

Electron-Beam Irradiation of Low-Density Polyethylene in the Presence of Phenolic Stabilizer, Carboxylic Acid Stabilizer, or Both

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ABSTRACT: The effects of Irganox 1010 and citric acid as antioxidants and modifiers of the network structure and mechanical and thermal properties of low-density polyethylene (LDPE) during electron-beam crosslinking with different irradiation doses (up to 120 kGy) were investigated. The results showed that the addition of these stabilizers had a retarding effect on the gel fraction of LDPE within the investigated range of electron-beam-irradiation doses. However, a noticeable effect on the gel fraction was found for the LDPE formulations compounded with citric acid alone or with its mixture with Irganox 1010 (in an equal ratio), as illustrated by a study of the gel-fraction/dose relationships. Tensile testing measurements showed that the addition of both stabilizers caused a slight reduction in the stress at break and an increase in the strain at

break. On the other hand, the thermal properties of the LDPE batches crosslinked with electron-beam irradiation were greatly improved as a result of the compounding with these stabilizers, as shown by thermogravimetric analysis studies. In this respect, the temperatures at different weight losses, the temperatures of the maximum rate of thermal decomposition, and the activation energies indicated that compounding with citric acid was more effective for stabilization against thermal decomposition than compounding with Irganox alone or a mixture. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1275–1286, 2005

Key words: LDPE; phenolic and carboxylic acid stabilizer; EB-Irradiation

INTRODUCTION

The high-energy irradiation of polymers produces several reactions; two of the most important are crosslinking and chain scission. These reactions proceed in parallel, and both are supposed to follow a free-radical mechanism. Most synthetic polymers susceptible to oxidative degradation require the addition of stabilizers to provide protection during processing and end use. The principle role of antioxidants is to transform highly reactive alkyl, alkoxy, and alkyl peroxy radicals into less reactive aromatic ones and simultaneously lower the total level of free radicals by recombination.

The stabilization of polyethylene (PE) is necessary against thermooxidative degradation either during its processing (i.e., melt conditions) or throughout its service life. In particular, crosslinked PE has higher service temperatures and needs more effective stabilizers. Both primary stabilizers (antioxidants) and secondary stabilizers (hydroperoxides) destroy scavenger free radicals and thereby interfere with oxidation degradation. Also, they inhibit the free-radical crosslinking of PE. Antioxidants are very important not just for the manufacture of plastics but primarily for their stabilization according to the application of the final product.¹

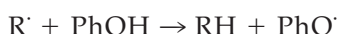
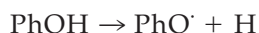
It is customary to incorporate antioxidants into PE in amounts beyond that usually added by a resin producer as an extrusion stabilizer before they are radiation-crosslinked. The radiolysis of PE and other polyolefins containing one or more of the many commercially available antioxidants often leads to a rapid loss of antioxidant activity with significant inhibition of radiation crosslinking. The list of commercially available antioxidants that do not inhibit radiolytic crosslinking, however, is quite small; for example, for peroxide crosslinking, only two or three types of antioxidants are known to survive a significant effect on the antioxidant. Several phenolic and aminic stabilizers survive exposure to radiation when present in polyolefin system with a significant retention of their antioxidant activity, even if some of them are still potent inhibitors of crosslinking.²

Even if an antioxidant inhibits chain scission, it can still cause a difference in the response because crosslinking in PE is a bimolecular process involving a reaction between two (migrating) secondary alkyl radicals, whereas chain scission is a unimolecular process. Thus, crosslinking is much more susceptible to inhibition than chain scission. The addition of an appropriate amount of a crosslinking agent to compositions, which, by virtue of an inherent tendency or because of significant scavenging, undergo significant chain scission, is very desirable as it should restore the properties to the level shown by the uncompounded resin (or to the level of a polymer exhibiting much less chain

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scission). On the other hand, if no appreciable chain scission occurs during the radiolysis of a polymer, then no penalty in physical properties results from the use of antioxidants that scavenge, and the decision to use a crosslinking agent becomes an issue of cost effectiveness.²

The antioxidant Irganox 1010 is a high-molecular-weight phenol that has *t*-alkyl substituents in ortho positions. During the irradiation of PE, the antioxidant forms phenoxyl radicals or takes part in a reaction with PE radicals:



Phenoxyl radicals ($\text{PhO} \cdot$) have a reasonably long lifetime at room temperature, and thus they are unable to initiate a new chain reaction. Therefore, the presence of a phenolic-type antioxidant influences the PE network formation (crosslinking) and the radical yield during the process of irradiation.²⁻⁴

Stabilizers such as antioxidants, metal deactivators, and UV absorbers are added to vinyl polymers. Polyols and other polymer systems are used to reduce degradation during manufacturing processes and throughout the lifetime of polymer products. These additives have been employed to improve the thermooxidative stability of polyolefins for many industrial applications (e.g., the wire and cable industry).⁵

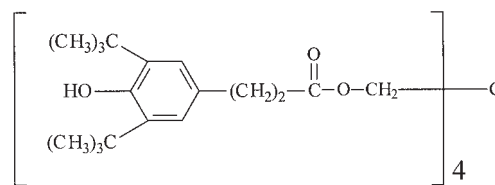
The purpose of this work was to determine the effect of an aromatic phenolic antioxidant (Irganox 1010) and an aliphatic carboxylic acid (citric acid) on the physicochemical properties of electron-beam (EB)-irradiated low-density polyethylene (LDPE) and to investigate the effectiveness of these additives on chain degradation and crosslinking.

EXPERIMENTAL

Materials

The LDPE (FT 5230 batch) used throughout this work was supplied in the form of pellets by Borealis A/S (DK-2800, Kongens Lyngby, Denmark). It had a density of 0.923 g/cm³, a melting point of 112°C, a softening temperature of 97°C, and a melt-flow index of 0.75 g/10 min. A phenolic antioxidant, commercially sold under the name Irganox 1010, was supplied by Ciba-Geigy (Bazel, Switzerland):

It was in the form of a white powder used as a nondiscoloring stabilizer for polyolefins. It had a specific gravity of 1.15 g/cm³, a bulk density of 0.530–0.560 g/L, a melting point of 116–125°C, and a flash point of 297°C. Citric acid (anhydrous, crystalline, and laboratory-grade) was supplied by Riedel-de Haën (Berlin, Germany).



