

Structure–Property Behavior of Polyethylene Exposed to Different Types of Radiation

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ABSTRACT: A detailed study was performed on unirradiated low- and high-density polyethylene (LDPE and HDPE) films as well as irradiated films with different types of radiation such as ⁶⁰Co γ rays, thermal and fast neutrons, and electron beam irradiation. The structural changes of PE films were characterized by Fourier transform infrared (FTIR), Fourier transform Raman (FT-Raman), and ultraviolet (UV) spectrometric techniques. The results showed significant radiation degradation, crosslinking, and changes in the crystalline and amorphous regions. The influence of γ -radiation on the structure of PE was found to be more prominent compared to that of thermal neutrons and electron beam irradiation. However, LDPE film was found to be more sensitive to these types of radiation in accordance with HDPE because of its lesser degree of crystallinity. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 179–200, 2000

INTRODUCTION

Intensive research of the application of radiation processing of polymers and food industry necessitates the examination of the effect of radiation on various plastic films. This is because different types of radiation may cause different structural changes, rearrangement, and fission or formation of chemical bonds in the polymeric film. As a result, the physical, chemical, microbiological, and mechanical properties of the plastic may suffer some detrimental changes. This might lead to the production of new polymeric materials with desired properties, which might fit one of the new technologies and specific applications.¹

Even though there is a clear relationship between property and structure of various polymeric materials, investigations have to start from the structural characteristics. Accordingly, studying the changes caused by ionizing radiation on

the properties of polyethylene (PE) films used widely in several technological applications is of special importance. The changes in the structure of the material were also recorded because an adequate answer to the question of applicability of the material can only be expected from the concomitant consideration of all of these observations.^{2–4}

PE, being one of the simplest polymers, has been the subject of a large number of investigations. When PE is subjected to γ -rays or electron beam irradiation, the main structural changes reported were crosslinking, degradation, and an increase or decrease in the unsaturation of some compounds.^{5–6} A detailed study of the effect of irradiation (γ -rays, electron beam, thermal neutrons, and fast neutrons) on PE films was studied earlier by Charlesby in 1953 showing that PE undergoes crosslinking after irradiation and its properties are largely dependent on the absorbed dose and conditions of irradiation.⁴ Also, Little⁷ and Lawton et al.⁸ reported that PE may be crosslinked by irradiation with fast electrons. Slovkhotova and Karpov⁹ investigated the modifi-

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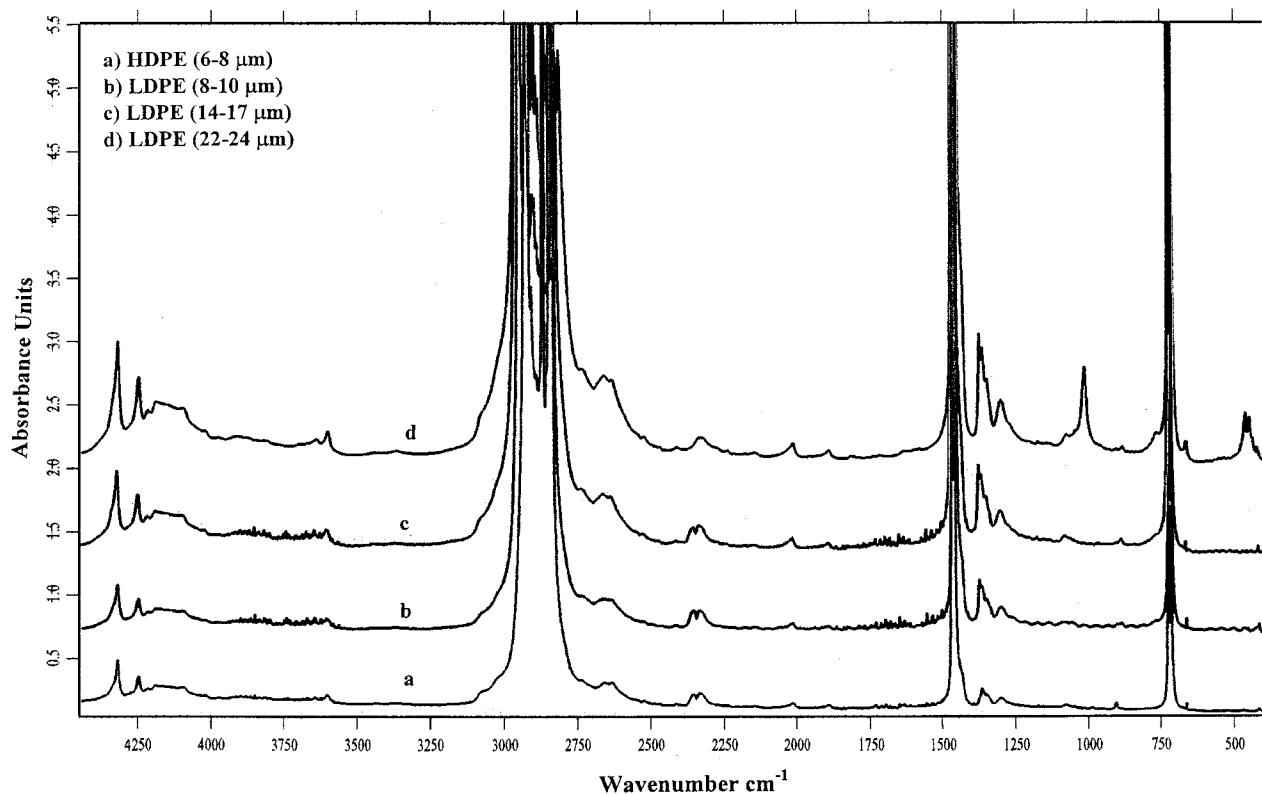


Figure 1 FTIR absorption spectra of unirradiated polyethylene (PE) films.

cation of the infrared (IR) spectra of PE film under electron and γ -irradiation, where the radiation-induced changes are identical to the changes that occurred by heating the PE.

Quantitative determination of the IR absorption bands at 1080 and 1303 cm^{-1} was used to investigate the changes in the degree of crystallinity as a function of the absorbed dose.¹⁰ Also, the radiation-induced changes of PE were studied using the UV absorption bands at several wavelengths (220, 225, 230, 236, 275 nm, etc.) against absorbed dose and dose rate.^{2,5,11}

The present work studies the changes caused by different types of radiation on LDPE and HDPE films used in industrial and technological applications. The structure and property changes in PE film induced by γ , neutron, and electron beam irradiation were characterized by FTIR, FT-Raman, and UV spectroscopic techniques. Because FTIR is the most sensitive technique, a good start would be to study in detail the IR spectrum changes of the unirradiated and irradiated PE films with different types of radiation.

EXPERIMENTAL

Materials

Commercial thin films of low- and high-density PE (LDPE, HDPE), produced by Al Shreef Company, Cairo, Egypt, were used. The LDPE films have a density of $\approx 0.92 \text{ g cm}^{-3}$, fusion index $> 300^\circ\text{C}$, crystallinity of 40%, melt flow index (MFI) of about 1.35 g/10 min, and various thicknesses of about (8–10 μm), (14–17 μm), and (22–24 μm) were used. The HDPE films have a density of $\approx 0.96 \text{ g cm}^{-3}$, fusion index of $> 350^\circ\text{C}$, crystallinity of $\approx 90\%$, MFI of about 1.5 g/10 min, and a thickness of about (6–8 μm).

Irradiation Sources and Procedures

γ -Irradiation Source

γ -Irradiation was carried out by using the NCRRT ^{60}Co γ cell (made in India) at a dose rate of 2.4–2.3 kGy h^{-1} in atmospheric air. The γ -irradiation of PE films was carried out at the central position of the γ -irradiator by using a specially designed poly(methyl methacrylate) holder (5-mm thick-

Table I The Characteristic FTIR Absorption Bands of Unirradiated, γ -Irradiated, and Reactor-Irradiated LDPE Film

Original Position of FTIR Bands				Intensity Change on γ -Radiation	Observed Shifts		
Bands Initially Present in Unirradiated PE	Bands Induced Due to γ -Radiation	Bands Induced Due to Reactor Radiation	Literature		Low γ -Dose	Middle γ -Dose	High γ -Dose
452					Constant		
456				Constant			
888				–	Disappeared	Disappeared	Disappeared
	965	967	965 (+)	+	965	965	963.98
1018	1017	1018		+	1017	1018	1018
1069			1068 (+)				
	1113			+			1114
	1131		1131 (+)	+	1131	1131	1130
	1175			+	1177	1177	1178
	1241			+			1241
1287				+			
1304			1306 (–)	+	1304	1302	1288
1377			1378 (+)	+	1378	1378	1377
	1411		1410 (+)	+		1411	1411
1456				Constant	1456	1457	1457
	1715	1714	1716 (+)	+	1714	1714	1701
	3420	3420		+			

ness). This insures that the films are exposed to the same radiation field in the most homogeneous region of the irradiated chamber (i.e., under conditions of electronic equilibrium). In other words, when the rack holding the PE films is fixed inside the irradiation chamber, the PE films are on an isodose cylindrical surface concentric with cylindrical irradiation chamber.

Mixed Radiation from the Egyptian Research Reactor

The neutron source used is the ET-RR-1 reactor (located in Anchas, Egypt) which is a 2 MW-WWR-S (Russian-type) research reactor. It is a tank-type reactor with 10% enriched-uranium oxide fuel. Distilled water is used as a moderator, coolant, and reflector. The maximum and average thermal neutron fluxes in the reactor core are 2.0×10^{13} and 1.1×10^{13} n cm⁻² s, respectively. The PE films were exposed continuously to the radiation from the reactor for 48 h to thermal neutrons of flux = 1.3×10^{13} – $1.5 \times 10^{13} \pm 5\%$ n cm⁻² s and fast plus epithermal neutrons of flux 1.4×10^{11} n cm⁻² s. The temperature inside the irradiation channel differed along the irradiation time and

the average temperature was about 38°C and its maximum temperature was about 42°C. (This is the temperature of the water steam coming out after cooling the channel.)

Thermal Neutron Source

Neutron fluxes obtainable from radioisotope neutron sources are much lower than those from ET-RR-I nuclear reactors and neutron generators. It was preferred, then, to irradiate the samples with thermal neutrons coming out from the ET-RR-1 reactor. The samples were irradiated at the exit of the curved neutron guide installed in front of the horizontal channel No. 9. The flux of pure thermal neutrons at the exit of this channel was about 6.7×10^{13} n cm⁻² s.

Electron Beam Irradiation

The electron beam (EB) irradiation was carried out by using a direct EB accelerator made by High Voltage Company, USA. The parameters of this accelerator are 1.5 MeV electron energy, 7.5 mA EB current, 70 cm scanner width, continuous EB pulse, and variable conveyor speed. The EB pa-

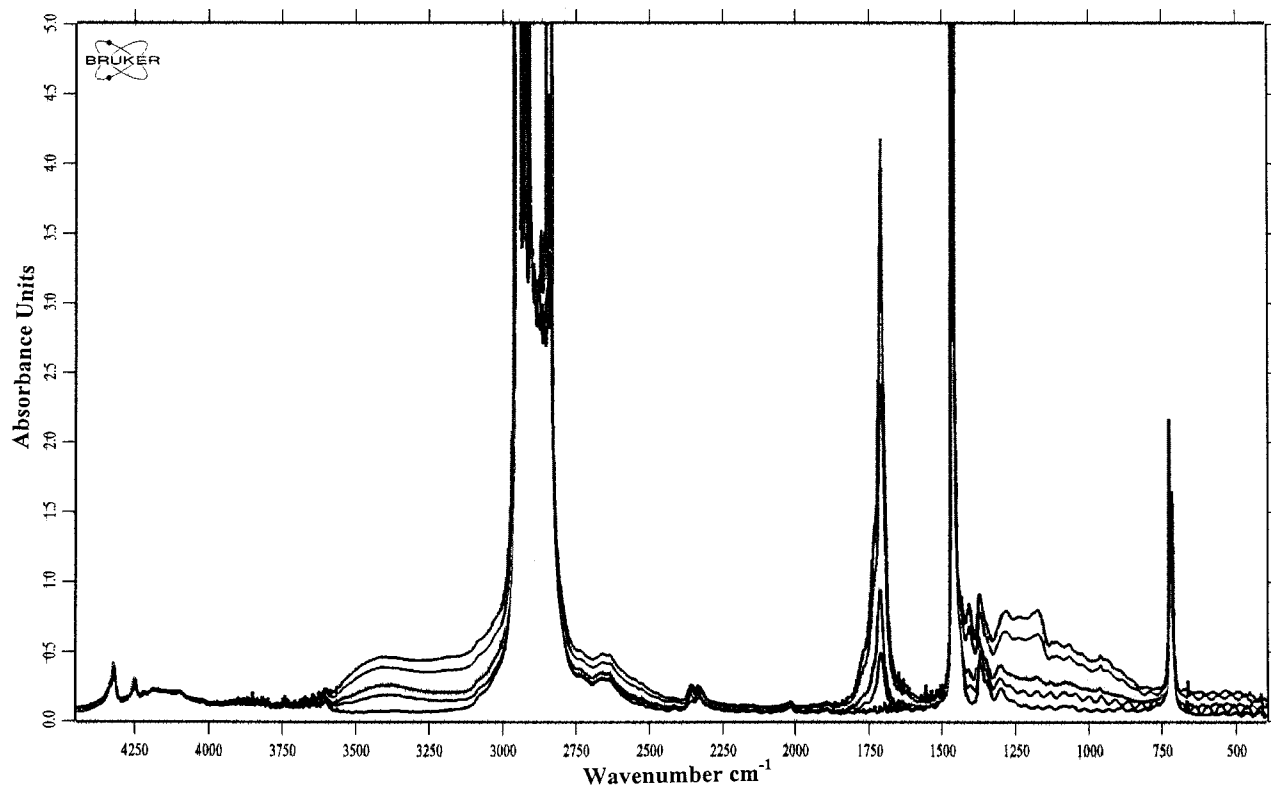


Figure 2 (a) FTIR absorption spectra of LDPE (8–10 μm) irradiated with different absorbed γ -doses up to 934 kGy in the wavenumber range 400–1000 cm^{-1} . (b) FTIR absorption spectra of LDPE (8–10 μm) irradiated with different absorbed γ -doses up to 934 kGy in the wavenumber range 1000–2000 cm^{-1} . (c) FTIR absorption spectra of LDPE (8–10 μm) irradiated with different absorbed γ -doses up to 934 kGy in the wavenumber range 2500–3600 cm^{-1} . (d) FTIR absorption spectra of LDPE (8–10 μm) irradiated with different absorbed γ -doses up to 934 kGy in the wavenumber range 4000–4500 cm^{-1} .

rameters were adjusted to give 5.0, 14.6, 26.2, 38.9, and 53.2 kGy.

