

Physicochemical Properties of Irradiated and Loaded LDPE Films with Polyfunctional Monomers

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ABSTRACT: Polyfunctional monomers (PFMs), namely, trimethylol propane trimethacrylate (TMPTMA), trimethylol propane triacrylate, ethylene glycol dimethacrylate, and diethylene glycol diacrylate were blended with low-density polyethylene (LDPE) and exposed to different doses of EB irradiation. Fourier transform infrared and ultraviolet and UV-vis spectroscopy of the unirradiated, irradiated, unloaded, and PFMs-loaded LDPE films were studied under various irradiation doses up to 300 kGy. The degree of crosslinking and oxidative degradation, as measured by the spectroscopic parameters, were dependent on both the irradiation dose and the type of loaded PFMs. For all of the loaded monomers, the extent of crosslinking increased at different rates as a function of irradiation dose. TMPTMA

monomer was the most efficient in enhancing the crosslinking of LDPE films compared to the other loaded monomers. However, the unloaded LDPE film showed the least extent of crosslinking. In addition, the EB-radiation-induced changes, such as *trans*-vinylene formation, a decrease in vinyl and vinylidene unsaturation; and carbonyl double-bond formation and change in crystallinity were correlated. The importance of these results on the prediction of the role of polyfunctional monomers in the production of crosslinked polymers is discussed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2025–2035, 2003

Key words: polyfunctional monomers; low density polyethylene; electron beam irradiation; FTIR; UV-vis spectroscopy

INTRODUCTION

The radiation modification of polymers refers to the production of beneficial changes by exposure to radiation. High-energy ionizing radiation is used most often to modify polymers because the high molecular mass of these materials means that comparatively low radiation doses can be produce significant changes in their physical and chemical properties. The more important physical and chemical changes that irradiation brings about in polymers (e.g., polyethylene) are crosslinking in the absence of air; oxidation in the presence of air or oxygen; degradation; formation of gaseous products such as H₂, CH₄, and CO; and changes in unsaturation (the formation of various types of double bonds).^{1–4}

The susceptibility of different polymeric materials to radiation crosslinking depends mainly on their chemical structure, irradiation dose, dose rate, and environmental conditions such as irradiation temperature and the absence or presence of air or oxygen. One can achieve production of a highly crosslinked network at a lower irradiation dose to prevent damage of the polymeric chain by loading the polymer with different types of polyfunctional monomers (PFMs).⁵ Among these PFMs, trimethylol propane trimethacrylate (TMPTMA), trimethylol propane triacrylate (TMPTA), ethylene glycol dimethacrylate, (EGDMA), and diethylene glycol diacrylate (DEGDA) (see Table I) enhance the crosslinking process, mechanical and thermal properties, volume shrinkage, and other physical properties at relatively low irradiation doses.^{6–8}

The main goal of this study was to examine the radiation-induced physical and chemical changes that occurred in LDPE films loaded with different PFMs with Fourier transform infrared (FTIR) and ultraviolet-visible (UV-VIS) spectroscopic techniques.

EXPERIMENTAL

Materials

Low-density polyethylene (LDPE)

LDPE pellets were produced by the CDF Co. (Lotrene, France). and supplied by EI Sewedy Co. for the plastic industry (Sedplast, 10th Ramadan City, Cairo, Egypt). The density of the LDPE was about 0.935 g/cm³, the melt flow index was about 3.5 g/10 min, and the crystallinity ratio was about 45%.

Techniques

Sample preparation

An accurate weight of LDPE pellets was mixed in a laboratory plasticorder mixer (Plasticorder PL 2100, Germany). The mixing process was carried out at

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TABLE I
PFMs (Crosslinking Coagents)

Trade name	Scientific name	Chemical Structure	Suppliers
TMPTMA	Trimethylol propane Trimetha crylate	$\text{CH}_3\text{—CH}_2\text{—C—(R)}_3$, where $\text{R} = [\text{—CH}_2\text{—O—C(O)—C—(CH}_3\text{)=CH}_2]$ Molecular weight = 338	Shin-Nakamura Chemical Co, Ltd. Japan
TMPTA	Trimethylol propane triacrylate	$\text{CH}_3\text{—CH}_2\text{—C—(R)}_3$, where $\text{R} = \{ \text{—CH}_2\text{—O—C(O)—CH=CH}_2 \}$ Molecular weight = 296	Shin-Nakamura Chemical Co.
EGDMA	Ethylene glycol dimethacrylate	$\text{CH}_2\text{=C(CH}_3\text{)—O—C(O)—(CH}_2\text{)—O—C(O)—C(CH}_3\text{)=CH}_2$ Molecular weight = 184	Musahi no Chemical Institute Co., Ltd., Japan
DEGDA	Diethylene glycol diacrylate	$\text{CH}_2\text{=CH—O—C(O)—(CH}_2\text{)}_2\text{—O—C(O)—CH=CH}_2$ Molecular weight = 170	Shin-Nakamura Chemical Co.

115°C at a mixing rate of 60 rpm for 5 min. Thereafter, the polyfunctional monomer (5 phr) was added gradually to the molten LDPE. The mixture was immediately transferred from the mixer to an open roll-mill sheet. The polymer sheet was then pressed under a hot press at 160°C for 5 min (2 min preheating and 3 min at 15 MPa) to obtain a rectangular sheet 0.70–0.75 mm in thickness. The molded sheet was then immediately transferred to a water-cooled press at the same pressure.

Irradiation process

EB irradiation was carried out in the atmosphere at ambient temperature with a 1.5-MeV, 25-mA, and 37.5-kW electron beam accelerator. All specimens were irradiated on one side with a current of 1.0 mA such that the specimens were exposed to about 10 kGy on each pass. Several passes under these conditions were required for high doses. The irradiation doses ranged from 50 to 300 kGy.

