

# Changes in crystallinity of HDPE films containing different amounts of an oxo-biodegradable additive due to UVC exposure

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Received: 12 May 2019, Accepted: 13 September 2019

## ABSTRACT

Crystallinities of high-density polyethylene (HDPE) films containing various amounts of an oxo-biodegradable additive (HES-W) were investigated immediately after preparation and 6 weeks after ultraviolet (UV) irradiation ( $\lambda=254$  nm). HDPE granules were mixed with oxo-biodegradable masterbatch in a twin-screw extruder and the extrudates were converted into films with thicknesses of  $35\pm 5$  micrometers. The films were exposed to UV light for 6 weeks. Crystallinities of the films are investigated by X-ray diffraction spectroscopy (XRD) and differential scanning calorimetry (DSC). The XRD results show that upon UV exposure, the crystallinities of the films enhance. The DSC thermograms have confirmed the XRD results and also show a decrease in melting points of the samples after UV exposure. Further investigations on viscosity average molecular weights ( $M_v$ ) of the samples show that their  $M_v$  decrease sharply after UV exposure. Scanning electron microscopy (SEM) shows clear cracks on the samples surfaces after 6 weeks exposure to UV irradiation. Investigating the functionalities of the polymers through Fourier transform infrared spectroscopy (FTIR) show the emergence of carbonyl peaks after UV irradiation so that the carbonyl index of the samples increases. It is concluded that maximum oxo-biodegradation enhancement of the HDPE film samples can be achieved by using a specific amount of the oxo-compound (3 wt%); furthermore the crystallinities of the samples show considerable enhancement after UV exposure which can be due to better packing ability of low molecular weight chains along with probable dipole-dipole attractions between the carbonyl groups on different newly formed short polar chains. **Polyolefins J (2020) 7: 25-32**

**Keywords:** Oxo-biodegradability, high density polyethylene, crystallinity, UV irradiation, supercooling effect.

## INTRODUCTION

Polyolefins as the most widely used polymers in the plastic industry have gained large attentions of academic and industrial research groups. Their acceptable physical and mechanical properties along with the low price and availability have caused them to be the most widely produced polymers and their production will approach approximately to 170 million metric tons in

2020 by the growth rate of 4.51% [1]. These polymers generally have high average molecular weights and are considered as bio-inert due to their resistance toward assimilation by fungi, algae, bacteria and other single-celled microorganisms. Their hydrophobic surface is not proper for the activity of these organisms. However, oxidative degradation of them results in the

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production of low molecular weight species bearing various oxygen-containing functionalities including carbonyl, hydroxyl and carboxyl groups which provide a suitable hydrophilic moiety for the activity of the microorganisms [2-5].

One of the main subclasses of polyolefins is polyethylenes which can be easily processed and converted into thin films and fibers. Right now these polymers have the largest use in packaging industries. Although these films and fibers are produced for short-term uses, their long life and non-biodegradable nature have caused them to be a serious source of environmental pollution after being discarded.

Biodegradation is an effective method in polyolefin degradation which happens through various oxidation processes along with assimilation of the products of the oxidation step by microorganisms. In this method, the first stage can be fulfilled through the action of water (hydro-biodegradation) or oxygen (oxo-biodegradation) [6-8]. Polyethylene can be degraded through two-stage oxo-biodegradation process. The first stage is oxidative degradation (also called peroxidation stage) which is abiotic and the second stage is biotic in which the oxidation product of the first stage is assimilated by microorganisms. The first stage in which polyethylene is oxidized and its molecular weight decreases is very important and the overall rate of the process is determined by this stage. In this stage, sunlight and temperature can play a vital role and the products are more compatible with microorganisms [9-11]. One of the methods for inducing the abiotic oxidation in polyethylene is the use of transition metal complexes in the polymer matrix. Usually, stearates of  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  or  $\text{Co}^{2+}$  are used for this purpose [5, 9]. In photo-oxidation reactions,  $\text{Fe}^{2+}$  acts as a source of free radicals while in thermo-oxidation reactions  $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$  act as initiators [5, 12-15]. Therefore, the polymer is being degraded through radical chain reactions in the presence of oxygen in air. The first products of the degradation process are hydroperoxides which can result in chain breakage, causing low molecular weight hydrophilic species which are appropriate for the activity of microorganisms [5].