Spectroscopic Analysis

A FTIR spectrometer (IFS 66/S) was used for measuring and scanning the IR absorption spectra of PE thin films with resolution of 2 cm^{-1} over the range of 400–5000 cm^{-1} . Besides, an ATI Mattson Genesis series FTIR spectrometer was also used to scan the same samples, and the data obtained from the two devices were compared when the same behavior was detected. High signal-to-noise ratio spectra were obtained by the collection of 100 scans for each sample and the resultant digitized spectra were stored for further data processing. The Bruker-FRA 106/RFS (100) used in this work contains all the components required for FT-Raman spectroscopy, and it con-

sists of Nd:YAG laser with maximum power of 500 mW, sample compartment, Raleigh filter, and the InGaAs detector. Unicam ultraviolet/visible (UV/VIS) UV2 spectrophotometer was used for measuring and scanning the absorption spectra and measuring the optical density at λ_{max} of the PE films before and after irradiation.

RESULTS AND DISCUSSION

FTIR Spectra of Unirradiated and γ -Irradiated PE Films

Figure 1 shows the IR absorption spectra of unirradiated PE thin films, and the obtained absorption bands are summarized in Table I. It is clear from Figure 1 that the intensity of the IR absorption bands of LDPE increases with

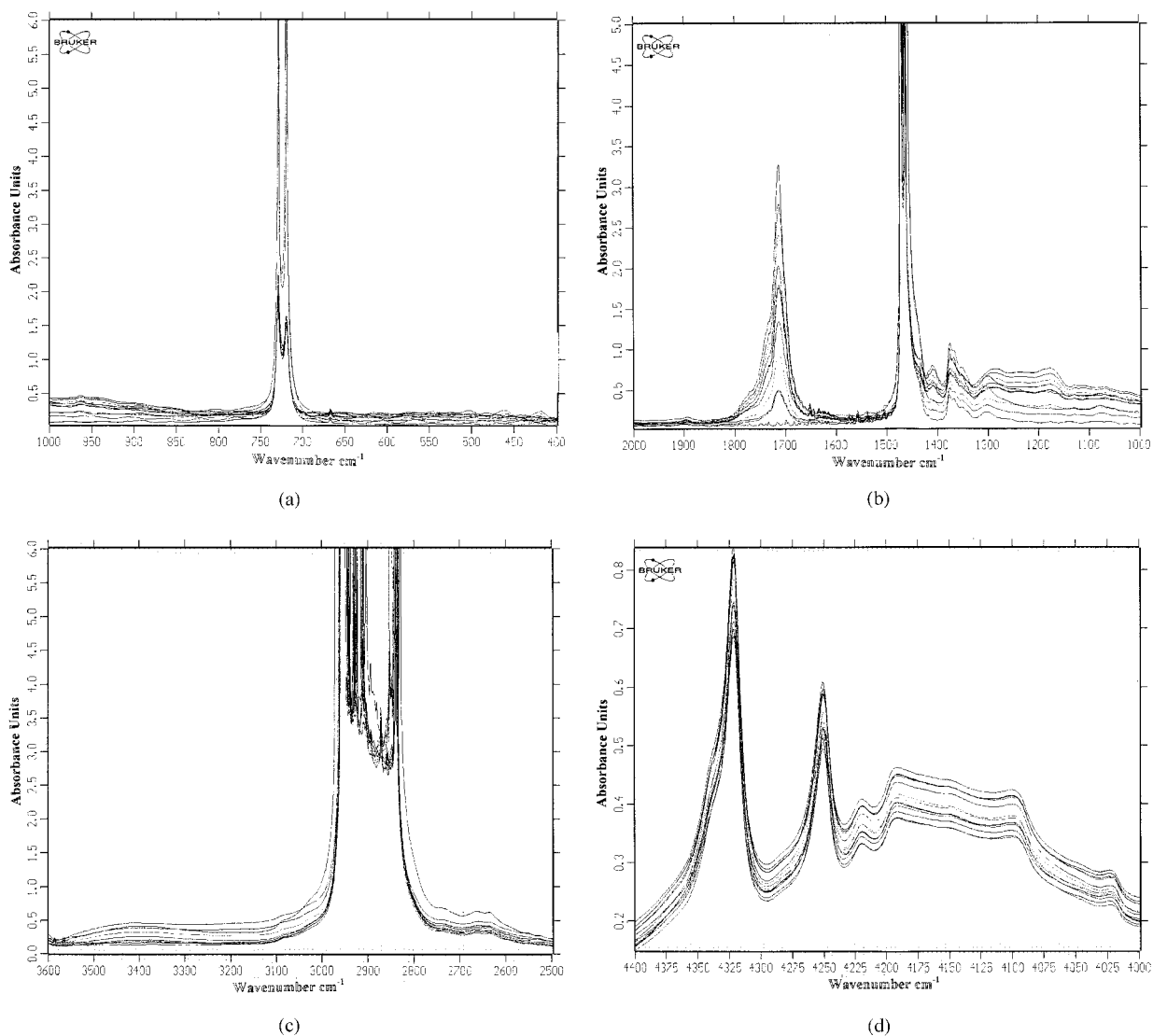


Figure 2 (Continued from the previous page)

increasing film thickness. Moreover, some of the bands were not monitored for small thickness such as the band at 1018 cm^{-1} , which was not detected before for PE. It is believed that this band may be due to the oxidation effects. It is known that as the thickness of the film increases, the amount of occluded oxygen in PE but not residual environmental will eventually increase. This oxygen could be present either as absorbed oxygen or as secondary peroxides, which it decomposes on production and storage to give ketonic carbonyl groups. Two absorption bands at 452 and 465 cm^{-1} , which are attributed to the $\beta(\text{C}\equiv\text{C}-\text{H})$, appeared in the IR spectra of the unirradiated films having a thick-

ness of $22\text{--}24\ \mu\text{m}$.¹² Moreover, the appearance of new modes with PE films of high thickness could be related to the increase of the crystallinity and ordering of the molecular segments.

Figures 2–4 show the IR absorption spectra of both unirradiated and irradiated LDPE and HDPE films to an absorbed dose of about 1 MGy of γ -radiation at room temperature. It should be noted that the IR analysis was carried out on various thicknesses of LDPE and $6\text{--}8\ \mu\text{m}$ of a HDPE. It can be seen that γ -irradiation resulted in several changes in the IR spectra with respect to those of the unirradiated ones.

On the basis of the obtained IR spectra, several prominent observations may be correlated.

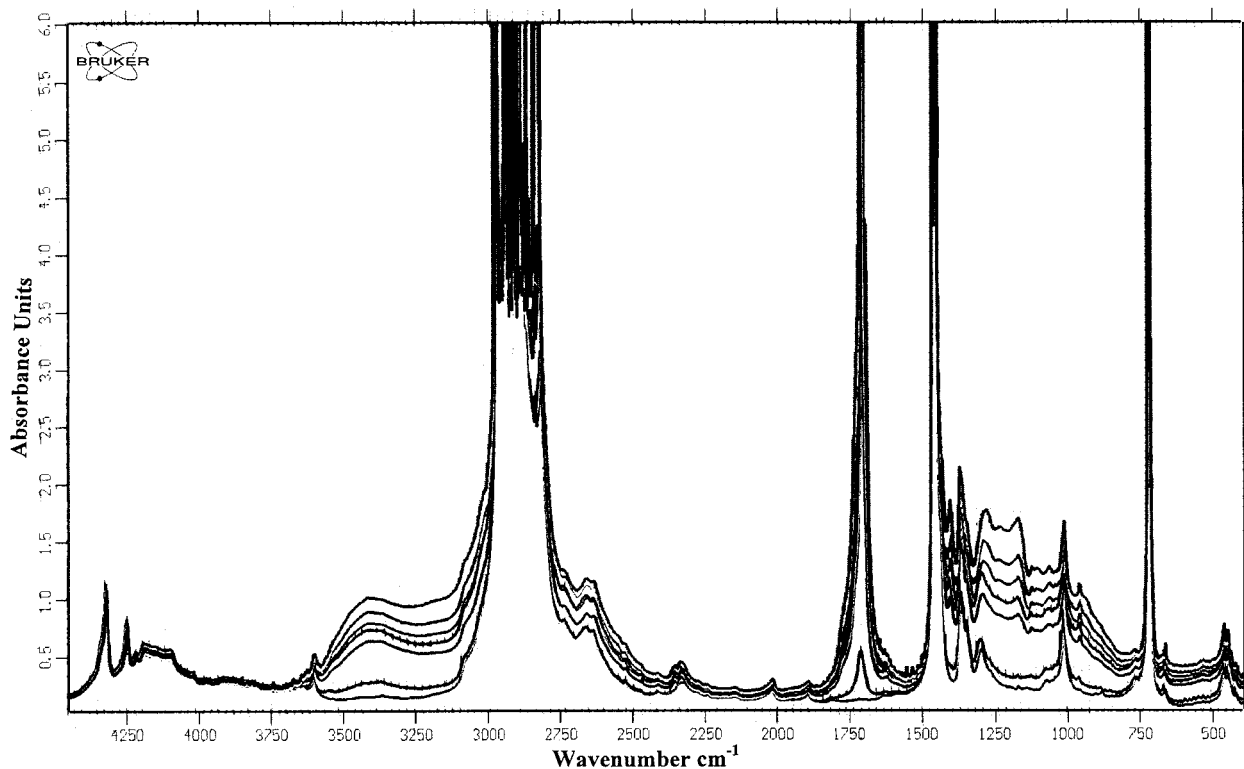


Figure 3 (a) FTIR absorption spectra of LDPE (22–24 μm) irradiated with different absorbed γ -doses up to 934 kGy in the wavenumber range 400–1000 cm^{-1} . (b) FTIR absorption spectra of LDPE (22–24 μm) irradiated with different absorbed γ -doses up to 934 kGy in the wavenumber range 1000–2000 cm^{-1} . (c) FTIR absorption spectra of LDPE (22–24 μm) irradiated with different absorbed γ -doses up to 934 kGy in the wavenumber range 2500–3600 cm^{-1} . (d) FTIR absorption spectra of LDPE (22–24 μm) irradiated with different absorbed γ -doses up to 934 kGy in the wavenumber range 4000–4500 cm^{-1} .

