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Effect of pro-oxidants on the photodegradability of recycled PE films containing calcium carbonate

Nguyen Thanh Tung, Pham Thu Trang*, Nguyen Van Khoi, Pham Thi Thu Ha, Nguyen Trung Duc

Institute of Chemistry, VAST, 18 Hoang Quoc Viet, Cau Giay, Ha Noi, Viet Nam

*Email: *thutrang90vhh@gmail.com*

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Abstract. In this study, calcium carbonate ($CaCO_3$) filled waste high density polyethylene (HDPE) films without and with prooxidants were prepared using a twin screw extruder. To control the degradation time, the HDPE film with pro-oxidants content varying from 0.5 - 2 wt.%, 25 wt.% taical and 0.5 wt.% antioxidant additive were investigated. The mechanical properties, Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC) and scanning electron microscope (SEM) were used to assess the changes of films during accelerated weathering according to ASTM G154 standard (340 nm UV lamp, 8 hours UV, 4 hours of condensation at 50 ^{o}C). The results showed that the degradation rate of HDPE increased by increasing of pro-oxidant content. After 6 days of accelerated weathering, FTIR spectra of oxidized HDPE films showed peaks of OH, C-O, C-O-C, C=O groups. The melting point decreased and the heat of fusion increased as the content of pro-oxidants increased.

Keywords: Calcium carbonate, waste polyethylene, polyethylene degradation, accelerated weathering, antioxidant, pro-oxidant.

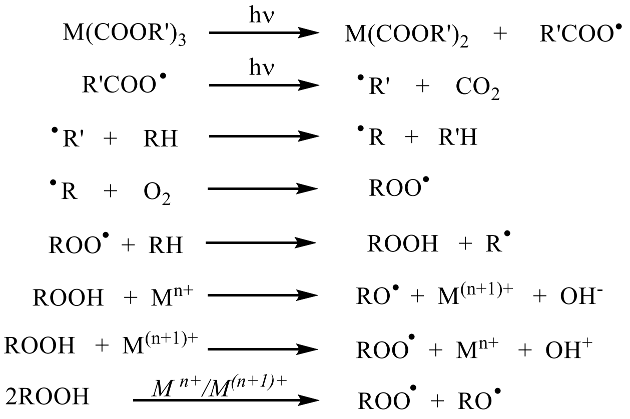
Classification numbers: 2.3.1, 2.9.3

1. INTRODUCTION

One of the main mineral fillers have been common used in polymeric materials is calcium carbonate, with an annual global consumption of approximately ten million tons. This is a naturally occurring substance that is plentiful and has the right characteristics for use as a filler in all types of polymers, including excellent whiteness, low refractive index, nontoxicity, good color, as well as being reasonably soft and easily milled to a fine size [1, 2]. Another important reason is that they contribute to lower product costs [3]. Calcium carbonate is commonly used to produce plastic films such as shopping bags, garbage bags and many other types of plastic products.

Polyolefins such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) or polystyrene (PS) are important packaging materials because they are flexible, have good barrier properties, and are inert to external influences like heat, radiation, chemicals and microorganisms. But environmental issues are also challenging when promoting the use of these plastics because they do not degrade easily [4]. In the natural environment, the degradation process can take centuries.

One of the research directions to promote the degradability of traditional polyolefins, especially PE, which is interesting in research by scientists around the world, is the use of pro-oxidant additives. These additives are usually transition metal ions (such as Ti, Mn, Co, Fe, Ni, Cu, Zn, etc.) in the form of salts or complexes with other organic compounds, in which the most effective is the stearate salt of Fe^{3+}, Mn^{2+} and Co^{2+} [5]. These additives will promote the degradation of PE to generate polar functional groups such as carboxyl, alcohol, aldehyde, ketone, ester, ether, etc. The following diagram (Figure 1) illustrates the mechanism of action of the pro-oxidant additives [6].



