




# Utilization of *Silybum marianum* extract as a high-performance natural antioxidant for polyethylene

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## ABSTRACT

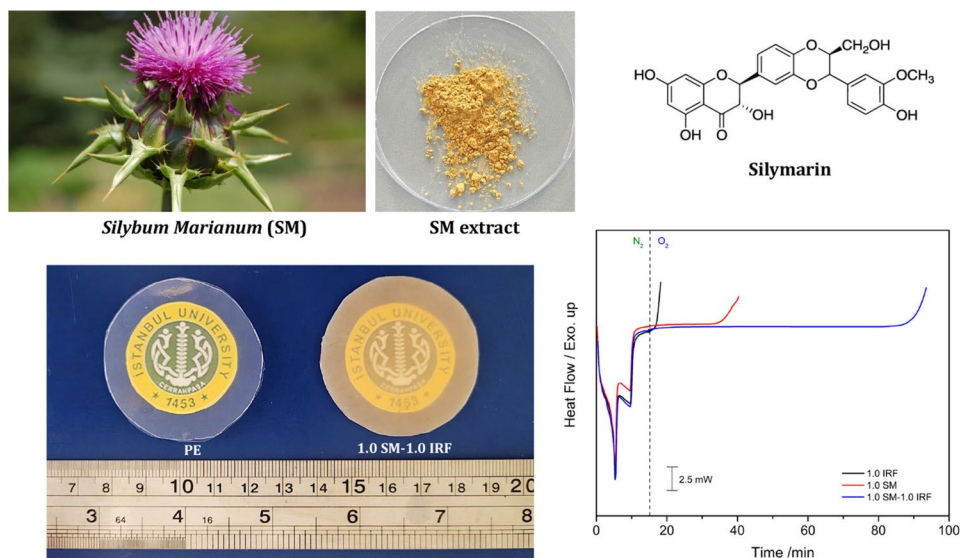
In this study, *Silybum marianum* extract powder was introduced into low density polyethylene (LDPE) as a primary polyphenolic antioxidant via melt blending method. Two synthetic and commercial polyphenol- and phosphite-based antioxidants (Irganox® 1010 and Irgafos® 168) were also used for comparing the antioxidant efficiency and performance of *Silybum marianum* extract with commercial ones. A systematic formulation study was achieved by varying the amount of *Silybum marianum* extract in the range of 0.1–1.0 wt% and the primary:secondary antioxidant ratio. Antioxidant efficiency of *Silybum marianum* extract was quantified with the oxygen induction time (OIT) and oxidation onset temperature values determined by thermal analysis in a differential scanning calorimeter depending on the compositional variations. Some physical properties of specimens such as transparency, color coordinates, contact angle, and degree of crystallinity values were also examined. It was found that 0.2 wt% of *Silybum marianum* extract and 0.2 wt% of Irgafos® 168 loaded sample showed an OIT value of 22 min. at 210 °C that could be regarded as a very successful commercial potential. Increasing amount of *Silybum marianum* extract and Irgafos® 168 significantly improved the oxidation stability of polyethylene under isothermal and non-isothermal conditions. It was also found that introducing *Silybum marianum* extract, even the loading content of 1.0 wt%, did not alter the transparency and physical properties of LDPE. It has been concluded that *Silybum marianum* extract can be successfully used as a natural antioxidant in polyolefins and these samples could be used in packaging film applications.

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## GRAPHICAL ABSTRACT



## Introduction

Polyolefins are the most extensively used thermoplastics in plastic industry and human life because of their several superior structural and physical properties such as simple and non-polar structure, flexibility, chemical and biological inertness, long-term durability, easy and versatile processability with commercial processing operations like extrusion, compounding, injection molding, rotational molding, film casting or blowing, etc., compared to other commodity plastics. Polyolefins, mainly polyethylenes, polypropylenes, and their copolymers, have been used to manufacture plastic parts in large number of applications such as packaging films, sheets, containers, and boxes, automotive parts, households, fibers, etc., for a long time and comprised almost a half of plastic production and consumption. Moreover, they can be safely used in food contact applications and medical parts such as catheters, implants, non-absorbable sutures, containers, clear bags, prescription bottles, disposable syringes, connectors, and finger joint prostheses because they are highly resistant to strong acids, alkaline liquids, organic solvents and aggressive conditions. They could also be sterilized in some cases [1].

Polyolefin chains consist of repeating unit of simple aliphatic hydrocarbons and having a completely saturated backbone. Thus, polyolefins are generally regarded as highly stable thermoplastics against

thermal and thermo-oxidative effects compared to other thermoplastics such as halogenated polymers (e.g., PVC and PVDF), polyesters (e.g., PET, PBT, PLA, etc.) and polyamides. However, polyolefins might be negatively influenced from some thermal and environmental effects which could deteriorate their structures and physical properties. Structural deteriorations are mainly initiated by chain scission reactions when they are exposed to high temperatures. Detecting and quantifying structural deteriorations in polyolefins are analytically very difficult phenomena. This effect is generally appeared with a loss of mechanical properties such as elongation, flexibility, tensile strength and the change in physical appearance and slowly growing destructive failures of materials [2].

Regarding the degradative environments exposed by polyolefins, degradation types are classified as thermal, thermo-oxidative, photo-oxidative, ozone-induced, mechanochemical, catalytic, and biodegradation [3]. Thermo-oxidative degradation is the most common degradation type that may occur during processing operations and service life of parts due to the presence of oxygen and elevated temperature conditions [4]. Therefore, polyolefins must be stabilized against oxidative degradation to maintain its chemical, physical, and mechanical properties for a long time under oxidative conditions. Specific additives, consisting of a combination of synthetic primary and secondary antioxidants are often used to inhibit

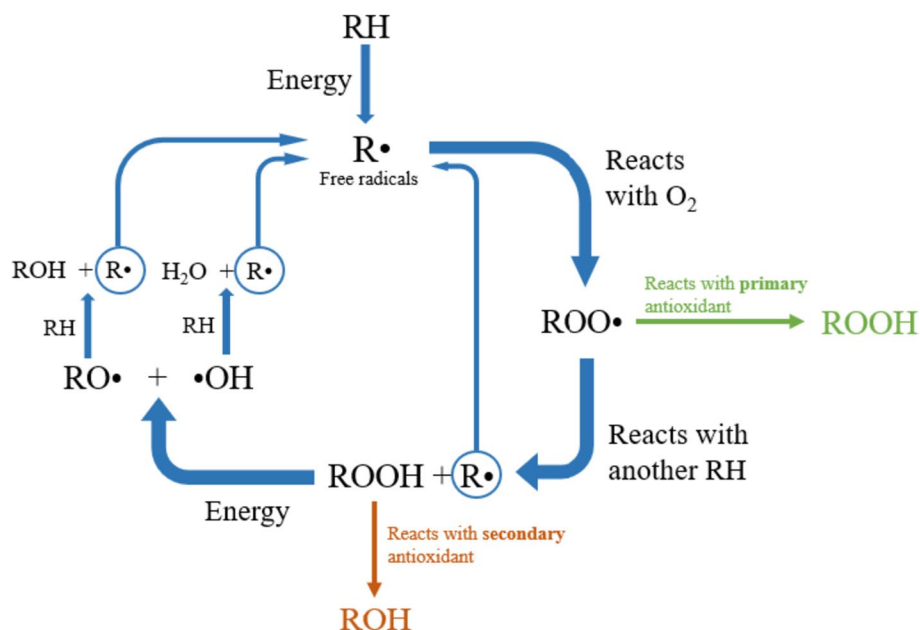
the degradation of polyolefins. Primary and secondary antioxidant classification is based on their functionality. The function of primary antioxidants, known as “radical scavengers”, is to interrupt the oxidation or oxidative degradation by rapidly reacting with peroxy free radicals. The majority of primary antioxidants used in polyolefins is sterically hindered phenols. Secondary antioxidants, frequently called as “hydroperoxide decomposers” decompose hydroperoxides (ROOH) that may generate free radicals during oxidation to yield non-radical, non-reactive and thermally stable products, also react with carbon-centered, peroxy and oxy radicals. Phosphorus (e.g., phosphates, phosphonites, phosphites) or sulfur-containing compounds could be used as secondary antioxidants for obtaining synergistic effect by combining with primary antioxidants [5].