In the polyethylene family, the high density and high molecular weight of HDPE have made it the most resistant polyethylene toward biodegradation

[16, 17]. In this semi-crystalline polymer most of the chains are packed and oriented and a limited number of chains are accessible for the activity of microorganisms. This packed structure along with hydrophobicity of the chains limits the probability of water and oxygen diffusion [18]. By introducing pro-oxidants in the polymer matrix and implementing UV irradiation, degradation of chains on the surface occurs and opens the way for diffusion of oxygen to the bulk of the sample and degradation continues. Degradation products are suitable for microorganisms to be assimilated simultaneously. In the present article the effect of UV irradiation is studied on crystallinity of HDPE samples containing various amounts of one of the widely used oxo-biodegradation additive i.e.

HES-W in the presence of air to find out what happens to the crystallinity of the sample during oxo-biodegradation process and whether the result can affect the biodegradation process or not.

## EXPERIMENTAL

### Material

High-density polyethylene (bulk density  $0.949 \pm 0.002 \text{ g.cm}^{-3}$ , with the commercial name of Ex-5) containing calcium stearate, zinc stearate and Irgafos 168 was provided by Jam Petrochemical Company (Asaluyeh, I.R.Iran). HES-W oxo-biodegradable additive was purchased from Add-X Biotech Company (Sweden).

### Film Preparation

According to Table 1, specified amounts of HDPE granules (Ex-5) were mixed with a constant amount of Addiflex oxo-biodegradable additive and melt blended in a ZSK co-current twin-screw extruder (Coperion, Germany) with a temperature profile shown in Table 2 at 100 rpm screw speed and the final blend was granulated using Accrapack instrument (series 750, England). Then the granules were converted into films with  $40 \mu\text{m}$  thicknesses using a film blowing instrument (Brabender, single screw, L/D=26, screw speed= 37 rpm, Germany) with a temperature profile shown in Table 3.

The thicknesses of the films were controlled by a digital caliper (Asimetco) and their thickness was

**Table 1.** Weight of each component present in the prepared samples

Entry	HDPE		Additive		
	g	wt%	g	wt%	wt% (active species <sup>(a)</sup> )
1	500	100	0	0	0
2	495	99	5	1	0.3
3	485	97	15	3	0.9
4	475	95	25	5	1.6

<sup>(a)</sup> The active species is 0.31 weight percent of the additive.

35±5 μm.

### Photo-Oxidation

The films were irradiated with UV light ( $\lambda=254\text{nm}$ ) in a UV chamber (Dimensions: 13×50×75 cm) equipped with a Hitachi (Japan) UV lamp (18-Watt, 60 cm length), at ambient temperature. The vertical distance between the films surface and the UV lamp was 30 cm (ASTM D6954-04). The samples were subjected to UV irradiation for six weeks (1008 h).

### Polymer Characterization

#### Crystallinity

To investigate the effect of oxo-biodegradation on crystallinity before and after UV exposure, the samples were analyzed by two well-known analysis techniques including XRD and DSC. The X-ray diffraction data were recorded between  $2\theta = 0^\circ$  to  $30^\circ$  on a Siemens D5000 instrument using  $\text{CuK}\alpha$  radiation of wavelength  $\lambda=0.154056\text{ nm}$ . To achieve degrees of crystallinity and also the melting points of the samples, differential scanning calorimetric analysis was carried out on a DSC-NEUZSCH 200 F3 (Germany). The heating cycle was from 25 to  $160^\circ\text{C}$ . The heating and cooling rates of the samples were the same and equal to  $10^\circ\text{C}/\text{min}$ .

