

## Synergistic effect of combining UV-sunlight–soil burial treatment on the biodegradation rate of LDPE/starch blends

H.A. Abd El-Rehim<sup>a,\*</sup>, El-Sayed A. Hegazy<sup>a</sup>, A.M. Ali<sup>b</sup>, A.M. Rabie<sup>b</sup>

<sup>a</sup> Department of Polymer, National Center for Research and Technology, P.O. Box No. 29, Nasr City, Cairo, Egypt

<sup>b</sup> Faculty of Science, Ain Shams University, Abassia, Cairo, Egypt

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### Abstract

The present work has focused on the possibility of accelerating the biodegradation process of low-density polyethylene (LDPE) by mixing it with starch and exposing the obtained blend to the effect of UV radiation and soil burial treatments. Comparable studies between the properties of untreated LDPE/starch blends and those exposed to UV irradiation and/or soil burial treatment were investigated. In reference to the mechanical properties of untreated blends. The tensile strength of the blends exposed to UV irradiation–soil burial treatments was reduced by 20–66%, meanwhile, the tensile strength of the blends exposed only to soil burial treatment reduced by 10–26% from the initial value according to the starch content in the blend. The changes in the thermal, structural, and morphological properties of the blends due to the photo-irradiation and/or microbial treatments were determined using differential scanning calorimetry (DSC), transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The obtained results showed that there is a synergistic effect on the LDPE/starch biodegradation process when the blends exposed to UV-sunlight and followed by soil buried treatment. This means that photo-radiation induced oxidation reaction enhanced and accelerated the biodegradability rate of LDPE/starch blends by creating oxidized LDPE/starch that is more susceptible to biotic reactions. The results suggested that it is possible to replace non-degradable polyethylene polymer by biodegradable one for controlling the lifetime of its waste.

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### 1. Introduction

During the past 20 years, there has been a continuous increase in the production of commodity and packaging plastic products such as polyolefin, accompanied by an ever-increasing amount of plastic waste. This is because such products tend to accumulate in nature due to their excellent mechanical properties, as well as chemical, weather and biodegradation resistance [1–3]. In recent years biodegradable polymers with controllable lifetimes are becoming increasingly important for application in the areas of waste management [4,5].

The degradation of most synthetic plastics in nature is a very slow process that involves environmental factors, followed by the action of wild microorganisms [6–8]. The primary mechanism for the biodegradation of high molecular weight polymer is the oxidation or hydrolysis by enzyme to create functional groups that improve its hydrophylicity.

Consequently, the main chains of polymer are degraded resulting in polymer of low molecular weight and feeble mechanical properties, thus, making it more accessible for further microbial assimilation [9–11].

Polyethylene (PE) is one of common synthetic polymers of high hydrophobic level and high molecular weight. In natural form, it is not biodegradable. Thus, their use in the production of disposal or packing materials causes dangers environmental problems [1,3]. To make PE biodegradable requires modifying its crystalline level, molecular weight and mechanical properties that are responsible for PE resistance towards degradation [6,8]. This can be achieved by improving PE hydrophilic level and/or reducing its polymer chains length by oxidation to be accessible for microbial degradation [12,13].

There is really only one way that PE can oxidize, even though there are a number of ways as ultraviolet light, heat, or oxygen to initiate the oxidation. Adding certain additives such as starch to the PE increases PE chain oxidation reactions; microbial consumption of starch increases the PE surface area by creating pores and enhances oxygen based

\* Corresponding author. Tel.: +20-2747413; fax: +20-2747498.  
E-mail address: [ha.rehim@hotmail.com](mailto:ha.rehim@hotmail.com) (H.A. Abd El-Rehim).

reaction [14–16]. The radiation by UV or sunlight also reduces the polymeric chain size of polyethylene and form oxidizing groups such as carbonyl, carboxyl, and hydroxyl. The intermediate products such as hydroperoxides, peroxides, alcohols, ketones, and perhaps some aldehyde resulted from the partial oxidation of PE are present in small amounts, but they continue to undergo oxidation. The relative amounts of some of these intermediate products is vary depending on whether the oxidation has been started by UV light. For example ketone groups fastened to PE molecules are decomposed by UV light however, hydroperoxide groups are decomposed both by UV light and by heat [7,17–19].

The combination of different environmental factors such as oxygen, temperature, sunlight, water, stress, living organisms and pollutants which are responsible for degradation of the polymer may result in synergistic effects on the polymer degradation rate [6,20,21]. In this connection the present work has focused on the possibility of replacing non-degradable polyethylene by biodegradable one for controlling lifetime of its plastic waste. The most frequently adopted approach to degradability design has been to introduce pro-degradant additives into synthetic polymers such as starch. Therefore, low-density polyethylene (LDPE) was blended with starch and the synergistic effect of combining UV-sunlight and soil burial on the degradability of such blends was investigated. The changes in the mechanical, thermal, and morphological properties of the blend exposed to UV-sunlight and/or soil burial treatments were studied and evaluated.

## 2. Materials and methods

### 2.1. Materials

The maize starch of commercial grade was supplied by El-Nasr Pharmaceutical Chemicals Co., Egypt. Low-density polyethylene (LDPE) granulates of density  $0.921 \text{ g/cm}^3$ , and melting temperature  $109^\circ\text{C}$  was obtained from Techno Co., Egypt. Polyethylene glycol (PEG) of molecular weight (Mw: 4000) was supplied by Adwic Co., Egypt.

