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Polyolefins Journal Vol. 10, No. 3 (2023)
DOI: 10.22063/POJ.2023.3288.1246
ORIGINAL PAPER

Acceleration of thermo-oxidative degradation of high-density polyethylene using oxidized polyethylene

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Received: 9 December 2022, Accepted: 31 March 2023

ABSTRACT

In the present study, the thermal oxidation behaviour of high-density polyethylene (HDPE) containing each of two types of oxidized polyethylene (OPE), one prepared using 500 ppm of iron (III) stearate as pro-oxidant and the other without the pro-oxidant, was investigated. Fourier-transform infrared spectroscopy (FTIR) showed that the carbonyl index of the HDPE increased from 1.03 to 6.37 upon the addition of 5.0 wt.% of OPE containing the pro-oxidant after 100 h of thermo-oxidative aging at 90°C. Moreover, it was observed that the rate of changes in retained tensile strength and retained elongation-at-break of the HDPE during the thermal oxidation increased in the presence of 5.0 wt.% of each type of OPE, especially, the one containing iron (III) stearate, which was consistent with the obtained data from gel content measurements. Lastly, the evolution in crystallinity of the film samples was monitored by density measurements as well as differential scanning calorimetry (DSC). It was revealed that the crystallinity of the tested films during thermo-oxidative degradation grows faster in the presence of OPE. Overall, the findings indicated that the utilization of OPE containing trace amounts of iron (III) stearate can accelerate the thermal oxidation of HDPE films and facilitate entering the final biodegradation stage, while resolving the need to use high concentrations of harmful heavy metal salts. **Polyolefins J (2023) 10: 149-157**

Keywords: High density polyethylene; oxidized polyethylene; iron (III) stearate; pro-oxidant; thermal oxidation.

INTRODUCTION

Because of the increased demand for plastics, global production of these materials has expanded dramatically in numerous industries, including packaging, agriculture, construction, healthcare, electronics, and automotive [1-3]. Petroleum-based hydrocarbon polymers, which include polyethylene (PE) and polypropylene (PP), are generally regarded in the above applications because of their exceptional mechanical properties, thermal stability, chemical resistance, low cost, and good processability [4-7]. However, these synthetic polymers are not biodegradable and make up half of the waste in landfills [8-11]. Due to their high oxidative stability, efforts have been made to accelerate their photo- and/or thermal oxidation to make them susceptible to attack by microorganisms. One of the proposed solutions to enhance the polymers photo-degradability is to incor-

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porate oxidized polyethylene (OPE) into the polymer [12,13]. OPE is manufactured by thermal oxidation of PE and is commonly utilized as a processing aid in plastic industry. In fact, the oxidation process fragments polymer chains into short, low-molecular-weight segments and introduces oxygen-containing groups, such as, hydroxyl, ketone and carboxylic acid groups, to the polymer chains [14].

Over the past few decades, polyethylene (PE) formulations containing catalysts or pro-oxidant additives have been introduced into the advanced materials market, rendering acceptable biodegradability [15]. Accordingly, some transition metal salts are utilized as pro-oxidant and catalyst in the thermal breakdown of polyolefinic plastic wastes [16-18]. It is worth noting that the transition metal salts have hazardous consequences for the human body, which have made governments to be concerned about [19].

There are not many relevant reports on the thermal degradation of HDPE in the presence of transition metal salts. For example, a study used various transition metal salts as catalytic agents in the thermal oxidation of high-molecular-weight polyethylene [20]. Researchers in this study discovered that the addition of metal salts accelerated the thermal oxidation of polymers. In another research [21] the thermal degradation of acrylonitrile-butadiene-styrene (ABS) copolymer in the presence of metal salts was investigated. The results showed that adding salts of transition metals accelerates the thermal oxidation of polymer.

