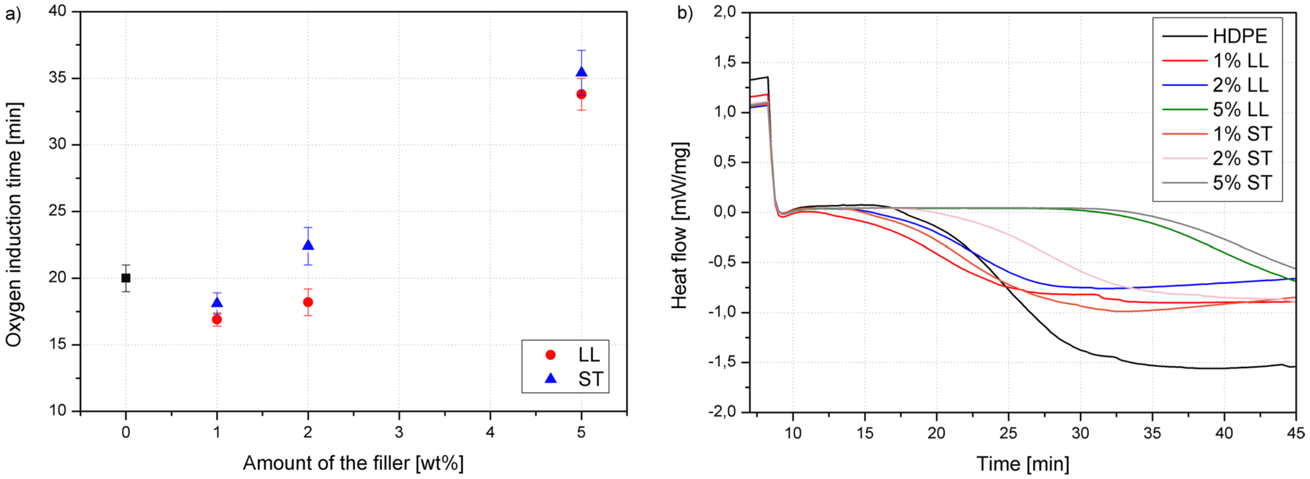


Fig. 7 Oxygen induction time (**a**) and course of DSC thermograms during OIT tests (**b**); exo down

between the chains (Iring et al. 1986). A two-stage increase in the storage modulus for the HDPE sample is observed, which can be related to the gradual formation of a spatially crosslinked structure. Both polymer composites showed different characteristics of the |G*|(t) course. Only an increase in viscosity in the range above 1,000 s is observed, preceded by a decrease in the value of the holding modulus. While the effect of viscosity reduction during oxidation in the molten state in dynamic conditions is mainly attributed to the consumption of stabilizers, in the considered case, it may be related to the effect of partial degradation of the plant component and migration of low-molecular products, and the formation of a porous structure in the sample subjected to rheological analysis. In addition, Fig. 8b shows the first derivative of the storage modulus vs. temperature. Proposing such an interpretation of the curves allows for determining the inflection of the |G*|(t) curves. Based on the results of the rheological analysis, it should be concluded that the addition of 5% ST caused a delay in the increase in polymer viscosity caused by the oxidation-induced polyethylene crosslinking process, which confirms the increased antioxidant capacity of this filler.

Samples subjected to rheological measurements were additionally analyzed using Fourier transform infrared spectroscopy. Figure 9 shows the FTIR spectra of the samples before and after rheological measurement in the set conditions of shear and oxidizing atmosphere taken in 60 min. In the case of polyethylene-specific absorption bands observed at 2913 and 2845 cm^{-1}, associated with symmetric and asymmetric stretching vibrations of C–H bonds, a decrease in peak intensity after the rheological test can be observed. This effect is particularly pronounced for unmodified HDPE samples, which the degradative phenomenon of chain scission can explain. Moreover, the absorption band