### 2.2. Preparation of polyolefins/starch blends

The blends were prepared by melt blending of the LDPE and LDPE/starch/PEG masterbatch in a Brabender Plastic order at temperature  $125^\circ\text{C}$ . For each composition, the LDPE was melted for 2 min and then the masterbatch was added accordance desirable concentration of starch such as (3, 5, 10, 15, and 25%) and mixer speed was set at 75 rpm. The mixing time was continued for 10 min, and then hot blend was removed from the mixer and converted to sheet by using a mill having two rollers. The sheets were cut into small pieces for preparation films by compression molding using a Carver Laboratory Press under a pressure of  $200 \text{ kg/cm}$  for 10 min using a spacer of 0.15 mm and 0.2 mm

at temperature  $125^\circ\text{C}$ . The material was immediately cooled between the two plates of cold-press at  $25^\circ\text{C}$ . Pure polyethylene samples were compression molded from pellets under the same conditions.

### 2.3. Mechanical properties

Measurements of the mechanical properties were performed using an Instron (model 1195) according to standard methods at a 50 mm/min crosshead speed [22]. Dumb-bell shaped specimens of 50 mm long and 4 mm neck width were used for the measurement of the tensile strength and percentage of elongation.

### 2.4. FTIR measurement

Fourier transform infrared spectroscopy (FTIR) spectra were acquired using a Mattson 1000 FTIR spectrometer product of Unicam Ltd., England. Samples were measured in the form of thin films of thickness about  $130 \mu\text{m}$ ; which prepared by hot-press moulding. Carbonyl index (CI) was calculated by means of the absorbance ratio of the IR bands at  $1712$  and  $1465 \text{ cm}^{-1}$  ( $A_{1712}/A_{1465}$ ) for LDPE [10].

### 2.5. Scanning electron microscope (SEM)

The morphology of the blends was studied using scanning electron microscope model JEOL JSM-5400. The treated blend was coated with gold before the examination.

### 2.6. Thermal gravimetric analysis (TGA)

Shimadzu TGA system of type TGA-50 was used for measurement of TGA. In the present study, nitrogen flow was kept at constant rate of about 50 ml/min to prevent thermal oxidation processes of polymer sample.

### 2.7. Differential scanning calorimetry (DSC)

Thermal parameters of the pure polymer and polymer blends; melting temperature ( $T_m$ ) and heat of melting ( $\Delta H_m$ ) at first heating run were determined by using DSC Perkin-Elmer equipped with DSC-7 data station. Specimens ( $\sim 6 \text{ mg}$ ) of the LDPE and LDPE-starch blends were used for DSC measurements. Indium and zinc standards were utilized to calibrate the temperature and thermal scale. The measurements were carried out in  $\text{N}_2$  atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$ . On the first heating up to  $140^\circ\text{C}$ . The heats of melting ( $\Delta H_m$ ) of pure polymer and polymer blends were determined from area of the corresponding transitions in the DSC scans.

### 2.8. X-ray diffraction

The X-ray diffraction patterns of the polymer films were measured with a modern SHIMADZU Diffractome-

ter XD-D1 series which is operated fully automatically. The X-ray copper target tube was operated at 40 kV and 30 mA. All the diffraction patterns were examined at room temperature and under constant operating conditions.

The estimation of the mean size of the crystalline particles of polymer was made by using the XRD data and the Scherrer equation [23], which is given by

$$L_{hkl} = \frac{K\lambda}{\beta \cos \theta}$$

where  $L_{hkl}$  represents the mean crystal dimension normal to the corresponding  $hkl$  plane;  $\beta$ , the half-height width of the scattering;  $2\theta$ , the scattering angle;  $\lambda$ , the wavelength; and  $k$  is a constant.

### 2.9. Soil burial treatment

The thin film dumbbell shaped samples were buried in sandy-clay Egyptian soil at a depth of 2 inch in glass boxes. The moisture contents of the soil samples were kept almost in the range of (48–68%) with drinking water in glass boxes and stored in room temperature. A control box contained only samples and no soil. The control and buried blend samples were removed after six months and then washed with distilled water and dried at 30 °C in vacuum oven for 24 h. Samples were then allowed to equilibrate to ambient temperature and for at least 24 h before testing.

### 2.10. Irradiation of samples by UV-sunlight

Outdoor unprotected exposure for one set of all the examined samples were performed on the roof of National Center for Radiation Research and Technology Nasr City, Egypt, in summer time 1999 (from August up to October). The LDPE and its blends were exposed to UV sunlight continuously for 15, 30, 60, and 90 days.