1. The complex contour of the IR absorption bands at 451 and 465 cm^{-1} appeared only in the case of LDPE samples of the largest thickness (22–24 μm) and seemed not affected by γ -irradiation, as shown in Figure 3(a).
2. The disappearance of the small band at 888 cm^{-1} is possibly due to the CH_2 out-of-plane deformation. This may be explained on the basis of evolution of hydrogen gas as a result of the degradation. This finding was first detected in this work, as shown in Figure 2(a).
3. The intensity of the IR absorption bands at 1017, 1113, 1130, 1175, and 1241 cm^{-1} is shown to increase with increasing irradiation dose, as shown in Figures 2(b) and 4(b). However, the IR absorption band at 1018 cm^{-1} , which appeared only in the case of the thickness (22–24 μm) [see Fig. 3(b)], were not seen in the IR spectra of either the smaller thickness of LDPE or that of HDPE. On the other hand, this band appeared in the IR spectra of unirradiated LDPE samples of thicknesses (22–24 μm) and its intensity was found to increase with the radiation absorbed dose. All these bands are attributed to the C—O stretching vibrations.
4. The intensity of the bands 1069, 1287, and 1377 cm^{-1} (which are initially present in the IR spectra of the unirradiated films) was found to increase remarkably with the radiation-absorbed dose, whereas the intensity of the sharp band at 1457 cm^{-1} was not affected at all [see Figs. 2(b)–4(b)]. These bands are attributed to C—C stretching, OH bending, symmetric defor-

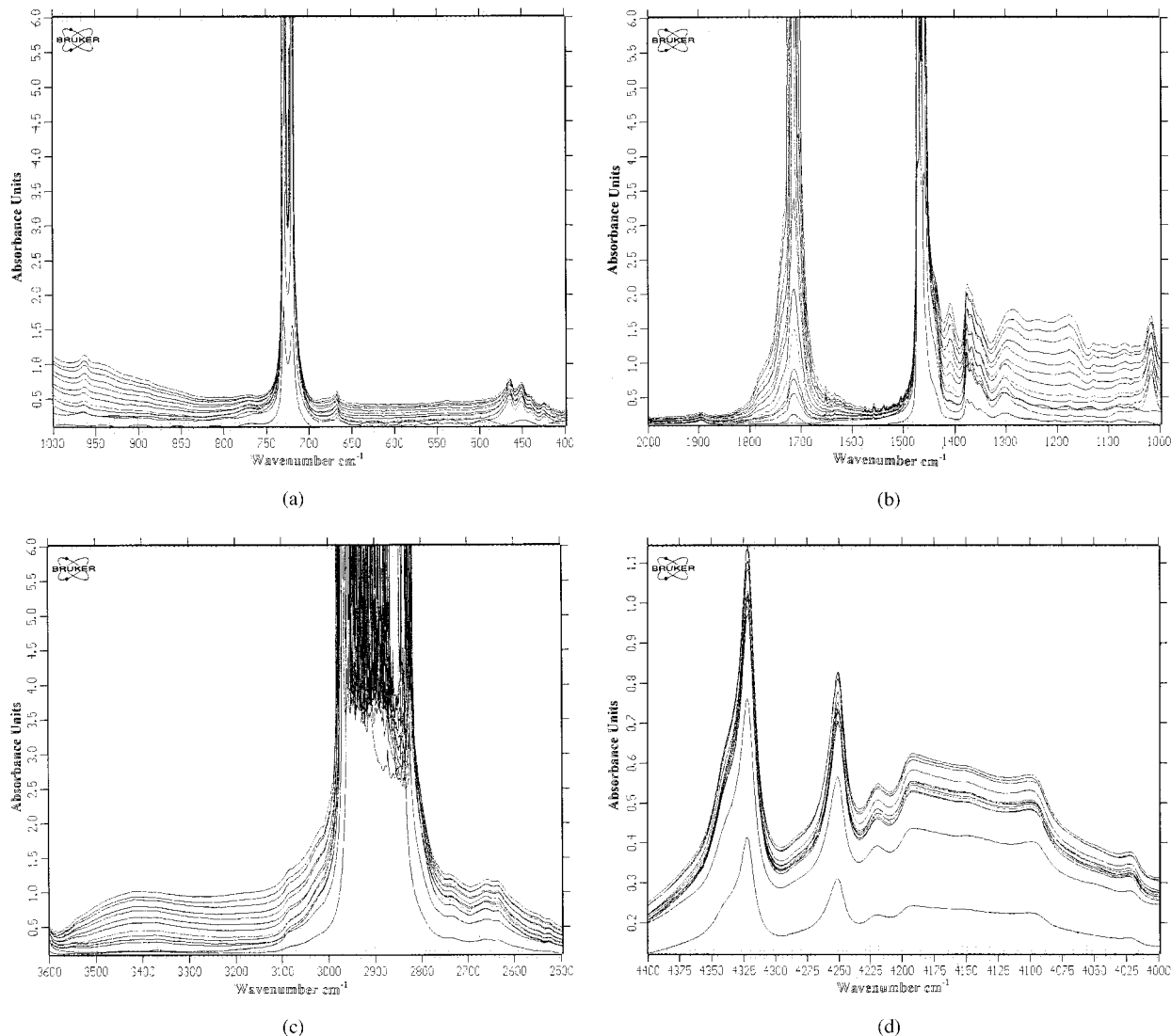


Figure 3 (Continued from the previous page)

mation of CH_2 (wagging), and CH deformation, respectively.

5. The following bands, 965, 1299, 1373, 1411, 1716, and 1879 cm^{-1} , had been monitored in a previous work describing the correlation and possible application for large dose-radiation dosimetry.¹³
6. The appearance of a broad band which is very obvious at high γ -radiation-absorbed dose in the range of 3100–3580 cm^{-1} [see Figs. 2(c)–4(c)] is attributed to the hydroxyl groups (O—H).¹⁴
7. The complex contour in the range of 4100–4220 cm^{-1} was not affected at all with γ -irradiation either in the peak position or height. Also, the bands at 4250–4322 cm^{-1}

were not affected with the γ -irradiation [see Figs. 2(d)–4(d)].

8. There was a shift in some bands (either the initially present bands or those produced because of γ -irradiation) toward higher or lower frequencies (Table I).
9. All of the above IR absorption bands increase as the thickness of the PE film increases, as shown in Figure 5.
10. The previously discussed remarks observed for LDPE are also clearly seen for HDPE films except that the relative height of the bands induced by the γ -irradiation are much less for HDPE than those bands corresponding to LDPE so that some of them are hardly detected.

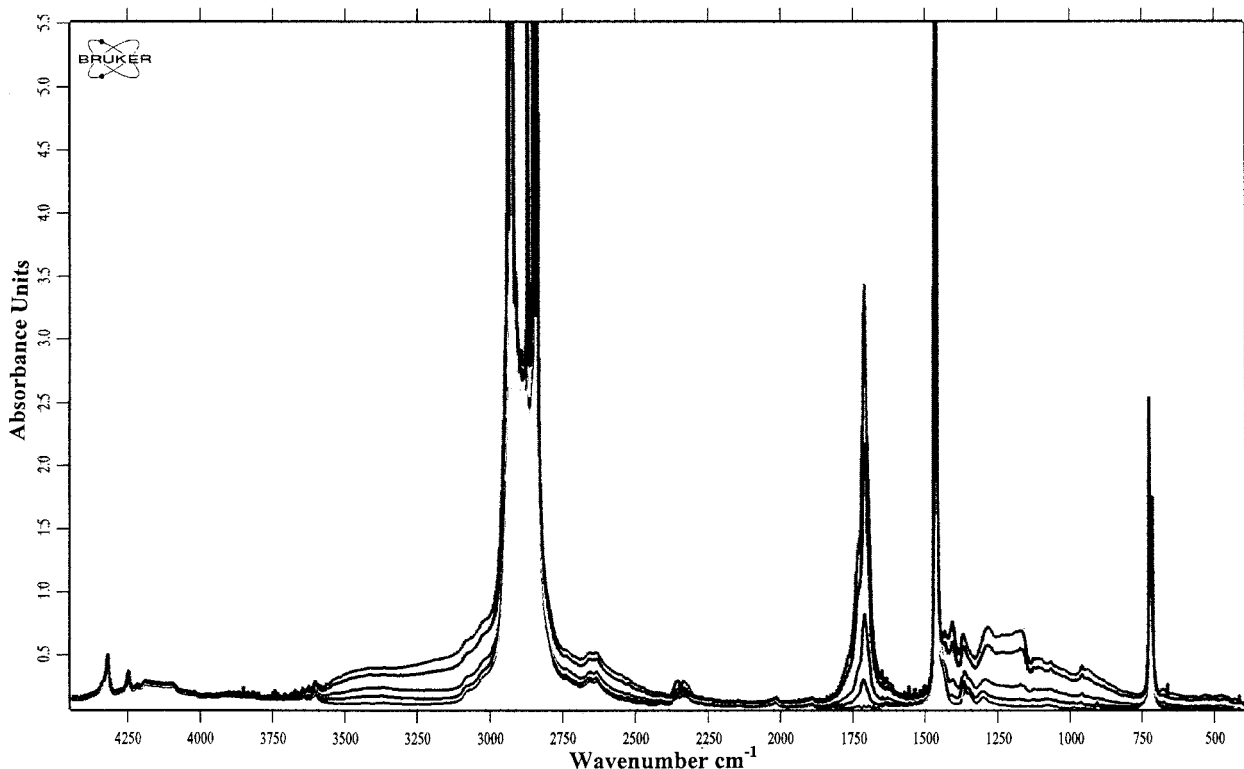


Figure 4 (a) FTIR absorption spectra of HDPE (6–8 μm) irradiated with different absorbed γ -doses up to 934 kGy in the wavenumber range 400–1000 cm^{-1} . (b) FTIR absorption spectra of HDPE (6–8 μm) irradiated with different absorbed γ -doses up to 934 kGy in the wavenumber range 1000–2000 cm^{-1} . (c) FTIR absorption spectra of HDPE (6–8 μm) irradiated with different absorbed γ -doses up to 934 kGy in the wavenumber range 2500–3600 cm^{-1} . (d) FTIR absorption spectra of HDPE (6–8 μm) irradiated with different absorbed γ -doses up to 934 kGy in the wavenumber range 4000–4500 cm^{-1} .

Effect of γ -Irradiation on the FTIR Band Parameters (Qualitative and Quantitative Analysis of FTIR Spectra for γ -Irradiated Samples)

The IR absorption bands are shown to have four parameters [viz., the band shape (φ), the absolute or integrated intensity $\{I(\nu)\}$, the frequency (ν), and the half-bandwidth ($\Delta\nu$), in addition to the band asymmetry]. These parameters can be calculated and represented by the (n) moments (μ_n) given by the following equation¹⁵

$$\mu_n = \frac{\int_{-\infty}^{+\infty} \varphi(x)x^n dx}{\int_{-\infty}^{+\infty} \varphi(x) dx} \quad (1)$$

where $\varphi(x)$ is the function describing the band shape, which could be either Lorentzian L or Gaussian G or a linear combination of both $\alpha_1 L + \alpha_2 G$. The zero moment is

$$(\mu_0) = \int_{-\infty}^{+\infty} \varphi(x) dx \quad (2)$$

where the zero moment (μ_0) is the integrated intensity of the band $\{I(\nu)\}$. The first moment is (μ_1), where $n = 1$ is the center mass of the band or the frequency (ν). The second moment (μ_2) is the half-bandwidth ($\Delta\nu$) of the band; finally, the third moment (μ_3) is the asymmetry of the band. The software used gives the values of these parameters directly for each IR band at different absorbed doses.

To study the effect of the γ -radiation dose on the IR band parameters, the bands, which appeared only because of the γ -irradiation, were considered. Among those IR bands, the bands at 965, 1177, 1303, and 1411, 1716, 3420 cm^{-1} , were chosen for this purpose. The small band appear-

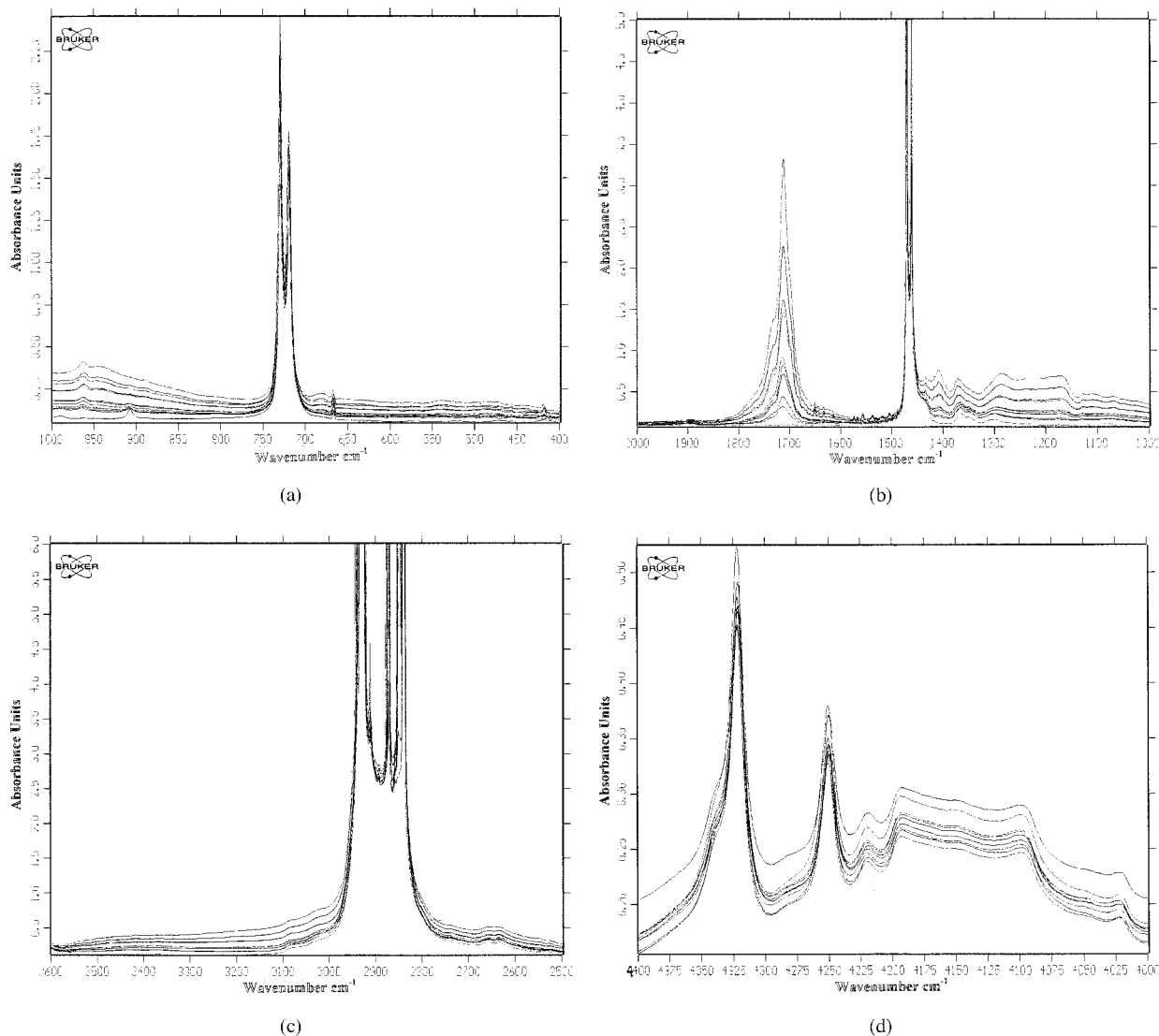


Figure 4 (Continued from the previous page)