#### Molecular Weight

The intrinsic viscosities of the samples before and after degradation were determined in decahydronaphthalene at  $135^\circ\text{C}$  using a SOFICA-CINEVISCO viscometer, serial No.V04/1CE. The Mark–Houwink– Sakurada

**Table 2.** Temperature profile in twin-screw extruder

Zone	Feed	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	Die
Temperature (°C)	160	170	180	185	190	195

**Table 3.** Temperature profile in film blowing instrument.

Die	2 <sup>nd</sup>	1 <sup>st</sup>	Feeding	Zone
200	195	180	170	Temperature (°C)

equation was used to calculate  $M_v$ . The required constants  $\alpha$  and  $K$  were 0.7 and  $0.062\text{ mL}\cdot\text{g}^{-1}$ , respectively [19, 20].

### FTIR

The changes in the chemical structures of the films, especially the emergence of polar functional groups on them due to oxidation, were monitored using IR analysis on an FTIR Bruker 55-EQUINOX (Germany) instrument. No further preparation was done on the film samples. By using the FTIR results, carbonyl indices of the samples were calculated by taking the area ratio of the carbonyl stretching band around  $1715\text{ cm}^{-1}$  to that of the C-H deformation band near  $1465\text{ cm}^{-1}$  using the integration limits of  $1705\text{ cm}^{-1}$  to  $1725\text{ cm}^{-1}$ , and  $1460\text{ cm}^{-1}$  to  $1475\text{ cm}^{-1}$ , respectively [21].

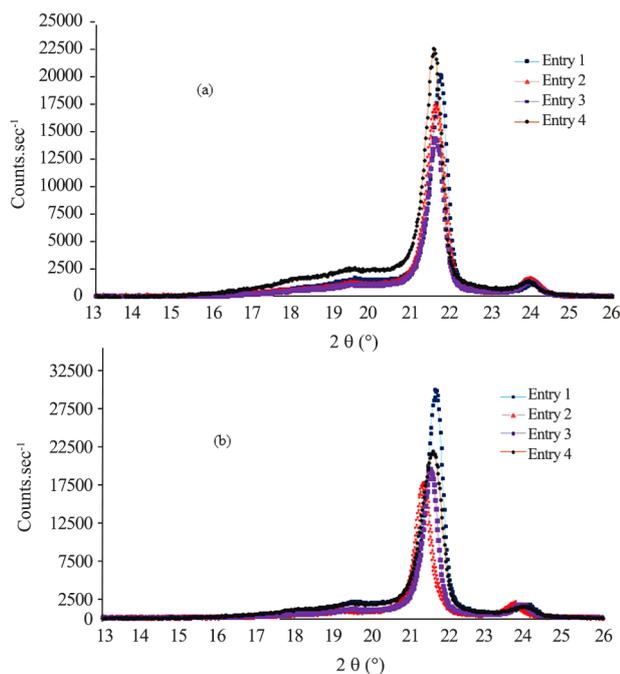
### Surface Morphology

The changes in surfaces morphologies of the film samples due to UV irradiation were monitored on a WEGA (TESCAN) scanning electron microscope after coating with gold. An accelerating voltage of 20.00 kV was used with a mean working distance of 14 mm.

## RESULTS AND DISCUSSION

Figure 1 illustrates the XRD patterns of the samples. As is clear from the figure, the addition of oxo-compound to neat HDPE and melt blending in the extruder did not alter the diffraction pattern of the samples which indicates that the inorganic species present in the oxo-compound did not affect the crystal structure of the samples. Also, after UV irradiation for 6 weeks, the diffraction patterns have not changed.