## 3. Results and discussion

### 3.1. Effect of UV-sunlight on the mechanical properties of LDPE and LDPE/starch blends

It is well known that UV-sunlight has a deterioration effect on many plastic materials including LDPE. These materials, when exposed to the outdoor environment, undergo significant changes, namely, photo-degradation, causing loss of mechanical characteristics and this depends on the sun intensity and other environmental factors. Therefore, the changes in tensile strength and elongation percent for LDPE and LDPE/starch blends exposed to UV-sunlight were investigated and shown in Fig. 1. It can be seen that, there are no significant changes in tensile strength of LDPE and LDPE/starch blend containing different ratios of starch with increasing sunlight exposure time. Also, it is observed that

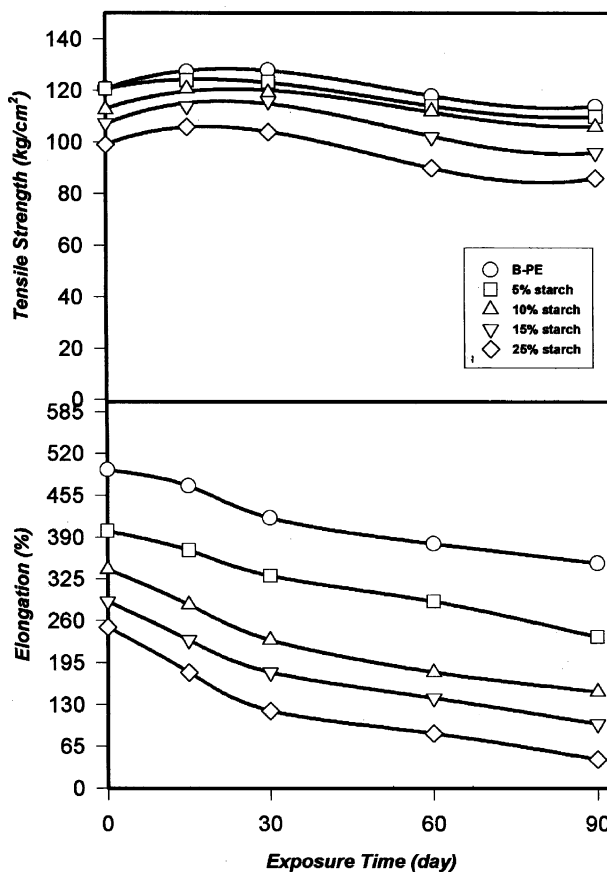


Fig. 1. Effect of UV-sunlight exposure dose on the mechanical properties of LDPE and LDPE/starch blends containing different amounts of starch.

the elongation percent decreases with increasing the sunlight exposure dose for both LDPE and LDPE/starch blends.

The results obtained assumed that the photo-oxidation of LDPE and LDPE/starch blend is characterized by an induction period in which oxygen uptake, that is responsible for the intermediate products formation includes hydroperoxides, peroxides, alcohols, ketones, occurs at a very low rate. Consequently, the photo-oxidation degradation of LDPE-blends in this stage is very limited. With increasing the exposure time, the oxygen uptake increases and the rate of formation of intermediate products increases leading to the rapid increase in carbonyl group concentration. In this stage, the effect of photo-irradiation on LDPE or LDPE/starch blend is mainly caused by slightly chain scission, which resulted in chain reorientation in the form of shorter, more readily crystallizable [24]. This results in forming a polymer of higher density and degree of crystallinity. Thereby, no significant effect on tensile strength of LDPE was occurred, however, significant decrease in elongation percent of LDPE and LDPE/starch blend was observed. This result agrees with that obtained by Yanai et al. [18] who found that the photo-degradation of polyethylene causes an increase in its elastic modulus and decrease in elongation.



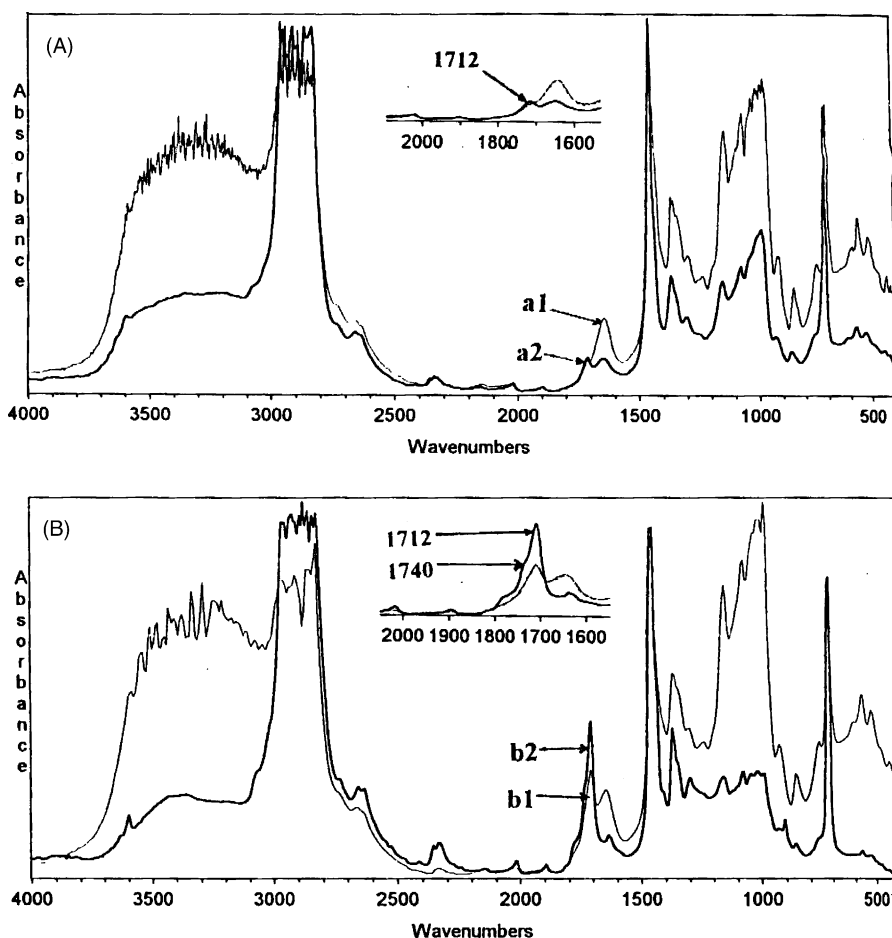


Fig. 4. FTIR spectra for LDPE/starch (75/25) blend. (A) (a1) Blank blend, (a2) blend after exposure to soil burial treatment; (B) (b1) blend after exposure to UV-sunlight for 60 days, (b2) blend after exposure UV-sunlight for 60 days followed by soil burial treatment.

