ESR and FTIR Studies on Electron Beam-Irradiated Low-Density Polyethylene Blends

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ABSTRACT: Low-density polyethylene (LDPE) composites modified with a resin based on ethylene/methacrylic acid copolymer (surlyn) and/or citric acid were electron beam-irradiated and investigated by electron spin resonance (ESR) at room temperature. ESR studies were carried out directly after irradiation and after various time intervals up to 72 h postirradiation. The irradiated samples showed the ESR spectrum of seven lines that was assigned to the formation of allyl radical. The nature and yield of the allyl radical of the different LDPE samples were analyzed as a function of time after irradiation. Also, the radical concentration, decay, decay rate, and kinetics of radical decay were evaluated. Fourier transform infrared (FTIR) analysis at a series of different temperatures upon cooling from room temperature to −175°C and the reverse heating to +125°C was also carried out. The structural changes while cooling and heating of LDPE samples were investigated using FTIR spectrometry. The results showed that cooling of unirradiated LDPE samples to −175°C results in a decrease of the intensities of IR bands. However, heating the samples from −175°C up to +125°C led to a consequence increase in the intensities of the IR bands. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3461–3469, 2007

Key words: LDPE; ionomer resin; citric acid; EB irradiation; ESR and FTIR analysis

INTRODUCTION

The studies on the mechanism of radiation-induced crosslinking and/or chain scission and radiation-induced grafting are closely related with the radical process, and the behavior of the free radicals in polyethylene was the major interest in the field of radiation chemistry.[1] The difference in the behavior of PE during irradiation depends not only on the nature of polymers but also on the polymer composition and the irradiation condition.[2] Important changes in the physical and chemical properties resulting from the incorporation of special additives permit their use in applications where the polymer alone would have had small chance to meet certain performance applications. The types of additives lead to important physical changes. Thus, blowing agent such as citric acid permits the production of cellular structure; crosslinking coagent improves the thermal, mechanical, and heat shrinkage properties.[3]

Many workers used electron spin resonance (ESR) to investigate the free radicals produced in irradiated polyethylene. According to the results in many reported studies, it was established that the major free radicals produced by irradiation of polyethylene are alkyl radicals ($\sim CH_2 \overset{\cdot}{-} CH{-}CH_2 \sim$), allylic free radicals ($\sim CH_2 \overset{\cdot}{-} CH{-}CH{=}CH\sim$), and the polyenyl free radicals [$\sim(CH{=}CH)_n \overset{\cdot}{-} CH\sim$].[1] The irradiation of polyethylene at −196°C causes the formation of the well-known alkyl free radicals. At this temperature they are quite stable and are observed in the ESR spectra as a sextet structure. When the irradiated PE sample is warmed up to room temperature, there is a substantial decrease in radical concentration and the ESR spectrum observed is a mixture of a sextet and a septet structure. On standing at room temperature, the contribution from the sextet disappears, leaving only the septet. This septet structure has been assigned to allyl radicals ($\sim CH_2 \overset{\cdot}{-} CH{-}CH{=}CH\sim$).[4–6] Allyl radicals are more stable than alkyl radicals under vacuum but decay more rapidly in reactive gases such as oxygen. Seguchi and Tamura in 1973 reported that the alkyl radical decay in the atmosphere of reactive gases (air or oxygen) can be well explained by the diffusion of radical in the crystallites regions of polyethylene.[6] Although, a part of alkyl radicals would decay by recombination or be converted to allyl radicals through the reaction with double bond in the crystalline regions.[6,7]

The influence of temperature on the structural, physical, and chemical changes of polymeric materials was studied by several groups of investigators over a wide range of temperature. Below −50°C, the radiation chemical yield for crosslinking is almost independent of temperature, whereas above this temperature,

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the yield of crosslinking steadily rises.[8] One of the characteristic features of the flexible polymer chain is the sensitive change of their conformations, depending on the external conditions. For example, the random coil in the melt changes its conformation to the regular form when it is cooled below the crystallization temperature. In some cases, the thus created crystal structure might be unstable and change furthermore to more regular and energetically more stable structure, i.e., the phase transition. The phase transition can also be caused by the application of the mechanical force, the electric field, etc., to the polymer solids. Many researches have been made so far to clarify the structure of polymers taken before and after the transitions. But it may also be important to reveal the structure changes in the process of transition and to solve the detailed mechanism of this physical structural transition.[9,10]

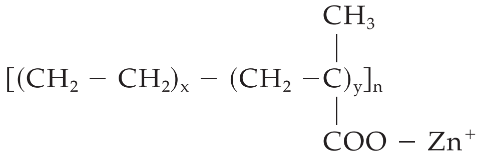
The low-temperature phase transition of unirradiated and γ-irradiated low density polyethylene (LDPE) samples was subjected to intensive investigation using both Fourier transform infrared (FTIR) and Fourier transform Raman (FT-Raman) techniques while cooling from room temperature down to liquid nitrogen temperature (−196°C) and re-heating up to +125°C.[11] In our previous work, thin films of LDPE and HDPE were intensively investigated using several techniques. The results of these investigations showed that γ-irradiation caused several changes in most of the physical and chemical properties of polyethylene. Moreover, the temperature dependence of polyethylene showed different behavior in the phase transitions of glassy–rubbery and rubbery–glassy for unirradiated samples than those of γ-irradiated ones.[11–13]

In the present work, ESR technique has been used to compare the concentration of the radicals formed in unmodified and modified LDPE samples when they are subjected to electron beam irradiation to a dose of 100 kGy at room temperature. Also, the decay of the radiation-induced radicals as a function of postirradiation effect up to 180 min was studied. It was also aimed to investigate the temperature dependence on the structural changes occurring in LDPE samples using FTIR technique.

