

Spectrophotometric Analysis of The Fuzzy Role of UV Irradiation In Commercial Polyethylene Films

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FOURIER transform infrared (FTIR) in combination with UV/Vis spectrophotometric analysis were performed to study the role of UV irradiation on the commercial samples of pristine high-density polyethylene (HDPE) films. X-ray diffraction data reveals an increase in the percent crystallinity which correlated and fitted linearly with irradiation times. FTIR experimental absorption spectra for commercial (HDPE) sample and other samples that irradiated with UV lamp for different prolonged time intervals shows the maintenance of main pseudo four characteristic bands in their positions with different intensities. Careful analysis of FT-IR bands reveals a clear variation in both band position and intensity for samples that irradiated up to 16 hours. UV/Vis. electronic spectra reveal the presence of charge transfer band in the UV region around 210 nm with a small change in their fundamental absorption edge and optical energy gap without any evidence for any other band till the end of measurements. Absorbance intensity was found to varies in relation to the irradiation time and sample thickness. Obtained data may be interpreted in terms of free radical and oxidation reactions of polyethylene.

Keywords: high-density polyethylene (HDPE); UV irradiation; FTIR; UV/Vis spectroscopy.

Introduction

During the last decades, polymeric materials attract the attention of scientists and decision makers according to their versatile uses and applications in the medical, industrial and other applications in our daily use. Therefore, a wide range of classifications was introduced from simple route depend on the structure (macromolecules) where a large number of atoms or groups multiplication linked to form linear, branched or cross-linked homopolymers or copolymers with capricious characteristics [1, 2]. Recently modified polymeric matrices were introduced to bring a specific physical or chemical property for specific applications [3-7].

Polyethylene (PE) represents a widely used semi-crystalline polymeric matrices with a simple chemical monomer $(-\text{CH}_2-\text{CH}_2-)$. Lamellae crystalline polyethylene phase offers a structural reliability while their non-crystalline phase

offers the elastic characteristics. PE epitomize an extensive material through industrial and daily used materials for different applications including coating, packaging, pipes, containers, toys and many other materials as a result for their low weight in comparison with other outmoded materials resulting in a cost-effectiveness reduction of transportation and installation. PE can be classified according to their density into low-density polyethylene (LDPE) and high-density polyethylene (HDPE) following the American Society for Testing Materials (ASTM) routine [8].

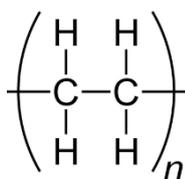
Degradable and biodegradable polymeric matrices considered as a material that can undergo a significant chemical change under specified environmental conditions. HDPE characterized by their low degree of branching combined with high tensile strength and density of about 0.940 g/cm^3 . The mechanisms of degradation may be

classified as microbial degradation in which microorganisms ingest the polymeric matrices and chemical degradation at which chemical reactions chop chemical bonds to reduce their molecular weight. Such mechanisms vary depending on polymeric matrices environment and anticipated application [9, 10].

The aim of the presented work is to introduce a simple routine that may be used to retrace the degradation processes of commercial HDPE and to illustrate the resulting structural variations based on spectrophotometric analyses. The work extended also to specify the best condition needed to obtain degradable materials.

Materials and Methods

Materials used include commercial films of high-density polyethylene (HDPE) supplied by Ahram Plastics company from Egyptian markets of the chemical structure shown in Scheme (1).