ing at 965 cm^{-1} is attributed to the C—H out-of-plane deformation of the *trans*-vinylene groups (*trans*-RCH=CHR).¹⁶ The absolute intensity of this band was found to increase linearly with absorbed dose and film thickness, as shown in Figure 6. However, the response of HDPE film is less than that for LDPE film. Such linear dependence on absorbed dose may lead to the conclusion that LDPE and HDPE thin films can be used as a γ -radiation dosimeter over a wide range of absorbed doses (0–1 MGy). Also, the frequency of this band decreases with increasing absorbed dose, as shown in Figure 6. In other words, it is clearly seen that this band is shifted toward lower frequency as the radiation-absorbed dose increases. This behavior may occur because of the

reorientation disorder of the molecular fragments as a result of γ -irradiation. It is also clear that this peak is shifted toward lower frequency (962 cm^{-1}) for HDPE and the rate of change with the irradiation dose is lower in this case.

The band at 1303 cm^{-1} is reported in literature to be one of the bands characterizing the amorphous phase in PE.^{2,13,14} This phase is expected to be affected inversely with the γ -irradiation because of the possibility of increasing the crystallinity of the sample with irradiation. However, the relation between the absolute intensity of this band versus γ -radiation-absorbed dose showed two stages of linear relationship with a kink in the range (330–500 kGy) for all PE films, as shown in Figure 7. The increase of the intensity

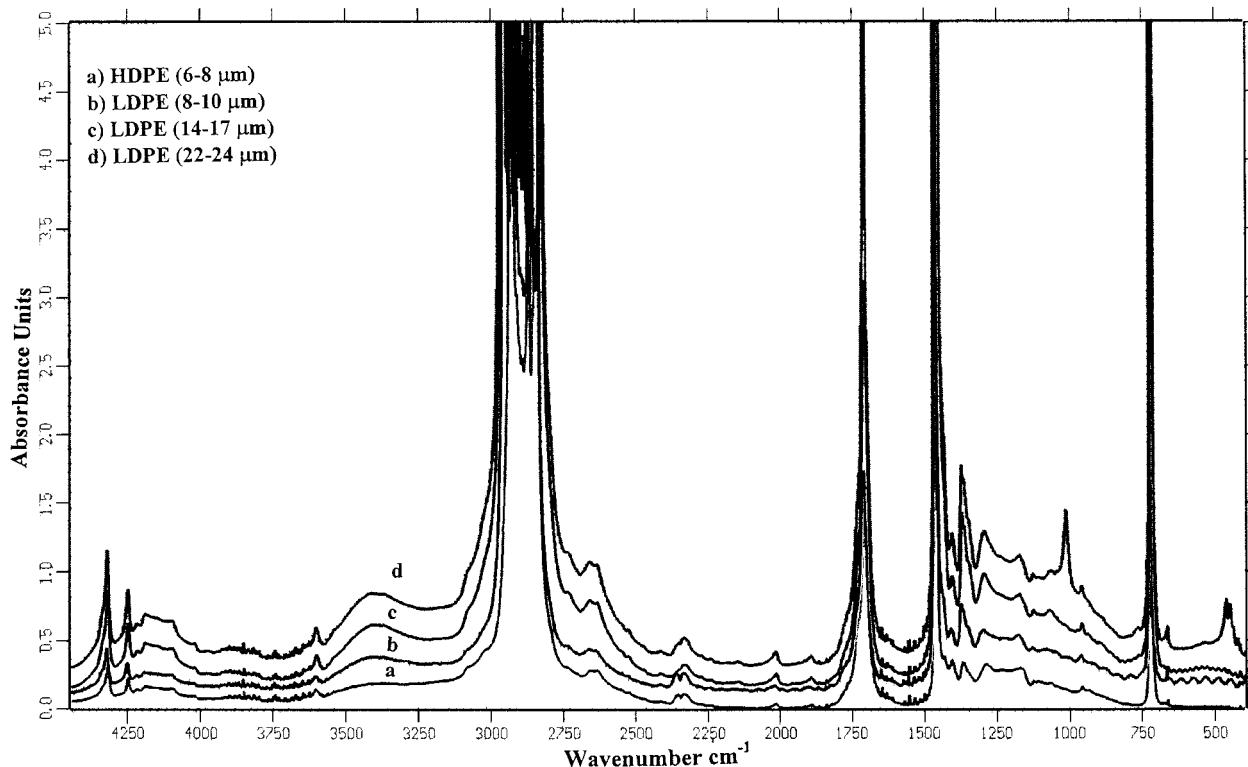


Figure 5 FTIR absorption spectra of PE (8–10, 14–17, and 22–24 μm for LDPE and 6–8 μm for HDPE) irradiated with γ -absorbed dose (505 kGy).

with the γ -radiation-absorbed dose in the first stage is much less than that in the second stage. This may be explained on the basis that in the first stage in which degradation is thought to be predominant, the decrease in crystallinity is much less than in the second stage. It follows that crosslinking is more predominant, and consequently, the decrease in crystallinity is expected to be more affected. As shown in Figure 7, there is a slight decrease in the frequency of this band at lower absorbed doses and then the rate of decrease tends to be larger at higher doses showing once again two stages of linear relationship. The half-bandwidth of the band at 1303 cm^{-1} showed a remarkable increase with increasing radiation dose up to 650 kGy and suddenly it started to decrease with absorbed dose, as shown in Figure 7. The half-bandwidth ($\Delta\nu$) is related to the lifetime of the level (or the relaxation time) (τ) by the relation $\tau = 1/(\pi c \Delta\nu)$, where c is the velocity of light.¹⁷ Using this equation, the lifetime τ (the time interval between two successive reorientations) could be estimated for the bands at 1303 and 3420 cm^{-1} as a function of the γ -radiation-absorbed dose, as shown in Figure 8. Once again

a two-stage linear dependence relationship with a kink lying in the same interval appear as obtained above in Figure 7.

The band at 1411 cm^{-1} , which is evidence to the occurrence of crosslinking due to the methylene deformation influenced by an adjacent carbonyl group, showed a linear relationship over a wide interval of γ -radiation-absorbed doses. This linear relationship again confirms the fact that PE can be used as a cheap and safe dosimeter. The frequency of this band was not affected with the radiation-absorbed dose, whereas the half-bandwidth showed an increase with a kink in the line within the same dose region (300–500 kGy). The relations between the absolute intensity and the half-bandwidth of this band versus the γ -radiation-absorbed dose are shown in Figure 9.

The intensity of the distinctive band at 1716 cm^{-1} , which is attributed to the stretching vibrations of the ketonic carbonyl group,^{13,14} was found to increase remarkably with γ -radiation-absorbed dose showing two stages of linear dependence, as shown in Figure 10. This two-stage linear dependence was detected before by Abdel Fattah et al. and Badr.^{13,17} As mentioned above, this kind of

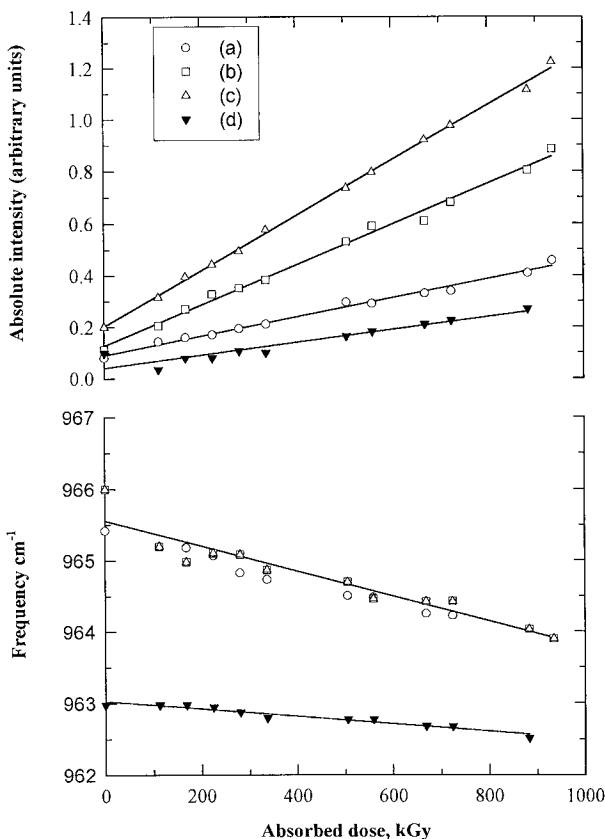


Figure 6 Variation in the absolute intensity and frequency of the absorption peak at 965 cm^{-1} as a function of the γ -absorbed dose. (a) LDPE ($8\text{--}10\ \mu\text{m}$), (b) LDPE ($14\text{--}17\ \mu\text{m}$), (c) LDPE ($22\text{--}24\ \mu\text{m}$), (d) HDPE ($6\text{--}8\ \mu\text{m}$).

two-stage linear relationship almost characterizes most of the variations of the band parameters with the absorbed dose.

The band parameters of the band in the range ($3370\text{--}3420\text{ cm}^{-1}$) were investigated as shown in Figure 11. The absolute intensity increases in general with the absorbed dose showing linear behavior for LDPE of various thicknesses. It should be noted that this band is very weak for HDPE because of its high crystallinity.

On the other hand, the half-bandwidth ($\Delta\nu$) for the same band at 3420 cm^{-1} showed different two-stage behavior where the value of $\Delta\nu$ increases linearly with increasing γ -radiation-absorbed dose up to 400 kGy and then decreases but with lower extensions, as shown in Figure 11. Also, Figure 11 shows the same two-stage linear dependence for the variation of the band frequency (ν) with the γ -radiation-absorbed dose for the band at 3420 cm^{-1} . Once again it is obvious that the range at which the kink occurs between the two linear stages is ($\sim 330\text{--}500\text{ kGy}$). The

frequency in each of the two stages is almost constant, which means that a sudden increase in the frequency occurs. This could be related to a sudden increase in the force constant due to a possible sudden rearrangement of the molecular segments in this interval separating the regions where chain degradation is predominant (intermediate absorbed doses). Nevertheless, the region where the crosslinking is more predominant is within the high absorbed doses.^{15,17} The above-mentioned observations may lead to the conclusion that γ irradiation has two stages of influence on PE, and the similar behavior of the dependence of the band parameters on the absorbed dose indicates that they all have the same origin.

