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ORIGINAL PAPER

Assessment of antioxidant performance of *Silybum marianum* extract as a natural antioxidant additive in polyethylene by time-dependent melt rheology tests

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Abstract

In this study, *Silybum marianum* (SM) extract as a natural primary antioxidant (PAO) additive was introduced into low density polyethylene. This primary antioxidant was supported by a commercial grade secondary antioxidant (SAO, Irgafos® 168). The effect of compositional variations, mainly amount of SM and the weight ratio of PAO: SAO in the composition, on the thermooxidative stability of low density polyethylene (LDPE) was characterized by determining the thermal parameters, oxygen induction time (OIT) and oxidation onset temperature (OOT) using conventional thermal analysis methods performed in a DSC in air atmosphere. Furthermore, time-dependent rheology test procedures were suggested for monitoring the thermooxidative degradation behavior of antioxidant-loaded compounds. It was found that SM loading of 0.2 or 0.5 wt% provided sufficient oxidation stability in polyethylene, at least 5 min at 240 °C under air when supported by introducing two- or three-fold of SAO. It can be concluded that these SM-Irgafos® 168 antioxidant packages can be successfully used in polyethylenes processed in conventional melt processing windows that can be varied in 180–240 °C, in processing devices (e.g., compounder, kneader, extruders, injection molding, rotomolding) because the obtained thermorheooxidative stability times are longer than the residence time of polymer melts, approximately in the range of 1–4 min from the melting zone to die during the extrusion process.

Keywords Silybum marianum · Natural antioxidant · Polyethylene, rheology, creep

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Extended author information available on the last page of the article

Introduction

Polyolefins are the most extensively used thermoplastics in the plastic industry and human life because of their superior structural and physical properties such as flexibility, chemical and biological inertness, long-term durability, and easy processability with commercial processing methods such as extrusion, compounding, injection molding, rotational molding, film casting, and blowing etc. [1]. Owing to their broad applications and technical advantages, polyolefins have been widely used in the production of various plastic products, including packaging films, sheets, containers, boxes, automotive components, household items, and fibers. This widespread application potential has made polyolefins a commercial polymer that accounts for nearly half of the global plastic production and consumption.

Owing to their simple structure composed of aliphatic units and a saturated backbone, polyolefins are thermally and thermo-oxidatively stable thermoplastics compared to other thermoplastics, such as halogenated polymers (e.g., PVC, PVDF), polyesters (e.g., PET, PBT, and PLA), and polyamides. However, exposure to elevated temperatures, shear stress, oxygen, and ultraviolet (UV) light can evenly initiate thermo-oxidative and photo-oxidative degradation reactions of polyolefin chains which primarily proceed via chain scission mechanisms. The most common type of degradation observed in polyolefins is thermo-oxidative degradation. Thermo-oxidative degradation refers to the chemical deterioration of polymer chains owing to the combined effects of heat and oxygen, leading to chain scission and/or crosslinking. It is well known that chemical deterioration results in significant loss of physical properties in thermoplastics. Therefore, various additives have been introduced into commercial polymers to improve their physical properties and provide durability over a long service time.

Among the various types of additives such as processing aids, anti-slips, anti-blocks, UV-stabilizers, anti-fog, anti-statics, and nucleating agents, antioxidants are one of the most crucial groups of additives for polyolefins because they should protect the polymer structure against oxidation under short-term aggressive or long-term moderate and bearable thermo-oxidative conditions. Antioxidants, or commercially called as “antioxidant packages”, used in polyolefins typically consist of a combination of synthetic primary and secondary antioxidants. The mechanism of thermo-oxidative degradation in polyolefins has been extensively studied in the literature, and the roles of primary and secondary antioxidants and detailed information on these phenomena can be found elsewhere [2–7]. The combination of synthetic phenolic and phosphorus antioxidants as primary and secondary antioxidants, respectively, is also a well-established practice in the polymer industry because of its cost-effectiveness and high antioxidant performance. However, numerous studies have recently focused on the replacement of synthetic phenolic antioxidants with natural alternatives and have investigated their effectiveness in inhibiting thermo-oxidative degradation of thermoplastics and elastomers compounded with natural antioxidants [8–17].