The oxidative degradation of polyethylene is divided into three stages: initiation, propagation, and branching. After the initiation of oxidation, each reaction can promote other reactions. One product can be reactant for another reaction, thus the oxidation process is referred as “autoxidation”. The simplified oxidation process and the roles of primary and secondary antioxidants are schematized in Fig. 1 for polyethylene as model polyolefin.

The initiation stage is basically the primary event in the autoxidation of polyethylene and results in radical formation. Then the propagation step begins with

the introducing of oxygen into the process. The alkyl radical ( $R\cdot$ ) reacts with oxygen and leads to intermediate unstable peroxy radicals ( $POO\cdot$ ) that will subsequently exchange a hydrogen atom from a different polymer molecule to yield a hydroperoxide (ROOH) and another alkyl radical. In the presence of oxygen, the generation of unstable peroxy is extremely fast and requires almost no energy. Branching consists of numerous reactions that involve the generation of new radical species from each hydroperoxide usually ending with the formation of alkyl radicals. As shown in the scheme, secondary phosphorus antioxidants react with hydroperoxide (ROOH) and yield non-radical, non-reactive and thermally stable products to interrupt the degradation reactions while primary phenolic antioxidants mainly take a role in the propagation steps by intercepting and reacting with free radicals faster than the substrate [6]. The efficiency of stabilization depends on the number of hydroxyl groups and the nature of substituents at the ortho- and para-positions to the phenolic  $-OH$  group of primary antioxidants. On the other hand, the synergistic effect of phenol/phosphorous antioxidant combinations is also a key parameter of polyethylene stabilization due to the autocatalytic free radical chain reaction mechanism. Additionally, the solubility and the mobility of both primary and secondary antioxidants in polyethylene should be taken into account for the efficiency to maximize the stabilization [7–9].

**Figure 1** Reaction scheme illustrating major reactions of the autoxidation and stabilization mechanism of polyethylene ( $R$ =polyethylene backbone).



The use of synthetic phenol/phosphorous antioxidant combinations is a well-established industrial practice for polyolefins because of their relatively low cost and high antioxidant efficiency. Nevertheless, regarding their possible hazards and toxicity effects on human health and the environment as well as other side effects such as carcinogenesis caused by the reaction of synthetic antioxidants, replacing of synthetic phenolic antioxidants with natural compounds has attracted a considerable scientific and industrial interest in recent years [10, 11]. A large number of plants, vegetables, and fruits that contain functional and renewable compounds showing antioxidant activity can be used as natural sources for antioxidant additives [12]. These natural antioxidants have been frequently used in foods and nutraceutical and pharmaceutical formulations [13–15]. In recent years, using of natural antioxidants such as various flavonoids [16–19], carotenoids [20, 21], caffeic acid [22], ellagic acid [23], phytic acid [24], curcumin [25], other natural phenols [26–28], natural lignocellulosic fillers and food industry wastes or side products [29], and phenolic polymers including lignin [30, 31], algae [32], chitosan-based biomass [33] in thermoplastics and rubbers have been studied and reported that these compound would promise considerable success for thermo-oxidative degradation. Thbayh and Fiser computed the antioxidant potential of several organic compounds and curcumin by calculating and comparing their bond dissociation enthalpy (BDE), ionization potential (IP), proton dissociation enthalpy (PDE), proton affinity (PA), and electron transfer enthalpy (ETE) values [34].

*Silybum marianum* (milk thistle) is a medicinal and herbal-remedy plant containing flavonoid mixture and obtained from the Asteraceae-family plants cultivated in the region from Southern Europe to Northern Africa. Surai reviewed well the properties of silymarin as a natural antioxidant [35]. The most important flavonoids are the flavonolignans which are known as the silymarin complex. Surai reported that *Silybum marianum* (SM) extract contains approximately 65–80% flavonolignans (silybin A and silybin B, isosilybin A, isosilybin B, silychristin and silydianin), with small amounts of flavonoids, and approximately 20–35% of fatty acids and polyphenolic compounds. They are mainly used for their hepatoprotective activity. Silymarin can promote liver cell regeneration, reduce blood cholesterol and help in the prevention of cancer.

This work investigates the using of *Silybum marianum* extract which includes silymarin, as a primary

phenolic antioxidant in low density polyethylene (LDPE). A systematic composition study was performed using *Silybum marianum* extract and commercial phenolic antioxidant (Irganox® 1010) and a phosphite antioxidant (Irgafos® 168) to determine optimum loading amount and quantify relationship between the compositional parameters and oxidation stability performance.

## Material and methods

### Materials

A film grade low density polyethylene (Petilen LDPE H2-21 T) used in this study was kindly supplied from Petkim. The LDPE used in this study includes no commercial and specific additive or agent such as antioxidant, anti-slip, and anti-block, processing aid, etc. *Silybum marianum* powder was kindly supplied by Aksuvital Natural Products and Food Supplier Co. with a purity of min 95%. Folin–Ciocalteu reagent, gallic acid, and quercetin standards, aluminum chloride hexahydrate, methanol, and sodium carbonate were obtained from Sigma-Aldrich. All other chemicals were analytical purity. Commercial grade antioxidants, Irganox® 1010 and Irgafos® 168 by BASF are also used as primary and secondary antioxidants, respectively. Chemical and physical properties of antioxidant compounds used in this study are listed in Table 1.

### Characterization of natural antioxidant


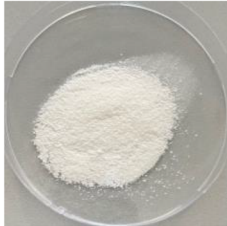

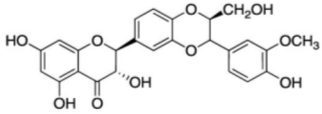
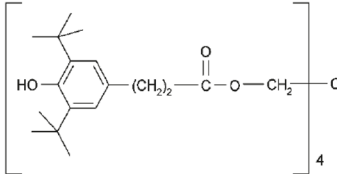
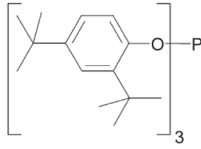
#### Determination of total phenolic content

Total phenolic content of *Silybum marianum* powder was determined by the Folin–Ciocalteu method [36] and reported as gallic acid equivalents (GAE) by used gallic acid standard curve measured at a wavelength of 765 nm in a UV–Vis spectrophotometer (Shimadzu UV1800).

#### Total flavonoid content

Total flavonoid content of *Silybum marianum* powder was colorimetrically determined and reported as quercetin equivalents (QE) [37]. The extract (1 mL) was mixed with 1 mL of AlCl<sub>3</sub> solution (20 g/L) in ethanol

**Table 1** Chemical and physical properties of antioxidant compounds used in this study

|                     | Silymarin   | Irganox® 1010  | Irgafos® 168  |
|---------------------|---|--|---|
| Classification      | Phenolic  | Phenolic   | Phosphite   |
| Physical appearance |  |  |  |
| Function            | Primary antioxidant   | Primary antioxidant  | Secondary antioxidant   |
| Source              | Natural   | Synthetic  | Synthetic   |
| MW (g/mol)          | 482.4   | 1178   | 646.9   |
| Chemical structure  |  |  |  |

and diluted to 25 mL with ethanol. After the mixture was kept at 20 °C for 40 min, the absorbance was measured at a wavelength of 415 nm by spectrophotometer device. A drop of acetic acid was added to 1 mL of extract, then the volume was diluted to 25 mL with ethanol and blank samples were prepared. A quercetin calibration curve was also used for flavonols prepared by mixing quercetin ethanol solutions with 2 mL AlCl<sub>3</sub> (20 g/L) and 6 mL sodium acetate (50 g/L). After 2.5 h of incubation at 20 °C, the absorbance value of the mixture was read at 440 nm with a UV–Vis spectrophotometer. The same procedure was performed with 2 mL of plant extract instead of quercetin solution. The content of flavonols was finally expressed as QE.

