IPPI
Polyolefins Journal, Vol. 7, No. 2 (2020)
DOI: 10.22063/poj.2020.2611.1149
ORIGINAL PAPER

Thermal and tensile behavior of LLDPE films containing limited amounts of an oxo-biodegradable additive and/or amorphous poly(1-hexene) before and after UV irradiation

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Received: 29 November 2019, Accepted 10 March 2020

ABSTRACT

Varying amounts of an amorphous poly(1-hexene) (PH, M_v 1.7×10^6 Da) were added to an LLDPE matrix containing 3% w/w Addiflex oxo-biodegradable additive (HES-W) and extruded and converted into films. Then the effect of presence of PH was investigated on microstructure, thermal and tensile behavior of polymer films before and after 6 weeks of ultra violet irradiation (UVR). Due to UVR, viscosity average molecular weight (M_v) of the sample without PH decreased from 9.6×10^4 to 4.6×10^3 Da and for the sample containing 3% w/w PH from 11.3×10^4 to 3.0×10^4 Da, also carbonyl index (CI) of the sample without PH increased from 0 to 28.7 while for the sample containing 3% w/w PH increased from 1.8 to 30.4. Moreover, differential scanning calorimetry (DSC) showed that crystallinity of the sample without PH increased from 34.4% to 36.9% and from 28.7% to 32.1% for the sample containing 3% w/w PH. Thermal gravimetric analysis (TGA) showed lower decomposition temperature for the samples containing PH. The elongation-at-break decreased from 723.0% to 88% for the sample without PH and from 410% to 10% for the sample containing PH. Atomic force microscopy (AFM) indicated smoother surfaces for samples containing 3% w/w PH before and after UVR. Although, the aforementioned results showed that the presence of limited amounts of PH in the LLDPE matrix deteriorated thermal and mechanical properties of the matrix, it hindered the oxo-biodegradablity of the matrix by opposing assimilation process perhaps due to high M_v and/or gelation. **Polyolefins J (2020) 7: 111-119**

Keywords: LLDPE; poly(1-hexene); oxo-biodegradability; UV irradiation; crosslinking.

INTRODUCTION

Today, plastic waste has become a serious problem for the environment, among which, the polyolefin films, particularly polyethylene films, are responsible for a considerable part of it. Hydrophobicity of these polymers along with their high molecular weights has caused them to be bio-inert and very resistant to various microorganisms like fungi or bacteria. However, their oxidized forms behave completely different and can be considered as eco-friendly compounds [1-3]. En route toward producing convenient and eco-friendly packaging materials, various approaches are being introduced every so often. Some of them replace polyolefins with papers, cardboard and other bio-based materials while others try to modify the already-in-use

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polyolefinic materials [4, 5]. Besides these methods, recycling, burning and burying are other approaches to reduce the amount of polyolefins released in the environment [6]. With the increasing annual consumption of plastics, the need for automatic biodegradation is fully felt.

Linear low-density polyethylene (LLDPE) is one of the most commonly used plastics in packaging due to its special properties like toughness, flexibility, strength, ease of processing, low cost, light weight and resistance to water. Various types of this polymer are widely used in making grocery bags, packaging, casings and many other disposable applications. Moreover more LLDPE is still entering traditional applications of LDPE. Since these applications are short-term ones, a considerable amount of this plastic is released into the environment as waste and due to its long life, significant environmental pollution is accompanied. In 2018, LLDPE accounted for about 32% of the total polyethylene market. World consumption of LLDPE is projected to grow at an average annual rate of almost 5% during 2018-2023[7]. Accordingly, the total global demand in 2020 would be approximately around 14 million metric tons. Therefore, working to improve the biodegradation of such high-demand polymer is an option to reduce its environmental pollution.

Addition of transition metals such as iron and cobalt is believed to promote the oxidation of polyethylenes thereby facilitating their biodegradation. In the first stage, which is abiotic, the oxygen present in the air oxidizes the polymer backbone in presence of the said transition metals and results in formation of smaller oxygen-containing molecular fragments. As a result, the polymer backbone becomes smaller, hydrophilic and can absorb water thereby providing a suitable place for microorganisms (bacteria, fungi and algae) that can consume the oxidized carbon backbone fragments to form CO_2, H_2O and biomass. The initial abiotic stage which is the rate-determining step (RDS) of the whole process can be accelerated by ultraviolet (UV) light or heat [6]. Accordingly, various types of masterbatches containing these types of cations along with stearate counter anion are now at hand, and by simply blending these masterbatches with the specified polymer, an oxo-biodegradable polymer is achieved [8-10].