EXPERIMENTAL

Materials

Low-density polyethylene (density ≈ 0.922 g/cm^3, melt flow index (MFI) ≈ 0.3 g/10 min, melting temperature ≈ 110°C, and softening temperature ≈ 96°C) was supplied in the form of pellets by Borealis A/S, Denmark. A commercial ionomer resin based on ethylene/methacrylic acid copolymer (Surlyn 1857) was supplied in the form of pellets from Dupont industrial polymer, Wilmington Delaware, USA. The acid group in the methacrylic acid of Surlyn resin is partially neutralized with zinc ion. Surlyn resin has a density of 0.94 g/cm^3, melting temperature of 87°C, softening temperature of 56°C, and MFI of 0.4 g/10 min (the structure is shown below). Anhydrous citric acid (extra pure) was supplied by Redel de Haen Chemical, Germany.



$$[(CH_2 - CH_2)_x - (CH_2 - \overset{\overset{\large CH_3}{|}}{\underset{\underset{\large COO\,-\,Zn^+}{|}}{C}})_y]_n$$

Zn salt of ethylene/methacrylic acid copolymer, (Surlyn 1857)

Preparation of LDPE samples

Pure LDPE sample and LDPE blends with different content of the ionomer resin (ethylene/methacrylate zinc salt, Surlyn) and/or citric acid (1.0 wt %) were mixed in a Brabender plasticcorder PL 2100 at 170°C and 60 rpm rotor speed. LDPE was first allowed to melt for 2 min, followed by the addition of Surlyn and/or citric acid for a total mixing time of 5 min. The melt mixes were immediately sheeted in an open roll mill. The sheets were compression molded for 3 min at 175°C and at a pressure of 15 MPa in a hot press to obtain thin films of thickness of ~0.4–0.5 mm for FTIR analysis and thick films of ~2.0–2.2 mm for ESR measurements. The samples were processed and specified in four formulations as follows:

I: Pure LDPE
II: LDPE + 1 wt % of citric acid
III: LDPE + 1 wt % of citric acid + 10 wt % of Surlyn
IV: LDPE + 1 wt % of citric acid + 20 wt % of Surlyn

Irradiation procedure

Irradiation was carried out at ambient temperature in the 1.5 MeV, 30 mA, and 25 kW electron beam accelerator. The irradiation doses up to 120 kGy were obtained by multipasses, by adjusting the conveyer speed and the electron beam parameters, in which the maximum irradiation dose per one pass was 20 or 40 kGy.

ESR investigation

The ESR spectra were recorded using Brucker EMX, X-band spectrometer, equipped with microwave power meter (E2 041XG) to determine the different radiation-induced free radicals of the irradiated samples at 40 kGy. All measurement were carried out at room temperature and at magnetic field modulation frequency of 100 kHz, amplitude modulation of 0.957 mT, sweep width of 20 mT, and microwave power of 7.96 mW. Concentration of free radicals was estimated by comparing, at room temperature, spectra of diphenyl picryl hydrazine–benzene solution. The number of accumulations and amplification was always adjusted according to the intensity of the obtained signal. The free radical concentrations were calculated by the double integration of the first derivative spectra.[7]

FTIR measurements

An FTIR spectrometer (ATI Mattson, Genesis series I, USA) was used for measuring and scanning the IR absorption spectra of samples under investigation with a resolution of 4 cm^{-1}, over the range 400–4000 cm^{-1}. The FTIR analysis of samples was carried out at room temperature and at a series of different temperatures using a variable automatic temperature controller cell (cryostat) of type Greasby/Specac P/N/12,573 (England). To achieve the best nitrogen hold time with this cell, it should be evacuated to a pressure of less than 0.05 Torr using a rotary vacuum pump. The investigated sample was placed and kept in the variable temperature controlled cell at the desired temperature for as much time as needed and at intervals of ±25°C to obtain the IR spectra at different temperatures. The methylene peak at 724 cm^{-1} (assigned to methylene CH$_2$ rocking vibration mode) was chosen as the reference peak (i.e., internal standard) for all LDPE samples as it remained constant during and after irradiation. Therefore, the carbonyl index and the other quantitative infrared analysis were calculated from the ratio of the absorbance of the respective peaks to the absorbance of the invariant reference infrared peak at 724 cm^{-1}.[14]