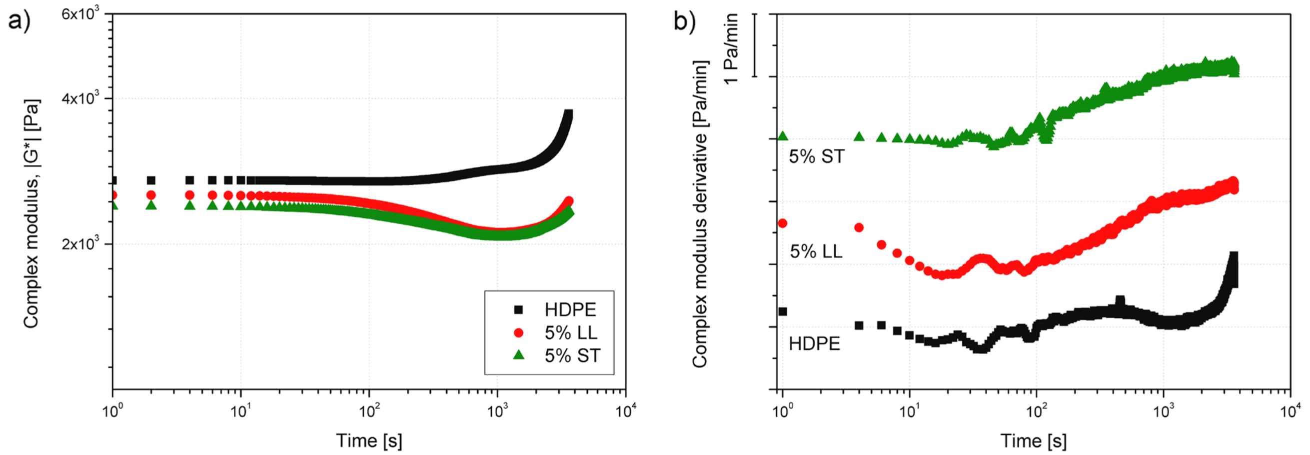


Fig. 8 Complex modulus vs. time measured during oscillatory rheological experiments conducted at constant shearing conditions and oxidizing atmosphere

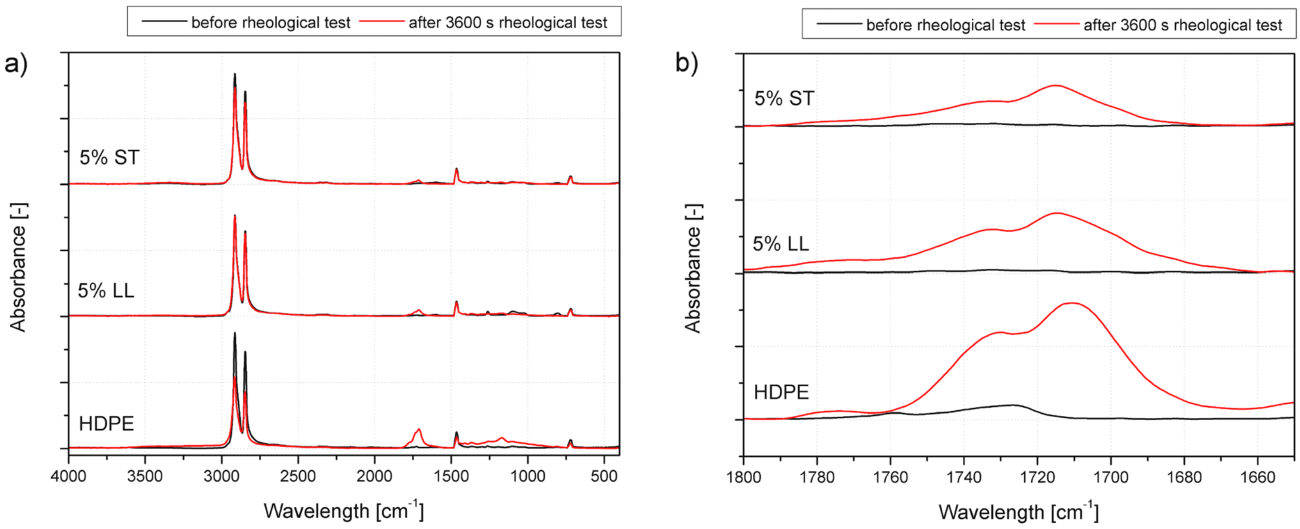


Fig. 9 FTIR spectra of HDPE and composites containing 5 wt% of the LL and ST, before and after 60 min rheological test in an oxidizing atmosphere

1100–1366 cm^{-1}, related to wagging and twisting deformations, shows higher intensity for the unmodified HDPE sample after oxidation. In the case of the other characteristic bands for polyethylene, i.e., 1466 cm^{-1} (bending deformations of C–H bonds) and 720–732 cm^{-1} (rocking vibrations of macromolecule), no significant intensity changes were noticed on spectra of both HDPE and composites (Gulmine et al. 2002).