To the best of our knowledge, there is no report on the influence of OPE on the thermal oxidation behavior of HDPE in the presence or absence of transition metal salts. Thus, for the first time, this study attempted to reduce the concentration of iron (III) stearate as a model transition metal salt through replacing all or at least most of its quantity with oxidized polyethylene (OPE). Accordingly, we studied the effects of two types of OPE, one containing trace amounts of iron (III) stearate and the other without the transition metal salt, on the thermo- oxidative degradation of HDPE during oven aging, utilizing qualitative and quantitative methodologies such as FTIR, tensile tests, and DSC studies in this paper.

EXPERIMENTAL

Materials

Amirkabir Petrochemical Company (Iran) provided additive-free HDPE powder (EX3 grade) for this study. The melt flow index, density, and crystalline melting point of this polymer are 0.45 g/10 min, 0.945 g/cm^3, and 130°C, respectively. Merck KGaA (Germany) supplied iron (III) stearate as well as xylene.

Sample Preparation

For 6 minutes, the polymer powder was mixed with 0.05 wt.% of stearate (III) iron as a pro-oxidant in a Brabender internal mixer at 180°C with a rotator speed of 60 rpm and a fill factor of 75%. The mixture was converted to film with a thickness of 210±20 μm using a Toyoseiki laboratory hot press at 190°C under 150 bar. A pure HDPE film without iron (III) stearate was also prepared under the same conditions to obtain a metal-ion-free additive. The two prepared sample films were subjected to oven aging at 90 °C for two aging times of 100 h and 400 h for the film containing pro-oxidant and the pure one, respectively, during which the progress of thermo-oxidative degradation in each film sample was monitored via taking FTIR spectra of the samples using a BOMEM FTIR spectrophotometer (Canada). The spectra were taken as an average of 20 scans at a resolution of 4 cm^{-1} in the range of 4,000-400 cm^{-1}. Carbonyl index change (ΔCI) of the films as a measure of the oxidation extent was evaluated using the following equation [22]:

$$\Delta CI = \frac{A_{1717}}{A_{2022}} - CI_0 \quad (1)$$

In which, A is the absorbance at the given wavenumber and CI_0 is the carbonyl index of films prior to the thermal degradation experiment. The absorbance at the wavenumber of 1717 cm^{-1} is assigned to the stretching vibration of ketone carbonyl groups. The absorbance at the wavenumber of 2022 cm^{-1} belongs to the combined rocking and wagging vibrations of the methylene group and was used as an internal thickness band to eliminate the effect of film thickness [23]. It should be noted that during the aging times specified above, the ΔCI of each film sample reached 6 units

and the films became fully brittle [24]. The pure and pro-oxidant-containing oxidized films were designated as OPE and OPE/Fe, respectively.

Finally, desired amounts of either of the two prepared oxidized PE samples were incorporated into the pure polymer powder utilizing the above-mentioned internal mixer. Accordingly, four HDPE samples containing 2.5 or 5.0 wt.% of either of OPE or OPE/Fe were prepared. A pure polymer sample without any additive was also prepared as the control sample. All the above samples were prepared under the same compounding conditions that were applied earlier for the incorporation of iron (III) stearate into HDPE powder. The formulated samples were compression molded at 190°C under 150 bar using the aforementioned hot press to obtain films with a thickness of 210±20 μm. The sample designations and their respective formulations are demonstrated in Table 1.

Analytical methods

The prepared HDPE film samples were put into the above-mentioned air draft oven at 90°C for a maximum of 100 h to perform aging studies. At 25, 52, and 100 h of aging, the samples were taken out of the oven and subjected to the following analyses.

FTIR analysis

Structural changes of the studied films upon exposure to oven aging were investigated by taking their FTIR spectra using the aforementioned conditions.