In the present work, the effect of addition of different amounts of a poly(1-hexene) (PH) to an LLDPE matrix containing 3% w/w of an oxo-biodegradable compound on the rate and amount of oxo-biodegradation of the matrix is studied. To the best of our knowledge the effect of addition of PH to LLDPE matrix as a probable oxidizing aid has not been systematically studied so far, and we believe that by the use of PH the amount of needed oxo-biodegradable compound to reach specified oxidation comes down. To pursue the changes in samples, FTIR spectra, thermal properties as well as mechanical properties of the samples were compared with those of extruded neat LLDPE and LLDPE containing 3% w/w oxo-biodegradable compound.

EXPERIMENTAL

Material

Granular film grade LLDPE (LL 0209AA) was purchased from Amirkabir Petrochemical Company (Mahshahr, Iran). Addiflex oxo-biodegradable additive (HES-W) was purchased from Add-X Biotech Company (Västra Frölunda, Sweden). Decahydronaphthalene (decalin) was purchased from Merck Chemical Company (Germany). PH (M_v 1.7×10^6 Da) was produced by polymerization of 1-hexene by a Ziegler-Natta catalyst [11].

Film preparation

According to Table 1, specified amounts of LLDPE granules were mixed with a constant amount of Addiflex oxo-biodegradable additive (1% w/w) and specified amounts of PH were added and melt-blended

Table 1. Weight of each of the components present in the blends.

Entry	LLDPE		PH		Additive		
	g	wt%	g	wt%	g	wt%	wt% (AS) [a]
1	700	100	0	0	0	0	0
2	677.4	97	0	0	22.6	3	1
3	666.9	95	10.5	1.5	22.6	3	1
4	656.4	94	21	3	22.6	3	1

[a]The active species is 0.31 weight percent of the additive.

in a ZSK co-current twin-screw (L/D=40) extruder (Coperion, Germany) at a 100 rpm screw speed and temperature profile (hopper to die) of 160-170-195-200-200-200°C. The final product was collected as granules. Then the granules were converted into films with 30 µm thicknesses using a film blowing process on a Brabender extruder (L/D=26, 37 rpm) equipped with a film blowing die. The temperature profile in the extruder (hopper to die) was set at 170-180-195-200°C.

Photo-oxidation

The films were irradiated with UV light (λ=254nm) in a UV chamber, equipped with a Hitachi (Japan) UV lamp, at ambient temperature. The vertical distance between the films surface and UV lamp was 30 cm. The samples were irradiated for different periods of time including 338 h (two weeks) and 1008 h (six weeks).

Polymer characterization

FTIR

To investigate changes in the chemical structures of the films, especially the appearance of new functional groups due to oxidation, IR analysis was carried out on a FTIR Bruker 55-EQUINOX (Germany) instrument. The film samples were used without any further preparation. By using the FTIR results, carbonyl indices (CI) of the samples were calculated by taking the area ratio of the carbonyl stretching band around 1715 cm^{-1} to that of the C-H deformation band near 1465 cm^{-1} using the integration limits of 1705 cm^{-1} to 1725 cm^{-1}, and 1460 cm^{-1} to 1475 cm^{-1}, respectively [4, 12].

Molecular weight

The intrinsic viscosities of the samples before and after degradation were determined in decahydronaphthalene at 135°C using a SOFICA-CINEVISCO viscometer, serial V04/1CE. For calculation of M_v, the Mark–Houwink–Sakurada equation was used. The requisite constants α and K were 0.7 and 0.062 mL/g, respectively [13,14].

Thermal analysis

The thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses of the film samples were recorded on a TGA METTLER TOLEDO instrument in air. The thermograms were recorded for the range from room temperature to 650°C at a heating rate of 20°C/min, and initial decomposition temperature (IDT), maximum rate of decomposition (MRD), maximum rate decomposition temperature (MRDT) and temperature of half decomposition (D1/2) were found out. DSC of the samples was recorded on a DSC-NETZSCH instrument with identical heating and cooling rates of 10°C/min. T_m, T_c , ΔH_f and ΔH_c were recorded and the percent crystallinity of the samples was calculated and compared.