The most crucial change in the chemical structure of polyethylene subjected to the oxidation process at elevated temperatures is the analysis of the absorption band originating from the carbonyl bonds C=O formed during oxidation (Guadagno et al. 2001). The intensity of the C=O band (Fig. 9) in the wavelength range of 1780–1600 cm^{-1} is noticeable for all samples after rheological measurements in oxidizing conditions. The most significant increase in absorbance in this range was noted for non-modified HDPE, while the 5% ST sample was characterized by the lowest susceptibility to oxidation. To quantify changes in the structure observed on the basis of the FTIR analysis, the carbonyl index values were determined following Eq. (1) and are summarized in Fig. 10. Considering the literature data (Andrady et al. 1993; Yang et al. 2006), the CI value for HDPE after a 3600 s rheological test of more than 1.7 should be regarded as significant. The introduction of both leaf varieties resulted in very favorable effects on HDPE. Due to their presence and indirect migration of active low-molecular compounds contained in them (Rangaraj et al. 2021; Quilez-Molina et al. 2022), CI for composites with 5 wt% content is many times lower compared to oxidized HDPE. Moreover, for composites, the CI value was negligibly small for samples before rheological measurement, while in the case of HDPE, the process of short-term formation of samples in the molten state caused degradation of the polymer structure.

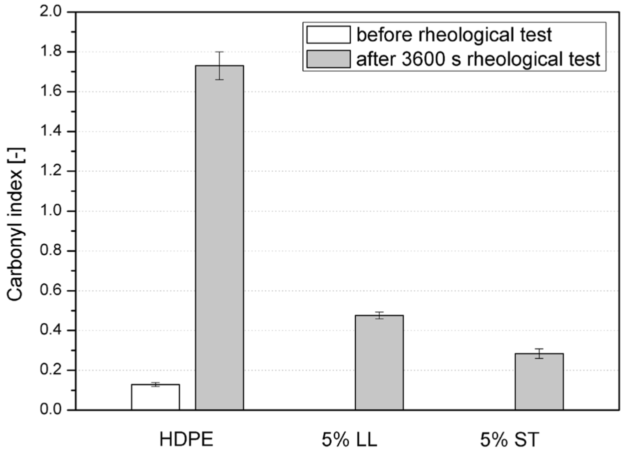


Fig. 10 Carbonyl index values measured for HDPE and 5% LL/ST composites before and after 60 min rheological test in an oxidizing atmosphere

The deconvolution of carbonyl bands was performed to further investigate the mechanism of HDPE composites oxidation during the rheological test. Figure 11 presents carbonyl peaks and their mathematical deconvolution. The number of peaks and their position is different for each sample. The HDPE sample before the rheological test was also slightly oxidized, confirmed in a carbonyl index measurement. After the deconvolution, the three peaks can be distinguished, and they correspond to the formation of three main oxidation products, which are ketones (1725 cm^{-1}), esters (1736 cm^{-1}), and carboxylic acid anhydride (1758 cm^{-1})