RESULTS AND DISCUSSION

ESR characterization

Unmodified and modified LDPE samples irradiated to 40 kGy were subjected to ESR analysis directly after irradiation (the least time taken to transfer the irradiated samples to ESR laboratory, ~1 min) and after time intervals up 72 h of postirradiation at room temperature. The ESR study was performed in terms of two parameters: (1) dependence of free radical type on sample composition and (2) dependence of free radical concentration on postirradiation stability. The first was determined by observing the variation in the structure of ESR spectrum, and the second by the double integration of the first derivative ESR spectrum. Figure 1 shows the typical ESR spectra of pure LDPE and modified LDPE composites tested directly and after various time intervals after irradiation. The characteristic peroxide ESR signal, known to appear in the ESR spectra of many polymers irradiated in air or in vacuum, was not observed. However, the ESR spectra of the 40 kGy irradiated pure LDPE and LDPE

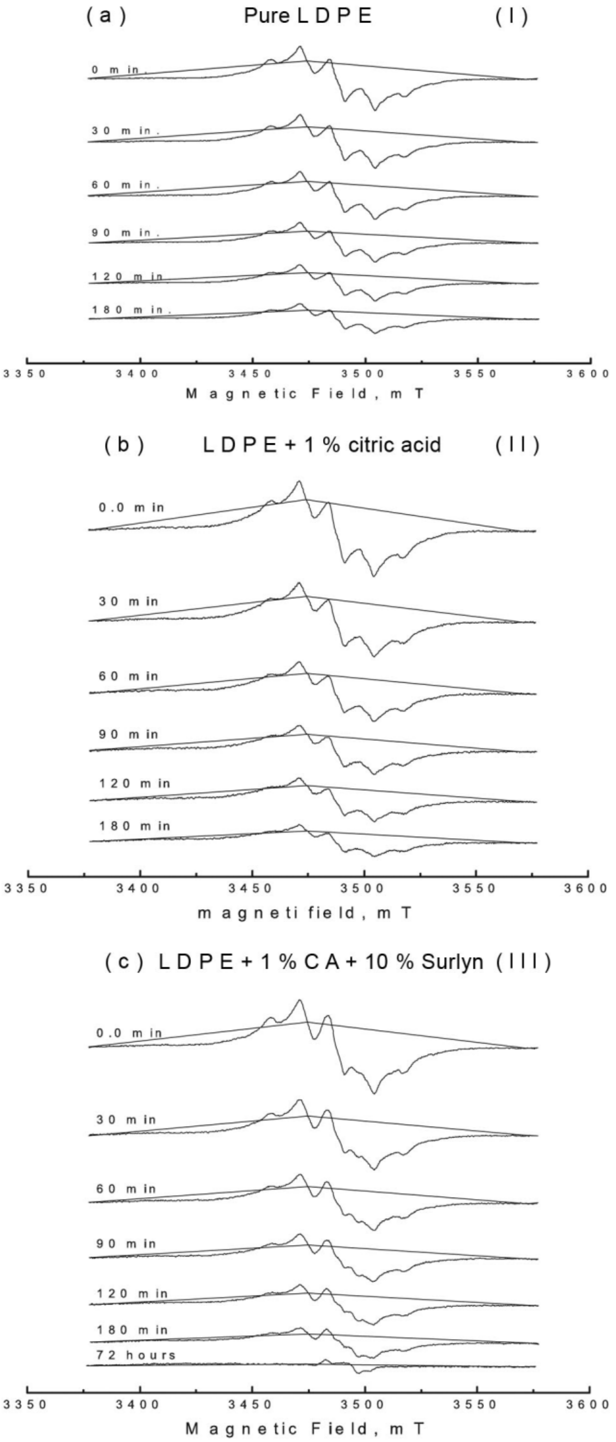


Figure 1 ESR spectra of 40 kGy irradiated pure and modified LDPE samples, tested immediately (~1 min) and at various time intervals elapsed after irradiation. (a) Pure LDPE sample, (b) LDPE/citric acid blend, and (c) LDPE/citric acid/surlyn blend.

TABLE I
Free Radical Concentration Parameters for Pure LDPE and LDPE Blends Tested after Various Time Intervals of Postirradiation[a]

Sample formulation	Time after irradiation (min)	Radical concentration (10^7) (arbitrary units)	Relative radical concentration (%)	Relative reduction (%)
Pure LDPE (I)	1	3.45	100.0	0.0
	30	2.97	86.09	13.91
	60	2.74	79.42	20.58
	90	2.35	68.12	31.88
	120	2.2	63.77	36.23
	180	1.87	54.20	45.8
	3 days	0.0	0.0	100
LDPE + citric acid (II)	1	3.22	100.0	0.0
	30	2.69	83.54	14.46
	60	2.31	71.74	28.26
	90	2.02	62.74	37.26
	120	1.89	58.70	41.30
	180	1.61	50.0	50.0
	3 days	0.0	0.0	100.0
LDPE + citric acid + surlyn (III)	1	3.79	100.0	0.0
	30	3.0	79.15	20.85
	60	2.54	67.7	32.30
	90	2.24	59.1	40.90
	120	1.99	52.51	47.49
	180	1.69	44.59	55.41
	3 days	0.77	20.32	79.68