Monitoring of thermo-oxidative degradation in polyolefins is largely based on thermoanalytical measurements, mainly the determination of the oxidative induction time (OIT) and oxidation onset temperature (OOT) performed by DSC. It is well known that all DSC measurements are carried out under quiescent conditions using a few miligrams of the sample in an aluminum crucible. Therefore, there are no physically destructive impacts on the sample other than thermal effects. However, thermoplastics are not only exposed to thermo-oxidative effects but also to shear forces, friction, localized hot spots along the screw and barrel surfaces, and deformations in melt processing operations. Understanding and modelling transport phenomena and related physicochemical issues during polymer processing operations is still a challenging aspect in polymer physics. Therefore, rheological measurements are particularly important for a better understanding of thermo-oxidative degradation and the associated structural changes under dynamic conditions. Moreover, rheology is a sensitive method for distinguishing structural changes, such as molecular weight, molecular weight distribution, branching, and cross-linking in polymers, and provides valuable insights into the degradation process. Some studies have reported the use of rheological analysis, specifically time-resolved rheometry, to investigate the thermal and thermomechanical degradation behaviors of polymers [18–27]. To the best of our knowledge, only a few studies have focused on monitoring the thermo-oxidative degradation of polyolefins by rheological measurements. Dordinejad et al. investigated the thermo-oxidative degradation behavior of linear low density polyethylene (LLDPE) by combining OIT and time-sweep test methods under air and nitrogen atmospheres [28]. They systematically evaluated the effects of antioxidant (Irganox® 1010 and Irgafos® 168) composition, temperature, and applied frequency on the oxidative stability of LLDPE. Their results showed that the combined use of primary and secondary antioxidants significantly improved thermal stability owing to synergistic effects. They also observed a considerable increase in storage modulus over time under air atmosphere and concluded that crosslinking and chain branching was the overall mechanism of polyethylene degradation in the presence of air at high temperature [28]. The time-sweep test enabled real-time monitoring of degradation and showed that the characteristic storage modulus remained stable in the presence of Irganox 1010, demonstrating its role as a long-term stabilizer. Drabek and Zatloukal studied the rheological behavior of virgin and thermally degraded branched polypropylene (PP) using rotational and Sentmanat extensional rheometers and gel permeation chromatography [29, 30]. They also employed four different constitutive equations, namely the Generalized Newtonian law, modified White-Metzner model, Yao and extended-Yao models to interpret the measured steady-state rheological data and describe structural changes during the thermal degradation of branched PPs. Koodehi and Koohi characterized the effect of three different commercial additives, antioxidants (Iraganox® 1010 and Irgafos® 168), carbon black, and nanoclay, on the thermal stability of high-density polyethylene (HDPE) by OIT analysis, rheological analysis, and melt flow index (MFI) measurement [31].

In this study, the effect of a natural antioxidant, *Silybum Marianum (SM)* extract, as a primary antioxidant that includes silymarin as an active phenolic compound, on the thermo-oxidative stability of low density polyethylene (LDPE) was investigated by OIT and OOT measurements and by monitoring the time-dependent rheological behaviors of the samples. The optimum SM extract loading amount was quantified based on the relationship between the compositional parameters and oxidation stability performance of the samples.

Materials and methods

Materials

The film-grade low density polyethylene (Petilen LDPE H2-21T) used in this study was supplied by Petkim. The LDPE used in this study includes no commercial or specific additives or agents such as antioxidants, anti-slips, anti-blocks, processing aids etc. *Silybum marianum* powder was supplied by Aksuvital Natural Products and Food Supplier Co. with a purity of min. 95%. Commercial-grade antioxidants, Irganox® 1010 and Irgafos® 168 (BASF) are also used as primary and secondary antioxidants, respectively. The chemical and physical properties of the antioxidant compounds used in this study have been reported previously [7].

Sample preparation

The SM extract was compounded with polyethylene via a melt blending method in an internal mixer operated at 75 rpm at 160 °C. Polyethylene melted in the chamber within 3 min and then the *Silybum marianum* extract was introduced and mixed for 7 min. The sample notations and composition are listed in Table 1. The film samples were prepared by compression molding in a hot press under a pressure of 50 kg/cm^2 for 2 min at 160 °C.

DSC analysis

The thermal properties and oxidation stability of the samples were characterized by performing different test procedures in a heat-flux-type differential scanning calorimeter (SII Nanotechnology ExStar, DSC6200) equipped with an electrical cooling device (Thermo-Scientific intracooler: EK90C/SII). Temperature and enthalpy calibrations of the instrument were conducted using indium (In), tin (Sn), and zinc (Zn) metals. The antioxidant performance of the PE compounds was characterized

Table 1 Notation and compositions of samples

Samples	Additive		Amount of additive (wt%)		
	Primer AO	Seconder AO	Primer AO	Seconder AO	Ratio (*P*/S)
LDPE	-	-	-	-	-
1.0 IRN	Irganox 1010		1.0	-	-
1.0 IRF		Irgafos 168		1.0	
1.0 SM	Silymarin	-	1.0	-	-
0.2 SM-0.2 IRF	Silymarin	Irgafos 168	0.2	0.2	1:1
0.2 SM-0.4 IRF	Silymarin	Irgafos 168	0.2	0.4	1:2
0.2 SM-0.6 IRF	Silymarin	Irgafos 168	0.2	0.6	1:3
0.5 SM-1.0 IRF	Silymarin	Irgafos 168	0.5	1.0	1:2
1.0 SM-1.0 IRF	Silymarin	Irgafos 168	1.0	1.0	1:1

by oxidative induction time (OIT) according to the modified conditions of ASTM D3895 and DIN EN ISO 11357-6 standards and oxidation onset temperature (OOT) analyses under isothermal and non-isothermal conditions, respectively.