mechanical properties, like tensile strength, toughness, and percentage of elongation. Again the biodegradation process of LDPE/starch blends can be improved by increasing the content of pro-degradant-starch in the blend as well as the UV-sunlight exposure dose.

### 3.3. FTIR studies on LDPE/starch blends exposed to UV-sunlight and/or soil burial treatment

Structural changes such as an oxidation level of LDPE due to the UV-sunlight and/or soil burial treatment can be accurately detected by FTIR [25]. Fig. 4 shows FTIR spectra for LDPE/starch blends exposed to UV-sunlight and/or soil burial treatment. The spectra show that the starch-hydroxyl group band of soil burial treated blends disappears meanwhile, a new carbonyl groups band at  $1712\text{ cm}^{-1}$  resulted from the degradation of LDPE/starch blends exposed to UV-sunlight and/or soil burial treatment clearly appears. In case of LDPE/starch blends exposed to UV-sunlight and followed by soil burial treatment the intensity of such carbonyl band is higher than that of microbial or UV-sunlight

treated blends. Moreover, a new band at  $1740\text{ cm}^{-1}$  for peroxide groups was observed for such treated blends [25,26].

To obtain quantitative information of the structural modification of treated LDPE and LDPE/starch blend, their carbonyl index values were estimated and shown in Fig. 5. It is clear that the carbonyl index value of LDPE exposed to UV-sunlight treatment increases as UV-irradiation dose increases. However, there is no significant change in the carbonyl index of UV-irradiated LDPE and that of UV-irradiated LDPE followed by soil burial treatment. On the other hand, the carbonyl index value of LDPE/starch blends which exposed to UV-sunlight following by soil burial treatments and those treated only with UV-sunlight increases as the irradiation dose increases. Moreover, the carbonyl index value of the former one is higher than that of the later one for all corresponding investigated irradiation dose. The carbonyl index of LDPE/starch blends, which exposed to UV-sunlight followed by soil burial treatments, is higher than that for LDPE treated in the same manner.

The results obtained indicated that the biodegradation rate of LDPE/starch blends which exposure to UV-sunlight/soil

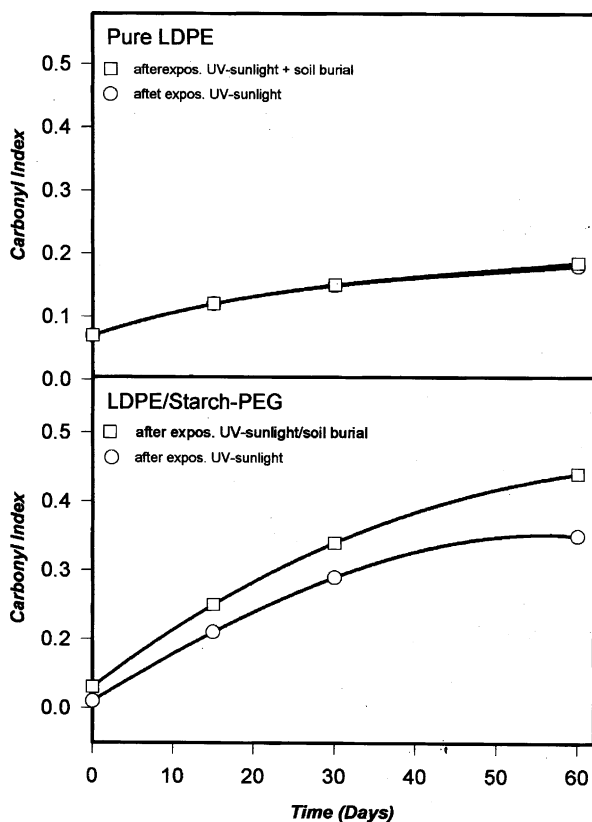


Fig. 5. Carbonyl index for LDPE and LDPE/starch (75/25) blend. Exposure to UV-sunlight of different doses and/or soil burial treatment.

burial treatment is much higher than that of LDPE treated with the same manner. This means that the starch plays an important role in enhancing the LDPE biodegradation rate.

### 3.4. Effect of UV-Sunlight and Soil Burial treatments on Thermal Stability of Blend

Typical TGA diagram obtained for LDPE/starch blend samples buried in soil and those exposed to UV-sunlight followed by soil burial treatment are shown in Fig. 6. It is clear that soil burial treatment for untreated blends caused reduction in the value of LDPE decomposition temperature from 504 to 497 °C. However, the decomposition temperature of the blends exposed only to UV-sunlight and those irradiated with UV-sunlight and followed by soil burial treatment was 501 and 478 °C, respectively, at 95% blend weight loss. This result reflected the positive effects of the UV-sunlight and biotic reaction on the improvement of LDPE/starch blends degradation process and indicated the reduction in blend molecular chains length due to UV-sunlight and soil burial treatments.