### Antioxidant activity

Antioxidant activity of *Silybum marianum* powder was determined using the DPPH (2,2-diphenyl-1-picrylhydrazil) radical method [38]. In this method, a 0.06 mmol of DPPH reagent solution in methanol was prepared. 300 µL of extract solution and 5700 µL of DPPH solution were mixed in a 10 mL test tube. The mixture was incubated for 30 min at room temperature in dark. The absorbance of the reaction mixture

against methanol was measured at 517 nm in a UV–Vis spectrophotometer. The antioxidant activity was calculated as:

$$\text{Antioxidant activity (\%)} = \left[ \frac{(A_c - A_t)}{A_c} \right] \times 100 \quad (1)$$

where  $A_c$  is the absorbance value of control sample at  $t=0$  and  $A_t$  is the absorbance value of antioxidant sample at  $t=60$  min. Ascorbic acid solutions with the concentrations of 100, 200, 300, 400 and 500 µg/mL were used as the control solutions in the analysis. The capacity of ascorbic acid solution to inhibit the DPPH radical was determined as 88%.

### Sample preparation

*Silybum marianum* extract was compounded with polyethylene via melt blending method in an internal mixer operated at 75 rpm at 160 °C. Polyethylene granules were melted in the chamber within 3 min then the *Silybum marianum* extract introduced and mixed for 7 min. Sample notations and composition are defined in Table 2. Films samples were prepared by compression molding method in a hot press under the pressure of 50 kg/cm<sup>2</sup> applied for 2 min at 160 °C.

**Table 2** Notation and compositions of samples

| Samples         | Additive     |              | Amount of additive (wt%) |              |             |
|-----------------|--------------|--------------|--------------------------|--------------|-------------|
|                 | Primary AO   | Secondary AO | Primary AO               | Secondary AO | Ratio (P/S) |
| LDPE            | –            | –            | –                        | –            | –           |
| 1.0 IRF         | –            | Irgafos 168  | –                        | 1.0          | –           |
| 1.0 SM          | Silymarin    | –            | 1.0                      | –            | –           |
| 0.1 IRN-0.2 IRF | Irganox 1010 | Irgafos 168  | 0.1                      | 0.2          | 1:2         |
| 0.2 IRN-0.2 IRF | Irganox 1010 | Irgafos 168  | 0.2                      | 0.2          | 1:1         |
| 0.1 SM-0.2 IRF  | Silymarin    | Irgafos 168  | 0.1                      | 0.2          | 1:2         |
| 0.2 SM-0.2 IRF  |              |              | 0.2                      | 0.2          | 1:1         |
| 0.2 SM-0.4 IRF  |              |              | 0.2                      | 0.4          | 1:2         |
| 0.2 SM-0.6 IRF  |              |              | 0.2                      | 0.6          | 1:3         |
| 0.33 SM-1.0 IRF |              |              | 0.33                     | 1.0          | 1:3         |
| 0.5 SM-1.0 IRF  |              |              | 0.5                      | 1.0          | 1:2         |
| 1.0 SM-1.0 IRF  |              |              | 1.0                      | 1.0          | 1:1         |

### Characterization of films

Some physical properties of films were characterized by (i) observing visual transparency and (ii) quantifying transparency by measuring in a UV spectrophotometer, (iii) determination of colorimetric parameters by a spectrophotometer (ColorFlex EZ), and (iv) evaluating surface polarity by contact angle measurements with a KSV Attension®, Theta Lite Goniometer device using the pendant drop method (5  $\mu$ L of water) taken at least 5 points on the film sample.

Thermal properties and oxidation performances of films 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. Antioxidant performances of PE compounds were characterized by oxidative induction time (OIT) according to the ASTM D3895 and DIN EN ISO 11357-6 standards and oxidation onset temperature (OOT) analyses under isothermal and non-isothermal conditions, respectively.

In OIT test, samples weighing 7–8 mg in an open aluminum pan were heated from 20 to 210  $^{\circ}$ C with a heating rate of 20  $^{\circ}$ C/min under inert atmosphere ( $N_2$  with a flow rate of 100 mL/min) and equilibrated at this temperature for 3 min. and kept at this temperature for 120 min. Onset of oxidation exotherm was considered as the OIT value as “minute”.

In OOT test, samples weighing 7–8 mg in an open aluminum pan were heated from 20 to 180  $^{\circ}$ C with a heating rate of 20  $^{\circ}$ C/min and equilibrated at this temperature for a minute under inert atmosphere ( $N_2$  with a flow rate of 100 mL/min). Then the furnace gas was automatically switched from  $N_2$  to pure oxygen ( $O_2$  with a flow rate of 100 mL/min.) at this temperature and a second heating run was started from 180 to 300  $^{\circ}$ C with a heating rate of 5  $^{\circ}$ C/min under oxygen flow. Onset temperature of oxidation exotherm was considered as the OOT value.

Degree of crystallinity ( $X_c$ , %) values of samples were also determined using the following equation;

$$\%X_c = \frac{\Delta H_m}{\Delta H_m^0(1 - \alpha)} \times 100 \quad (2)$$

where  $\Delta H_m$  is the melting enthalpy of samples (J/g),  $\Delta H_m^0$  is the melting enthalpy value of 100% crystalline form of polyethylene (293 J/g) [39], and  $\alpha$  is the weight fraction of additive(s) by taking into account of OIT heating runs of samples.

## Results and discussion

### Properties of natural antioxidant

The TPC, TFC, and AA values of *Silybum marianum* extract are listed in Table 3. Akbel et al. reported the TPC value of 56 mgGAE/g, TFC value of 85 mgQE/g, and DPPH value of 77.7% for the *Silybum marianum* extract [40]. Caglayan found these parameters

**Table 3** Physicochemical properties of natural antioxidant

| TPC(GAE, mg/g dry sample) | TFC (QE mg/g dry sample) | AA inhibition (%) |
|---------------------------|--------------------------|-------------------|
| 80.9                      | 111.2                    | 79.2              |

to be 74 mgGAE/g, 98 mgQE/g, and 79.23% for the TPC, TFC, and DPPH of *Silybum marianum* [41]. In another study, Akhtar et al. reported the TPC value of 21.79 mgGAE/g, TFC value of 129.66 mgQE/g, and DPPH value of 63.8% [42]. It is seen that our antioxidant parameters are very consistent with the previously reported values. According to the literature, there is a linear correlation between the antioxidant activity and phenol and flavonoids contents of medicinal plants. It can be concluded that the antioxidant capacity of *Silybum marianum* extract mainly depends on the content of phenolic species present in the powder.

### Physical properties of films

Figure 2 shows the visual transparency of PE films having different compositions. It is seen that all samples yield transparent films but the PE can be regarded as the most transparent film on the first sight. It can also be inferred that the increasing amount of additives slightly improves the haziness and yellowishness of films, particularly by comparing the appearances of specimen 2 and 8. But, we also conclude that such

a slight increase in haziness cannot be regarded as a technical handicap for the commercial application potential of specimens. An interesting finding is that the color of specimen 9 which only includes 1.0 wt% of IRF is not yellowish compared to *Silybum marianum* loaded films. This result clearly implies that the *Silybum marianum* powder slightly induces the yellowing of films.