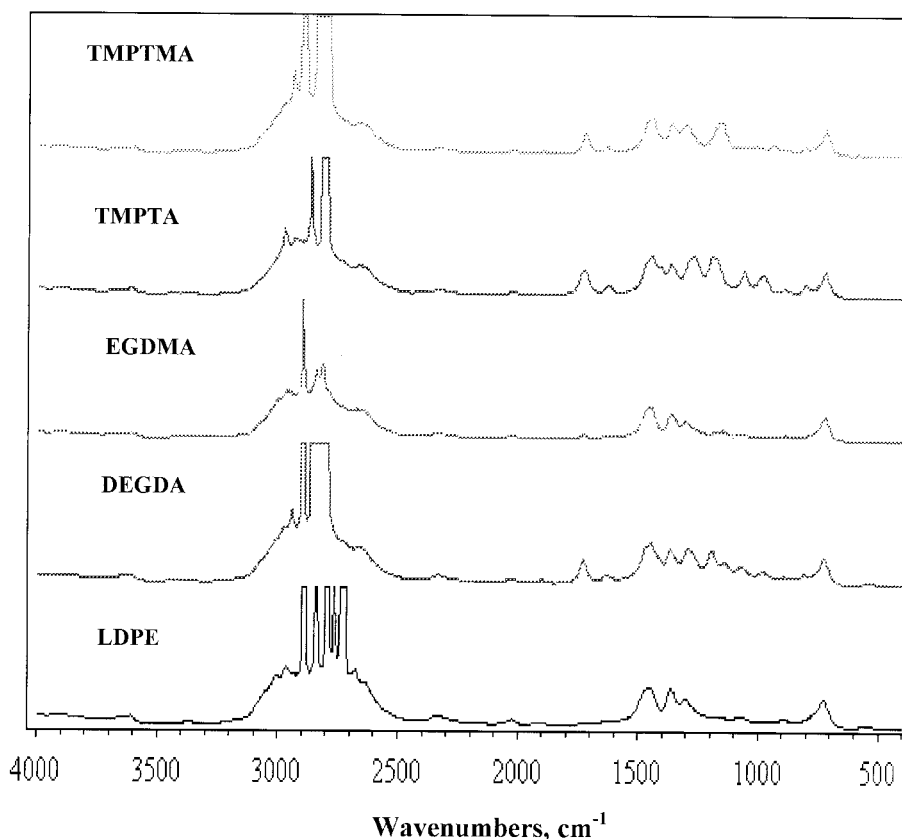


Figure 1 FTIR absorption spectra of unirradiated unloaded LDPE samples and LDPE samples loaded with different monomers.

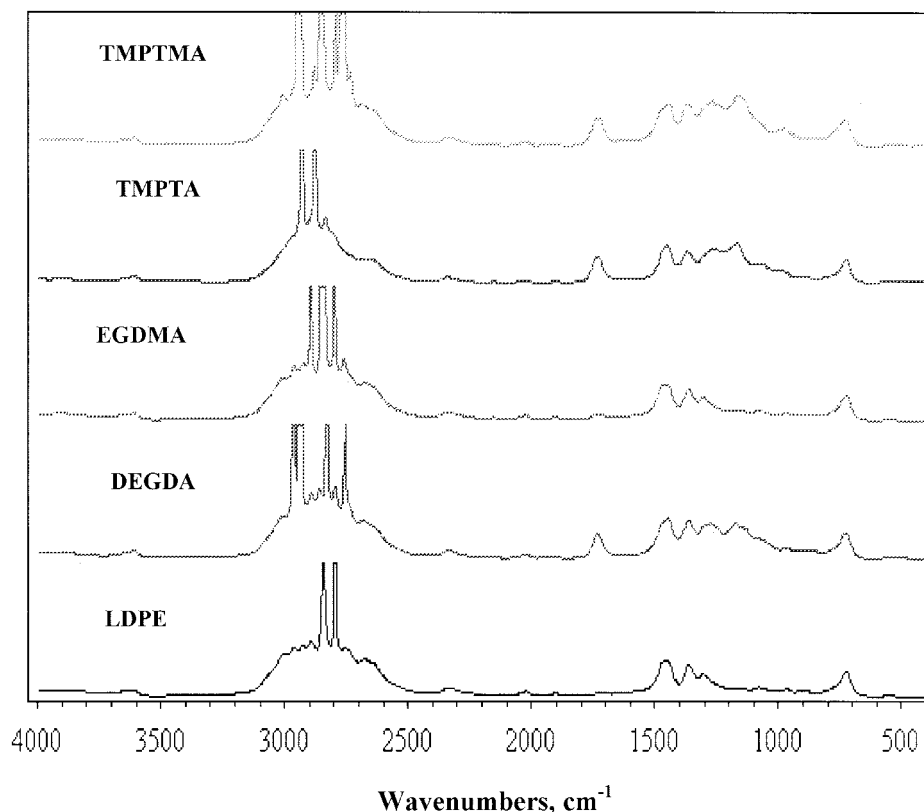


Figure 2 FTIR absorption spectra of irradiated (300 kGy) unloaded LDPE samples and LDPE loaded with different monomers.

Spectroscopic analysis

FTIR

An ATI Mattson (Genesis series, Unicam, England) FTIR spectrometer was used to scan and measure the absorption spectra at a resolution of 4 cm^{-1} . High signal-to-noise spectra were obtained by the collection of 100 scans for each sample. The resultant digitized spectra were stored for further data processing. For quantitative analysis, the resolution was at 16 cm^{-1} to improve quantitative accuracy. The spectra of unirradiated and irradiated samples were measured before and directly after irradiation with a designed sample holder $2 \times 2\text{ cm}$ in dimension. From the spectra and the obtained data, the changes in absorbance (peak intensity) at the characteristic peak wavenumber (cm^{-1}) were recorded.

UV-vis spectroscopy

A UV2 double-beam Unicam UV-vis spectrometer was used to scan the absorption spectra in the wavelength range 190–400 nm and to measure the optical density at λ_{max} for the unirradiated and irradiated samples. The unirradiated and irradiated samples were cut into $1 \times 1\text{-cm}$ pieces that were suitable for the holder designed specially for reproducible fitting into

the beam of the spectrometer. Also, the irradiated samples were measured before and directly after irradiation.

RESULTS AND DISCUSSION

The irradiation of polymeric materials, especially LDPE films, induce the following physical and chemical changes.^{3,4,9}

- The production of hydrogen gas and gaseous low-molecular-weight hydrocarbons.
- Oxidation, mostly on or near the surface of the film, which finally leads, to chain degradation at higher doses.
- Changes in the vinyl, vinylene, and vinylidene unsaturated double-bond extent.
- The formation of crosslinks, that is, the formation of an insoluble gel.
- Changes in the degree of crystallinity and other physical properties.