Scheme (1) chemical structure of HDPE

Samples were irradiated with coherent eglamp 2-W operating at $\lambda = 254$ nm for different

time intervals up to 96 h was used as a source of UV light. Treatments were done using unfocused fluctuated beam at a distance about 10 cm for all samples. Optical absorption FT-IR spectra were recorded using 32 runs on Nicolet is10 single beam spectrophotometer within the spectral range 4000-400 cm^{-1} at room temperature. UV/Vis. electronic absorption spectral data was measured using Jasco 570 instrument within the spectral range 200-1100 nm. X-ray diffraction (XRD) recorded to identify various crystalline and amorphous phases within the Bragg's angle (2θ) 5:70° PANalytical X'Pert PRO adopting Cu K α target using wavelength $\lambda = 1.540$ Å and tube operating at 45 kV-40 mA. Crystallinity index of studied samples was calculated using the area of two sharp bands located at 21.4° and 23.9° to the area integral over the complete diffraction spectra using the equation:

$$\text{Crystallinity index} = \frac{A_{\text{Crystalline}}}{A_{\text{Crystalline}} + A_{\text{Amorphous}}}$$

Where $A_{\text{Crystalline}}$ represent the area of crystalline bands and $A_{\text{Amorphous}}$ represent the area of amorphous region [11].

Results and Discussion

X-ray diffraction analysis

Figure (1) illustrates the change in structural rearrangement of building units in commercial HDPE matrices correlated to the treatment

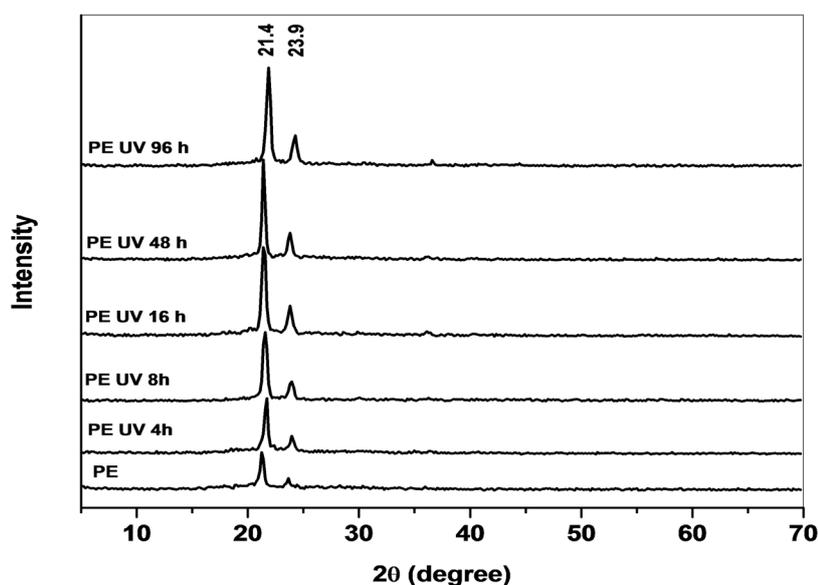


Fig.1. illustrates the change in structural rearrangement of building units in PE matrix

regime and time when irradiated samples for different prolonged time intervals.

XRD diffractogram of PE samples in the Bragg's angle range $5:70^\circ$ generally shows two sharp crystalline characteristic bands at about 21.4 and 23.9° corresponding (110) and (200) planes respectively. It was also observed that crystallinity behavior changes with immersion times. The crystallinity index for PE samples studied by different authors [12]. Obtained crystallinity index was calculated for all samples before and after being irradiated with UV radiation for different time intervals are tabulated in Table (1) and plotted in Fig. (2).

Obtained data fitted to a linear behavior using the following equation:
Crystallinity % = 0.059 (time) + 54.94

Fourier Transform Infrared (FT-IR) absorption spectra

FT-IR considered as fast, non-destructive and informative tool that can describe the structural variations in polymeric matrices while the

degradation process of plastics (a type of polymeric matrices) is in the focus of scientist during the last decades. FT-IR optical absorption spectra of untreated commercial high-density polyethylene sample from Egyptian market was measured in addition to other sample that irradiated with UV lamp for different time intervals up to 96h. Fig. (3) reveals FT-IR spectra of studied samples before and after different irradiation time.