In the OIT test, samples weighing 7–8 mg in an open aluminum pan were heated from 20 °C to 240 °C at a heating rate of 20 °C/min under an inert atmosphere with a flow rate of 100 mL/min and equilibrated at this temperature for 3 min. The furnace atmosphere was then automatically switched from N_2 to air at a flow rate of 100 mL/min and maintained at this temperature for 120 min. The onset of the oxidation exotherm was considered as the OIT value as “minute.”

In the OOT test, samples weighing 7–8 mg in an open aluminum pan were heated from 20 °C to 180 °C at a heating rate of 20 °C/min under an inert atmosphere at a flow rate of 100 mL/min and equilibrated at this temperature for two minutes. The furnace gas was automatically switched from N_2 to air at a flow rate of 100 mL/min at this temperature, and a second heating run was started from 180 °C to 300 °C at a heating rate of 5 °C/min under air flow. The onset temperature of the oxidation exotherm was considered as the OOT value.

Melt rheology tests

The thermo-oxidative degradation of the samples was also analyzed by melt rheology tests performed using a rotational rheometer (TA Instruments, Discovery HR-2) equipped with a convection heating chamber and 25 mm parallel plates with a gap distance of 1 mm.

Time-sweep tests were conducted by applying a constant strain (10%) within a linear viscoelastic region with a frequency of 1 Hz at 240 °C in air for 600 s.

Creep tests perfortmed out at 240 °C in air by instantaneously applying a shear stress of 50 Pa for 3 min. Creep tests were performed before and after the time sweep tests to evaluate the effect of thermorheooxidative degradation during the 600-second time sweep runs under air on the viscoelastic responses of the specimens. This strategy allowed us to compare the antioxidant effects of the additives and compositional dependence of the thermorheooxidative degradation.

Results and discussion

Properties of extract and film samples

The SM extract used in this study was characterized by determining its total phenolic content, total flavonoid content, and antioxidant activity according to the DPPH (2,2-diphenyl-1-picrylhydrazil) radical method and reported before [7].

Some physical properties of the films, such as (i) visual transparency and quantitatively measured transparency by UV-Vis spectrophotometry, (ii) colorimetric parameters and (iii) surface polarity by contact angle measurements, have been previously reported [7].

In the previous paper, it was shown that the *Silybum marianum* extract possessed a considerable antioxidant capacity for use as a natural, primary antioxidant additive in polyolefins due to the phenolic species in the extract; the introduction of *Silybum marianum* powder into polyethylene yielded highly transparent films but an increase in extract loading slightly induced the yellowing of films. It was also reported that the addition of *Silybum marianum* extract did not change the contact angle values of PE films and significantly improved the thermo-oxidative degradation stability of PE under a pure oxygen atmosphere at 210 °C.

In this study, the thermo-oxidative degradation behaviors of *Silybum marianum* extract loaded PE samples were examined in an air atmosphere considering the commercial polymer processing conditions.

Thermooxidative stability of samples

Figure 1 compares the OIT thermograms of the different groups of samples to those of LDPE. As seen in Fig. 1(a), LDPE and 1.0 wt% Irgafos 168 loaded sample were quickly oxidized when the furnace purge gas was switched to air at 240 °C thus, the OIT values of these samples were reported to be zero (Table 2). This result indicated that 1.0 wt% of phosphite-based secondary AO (Irgafos 168, IRF) cannot solely exhibit oxidative stability in air. On the other hand, phenolic compounds as primary antioxidants, such as Silybum marianum extract and Irganox 1010 (IRN) showed considerable antioxidant activity at this temperature. The OIT value of 1.0 SM was found to be 10.3 min. while 1.0 IRN exhibited much higher OIT value (> 85 min.) compared to 1.0 SM. It is well known that the OIT value of a polymer strongly depends on its temperature and oxygen concentration. This combined effect could be called as “thermo-oxidative stress” in the sample. In addition, compositional parameters such as chemical structure, antioxidant capacity, and loading amount of antioxidant additives are also primary factors affecting the thermooxidative stability of polymers. Although the thermo-oxidative test conditions are different from the standard OIT test (ASTM D3895 and DIN EN ISO 11357-6) in this study, it can also be concluded that the OIT values of 1.0 IRF and 1.0 SM will not be sufficient for commercial applications. However, only 1.0 wt% IRN addition provided significant thermo-oxidative stability to LDPE. However, it should be noted that primary (PAO) and secondary antioxidants (SAO) play crucial roles in scavenging and pacifying the oxygen species formed at high temperatures. Thus, PAO and SAO are always used together to obtain much better thermo-oxidative stability in commercial thermoplastics. Furthermore, lower PAO and SAO loadings might yield sufficient thermooxidative stability instead of using only 1.0 wt% PAO. This composition strategy also provides additional advantages such as transparency, good dispersion of additives, and cost of additives. Therefore, the effect of compositional variation on the OIT and OOT values of the samples was investigated in this study by varying the PAO: SAO ratio.