FTIR Spectra of Neutron-Irradiated PE Films

On exposing PE thin films to the thermal neutron source, almost no changes were detected for both

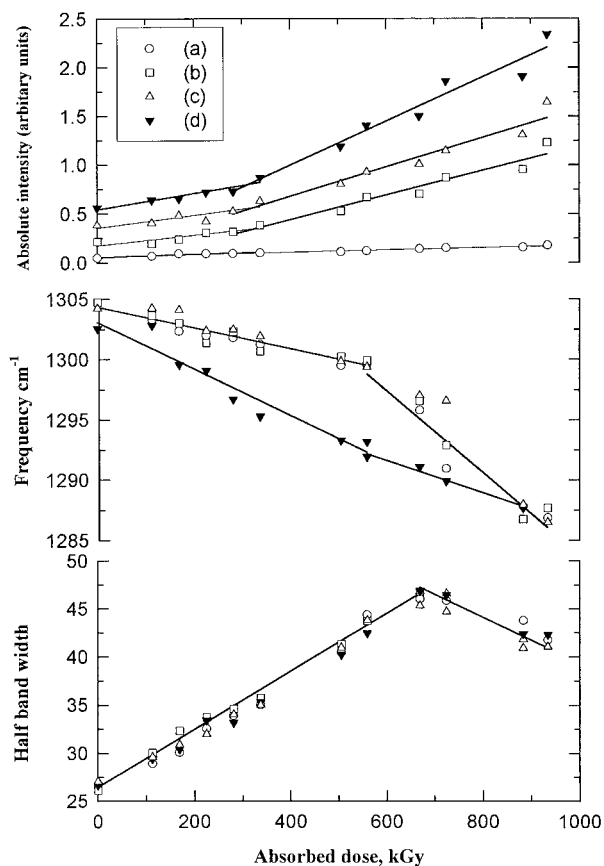


Figure 7 Variation in the absolute intensity, frequency, and bandwidth of the absorption peak at 1303 cm^{-1} as a function of the γ -absorbed dose. (a) LDPE ($8\text{--}10\ \mu\text{m}$), (b) LDPE ($14\text{--}17\ \mu\text{m}$), (c) LDPE ($22\text{--}24\ \mu\text{m}$), (d) HDPE ($6\text{--}8\ \mu\text{m}$).

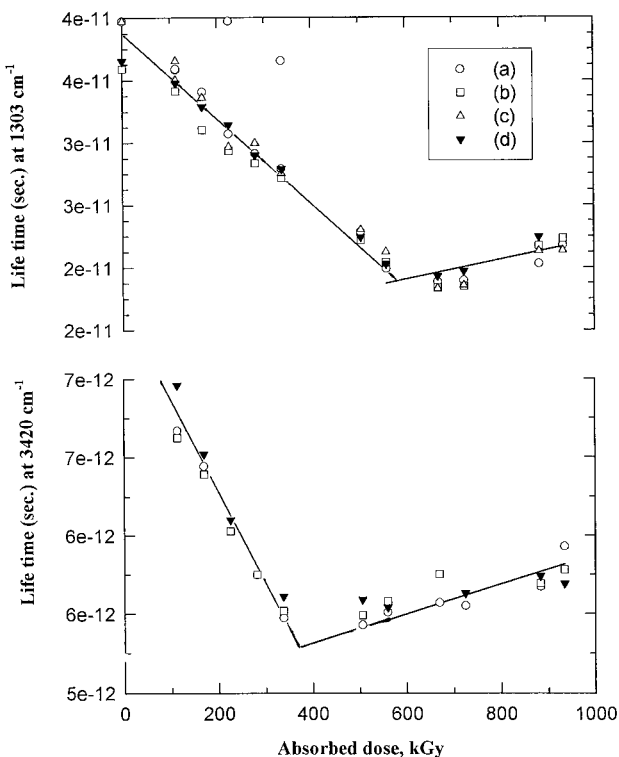


Figure 8 Variation in the lifetime of the absorption peaks at 1303 and 3420 cm^{-1} as a function of the γ -absorbed dose. (a) LDPE (8–10 μm), (b) LDPE (14–17 μm), (c) LDPE (22–24 μm), (d) HDPE (6–8 μm).

FTIR and FT-Raman spectra in which no remarkable changes in peak intensities or shifts in peak position were observed. This may reflect the fact that PE shows good resistance to thermal neutrons up to doses of about $6.7 \times 10^{13} \text{ n cm}^{-2} \text{ s}$. These observations are in good accordance with literature where a similar observation was reported for polypropylene.^{17,18}

On the other hand, on using fast neutrons with the abovementioned flux, the following changes were detected, as shown in Figure 12.

1. As can be seen from Figure 12(a), the small IR absorption band at 770 cm^{-1} was not identified in the case of PE films with the smallest thickness and began to appear with increasing film thickness. Moreover, the shape of this band turned out to be a broad shoulder attached to the neighboring sharp band at 727 cm^{-1} with the PE films of the largest thickness. However, the relative intensity between these two bands was not affected with increasing irradiation dose of ^{60}Co γ -rays. This band at 770

cm^{-1} is attributed to the C—H out-of-plane deformation for five adjacent free hydrogen atoms.¹⁹

2. A broad complex band at about 875 cm^{-1} showed up as a result of irradiation with fast reactor neutrons. It should be noted that this band did not appear in the case of γ -irradiation to the highest absorbed dose. The only observed variation due to γ -irradiation was the remarkable increase of the baseline within this region of γ -irradiation dose. This band is attributed to the CH_2 out-of-plane deformation.
3. The appearance of a sharp and highly intense band at about 967 cm^{-1} is due to the C—H out-of-plane deformation of the *trans*-vinylene groups [*trans*-(R—CH=CH—R')] or the substitutions of =C—H is eventually due to γ -irradiation.

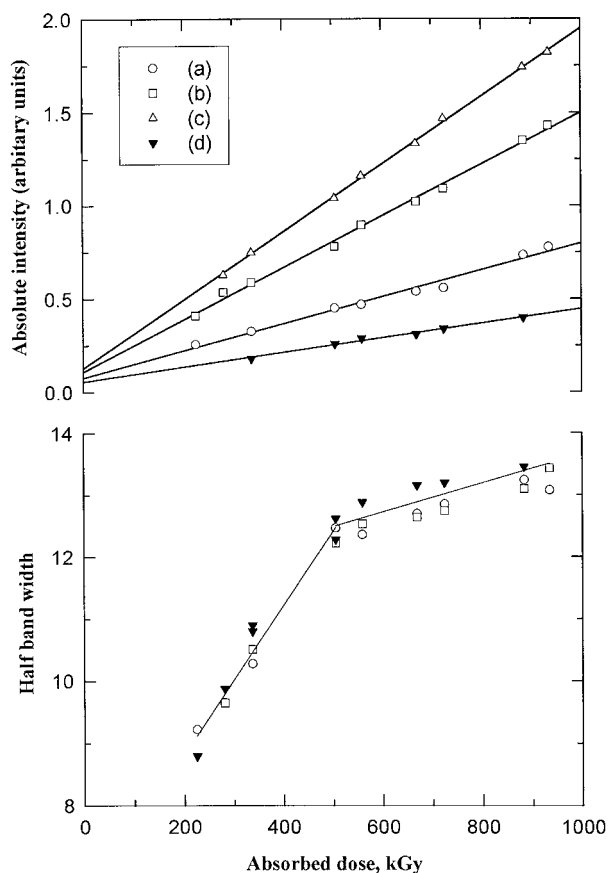


Figure 9 Variation in the absolute intensity and bandwidth of the absorption peak at 1411 cm^{-1} as a function of the γ -absorbed dose. (a) LDPE (8–10 μm), (b) LDPE (14–17 μm), (c) LDPE (22–24 μm), (d) HDPE (6–8 μm).

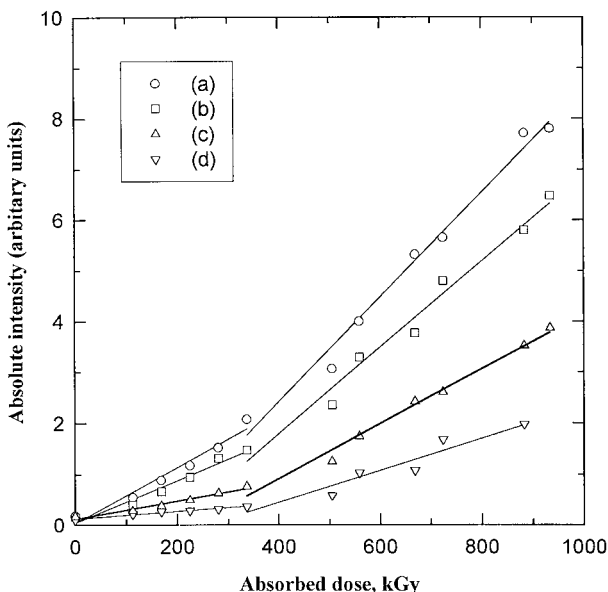


Figure 10 Variation in the absolute intensity of the absorption peak at 1716 cm^{-1} as a function of the γ -absorbed dose. (a) LDPE ($8\text{--}10\ \mu\text{m}$), (b) LDPE ($14\text{--}17\ \mu\text{m}$), (c) LDPE ($22\text{--}24\ \mu\text{m}$), (d) HDPE ($6\text{--}8\ \mu\text{m}$).

4. The band at about 1018 cm^{-1} , which was seen only with unirradiated LDPE films with thickness of ($22\text{--}24\ \mu\text{m}$), was found to appear after irradiation with fast neutrons for all thicknesses even for HDPE. Regarding the LDPE film of thickness ($22\text{--}24\ \mu\text{m}$), the intensity of this band was found to increase after irradiation with a shift of about 2 cm^{-1} toward higher frequency. For a small thickness, the band under investigation was found to be a small broad symmetric one and its intensity increases slightly as the thickness was increased. For a LDPE sample of a larger thickness, a small shoulder a few reciprocal centimeters apart appeared with a complex broad contour compared with samples with a smaller thickness. The complexity of this band was also observed for an unirradiated sample of a larger thickness but with lower intensity only. Thus, these differences in IR spectra of PE films can be attributed to the difference in the thickness of the films. In this regard, PE films of $22\text{--}24\ \mu\text{m}$ is characterized by high ordered structure with high crystallinity compared to PE films of a thickness of $8\text{--}10\ \mu\text{m}$. This finding was clearly observed in a future work dealing with X-ray diffraction analysis of

PE film. This work has been submitted for publication. It is worthwhile to mention once more that this band is detected here for the first time for PE and that it is not specified in literature for PE films but it is attributed in literature as the C—H stretching frequencies in cyclopropane ($1000\text{--}1020\text{ cm}^{-1}$). On the basis of that, this conjugated $(\text{CH}_2)_5$ resulted in PE as a result of the fast neutron irradiation. It is believed, in our point of view, that this band could be related to the oxidative effects of the fast neutrons.¹⁶

5. Moreover, a band at 1714 cm^{-1} was also induced by neutrons and its intensity was found to be equivalent to that band produced by a γ -dose of about 169 kGy [see Fig. 12(b)], but the position for the band induced by γ -irradiation was noticed to be shifted toward a higher frequency. Besides,

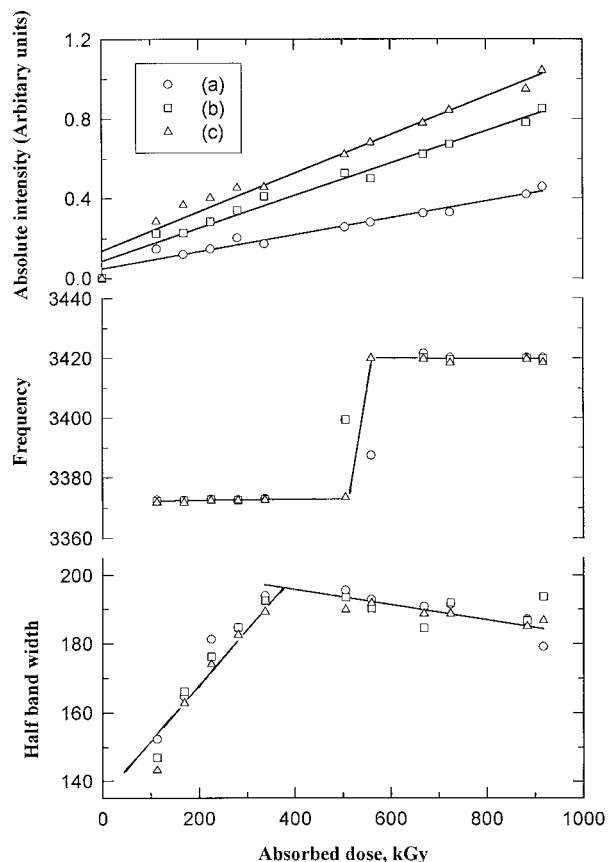


Figure 11 Variation in the absolute intensity, frequency, and bandwidth of the absorption peak at 3420 cm^{-1} as a function of the γ -absorbed dose. (a) LDPE ($8\text{--}10\ \mu\text{m}$), (b) LDPE ($14\text{--}17\ \mu\text{m}$), (c) LDPE ($22\text{--}24\ \mu\text{m}$).