Several parameter can be drawn from these measurement considering the following regions:

Region I $3000-2800\text{ cm}^{-1}$

Region II $1490-1440\text{ cm}^{-1}$

Region III $750-700\text{ cm}^{-1}$

Generally, PE polymer characterized by four fingerprint sharp bands originally located at 2919 , 2850 , 1473 , and 725 cm^{-1} characterized different vibrational groups in polyethylene structure but with different intensities. Band position and their assignment introduced in Table (2).

A small variation in both band position and

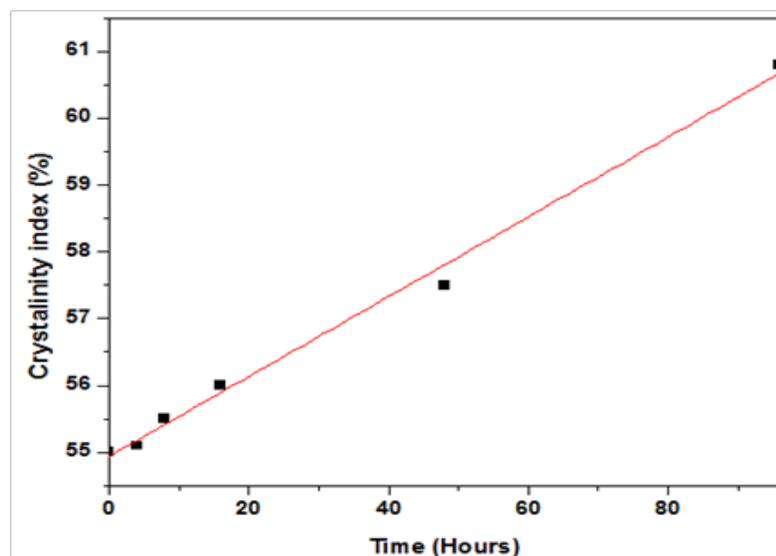


Fig. 2. Crystallinity index for all samples before and after immersion in acidic media.

TABLE 1. Crystallinity index of PE samples before and after UV irradiation.

Radiation times (Hours)	Crystallinity index (%)
0	55
4	57
8	58
16	61
48	62
96	64

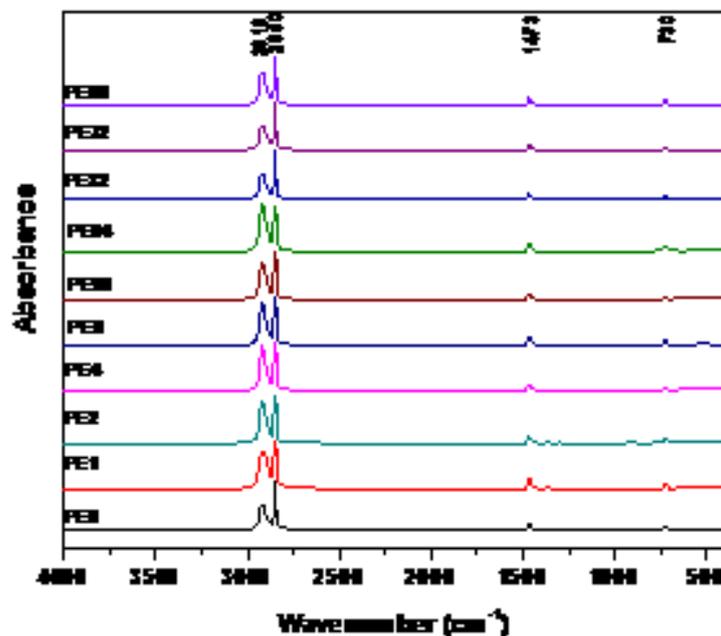


Fig. 3. FT-IR spectra of studied PE samples before and after different irradiation time.

TABLE 2. Band position and their assignments of sharp FT-IR characteristic peaks of PE.