Figure 3 compares the light transmission of representative specimens analyzed in a UV–Vis spectrophotometer as a function of composition. It should be noted that the thicknesses of film specimens were approximately  $100 \pm 10 \mu\text{m}$  therefore it can be accepted that the UV spectrums were not influenced by the variation in thickness. It should also be noted that degree of crystallinity ( $X_c\%$ ) values of samples were found to be in the range of 28–34% (DSC melting endotherms are not shown, separately) and did not show a correlation with the amount of AOs. Therefore, it can be accepted that such a relatively small variation in  $X_c$  (%) did not affect the film transparency much. As seen in Fig. 3a, increasing amount of Irgafos® 168 (IRF) reduced the light transmission in the visible region. This effect is more pronounced for the doubling of IRF amount from 0.2 to 0.4 wt%. Figure 3b compares the UV spectrums of specimens including a particular amount (0.2 wt%) of secondary AO (IRF) and different amount of primary AOs. It was found that the type and relatively low amount of primary AO did not affect the transparency of films.

**Figure 2** Visual transparency of PE films.

**Figure 3** **a** Representative UV spectrum of film specimens having a particular SM (0.2 wt%) and different Irgafos® amount and **b** Comparison of UV spectra of film specimens having a particular Irgafos® (0.2 wt%) amount.

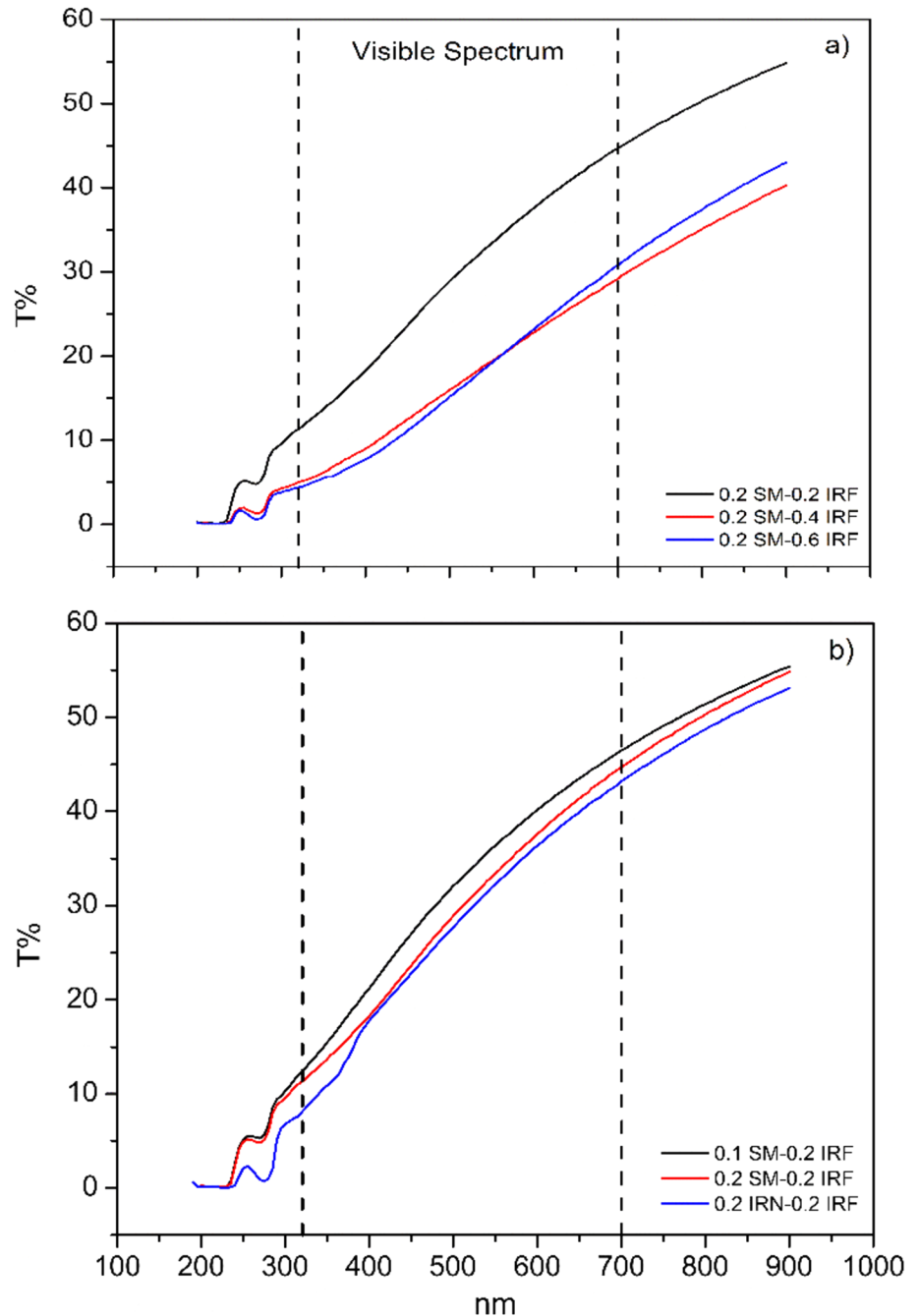


Table 4 lists the color coordinates of film specimens. The values of  $L^*$  (lightness),  $a^*$  (red to green), and  $b^*$  (yellow to blue) parameters were calculated based on the color difference between two samples ( $\Delta E^*_{ab}$ ) with the following equation;

$$\Delta E^*_{ab} = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (3)$$

where  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  correspond to the differences in  $L^*$ ,  $a^*$ , and  $b^*$  coordinates, respectively, between the

**Table 4** Color coordinates and difference of films

| Sample name     | $L^*$ | $a^*$ | $b^*$ | $\Delta E^*_{ab}$ |
|-----------------|-------|-------|-------|-------------------|
| 0.1 SM-0.2 IRF  | 43.60 | -0.22 | -2.38 | 2.00              |
| 0.2 SM-0.2 IRF  | 44.22 | -0.54 | -0.51 | 2.94              |
| 0.2 SM-0.4 IRF  | 44.03 | -0.49 | 0.52  | 3.49              |
| 0.2 SM-0.6 IRF  | 45.44 | -0.38 | 2.33  | 3.96              |
| 0.33 SM-1.0 IRF | 44.60 | -0.62 | 0.94  | 5.06              |
| 0.5 SM-1.0 IRF  | 43.93 | -0.02 | 1.56  | 7.05              |
| 1.0 SM-1.0 IRF  | 44.97 | -0.20 | 4.54  | 7.88              |