$$M(COOR')_3 \xrightarrow{h\nu} M(COOR')_2 + R'COO^\bullet$$
$$R'COO^\bullet \xrightarrow{h\nu} {}^\bullet R' + CO_2$$
$${}^\bullet R' + RH \longrightarrow {}^\bullet R + R'H$$
$${}^\bullet R + O_2 \longrightarrow ROO^\bullet$$
$$ROO^\bullet + RH \longrightarrow ROOH + R^\bullet$$
$$ROOH + M^{n+} \longrightarrow RO^\bullet + M^{(n+1)+} + OH^-$$
$$ROOH + M^{(n+1)+} \longrightarrow ROO^\bullet + M^{n+} + OH^+$$
$$2ROOH \xrightarrow{M^{n+}/M^{(n+1)+}} ROO^\bullet + RO^\bullet$$

Figure 1. Mechanism of action of the pro-oxidant additives [6].

Currently, there are many studies on the degradation process of PE films containing pro-oxidants. Maryudi *et al.* [7] studied the thermal degradation of high density polyethylene (HDPE) films containing 0 - 1 wt.% of manganese laurate at 70 °C for 1000 hours. Manganese laurate accelerated the thermal degradation of HDPE films. The tensile strength and elongation at break of the sample containing 1 % wt.% of manganese laurate decreased by 43.33 and 55.85 %, respectively, while those of pure film decreased by only 11.74 and 16.21 %, respectively. Roy *et al.* [8] synthesized and characterized two cobalt complexes (cobalt maleate - styrene copolymers and cobalt stearate), and studied the influence of these complexes on the thermal and photodegradation processes of low density polyethylene (LDPE) film. The results showed that cobalt stearate accelerated the degradation of LDPE but cobalt maleate - styrene did not. Fontanella *et al.* [9] studied the degradability of PE resins (LDPE, HDPE, linear low density polyethylene (LLDPE)) in the presence of pro-oxidants and found that HDPE was oxidized more slowly than LDPE and LLDPE. However, most of the studies focus on assessing the degradability of PE films without fillers, whereas the commercial products of PE such as shopping bags, and garbage bags usually contain carbonate fillers. Therefore, this paper aims to evaluate the effect of pro-oxidants on the photodegradability of recycled PE films containing calcium carbonate.

2. MATERIALS AND METHODS

2.1. Materials

Recycled high density polyethylene (HDPE) pellets with melt index (MFI) (190 ^oC/2.16 kg) of 5 g/10 min was from Viet Nam. Metallocene linear low density polyethylene (mLLDPE) with a density of 0.93 g/cm^3, MFI (2.16 kg/190 °C) of 3,5 g/10 min was from China.

The pro-oxidant additives (Cobalt (II) stearate, manganese (II) stearate and ferric stearate) were supplied by Jingjiang Hangsun Plastic Additives Co., Ltd (China). In order to uniformly disperse in the HDPE film, the pro-oxidant additives were added to the film in the form of a masterbatch (10 wt.% of pro-oxidants mixture, manganese/ferric/cobalt stearate with a weight ratio of 18:4:1).

Taical with 80 wt.% of calcium carbonate ($CaCO_3$) (an average particle diameter of 3 μm) was from China. Antioxidant additive (Irganox 1010) was supplied by BASF Corporation (Charlotte, Carolina), density at 20 ^oC: 1.15 g/ml, melting range: 110 - 125 ^oC. Stearic acid (Aldrich, ≥ 95 %) was used to modify the calcium carbonate particles. Because the produced garbage bags were usually black, black colorant (China) was used to color the film.

2.2. Film Preparation

HDPE films were prepared with a thickness of 30 µm in a film-blowing machine using an XD-35 extruder with a 35 mm screw with an L/D ratio of 28:1. Because molten PE was very sensitive to oxidation with air–oxygen during processing, especially PE film containing pro-oxidants. Therefore, it was necessary to add a certain amount of antioxidant additive so that the PE film could maintain its mechanical properties during a certain period of storage and use. The antioxidant additive was incorporated into the film formulation with a content of 0.5 wt.%. Pro-oxidant masterbatch was added with various concentrations, as shown in Table 1.