Figure 1(b) illustrates the OIT thermograms of the samples loaded with various amounts of SAO and a particular amount of PAO (0.2 wt%). The inset shows an exponential improvement in the OIT values of the samples as a function of the PAO: SAO ratio. A lower IRF amounts (0.4 or 0.6 wt%) retarded oxidation significantly in the case of loading with 0.2 wt% of SM while 1.0 wt% of IRF did not yield an oxida-

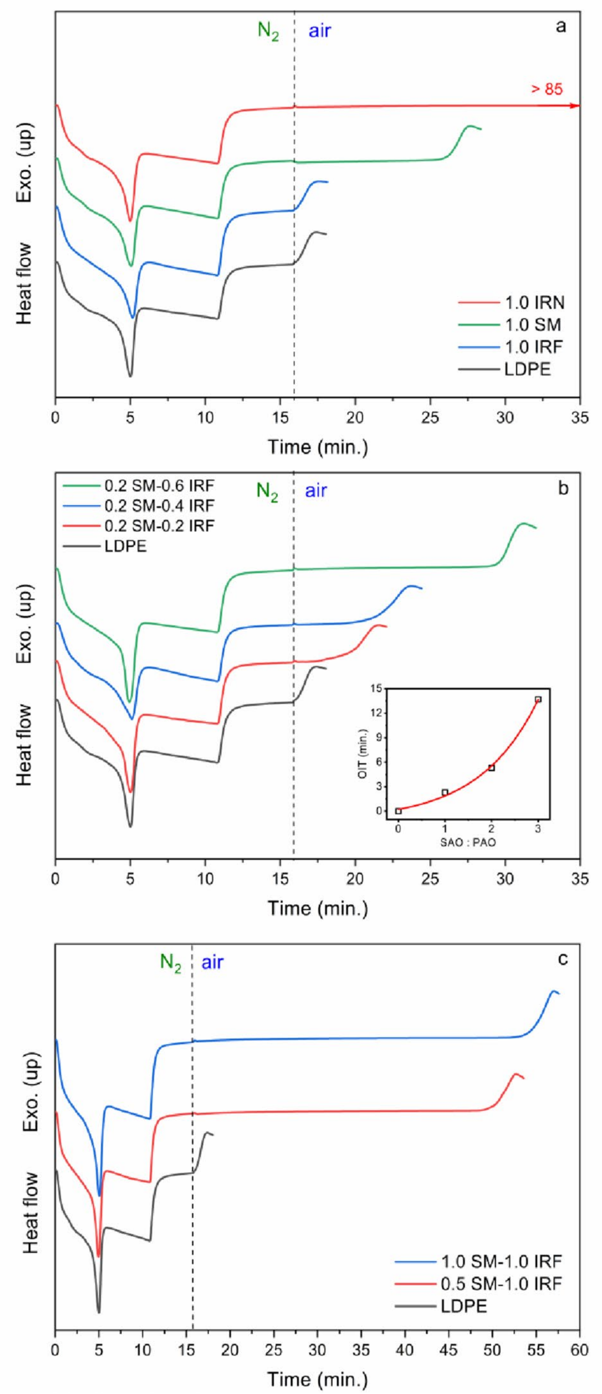

Fig. 1 Comparing the OIT thermograms of LDPE and compounds having (**a**) a constant amount (1.0 wt%) of PAOs and SAO loaded specimens, (**b**) a constant SM of 0.2 wt% with different IRF amounts and (**c**) a constant IRF of 1.0 wt% with different SM amounts tested at 240 °C under air flow

Table 2 OIT and OOT values of samples

Samples	OIT@240°C (min.)	OOT (°C)
LDPE	0	201.0
1.0 IRN	>85	276.8
1.0 IRF	0	219.8
1.0 SM	10.3	248.0
0.2 SM-0.2 IRF	3.6	234.0
0.2 SM-0.4 IRF	5.3	237.0
0.2 SM-0.6 IRF	13.7	250.3
0.5 SM-1.0 IRF	34.2	258.2
1.0 SM-1.0 IRF	38.4	271.0

tive stability. This result indicated the synergistic effect of PAOs and SAOs and their efficient mechanism of action, as previously reported [32].

Figure 1(c) compares the antioxidant activity of samples loaded with higher amounts of PAO and SAO. These samples exhibited OIT values greater than 30 min at 240 °C. It can be expected that these compositions can resist oxidation for more than 30 min during standard measurements (210 °C). The synergistic effect of PAO and SAO can be clearly inferred from the exponential increase in the OIT values. For example, 2.5 times increase in antioxidant levels from 0.2 PAO-0.4 SAO to 0.5 PAO-1.0 SAO improves the OIT value about 6.5 times. Similarly, 5.0 times increase in antioxidant levels from 0.2 PAO-0.2 SAO to 1.0 PAO-1.0 SAO improves the OIT value about 10.7 times.