Roughness studies

Surface roughness (topology) of the film samples before and after degradation was investigated by atomic force microscopy (AFM) using a DME Dualscope/Rasterscope C26 instrument fitted with a silicon rectangular cantilever. An AC probe with a conical tip in tapping mode (non-contact mode) within 0.1 nN force was used. Sample surface features such as average roughness (R_a) and root mean square roughness (R_q) were obtained through the instrument software (DUALSCOPE (tm)/ RASTERSCOPE (tm) SPM, Version 2.1.1.2) [15].

Mechanical properties

The changes in tensile properties (tensile strength and elongation-at-break) of the film samples were recorded on a tensile machine according to ASTM D638 before and after UV irradiation. The test was done at 50 mm min^{-1} and constant temperature (25°C) on a Gotech Instrument (Al-7000-LA). The samples were prepared as sheets of 1mm thickness using a hot press (Toyoseiki Mini Test Press, Japan) and they were punched according to ASTM D638 Type IV. The prepared samples were free from any bubbles or defects.

RESULTS AND DISCUSSION

FTIR

Figure 1a illustrates the FTIR spectra of samples immediately after mixing while Figures 1b and 1c show the spectra after 2 weeks and 6 weeks of UV irradiation. The spectra were obtained in the range of

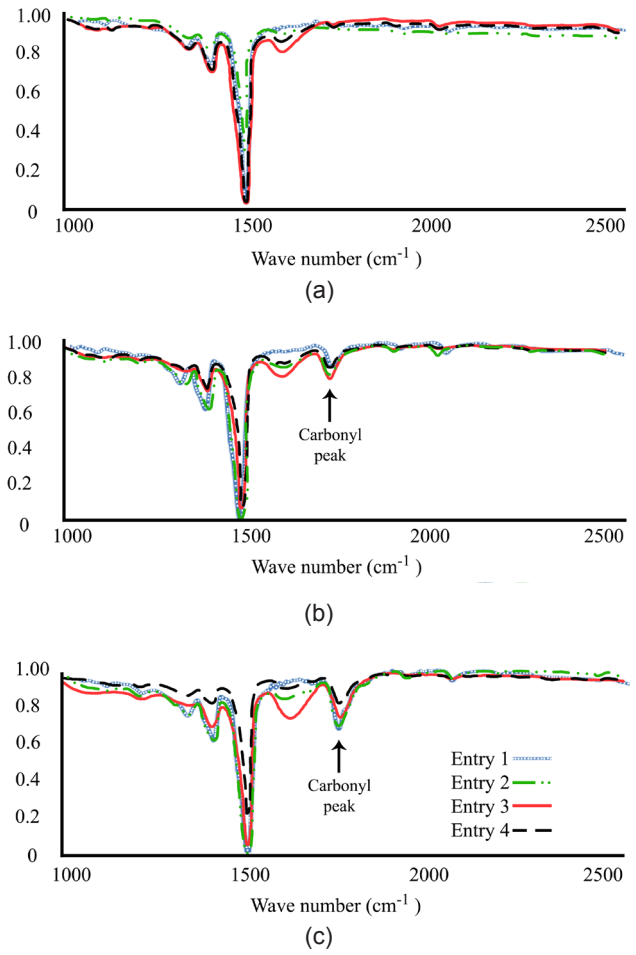


Figure 1. FTIR spectra of the film samples (a). Immediately after mixing, (b). After 2 weeks UV irradiation, (c). After 6 weeks UV irradiation.

400 to 4000 cm^{-1} but for better clarification the ranges in the figure are shown from 1000 cm^{-1} to 2500 cm^{-1}. As is clear from the figures after 2 to 6 weeks of UV irradiation, strong carbonyl peaks (1680 cm^{-1} to 1750cm^{-1}) appeared in FTIR spectra of the samples. It can be concluded that due to abiotic degradation (and oxidation) of the polymeric samples, smaller molecular fragments having oxygen-containing functional groups such as ester (-COOR), aldehyde (-CHO), alcohol (-OH) and acid (-COOH) are produced.