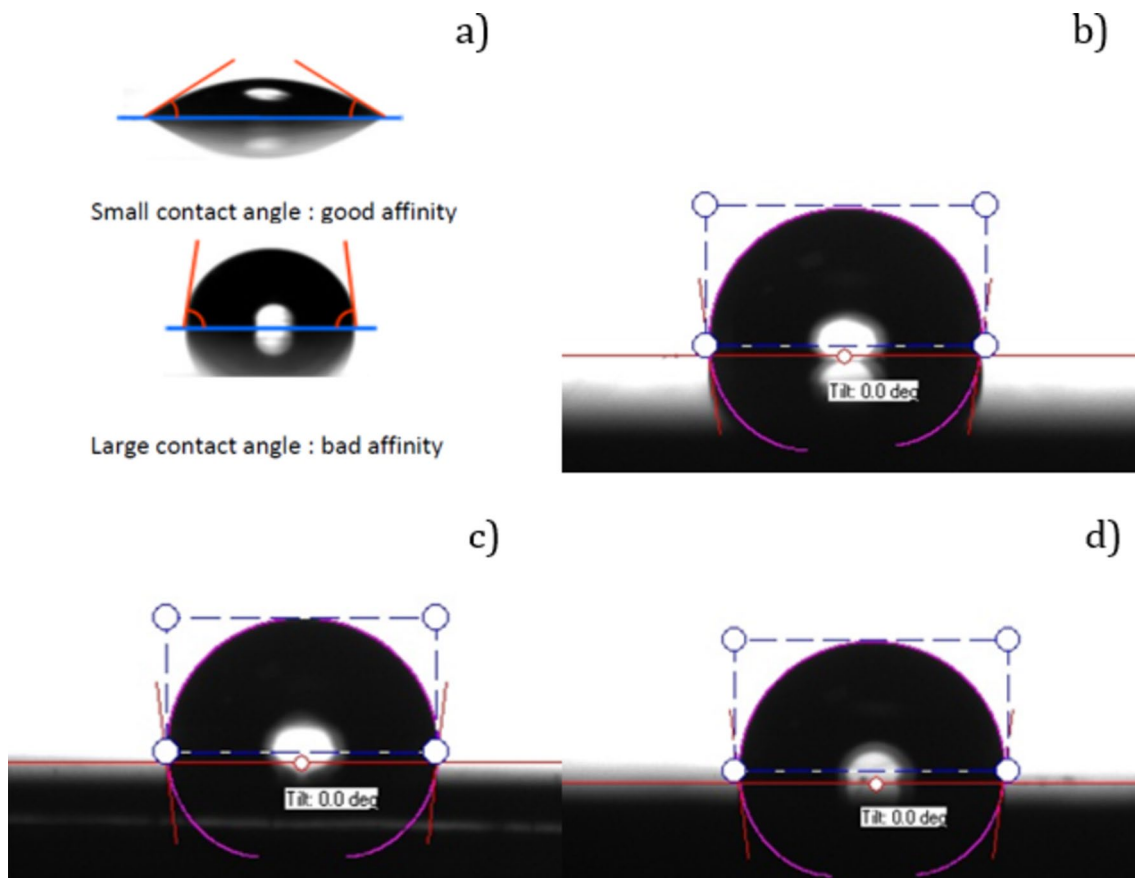


LDPE film and AO loaded films. Five measurements were performed for each composition and the average values of parameters are listed in Table 4.

It is known that the  $\Delta E_{ab}^*$  value  $< 1$  and a value between 1 and 2 correspond to an unnoticeable difference and a slight difference that could only be noticed by an experienced observer in color, respectively. All the samples yielded higher  $\Delta E_{ab}^*$  values than 2 referred to the fact that specimen colors changed in somewhat depending on the film composition. The  $\Delta E_{ab}^*$  values in the range of 2.0–3.5 are attributed to a noticeable difference in color by unexperienced observer. In this study, the first three samples including relatively low amount of SM and IRF resulted in  $\Delta E_{ab}^*$  values in this range. The  $\Delta E_{ab}^*$  values between 3.5 and 5.0 refer to a clear noticeable difference while the higher values than 5 may correspond to different colors are noticeable [11]. It was found that the  $\Delta E_{ab}^*$  value exceeded 5 when the IRF amount was 1.0 wt%. It was found that tripling the IRF amount from 0.2 to 0.6 wt%

for a particular SM amount of 0.2 wt% improved the  $\Delta E_{ab}^*$  value about 35% which implied slight increase in yellowishness. Nevertheless, high  $\Delta E_{ab}^*$  values of samples including 1.0 wt% of IRF did not deteriorate much the transparency of specimens. Even though the dark yellowish and almost light brownish color of *Silybum marianum* powder as seen in Table 1, it could be concluded that all film specimens can be employed as transparent packaging materials.

Figure 4 shows the contact angle images of representative samples and Table 5 lists the average left (L) and right (R) angles of five measurements onto film samples. It was found that all specimens exhibited contact angle values higher than 90 which clearly implied non-polar surface character as expected and SM and IRF addition did not change the contact angle values of LDPE, significantly. This very stable contact angle values in the range of 94–97 could be attributed to the fact that primary and secondary AO addition in this composition range did not influence the surface



**Figure 4** a Description of contact angle appearance. Contact angles of representative samples; b LDPE, c film having 1.0 wt% of SM and IRF, and d 1.0 wt% of SM.

**Table 5** Contact angle values of film samples

| Sample name     | L  | R  |
|-----------------|----|----|
| LDPE            | 97 | 97 |
| 0.1 SM-0.2 IRF  | 96 | 97 |
| 0.2 SM-0.2 IRF  | 94 | 93 |
| 0.2 SM-0.4 IRF  | 95 | 96 |
| 0.2 SM-0.6 IRF  | 96 | 95 |
| 0.33 SM-1.0 IRF | 95 | 94 |
| 0.5 SM-1.0 IRF  | 95 | 94 |
| 1.0 SM-1.0 IRF  | 96 | 96 |
| 1.0 SM          | 96 | 95 |

and bulk polarity of specimens. This result also indicated that SM and IRF did not show a migration from the structure and alter the surface polarity in short-term, at room temperature for a few weeks. But, it should be noted that long-term migration stability of organic additives might be different in polyolefins by regarding their highly non-polar structures and semi-crystalline natures as well as chain dynamics due to possessing extremely low glass transition temperature.

### Thermal properties of films

Figure 5a and b describe the OIT and OOT in the representative isothermal and non-isothermal thermograms, respectively. Table 6 lists the OIT and OOT values of samples prepared with various composition.

As seen in Table 6, LDPE was quickly oxidized when the furnace purge gas was switched to oxygen thus OIT value was reported as zero. It was also showed an oxidation onset temperature (OOT) at 200.6 °C under non-isothermal oxidative conditions. It was found that 1.0 wt% of IRF did not singly improve the OIT performance of LDPE while it increased the OOT of LDPE by 10 °C. On the other hand, 1.0 wt% of SM yielded an OIT value of 21 min. and improved the OOT of LDPE about 40 °C. But, it is a well-known fact that primary and secondary antioxidants act crucial roles for scavenging and pacifying of oxygenic species formed at high temperatures. This synergic effect is shown in Fig. 6. The 1.0 wt% of phosphite-based secondary AO (Irgafos® 168) cannot solely show an oxidative stability at 210 °C. The same amount of SM, as natural phenolic primary AO, provided much better oxidative stability. But, in the case of using PAO and SAO together, these AOs yielded an OIT value of 75 min. Synergic effect of PAOs and SAOs and