Table 1. Compositions of HDPE film samples (%).

Sample	Waste HDPE	mLLDPE	Pro-oxidant masterbatch	Taical	Color masterbatch	Antioxidant additive
HD0	62.5	10	0	25	2	0.5
HD0.5	62.0	10	0.5	25	2	0.5
HD1	61.5	10	1	25	2	0.5
HD2	60.5	10	2	25	2	0.5

2.3. Accelerated weathering testing

The film samples with size 7 × 14 cm were tested in accelerated weather testing according to ASTM G154 standard. The accelerated conditions for one cycle were 8 hours UV at 70 ^oC, 4 hours condensation at 50 ^oC and 340 nm UV lamp. The film samples were accelerated aging for 12 days.

2.4. Characterization

2.4.1. Mechanical properties

Tensile properties of film specimens were measured by BP1068 Testing Machine (Dongguan Baopin Precision Instrument Co., Ltd, Dongguan, China), according to ASTM D882 at a crosshead speed of 10 mm/min.

2.4.2. Scanning electron microscope (SEM)

The surface morphology of film samples was analyzed by a scanning electron microscopy (SEM) (JEOL 6490, Tokyo, Japan) at 15 kV. The surface of the samples was coated with platinum using a sputter coater before the examination.

2.4.3. Fourier transfer infrared spectroscopy (FTIR)

The chemical changes in the structure of PE films before and after accelerated weathering testing were observed by using a Fourier transform infrared (FTIR) spectrometer (Nicolet Impact model 410, Nicolet, Madison, WI, USA). The equipment was operated with a resolution of 4 cm^{-1}, and scanning ranged from 4000 to 400 cm^{-1}. The carbonyl index (CI) was calculated from the ratio of the total area of the absorption band at 1713 cm^{-1} (carbonyl peak) to the total area of the absorption band at 1465 cm^{-1} ($-CH_2-$ scissoring peak) [10], the hydroxyl index (HI) was calculated from the ratio of the total area of the absorption band at 3350 cm^{-1} (hydroxyl peak) to the total area of the absorption band at 1465 cm^{-1} ($-CH_2-$ scissoring peak).

2.4.4. Differential scanning calorimetry (DSC)

Differential scanning calorimetry analysis was conducted using NETZSCH DSC 204F1 Phoneix (Netzsch, Selb, Germany). The sample was heated at a rate of 10 ^{o}C/min from room temperature to 200 ^{o}C.

3. RESULTS AND DISCUSSION

3.1. Mechanical properties

The changes in mechanical properties of the HDPE film samples during photooxidation were shown in Figures 2 and 3.

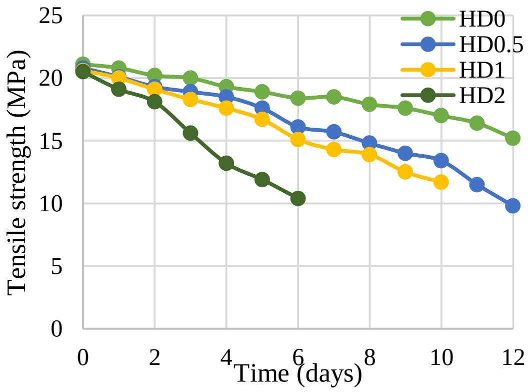


Figure 2. Tensile strength of films during photo-oxidation time.

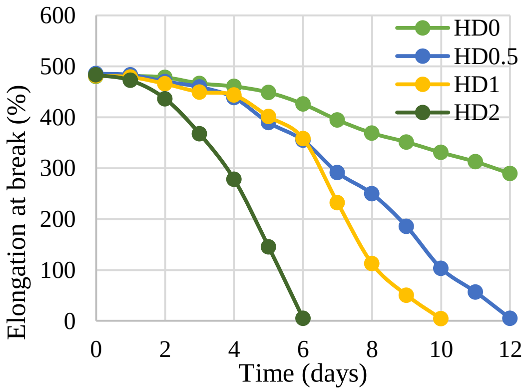


Figure 3. Elongation at break of films during photo-oxidation time.