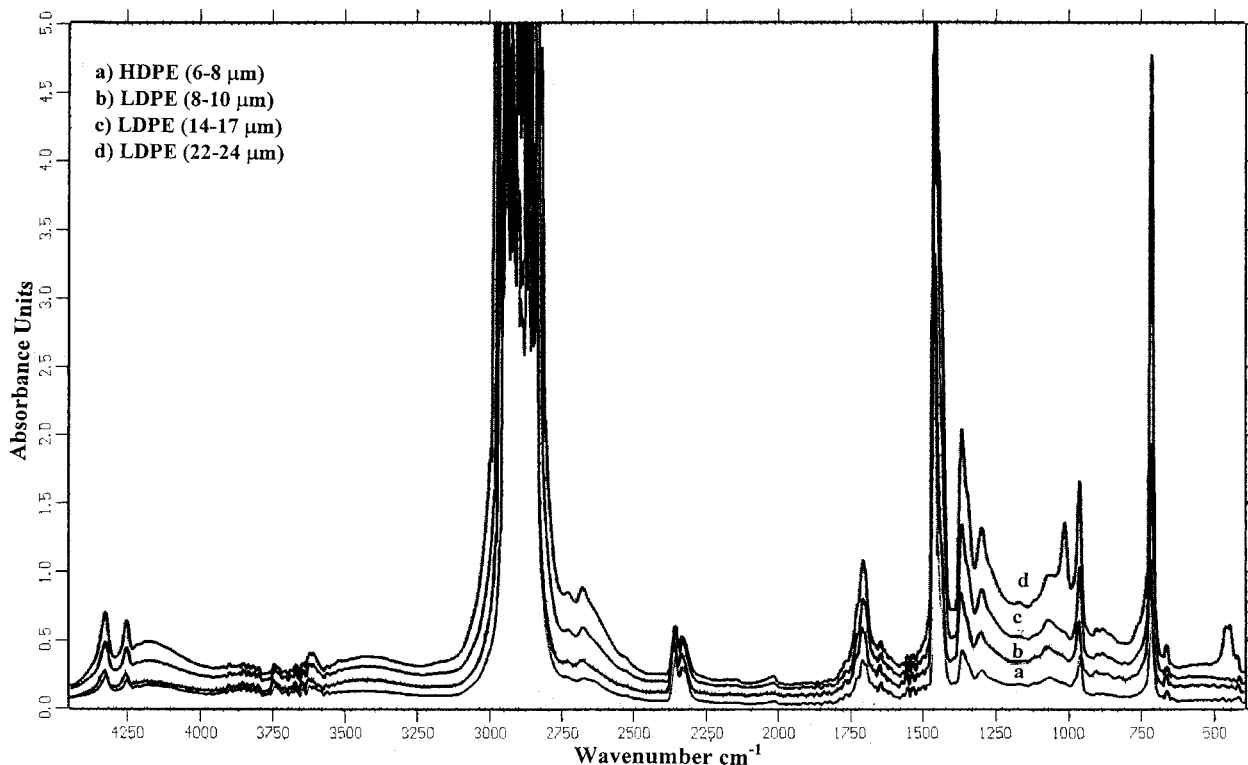


Figure 12 (a) FTIR absorption spectra of irradiated (PE) film with fast neutrons from the reactor in the wavenumber range 500–1100 cm^{-1} . (b) FTIR absorption spectra of irradiated (PE) film with fast neutrons from the reactor in the wavenumber range 1100–1800 cm^{-1} . (c) FTIR absorption spectra of irradiated (PE) film with fast neutrons from the reactor in the wavenumber range 2500–3600 cm^{-1} .

the contour of the band induced by neutrons was different in its shape than that induced by γ -irradiation as it had a small shoulder in the higher frequency side in the former case.

6. Figure 13 shows the IR spectra of unirradiated and irradiated LDPE films with γ -rays and fast neutrons. A new broad band appeared at about 3420 cm^{-1} , as shown in Figures 12(c) and 13. A similar band was previously detected for γ -irradiated samples. The intensity of this band due to reactor neutron irradiation was found to be equivalent to that produced by a γ -dose of about 169 kGy.
7. The complex contour in the range of 4000–4250 cm^{-1} , which appeared in the case of unirradiated and γ -irradiated PE samples without remarkable change, was found in the case of reactor neutron irradiation to be a smooth and broad band, which has an intensity increasing with the sample thickness. The same behavior was found to oc-

cur in the complex contour at the range of 2635–2664 cm^{-1} . The first three remarks for the appearance of the small band in the range of 750–900 cm^{-1} might reflect the fact that the frequency of the C—H out-of-plane deformation could be affected by the existence of the adjacent five free hydrogen atoms as a result of the irradiation by fast neutrons.¹⁸ A comparative study of the effects of both γ -irradiation and reactor neutron irradiation on the FTIR spectra of PE is summarized in Table I.

FTIR Spectra of EB-Irradiated PE

The IR spectroscopic analysis of PE thin films of different thickness irradiated by various doses of electrons showed no variations in the spectra due to this type of irradiation. Moreover, the energy and the high dose rate of the EB used in this investigation was found to be not enough to produce structural changes resulting in the IR spectra of PE. The difference in behavior between the

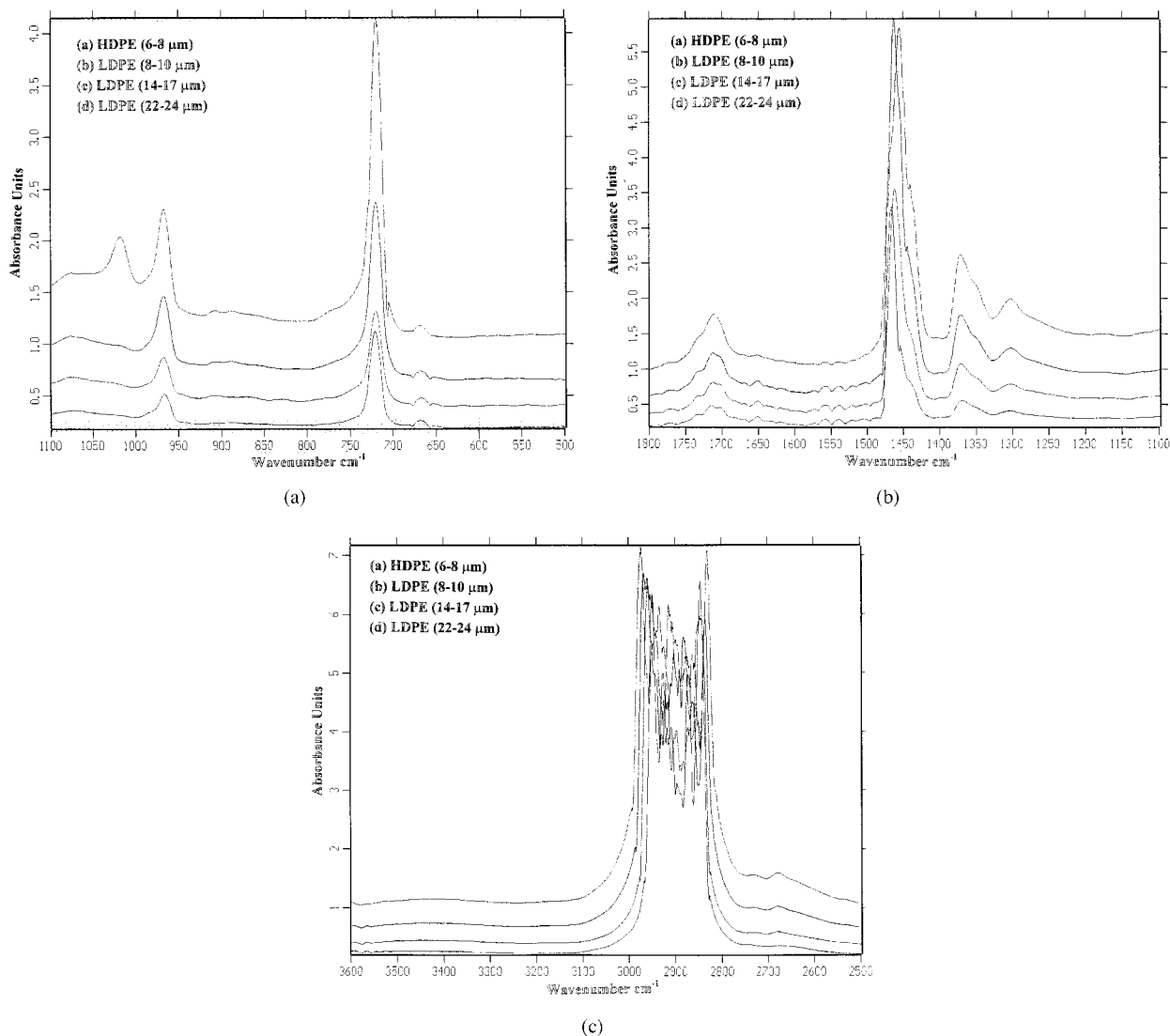


Figure 12 (Continued from the previous page)

two types of radiation (γ -irradiation and EB irradiation) can be correlated by the oxygen diffusion phenomena. At relatively low dose rate (i.e., typical for γ -irradiation), oxygen diffusion is efficient enough to produce structural changes in the IR spectra and disappears if the film is irradiated at a high dose rate (i.e., EB irradiation).²⁰

FT-Raman Analyses of Unirradiated, Gamma- and Neutron-Irradiated PE Thin Films

The FT-Raman spectra of unirradiated PE films of various thicknesses are shown in Figure 14. It is obvious that the only difference between the spectra of various thicknesses is an increase in the intensity of all the Raman bands. Also, no

shifts in the peak positions and no change in the relative intensities between the peaks were observed. The most pronounced Raman bands are given in Table II.

The Raman spectra of LDPE and HDPE were not affected by γ -irradiation compared to the neutron irradiation, as shown in Figure 15. This observation may be attributed to the fact that the source of excitation in the used Raman spectrometer is of a maximum intensity of 500 mW, whereas the intensity falling on the sample is much less than that (300 mW). This variation yields small intensities for most of the Raman active-mode spectra at 1062, 1127, 1294, 1439, 2727, 2847, and 2881 cm^{-1} . The only change occurring in the spectrum because of γ -irradiation

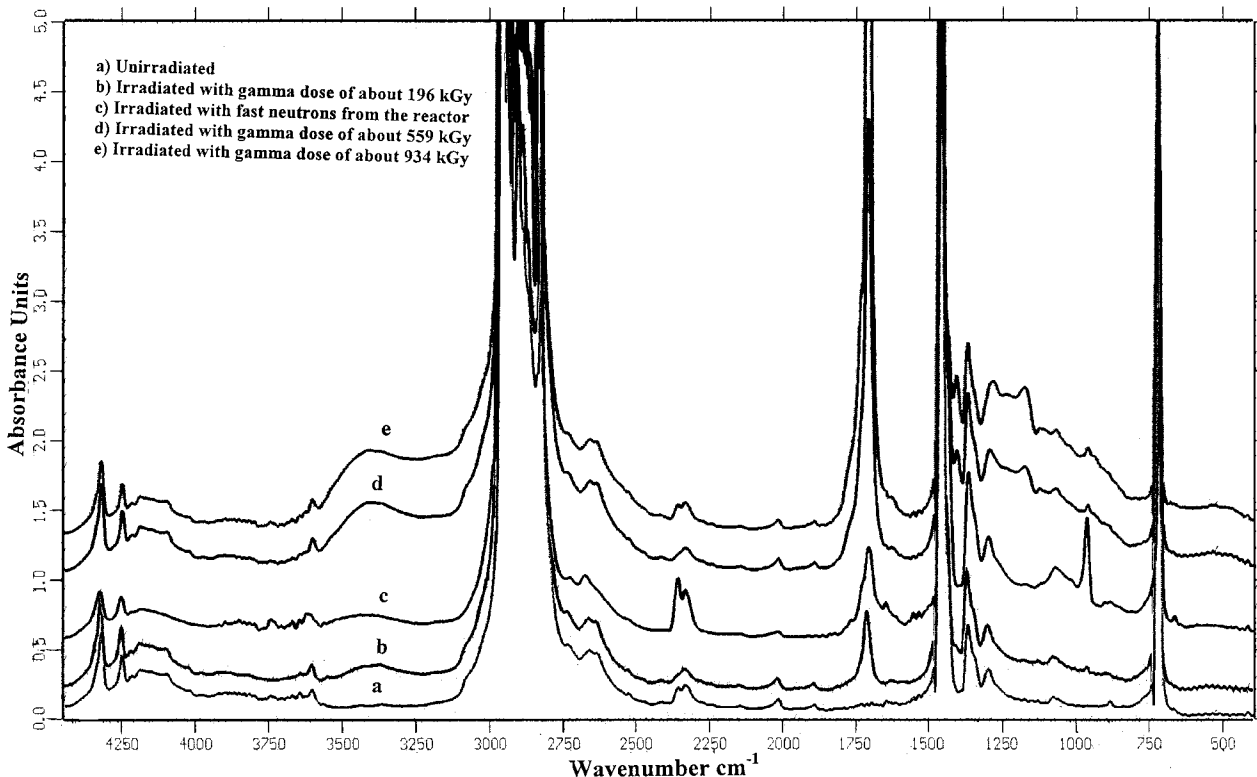


Figure 13 FTIR absorption spectra of unirradiated as well as gamma and fast neutrons irradiated LDPE films (14–17 μm).

is the appearance of the band at 1716 cm^{-1} , which is detected as a very small intensity in the present spectrum. It is believed that better results could be obtained if the system is upgraded by 1.5 W Nd-Yag laser and replacing the present detector by another liquid-nitrogen-cooled one, which will result in an increase in the intensity of the Raman bands by a factor of 15.

The results of the FTIR analysis of PE irradiated by neutrons showed that only the reactor neutrons affect PE, whereas it showed good resistance to thermal neutrons. On the basis of the Raman spectra of γ - and neutron-irradiated films, a few points may be indicated.