Band Position (cm ⁻¹)	Assignments	References
2919	Vibration of CH ₂ asymmetric stretching	13, 14, 15
2850	Vibration of CH ₂ symmetric stretching	
1473	Bending deformation	
725	Rocking deformation	

intensity combined in some cases with a splitting of bands originally located at 1473 and 725 cm⁻¹ were observed especially for samples irradiated with UV radiation for 24 hours and thereafter.

The variation of band position, splitting and intensity of different peaks will be introduced in the magnified image of the spectrum for the specific regions in Fig.(4)

Region I 3000-2800 cm⁻¹

Figure (4.a) shows the magnified spectral variation of the bands located in the spectral region between 3000-2800 cm⁻¹. It was clear that the full width at half maximum (FWHM) or the broadness of the band originally located at 2850 cm⁻¹ was decreases with increasing of the irradiation time

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combined with increase in broadness of the band at 2919 cm⁻¹.

Region II 1490-1440 cm⁻¹

Figure (4.b) shows the magnified spectral variation of the bands located in the spectral region between 1490-1440 cm⁻¹. It was clear that there is no clear change in both intensity and full width at half maximum (FWHM) for all samples subjected to UV irradiation up to 16 hours. A splitting of the band originally located at 1473 cm⁻¹ into two bands at about 1472 and 1462 cm⁻¹ was observed for the remind samples that subjected to UV radiation for a time interval greater than or equal to 24 hours.

Region III 750-700 cm⁻¹

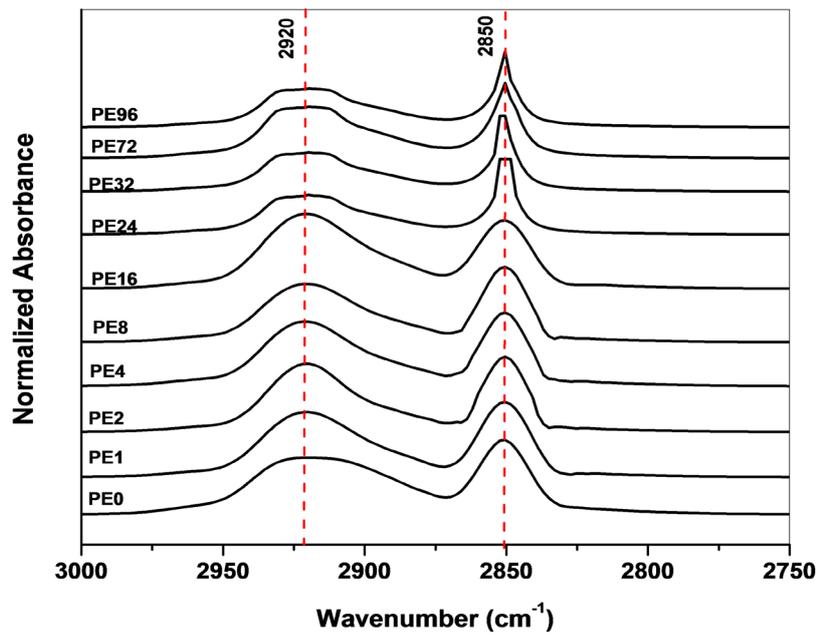


Fig. (4.a) magnified spectral variation of the bands located in the spectral region between 3000-2800 cm^{-1} .