The results showed that the mechanical properties of the original film samples were of insignificant difference. Thus, the pro-oxidant additives unchanged the mechanical properties of the original film samples. Under the impact of heat and UV radiation, the polymer chains were broken into shorter chains, leading to a decrease in the mechanical properties of the samples. The results in Figures 1 and 2 also showed that the photo-oxidation of the control film samples without pro-oxidatns (HD0) took place very slowly. After 12 days of photooxidation aging, the tensile strength and elongation at break of HD0 film decreased by only 27.9 and 39.7 %, respectively. For film samples with pro-oxidant additive, the mechanical properties of the HD films decreased as soon as they were exposed to UV radiation. When increasing the pro-oxidant content, the degradation rate of the films increased and was much faster than that of the control sample. After 6 days of accelerated aging, the elongation at break of HD0, HD0.5, HD1 and HD2 films decreased by 11.3 %, 27.0 %, 25.6 % and 99.0 %, respectively. The elongation at break of the HD0.5, HD1, HD2 films was < 5 % after 12, 10 and 6 days of accelerated aged, respectively. Therefore, the HD0.5, HD1; HD2 films were considered to self-destruct after 12, 10 and 6 days of photooxidation, respectively.

3.2. FTIR-spectra

The degradation of the polymer resulted in structural changes and was assessed by FTIR. FTIR spectra of original and photo-oxidized HDPE films were shown in Figure 4.

The results showed that the IR spectra of the HDPE films containing pro-oxidants after 6 days of accelerated weathering appeared peak at 1700 cm^{-1}, which was assigned to the carbonyl group (C=O). This peak was specific for various oxidized products such as carboxylic acids (1700 cm^{-1}), ketones (1714 cm^{-1}), aldehydes (1733 cm^{-1}), esters (1733 cm^{-1}) and lactones (1780 cm^{-1}) [11, 12]. In addition, there was a wide peak at 3351 cm^{-1}, which was assigned to the stretching vibration of OH group. These results were also consistent with the study of Maryudi *et al.* [7]. The IR spectra band of the HDPE films with pro-oxidants, also appeared peak at 1000 - 1100 cm^{-1}, was assigned to C-O and C-O-C group. The formation of these products could be explained as follows: hydroperoxide was one of the main oxidation products of polymers, under the influence of UV/temperature or combination with another free radical to form the different oxidation products shown in Figure 5.

The carbonyl and the hydroxyl index were parameters used to assess the degree of degradation. The CI, HI of the original and photo-oxidized HDPE films were shown in Figures 6 and 7.

It could be seen that in the control sample (HD0), the CI and HI were almost unchanged in the early aging stage, only slightly increased after 6 days of photo-oxidation. The CI, HI of films containing pro-oxidant increased slowly in the early stages because the degradation of polyethylene was characterized by an induction period (forming free radicals) so at this stage the oxidation reactions occurred very slowly.

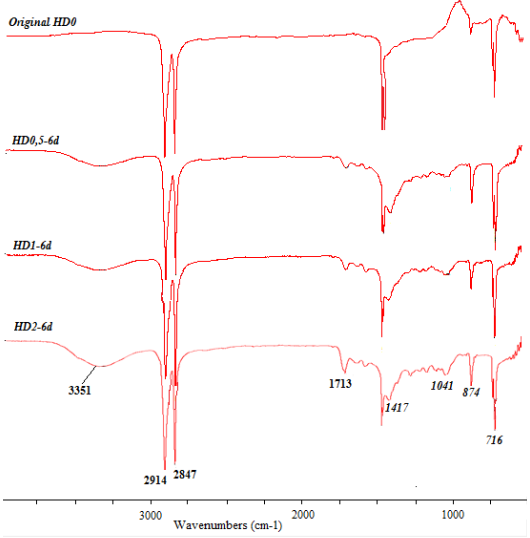


Figure 4. FTIR spectra of original and photo-oxidized HDPE films.