Mechanical properties

The mechanical properties considered in this project, i.e., tensile strength and elongation-at-break, were measured using a tensile testing machine made by the ELIMA Company (Iran). Following the ASTM D882 standard, the test specimens were cut with a length of 100 mm and a width of 10 mm. All tensile tests were performed at a temperature of 25±2 °C and a relative humidity of 40±5%. The distance between the two jaws of the testing machine was adjusted to 50 mm, and the grip separation speed of 25 mm/min was applied for all specimens. The percentage of retained elongation-at-break for each film specimen, which is denoted by ε_r, was obtained and reported from the elongation values of the film at the breakpoint before the oven aging (ε_0) and after being exposed to the aging for t hours (ε_t), using the equation below:

$$\varepsilon_r = \frac{\varepsilon_t}{\varepsilon_0} \times 100 \quad (2)$$

Subsequently, the percentage of the retained tensile strength (σ_r) was also calculated in a similar way:

$$\sigma_r = \frac{\sigma_t}{\sigma_0} \times 100 \quad (3)$$

Where σ_t is the tensile strength after being exposed to the aging for t hours and σ_0 is the initial tensile strength.

Gel content

Gel content measurement was conducted according to the ASTM D2765 standard.

Determination of density

The densities of the specimens were measured using a density gradient column as stated by ASTM D1505 standard. Crystallinity of the samples was calculated using the measured densities according to the following equation [25]:

$$\%\ \text{crystallinity} = \frac{\rho - \rho_a}{\rho_c - \rho_a} \times 100 \quad (4)$$

Where, ρ, ρ_c, and ρa are the densities of a studied specimen and the perfect crystal and the amorphous phase of PE, respectively. The ρ_c and ρ_a of HDPE were adopted as 1.00 and 0.850 g/cm^3, respectively [26].

DSC analysis

Crystallization characteristics were investigated using DSC experiments, which were performed with a DSC 214 Polyma model NETZSCH instrument (Germany). About 5 mg of each sample was tested under a nitro-

Table 1. Formulations of the prepared HDPE film samples.

Sample designation	HDPE (wt. %)	OPE/Fe (wt. %)	OPE (wt. %)
HDPE	100.0	-	-
OPE-2.5	97.5	-	2.5
OPE-5.0	95.0	-	5.0
OPE/Fe-2.5	97.5	2.5	-
OPE/Fe-5.0	95.0	5.0	-

gen atmosphere. Every sample was firstly heated from ambient temperature to 180°C in order to delete its thermal history. Then, it was cooled to room temperature and heated again to 180°C. The heating and cooling rates were both 10°C/min. The crystallinity (X_c, dsc) was calculated using the following equation [27]:

$$X_{c,dsc} = \frac{\Delta H_m}{\Delta H_{100\%}} \times 100 \quad (5)$$

where ΔH_m is the enthalpy associated with the melting of the polymer in the second heating run, and $\Delta H_{100\%}$ is the enthalpy of 100 % crystalline HDPE reported in the literature to be 293 J/g [28, 29].