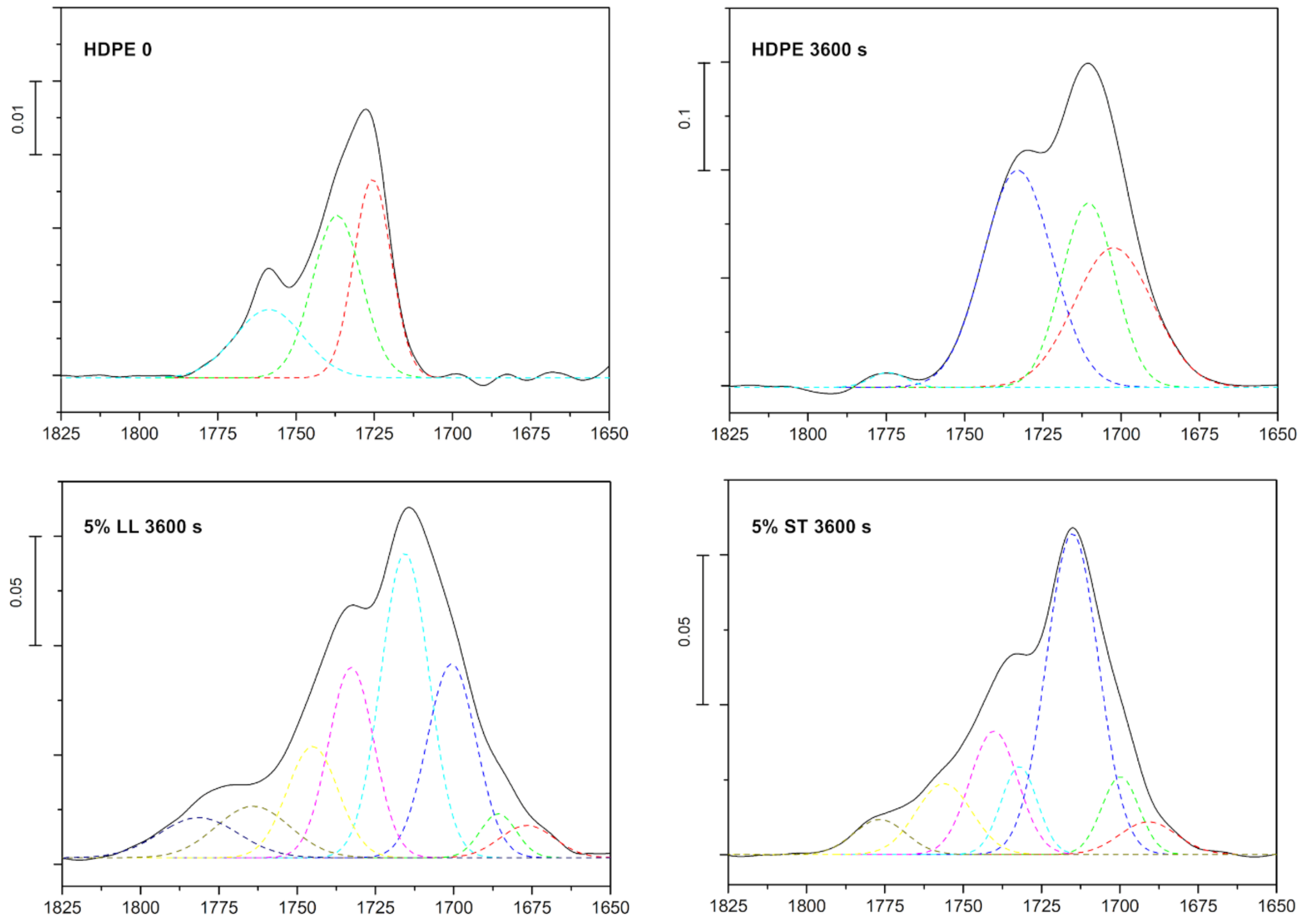


Fig. 11 Deconvoluted carbonyl bands for HDPE before and after rheological test and composites with 5 wt% lemon and stevia leaves after rheological test

(Gardette et al. 2013). The HDPE sample after the rheological test is characterized by the highest carbonyl index and four deconvoluted oxidation products: γ-Ketoacids (1702 cm^{-1}), carboxylic acids (1710 cm^{-1}), aldehydes (1733 cm^{-1}) and peresters (1774 cm^{-1}) (Yagoubi et al. 2015). The main focus should be the appearance of an aldehydes oxidation product; not only is it linked with a thermal oxidation mechanism, but it also tends to appear in earlier stages of thermal oxidation (Antunes et al. 2017). Carbonyl compounds formed in HDPE composites after the rheological test are all presented in Table 3. There can be distinguished ten different carbonyl compounds in a C=O band. The peak with the highest share for unfilled HDPE samples is aldehyde or ketone, but in the case of lemon and stevia leaves composites, the highest intensity and peak area is for the carboxylic acid band (1715 cm^{-1}). This behavior can be attributed to the thermally aged crosslinked polyethylene, and Sugimoto et al. reported this conduct for XLPE samples thermally aged in the air for 200 h at 155 °C (Sugimoto et al. 2013).