For better evaluation of the FTIR spectra, CI of all samples are calculated and shown in Table 2. As is clear from the table, CI of entries 3 and 4 immediately after mixing is higher than that of entries 1 and 2 which did not contain any PH and/or oxo-biodegradable additive in their matrix. This index is higher for entry 4 which contained more PH than entry 3 in addition to oxo additive. These observations can be attributed to the

Table 2. Carbonyl indices (CI) of the films after UV exposure for different periods of time.

Entry	Carbonyl Index (CI)		
	Immediately After Mixing	After 2 Weeks of Irradiation	After 6 Weeks of Irradiation
1	0	12.0	30.6
2	0	15.6	28.7
3	1.7	21.1	27.3
4	1.8	17.9	30.4

degradation which takes place during mixing process. In this stage, only abiotic degradation takes place. The higher CI of entries 3 and 4 than entry 2 can be attributed to high number of tertiary carbon atoms in the PH chains. After 2 and 6 weeks of UV irradiation the CI of all of the entries increased considerably but the amount of the increase was different. After 2 weeks of irradiation entry 3 shows the highest CI even compared to entry 4. This observation could be due to more intense biotic degradation of entry 4 than entry 3 which could result in higher conversion of entry 4 to CO_2 [4, 16], which leaves the sample as a gas, resulting in lower concentrations of carbonyl compounds in the sample matrix. By increasing the exposure time to 6 weeks, entry 3 shows the lowest CI which can be indicative of its better assimilation by micro-organisms and conversion to CO_2 which can result in lower amounts of carbonyl groups in the chains [4, 16]. Also, it can be said that due to crosslinking and gelation of entry 4, due to higher amounts of radicals originated from tertiary carbons of PH and longer UV irradiation period, the assimilation process is hindered. Comparing entries 1 and 2 with each other also shows that the assimilation process in entry 2 has occurred more due to the presence of the oxo compound.

Molecular weight

Table 3 shows the viscosity average molecular weights (M_v) of the samples. The results show that upon extruding at aforementioned conditions, neat LLDPE (entry 1) experiences a severe decrease in molecular weight (approximately 60% decrease). This decrease can be attributed to the heat and shear in the extruder which can result in chain scission. Furthermore, as is shown in the table for estimating the effect of PH on the amount of degradation of LLDPE matrix immediately after mixing in extruder, LLDPE was purified by Soxhlet and its M_v was measured. As is shown in

Table 3. Viscosity average molecular weights.

Entry	Before Mixing	Viscosity Average Molecular Weights (M_v)			
		Immediately After Mixing	Reduction in M_v (%)	After 6 Weeks of Irradiation	Reduction in M_v (%)
1	2.5×10^5	10.3×10^4 [a]	59	--------	----
2	2.5×10^5	9.6×10^4	62	4.6×10^3	98
3	2.7×10^5 [b]	10.5×10^4	61	1.8×10^4	93
4	2.9×10^5 [b]	11.3×10^4	61	3.0×10^4	90
3[c]	2.5×10^5	8.8×10^4	65	---------	----
4[c]	2.5×10^5	9.8×10^4	61	---------	----
Neat PH	1.7×10^6	----------	----	---------	----

[a] Neat LLDPE after extrusion (mixing with nothing)
[b] Calculated values
[c] After omitting PH by Soxhlet (PH is completely soluble in boiling *n*-heptane)

the table, the molecular weights are lower than those of extruded pure LLDPE but the decreases are not considerable. These measurements were performed just to see the effect of extruding condition on the matrix to help us better justification of the results. As the table shows, entry 2 shows a larger decrease in M_v after mixing. Compared to entry 1 it can be said that the oxo additive has affected the degradation of the matrix. After putting entry 2 under UV irradiation for 6 weeks, M_v decreased considerably. This decrease can be attributed to the function of the oxo compound and/or UV. Entries 3 and 4 which contain 1.5% w/w PH and 3% w/w PH, respectively, show higher molecular weights than entry 2 after mixing. This is simply because of high molecular weight of the PH mixed with the matrix. Although PH tends to degrade easier than LLDPE, its M_v is so high that the specimens produced after degradation still have high M_vs, and therefore, the overall M_v increases. The increase is more pronounced for entry 4 which contains higher amounts of PH than entry 3. After 6 weeks of UV irradiation, entries 3 and 4 continue to degrade and their M_v comes down and the decrease is more pronounced for entry 3 (83% decrease). These observations can be attributed to lower resistance of entries 3 and 4 to degradation due to the PH impurity which can destroy the crystallinity and integrity of LLDPE matrix besides producing higher amounts of free radicals due to greater number of tertiary carbon atoms in its molecules. In entry 4, possible crosslinking of the chains may also be responsible for the observed higher M_v.