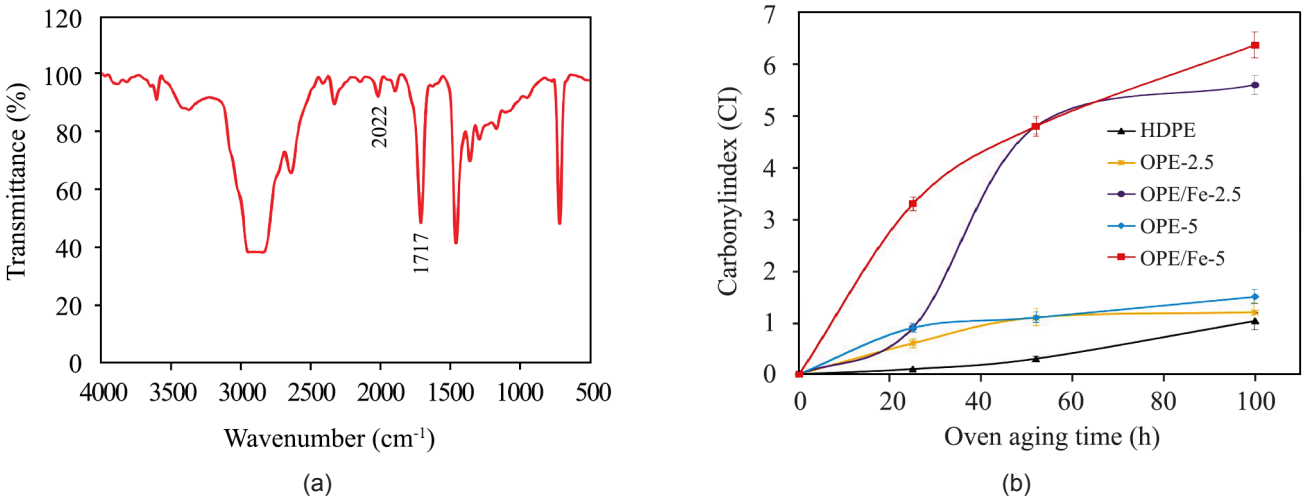
RESULTS AND DISCUSSION

Analyzing carbonyl index through FTIR spectrum

FTIR was utilized to track the changes occurred in the chemical structure of PE upon oven aging in both phases of the preparation of OPE and the thermo-oxidative degradation studies performed on the final film samples. Figures 1a and 1b illustrate FTIR spectrum of the neat PE film (without ferric stearate) after exposure to oven aging at 90°C for 400 h and the variations in carbonyl index change (ΔCI) of the studied film samples as a function of thermal oxidation time, respectively. As shown in Figure 1a, a sharp and intensive absorption band at 1717 cm^{-1}, which is assigned to the stretching vibration of carbonyl group, is present in the FTIR spectrum of neat PE film upon aging for 400 h, indicating that the thermal oxidation process was successful [22, 30-34].

Figure 1b indicates that the concentration of carbonyl groups in all the studied samples increased with aging time. However, the carbonyl index of neat HDPE grew less significantly than that of other samples. It is clear that the rise in carbonyl index of the neat HDPE film increased somewhat with the addition of OPE. Moreover, the ΔCI of the films containing OPE/Fe-2.5 and OPE/Fe-5 shows a more substantial enhancement than neat HDPE and HDPE containing OPE, indicating their faster thermo-oxidative degradation. Using manganese stearate as a pro-degradant, similar findings were obtained elsewhere [35]. As demonstrated in reactions 1 and 2, this phenomenon can be attributed to the much faster production of radicals in the presence of heavy metal ions [36]. In brief, Mn^{+1} (Fe^{3+}) catalyzes thermal decomposition of the hydroperoxides (POOH) of polymer, which consequently produce carbonyl groups [34]. It should also be noted that raising the OPE/Fe concentration results in more acceleration in the oxidation process. This can be explained by the fact that the radicals develop faster when more iron (III) stearate as pro-oxidant is added to the matrix.

$$M^{n+1} + POOH \longrightarrow M^{n} + POO^{\circ} + H^{+} \quad (1)$$



(a) (b)

Figure 1. (a) FTIR spectra of OPE after 400 h oven aging time and (b) carbonyl index change (ΔCI) of HDPE films over oven aging time.

$$M^n + POOH \longrightarrow M^{n+1} + PO^\circ + OH^- \quad (2)$$

Mechanical properties

Due to their extraordinary sensitivity to presence of any defects in the structure of polymer, ultimate tensile characteristics are commonly utilized to examine polymer degradation behavior [34]. In this study, the retained tensile strength and retained elongation-at-break of films were used as relevant parameters to assess the extent of thermo-oxidative degradation and the effect of OPE and OPE/Fe additives on the thermal oxidation rate of HDPE. Figures 2 and 3 illustrate retained elongation-at-break (ε_r) and retained tensile strength (σ_r), which were computed using Equations 2 and 3 for the film samples, respectively, in terms of oven aging time. As can be observed, the trends of variations in the values for all samples followed a similar pattern, in which the two values increased over the first 52 h (first phase), then exhibited a significant drop in both ε_r and σ_r (second phase). Such changes in the ultimate mechanical properties of the HDPE specimens can be attributed to the competition between crosslinking and chain scission reactions during PE oxidation [37, 38]. In another research, similar observations were made [22]. As suggested, the addition of OPE, and especially OPE/Fe, increases the variations of retained tensile strength and retained elongation-at-break of the HDPE samples in the initial phase of degradation, demonstrating a higher thermo-oxidative degradation by chain crosslinking phenomenon. The OPE/Fe-5.0 showed the most remarkable results, with a 50 and 40 % increase in changes of σ_r and ε_r, respectively, upon 52 h of aging, compared to the neat HDPE film sample. In addition, it is evident that the inclusion of OPE, particularly OPE/Fe, led to a more severe deterioration of the ultimate mechanical properties compared to the neat HDPE in the second phase, where the chain scission process predominates and causes a reduction in the molecular weight of the polymer.