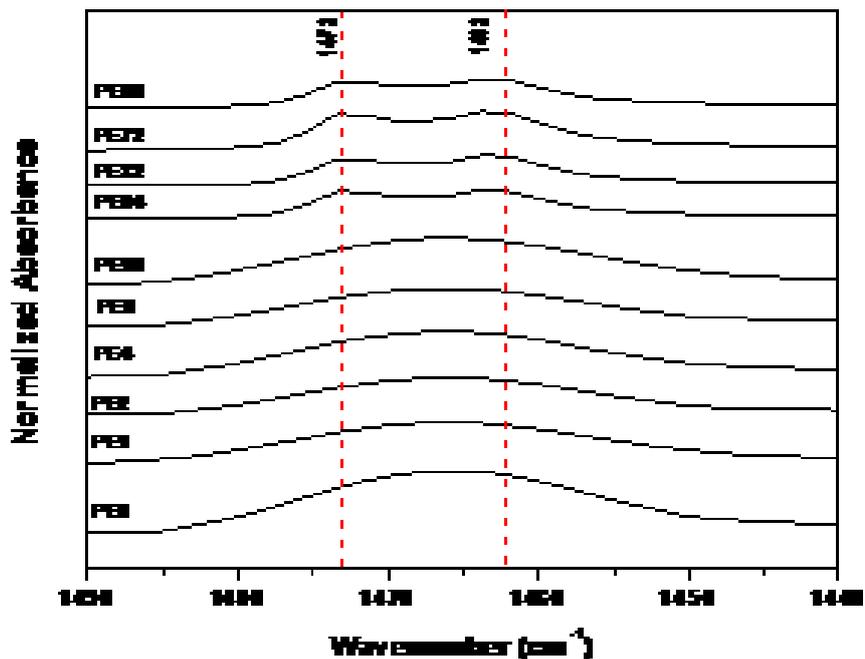


Fig. (4.b). magnified spectral variation of the bands located in the spectral region between 1490-1440 cm^{-1} .

Figure (4.c) shows the magnified spectral variation of the bands located in the spectral region between 750-700 cm^{-1} . It was clear that there is no clear change in both intensity and full width at half maximum (FWHM) for all samples subjected to UV irradiation up to 16 hours. A splitting of the

band originally located at 725 cm^{-1} into two bands at about 730 and 720 was observed for the remind samples that subjected to UV radiation for a time interval greater than or equal to 24 hours.

UV/vis. optical absorption spectra of commercial

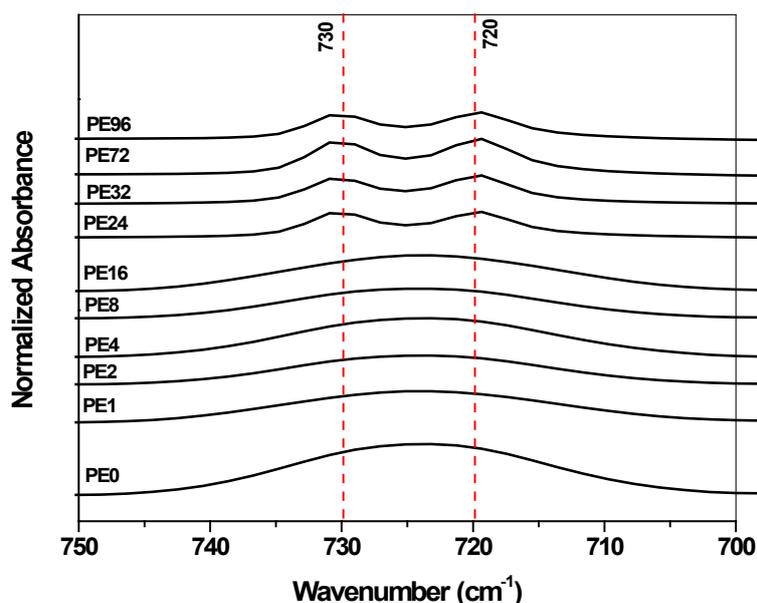


Fig. (4.c) magnified spectral variation of the bands located in the spectral region between 750-700 cm^{-1} .

HDPE samples before and after different UV irradiation times

Figure (5) reveals UV/Vis optical absorption spectra of commercial polyethylene samples before and after subjecting to successive UV irradiation type B with a constant illumination for different time periods up to 96 hours.

Obtained spectra shows the maintenance of main absorption UV band located at about 210 nm but with different intensities depending on

the irradiation and without any evidence for other peaks in the extended visible region till end of measurements. It was noted also that increasing of irradiation time results in an obvious change in absorption intensity especially in the visible region and also with change in the irradiation time. Such behavior may be attributed to defect creation or dissociation behavior of PE chain combined with irradiation regime.