Figure 2 shows the oxidation onset temperature (OOT) thermograms of LDPE and different groups of samples. It was found that the OOT of LDPE at 201.0 °C under non-isothermal oxidative conditions in air. OOT values of antioxidant loaded samples were found to be 219.8, 248.0, and 276.8 °C for the 1.0 IRF, 1.0 SM, and 1.0 IRN, respectively. This result implied that the oxygen capturing performance of antioxidants increased in the order of IRF < SM< IRN at a particular loading amount. The effect of compositional variations, such as the PAO: SAO ratio, on the OOT values of the samples is shown in Fig. 2(b). It was found that doubling SAO amount from 0.2 wt% to 0.4 wt% (SAO: PAO ratio of 2) only improved the OOT value as 3 °C but, increasing the SAO: PAO ratio up to 3 significantly enhanced the OOT value. This finding demonstrates that the SAO: PAO ratio is an important compositional parameter for determining the thermooxidative stability of polyolefins. This result was also verified for higher PAO and SAO loadings as shown in Fig. 2(c); however, in this case, the SAO (IRF) amount was kept constant at 1.0 wt%. It was found that these samples, which included relatively high amounts of antioxidants, showed sufficiently high oxidation stability.

Thermorheooxidative stability of samples

Figure 3 illustrates the time-sweep curves of the different groups of samples. It is well known that the time sweep test is a perfect tool for monitoring variations in the rheological behavior of a specimen with time depending on chemical and/or physical interactions or changes. As shown in Fig. 3(a), the G' of LDPE readily increased within 10 min. This behavior clearly implies that the thermooxidative degradation

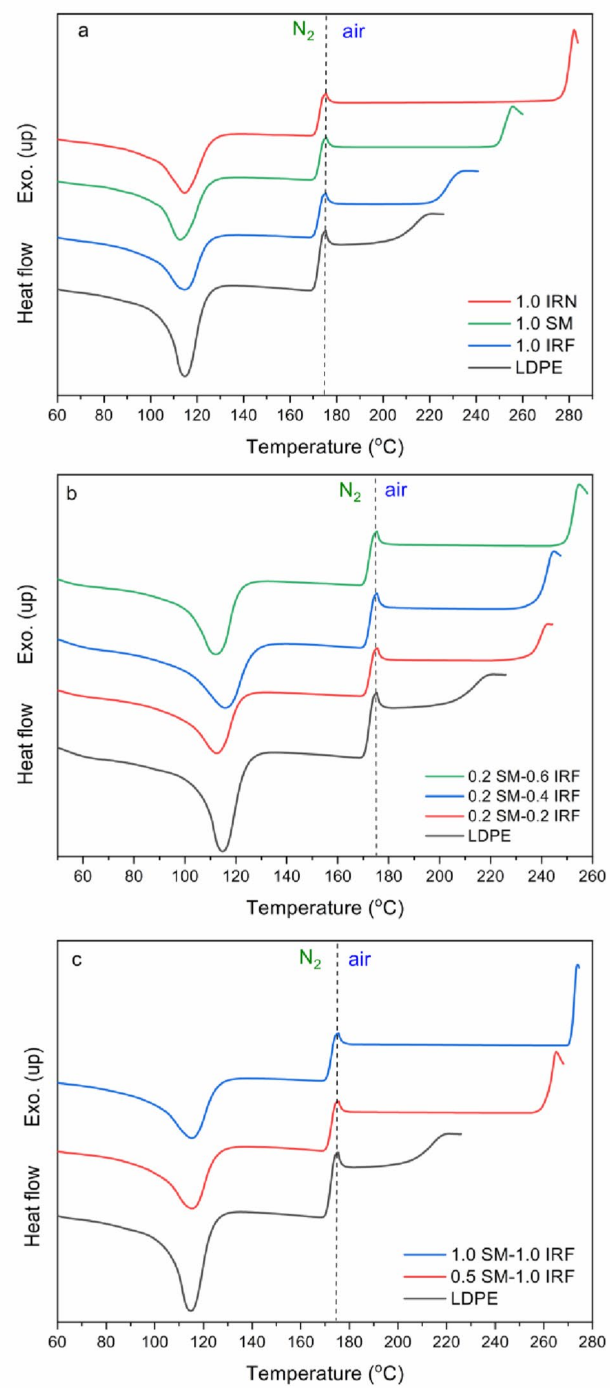

Fig. 2 Comparing the OOT thermograms of LDPE and compounds having (**a**) a constant amount (1.0 wt%) of PAOs and SAO loaded specimens, (**b**) a constant SM of 0.2 wt% with different IRF amounts and (**c**) a constant IRF of 1.0 wt% with different SM amounts tested under air flow