(Irganox 1010)

(Pentaerythritol tetrakis - (3-(3,5-di-tert-butyl-4-hydroxyphenyl) - propionate)

Preparation of the LDPE formulations

The compounding and sheeting of the different LDPE formulations were performed during double extrusion and granulation in the mixing chamber of a Brabender (Berlin, Germany) Disburg PLV-151. The temperatures of the three zones were as follows: 145°C for zone I, 180°C for zone II, and 185°C for zone III. The temperature of the extrusion head was 180°C at 30 rpm. The different formulations were then processed to obtain uniform sheets 10 cm wide and 0.1 cm thick. The different LDPE compositions were specified as follows: LDPE 1 was pure LDPE, LDPE 2 was an LDPE composite with 1 wt % citric acid, LDPE 3 was an LDPE composite with 1 wt % Irganox, and LDPE 4 was an LDPE composite with a mixture of citric acid and Irganox in an equal ratio of 1 wt %.

EB irradiation

The LDPE formulations were irradiated in air at room temperature with a 10-MeV high-energy-EB linear accelerator (LAE 13/9, installed at the Institute of Nuclear Chemistry and Technology, Warsaw, Poland) at doses as high as 120 kGy. The total irradiation doses (60, 80, 100, and 120 kGy) were collected in multipass runs in which one pass of the absorbed dose level was not higher than 20 kGy.

Gel fraction

The gel fraction was measured gravimetrically by the extraction of the soluble component of the irradiated samples in boiling xylene for 8 h with a Soxhlet apparatus. The initial weight (w_1) and final weight (w_2), after extraction and 24 h of drying at 60°C, were recorded, and the gel fraction was calculated as follows:

$$\text{Gel fraction (\%)} = (w_2/w_1) \times 100$$

Mechanical properties

The tensile strength and elongation at break were measured on dumbbell-shaped specimens with an Instron (High Wycombe, UK) model 5565 machine. The stress-strain measurements were carried out at the ambient temperature at a stretching rate of 10 mm/min. The machine was equipped with digital signal processing and Merlin testing software. The averages

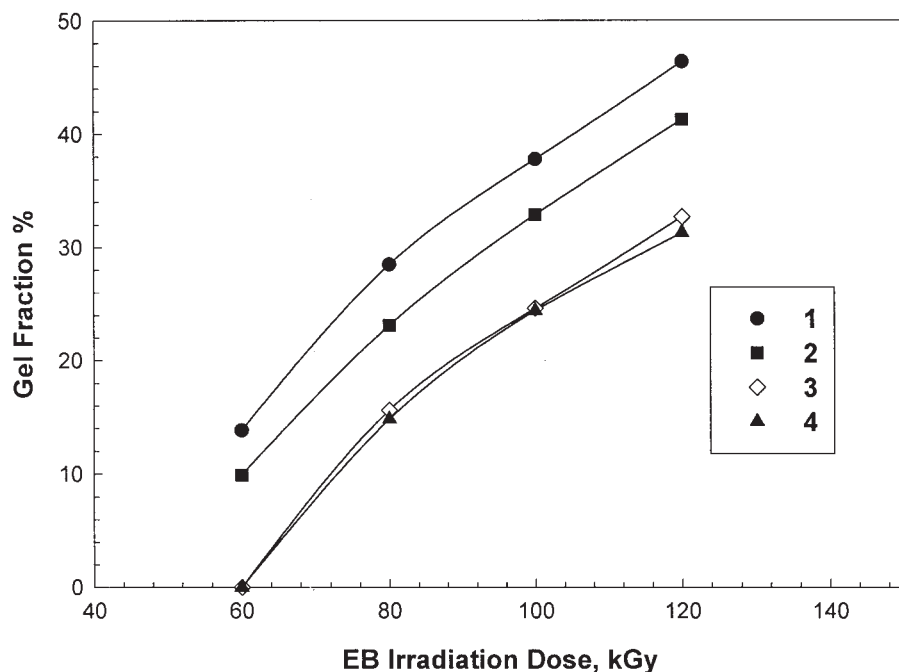


Figure 1 Gel fraction as a function of the EB-irradiation dose for different LDPE formulations (pure LDPE and composites with Irganox, citric acid, or both).

and standard deviations of five specimens representing the values of the tensile strength and ultimate elongation at break were recorded.

Fourier transform infrared (FTIR) spectrometry analysis

An ATI Mattson Genesis series (Madison, WI) FTIR spectrometer was used for scanning and measuring

the absorption spectra at a resolution of 16 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.

Thermogravimetric analysis (TGA)

TGA was carried out with a TG-50 instrument from Shimadzu (Tokyo, Japan) at a heating rate of 10

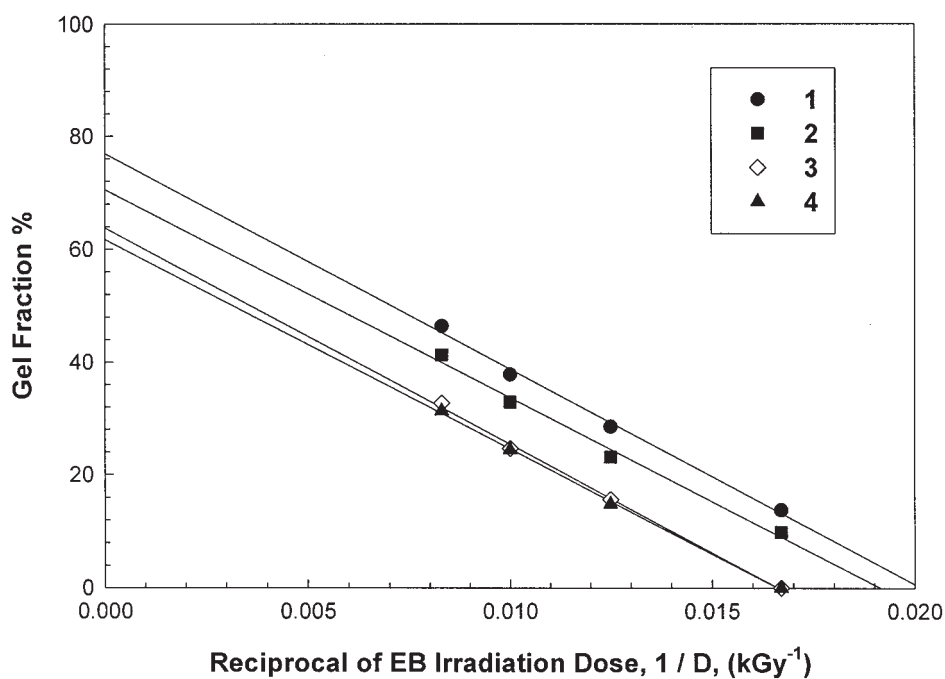


Figure 2 Gel fraction as a function of $1/D$ for different LDPE formulations (pure LDPE and composites with Irganox, citric acid, or both).