Although melt blending and UV irradiation did not show a considerable effect on the diffraction pattern of the samples, the calculated degrees of crystallinity of all entries (Table 4) increased after UV irradiation. This increase can be considered as a clue for degradation of the polymer due to UV irradiation;



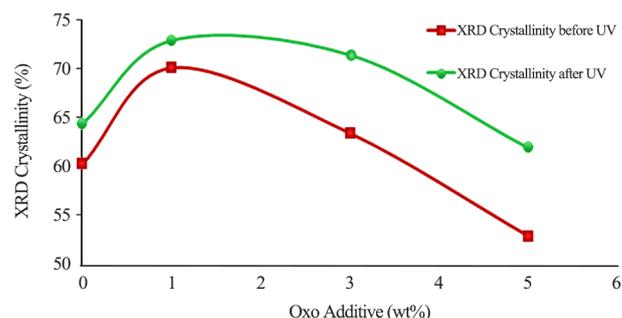
**Figure 1.** XRD patterns of samples (a). Immediately after mixing; (b). After 6-weeks of UV irradiation.

in fact due to degradation the chains become shorter and they can pack beside each other more easily and as a result, the degree of crystallinity goes up [22]. In this characterization method since the sample is solid (thin film), the chains cannot be oriented and ordered through translational motion but it can be said that during UV irradiation, the temperature of the samples increases and enough kinetic energy for annealing of the degrading chains is provided. During annealing, the chains can reorient through limited rotational motions of various segments (trans-gauche transformations) of the chains. Entry 4 showed lower crystallinities than the other entries (Figure 2) which can be due to crosslinking of the chains due to overdosing of the oxo-additive [24].

For better evaluation of the XRD results, the samples were also studied by DSC. As is clear from Table 5 and Figure 3, the DSC results show that the

**Table 4.** Crystallinity of samples according to X-ray diffraction data

Entry	Crystallinity (%)	
	Immediately after mixing	After 6 weeks of UV exposure
1	60.4	64.5
2	70.2	73.0
3	63.5	71.5
4	53.0	62.0



**Figure 2.** Crystallinity trends of samples before and after UV irradiation obtained by XRD.

crystallinities (obtained from the 2nd heating cycle) of all of the entries are increased after UV exposure while their corresponding melting points (Figure 4) are decreased and they are not broad anymore. These findings can be indicative of the presence of higher amounts of crystals but with smaller dimensions in samples after UV exposure. By considering the results of molecular weight studies (Table 6) it can be said that UV irradiation has caused the samples to degrade and as a result shorter polymeric chains are produced which can be ordered and packed more easily beside each other during the 1<sup>st</sup> heating and cooling cycle. The shorter dimensions of degraded chains along with the presence of inorganic impurities coming from oxo-compound and acting as a nucleating agent can decrease crystal dimensions, and therefore lowering melting points. The difference between crystallinities obtained from XRD and DSC can be probably originated from the removing thermal history of samples in the first scan of DSC. By considering the results of crystallinities and molecular weights of the samples before UV irradiation (Tables 5 and 6) it can be concluded that the degradation is started during the mixing process in the extruder which results in lower molecular weights and crystallinities (entries 2 and 3 but not 4). The high molecular weight of entry 4 is probably due to high amounts of crosslinking in this stage because of overdosing of the oxo-additive. Another result which can be deduced from Table 5 is the difference between the amounts of increase in crystallinities of different entries after UV exposure. Entry 1 which contained no oxo-additive showed the lowest amount of increase in crystallinity due to UV exposure. For the other entries a probable cause of this observation can be the presence of oxo-compound in

**Table 5.** DSC results.

Entry	Immediately after mixing				After 6 weeks UV irradiation			
	2 <sup>nd</sup> Heating cycle		Cooling cycle		2 <sup>nd</sup> Heating cycle		Cooling cycle	
	X <sub>n</sub> (%)	T <sub>m</sub> (°C)	X <sub>c</sub> (%) <sup>(a)</sup>	T <sub>c</sub> (°C)	X <sub>n</sub> (%)	T <sub>m</sub> (°C)	X <sub>c</sub> (%) <sup>(a)</sup>	T <sub>c</sub> (°C)
1	62.8	130.2	64.0	109.0	64.2	128.2	68.9	114.3
2	53.7	132.2 <sup>(b)</sup>	62.0	110.3	60.9	128.2	64.0	113.2
3	53.2	131.4 <sup>(b)</sup>	62.2	111.5	58.7	128.8	64.0	112.5
4	51.6	131.8 <sup>(b)</sup>	61.8	110.7	60	129.3	65.1	113.6