The incorporation of PFMs (crosslinking agents), such as DEGDA, EGDMA, TMPTA, and TMPTMA, into the LDPE samples enhanced the physical and chemical properties on irradiation. So, FTIR was used to elucidate the changes that occurred in the unloaded and

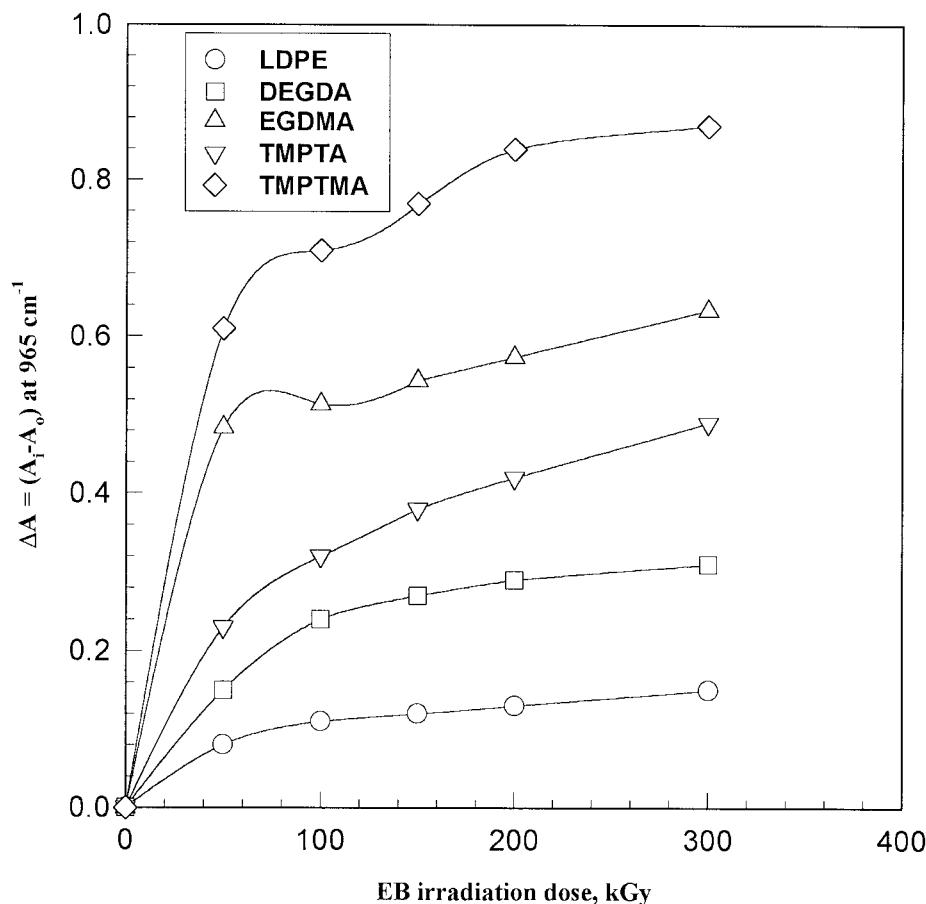


Figure 3 Variation of the absorption intensity [$\Delta A = (A_i - A_0)$] of the IR peak at about 965 cm^{-1} for unloaded LDPE samples and LDPE samples loaded with different monomers as a function of EB irradiation dose.

loaded samples with monomer and in the unirradiated and irradiated LDPE films. This elucidation was emphasized throughout the determination of the IR absorption intensity for the characteristic peaks. The most interesting characteristic peaks were *trans*-vinylene ($-\text{HC}=\text{CH}-$) double bonds at about 965 cm^{-1} vinyl and vinylidene double bonds at 1640 and 890 cm^{-1} , C=O vibrations in the range $1735\text{--}1700 \text{ cm}^{-1}$, OH groups in the range $3300\text{--}3500 \text{ cm}^{-1}$, methylene deformation influenced by an adjacent C=O group at about 1410 cm^{-1} , and finally amorphous and crystallinity ratio at about 1300 and 1900 cm^{-1} .^{5,10-12}

IR absorption spectra of unloaded and PFM-loaded LDPE films

Figure 1 shows the IR spectra ($400\text{--}4000 \text{ cm}^{-1}$) of unirradiated unloaded and loaded LDPE films with different monomers (DEGDA, EGDMA, TMPTA, and TMPTMA). There were several peaks at nearly 942 , 1161 , 1640 , and 1724 cm^{-1} , which appeared only in the PFM-loaded LDPE samples. These peaks were characterized to the C=C and C=O groups present in the loaded PFMs monomers, and the intensity of these peaks depended on the type of loaded monomer. The

IR spectra of the irradiated (300 kGy) unloaded and loaded LDPE samples are presented in Figure 2. The characteristic peaks for the C=C double bonds first decreased and then disappeared due to irradiation, whereas the characteristic one for the C=O group still appeared. The intensity of the latter peak was of higher value compared to the unirradiated samples, as shown in Figure 1.

The change in IR spectra of unloaded LDPE and that irradiated at various doses was insignificant. This was due to the low EB irradiation dose, highly dosed rate, and absence of crosslinking agents (PFMs). However, the change in IR spectra of the loaded and irradiated samples ($0\text{--}300 \text{ kGy}$) was more pronounced and is clarified throughout the following discussion.

Double-bond formation to-*yield trans*-vinylene ($-\text{HC}=\text{CH}-$)

The formation of unsaturated double bonds is closely related to radiation-induced hydrogen gas evolution. Hydrogen gas evolution can occur only if, for each molecule of hydrogen gas liberated, the formation of one double bond or one interchain or intrachain crosslinks occur. In other words, the liberation of hy-