[a] Electron beam irradiation dose = 40 kGy.

blends with surlyn and/or citric acid at room temperature showed only the septet structure of allyl radicals ($\sim CH_2\dot{-}CH - CH{=}CH\sim$) with a splitting width (hyperfine structure) of 1.25 mT. The decay of the allyl radicals is fast, in which they were completely disappeared after 3.5 h of irradiation. Previous ESR studies on irradiated polyethylene at room temperature claimed that the dominant component of signals of polyethylene radiolysis is the one originating from the allyl radicals of septet spectra.[2,6,15,16]

Because the used citric acid concentration (1.0 wt %) in LDPE blends is relatively small, it does not allow to observe its effect on the radical processes after irradiation. This may explain the similar shape of the septet structure of allyl radicals for pure LDPE and LDPE modified with 1 wt % of citric acid. Citric acid is a tricarboxylic acid, which may be considered as a blowing agent; it is expected to impose a stabilizing influence by either OH group and/or C═C double bond. The results showed that citric acid has a slight effect in inhibiting free radical formation in irradiated samples. The ESR spectra of LDPE modified with 1 wt % citric acid and 10 wt % surlyn (Sample III) showed the dominant septet of the allyl radical spectra with superimposed structure which can be related to the radiation-induced radical from the Surlyn present in the polymer matrix. Therefore, the total concentration of radicals in Sample III may not be due to allyl radicals but to others; probably radiation-induced radicals from the surlyn additive. The obtained data illustrated that the radiation-induced radical in Sample III is more stable than those in Samples I and II.

Table I summarizes the calculated parameters from the ESR spectra for pure LDPE and LDPE modified with citric acid and the mixture of citric acid and Surlyn (40 kGy irradiation dose) tested directly after irradiation (~1 min) and after various periods of time. Here, the concentration of allyl radicals was calculated by the double integration of the first derivative ESR spectra. It can be seen that the initial radical concentration measured directly after irradiation, decreased as the time after irradiation increased for all LDPE samples. Also, the initial radical concentration of the modified LDPE samples with citric acid alone (Sample II) was lower than that for unmodified one. On the other hand, the initial radical concentration of irradiated Sample III was higher than that for pure LDPE sample and up to 30 min of postirradiation. After that, the situation is reversed, where the initial radical concentration of Sample III was lower than that for pure LDPE sample. In general, it can be seen that the relative radical concentration of LDPE samples follows the order: Sample I > Sample II > Sample III. Although, the radicals of LDPE sample modified with citric acid/Surlyn mixture (Sample III) were more stable (the radicals can be detected even after 72 h), this

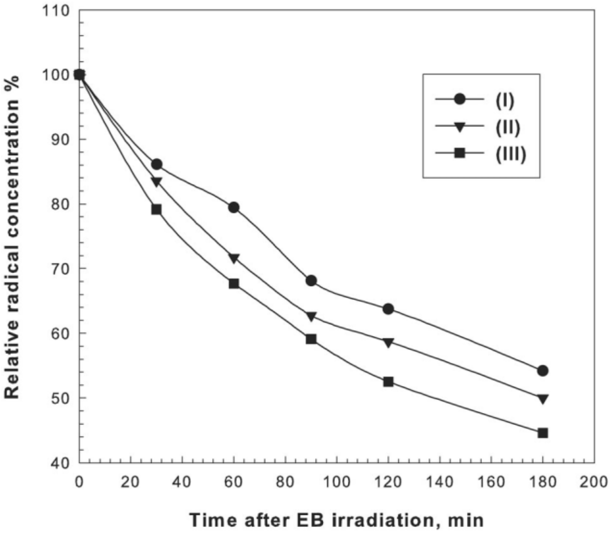


Figure 2 Relative radical concentration % for 40 kGy irradiated LDPE samples (Samples I–III) as a function of measurement time elapsed after irradiation.

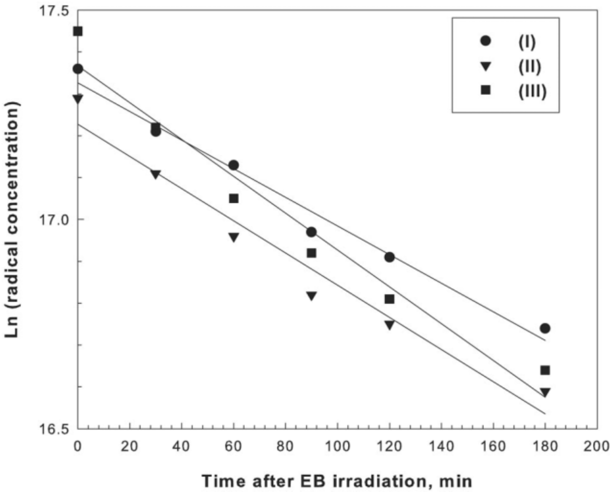


Figure 3 Plots of logarithm of radical concentration for 40 kGy irradiated LDPE samples (Samples I–III) as a function of time elapsed after irradiation.

sample exhibits higher decay rate compared to the other LDPE samples (Samples I and II, see Fig. 2).

