ORIGINAL ARTICLES

Gamma-Ray Induced Modifications in Structure and Optical Properties of High Density Poly-ethylene Thin Films


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ABSTRACT

The effect of gamma-ray radiation on the crystalline structure and optical properties of high density polyethylene (HDPE) thin films has been investigated. Gamma irradiation was carried out in air to a maximum dose up to 400 kGy. The structure and chemical changes of the polymer were studied using X-ray Diffraction (XRD) and Fourier-Transform Infrared Spectrophotometry (FTIR) techniques. The optical parameters such as (optical energy gap, absorption coefficient, and activation energy) were determined from transmission, reflection and absorption spectra for these films. The obtained results show that the gamma-ray irradiation increased the crystallinity of the polymer films. Meanwhile, the optical energy band gap and the optical activation energy of the films exhibit a decrease with increasing the irradiation dose.

Key words: High Density Polyethylene Polymer thin film, FTIR, UV-Vis spectrophotometry, γ-ray irradiation.

Introduction

Polyolefin’s are plastics of great commercial and economic importance, especially high density polyethylene (HDPE). It is an attractive material for scientific and technological aspects due to its low cost, good properties and versatility (Mends et al., 2003). Many investigations were reported on high-energy irradiation of polyethylene (PE) and the effects on chemical structure and properties (Calcagno et al., 1993; Baojum and Bengt, 1995). The exposure of PE to high energy radiation results in the following changes: crosslinking, main-chain scission, evolution of hydrogen and increase or decrease of unsaturation (Calcagno et al., 1993). These reactions are related to the chemical and physical state of the polymer and the nature of the irradiation and the environment (Baojum and Bengt, 1995). Singh (1990) presented two phenomena which occur as a consequence of gamma-ray irradiation for HDPE: the cross-linking and oxidative degradation. In general, equation (1) shows the reaction between free radicals (PE.) of HDPE, produced by the loss of a hydrogen atom of HDPE (represented as PE), forming cross-linking between polymer molecules. This recombination reaction is predominant in cases of irradiation in vacuum or inert atmospheres.

\[
\text{PE.} + \text{PE.} \rightarrow \text{PE} - \text{PE} \quad (1)
\]

When the irradiation is performed in air, the formation of peroxide radical (equation (2)) and the reaction between PE free radical and peroxide radical (equation (3)) is predominates.

\[
\text{PE.} + \text{O}_2 \rightarrow \text{PEO}_2 \quad (2)
\]
\[
\text{PE.} + \text{PEO}_2 \rightarrow \text{PEOOPE} \quad (3)
\]

The complexity of the phenomena occurred during high energy source irradiation for HDPE is also discussed by Premnath et al. (1999). Specific effects of irradiation for polyethylene irradiation may differ depending on factors such as polymer molecular weight, the presence of additives, storage temperature under atmospheric conditions before, during and after irradiation, and size of samples, among others.

The effect of irradiation on the physical properties and structure of their polymers and their chemical properties has been studied (Kellr and Ungar, 1983; Charlsky, 1952; Chawla and Pierre, 1972; Saito et al., 1972; Kitamaru and
Mandelkern, 1964 and Charlsby, 1954). The finding results for studied are widely being used in most commercial application. Also, cross linked polyethylene has been used in hot water piping installation, wire and cable industries (Mateey & Karageorgiey 1996; Oshima et al., 1997; Dalla et al., 1996 and Mandelkern 1985).

The optical characterization is the best method for studying the material properties. Spectrophotometry measurements give a clear picture of the electron transitions of these materials. These transitions provide information to determine the main optical parameters of these materials such as the band structure, optical band gap energy, and oscillation and dispersion energy for these materials. The principle of this technique is that photons with energies greater than the band gap energy will be absorbed. The absorption edge in many materials follows the Urbach rule (Urbach 1953).

In this work, we investigate the effect of gamma-ray irradiation on the structure, optical properties as well as the optical band gap energy of HDPE.

Materials and Methods

A commercial grade of HDPE films, with an area of 2x2 cm² and a thickness of 40 µm (Hema plastic and Hem foam company, Cairo, Egypt), were irradiated by gamma-ray radiation. The irradiation were performed in air at room temperature using a 60Co source of the Indian gamma cell type (NCRRT, AEA, Cairo, Egypt). The samples were subjected to various irradiation doses up to 400 kGy. The dose rate during the irradiation was 2.7 kGy/h. A Shimadzu X-ray diffractometer working in reflection geometry was used in the present work. The device, working at 40 kV and 30 mA, uses a Cu anode to produce an 8.047 keV (= 0.15425 nm) highly collimated X-ray beam. Scattering angles from 2º up to 45º were scanned with a scan rate 8º/min. The systematic error for XRD measurements was found to be about 3%. Molecular vibration modes of bonds in polymers were characterized by transmission of FTIR spectra (ATI Mattson Genesis series, made by Unicom). All the measurements were done in the 400-4000 cm⁻¹ wave number range at a resolution 4 cm⁻¹, keeping air as a reference. The variation of crystallinity has also been determined by FTIR.