1. A small broad band at about 854 cm^{-1} appeared due to neutron irradiation. A similar band in the same region showed up in the IR spectra due to the same sort of irradiation.
2. The two sharp bands at 1062 and 1128 cm^{-1} , which appeared in the unirradiated samples, were found to be changed to one complex broad band and appeared at about 1065 cm^{-1} .

3. A second new band can be seen at about 1655 cm^{-1} due to neutron irradiation, which is thought to be due to $\text{C}=\text{C}$ and may lead to the conclusion that fast neutrons induced the formation of $\nu(\text{C}=\text{C})$, $\text{R}-\text{CH}=\text{CH}_2$ in PE films.¹⁴
4. A remarkable decrease in the absolute intensities of all the bands was observed due to the irradiation with neutrons as shown in Table II in terms of a comparative study between the FT-Raman spectra of unirradiated and fast neutron-irradiated PE films.

UV Absorption Spectra for Unirradiated PE and the Effect of Thickness

Figure 16 shows the UV absorbance spectra within the range 200–400 nm for unirradiated PE films having different thicknesses. It is obvious that the UV absorbance of LDPE film increases as the thickness was increased. For HDPE, although it showed the highest UV absorbance within the wavelength range 250–400 nm, it showed lower UV absorbance within 200–225 nm.

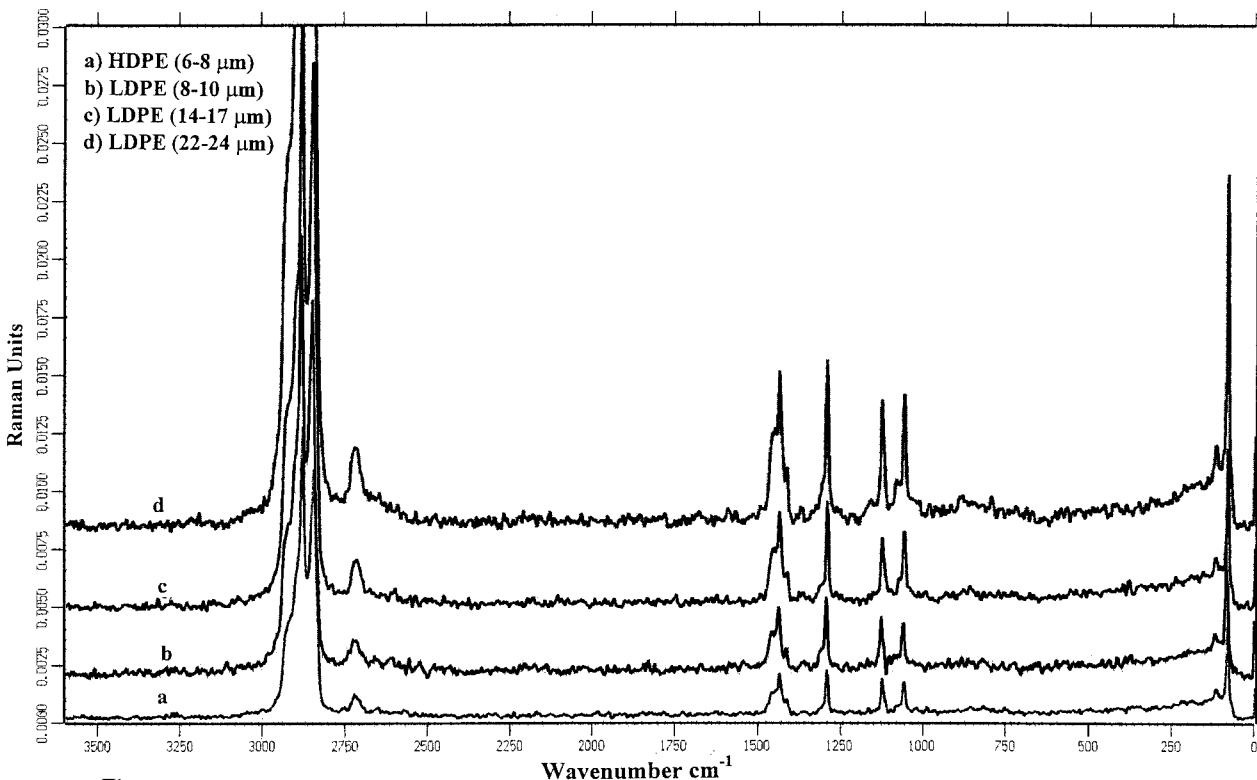


Figure 14 (a) FT-Raman scattered spectra of unirradiated (PE) film in the wavenumber range 1100–1800 cm^{-1} . (b) FT-Raman scattered spectra of unirradiated (PE) film in the wavenumber range 2500–3600 cm^{-1} . (c) FT-Raman scattered spectra of unirradiated (PE) film in the wavenumber range 2500–3100 cm^{-1} . (d) FT-Raman scattered spectra of unirradiated (PE) film in the wavenumber range 3500–4300 cm^{-1} .

UV Absorption Curves for γ -Irradiated PE

Figure 17 shows the variation of the UV absorption spectra of LDPE (8–10 μm) irradiated to various doses of γ -radiation. The exposure of thin PE films to γ -irradiation leads to the appearance of two absorption bands at 220 and 270 nm, as shown in Figure 17. The absorption band at 220 nm is attributed to the presence of the ketonic carbonyl group due to the oxidation of PE on γ -irradiation in air, whereas the other absorption band at 270 nm is indicative for the presence of conjugated double bonds of polyenes.^{14,21,22} It can be seen that not only the optical absorbance increases with increasing γ -irradiation dose increases, but also a slight shift toward high wavelength occurs. Meanwhile, two main absorption peaks at wavelengths 270–280 and 230–235 nm can be observed after irradiation. The values of optical density against absorbed dose for the selected wavelength at 230 nm were plotted as

shown in Figure 18. It is clear that the variation of optical density versus the absorbed dose yields a two-stage linear relationship for all absorbed doses.

The absorbance at 225 nm is thought to be related to the presence of the ketonic carbonyl group.¹⁴ This can be confirmed by the increase of the ketonic carbonyl peak in the corresponding IR spectrum at 1716 cm^{-1} with the γ -dose. On the other hand, the second absorption maximum at 275 nm is indicative to the presence of the conjugated double bonds of polyenes.¹⁴ Also, it can be confirmed by the increase of the C–H out-of-plane deformation of the *trans*-vinylene group which is induced by the γ -irradiation in the IR spectrum at 965 cm^{-1} . Figure 19 shows the variation in the UV absorbance spectra for irradiated PE films (337 kGy) of different thickness. It is obvious that in this figure the variation produced is due to γ -irradiation.

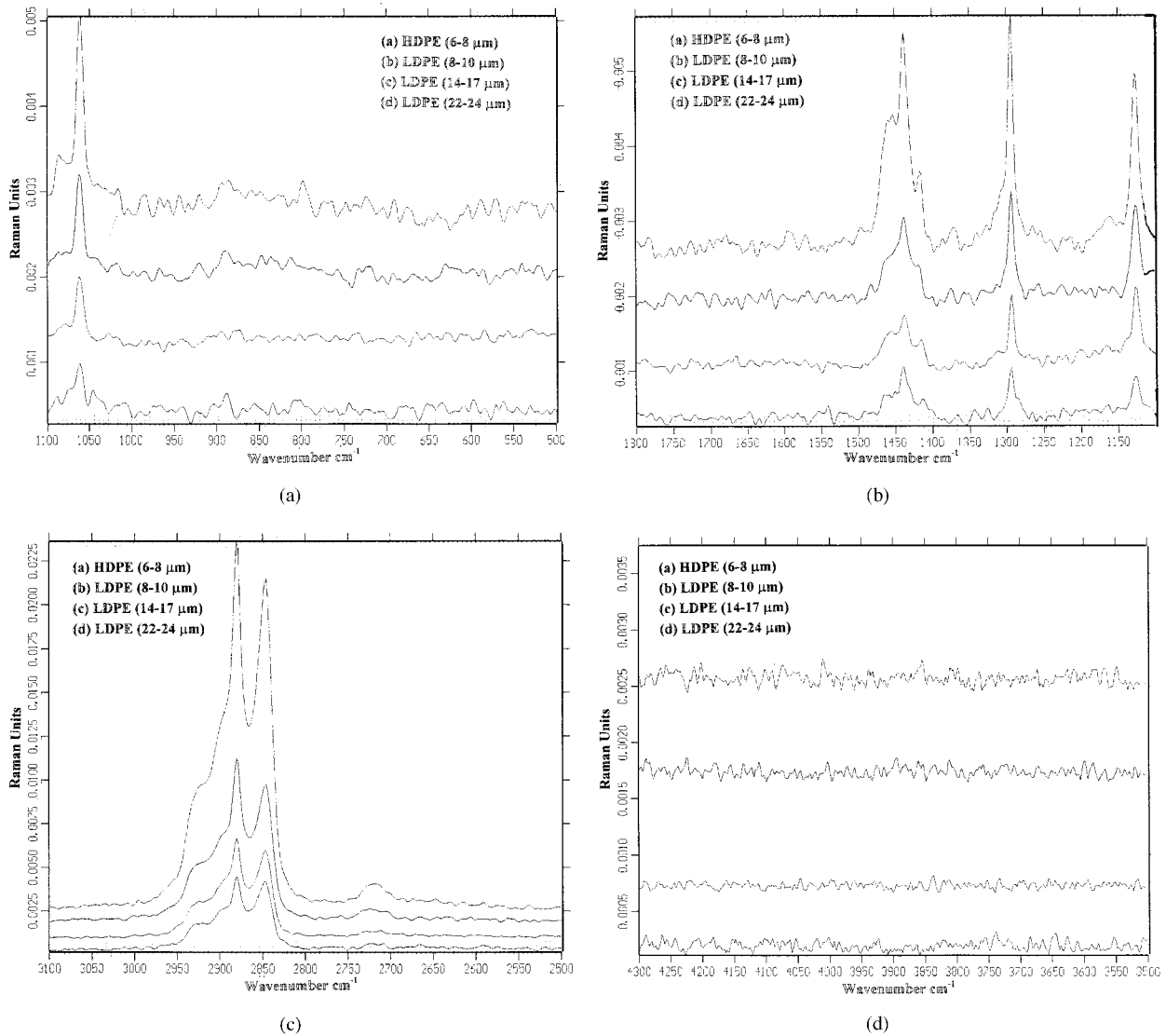


Figure 14 (Continued from the previous page)

UV Absorption Spectra of Irradiated PE Films with Fast Electrons

Thin films of PE of different thicknesses were subjected to EB irradiation, and the UV spectra were shown in Figure 20. From this figure, it is clearly seen that there is only one absorption maximum appearing at 225 nm, which is related to the presence of the ketonic carbonyl group,¹⁴ whereas the maximum due to the conjugate double bond of polyenes {triene(-CH=CH-)₃} at 275 nm cannot be detected. Moreover, for a high thickness of 22–24 μm, a new absorbance maximum appeared at 200 nm. This band may be related to the appearance of a new band in the IR spectra for this thickness.

UV Absorption Spectra of Irradiated PE Films with Fast Neutrons

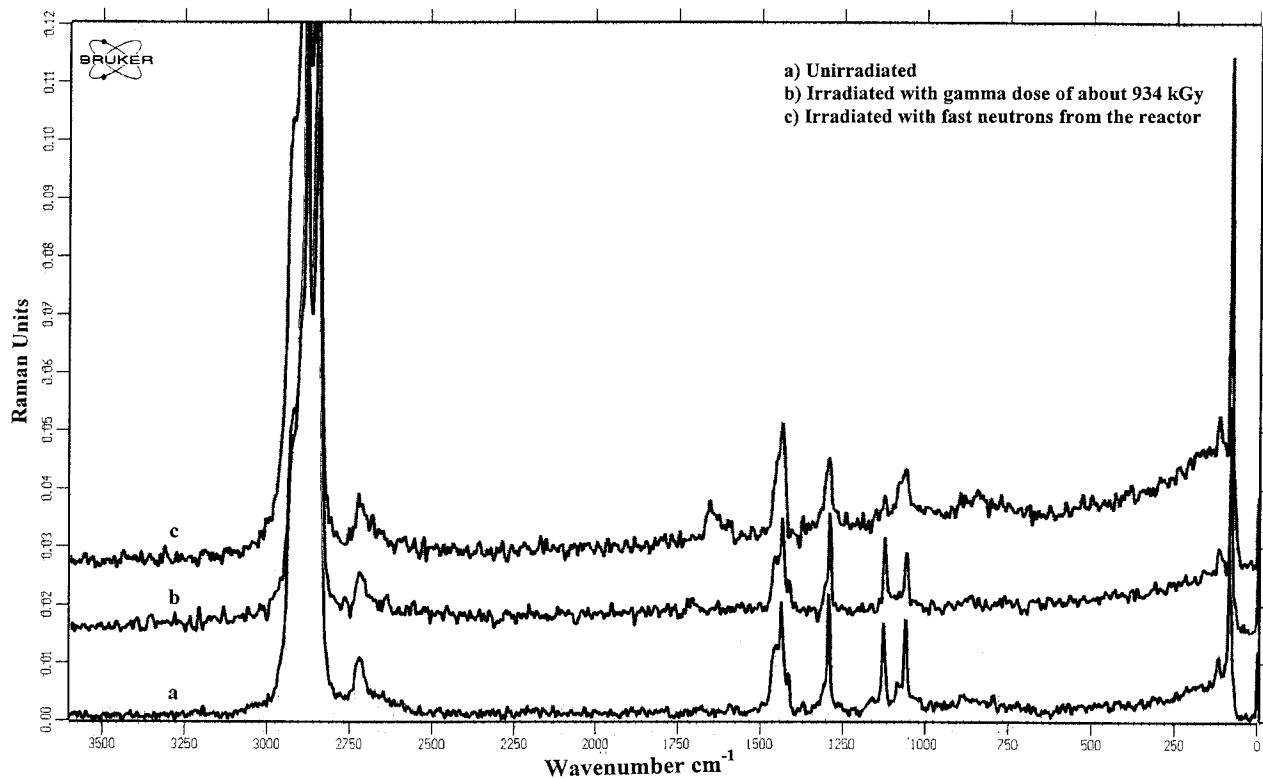
Figure 21 shows the UV optical absorbance for HDPE and LDPE thin films irradiated with fast neutrons in the range of 300–440 nm. It is clear that a new absorption band appeared because of neutron irradiation at about 310 nm. Once again, similar trends to those observed, the curve of HDPE intersects with the curves of LDPE as in Figure 16. Obviously, neutron irradiation produces a more pronounced effect than that of γ -irradiation, either in the increase in the optical absorbance, the observed shift, or the appearance of a new peak > 300 nm. The appearance of the absorption maximum in the UV spectrum at 310