All previous observations suggests a type of

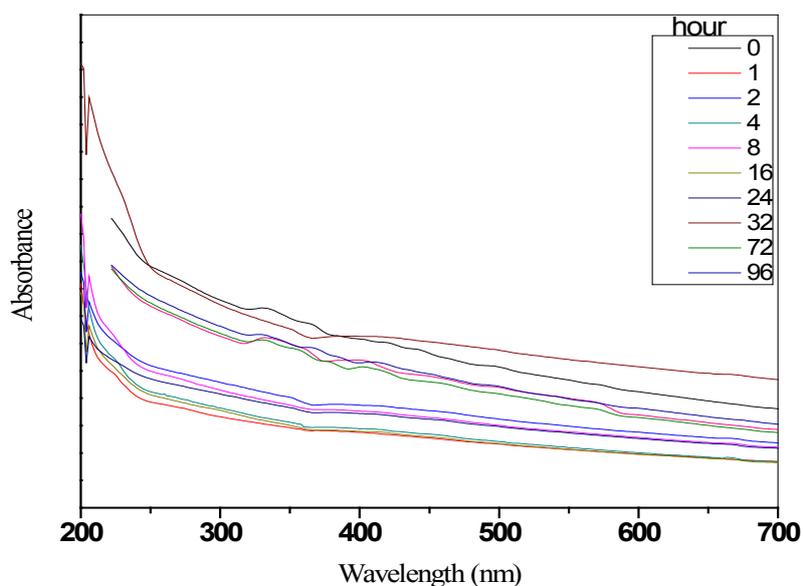


Fig.(5) UV/vis optical absorption spectra of polyethylene sample before and after successive UV irradiation using type B with constant illumination.

polymer degradation or chain dissociation in the polymeric backbone that start at UV irradiation dose of 24 hours and increases up to 96 hours. A complementary study of the UV/visible spectra of all samples before and after different irradiation times may be used to support these idea and help in choosing a suitable samples to complete the study and satisfy the principle aims.

The most effective method for the description of electron transition and reward a precise information about their internal structure and possible application can be supplied using the well-known formula reported by Mott and Davis [16]

$$E_{opt} = h\nu - \frac{(ah\nu)^{2/3}}{B} \quad (1)$$

$$E_{opt} = h\nu - \frac{(ah\nu)^2}{B} \quad (2)$$

Where B is a constant

α absorption coefficient

E opt is the optical energy gap

h is a Planck constant

on basis of these two equation reported for direct allowed and indirect allowed transitions respectively, one can introduce what is called Tauc's plot which is a representation for the relation between photon energy ($h\nu$) against

$(ah\nu)^{1/2}$ and $(ah\nu)^2$

Values of the optical energy gap was found to be nearly equal due to the small structure changes.

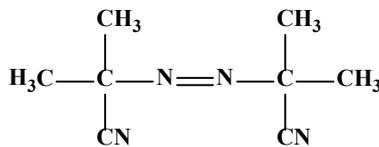
The observed behavior may be discussed also in terms of free radical reaction caused by UV irradiation discussed by different authors [17-19]. An example of such reactions can be shown in Scheme (1)

In these reaction initial pristine polyethylene becomes enriched by a double bonds, condensed aromatic rings, amorphous carbons and finally transformed to a highly cross-linked amorphous carbon. Resulting reactions followed usually by oxidation reactions (Scheme (2)) when samples