If the percentage relative reduction in the free radicals concentration was taken as a measure for the extent of free radical decay (relative radical reduction), then the different LDPE samples can be arranged in the following order: Sample III Sample II Sample I, as shown in Figure 2. Thus, it can be seen that the rate of the relative allyl radical reduction in all investigated samples is not the same and depends on the LDPE composition. In addition, the data in Table I implied that the rate of the allyl radical reduction and consequently the half-life (i.e., time at which relative radical reduction is 50%) depends on the initial radical concentration. As shown in Figure 3, the plotting of logarithm of the initial radical concentration as a function of time after irradiation displayed straight line relationships giving a first-order kinetics in accordance with previous work.[16] From the slope of the straight lines, the first-order rate constant for the allyl radical decay was found to be 17.33, 17.23, and 17.37 min^{-1} for LDPE samples I, II, and III, respectively.

ESR signals for LDPE blend with Surlyn can be interpreted based on the superimposition of two signals. The first is due to the polymer allyl radical and the second to Surlyn radical. Change in the radical concentration (allyl and superimposed surlyn radical) during postirradiation stability was investigated by subtracting the recorded ESR spectra from that corresponding to each one as shown in Figure 4. It can be seen that the change in the relative concentration of allyl radical and superimposed surlyn radicals were observed only in Sample III, as function of time after irradiation. Also, the relative allyl radical concentration gradually decreased, whereas the relative concentration of radiation-induced Surlyn radicals slightly increased as the time after irradiation increased. However, the rate of allyl radical decay was being higher than the rate of growth of superimposed radical.

FTIR analysis of LDPE samples at room temperature

Figure 5 shows the IR spectra at room temperature of unirradiated and 100 kGy irradiated LDPE samples. It can be seen that the IR spectra of unirradiated LDPE samples showed the appearance of IR bands at 1640 and 1720 cm^{-1} due to C=C and C=O stretching for Samples II–IV. The intensity of these bands was found to increase with the addition of Surlyn and/or citric

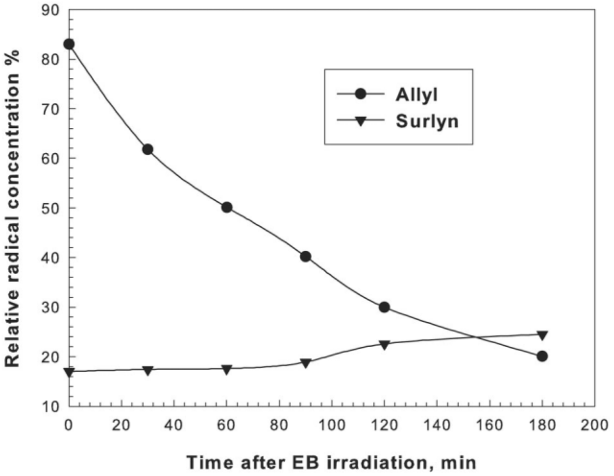


Figure 4 Relative radical concentration % (allyl and surlyn radicals) for 40 kGy irradiated LDPE sample III (LDPE/citric acid/surlyn) as a function of measurement time elapsed after irradiation.