The optical transmission, reflection and absorption spectra for these films were measures using Spectrophotometer (V-570, Jasco, Japan) in the range of wave length (190 – 2500 nm). The spectra were obtained for the polymers' absorbance as a function of wave number. The variation in absorbance before and after irradiation was compared and the peak analysis was done to study the variation in position and relative intensity of the bands, the disappearance of some existing bands and emergence of new bands.

Results and Discussion

3.1. Structure Analysis:

X-ray chart pattern for the all investigated samples with different gamma doses (0-300 kGy) are shown in Fig. 1. For the virgin sample, XRD pattern consists of three peaks belong to the orthorhombic unit cell of polyethylene (Dalai & Wenxiu 1996) at 2θ = 21.588° (110), 24.095° (200) and 36.356° (020), respectively. The most intense peak was found to be at 2θ = 21.588°. For the gamma-ray irradiated HDPE films, the same peaks were identified. The full-width at half maximum FWHM of the peaks shows slight decrease with increasing the gamma-ray dose, which indicates an increase in the crystallinity of the irradiated films.

For the determination of the ratio of amorphous to crystalline phase in these samples, all irradiated samples were studied with FTIR measurements. The FTIR spectrum for virgin HDPE and samples with different radiation doses are shown in Fig. 2. All the observed dominant bands are the characteristic bands of the control (non-irradiated) sample that pointing out the isotactic nature of the polymer. The presence of the almost the same main bands in irradiated samples indicates that the isostatic nature of HDPE has been kept (not destroyed) during gamma irradiation (Bakshi et al., 2007). FTIR is proved to be a powerful tool to follow up the changes in polymerization (Ibrahim & Koglin 2005) and is a technique of concern for studying both natural and synthetic polymers (Ibrahim & Osman 2009 and Ibrahim et al., 2010). Fig.3 a, b show the spectral zones studied to determine the crystallinity (2700-3100 and 2800-2960 cm⁻1) of virgin and gamma-ray irradiated samples at 300 kGy, respectively (i.e. minimum and maximum irradiation dose).

The crystallinity ratios were calculated by (Zerbi et al., 1989)

\[ x = \frac{(I_a - I_b)}{(I_a + I_b)} \times 100 \]  

(4)

Where x is percentage of amorphous content, \( I_a \) and \( I_b \) are the intensities of the bands 2700 and 3100 cm⁻¹ or alternatively, 2800 and 2960 cm⁻¹ bands. The constant 1.3462 corresponds to the relation of intensities of these bands in the fully crystalline HDPE spectrum.
Fig. 1: X-ray diagram for HD PE thin films with different gamma radiation doses (a) unirradiated, (b) 100 kGy, (c) 200 kGy and d) 300 kGy

Fig. 2: FTIR spectra for unirradiated and irradiated HDPE films with different gamma radiation doses (a) unirradiated, (b) 100 kGy, (c) 150 kGy (d) 200 kGy and 300 kGy

Fig. 4 illustrates the variation of the amorphous and crystalline content of HDPE samples versus the irradiation dose. Results in Table (1) show relevant discrepancies according to the spectral bands selected for the evaluation of the content in both the amorphous and crystalline phases. The intensity ratio 2800/2960 leads to crystalline contents ranging from 82.2% to 92.2% and the bands 2700/3100 lead to crystallinity values between 82.8% and 92.5%.

The results illustrated in Fig.4 indicated that the HDPE crystallinity takes random values in both cases. It can be confirm that the structural modifications and chemical changes are really very complex. Certain changes lead to a crystallinity increase and others to a crystallinity decrease, the final result leading to a small crystallinity variation. Therefore, the gamma-ray irradiation has slightly increased the HDPE crystallinity.

3.2. Optical Analysis:

Figure 5 shows the absorption spectra of virgin and gamma irradiated HDPE films. It is clear that the absorbance increases with the increase of the radiation doses in range (100 – 400 kGy). This could be due to the increase of the crystallinity of these films with increasing the irradiation dose of as shown in Fig.4. Furthermore, the increase could be due to the increase of conjugated double C=O bonds (Abdel-Fattah et al., 2002).
Fig. 3: FTIR studied zone (2700-3100 cm\(^{-1}\)) for HDPE a) unirradiated, (b) irradiated at 300 kGy

Fig. 4: FTIR studied zone (2960-2800 cm\(^{-1}\)) for HDPE a) unirradiated, (b) irradiated at 300 kGy

Table 1: Amorphous and crystalline contents evaluated by means of Zerbi et al equation

<table>
<thead>
<tr>
<th>Irradiation dose (KGY)</th>
<th>Spectral bands</th>
<th>Amorphous content (%)</th>
<th>Crystalline content (%)</th>
<th>Spectral bands</th>
<th>Amorphous content (%)</th>
<th>Crystalline content (%)</th>
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<td></td>
<td>I(_a) = 2700 cm(^{-1}) and I(_b) = 3100 cm(^{-1})</td>
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<td></td>
<td>I(_a) = 2800 cm(^{-1}) and I(_b) = 2960 cm(^{-1})</td>
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<tr>
<td>0</td>
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<td>92.50</td>
<td>7.80</td>
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</table>