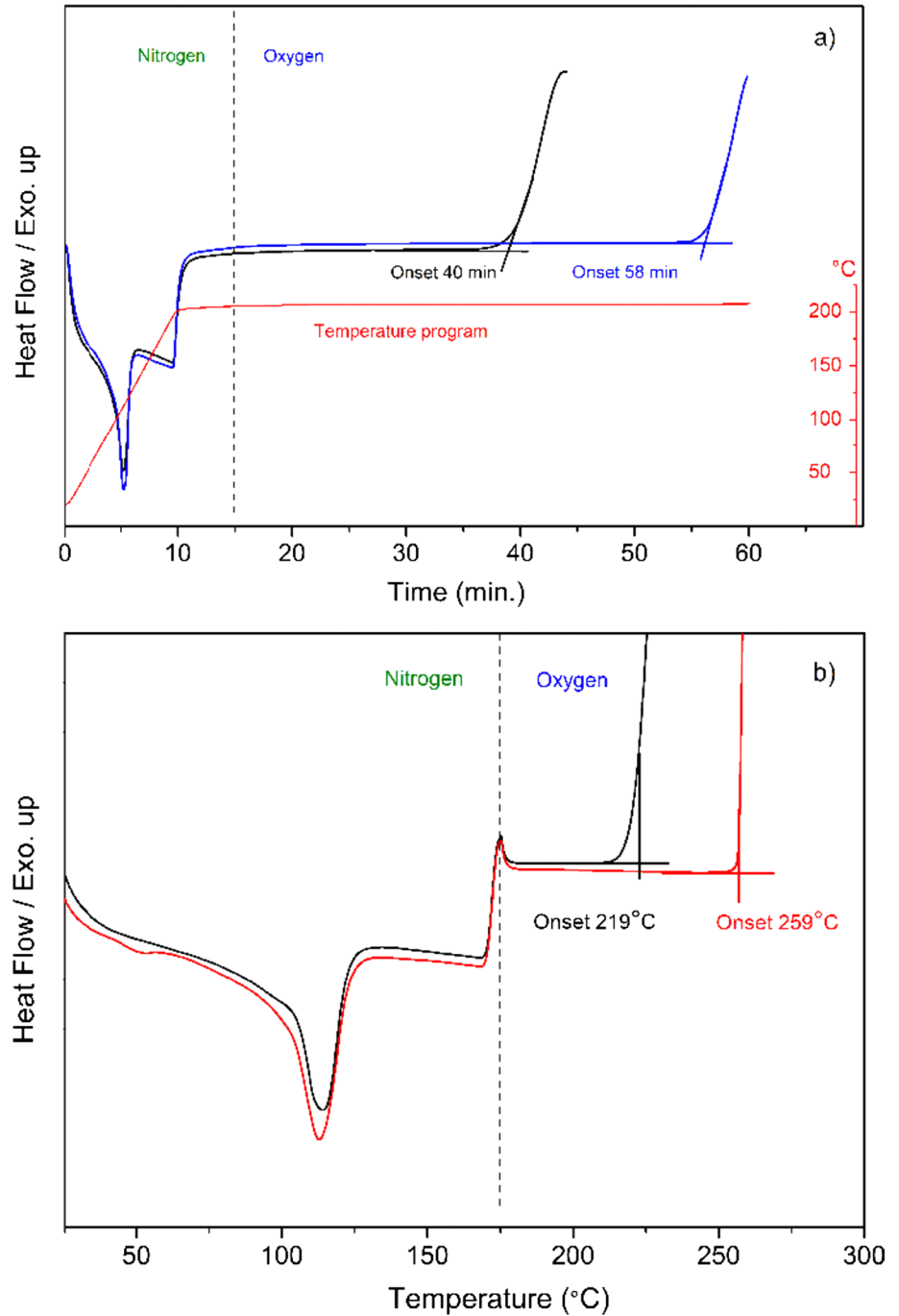
inhibition mechanism for chain scissions have already been explained in the relevant literature [7–9].

In this study, two compositions prepared with commercial AOs, denoted as “0.1 IRN-0.2 IRF” and “0.2 IRN-0.2 IRF”, could be regarded as control samples for comparing the antioxidant performance of SM to the commercial ones. We intended to reach or surpass the antioxidant performances of these samples by using SM as primary AO. It is clearly seen that the 0.2 IRN-0.2 IRF sample exhibited a superior performance, 78 min as OIT and 246 °C as OOT. These values can be accepted as a quite high performance for commercial applications. Starting with relatively low loading amounts of primary and secondary AOs, first we tested oxidative performances of SM loaded specimens prepared with the same compositions of control samples. It was found that 0.1 SM-0.2 IRF exhibited lower oxidation stability than 0.1 IRN-0.2 IRF. But, in the case of doubling the SM amount (0.2 SM-0.2 IRF) yielded a considerable improvement in the oxidation stability and reached to performance of 0.1 IRN-0.2 IRF. Then a systematic composition approach was applied by keeping the SM amount as 0.2 wt% and varying the secondary AO amount as 0.2, 0.4, and 0.6 wt% and thus the PAO/SAO ratio of 1:1, 1:2, and 1:3. OIT thermograms of these samples is given in Fig. 7a. It was found that all these samples showed a superior OIT performance, above 20 min, and increase in IRF amount enhanced the OIT performance, as expected. It is also noticeable that the slope of the oxidation exotherms of specimens appears similar. This slope can be regarded as a rapid and simple indicator for the rate of oxidation.

Figure 7b illustrates the OIT thermograms of samples having 1.0 wt% of IRF and different amounts of SM. It was obtained that the increase in SM amount readily improved the oxidation stability when the SAO amount was sufficiently high and reached 75 min. and for the maximum loading amounts. Introducing 1.0 wt% of SM and IRF into LDPE also shifted the OOT value about 57 °C.

Table 7 compares the OIT values of samples having the SM:IRF ratio of 1, but low and high amount of loadings at different isothermal temperatures. The corresponding OIT thermograms of 0.2 SM-0.2 IRF sample are given in Fig. 8a. It is seen that the OIT value is inversely proportional with the isothermal test temperature. Another clear observation in Fig. 8a is the increase in slope of oxidation exotherms with temperature. This slope ( $\alpha_R$ ) was qualitatively determined by

**Figure 5** Graphical description of **a** OIT and **b** OOT analysis in DSC.



considering the change in heat flow within a unit of time as “mW/min” and illustrated in Fig. 8b.

It can qualitatively be concluded that a 30 °C increase in temperature accelerates the rate of initial oxidation approximately 17 times. Figure 8c represents the correlation between the OIT and the isothermal test temperature. This figure implies that the amount of antioxidant is a more pronounced parameter at low

temperatures. In the case of temperature increase, amount of AOs becomes less important for the oxidation stability.

Figure 9 shows the OOT thermograms of specimens. It is seen that increasing amount of IRF at a particular SM content (0.2 wt%) and increasing amount of SM at a particular IRF content (1.0 wt%) improve the oxidation temperature, as expected.

**Table 6** OIT and OOT values of LDPE and compounds

| Samples                | OIT@210 °C (min.) | OOT (°C)     |
|------------------------|-------------------|--------------|
| LDPE                   | 0                 | 200.6        |
| 1.0 IRF                | 2.5               | 210.6        |
| 1.0 SM                 | 21.0              | 240.4        |
| <b>0.1 IRN-0.2 IRF</b> | <b>27.7</b>       | <b>224.3</b> |
| <b>0.2 IRN-0.2 IRF</b> | <b>77.8</b>       | <b>246.2</b> |
| 0.1 SM-0.2 IRF         | 10.0              | 219.0        |
| 0.2 SM-0.2 IRF         | 22.3              | 229.5        |
| 0.2 SM-0.4 IRF         | 25.0              | 231.2        |
| 0.2 SM-0.6 IRF         | 41.6              | 240.0        |
| <b>0.33 SM-1.0 IRF</b> | <b>52.0</b>       | <b>246.8</b> |
| <b>0.5 SM-1.0 IRF</b>  | <b>72.7</b>       | <b>251.2</b> |
| <b>1.0 SM-1.0 IRF</b>  | <b>75.0</b>       | <b>257.2</b> |

Figure 10a and b illustrate the TGA and DTG thermograms of LDPE and two of samples, respectively. It was found that all samples showed a rapid and similar decomposition behaviors in the temperature range of 350–420 °C. DTG thermograms implied that samples decomposed in two steps and AO loaded samples decomposed slightly broader temperature range than LDPE. Consequently, TGA analysis implied that type and amount of AOs do not affect