Table 3 Carbonyl compounds distinguished after the deconvolution of carbonyl bands after the rheological test for 5% LL and 5% ST

		Wavenumber (cm^{-1})	5% LL	5% ST
1	Ketones conjugation with phenyl	1676	+	
2	Ketones, acids a,b unsaturated	1686	+	
3	Ketones, aldehydes α, β unsaturated	1690		+
4	γ-Ketoacids, keto group	1700	+	+
5	Carboxylic acids	1715	+	+
6	Aldehydes	1732	+	+
7	Esters	1745	+	+
8	Carboxylic acids anhydride	1764	+	+
9	Peresters	1781	+	+

(+) Confirmation of specific band components in the carbonyl range from absorption peak deconvolution analysis

The HPLC chromatographic analysis allows to describe qualitatively the following active compounds, exhibiting antioxidant activity contained in both used plant fillers:

lemon leaves (LL): gallic acid, 2,5-dihydroxybenzoic acid, 4-hydroxybenzoic acid, vanilic acid, caffeic acid, syringic acid, vanilin, p-coumaric acid, benzoic acid, ferulic acid, sinapic acid, t-cinnamic acid, chlorogenic acid, protocatechuic acid, rosmarinic acid, salicylic acid, apigenin, hesperidin, limocitrin, catechin, kaempferol, luteolin, naringenin, quercetin, rutin, vitexin; stevia leaves (ST): gallic acid, 4-hydroxybenzoic acid, vanilic acid, caffeic acid, syringic acid, vanilin, p-coumaric acid, benzoic acid, ferulic acid, sinapic acid, t-cinnamic acid, chlorogenic acid, protocatechuic acid, rosmarinic acid, salicylic acid, catechin, kaempferol, luteolin, rutin, pyrogallol. The obtained list of compounds is in line with the literature data on active compounds contained in the leaves of the considered plants (Covarrubias-Cárdenas et al. 2018; Klimek-Szczykutowicz et al. 2020; Chi et al. 2020; Asker et al. 2020).

Tables 4 and 5 present the antioxidant properties of lemon and stevia leaves. At first sight, it is clearly seen that stevia is a stronger antioxidant since their extract that has a 50% ability to scavenge free radicals is equivalent to 65.89 mg of Trolox per 1 g of dry mass, which is over 40 times higher than for the extract of lemon leaves. The significantly lower antioxidant activity is represented by lemon leaves; the methanolic extracts at 5 different concentrations exhibit similar inhibition even though the extract with the lowest concentration is 40 times diluted in comparison with the highest concentrated extract. This means that the changes in extract concentration did not influence the ability to scavenge free radicals of lemon leaves extract. A different mechanism is represented by the stevia leaves extract, where the 2 g per liter extract shows almost eight times higher ability to scavenge free radicals than the 0.05 g/l extract. In the literature, we can find works where the antioxidant activity of citrus leaves is commonly analyzed for essential oils extracted from them (Ouedrhiri et al. 2015; Ben Hsouna et al. 2017; Chi et al. 2020). The concentration of citrus leaves essential oils in methanol with the 50% antioxidant activity examined by Chi et al. is 1.21, 1.49, and 2.18 g/l for *citrus aurantifolia*, *citrus sinensis* and *citrus grandis,* respectively (Chi et al. 2020). A similar investigation to ours was performed by Ordonez-Gomez et al., and they discovered that the methanolic extracts of dried lemon leaves with the ability to scavenge 50% of free radicals (IC_{50}) are in concentration between 0.92 and 1.85 g/l for different lemon spices (Ordoñez-Gómez et al. 2018). The value of IC_{50} calculated in this work for dried lemon leaves extract gives a value of 51.92 g/l; such a big difference may be caused by the insufficient extraction process, which can rely on too short an extraction time. In the previously mentioned work, the extraction time was 24 h in an 80% methanolic solution, and the used DPPH assay method is similar to the one presented in this work. Proceeding to analyze the antioxidant properties of stevia leaves (Table 5), it is important to mention that they show better free radical scavenging ability than lemon leaves, which were confirmed by the DPPH assay. A similar investigation performed by Periche et al. provides data about the antioxidant activity of aqueous extracts obtained at three temperatures (50, 70, and 90 °C) (Periche et al. 2014). The information collected from that study shows that with the increase in temperature of extraction, the value of antioxidant activity presented in Trolox equivalent also increases, and this is 62.45 mg Trolox per gram of stevia dried leaves at 50 °C, 106.68 at 70 °C and 119.12 at 90 °C. This data for extract prepared at 50 °C aligns with the DPPH radical