To study the effect of gamma-ray irradiation on the optical band-gap energy of HDPE, the absorption coefficient (\(\alpha\)) was calculated from Urbach rule as (Belal et al., 2002)

\[
I_{(i)} = I_{o} e^{\alpha i}
\]  

(5)
Fig. 5: The absorbance spectra for HDPE samples with different radiation doses, (a) unirradiated, (b) 100 kGy, (c) 200 kGy (d) 300 kGy and (e) 400 kGy

where \( I_0 \) and \( I(t) \) are the intensities of the incident and transmitted light, respectively and \( t \) is the film thickness.

Figs 6 and 7 show the transmittance and reflectance spectra for HDPE samples with different radiation doses. From figure 6, it could be observed that the transmittance is not affected by the radiation doses, while as shown in Fig. 7 the reflectance decreases with increasing radiation doses that is due to the crystallinity increases with increasing the radiation doses, this result is in agree with that shown in Fig. 5. In order to deduce the optical band gap of the studied samples, the spectral dependence of absorption coefficient on the photon energy could be described by the following equation (Gaffar & AbuEl-Fadl 1999):

\[
(\alpha h\nu) = A(h\nu - E_g)^p
\] (6)

where \( h\nu \) is the photon energy, \( A \) is a parameter that depends on the transition probability, \( \alpha \) is the absorption coefficient, \( E_g \) is the optical band-gap energy and the exponent \( p \) depends on the type of the optical transition between the valence and conduction band; direct or indirect optical transitions. The simplest way to determine what type of transition occur is to examine the value of \( p \) which fits \( h\nu \) to \( \alpha h\nu \) with a straight line relationship [30]. In this study, we got straight lines when we analysis the data with \( p = 2 \) which means the energy band gap is an allowed direct transition. Fig. 8(a) shows the relation between \( \alpha^{1/2} \) and the photon energy \( (h\nu) \) for the HDPE films with different gamma-ray radiation doses. The value of \( E_g \) is deduced from the intersection of the extrapolated lines, from the linear part of the curves, with the photon energy axis, while Fig. 8 (a) shows the
The relation between \( \alpha^{1/2} \) and the photon energy \( (h\nu) \) for the HDPE films with different gamma radiation doses. The common method for determining the optical band gap is to plot a curve between \( (\alpha h\nu)^{1/p} \) (\( p=1/2 \) or 2 for direct allowed transition and non-direct transition between valence and conduction bands) and the photon energy \( h\nu \), which tends asymptotically towards a linear section in the high photon energy. The optical activation energy can be determined using the Urbach rule as \[ \alpha = B \exp \left( \frac{h\nu}{E_a} \right) \] for determining the optical band gap is to plot a curve between \( (\alpha h\nu)^{1/p} \) (\( p=1/2 \) or 2 for direct allowed transition and non-direct transition between valence and conduction bands) and the photon energy \( h\nu \), which tends asymptotically towards a linear section in the high photon energy. The optical activation energy can be determined using the Urbach rule as \[ \alpha = B \exp \left( \frac{h\nu}{E_a} \right) \] (7)
optical activation energy of HDPE films. From the first insight, one can observe that the optical activation energy decreases with increasing the gamma radiation dose. The activation energy value was found to be 3.16 eV for the virgin HDPE film. It exhibits sharp decrease to be 1.64 eV for the film irradiated with 100 kGy, then followed by slight decrease to reach 1.49 eV of the 300 kGy irradiated film. This trend confirmed the energy gap behavior of these films (Fig. 9). It belongs to the increase in the polymer crystallinity as well as the formation of the conjugated C=C bonds in the present material.

Fig. 9: Gamma radiation doses effect on the a) direct energy gap b) indirect energy gap for HDPE films

Fig. 10: Activation energy dependence on the gamma radiation doses for HDPE samples

Conclusion:

The effect of gamma-ray irradiation on the structure and optical properties were studied for HDPE thin films. The crystallinity of the investigated films increased with increasing gamma-ray doses especially at high doses. Which causes the direct energy band-gap of the irradiated films exhibits a decreasing with gamma radiation. Also, the indirect energy band-gap shows a decrease with increasing gamma dose, but for the low radiation doses with radiation dosed range (0-80 kGy) this decrease was non-significant. Moreover, the optical activation energy shows an inverse proportion to the irradiation dose. It could be referred to both the increase in the crystallinity and the formation of conjugated C=C bonds inside the polymer due to the chain scission resulted from the gamma irradiation. The influence of the gamma radiation on both direct and indirect energy band-gaps make HDPE is very good candidate to be usable for UV detector and in many industrial and technological fields with a low-cost.

References


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