### 3.5. Effect of UV-sunlight and soil burial treatments on the crystallinity of LDPE/starch blends

The capability of UV-sunlight irradiation and/or growth of microorganisms on the plastic to cause changes in some

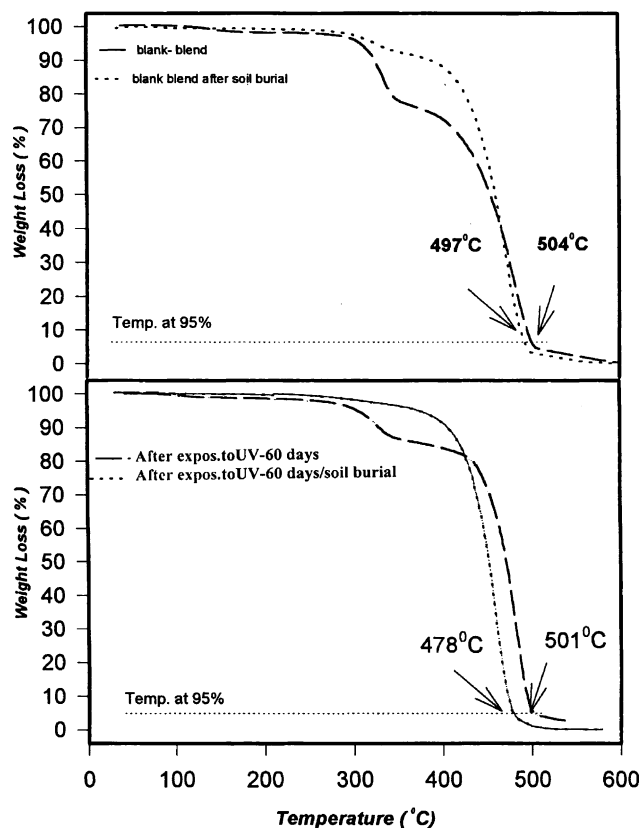


Fig. 6. Thermal diagram for LDPE/starch (75/25) and LDPE after exposure to UV-sunlight for 60 days and/or soil burial treatment.

of its measurable physical and chemical properties can be detected by thermal analysis. To determine the morphological and structural changes in the polymers, the change in thermal parameters such as the melting temperature ( $T_m$ ) and heat of fusion ( $\Delta H_m$ ) of LDPE and LDPE/starch blends exposed to UV-sunlight at different doses and those exposed to UV-sunlight and followed by soil burial treatment for six months were investigated by DSC (Figs. 7 and 8).

From the DSC thermal diagrams (Fig. 7), it can be seen that there is no significant change in the  $T_m$  of the original LDPE/starch blend after exposure to UV-sunlight at different doses. While, by increasing UV-sunlight exposure dose, a shoulder appeared in the  $T_m$  peak and seemed to broaden with increase of exposure dose. Meanwhile, in case of the blends which were exposed to UV-sunlight and followed by soil burial treatment, a significant change in  $T_m$  value is observed (Fig. 8). The original  $T_m$  split into two new melting peaks appeared at 107 and 110 °C however, the  $T_m$  of untreated blend appeared at 109 °C. As the UV-sunlight dose increases the intensity of blend melting peak that appeared at 107 °C increases on the expense of that appeared at 110 °C [17,18].

The appearance of  $T_m$  peak with a shoulder for the blend treated with high dose UV-sunlight indicated that the UV irradiation caused some structural changes in the blend chains, however, the  $T_m$  value of UV irradiated blends was the same

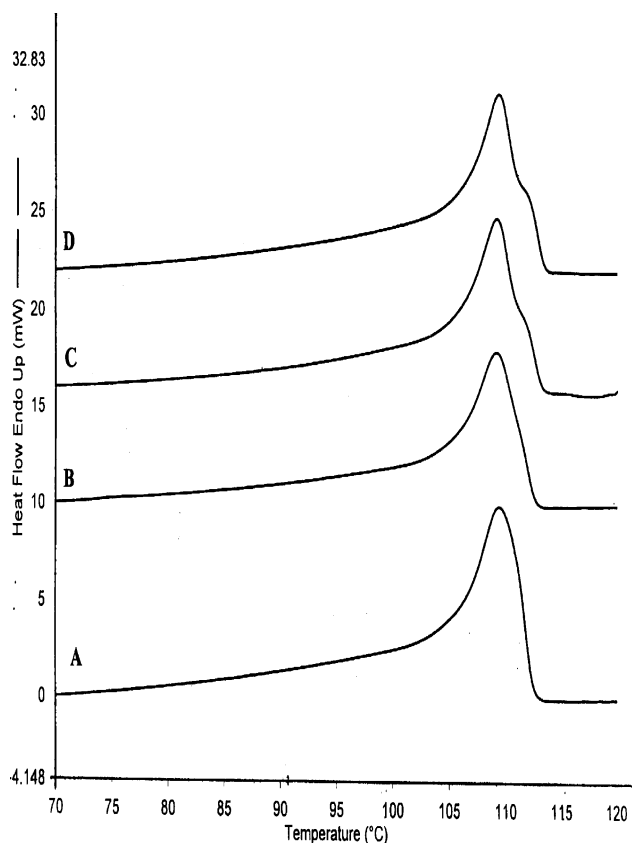


Fig. 7. DSC thermal diagram for LDPE/starch (75/25) blend after exposure to UV-sunlight of different times (days) (A) 0; (B) 30; (C) 60; and (D) 90.