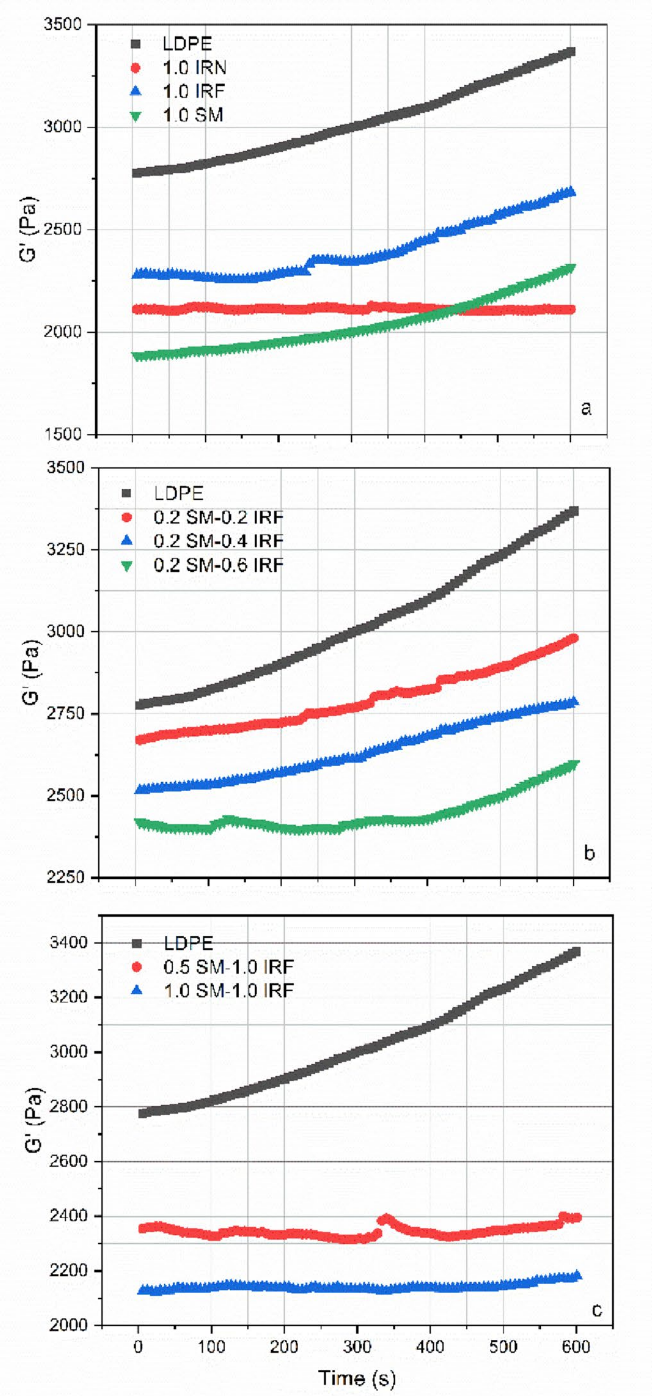

Fig. 3 Time sweep curves of LDPE and compounds, (**a**) a constant amount (1.0 wt%) of PAOs and SAO loaded specimens, (**b**) a constant SM of 0.2 wt% with different IRF amounts and (**c**) a constant IRF of 1.0 wt% with different SM amounts tested under air flow

of polyethylene proceeded toward crosslinking, as reported previously (Dordinejad et al., 2018). This observation also indicated that the slope of the increasing trend of the G' curve could be used to characterize the structural changes in the sample as a result of thermooxidative degradation. Samples 1.0 SM and 1.0 IRF exhibited similar increasing trends in the G' curve, whereas 1.0 IRN showed a plateau behavior and no change in G' within 10 min. This result is consistent with the OIT and OOT analysis of 1.0 IRN and implies that the sole use of 1.0 wt% of IRN inhibits thermooxidative degradation of LDPE exposed to dynamic shearing under air.

Figure 3(b) compares the time sweep curves of LDPE and compounds including a constant SM of 0.2 wt% with different IRF amounts. The slopes of the antioxidant-loaded samples are lower than that of the LDPE. The 0.2 SM-0.6 IRF sample exhibits a plateau up to 350 s, after which G' begins to increase. Figure 3(c) shows the time-sweep curves of the compounds loaded with higher amounts of SM and IRF. Introducing higher amounts of PAO and SAO yielded a steady rheological behavior and did not exhibit an increase in G' as observed for other compounds. This behavior can be attributed to the effective protection of 0.5 wt% Silybum marianum extract loaded with a secondary antioxidant. The SAO loading can be the same as the amount of SM or doubled. It can be concluded that both formulations can be used as thermally stable compounds for thermorheooxidative stress on polyethylenes during melt processing. LDPEs can be processed within a broad processing window, roughly in the range of 150–200 °C, and are exposed to various shear conditions in conventional melt processing equipment such as compounders, kneaders, and extruders. The process conditions can vary depending on the structural and molecular features of the polyethylenes. The melt flow index (MFI) and melt viscosity values of different grades of PEs are considered as the main and distinctive parameters for processing operations. Low MFI grades are generally processed at higher temperatures than high MFI grades because an increase in temperature results in a reduction in the melt viscosity of the thermoplastics. Rheological measurements conducted in this study confirmed that a SM loading of 0.2 or 0.5 wt% provided sufficient oxidation stability in polyethylene for, at least 5 min at 240 °C under air when supported by introducing two- or three-fold of secondary antioxidants. It can be concluded that such a stability time is longer than the residence time of polymer melts, approximately in the range of 1–4 min from the melting zone to die, in processing devices. It should also be noted that the rheological measurements were performed at a higher temperature than the conventional processing temperatures of polyethylenes; thus, the thermorheooxidative stability times obtained at 240 °C are much longer than 5 min in the industrially applied processing window. Based on the aforementioned findings and relationships, it can also be concluded that these antioxidant packages, including SM and IRF, protect polyethylene, probably for decades, against oxidation under ambient conditions.