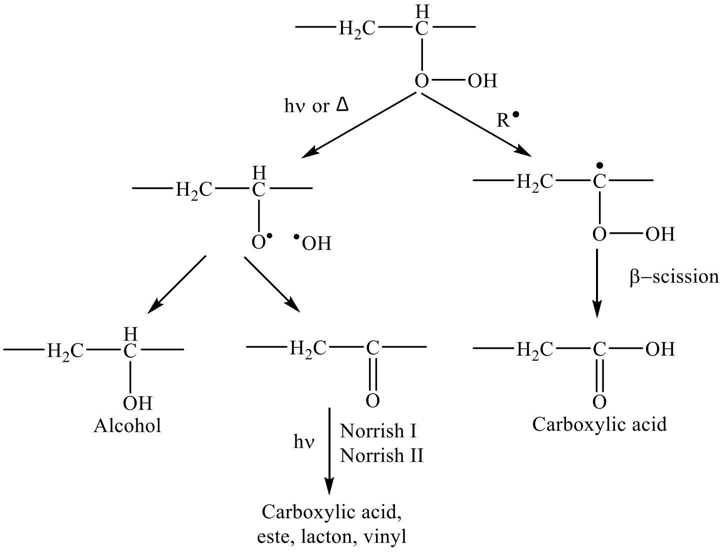


Figure 5. Decomposition mechanism of hydroperoxide to form different degradation products [13].

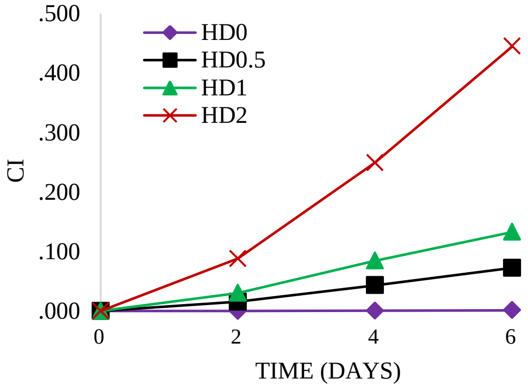


Figure 6. The CI of original and photo-oxidized HDPE films.

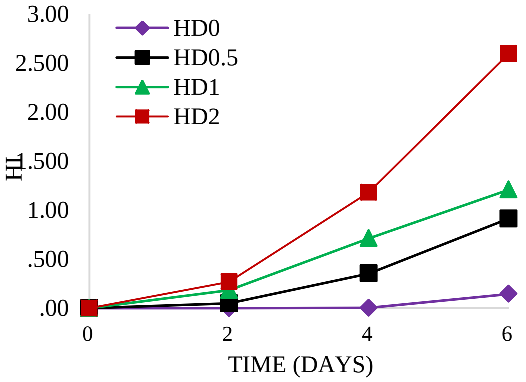
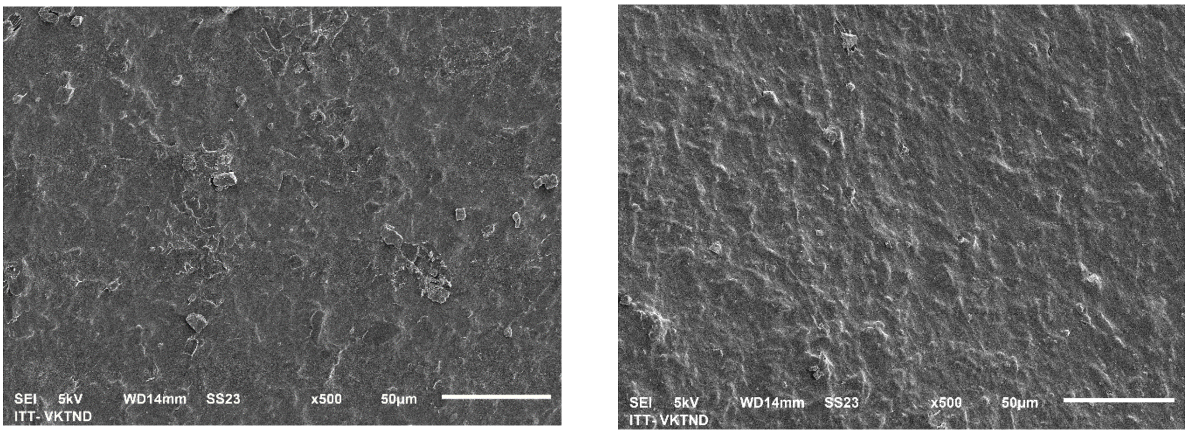