TABLE I
 g_{\max} , D_{gel} , and $G(s)/G(x)$ Values of the Investigated
 LDPE Formulations

Sample	g_{\max} (%)	D_{gel} (kGy)	$G(s)/G(x)$
1	77	50	0.784
2	71	54	0.984
3	64	61	1.014
4	61	61	1.048

K/min under a nitrogen atmosphere. The nitrogen flow was kept at a constant rate of 20 mL/min to prevent the thermal oxidation of the polymers. The TGA curves were taken from room temperature to 600°C. The primary TGA thermograms were used to determine the different kinetic parameters, such as the decomposition temperature (T_d) at different weight losses, the onset temperature (T_i) at which the decomposition reaction started, the inflection temperature point (T_f), the temperature at which the rate of the thermal decomposition reaction (dw/dt) reached its maximum (T_s), and the activation energy [E^* (kJ mol⁻¹)].

RESULTS AND DISCUSSION

Gel fraction dependence on the EB irradiation dose

The degree of crosslinking for EB-irradiated pure LDPE, LDPE/Irganox, LDPE/citric acid, and LDPE/Irganox/citric acid formulations was determined by the gel content at various irradiation doses of acceler-

ated electrons, as shown in Figure 1. The gel content for all the samples gradually increased as the irradiation dose was increased up to 120 kGy. The highest gel content obtained for all the irradiated samples at 120 kGy ranged between 30 and 50%. All the modified samples (LDPE 2, LDPE 3, and LDPE 4) had lower gel contents than pure LDPE. The smallest reduction of the gel content was observed for the LDPE/citric acid formulation (sample 2, which contained 1% citric acid). In addition, the biggest reduction of the gel content was observed for the samples containing different ratios of citric acid and Irganox 1010 (samples 3 and 4). Also, the gel contents for these formulations were quite close to each other. Furthermore, the incorporation of 1% citric acid in the presence of Irganox had no significant effect on the enhancement of the gel content; this was due to the retardation effect on the radiation-induced crosslinking reaction.

Through the plotting of the gel fraction percentage versus the reciprocal of the irradiation absorbed dose [$1/D$ (kGy⁻¹)], the maximum gel content (g_{\max}) was obtained by extrapolation to an infinite dose, that is, $1/D = 0$, as shown in Figure 2.^{6,7} The crosslinking efficiency (g_{\max}) was reduced from 77% for pure LDPE to 61% for the PE sample incorporated with citric acid and Irganox, as shown in Table I.

When PE is subjected to ionizing radiation, crosslinking and chain scission possibly exist. The processes ultimately cause the formation of an insoluble gel if crosslinking predominates over chain scission. Charlesby and Pinner⁶ obtained an expression relating the sol fraction (S) to D :

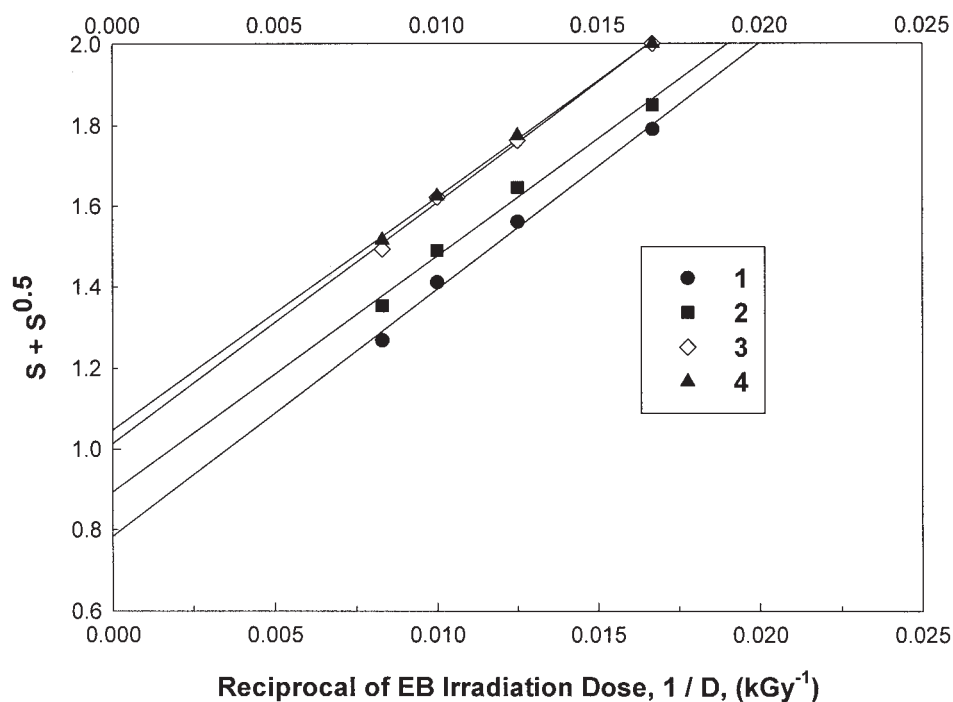


Figure 3 Charlesby–Pinner plots for different LDPE formulations crosslinked by EB irradiation.

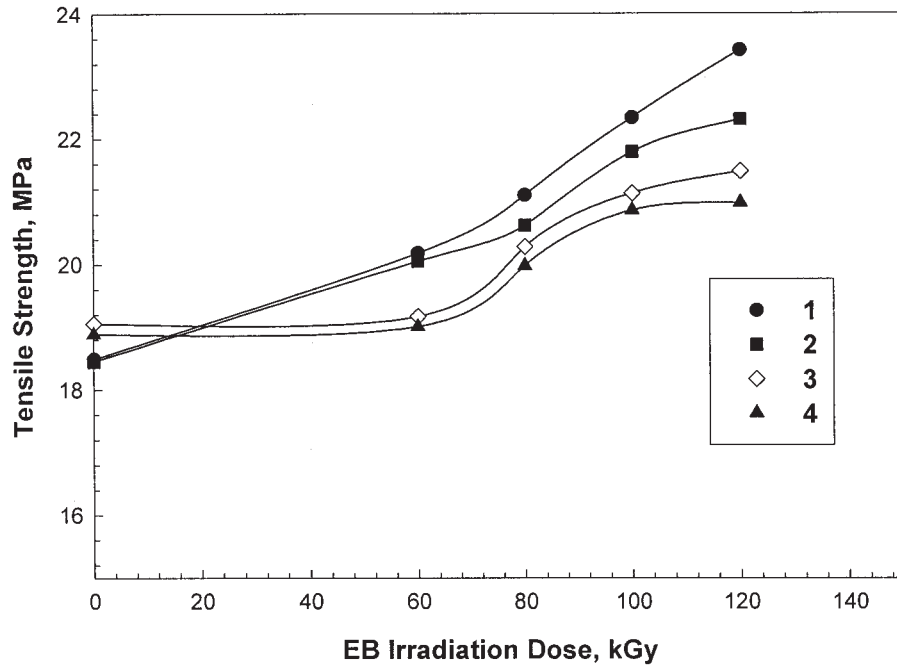


Figure 4 Tensile strength as a function of the irradiation dose for different LDPE compositions with Irganox, citric acid, or both.