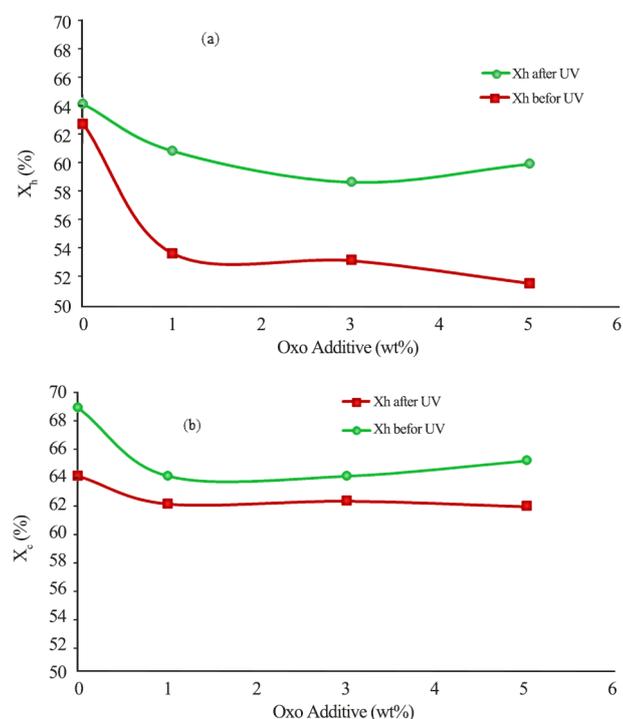
<sup>(a)</sup> Latent heat of diffusion for fully crystalline polyethylene: 293.7 J/g

<sup>(b)</sup> T<sub>m</sub> and T<sub>c</sub> are derived after fitting a Lorentzian distribution curve on the primary curves. broad

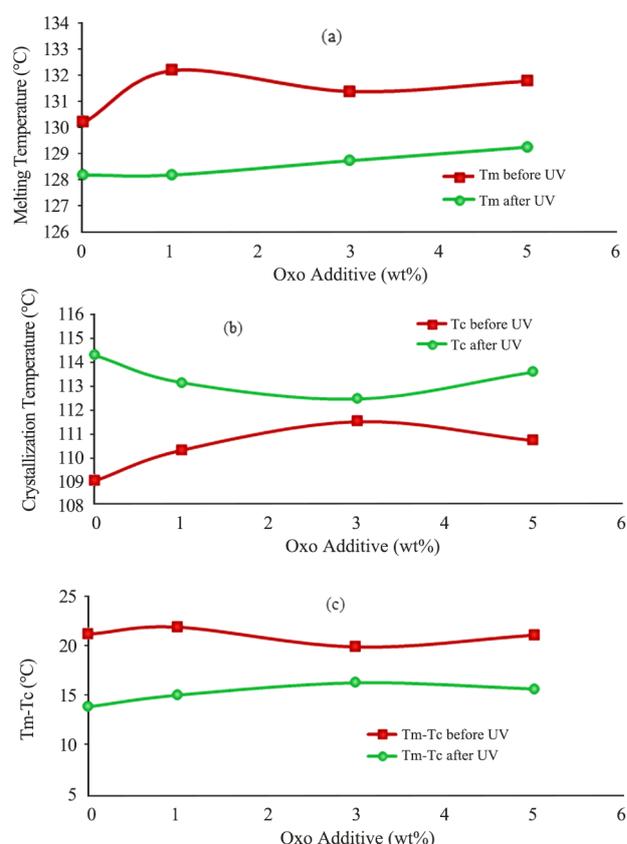
the polymer matrix which can act as an impurity and result in lower packing and lower crystallinity before UV irradiation; but after UV the oxo-compound is degraded and converted into radical-bearing species that can attack matrix chains and shorten them which can be packed beside each other readily. Moreover during the mixing process since no UV light is present and also the matrix (purchased PE granules) contains limited amounts of antioxidants (Irgafos 168), degradation of the chains is lower (compared to UV degradation) and as a result lower amounts of polar groups are emerged on the chains. But during