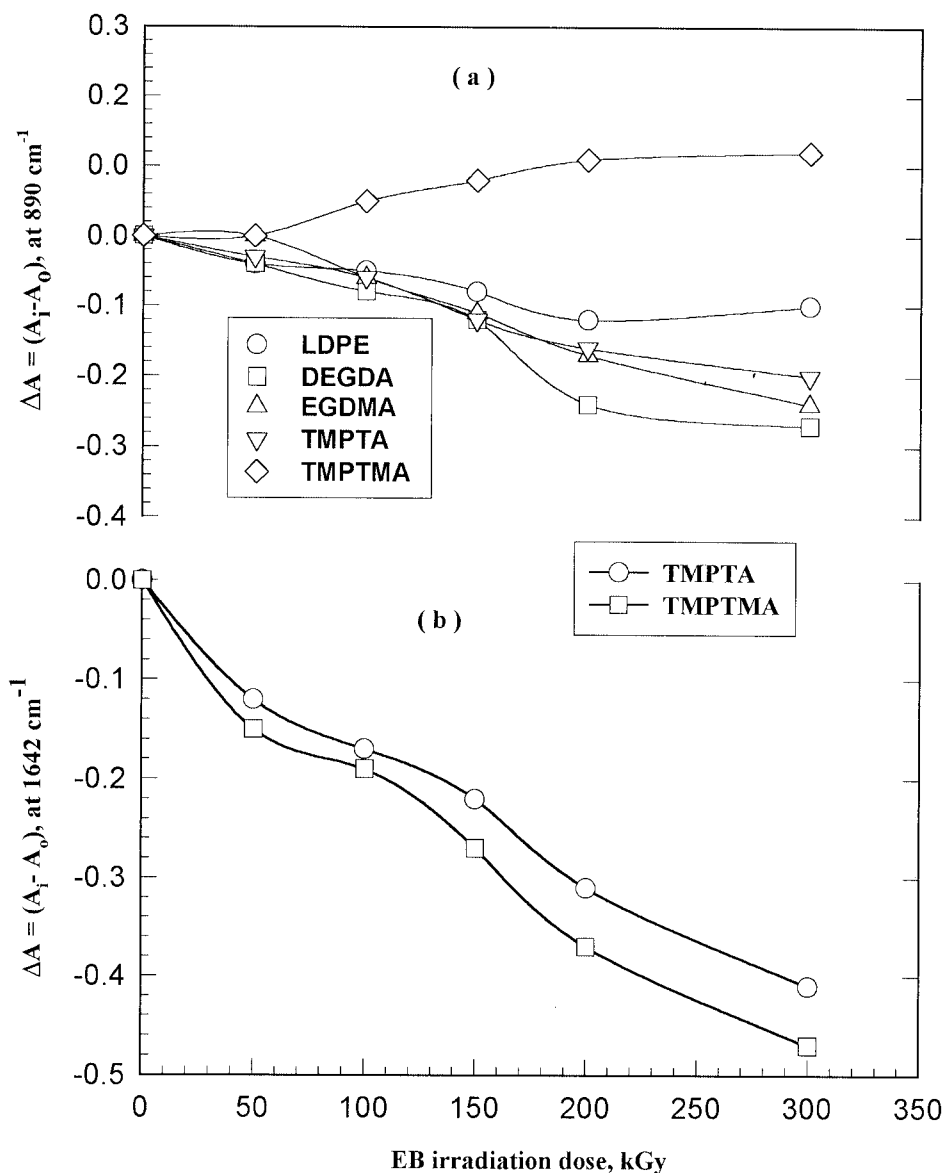


Figure 4 Variation of the absorption intensity [$\Delta A = (A_i - A_0)$] of the IR peaks at about 890 and 1642 cm^{-1} for unloaded LDPE samples and LDPE samples loaded with different monomers as a function of EB irradiation dose.

drogen gas consequently leads to the formation of crosslinks. In addition, this phenomena yields *trans*-vinylene ($-\text{HC}=\text{CH}-$) double bonds, conjugated diene, and higher polyenes. Hence, the pronounced absorption peak of the *trans*-vinylene unsaturated double bond at about 965 cm^{-1} , determined by the IR data, was used in the estimation of crosslinking degree.^{2,3,11,12}

Figure 3 shows the change in the IR absorption intensity [$\Delta A = (A_i - A_0)$], where A_i and A_0 are the intensities after and before irradiation) at 965 cm^{-1} as a function of EB irradiation dose for unloaded LDPE and LDPE loaded with PFM monomers. Clearly, the intensity of the *trans*-vinylene unsaturated double bond at 965 cm^{-1} gradually increased with increasing irradiation dose. Also, the highest increase in the peak

intensity appeared for LDPE samples loaded with TMPTMA monomer. In addition, the unloaded LDPE sample showed the lowest increase in the absorbance of this peak. The order of crosslinking increase in the PFM-loaded samples was as follows:

TMPTMA > EGDMA > TMPTA
> DEGDA > Unloaded LDPE

The obtained results indicate that the extent of radiation-induced crosslinking of LDPE samples, as measured by the increase of the IR absorption peak at 965 cm^{-1} , increased with increasing irradiation dose beside the presence of crosslinking agent. This means that the degree of crosslinking was dependent on both

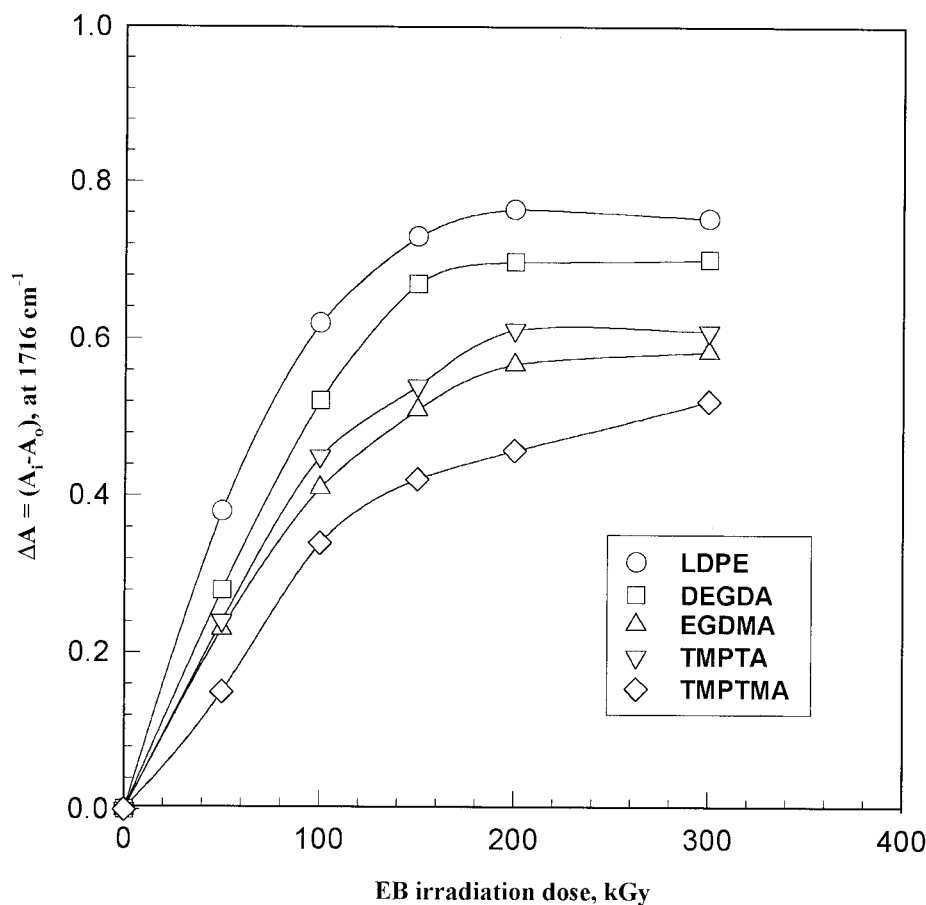


Figure 5 Variation of the absorption intensity [$\Delta A = (A_i - A_0)$] of the IR peak at about 1716 cm^{-1} for unloaded LDPE samples and LDPE samples loaded with different monomers as a function of EB irradiation dose.