Gel content

Monitoring the changes in gel content of the samples during the oven aging period, as shown in Figure 4, allows researchers to evaluate the aforementioned explanation for the observed trends of alterations in the mechanical properties of HDPE. It can be seen in Figure 4 that all the changes in the gel content of the samples follow the same trend, which is characterized by an initial increase followed by a decrease in this value. Dominations of crosslinking in the first phase and chain scission reactions in the second phase can be the main reasons for the increase and eventual decrease in gel content, respectively [39]. The current findings agree with those made about the mechanical properties by other authors. Additionally, Figure 4 shows that the film samples containing OPE and OPE/Fe, especially those having OPE/Fe, had higher initial gel contents than the neat HDPE film, indicating that they are more prone to thermal oxidation compared to the neat HDPE film. This can be inferred from the higher formation of gel in the OPE-containing samples during the melt processing of the samples through compression molding. Furthermore, the fact that the first gel formation of the OPE/Fe-5 sample is more

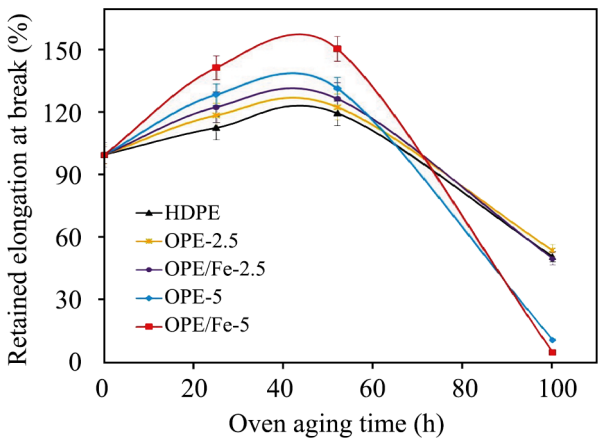


Figure 2. Percentage of the retained elongation-at-break (ε_r) of the HDPE films over the oven aging time.

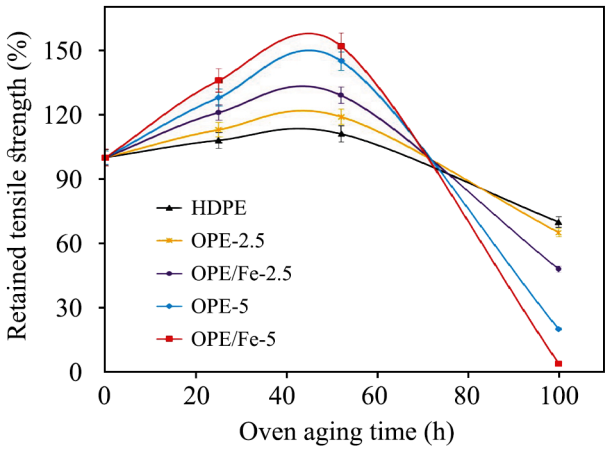


Figure 3. Percentage of the retained tensile strength (σ_r) of the HDPE films over the oven aging time.

pronounced (about 8%) confirms the lower thermo-oxidative stability of this sample. So, it seems that iron (III) stearate could accelerate the thermal oxidation of HDPE outstandingly.