Thermal analysis

DSC analysis

The DSC results are shown in Table 4. As is clear from the table, by adding PH to the samples the crystallinity is decreased at first but by increasing the amount of added PH, it increases and this trend is observed for all UV exposure times. The initial decrease can be attributed to the presence of long PH chains which hinder the crystallization of the chains but by increasing its amount due to higher amounts of tertiary carbons the degradation occurs more and

Table 4. DSC results of the samples.

Entry	UV exposure time (wk)	T_m (°C)[a]	ΔH_m(j/g)[a]	Crystallinity (%)	T_c (°C)	ΔH_c(j/g)	T_m-T_c (°C)
2	0	123.3	-100.7	27.65	107.5	79.64	15.8
3	0	124.7	-71.04	22.07	106.2	63.58	18.5
4	0	124.6	-84.05	26.45	106.4	76.2	18.2
2	2	123.6	-101.8	34.75	108.6	100.1	15
3	2	123	-96.07	31.66	108.2	91.2	14.8
4	2	123.7	-96.61	32.61	108.3	93.93	15.4
2	6	123.4	-107.8	34.57	109.6	99.59	13.8
3	6	123.1	-94.9	29.09	109.8	38.78	13.3
4	6	123.0	-40.0	29.62	110.2	85.32	12.8

[a] Obtained from the second scan.

smaller chains are produced which can crystallize more readily. Increasing UV exposure time to 2 weeks causes the crystallinities to increase at first but by extending the exposure time to 6 weeks the crystallinities decrease. The initial increase can be attributed to the degradation of the chains and their easier crystallization but by increasing the exposure period, UV light starts to degrade the crystallites present in the crystals, and therefore, crystallinity starts to decrease. Also extensive crosslinking causes high chain rigidity and restricts molecular mobility which can prevent crystallization. Before UV irradiation by increasing the amount of added PH, T_c of the samples decreases at first and then increases. Adding 1.5 w/w% of PH to the samples causes the chains to become ordered less readily in the cooling cycle, and therefore, a supercooling effect is observed. But by adding more amounts of PH to the samples since radical formation and subsequent crosslinking occurs more, the chains become ordered in crystalline forms more readily, and therefore, supercooling effect is less and T_c approaches T_m. By extending UV exposure time to two weeks since the degradation (or crosslinking) occurs more therefore the amounts of shorter segments are more and they can be ordered in crystal form more rapidly and T_c approaches T_m and supercooling is less. By extending the UV exposure time to 6 weeks, the supercooling effect for all of the samples continues to decrease but the decrease for entry 4 is more pronounced; this observation confirms the presence of crosslinking besides degradation in entry 4 after 6 weeks of UV irradiation. The heat released during the crystallization of the samples in the cooling cycle (ΔH_c) shows a similar trend to the T_c for the same reasons.

TGA analysis

Figure 2 and Table 5 show the TGA/DTG results of the samples after UV irradiation. As is clear from the results, the samples containing PH (entries 3 and 4) show lower IDT, MRD and $D_{1/2}$. This means that PH has caused LLDPE to degrade at lower temperatures but at lower decomposition rate. Also, as the amount of PH increases in the samples the aforementioned parameters show lower values. It can be said that PH has decreased the thermal stability of the LLDPE

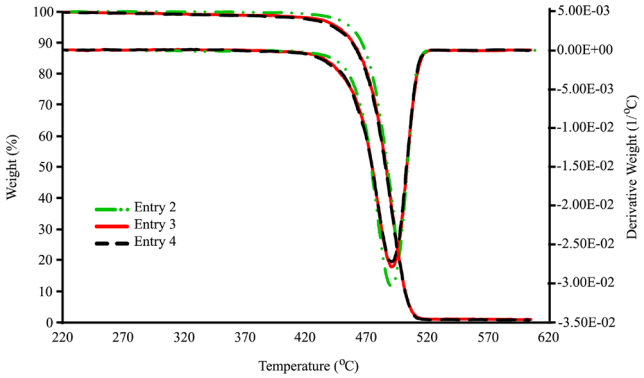


Figure 2. TGA/DTG curves of the samples after UV exposure.

matrix perhaps due to lower crystallinity and higher amounts of tertiary carbon atoms. The decrease of the parameters in entry 4 in comparison to entry 3 indicates easier degradation. It should be noted that this degradation is mostly governed by non-crosslinked chains present in the blend. This conclusion is derived from the comparison of the broadness of the DTG peaks in which the order of broadness is entry 4 > entry 3 > entry 2.