irradiation dose and type of loaded PFM (i.e., number of functional group and induced steric hindrance). Monomers are classified by their functionality and chemical structure; for example, methacrylate and monomers with higher double bonds exhibit higher crosslinking densities than do acrylate and monomers with fewer double bonds. In addition, the added methyl group of methacrylates introduces a somewhat stiffer chain compared to acrylates. The chain stiffness results in a higher crosslinking density.^{5,7} This investigation showed that the TMPTMA monomer was the most efficient in crosslinking the of the LDPE sample compared to the other loaded monomers.

Vinyl and vinylidene unsaturated double-bond changes

One of the most notable aspects of the high-energy irradiation of LDPE the initial rapid disappearance of vinyl and vinylidene olefinic groups, consistent with the production of vinylene unsaturation.² The radiolytic decay of the vinylidene double bond in LDPE was measured by the IR technique, with the absorption band at 890 cm^{-1} , as a measure of the vinylidene concentration.³ In addition, the initial amount of un-

saturated double bonds present in the loaded monomers was expected to decrease rapidly throughout the crosslinking reaction in the early stages of irradiation. The destruction of the initially present unsaturation was ascribed to the reaction of H atoms liberated by irradiation, with the unsaturated functional groups acting as scavengers.^{5,10,12}

The IR characteristic peaks for vinylidene and vinyl unsaturated double bonds were assigned at frequencies near 890 and 1640 cm^{-1} , respectively. Figure 4 illustrates the decrease in the vinyl unsaturated double bonds (as measured by the intensity of IR peak at 890 cm^{-1}) with increasing irradiation dose. However, for the TMPTMA-loaded LDPE sample, there was a slight increase with increasing irradiation dose, and the extent of the increased levelled off at a higher dose. Figure 4(b) shows the decrease in the intensity of the absorption peak for TMPTA- and TMPTMA-loaded LDPE samples at 1640 cm^{-1} , which was assigned to the vinyl unsaturated double bond. The intensity of this characteristic IR peak gradually decreased with increasing irradiation dose. The rate of the decrease for the TMPTMA-loaded sample was higher than that with the TMPTA monomer. However, the IR spectra

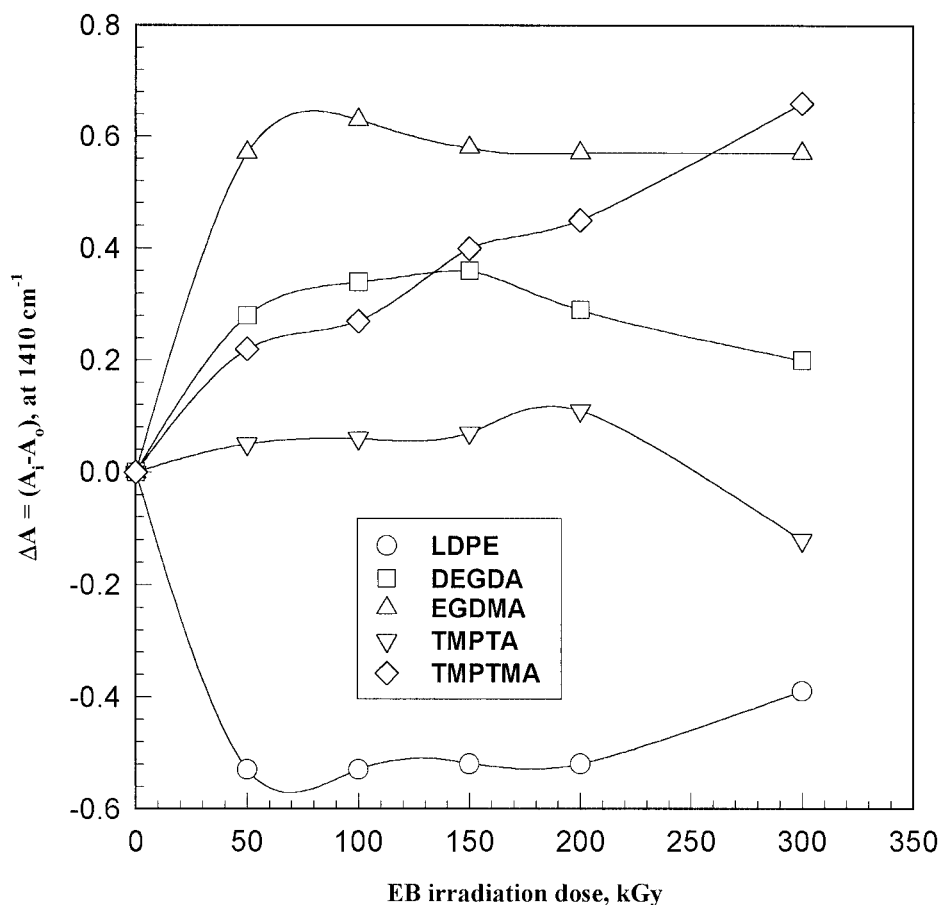


Figure 6 Variation of the absorption intensity [$\Delta A = (A_i - A_0)$] of the IR peak at about 1410 cm^{-1} for unloaded LDPE samples and LDPE samples loaded with different monomers as a function of EB irradiation dose.

at this characteristic peak corresponding to unloaded and loaded samples with the EGDMA and DEGDA monomers completely disappeared on irradiation. This rapid decrease or the disappearance in the IR intensity indicated that the monomer molecules completely participated in the crosslinking of LDPE during irradiation.