$$S + (S)^{0.5} = p_0/q_0 + 2/q_0\mu D$$

where p_0 is the degradation density (average number of main-chain scissions per monomer unit and per irradiation dose unit), q_0 is the crosslinking density (proportion of monomer units crosslinked per dose unit), and μ is the initial weight-average degree of polymerization.^{6,7} A plot of $S + S^{(0.5)}$ versus $1/D$

(kGy^{-1}) is linear, with the intercept at $1/D = 0.0$ equal to p_0/q_0 . The dose corresponding to the beginning of gelation is called the gelling dose (D_{gel}), and it was obtained from the extrapolation of a conventional Charlesby-Pinner plot to $S + S^{(0.5)} = 2$, as shown in Figure 3. The value of D_{gel} increased because of the incorporation of PE with citric acid, Irganox, or both; the lowest value of D_{gel} was observed for pure LDPE

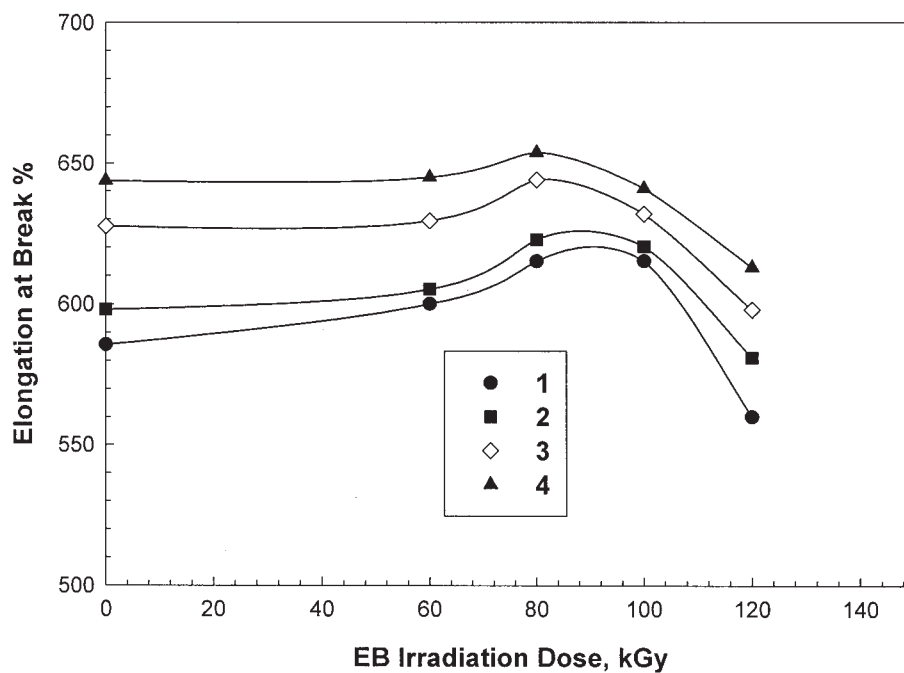


Figure 5 Elongation at break as a function of the irradiation dose for different LDPE formulations (pure LDPE and composites with Irganox, citric acid, or both).

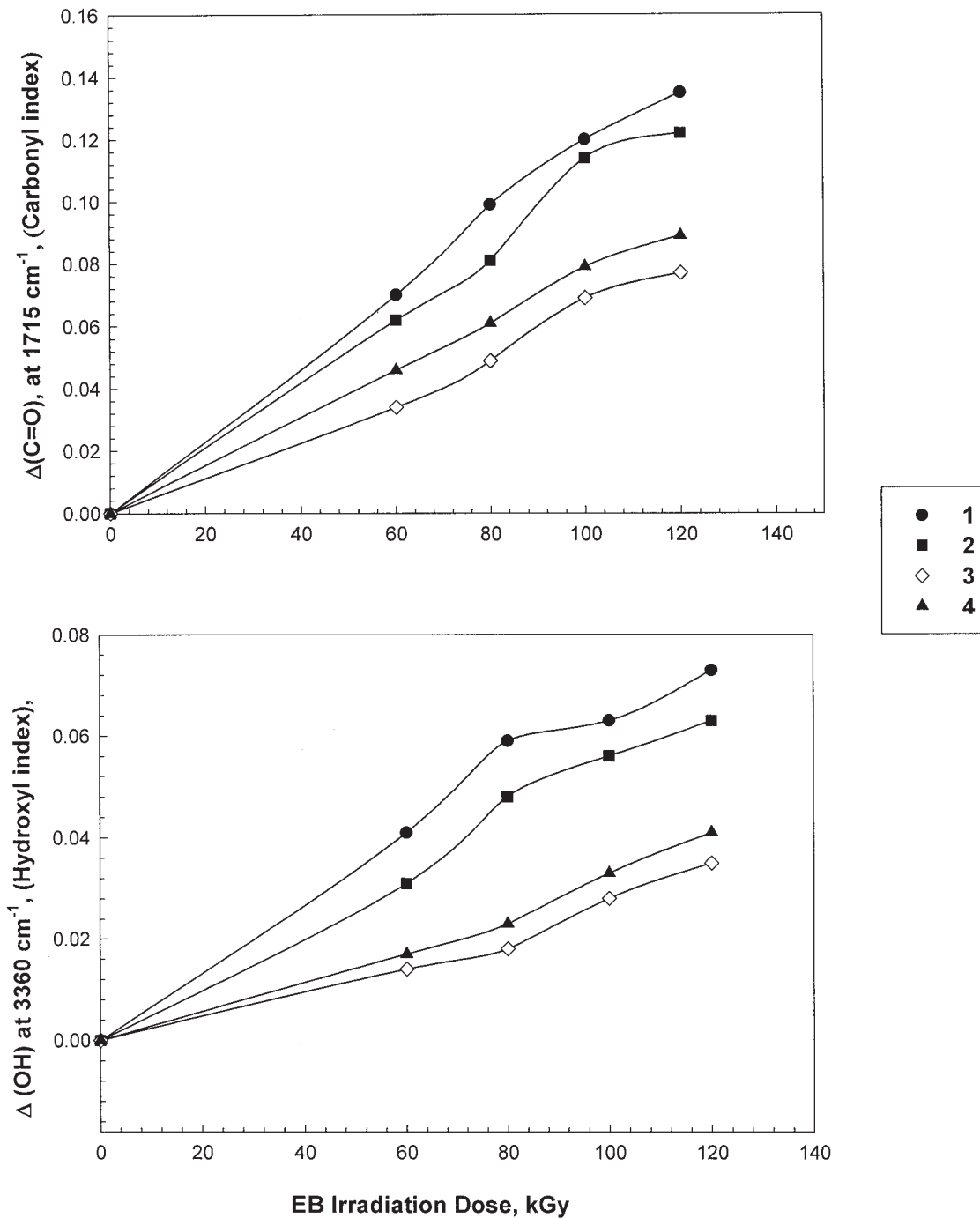


Figure 6 Changes in the carbonyl and hydroxyl indices as a function of the irradiation dose for different LDPE formulations (pure LDPE and composites with Irganox, citric acid, or both).