UV irradiation the amount of produced free radicals is so high that the antioxidant cannot temper their effect. (This issue is proved by the FTIR results, in Table 7 and Figure 5)

The results obtained from FTIR showed appearance of carbonyl groups after UV irradiation for all of the entries. Figure 5 shows FTIR spectra of the entries immediately after mixing and after receiving UV irradiation for 6 weeks. As is clear from the figure



**Figure 3.** Comparing DSC crystallinities of the samples before and after UV irradiation (a): The crystallinities obtained through enthalpy of fusion in the 2<sup>nd</sup> heating cycles, (b): The crystallinities obtained through enthalpy of crystallization in the cooling cycle.



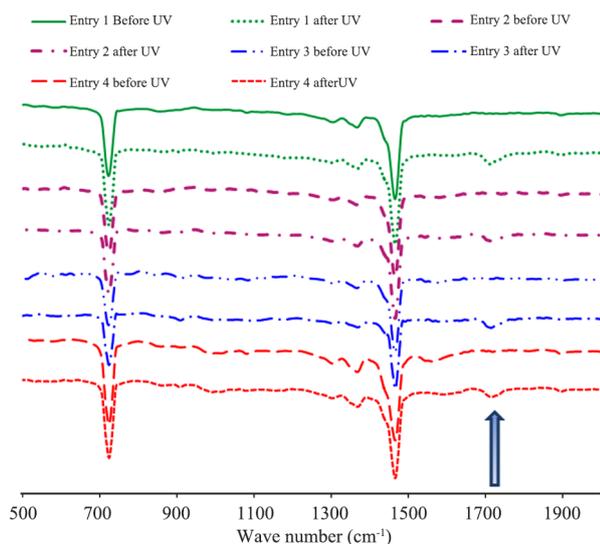
**Figure 4.** Comparing transition temperatures before and after UV irradiation; (a): Melting points (T<sub>m</sub>); (b): Crystallization temperature of samples (T<sub>c</sub>); (c): T<sub>m</sub>-T<sub>c</sub> which shows supercooling effect. All of the samples showed lower supercooling effect after UV exposure.

**Table 6.** Viscosity average molecular weights.

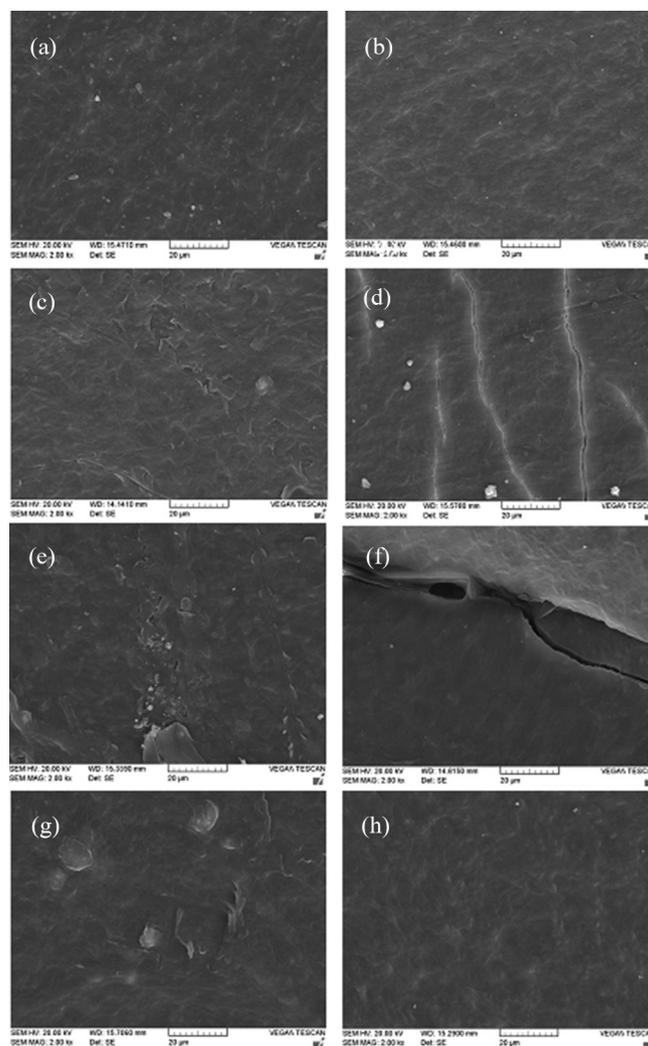
Entry	Viscosity average molecular weight (Da)	
	Immediately after mixing	After 6 weeks of UV exposure
1	$10^5 \times 3.4$	$10^4 \times 4.5$
2	$10^5 \times 3.2$	$10^4 \times 3.5$
3	$10^5 \times 2.5$	$10^4 \times 2.5$
4	$10^5 \times 3.7$	$10^4 \times 2.7$