Formation of carbonyl double bonds and hydroxyl groups

The radiation-induced oxidation of LDPE was dependent on the irradiation dose, dose rate, absence or presence of air or oxygen, temperature during irradiation, and environmental conditions. At a lower irradiation dose, the oxidation reaction predominated, where all primary radicals formed in the amorphous regions reacted preferentially with oxygen and initiated a chain process whose main consequences were carbonyl formation and chain scission.¹³

However, at a higher irradiation dose, the extent of the oxidative reaction became less pronounced where the crosslinking reaction began to appear, and then it predominated.¹⁴ In addition, the presence of loaded

PFMs in the LDPE sample played an important role in enhancing the degree of crosslinking at higher doses.

The oxidative reaction in LDPE loaded with PFMs during EB irradiation was estimated with quantitative IR measured at a characteristic peak ($1700\text{--}1735 \text{ cm}^{-1}$). Figure 5 clearly shows the effect of the EB irradiation dose on the oxidation of LDPE loaded with PFMs. As shown in this figure, the oxidation reaction predominated and increased with increasing irradiation dose up to about 100 kGy (i.e., at the early stage of irradiation); after that, the level of oxidation levelled off at higher doses (150–300 kGy). For LDPE sample loaded with DEGDA monomer, the extent of oxidation was more pronounced compared with the other loaded monomers. The order of oxidation extent at any irradiation dose was as follows:

Unloaded LDPE > DEGDA > TMPTA
> EGDMA > TMPTMA

This obtained result indicated why the TMPTMA monomer appeared to be the best at enhancing the extent of crosslinking in the LDPE sample.

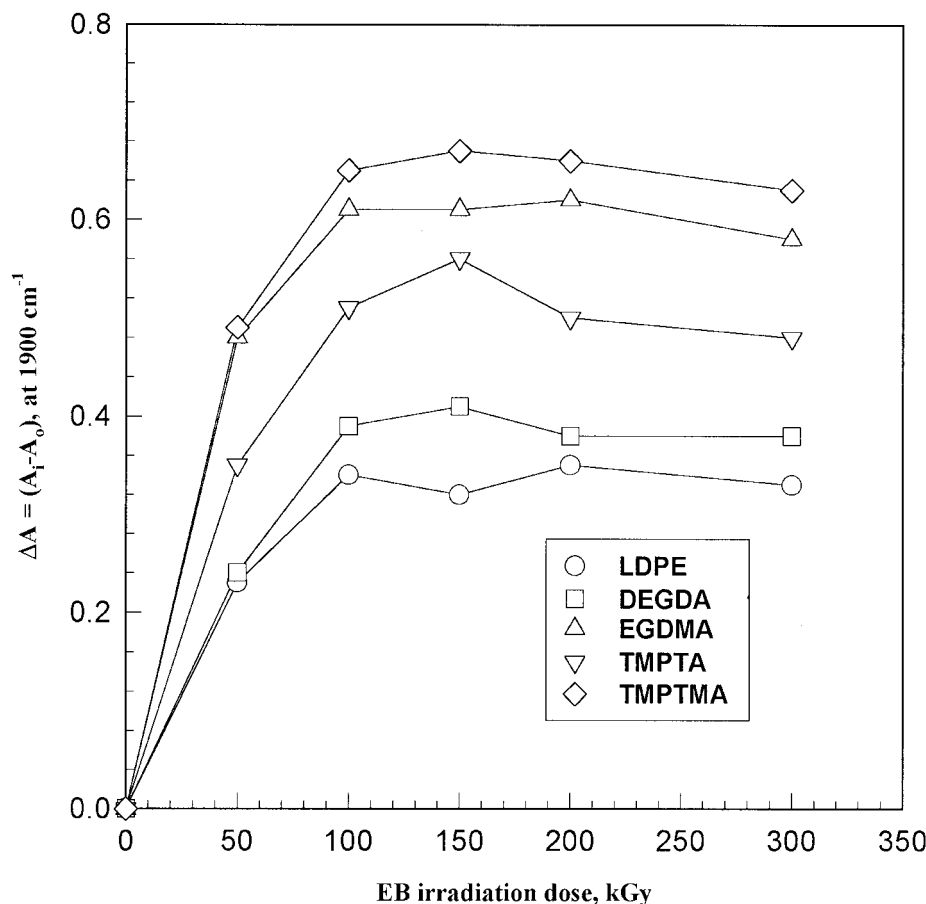


Figure 7 Variation of the absorption intensity [$\Delta A = (A_i - A_0)$] of the IR peak at about 1900 cm^{-1} for unloaded LDPE samples and LDPE samples loaded with different monomers as a function of EB irradiation dose.

Radiation-induced methylene deformation

Figure 6 shows the change in the IR absorption intensity measured at 1410 cm^{-1} (assigned to methylene deformation influenced by an adjacent C=O group) with increasing EB irradiation dose for unloaded LDPE and LDPE loaded with PFMs. The intensity of this peak slightly increased up to 100 kGy for the LDPE samples loaded with EGDMA, DEGDA, and TMPTA monomers, and then, it decreased as the irradiation dose was increased. Also, the IR intensity for LDPE loaded with the TMPTMA monomer gradually increased with increasing irradiation dose. However, the unloaded LDPE sample showed the opposite behavior, where the intensity of this peak sharply decreased at 50 kGy, then displayed a saturated region from 50 to 200 kGy, and after increased up to 300 kGy.

Changes in crystallinity

The crystallinity of several types of polymers (semicrystalline crosslinked polyolefins) depend on irradiation dose, temperature, and some competing processes, those are, the formation of double bonds and

crosslinking in the amorphous regions or the destruction of crystalline regions.¹³⁻¹⁶ Crosslinking occurs mainly in the amorphous regions of the polymer, as macromolecules in the amorphous regions of the polymer are interwoven, which is favorable to crosslinking. In the crystalline regions, radiation-induced free radicals become localized near the surface of the crystallites, and crosslinks are formed at these sites. With polyethylene, crosslinking occurs throughout the amorphous regions of the polymer and predominantly on the surface of the crystallites present.^{3,16} However, crystal destruction predominates at high doses ($> 1 \text{ MGy}$), which creates a structure defect responsible for the decrease in crystallinity.¹⁷

The change in crystallinity of the unloaded LDPE and LDPE loaded with PFMs, as measured by the intensity of IR absorption at 1900 cm^{-1} , is shown in Figure 7. As the EB irradiation dose increased, the crystallinity increased gradually up to 150 kGy, beyond which the degree of crystallinity levelled off. The increase in the degree of crystallinity was correlated to the preferential crosslinking of the amorphous regions to the crystalline regions as a result of irradiation.¹⁸