Table II Comparative Study for the FT-Raman Spectra of Unirradiated and γ -Irradiated LDPE (22–24 μm)

Unirradiated PE	γ -Irradiated PE at Maximum Dose	Neutron-Irradiated PE	Assignment
Absent	Absent	854.3	CH_2 out-of-plane deformation
1063	1062	1065	$\nu_a(\text{C—O—C})$
1127	1127	Absent	C—O Stretching vibration
1294	1295	1299	C—C Stretching vibration
1439	1438	1436	$\delta(\text{CH}_2)$, $\delta_a(\text{CH}_3)$
Absent	Absent	Absent	Nonconjugated double bond, R—CH=CH ₂ , $\nu(\text{C=C})$
2727	2723	2714	
2847	2847	2848	(Doublet) Symmetric and asymmetric vibration of the CH_2 group
2881	2881	2883	

nm is attributed to the tetraene, which is related to the conjugated double bond given by $(-\text{CH}=\text{CH}-)_4$.¹⁶ The band at 310 nm is related to the oxidative effects accompanying the neutron irradiation in which the diene group was converted to some structures that do not absorb the

UV in the 270–290 nm range.²¹ In addition, on irradiation by fast neutrons, a significant increase in the optical absorption was observed which resulted in an increase in the wavelengths range of 200–300 nm, which makes it out of the range of the system used.

**Figure 15** FT-Raman scattered spectra of unirradiated as well as γ and fast neutrons irradiated LDPE films (22–24 μm).

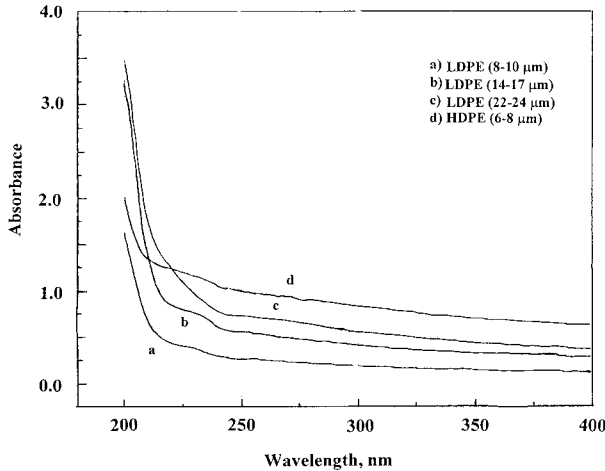


Figure 16 UV absorption spectra of unirradiated (PE) film with different thickness.

CONCLUSIONS

The main conclusions of the present work can be summarized as follows.

1. The IR spectra studied for LDPE and HDPE covered all the possible vibrational bands that arose because most functional groups are in good agreement with literature.
2. The intensity of the IR absorption bands of PE was found to increase as the thickness increases. Moreover, it was able to detect a

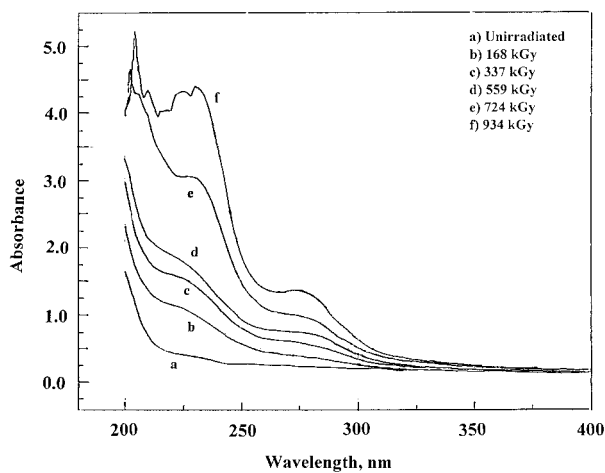


Figure 17 The UV absorption spectra for irradiated LDPE films of thickness (8–10 μm) in the range 200–400 nm. (a) unirradiated, (b) 168 kGy, (c) 337 kGy, (d) 559 kGy, (e) 724 kGy, (f) 934 kGy.

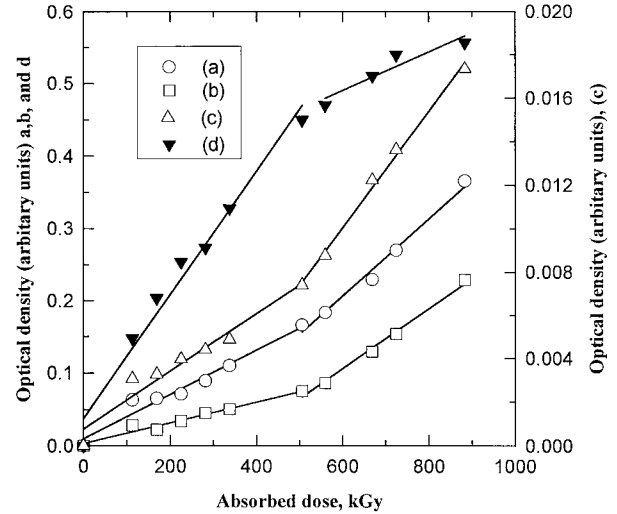


Figure 18 Variation in the optical density at 230 nm of LDPE (8–10, 14–17, and 22–24 μm) and HDPE (6–8 μm) films.

vibrational band at 1017 cm^{-1} with PE films having the largest thickness. This band was not detected before for PE and is recorded in the present work for the first time. The appearance of this band is related somehow to the oxidative effects due to oxygen included in PE and not residual environmental oxygen. In addition, the PE film with a large thickness requires higher temperature and pressure during processing. Moreover, the appearance of new

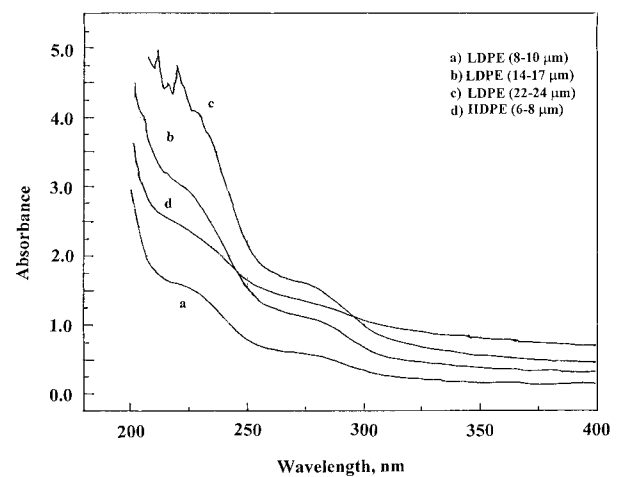


Figure 19 The UV absorption spectra of irradiated (337 kGy) PE films of different thicknesses. (a) LDPE (8–10 μm), (b) LDPE (14–17 μm), (c) LDPE (22–24 μm), (d) HDPE (6–8 μm).

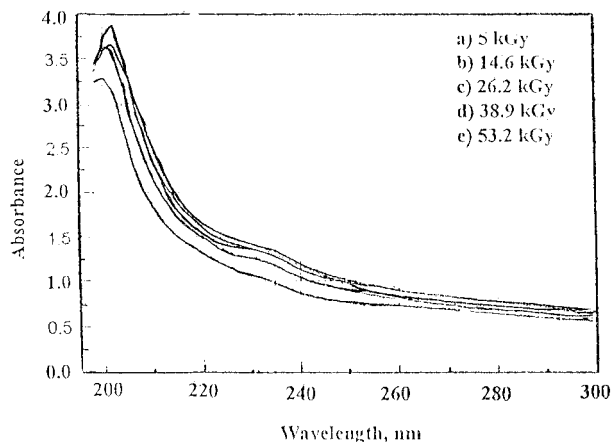


Figure 20 UV absorption spectra of electron beam irradiated LDPE (22–24 μm) films with absorbed doses from 5.0 up to 53.0 kGy.

modes with large thicknesses could be related to the increase of crystallinity and the order of the molecular segments.

3. The quantitative analysis carried out to illustrate the dependence of the IR band parameters $\{I(\nu), \nu, \Delta\nu\}$ on the γ -irradiation dose showed a good linear dependence of the intensity of absorption bands on the γ -dose, which suggests the possible use of PE thin films as a simple and cheap dosimeter over a wide range of doses (0–1 MGy). The dependence of the other parameters ($\nu, \Delta\nu$) showed a two-stage linear dependence on γ -doses, gives support to the assumption that there are mainly two mechanisms due to γ -irradiation. These mechanisms are the degradation that is thought to be predominant within the low dose levels (up to about 300 kGy) and crosslinking that could be predominant at high doses > 500 kGy. The kink between the two stages of the dependence of the band parameters on γ -doses was found to lie in the interval (300–500 kGy) for most of the analyzed absorption bands. Suitable interpretation was given for most of the changes caused by gamma irradiation.
4. Similar FTIR analysis was carried out for the effect of different types of radiation such as thermal and fast reactor neutrons, in addition to the abovementioned γ -irradiation. It was shown that PE thin films possess good resistance to thermal and fast reactor neutrons and are slightly affected by EB irradiation. Moreover, some bands

appeared only after irradiation with fast neutrons (e.g., at 967 cm^{-1}). This band is attributed to be due to C—H out-of-plane deformation of *trans*-vinylene groups affected by five free hydrogen atoms.

5. A detailed analysis for the effects of different radiation on PE thin films was carried out by using the FT-Raman spectroscopy. The obtained data showed almost the same effects obtained by FTIR spectroscopy. This similarity reflects the fact that the observed changes using the two techniques may have the same origin.
6. The quantitative analyses using UV spectrophotometry showed the same two-stage linear dependence of the parameters in good agreement with FTIR spectra band parameters. Once again, this reflects the fact that the structural changes observed experimentally using different techniques have the same origin. Finally, the properties of polymeric materials are highly affected by irradiation and can be useful for obtaining PE films with the desirable properties using the suitable types of irradiation. The changes occurring because of irradiation are certainly related to the sensitivity of PE films to any changes (either structural or even reorientation) in the molecules, molecular segments, and functional groups.

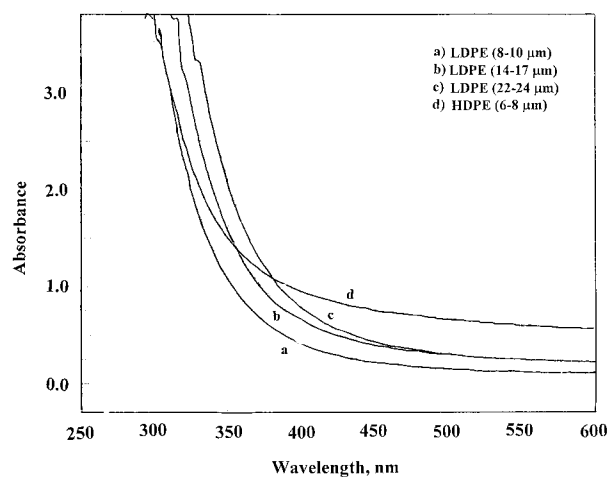


Figure 21 UV absorption spectra of fast neutron irradiated LDPE and HDPE films. (a) LDPE (8–10 μm), (b) LDPE (14–17 μm), (c) LDPE (22–24 μm), (d) HDPE (6–8 μm).

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