Tensile properties

As is shown in Table 6, before UV exposure the samples containing PH show lower values of tensile strength-at-yield, elongation-at-yield, tensile strength-at-break and elongation-at-break than the samples without PH. This shows that PH weakens the tensile properties of LLDPE matrix.

A contributing explanation for this is the action of PH as an impurity in LLDPE matrix; the long chains of PH can create spaces between LLDPE chains and causes the matrix to be less crystalline (which is proved in Table 4) and as a direct result of lower crystallinity, mechanical properties deteriorate. In other words, although it is expected that the presence of PH in the blend can increase the said mechanical properties due

Table 5. TGA results[a].

Entry	IDT	MRD	MRDT	$D_{1/2}$
2	467.6	-3.03×10^{-2}	490.3	487
3	464.7	-2.78×10^{-2}	491.3	486
4	461.5	-2.70×10^{-2}	490.7	485.7

[a] IDT: Initial decomposition temperature, MRD: Maximum rate of decomposition, MRDT: Maximum rate decomposition temperature, $D_{1/2}$: Temperature of half decomposition.

Table 6. Tensile properties of the samples.

Entry	UV exposure time (hr)	Tensile strength-at-yield (MPa)	Elongation-at-yield (%)	Tensile strength-at-break (MPa)	Elongation-at-break (%)
2	0	10.8	14.2	27.7	723
3	0	10.7	13.4	18.5	454
4	0	10.7	13.7	16.3	410
2	6	12.0	11.6	9.4	88
3	6	N.O.	N.O.	10.5	11
4	6	N.O.	N.O.	11.8	10

N.O.: Not observed

to higher amounts of entanglement, it seems that its role as an impurity outbalances, and therefore, the mechanical properties diminish. As is clear from the table, all of the entries show very different tensile behaviors before and after UV exposure especially at break point. In entry 2 the differences in the yield point can be attributed to the shorter polymer chains after UV irradiation. Shorter chains result in higher stress-at-yield due to crystallization, and lower elongation-at-yield due to lower amount of entanglement. Before UV irradiation, the sample shows a considerable resistance toward breaking while after UV irradiation it simply breaks at low stresses and elongation. This observation also can support the role of UV in degradation of the samples; shorter chains cannot be elongated too much due to lower amounts of gauche and trans conformations in their microstructures, and therefore, they have higher restrictions to change their conformations to alleviate the effects of tensile stresses. In other words, the longer the chains are, the more they can be elongated. After UV irradiation, entries 3 and 4 do not show any yield point at all and they simply break after a few percent of elongation and low amounts of tensile stresses. This can be due to shorter chains and/or crosslinking of the chains and/or absence of entanglements. All of these obtained values show the occurrence of degradation in the LLDPE polymer matrix but this degradation is less for the samples containing PH, especially entry 4. The number of radicals is more in entry 4 than 3 which can result in higher crosslinking, and therefore, lower EB% and higher tensile strength-at-break in entry 4.

Atomic force microscopy

The results of topography and phase image investigations by AFM analysis of the film samples are shown in Figure 3 and Table 7. In the pure LLDPE (entry 1) and LLDPE with 3% oxo additive in its