and LDPE compounded with citric acid alone, as shown in Table I. Apparently, in all the LDPE formulations, the basic effect was an increase in D_{gel} in the presence of stabilizers and an increase in the $G(s)/G(x)$ ratio. $G(s)$ and $G(x)$ are the numbers of chain scissions and crosslinks produced per 100 eV of absorbed radiation energy, respectively. The effect may be mainly attributed to the reduction of the $G(x)$ values, except in the presence of citric acid; there, $G(s)$ probably increased. From the obtained swelling parameter data,

we can say that the compounding of the LDPE sample with citric acid alone caused a slight increase in the D_{gel} value and a lowering of the rate and level of gelation, and this led to a lower crosslinking density. This change in the swelling parameter became higher for samples containing citric acid, Irganox, or both. Also, all corresponding swelling parameter values for stabilized LDPE samples (i.e., formulations containing citric acid, Irganox, or both) were lower than those of unstabilized samples. Therefore, the irradiated

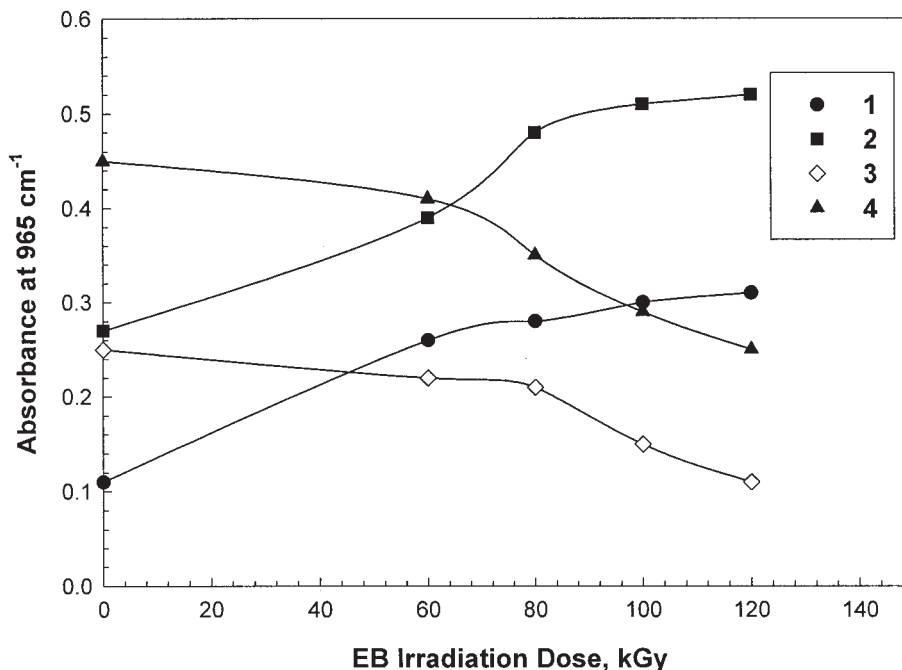


Figure 7 Absorbance intensity of the *trans*-vinylene double bond as a function of the irradiation dose for different LDPE formulations (pure LDPE and composites with Irganox, citric acid, or both).

pure LDPE samples were susceptible to radiation crosslinking, whereas the compounded samples with a stabilizer, a modifier, or both were less susceptible.^{4,6,8}

For the antioxidant Irganox 1010 and the stabilizer citric acid, the following generalizations may be made:

1. Their presence postponed the beginning of gelation.
2. With a change in the additive content, the probability of scission with respect to crosslinking $[G(s)/G(x)]$ increased.
3. The radiolysis of PE containing an antioxidant often led to a rapid loss of antioxidant activity with significant inhibition of radiation crosslinking.

On the other hand, citric acid, acting as a stabilizer (radical scavengers), a modifier (crosslinking agent), or both accelerated the gelation at lower irradiation doses in comparison with that of samples containing an antioxidant.

It is generally believed that PE undergoes significant chain scission and crosslinking upon irradiation. If this is the case, the incorporation of any stabilizer, such as citric acid (which has an inhibitory effect; that is, citric acid is a scavenger for radiolytic crosslinking but not chain scission), into PE should cause the resin to exhibit a lower gel content than it would if it did not contain the stabilizer.² Even if an antioxidant also inhibited chain scission, it would still cause a difference in the response

because crosslinking in PE is a bimolecular process involving a reaction between two (migrating) secondary alkyl radicals, whereas chain scission is a unimolecular process. Thus, crosslinking would be much more susceptible to inhibition than chain scission. This is consistent with the hypothesis that the presence of the antioxidant inhibits part of the reaction induced by radiation, delaying the growth of crosslinking density. The net effect of the addition of an antioxidant is neutralizing some of the reactions induced uniformly throughout the radiation process.^{3,9}

Tensile mechanical properties

Mechanical properties are very important in assigning useful applications of PE formulations for specific purposes. In particular, the tensile strength, elongation at break, and modulus of elasticity are primary characteristics of a polymer film for the determination of its general applications in a wide range of fields. Changes in the mechanical properties are strongly related to radiation-induced chemical reactions, such as chain scission and the formation of crosslinks through excitation, ionization, the formation of active species, and their reaction.^{10,11}

The variation of the tensile strength with the irradiation dose is shown in Figure 4. The tensile strength increased with increasing irradiation dose as a result of the dominance of crosslinking over chain scission. The crosslinking efficiency of the LDPE formulations