without receiving UV irradiation, the samples do not show any peaks in  $1700 \text{ cm}^{-1}$  region while after UV exposure a clear peak is observed for all of them. Table 7 tracks the changes in carbonyl indices of the samples. As is clear from the table, entry 3 which contains 3 wt% oxo-compound shows the lowest carbonyl index. This can be due to better degradation of the sample which results in conversion of carbonyl groups to  $\text{CO}_2$  which leaves the sample as gas. [23]

Figure 6 shows the surface morphology of the entries before and after UV irradiation obtained by SEM. As is clear from the figure, entries 2 and 3 showed clear cracks on their surface after UV exposure, confirming the results obtained from the aforementioned analyses. Entries 1 and 4 did not show any cracks on their surfaces and according to results of the other analyses, it can be said that degradation in entry 1 was low while in entry 4 crosslinking occurred due to high amounts of radicals.

**Figure 5.** FTIR spectra of all entries immediately after preparation and after being exposed to UV irradiation for 6-weeks. The peak corresponding to carbonyl group is appeared around  $1700 \text{ cm}^{-1}$  after 6-weeks UV irradiation in the presence of air.**Table 7.** Carbonyl Indices of samples before and after UV exposure.

Entry	Immediately after mixing	After 6 weeks of UVR
1	4.03	8.69
2	4.12	7.24
3	4.01	3.84
4	3.99	9.04

**Figure 6.** SEM micrographs of samples: (a): Entry 1 before UV exposure; (b): Entry 1 after 6 weeks UV exposure; (c): Entry 2 before UV exposure; (d): Entry 2 after 6 weeks UV exposure; (e): Entry 3 before UV exposure; (f): Entry 3 after UV exposure; (g): Entry 4 before UV exposure; (h): Entry 4 after UV exposure.

## CONCLUSION

Investigating the effect of UV-induced abiotic degradation of HDPE films containing limited amounts of an oxo-biodegradable additive showed that maximum oxo-biodegradability of the samples occurs at specific amounts of oxo-additive i.e. 3wt%;

also, it was found that UV irradiation can result in higher crystallinities in the samples. The main factors which were identified to play role in this regard were the appearance of polar short chains in the samples after UV irradiation which were confirmed by FTIR and molecular weight studies. Short chains can pack beside each other more easily due to lower entanglements and the polar groups can result in better packing of the chains beside each other by dipole-dipole attraction. Totally it can be concluded that although UV irradiation increased the crystallinity of samples which can hinder the decomposition of them but low molecular weight polar chains can enhance the oxo-biodegradation due to providing more favorable conditions for activity of microorganisms.

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