Density measurements

It is well established that the density of HDPE grows during thermo-oxidative degradation [33, 40]. Figure 5 shows the samples density that was measured during oven aging. As can be seen, all samples experienced a significant rise in density. Firstly, the incorporation of oxygen atoms into polymer chains upon oxidation, whose atomic mass is higher than carbon, raises the density [24]. Secondly, this increment can be assigned to an increase in crystallinity. To elaborate, the chain scission caused by thermal aging in the amorphous phase enhances the chains mobility, resulting in more crystal formation [41]. Based on this argument, the variations in density can be due to changes in the morphology of HDPE samples upon oven aging. For better understanding, the crystallinity was calculated according to Equation 4. The calculated values for different HDPE films are demonstrated in Figure 6. It is evident that the crystallinity of all specimens increased over aging time, while the OPE/Fe-5.0 sample exhibited the most prominent values because of the higher rate of thermal oxidation. Furthermore, it is seen in Figure 5 that the initial density of neat HDPE rose from 0.945 to 0.954 g/cm^3 as 5.0 wt. % of OPE was incorporated into the polymer matrix, and this was made more significant by adding 5.0 wt. % of OPE/Fe, as this value increased from 0.945 to 0.959 g/cm3. This is because

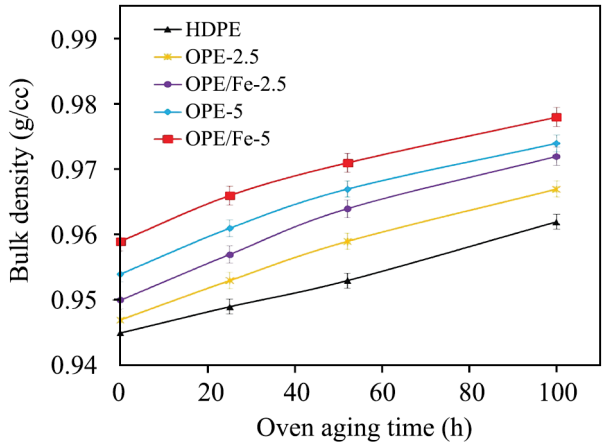


Figure 5. Changes in the density of HDPE films over oven aging time.

of the higher density of both OPE and OPE/Fe compared to neat HDPE, which, in turn, is due to the extensive oxidation in the presence of the two additives. As mentioned earlier, this phenomenon is related to polymer chain scission reactions, where shortened polymer chains can enter the crystal structure due to their high mobility.

To be more specific, DSC analysis was employed to measure the more precise amounts of crystallinity of the neat HDPE, OPE-5 and OPE/Fe-5 samples after 100 h of aging. The DSC curves of the above-mentioned samples are demonstrated in Figure 7. Using Equation 5, the values of crystallinity of neat HDPE, OPE-5, and OPE/Fe-5 samples were calculated as 70.1, 76.3 and 81.6%, respectively. Also, these values are a bit lower than those obtained from the density measurements, which is credited to the heavy

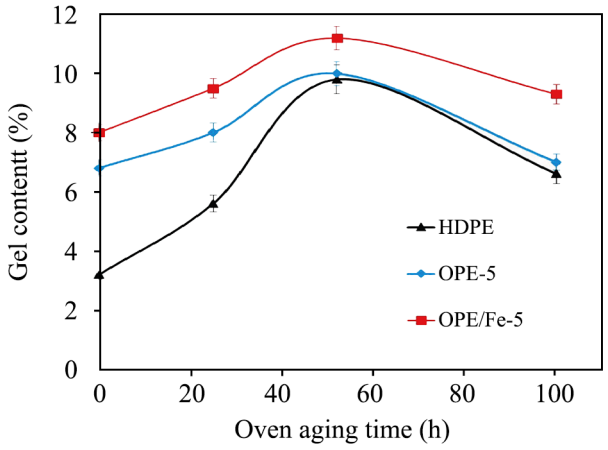


Figure 4. Changes in gel content of some HDPE films during oven aging time.