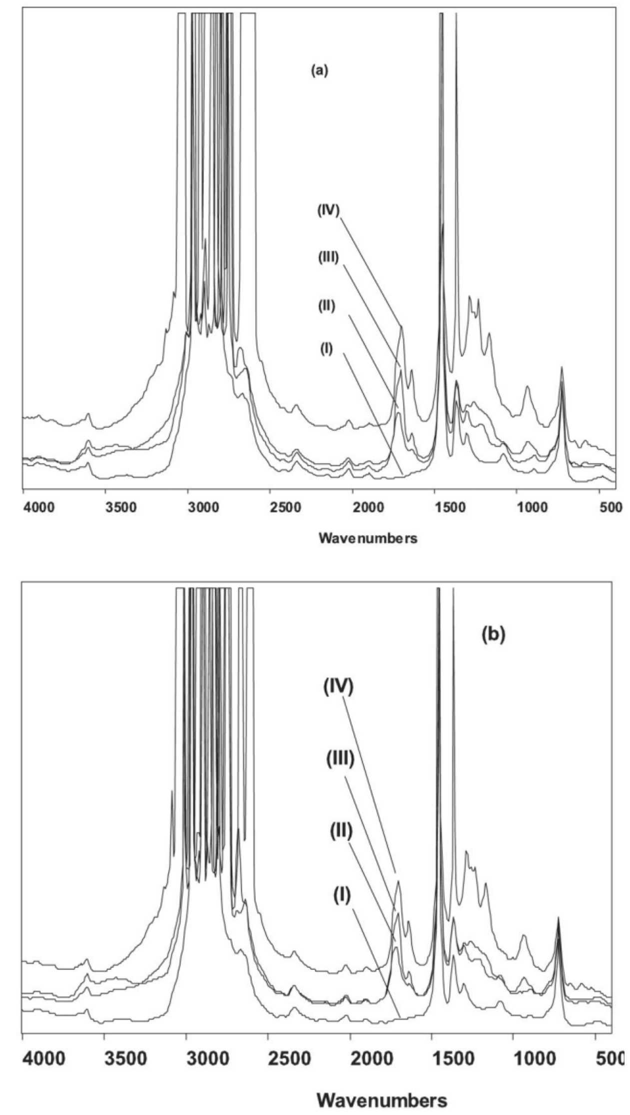


Figure 5 Room temperature IR spectra of unirradiated and 100 kGy irradiated LDPE samples (Samples I–IV). (a) Unirradiated and (b) 100 kGy irradiated samples.

acid. The addition of 10 wt % of Surlyn caused a shift to lower wavenumber and this shift increased with increasing the content of Surlyn. The carbonyl band in the IR spectrum of Sample II was appeared as a well-resolved peak centered at ~1720 cm^{-1}, which is correlated to the C=O group of the carboxylic group of citric acid alone. The observed shift of the carbonyl band toward lower wavenumber for LDPE Samples III and IV (i.e., as a result of addition of Surlyn in the presence of citric acid) may be explained on the basis of the overlapping of two peaks corresponding to carbonyl groups of two different types of carboxylic groups. Therefore, the carbonyl band in Samples III (10 wt %) and IV (20 wt %) appeared as two overlapping peaks with a maximum at 1710 cm^{-1} and 1701 cm^{-1} is due to the C=O of the carboxylic group of Surlyn, while the shoulder at 1720 cm^{-1} is due to the C=O of carboxylic group in citric acid. In this respect, the shift in the wavenumber of the carbonyl groups of the two different carboxylic groups could be related to some sort of inter and/or intra chemical reaction between the carboxylic groups of the additives. In addition, the 965 cm^{-1} band (*trans*-vinylene double bond) appeared only in the sample modified with surlyn (Samples III and IV) and its intensity increases with increasing Surlyn content. The intensity of the IR band at 1080 cm^{-1} (C—O vibration) was increased upon irradiation and due to the blending of LDPE samples with surlyn and/or citric acid.[11,17,18]

Figure 6 shows the variation in the carbonyl index for the investigated samples as a result of EB irradiation. It can be seen that the carbonyl index increases slightly with increasing the irradiation dose according to the type and concentration of additive. Also, it is clear that there is a big difference in the level of carbonyl index due to the change of LDPE sample composition. The increase of IR absorbance ratio ($A_{x\,\mathrm{cm}^{-1}}/A_{724\,\mathrm{cm}^{-1}}$) at the selected IR peaks (965, 1080, and 1640 cm^{-1}) due to the EB-irradiation and addition of Surlyn and/or citric acid may give support to the occurrence of radiation-induced crosslinking reaction. The intensity ratios of the different absorption bands for unirradiated and 100 kGy irradiated LDPE samples are summarized in Table II.

Thermal dependence of FTIR analysis of unirradiated and irradiated LDPE samples

The FTIR spectra of unirradiated and 100 kGy irradiated LDPE samples I–IV were recorded using the temperature controller cell at a series of different temperatures. In this regard, the room temperature IR spectrum was recorded and then the sample was cooled gradually down to −175°C. On the same sample, the

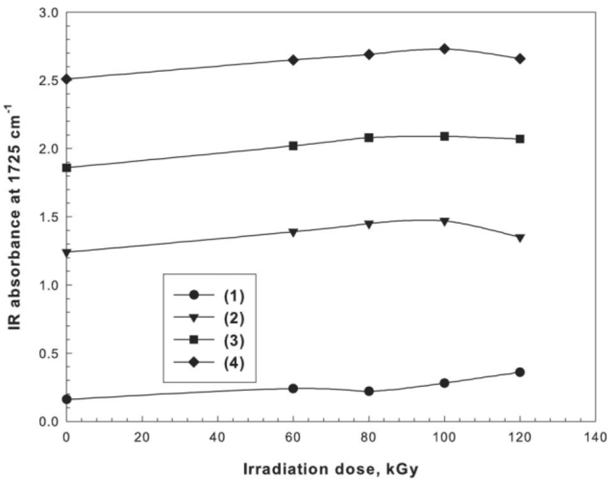


Figure 6 The variation in the carbonyl index ($A_{1720\,\mathrm{cm}^{-1}}/A_{724\,\mathrm{cm}^{-1}}$) for LDPE samples as a function of irradiation dose.