Figure 7. The HI of original and photo-oxidized HDPE films.

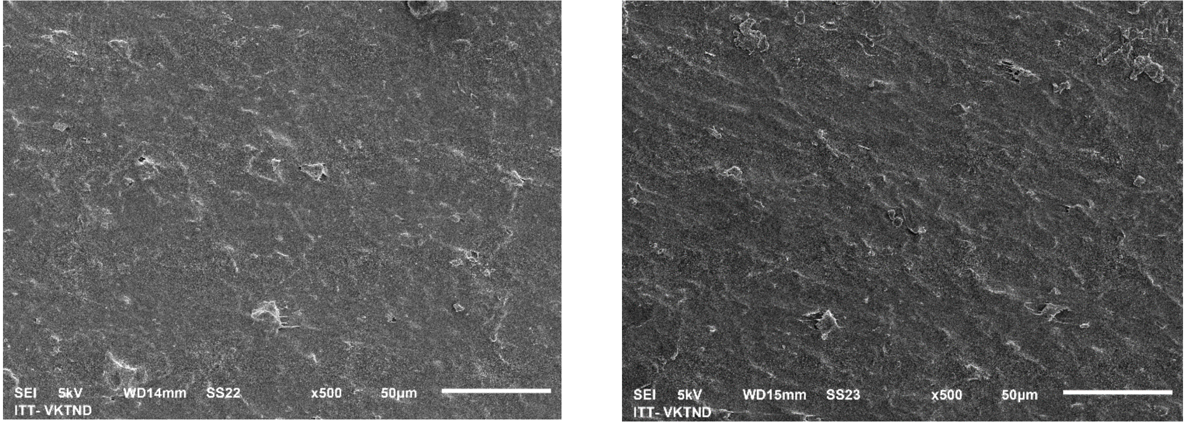
The results also showed that the CI, HI index increased by increasing the content of pro-oxidants. The higher the carbonyl index was, the stronger the sample's oxidation was. Thus, under the influence of UV radiation, heat and humidity, the pro-oxidants were decomposed, generating free radicals, initiating the reaction, promoting the oxidation of PE films leading to accumulation of carbonyl and hydroxyl groups.

After 6 days of accelerated weathering the carbonyl index in HD0, HD0.5, HD1 and HD2 samples were 0.001, 0.073, 0.133, 0.445, the hydroxyl index of these samples was 0.145, 0.913, 1.208, 2.597, respectively.

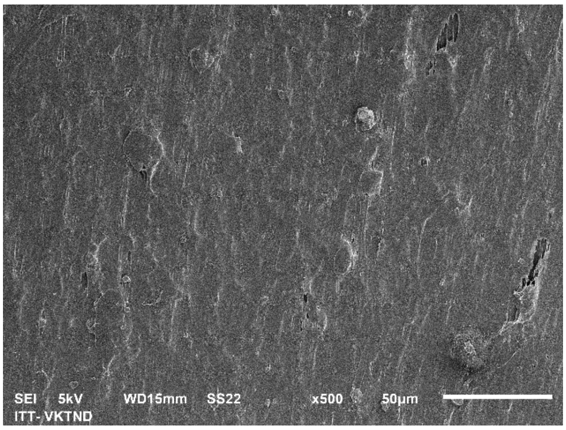
3.3. Surface morphology of HDPE films



Original HD0 HD0 – 6d



HD0.5 – 6d HD1 – 6d



HD2 – 6d

Figure 8. Surface SEM images of the original HDPE films and HDPE films after 6 days of accelerated weathering.