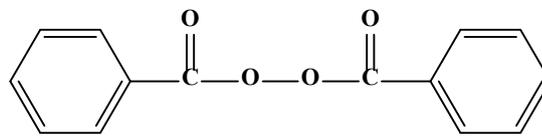
Free Radical Polymerization

1. INITIATION step

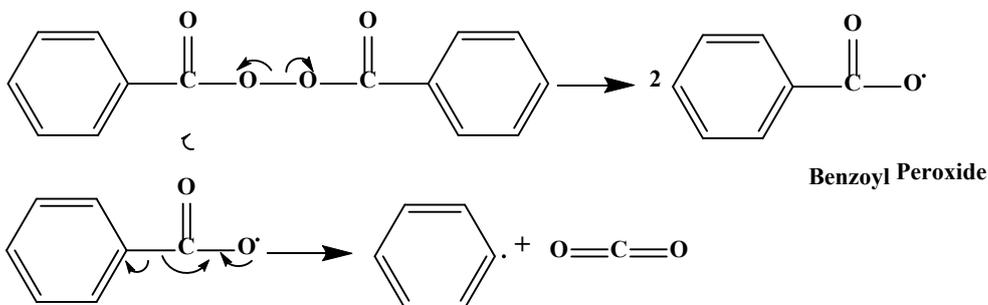
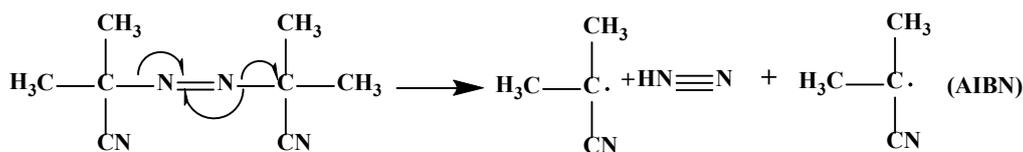
• Initiator



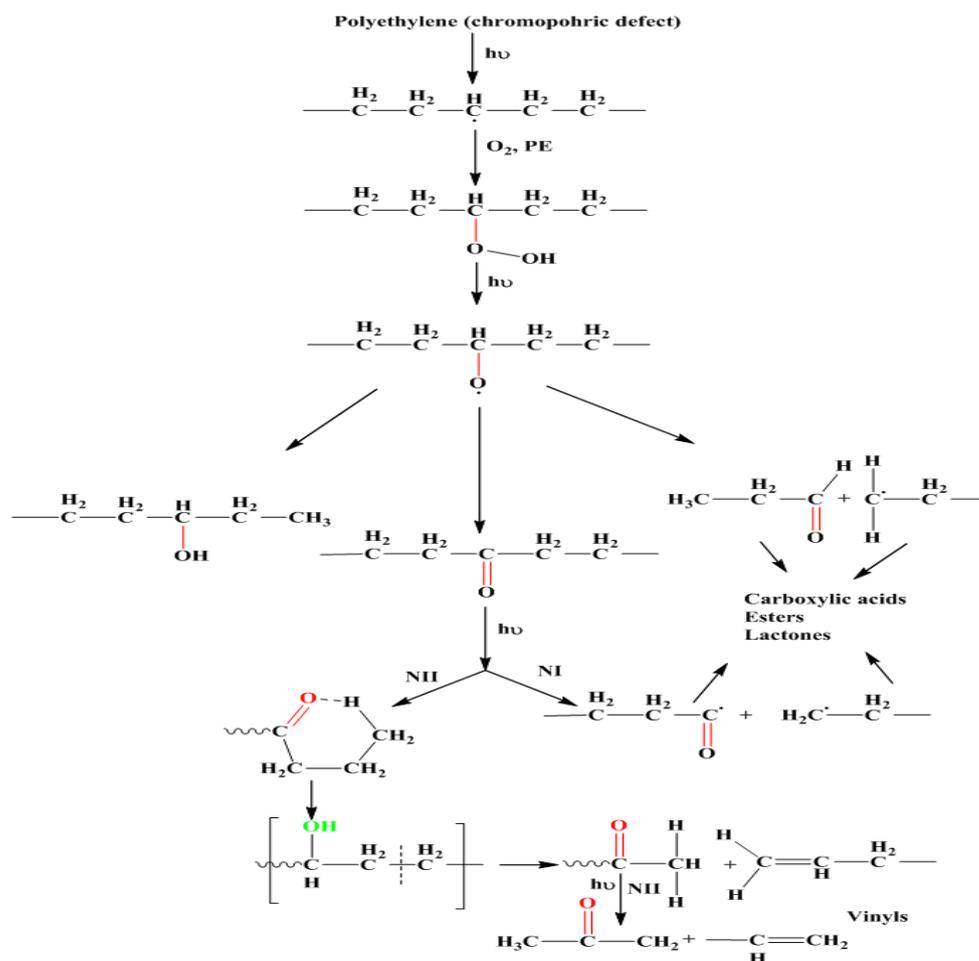
2,2'-azobisisobutyronitrile (AIBN)