TABLE II
IR Absorbance Intensity Ratios ($A_{x\,\mathrm{cm}^{-1}}/A_{724\,\mathrm{cm}^{-1}}$) of Selected Bands for Different LDPE Samples[a]

Dose (kGy)	Samples	Absorbance ratios of selected IR peaks		
		965 cm^{-1}	1080 cm^{-1}	1640 cm^{-1}
0	I	—	0.375	—
	II	—	0.423	0.389
	III	0.422	0.528	0.539
	IV	0.933	0.667	1.09
100	I	0.146	0.377	—
	II	0.322	0.477	0.397
	III	0.454	0.657	0.515
	IV	0.853	0.702	0.980

[a] The IR spectra were performed at room temperature.

IR spectra were recorded while heating from −175°C up to near the melting temperature of LDPE (+125°C). In addition, the IR spectra were recorded while re-cooling from +125°C down to +25°C. Figure 7 shows the IR spectra of unirradiated and 100 kGy irradiated pure LDPE samples (as an example) at different temperatures while cooling from room temperature down to −175°C and then re-heating to room temperature. To understand the temperature-induced structural changes, the intensity ratios ($A_{x\,\mathrm{cm}^{-1}}/A_{724\,\mathrm{cm}^{-1}}$) of selected IR bands (1302 for CH_2 twisting vibration, 1451 for CH_2 asymmetric bending, and 1720 cm^{-1} for C=O vibration) were estimated at different temperatures as shown in Figure 8.

Based on Figures 7 and 8, few points may be addressed: (1) During cooling from +25°C to −175°C, it can be seen that the intensity of the selected IR bands gradually decreased; (2) During heating from −175°C to −75°C, the intensity of all the IR bands was found to decrease and then tends to increase up to +125°C; (3) The re-cooling of the samples from +125°C to +25°C leads to a gradual decrease in the intensity of all the IR bands; and (4) The sharp IR band around 2800–3200 cm^{-1} for unirradiated pure LDPE at room temperature appears as a broad one upon cooling to −175°C as shown in Figure 7. The broadness of this band was also observed upon heating up to +25°C and no longer occurred upon further heating to +125°C. This structure change in unirradiated pure LDPE sample was not observed in the case of irradiated pure LDPE and unirradiated or irradiated modified LDPE samples upon cooling from +25°C down to −175°C.

These structural changes upon cooling and heating and re-cooling may be explained on the basis of the following points: (a) Cooling the LDPE sample will lead to freezing the re-orientation or limiting the possible orientation motions of polymer molecular segments[10,11]; (b) The appearance of broadness of the peak structure over the range 2800–3200 cm^{-1} may be correlated to a certain kind of physical phase transition at low temperature. Physical phase transition might occur in unirradiated pure LDPE sample due to the freezing of re-orientational vibration of molecular segments. The inhibition or disappearance of this physical phase transition in the other samples can be attributed to the induced crosslinking during sample processing and irradiation in the presence of Surlyn and citric acid. The incorporation of citric acid in LDPE samples as a modifier and/or blowing agent may lead to the existence of a very weak van der Walls intermolecular force which in turn limits these structural changes. Also, EB irradiation and the addition of Surlyn as a crosslinking agent for LDPE enhanced the radiation crosslinking reaction in the polymer matrix. Because of such crosslinks, the distance between the molecular chains of polyethylene was mostly fixed and consequently the re-orientational vibration was hindered.

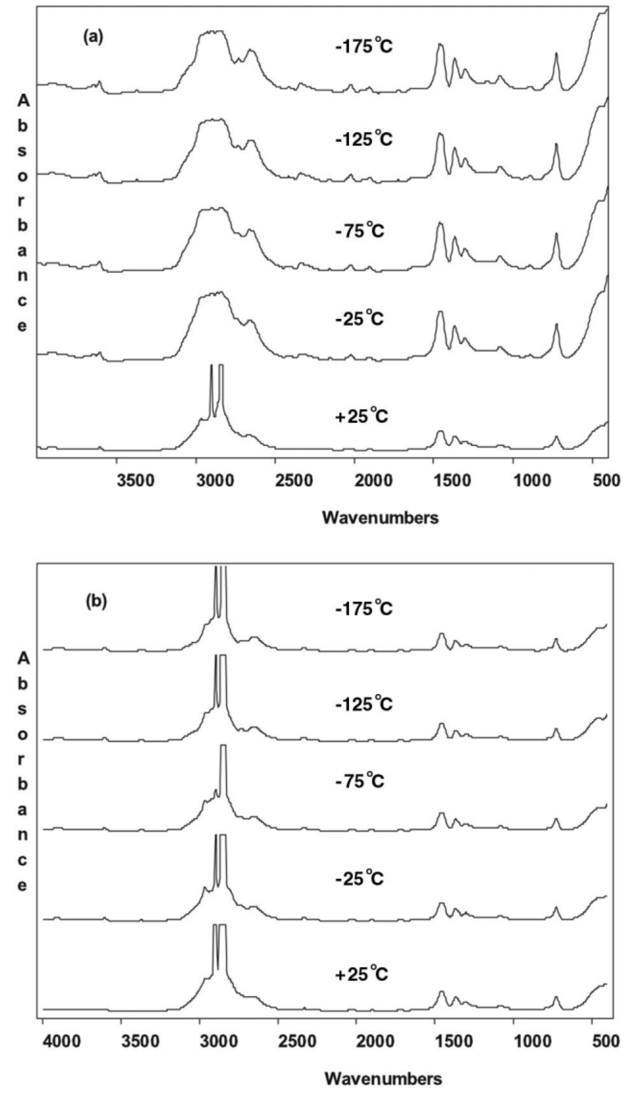


Figure 7 IR spectra of (a) unirradiated and (b) 100 kGy irradiated pure LDPE samples at a series of different temperatures upon cooling from +25°C to −175°C.