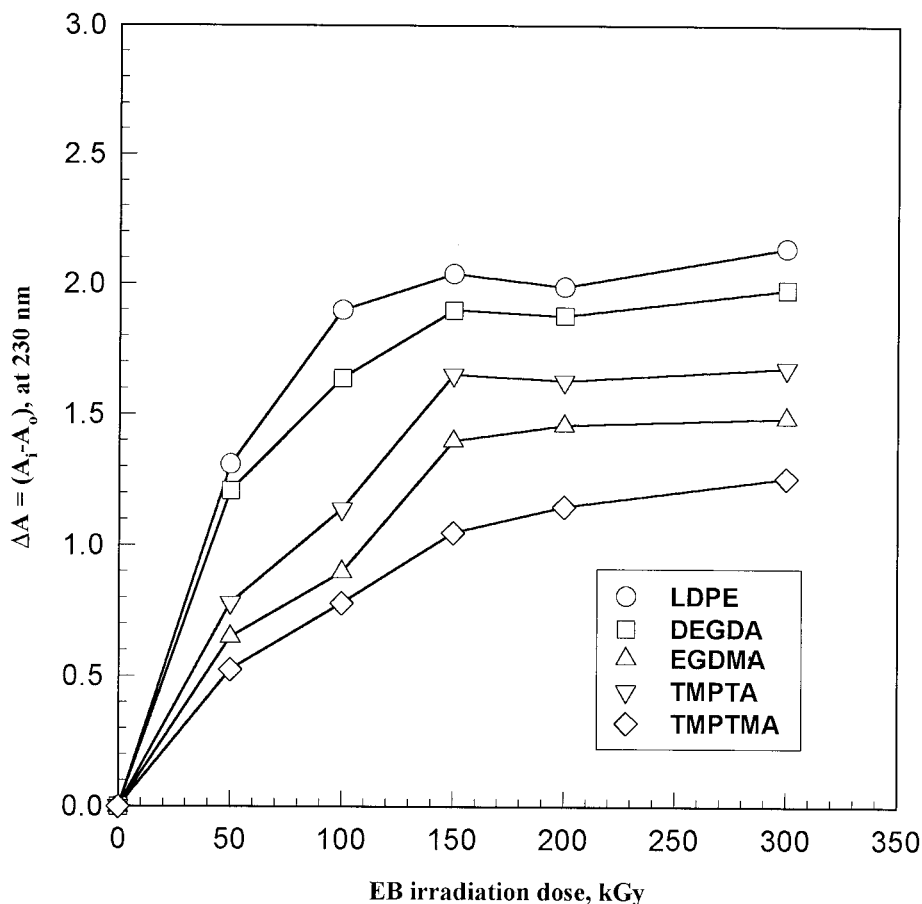


Figure 8 Variation of the UV absorption intensity [$\Delta A = (A_t - A_0)$] at about 230 nm for unloaded LDPE samples and LDPE samples loaded with different monomers as a function of EB irradiation dose.

The order of increasing crystallinity of the LDPE samples was dependent on type of loaded PFM_s and was as follows:

TMPTMA > EGDMA > TMPTA
> DEGDA > Unloaded LDPE

Hence, the degree of crystallinity was dependent on both irradiation dose and type of loaded PFM. In consequence, the increase in the degree of crystallinity was consistent with the increase in crosslinking by the action of loaded PFM_s.

(UV) spectroscopy of unloaded and loaded LDPE samples with PFM_s

The assignment of the uv absorption of bands observed in irradiated LDPE led to the division of the bands into two groups, group A, which was thought to be polyene free radicals, and group B, which corresponded to polyenyl groups. Thus, the band at about 275–285 nm was attributed to polyenylfree radicals. The bands at 236 and 258 nm were probably the allyl free radicals (conjugated diene groups). Also, the ab-

sorption at 225 nm was related to the presence of ketonic carbonyl groups.^{3,4,19–22}

Figure 8 shows the quantitative UV data at 230 nm for the samples as a function of EB irradiation dose. As is known, the UV absorption peak at about 230 nm was characteristic of ketonic carbonyl groups (C=O). The radiation-induced carbonyl group increased with increasing irradiation dose up to about 100 kGy. At an irradiation dose in the range 100–300 kGy, the change in the intensity of the UV absorption peak (230 nm) was insignificant or levelled off. In addition, the extent of carbonyl group formation was dependent on the type of loaded monomer.

Figure 9 illustrates the change in UV absorbance at 250 nm (assigned to the formation of allyl free radicals) in accordance with the increase of irradiation dose. As shown in this figure, the intensity of the UV absorbance gradually increased with increasing irradiation dose up to 150 kGy. The maximum rate of increase was observed with the samples loaded with TMPTMA or EGDMA monomers, whereas the rate of other two loaded monomers increased nearly with the same order. These observations indicated that the loaded monomers in the LDPE samples participated