Figure 4 reports the creep curves of different groups of samples before and after 10-minute time sweep tests depending on the compositional variations.

In this study, the melt state creep behaviors of the samples were used to assess the effect of structural changes (e.g., chain scission or crosslinking/branching due to thermal degradation) during shearing under an oxidative atmosphere in a time sweep test on the rheological response of the samples. All samples were grouped in these curves with a classification similar to that in the previous figures. As seen in

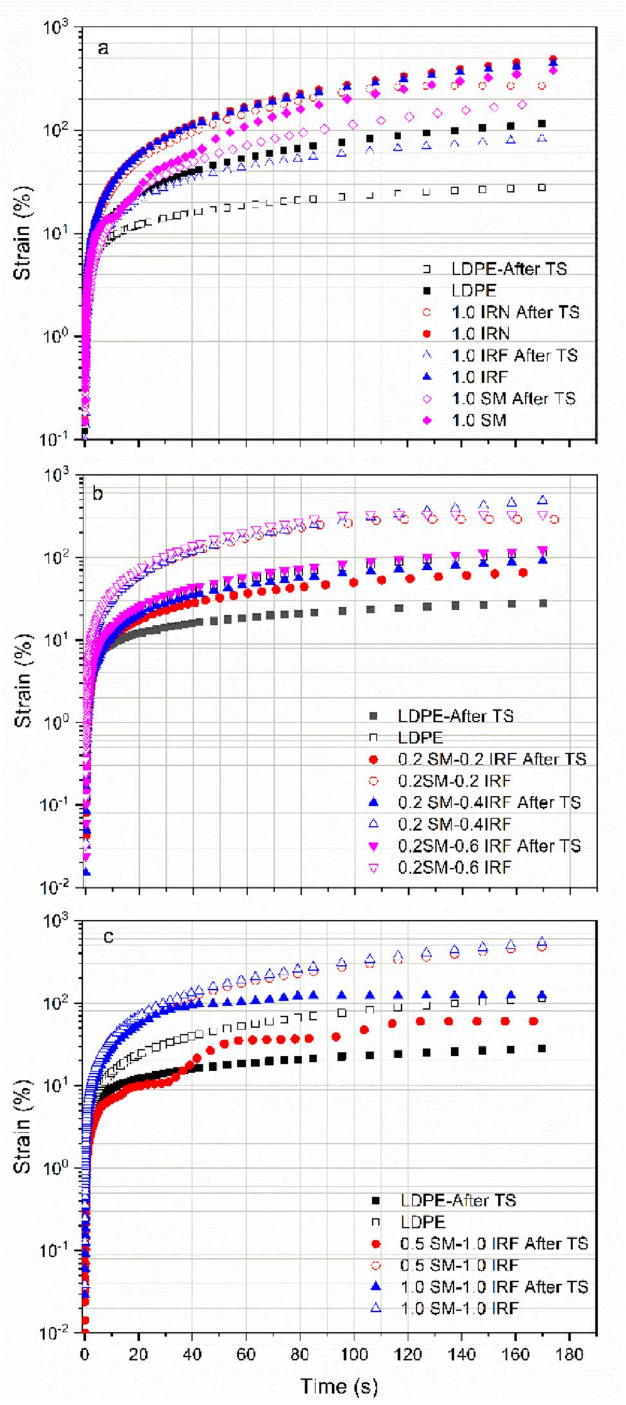

Fig. 4 Comparing the melt state creep curves of samples (@240°C) before and after time sweep