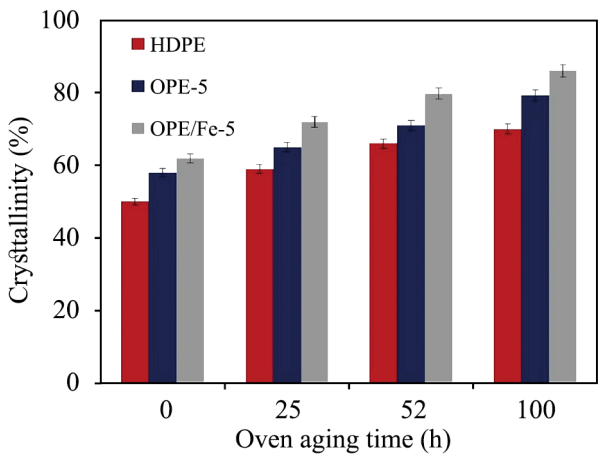


Figure 6. Changes in the crystallinity of HDPE films over oven aging.

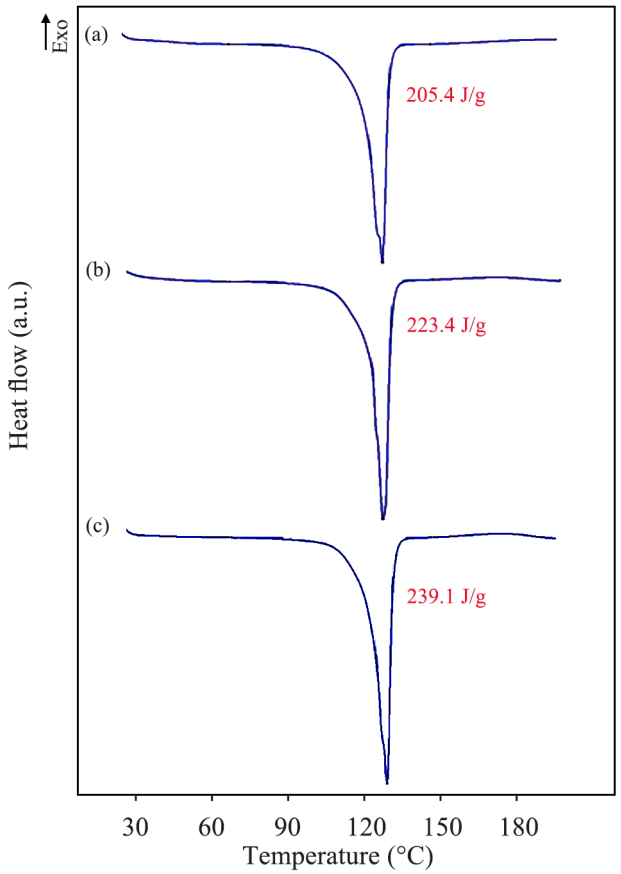


Figure 7. DSC curves of neat (a) HDPE, (b) OPE-5 and (c) OPE/Fe-5 samples after 100 h of aging.

oxygen-containing groups on the polymer chains as a consequence of oxidation, which, in turn, leads to extra grows in density values. To recapitulate, in this section it is shown that the incorporation of either of the two additives, especially OPE/Fe, into the polymer enhanced the rate of changes in density and crystallinity of HDPE, indicating the acceleration of the thermo-oxidative process of the polymer.

CONCLUSION

In this study, two types of OPE, one containing 50 ppm of iron (III) stearate and the other one, without any external impurity were used as additives for HDPE to catalyzes thermal oxidation of the polymer. By performing several experimental studies, including FTIR spectroscopy, gel content and density measurements, stress-strain test and differential scanning calorimetry, it was shown that the both additives are able to accelerate of the oxidation of the polymer and their effects are proportional to their concentration in the polymer. However, the effects of OPE/Fe were more pronounced, which can be due to the presence of iron (III) that acts as pro-oxidant. Overall, the obtained results proved that OPE has the potential to reduce the need for using high concentrations of iron (III) ion as a model transition metal ion to acquire the desired degradability. The lower the concentration of transition metal ions in the formulation of oxo-biodegradable polyethylene films, the less harmful side effects of their waste on the environment and human health.

CONFLICT OF INTEREST STATEMENT

The authors declare that they do not have a conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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