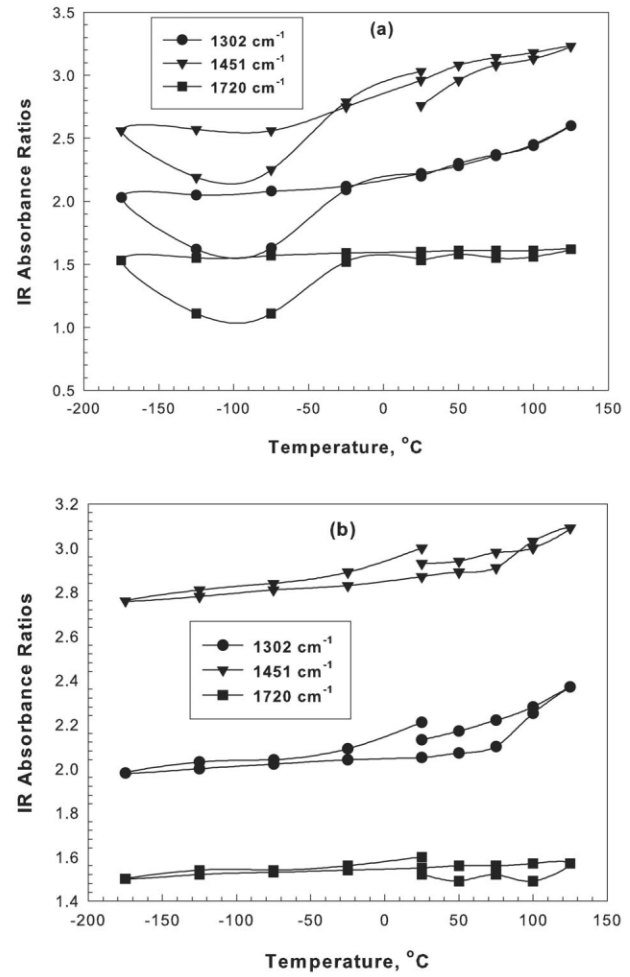


Figure 8 The change in the ratio of the IR absorption bands at 1302, 1451, and 1720 cm^{-1} to the invariant reference band at 724 cm^{-1} of (a) unirradiated and (b) 100 kGy irradiated pure LDPE samples as a function of temperature upon cooling from +25°C to −175°C and heating from −175°C to +25°C and +125°C.

The observed decrease and increase in the absorption intensities of IR band while cooling and heating may be interpreted based on the reduction and increment of the thermal energy according to Boltzmann distribution equation:[10,11,19]

$$I = I_0 e^{-\Delta E/KT}$$

where, ΔE is the vibration energy (the height of the vibrational energy barrier) activating a re-orientational motion, I and I_0 are proportional to the number of ions in the energy levels U_1, and U_2, K is Boltzmann constant, and T is the absolute temperature in Kelvin. It was reported that the value of the height of energy barrier ΔE changes with temperature; ΔE increases as the temperature decreased while cooling, whereas at high temperature, the energy barrier decreases under the effect of thermal agitation.[19] This fact might suggest that cooling of the LDPE samples will lead to an increase in the value of ΔE which means an increase in the height of energy barrier; thus leading to freezing of re-orientational motion and hence led to reduction of the intensities of IR bands corresponding to these re-orientational vibration modes. On the other hand, the decrease of the energy barrier (ΔE) while heating makes the re-orientational motion much easier resulting in an increase in the IR band intensities.

CONCLUSIONS

This work presents a comparative study on the nature and structure of free radical formation in LDPE composites just after electron beam irradiation to various doses and those remained after long time of irradiation. Also, the irradiated LDPE samples were IR analyzed at room temperature and at a series of cooling and heating processes. The ESR spectra showed that the structure, concentration, and stability are largely dependent on the LDPE composition. In this regard, citric acid has a slight effect on the concentration or the decay of the formed allyl free radicals. However, when the ionomer resin (Surlyn) was as an additive, the septet allyl radical with superimposed structure was the dominant feature. LDPE samples modified with citric acid and surlyn showed the highest stability of the radical. The kinetic study of the radical concentration proposed a first-order reaction.

The IR analysis suggests the occurrence of structural change in unirradiated pure LDPE samples during cooling and heating in the temperature range −175 °C → +125°C, in which this change appeared nearly at about −50°C. The induced crosslinking of LDPE samples modified with Surlyn and/or citric acid (during sample processing and irradiation) inhibited or blocked the occurrence of structural change in these LDPE samples.

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