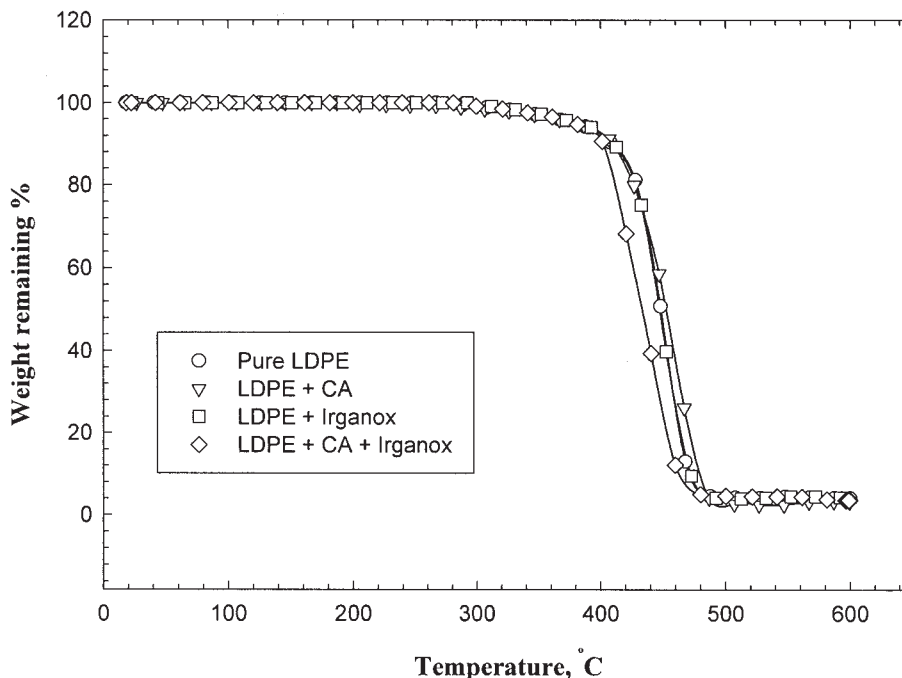


Figure 8 TGA thermograms for different LDPE formulations (pure LDPE and composites with Irganox, citric acid, or both).

decreased because of inhibition via radical scavenging by the incorporated additives. This can be clearly seen from the lower values of the tensile strength for the LDPE formulations containing stabilizers in comparison with those of the pure LDPE sample.

The elongation at break of the LDPE formulations as a function of the irradiation dose is given in Figure 5. There was a slight increase in the elongation at break with an increasing irradiation dose up to 80 kGy, and then it tended to decrease as the irradiation dose was increased up to 120 kGy. The lowest value of the elongation at break was observed for pure LDPE samples. The elongation at break of LDPE blended with citric acid alone showed the lowest response in comparison with those of the other stabilized formulations. These results agreed with the gel fraction measurements, proving that the stabilizers (citric acid and Irganox 1010) affected the radiation-induced crosslinking of PE to some extent.

The influence of irradiation on the mechanical properties of polymers has been established to depend on polymer crosslinking or degradation. Radiation-induced degradation always degrades the mechanical properties, whereas radiation crosslinking may improve the mechanical properties of polymers. Also, the stabilization of LDPE reduces chain scission (i.e., oxidative degradation) and consequently improves the elongation at break. In this respect, stabilizers such as Irganox 1010 and citric acid retard oxidative degradation through rapid free-radical scavenging (radical-radical termination) in the presence of radiation, and this helps to inhibit or reduce the oxidative chain scission.¹²⁻¹⁴

FTIR spectroscopy analysis

The changes in the intensities of the absorption bands characteristic of the carbonyl and hydroxyl groups were followed by the absorption peaks at 1715 and 3360 cm^{-1} , respectively. The absorption peak at 724 cm^{-1} was chosen as a reference for all the investigated LDPE formulations because its intensity did not change during EB irradiation.¹⁵ The carbonyl and hydroxyl indices of these peaks were calculated by the division of the intensities of the absorption of the characteristic peaks by the absorption of the reference peak. The changes in the difference of the calculated values before and after the irradiation of the carbonyl and hydroxyl indices [$\Delta(\text{C}=\text{O})$ and $\Delta(\text{O}-\text{H})$] of the LDPE formulations as a function of the EB-irradiation dose are shown in Figure 6. Irganox was more effective than citric acid. In other words, the LDPE formulation containing 1.0% Irganox had the highest retarding oxidation effect, that is, the lowest values of the $\text{C}=\text{O}$ and $\text{O}-\text{H}$ indices. Also, the pure LDPE formulation had the highest oxidation level. The changes in the levels of the carbonyl and hydroxyl indices could be attributed to the type of added stabilizer and its concentration.

TABLE II
 T_d ($^{\circ}\text{C}$) Values of the LDPE Formulations at Different Weight Losses

Sample	2%	10%	50%	80%	90%
1	285	389	432	452	462
2	332	409	454	470	495
3	328	406	448	466	478
4	316	400	443	461	478

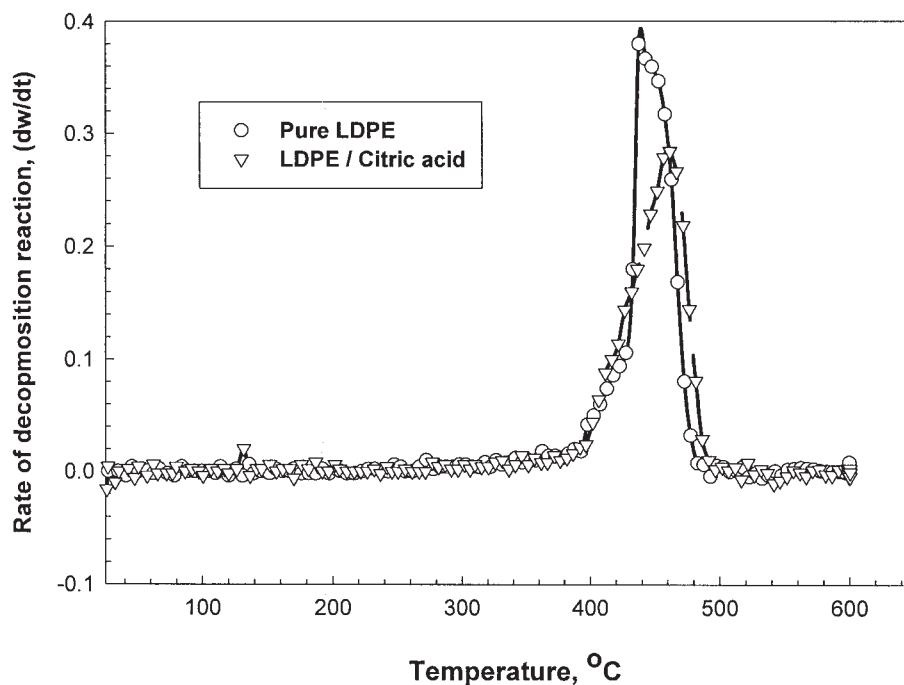


Figure 9 dw/dt as a function of the temperature for pure LDPE and LDPE/citric acid compositions.