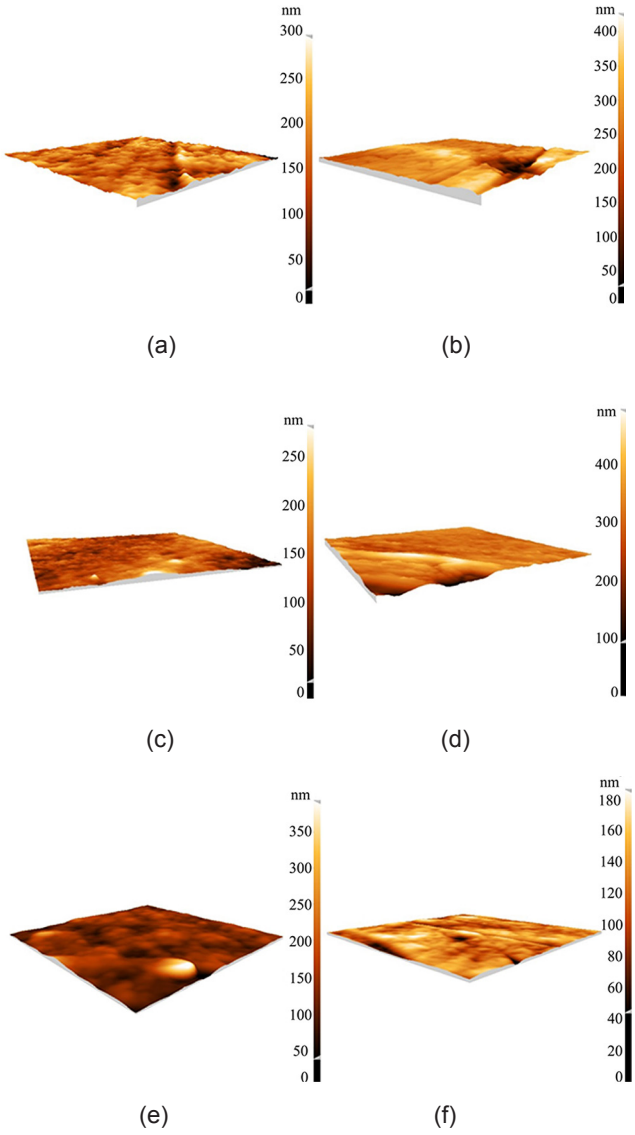


Figure 3. AFM topographic images of the samples: (a) Entry 1 immediately after mixing, (b) entry 1 after 6 weeks of UV exposure, (c) entry 2 immediately after mixing, (d) entry 2 after 6 weeks of UV exposure, (e) entry 4 immediately after mixing, (f) entry 4 after 6 weeks of UV exposure.

Table 7. Effect of accelerated aging on the roughness parameters of the samples obtained through AFM.

Entry	Arithmetic Mean Deviation (Average Roughness) S_a or R_a (nm)		Root Mean Square Deviation (RMS) S_q or R_q (nm)		Arithmetic Average Height S_z or R_z (nm)	
	No UV Exposure	After 6 wk UV Exposure	No UV Exposure	After 6 wk UV Exposure	No UV Exposure	After 6 wk UV Exposure
1	35.3	46.9	44.6	64.1	301	399
2	29.5	30	37.7	44.8	280	333
4	25.9	19.3	38.4	24.2	266	142

matrix (entry 2), after 6 weeks UV irradiation, all of the three parameters in the table increase. Meanwhile, for the sample with 3% oxo additive plus 3% PH (entry 4), after this period, not only the above parameters do not increase, but also they decrease drastically. This observation could be due to the overdosing effect and/or the presence of a high molecular weight polymer (PH and/or crosslinked chains) in the sample. In the topographic images, dark and bright regions correspond to ups and downs of the scanned surfaces, respectively. According to these results, it can be said that the intensity of surface degradation of the samples was as entry 1 > entry 2 > entry 4. In entries 1 and 2, UV exposure caused the samples to have a rougher surface showing more degradation while in entry 4 an opposite trend was observed and UV exposure caused the sample to be more smooth which can be due to crosslinking of the chains on the surface.

CONCLUSION

Addition of limited amounts of high molecular weight amorphous poly(1-hexene) to LLDPE/oxo-compound can result in inferior mechanical properties of LLDPE, and UV exposure can cause the blend to become even weaker. Samples containing PH show higher carbonyl indices before and after UV irradiation perhaps due to higher amounts of tertiary carbon atoms in their structure and their lower assimilation because of their higher M_vs and/or crosslinked chains. PH-containing blends show lower degradation temperatures perhaps due to presence of higher population of low molecular weight species in their matrix. Higher crystallinities are obtained for the blends perhaps due to presence of low molecular weight species and/or crosslinking. Totally, it can be said that the presence of PH in LLDPE matrix can deteriorate its oxo- biodegradability; although it enhances the formation of oxygen-containing groups on the chains, the produced polar chains cannot be assimilated by microorganisms due to their high molecular weights and/or crosslinked nature.

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