as untreated one. This suggested that the degradation by UV results in fragment have a capability to reorient again in crystal form, therefore, there is no significant change in  $T_m$  of irradiated blend. These results confirmed the mechanical testing results, in which the blend tensile strength was not significantly changed when exposed to UV-sunlight. For the UV-irradiated blends followed by soil burial degradation the results assumed that the change in  $T_m$  values of such blends is corresponding to the change in their molecular weight as well as crystal size caused by both photo- and

biodegradation treatments. As the crystal size and/or polymeric chain length decreases the  $T_m$  of the blend decreases. Table 1 shows the heat of fusion of UV-sunlight irradiated blends and those treated with UV-irradiation and followed by soil burial treatment for six months. For the blend treated only with UV-sunlight it is clear that the heat of fusion of irradiated blend is increased with radiation dose to reach a maximum at 60 days thereafter, it gradually decreases as the irradiation dose increases. The UV radiation causes an increase in the crystalline level of LDPE and consequently, the heat of fusion increases. Increasing the UV irradiation leads to chain scission, reduction in molecular weight and decrease in heat of fusion. Meanwhile, the heat of fusion of the blends exposed to UV-sunlight and followed by soil burial treatments increases as the irradiation dose increases. This can be attributed to the biotic reactions that consume the starch as well as the amorphous part of LDPE. In this way, the weight ratio of LDPE/crystalline part increases, i.e. the apparent increase in the crystallinity of the sample is mainly due to the whole amorphous phase beside starch in the blend that is consumed by the effect of microorganisms.

### 3.6. XRD studies

The degree of crystallinity of LDPE/starch blends treated with UV-sunlight and those irradiated with UV-sunlight followed by soil burial treatment was also determined by X-ray diffraction. The XRD spectra show sharp distinguished peaks at 23.7 and 21.5 of the angular position  $2\theta$  for LDPE (Fig. 9). The intensity of the peaks of UV irradiated blend is higher than that of un-irradiated one. These results indicated that the degree of polymer blend crystallinity increased when exposed to UV-irradiation. Meanwhile, XRD pattern of the LDPE/starch blend exposed to UV-sunlight and followed by soil buried treatment shows the same peaks at the same angular position  $2\theta$  but, of lower intensity. This means that the crystal sizes for LDPE/starch blends decreases during biodegradation process.

Main crystal size of LDPE/starch blends treated with UV-sunlight and those exposed to UV-sunlight followed

Table 1  
Effect of UV-sunlight and/or soil burial treatment on the  $\Delta H_m$  and  $T_m$  for LDPE/starch (75/25) blend

Condition LDPE/starch blend		Action	$T_m$ (°C)	$\Delta H_m$ (J/g)
After exposure to UV-sunlight	After soil burial for six months			
–	–	Non	109.33	74.76
15	–	Single	109.83	75.5
30	–	Single	109.16	75.2
60	–	Single	109.16	75
90	–	Single	109.33	74
–	Burial	Single	108	77.2
15	Burial	Double	110	107.2
30	Burial	Double	110	107
60	Burial	Double	110.16	106.8
90	Burial	Double	110.33	106.5