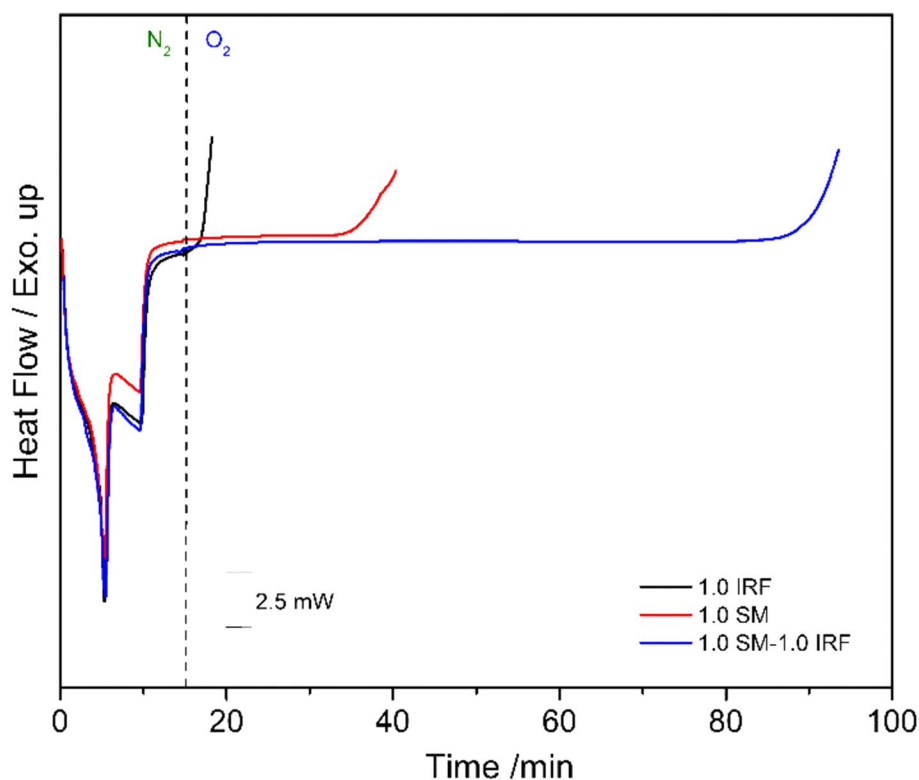
the high temperature decomposition behaviors of polyolefins.

## Conclusion

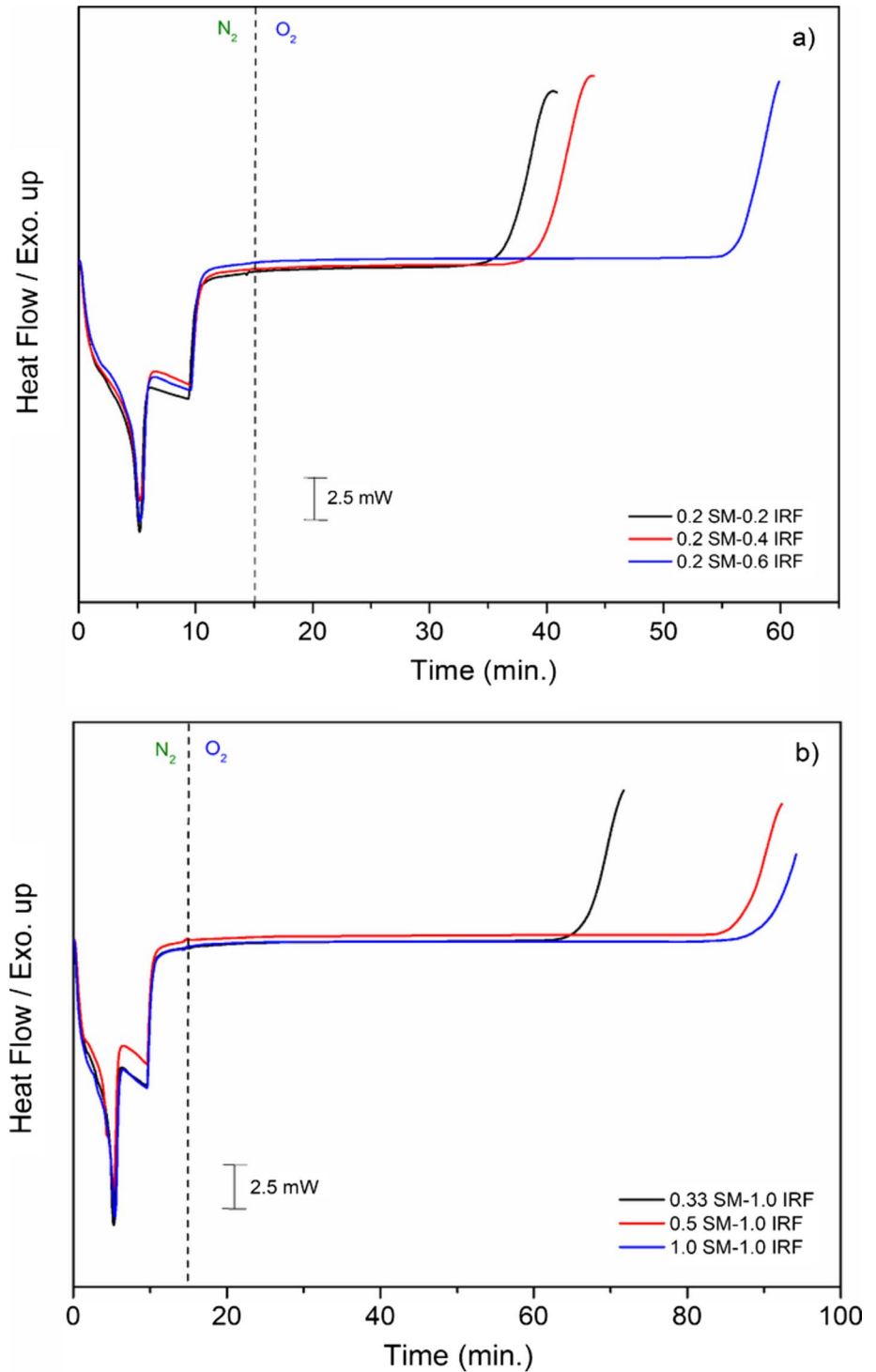
This study systematically examined the effect of *Silybum marianum* extract as a natural primary antioxidant in polyethylene. Composition study showed that the 0.2 SM-0.2 IRF sample exhibited an OIT value above 20 min and similar performance to the 0.1 IRG-0.2 IRF prepared with commercial antioxidants. It can be concluded that *Silybum marianum* extract could be successfully used as an alternative compound to the phenolic synthetic antioxidants without deteriorating the transparency, surface nature, polarity, and other physical properties of LDPE.

From the biochemical point of view, it has been known that the *Silybum marianum* can exhibit a superior antioxidant effect in different ways; (i) by direct free radical scavenging (ii) by preventing free radical formation by inhibiting the activities of specific, free radical producing enzymes, and (iii) by optimizing the redox status of the cell by activating a range of antioxidant enzymes and non-enzymatic antioxidants. The result showed that the *Silybum marianum* extract

**Figure 6** OIT thermograms of antioxidants and the synergistic effect of PAO and SAO.



**Figure 7** OIT thermograms of specimens having **a** a constant SM of 0.2 wt% with different SAO amounts and **b** a constant SAO of 1.0 wt% with different SM amounts.