It has previously been shown that phenolic-type antioxidants such as Irganox 1010 are capable of stabilizing polymers against radiation-induced oxidative degradation, and they are converted into their corresponding nonreactive species by radical scavenging.^{1,3} The data show that Irganox 1010 strongly retards the formation of carbonyl and hydroxyl groups at different irradiation doses, whereas citric acid accelerates the crosslinking reaction.

Figure 7 shows the changes in the *trans*-vinylene absorption peak at 965 cm^{-1} for the investigated samples, this being considered a reliable measure of the radiation-induced crosslinking of PE. There were large differences in the absorbance values at 965 cm^{-1} for the different unirradiated LDPE samples. This could be attributed to the variation of the composition and structure of the investigated LDPE formulations. The obtained data show that the intensity of the *trans*-vinylene unsaturation of the pure LDPE and LDPE formulation containing 1% citric acid increased with increasing irradiation dose. In addition, the LDPE/citric acid composite showed the highest value of the absorption peak intensity, that is, the highest level of radiation-induced crosslinking. On the other hand, the data obtained for the other stabilized LDPE formulations (samples 3 and 4) decreased with an increasing irradiation dose. This could be attributed to the reduction of radiation-induced crosslinking.

TGA

The effect of stabilization with Irganox 1010 and citric acid on the thermal decomposition behavior of the

LDPE samples was investigated with TGA. Figure 8 shows the initial TGA thermograms for the thermal decomposition of the LDPE samples irradiated at a dose of 100 kGy of accelerated electrons. The TGA thermograms indicate that all the investigated LDPE formulations underwent thermal decomposition in a similar manner; the major weight loss occurred within the temperature range of 350–480°C. The T_d values at different weight losses for the samples are summarized in Table II. Up to a 90% weight loss, the LDPE samples stabilized with citric acid, Irganox, and their mixtures showed higher thermal stability than pure LDPE. However, the LDPE formulation with citric acid alone possessed higher thermal stability than those containing Irganox or a mixture of the two.

The efficiency of citric acid as a thermal stabilizer, compared with that of Irganox, may be explained by the average dissociation energy of the bonds forming the stabilizers. It has been reported that the heating of citric acid up to 150°C results in the formation of aconitic acid through the elimination of water molecules:¹⁶

TABLE III
 T_i, T_s, T_f, E^*

Sample	T_i (°K)	T_s (°K)	T_f (°K)	Weight loss (%) at T_s	E^* (kJ/mol)
1	272	435	400	66	200.1
2	283	439	408	47	233.6
3	307	458	420	31	216.2
4	310	462	425	27	219.3

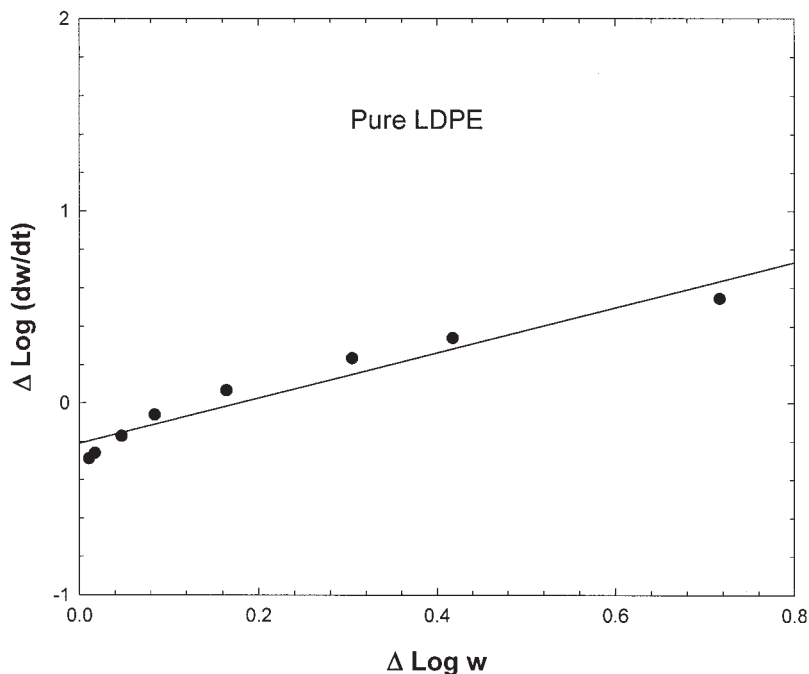
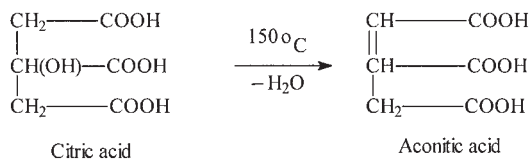


Figure 10 Temperature dependence plot of $\Delta \log dw/dt$ versus $\Delta \log w$ for pure LDPE.



The LDPE formulation containing citric acid possessed higher thermal stability than the formulation

containing Irganox. Irganox is considered a sterically hindered phenolic antioxidant, whereas citric acid acts here as a modifier or crosslinking agent. The steric hindrance effect of Irganox has a pronounced effect on the lowering of thermal stability. On the other hand, the modification of LDPE induced by the addition of citric acid in the presence of EB radiation is responsible for the enhancement of the thermal stability.

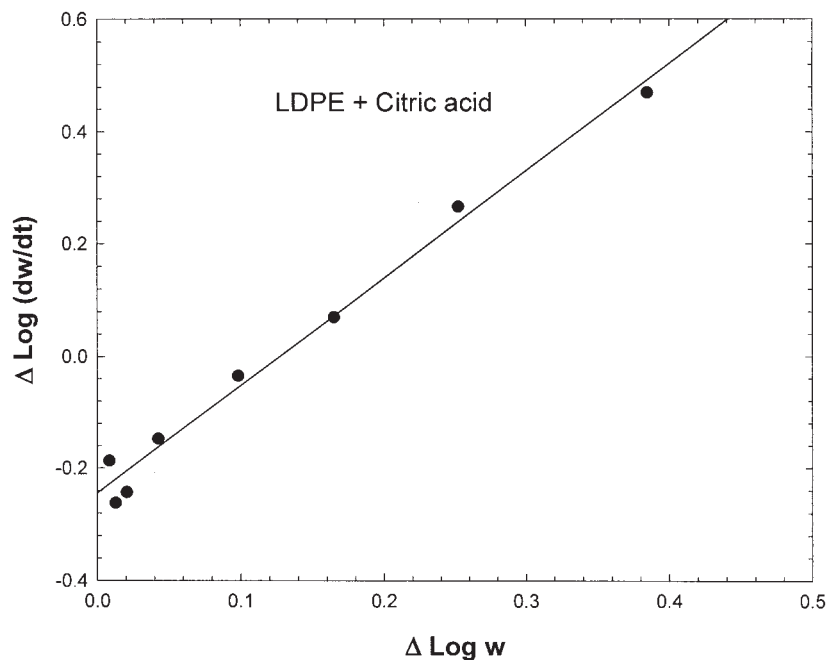


Figure 11 Temperature dependence plot of $\Delta \log dw/dt$ versus $\Delta \log w$ for LDPE composites with citric acid.