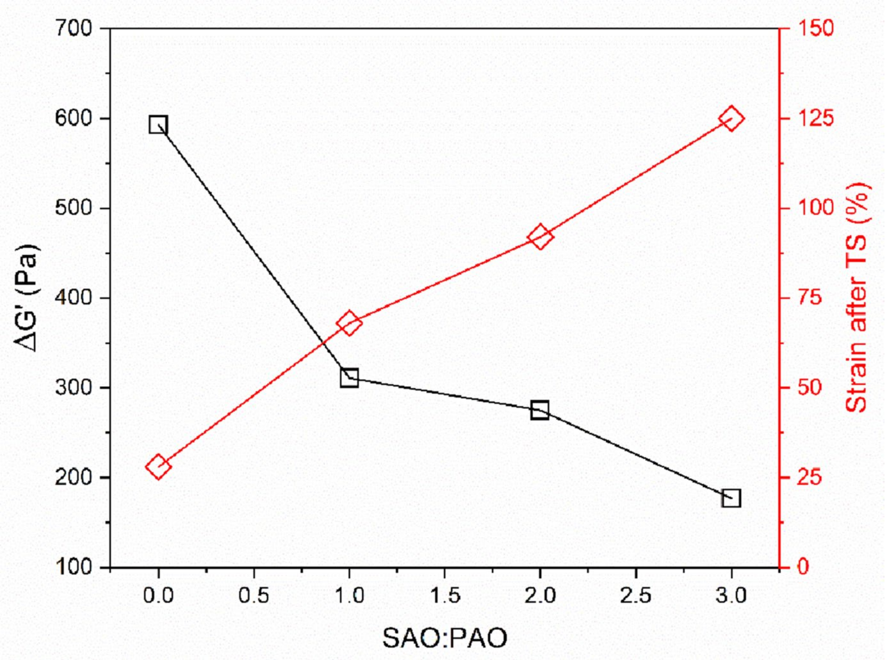

Fig. 5 Dependence of experimentally measured thermorheooxidative parameters on SAO: PAO ratio at 240 °C

these figures, the total creep strain of LDPE containing no antioxidants dramatically decreased after the time sweep run. The decrease in creep deformation after a thermorheooxidative shearing step can be explained by a decrease in creep compliance [J (1/Pa), the reciprocal of storage modulus (G')], and an increase in melt viscosity. It is obvious that shearing of "non-AO LDPE" in oxidative conditions lead to formation of crosslinking and increase in melt viscosity resulting lower deformation. The gap in the total creep deformation values of the samples before and after the time sweep can be used to quantify the level of structural change. It was found that all PAO and SAO loaded samples exhibited higher creep deformations than thermally degraded LDPE (LDPE-After TS), as shown in Fig. 3(b) and (c), and the gap between the two cases before and after TS decreased with the increasing amount of AO. This finding confirmed that the thermooxidative stability of the AO package formed SM and IRF.

Figure 5 shows the changes in two simple thermooxidative parameters determined by the time sweep and creep tests as a function of the SAO: PAO ratio.

The parameter ΔG' represents the difference in the storage modulus values at the starting and end points of the time sweep curves. A lower ΔG' value corresponds to a smaller change in the structural properties and better protection against thermooxidative degradation. The variation in G' significantly decreases with increasing SAO: PAO ratio. This relationship indicates that low amounts of PAO and SAO can exhibit a fair thermooxidative protection performance when natural phenolic PAO is supported by a sufficient amount of SAO. It is also seen in Fig. 5 that the creep strain (%) values of this group of samples significantly improved with increasing SAO: PAO ratio. An increase in creep strain as a function of antioxidant amount indicates that less crosslinking developes in the polyethylene structure during the time sweep test because it is well known that the creep strain is inversely proportional to the degree of crosslinking.

Conclusion

This study investigated the utilization of *Slybum marianum* (SM) extract as a natural and sustainable primer antioxidant with a phenolic compound, silymarin, in polyolefins. The antioxidant performance of the SM extract was quantified by classical calorimetric analysis using DSC and time-dependent melt rheology tests conducted in an oscillatory melt rheometer in air atmosphere. It was found that SM extract exhibited high antioxidant performance as a radical scavenger and yielded sufficiently high thermal stability when supported by two- or three-fold (wt%) of a secondary antioxidant. It was found that the thermal degradation of LDPE led to the formation of crosslinking, based on the rheological observation of a dramatic increase in G' with time in this study, in consistent with the previously reported studies. But the addition of SM and SAO significantly suppressed or annihilated the increase in G' owing to efficient oxygen capture and radical scavenger at high temperatures. A new and very-fast (3-minute run) experimental methodology, monitoring the melt state creep deformations as a function of compositional variations, in addition to classical time-dependent measurements was also suggested to assess and compare the thermooxidative behaviors of polyolefin compounds. Consequently, it was concluded that SM extract can be successfully used in polyethylene compounds as a primary antioxidant and exhibits thermooxidative stability for a long time at the melt processing temperature of polyethylene.

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Author contributions Mine Begum Alanalp: Methodology, Formal analysis, Investigation; Gizem Şıdım: Resources, Formal analysis, Data curation; Esra Mirmahmutogullari: Methodology, Visualization, Investigation; Ozlem Pınar: Methodology, Visualization, Formal analysis, Ali Durmus: Conceptualization, Writing - Original Draft, Writing - Review & Editing, Supervision, Project administration.

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Data availability Not applicable.

Declarations

Competing interests The authors declare no competing interests.

Ethical approval Not applicable.

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