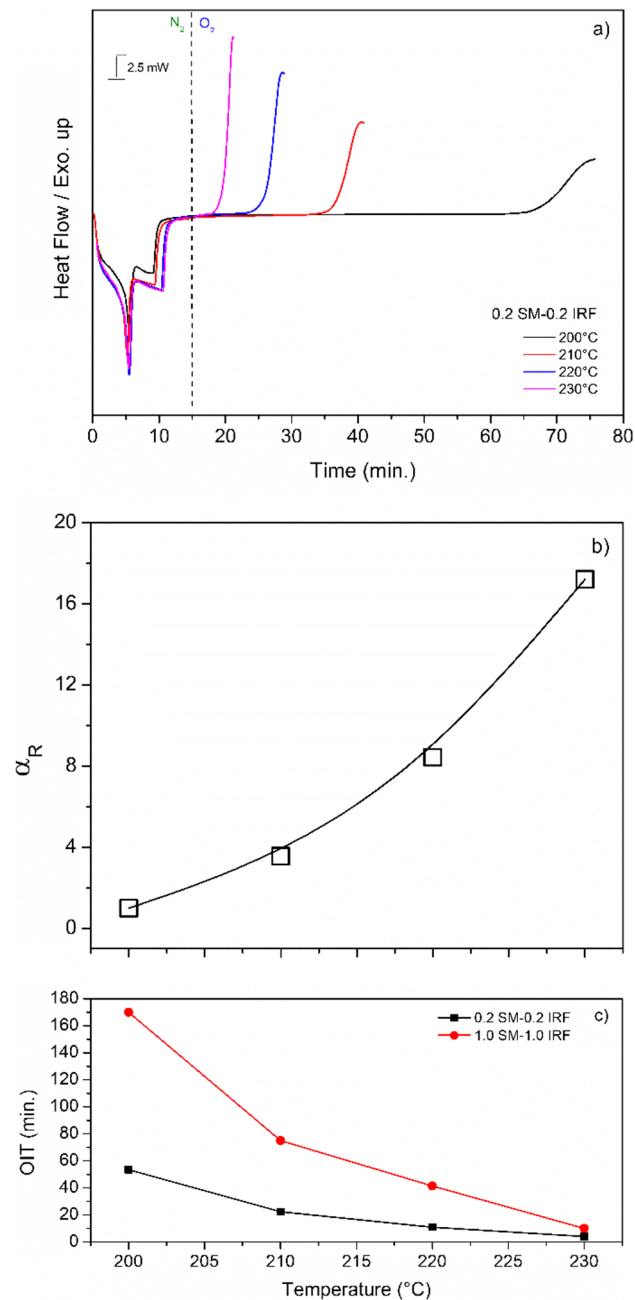
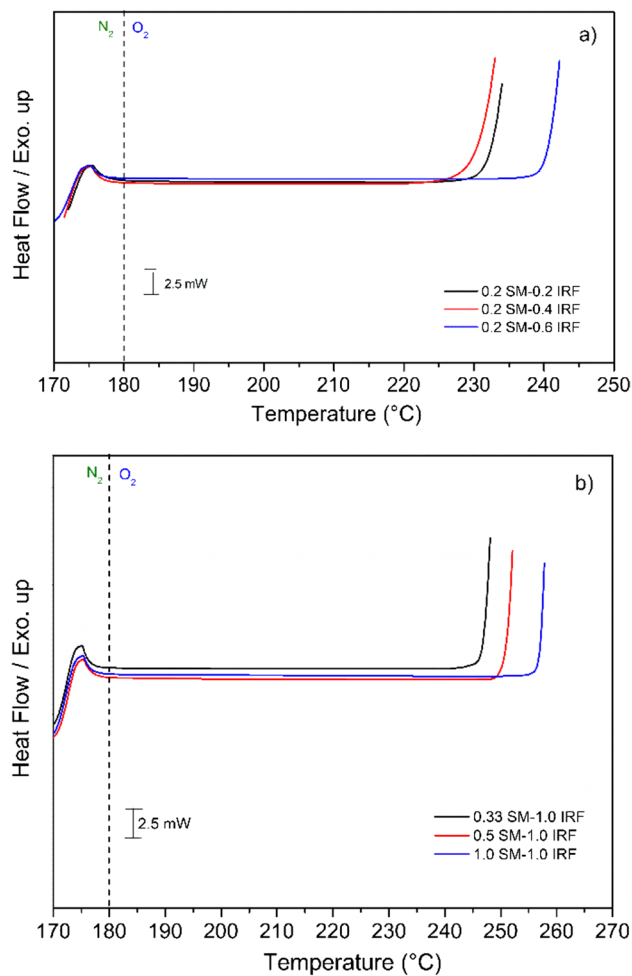
can also exhibit an excellent antioxidant efficiency by scavenging the free radicals in the thermo-oxidative conditions during polymer processing operations at high temperatures. It should be remarked that the most astonishing finding was the fact that relatively

low loading amounts (<0.5 wt%) yielded a quite high oxidative stability compared to other natural antioxidants used in literature.

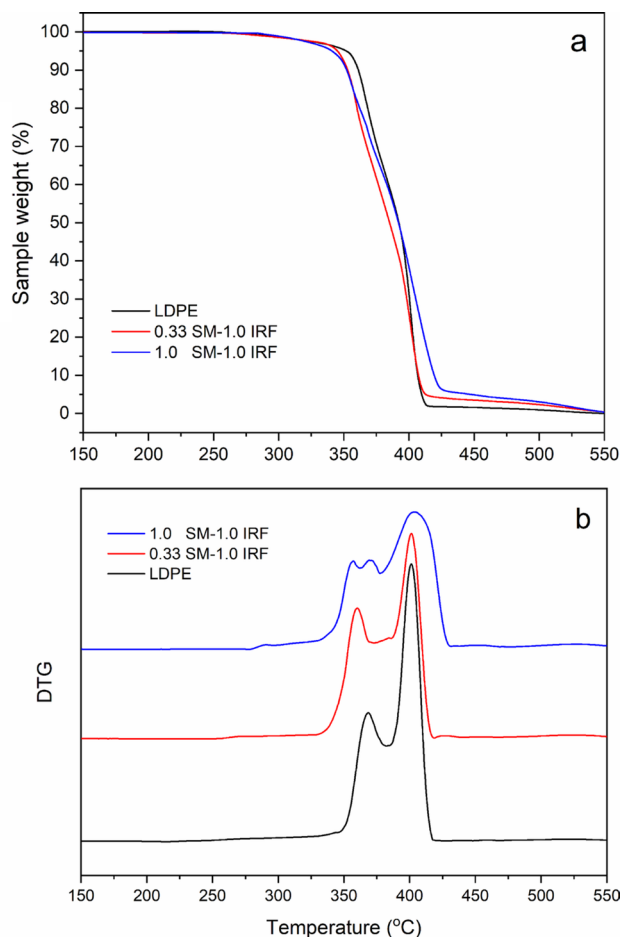
Consequently, it has been concluded that the important benefit of *Silybum marianum* extract usage

**Table 7** OIT values of the samples having the PAO:SAO ratio of 1 at different test temperatures

| Samples               | OIT (min.) |      |      |      |
|-----------------------|------------|------|------|------|
|                       | 200        | 210  | 220  | 230  |
| Test temperature (°C) | 200        | 210  | 220  | 230  |
| 0.2 SM-0.2 IRF        | 53.5       | 22.3 | 10.8 | 4.0  |
| 1.0 SM-1.0 IRF        | > 120      | 75.0 | 41.4 | 10.0 |

**Figure 8** a OIT thermograms of 0.2 SM-0.2 IRF sample at different temperatures. b Slope of oxidation exotherm as a function of test temperature. c Correlation between the OIT and the test temperature depending on different antioxidant amount.**Figure 9** OOT thermograms of specimen having a a constant SM of 0.2 wt% with different SAO amounts and b a constant SAO of 1.0 wt% with different SM amounts.

in packaging film applications as a natural antioxidant, particularly in food packaging materials, is an achievement in terms of chemical safety and renewability issues because these compounds are classified as plant-based (or herbal-based) chemicals. Many of plant-based natural antioxidants have been extensively used in nutraceutical and pharmaceutical formulations. This fact implies that these compounds are non-toxic chemicals. In the worst scenario as the migration of additive from packaging material to foods, there is no adverse or toxic effect to living organisms when natural additives are used into synthetic thermoplastics.



**Figure 10** **a** Thermogravimetry and **b** DTG thermograms of LDPE and representative samples under air.

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## Author contributions

OP contributed to methodology, visualization, formal analysis, investigation, data curation, and writing—original draft; FEK contributed to methodology, formal analysis, investigation, validation, and writing—original draft; MBA contributed to methodology, formal analysis, and investigation; NS contributed to methodology, visualization, and investigation; AE contributed to resources, formal analysis, and data curation; AD contributed to conceptualization,

writing—original draft, writing—review and editing, supervision, and project administration.

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## Data and code availability

Not applicable.

## Declarations

**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.

**Ethical approval** Not applicable.

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