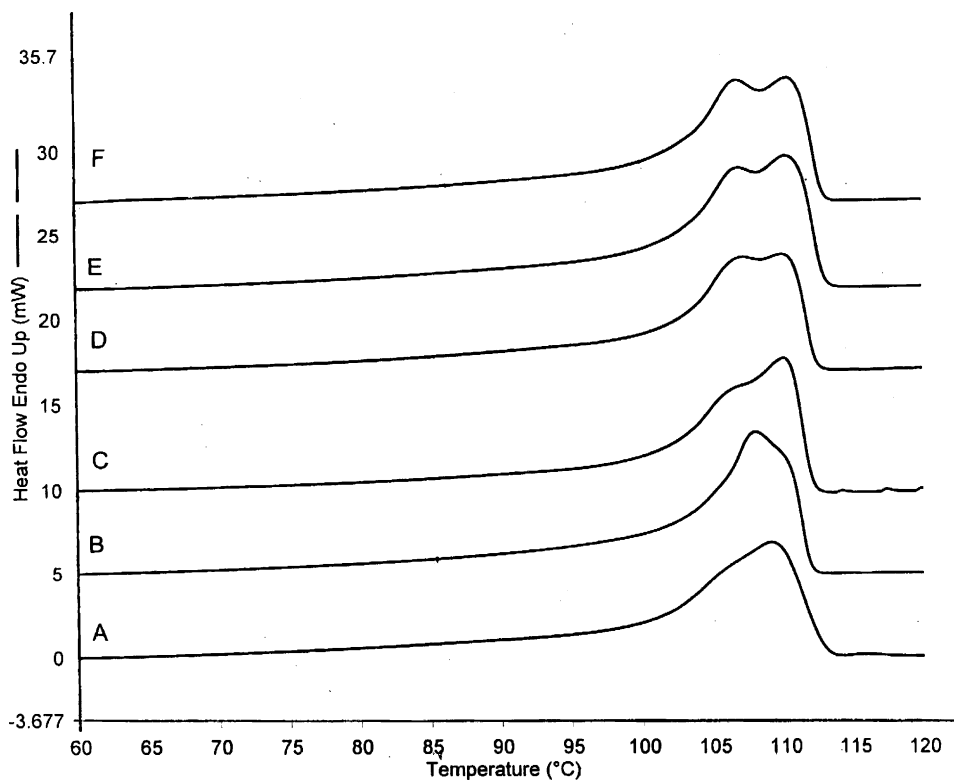


Fig. 8. DSC thermal diagrams for (LDPE/starch-75/25) blend before and after exposure to UV-sunlight or/and soil burial treatment for six months. (A) Blank-blend; (B) blend after exposure to soil burial treatment; (C) blend after exposure to UV-sunlight 15 days/soil burial; (D) blend after exposure to UV-sunlight 30 days/soil burial; (E) blend after exposure to UV-sunlight 60 days/soil burial; (F) blend after exposure to UV-sunlight 90 days/soil burial.

by soil burial treatment was determined, and shown in Fig. 10. It was found that there is no significant changes in the main crystal size of blends that treated with various UV-irradiation doses. However, the main crystal size of blends exposed to UV-sunlight of different doses and followed by soil burial treatment decreases. These results indicated that as the UV irradiation dose increases the rate of biodegradation increases and consequently, the blend crystal size decreases.

### 3.7. SEM studies

The surface topography of UV-irradiated LDPE/starch blend containing different amount of starch before and after soil burial treatments for six months was investigated by using SEM. The SEM examination clearly showed the created holes and cavities at the surface of the blend exposed to different treatments (Fig. 11A–D). Many of these cavities could be seen to have fungal hyphae growing. Also, it can be seen that the degree of deterioration caused by the biotic reaction tends to increase with increasing starch content in the blend (Fig. 11B,C) and enhances when the blend exposure to UV-sunlight before soil burial treatment (Fig. 11C,D).

The results suggested that the microbes in soil degraded the starch and also oxidized the LDPE amorphous regions. Again, the microbes created pores on consumption of starch, plasticizer PEG as well as the oxidized amorphous regions

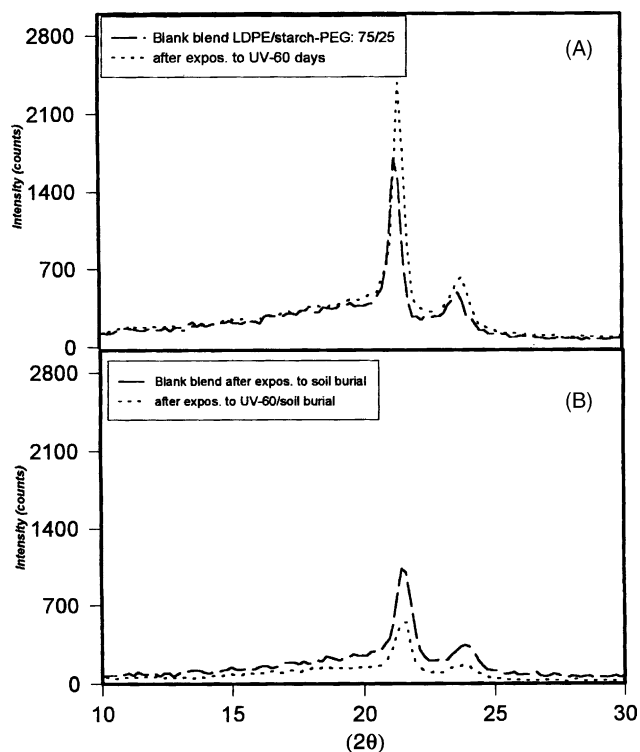


Fig. 9. XRD spectra for LDPE/starch (75/25) blend at different conditions: (A) before and after exposure to UV-sunlight; (B) after exposure to UV-sunlight and/or soil burial treatment.



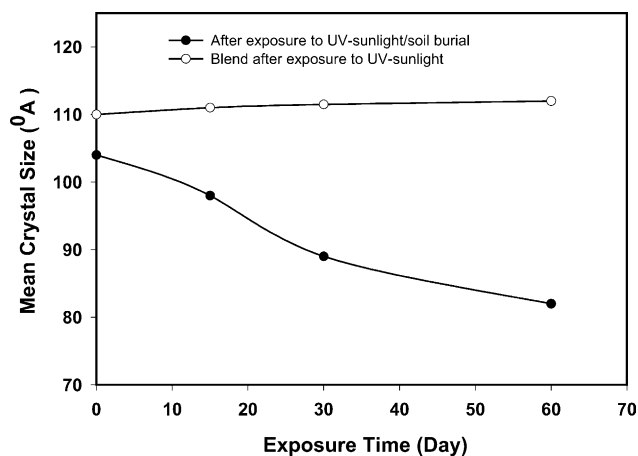


Fig. 10. Mean crystal size for LDPE/starch blend after exposure to UV-sunlight and UV-sunlight followed by soil burial treatments.

of LDPE resulted from UV-sunlight treatments. Thereby, the surface area of polymer blends increased and this improves oxygen-based reactions, that enhances and increases LDPE chain oxidation reaction. Creating oxidized LDPE chains ends in a degraded LDPE/starch makes LDPE more susceptible to the biotic reactions continuation. The high deterioration, of the blend exposed to sunlight and followed by soil burial treatments indicated that the pre-oxidation by UV-sunlight radiation before soil burial treatment played significant role to improve and accelerate the biodegradation process of LDPE/starch blends.