Table 4 Antioxidant properties of lemon leaves obtained in a DPPH free radical scavenging assay

	Extract	Concentrations (g/l)	Inhibition (%)	Trolox equivalent (mg/l)	IC_{50} (g/l)	DRSC (mg/g dry mass)
1	LL 2	2	10.04	6.52	51.92	1.52
2	LL 1	1	9.33	5.22		
3	LL 0.5	0.5	7.17	1.33		
4	LL 0.1	0.1	9.33	5.22		
5	LL 0.05	0.05	8.32	3.41		

Table 5 Antioxidant properties of stevia leaves obtained in a DPPH free radical scavenging assay

	Extract	Concentrations (g/l)	Inhibition (%)	Trolox equivalent (mg/l)	IC_{50} (g/l)	DRSC (mg/g dry mass)
1	ST 2	2	75.04	124.09	1.20	65.89
2	ST 1	1	49.50	77.89		
3	ST 0.5	0.5	24.39	32.48		
4	ST 0.1	0.1	11.05	8.34		
5	ST 0.05	0.05	9.90	6.26		

scavenging capacity (DRSC) calculated and presented in Table 5. The more similar study was performed by Tadhani et al., the extracts were obtained by the extraction in methanol and water for one hour (Tadhani et al. 2007). The antioxidant activity described as Trolox equivalent of this way prepared extracts is 38.24 mg Trolox/g dry mass and 37.40 mg Trolox/g dry mass for water and methanol extracts, respectively. This time the value of DPPH radical scavenging capacity calculated by us is 2 times higher; this can be caused by a slightly different DPPH assay method. All the mentioned literature references about antioxidant activity give one conclusion that the antioxidant compounds in stevia leaves are more soluble in the aqueous and methanolic solvents which gives more concentrated extracts for DPPH assay in a shorter time than for lemon leaves where the extraction process should be longer. The higher antioxidant activity of stevia leaves than the lemon leaves is also reflected in the carbonyl index measurement after the oxidation of HDPE composites (Fig. 10). This can suggest that the migration of low molecular compounds in the polymer matrix is also more likely to happen for stevia leaves.

Conclusions

The production of composites with a matrix of high-density polyethylene filled with ground lemon and stevia leaves allows for obtaining advantageous functional properties of the sustainable composite compared to the unmodified matrix. Using as little as 5 wt% of the filler caused the phytochemicals active in both fillers to increase the composites' antioxidant resistance. In the considered case, the resistance to oxidation of the polymer in the molten state, verified using three experimental methods, confirmed the greater effectiveness of the impact of stevia leaves. In addition, the combined use of rheological analysis in an oxidizing atmosphere with the quantification of the degree of oxidation based on the FTIR carbonyl index is an essential tool for the short-term determination of both the course of the thermo-oxidation process and the effectiveness of the introduced active agents. The thermal properties assessed by DSC allowed to conclude that the introduced fillers do not significantly impact the change in the course of the solidification process and the crystalline structure of HDPE composites. This allows concluding that the addition of both LL and ST should not have an adverse effect on the composite processing process. Furthermore, the presence of renewable lignocellulosic fillers, although they are characterized by lower thermal stability than the polymer matrix, caused an increase in the thermal stability of the composites, already in a minor concentration.

Author contributions MB, JA, AH contributed to the study conception and design; MB, AH, OM, PK contributed to material preparation; MB, OM, PK, JA, KS, AP-B, KS-S contributed to data collection and analysis; and MB, JA, AH, OM, KS, AP-B, KS-S, AB contributed to the first draft of the manuscript writing and edition. All authors read and approved the final manuscript.

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Data availability Data are available on request from the corresponding author.

Declarations

Competing interests The authors declare no competing interests.

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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