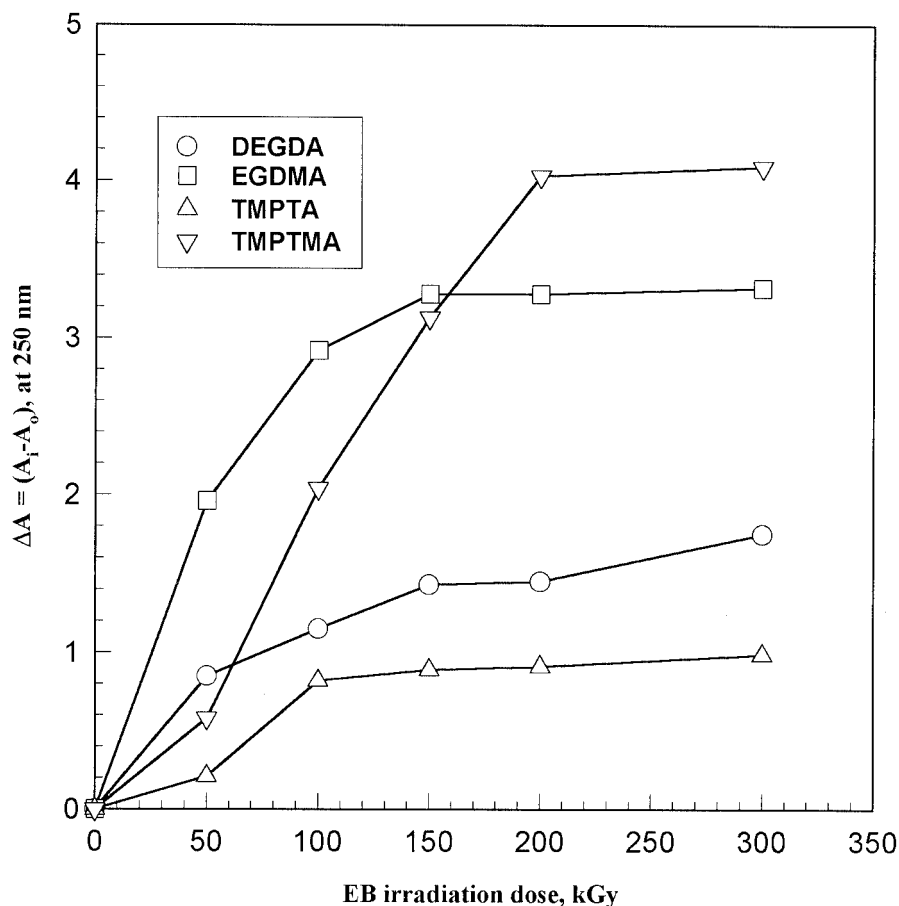


Figure 9 Variation of the UV absorption intensity [$\Delta A = (A_t - A_0)$] at about 250 nm for LDPE samples loaded with different monomers as a function of EB irradiation dose.

by different orders during irradiation to produce the crosslinked LDPE samples.

Finally, Figure 10 shows the relation of the change in the totally conjugated diene, as measured by the UV absorbance at 280 nm, with increasing irradiation dose. The obtained results indicated that the extent of unsaturated double bonds increased at an early stage of irradiation, whereas at irradiation dose range of 100–300 kGy, the value of unsaturation decreased. This observation led us to conclude that the produced conjugated diene was involved in the crosslinking of LDPE film, especially at relatively high doses (>150 kGy). The UV data were in a good agreement with that obtained through FTIR.

CONCLUSIONS

The EB irradiation of LDPE samples loaded with different monomers exhibited a high degree of crosslinking at lower doses. The extent of radiation-induced crosslinking of the LDPE samples as measured by the increase in the IR absorption peak at 965 cm^{-1} , increased with irradiation dose. Also, the degree of crosslinking was dependent on both irradiation dose

and type of loaded PFM. The order of monomer efficiency was as follows:

TMPTMA > EDGMA > TMPTA
> DEGDA > Unloaded LDPE

The change in the degree of unsaturation, (vinyl at 1640 cm^{-1} and vinylidene at 890 cm^{-1}), for both PFM-loaded and unloaded LDPE samples decreased with increasing irradiation dose. The rate of decreasing unsaturation for the TMPTMA-loaded sample was higher than that with the TMPTA monomer. This decrease or the disappearance in the IR intensity indicated that monomer molecules participated in the crosslinking reaction of LDPE due to irradiation.

The oxidation reaction predominated and increased with increasing irradiation dose up to about 100 kGy; after that, the level of oxidation was nearly constant up to 300 kGy. The order of oxidation extent at any irradiation dose in this case was opposite in behavior to that of crosslinking extent and was as follows:

Unloaded LDPE > DEGDA > TMPTA
> EGDMA > TMPTMA

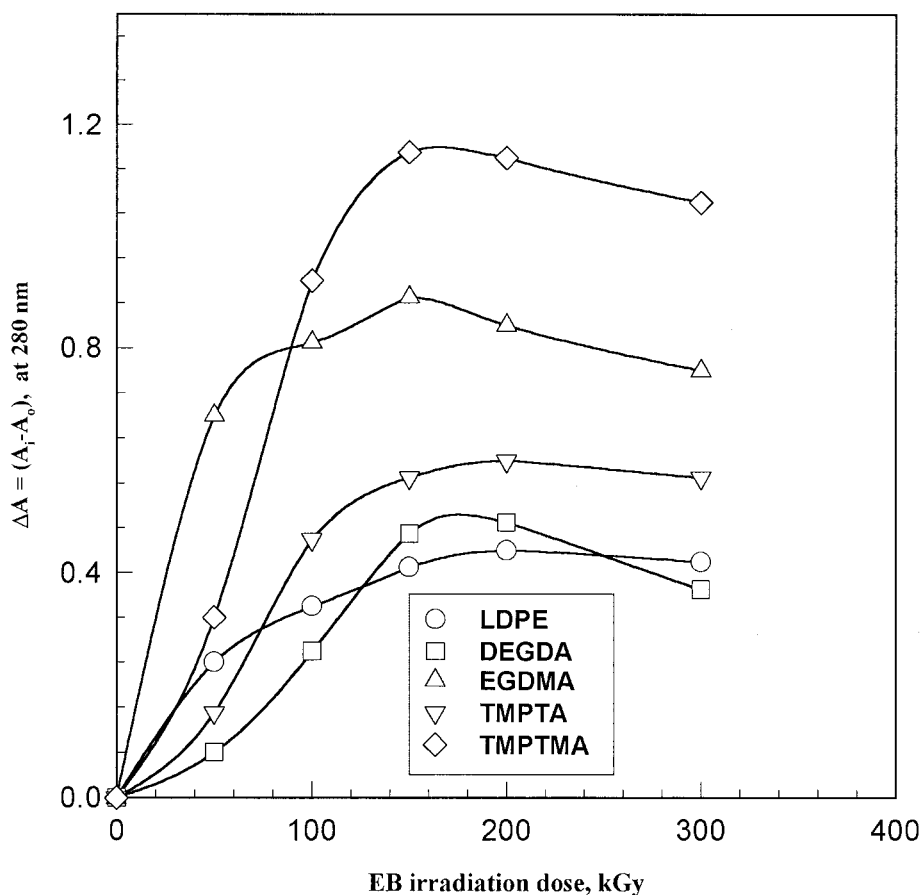


Figure 10 Variation of the UV absorption intensity [$\Delta A = (A_i - A_0)$] at about 280 nm for unloaded LDPE samples and LDPE samples loaded with different monomers as a function of EB irradiation dose.

The crystallinity increased gradually up to 150 kGy, beyond which the degree of crystallinity levelled off. The order of increasing crystallinity of the LDPE sample was dependent on the type of loaded PFM. The increase in the degree of crystallinity was due to the preferential crosslinking of the amorphous regions to the crystalline regions as a result of irradiation in the presence of PFMs.

TMPTMA monomer was the most efficient crosslinking agent compared to other monomers; it showed the highest extent of crosslinking and crystallinity and the lowest extent of oxidation of the LDPE samples.

The UV obtained data was in a good agreement with the FTIR data.

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