#### 4. Conclusion

Many solutions have been proposed for waste management of LDPE. In the present work the effort was towards

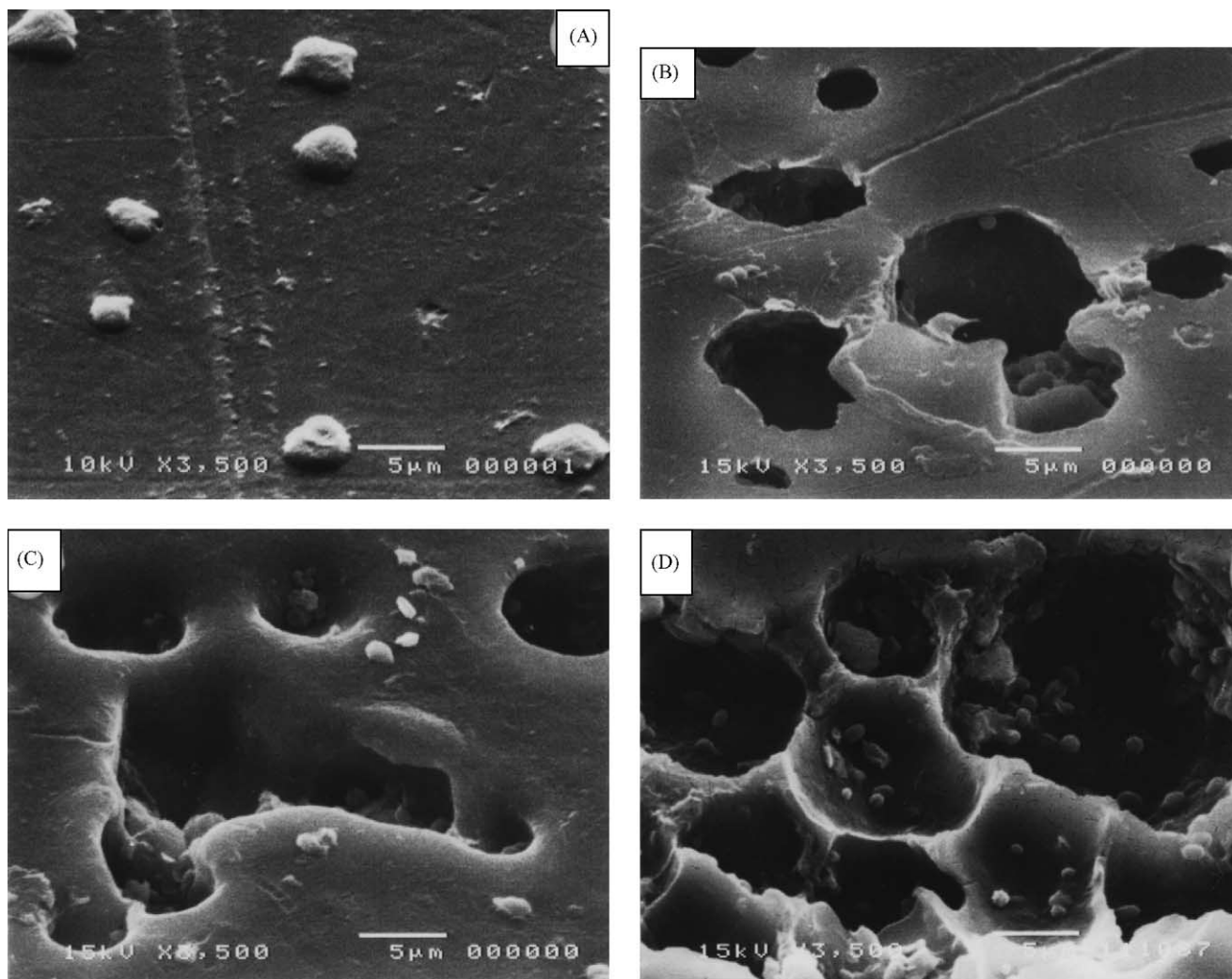


Fig. 11. SEM micrographs of (A) Untreated (LDPE/starch: 75/25); (B) (LDPE/starch: 85/15) after exposure to soil burial treatment for six months; (C) (LDPE/starch: 75/25) after exposure to soil burial treatment for six months; (D) (LDPE/starch: 75/25) after exposure to UV-sunlight (60 days) followed by soil burial treatment for six months.

imparting the biodegradability property to LDPE. This was achieved by mixing the polymer with natural biodegradable materials such as starch followed by creating oxidized groups on the LDPE through the exposure of the polymer blend to UV radiation and/or soil burial treatment. The structural and morphological changes on the treated PE with UV-sunlight irradiations and biotic reaction were evaluated by using, mechanical testing, SEM, TGA, DSC, and FTIR. The obtained results indicated that the blend bio-degradation rate could be enhanced when the blend exposed to UV-sunlight and followed by soil burial treatment. It might be concluded that synergistic effect of combining UV-sunlight and soil burial treatments on biodegradation rate of LDPE/starch blend put up this blend as one of bio-degradable plastic that could be used in the production of disposal and packaging plastic products.

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