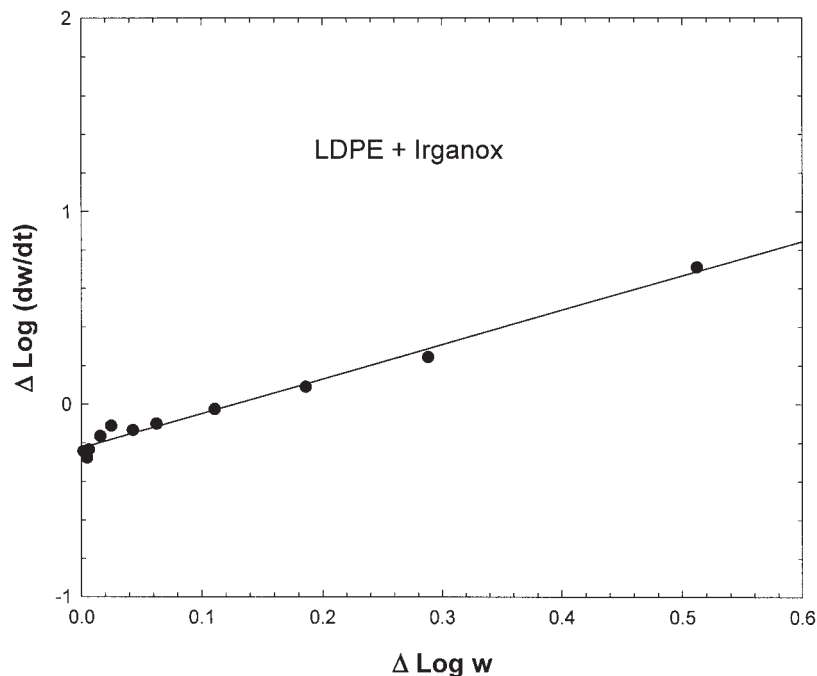


Figure 12 Temperature dependence plot of $\Delta \log dw/dt$ versus $\Delta \log w$ for LDPE composites with Irganox.

dw/dt is plotted versus T_d for pure LDPE and LDPE/citric acid formulations irradiated at 100 kGy in Figure 9. All the LDPE formulations showed only one maximum with increasing T_d , and this could be attributed to the decomposition of the LDPE formulations. T_i , T_f , and T_s are summarized in Table III. The LDPE/citric acid formulation started to decompose at a higher temperature than the other LDPE formulations. These results agreed

with the obtained data representing the T_d values at different weight losses (see Table II).

The TGA thermograms of the different LDPE formulations showed that the majority of the thermal decomposition reactions occurred in the temperature range of 350–480°C; the weight loss increased from 5 to 95%. The thermal stability of the different LDPE formulations was further investigated by the calculation of the kinetic pa-

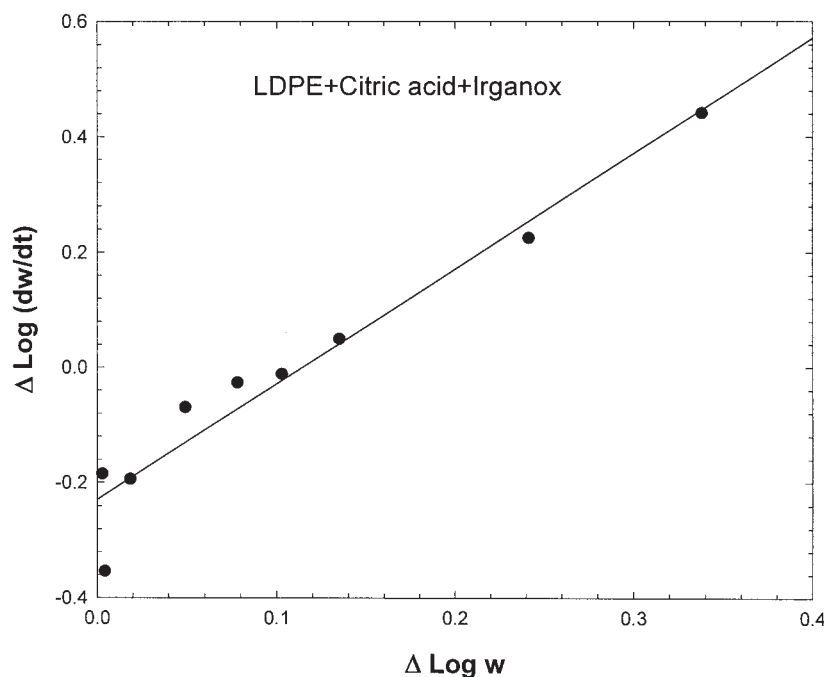


Figure 13 Temperature dependence plot of $\Delta \log dw/dt$ versus $\Delta \log w$ for LDPE composites with a mixture of citric acid and Irganox (equal ratio).

rameters of thermal decomposition, such as E^* and the order of reaction, with the Anderson and Freeman method.^{17,18} This method involves the calculation of the quantities $\Delta \log(dw/dt)$ and $\Delta \log w$ [where w is the reactant weight (mg)] corresponding to a small constant difference in the temperature from the initial TGA thermograms. The linear relationship correlating these quantities is given by the Anderson–Freeman equation as follows:

$$\Delta \log(dw/dt) = n\Delta \log w - (E^*/2.303R)[\Delta(1/T)]$$

where n is the order of the thermal decomposition reaction, R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and T is the absolute temperature. When $\Delta \log(dw/dt)$ was plotted versus $\Delta \log w$, it yielded a straight line of slope n , and the intercept was E^* .^{19,20} Plots of $\Delta \log(dw/dt)$ versus $\Delta \log w$ over the entire temperature range are shown in Figures 10–13. The calculated E^* values for all the LDPE formulations are presented in Table III. On the basis of these values, it may be concluded that the LDPE formulation stabilized with citric acid possessed the highest thermal stability. This may be attributed to the stabilization of the LDPE/citric acid formulation through induced crosslinking during EB irradiation. In other words, the formation of more compact three-dimensional structures as a result of irradiation can improve the thermal stability. Also, the irradiation of LDPE formulations in the presence of an antioxidant or stabilizer can reduce, to some extent, chain scission because of the action of radical scavengers produced from the additive.²¹

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