The degradation of HDPE films led to changes in the surface morphology of films. Surface SEM images of the original and oxidized HDPE films were shown in Figure 8.

Because the surface of original films with $CaCO_3$ was rough, making it more difficult to observe the surface change after degradation. The surface of HD0 film was almost no change while the surface of the HD0.5, HD1; HD2 films appeared craters, especially at the phase separation between the resin matrix and $CaCO_3$. The craters become more and more extensive as the content of pro-oxidant additives in the film increases.

3.4. DSC diagrams of the HDPE film

Figure 9 showed the DSC curves of the HDPE films. The analytical data from the DSC diagram of the HDPE films before and after photo-oxidation were summarized in Table 2.

Table 2. Differential scanning calorimetry results of HDPE films.

Sample	Original		After 6 days of accelerated weathering	
	T_m (°C)	ΔH_f (J/g)	T_m (°C)	ΔH_f (J/g)
HD0	135.1	125.1	134.8	125.9
HD0.5	135.3	125.0	133.7	130.7
HD1	135.2	125.4	132.1	135.3
HD2	135.5	125.7	131.4	143.9

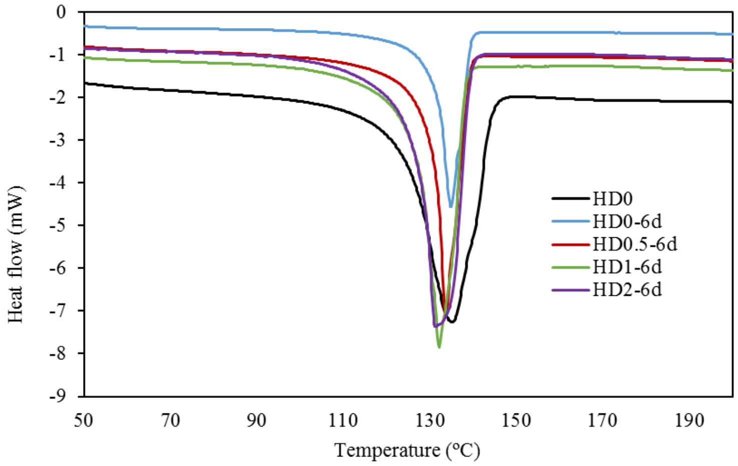


Figure 9. DSC curves of the HDPE films.

The results showed that, the melting temperature of HD0 film was almost unchanged after 6 days of photo-oxidation. Melting temperatures of the HD0.5, HD1, HD2 films decreased. The heat of fusion of the films had the opposite trend, it increased after 6 days of photo-oxidation. As the content of pro-oxidant additives in the film increased, the melting temperature decreased but the heat of fusion increased. The heat of fusion of the films increased, indicating that their crystallinity increased. This was due to the fact that under the impact of the pro-oxidant additives, the amorphous region of the material was decomposed first, leading to a decrease in the content of the amorphous region and an increase in the content of the crystalline region [14].

4. CONCLUSIONS

The effect of pro-oxidants on the degradability of recycled HDPE films containing calcium carbonate was studied by accelerated weathering test. The degradation rate of the oxo-HDPE films was much faster than that of the controlled PE film and increased by increasing pro-oxidants content. The tensile strength and elongation at break was found to be decreased with increasing amount of pro-oxidants loading due to the chains rupture of the HDPE molecular caused by the oxidation of the aged plastic. After accelerated weathering treatment, IR spectra of oxo-HDPE films showed the appearance of the polar functional groups such as carbonyl groups, OH, C-O and C-O-C group which were the results of oxidative degradation process. The melting temperature were found to be decreased more significantly for samples with pro-oxidants than that of pure samples. In addition the heat of fusion increased, indicating an increase in the degree of crystallinity of the samples. The results indicated that pro-oxidants accelerated the degradation of HDPE under accelerated weathering. It was found that the extent of degradation depended on the amount of added pro-oxidants.

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

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