Benzoyl Peroxide



Scheme (1) free radical reaction of irradiated PE sample.



Scheme (2) oxidation reaction of irradiated PE sample.

exposed to the surrounding atmosphere.

The process of polymer irradiation combined with dominating chain scission, low molecular weight fragments, gas evolution (odor) and unsaturated bonds (color) may appear. Free radicals determine the initiating centers for scissioning and/or crosslinking. The mechanism occurring during irradiation has three distinct stages, namely, initiation, propagation and termination shown in Scheme (1)

Conclusion

The role of UV irradiation times in HDPE commercial samples were studied using FTIR and UV/Vis spectrophotometric analysis. FTIR experimental absorption spectra for commercial (HDPE) sample and other samples that irradiated with UV lamp for different prolonged time intervals shows the maintenance of main pseudo four characteristic bands in their positions with different intensities. Careful inspection of the

spectral data shows a clear variation in both band position and intensity for samples that irradiated up to 16 hours. UV/Vis. electronic spectra reveal presence of charge transfer band in the UV region around 210 nm without any evidence for any other band till the end of measurements but with different absorption that related to the irradiation time and sample thickness. Obtained data may be interpreted in terms of free radical and oxidation reactions of polyethylene.

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التحليل الطيفي لدور التشوه بالأشعة فوق البنفسجية في أفلام البولي إيثيلين التجارية

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الفيزياء - كلية العلوم - جامعة المنصورة - ٣٥٥١٦ - المنصورة - مصر

أستخدم تحويل فورير لأطياف الأشعة تحت الحمراء ممزوجا بطيف الأشعة فوق البنفسجية والمرئية لدراسة دور التشعيع بالأشعة فوق البنفسجية لعينات تجارية من البولي إيثيلين ذو الكثافة العالية. أوضحت نتائج حيود أشعة أكس زيادة في درجة التبلور المرتبط خطياً بزمان التشعيع. كما أوضحت اطياف الأشعة تحت الحمراء للعينات قبل وبعد عملية التشعيع لفترات زمنية مختلفة استقرار في نطاقات الامتصاص الاربعة الزائفة في أماكنها وبشدة امتصاص مختلفة. كما وأن التحليل الدقيق لهذه الاطياف يظهر تغيرات واضحة سواء في النطاق او الشدة للعينات المعرضة للتشعيع فترات زمنية تزيد عن ١٦ ساعة. أوضحت أطياف امتصاص الأشعة فوق البنفسجية والمرئية وجود حافة امتصاص في منطقة الاشعة فوق البنفسجية ذات قمة عند حوالي ٢١٠ نانومتر مع تغير بسيط في قيم حافة الامتصاص الرئيسية مع عدم وجود اي احتمال لعملية الامتصاص في مدى الضوء المرئي وحتى نهاية مدى القياس. كما وأن شدة الامتصاص تتغير بتغير زمن تشعيع العينات وسمكها. كما وتم تفسير النتائج في ضوء الشحنات الحرة وتفاعلات الأكسدة للبولي إيثيلين.