

TGA Analysis of γ -Irradiated Linear Low-Density Polyethylene

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ABSTRACT: Linear low-density polyethylene (LLDPE), based on butene-1 or hexene-1, was irradiated with γ -rays under vacuum or in the presence of air. The study focused on the influence of the dose rate and the γ -dose on the thermal properties of LLDPE. Differential scanning calorimetry, thermogravimetric analysis (TGA), and TGA/FTIR techniques were used to address the thermal behavior as a result of γ -irradiation. During this irradiation, competition between crosslinking and scission reactions, subsequent to oxidation reactions, occurred in the polymeric material, which strongly depends on the experimental conditions. A decrease of the crystallinity for γ -irradiated samples was

observed in particular for samples irradiated under vacuum. This observation may be explained by increased hindrance of segment mobility due to crosslinking reactions that prevent crystal growth. TGA investigations revealed an enhancement of the thermal stability for samples irradiated under vacuum but not for those irradiated in air. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2790–2795, 2006

Key words: linear low-density polyethylene; γ -irradiation; thermogravimetric analysis; differential scanning technique; Fourier transform infrared; thermal stability

INTRODUCTION

For the past few years γ -oxidation of polyolefins has gathered the attention of many research groups because of its practical and fundamental importance. γ -Irradiation has the advantage of being a clean method with good control, because the production of radicals can be identified and quantified,¹ and due to the linear production of oxidation products, γ -oxidation has helped lead to an understanding of several mechanisms of oxidation.^{2,3} In more recent times, sterilization of plastic medical equipment, with γ -rays, is gaining ground over other techniques such as autoclaving or the use of ethylene oxide. Nuclear plants and irradiation facilities may use equipment made of polymeric materials that can experience modifications in use. The effects of γ -irradiation on polymers may involve chemical modification (crosslinking, chain scission, and double bond formation, etc.) and mechanical changes (Young's modulus, elongation at break, etc.).

We have previously studied the γ -oxidation of polypropylene (PP) and linear low-density polyethylene (LLDPE) using the FTIR procedure coupled with chemical derivatization (SF₄ and NO treatments).^{4,5} These studies were performed using different dose rates of irradiation. Figure 1 illustrates concentration

changes in the oxidation products in response to different integrated doses. To avoid overloading the figure, only ketone and secondary hydroperoxide plots are displayed but the tendency is the same for most oxidation products quantified. The kinetic accumulation of oxidation products increases when the dose rate decreases. Our findings clearly establish that the degradation is much more severe at a low dose rate than, at a high rate. We hypothesized that, at high dose rates, one should expect an excess production of alkyl radicals that steadily combines before they can be reached by oxygen molecules to propagate the oxidation and thus favor crosslinking over oxidation. On the other hand, macroradicals generated at a low dose rate combine easily with oxygen, leading to oxidation products.

The direct consequence of this is a much higher production of oxidation products at low dose rate as shown in Figure 1.

The objective of this work is to verify this hypothesis using thermogravimetric analysis (TGA). This technique has proved to be very useful for studying the thermal stability of polymers. Since it is commonly believed that a crosslinked polymer will be inherently more thermally stable than the corresponding thermoplastic polymer,⁶ TGA is an appropriate technique. We shall discuss thermal properties, such as degree of crystallization, specific melting enthalpy, melting temperature of unirradiated and irradiated LLDPE, using differential scanning calorimetry (DSC).

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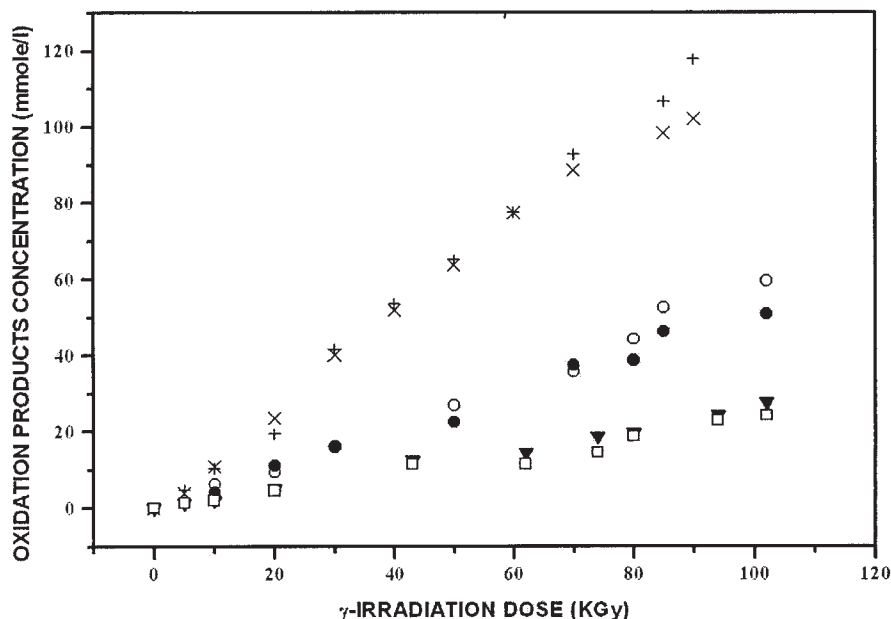


Figure 1 Kinetic accumulation of LLDPE γ -initiated oxidation products at different dose rates. At 7.2×10^{-2} KGy/h: ketone (+), secondary hydroperoxide (\times); at 0.72 KGy/h: ketone (O), secondary hydroperoxide (●); at 3.6 KGy/h: ketone (▼), secondary hydroperoxide (□).

EXPERIMENTAL

Polymers

Linear low-density polyethylene (LLDPE), based on butene-1 (containing 9 ethyl branches per thousand carbon atoms) or hexene-1 comonomer (containing 8.1 butyl branches per thousand carbon atoms), was provided in the form of a thin film by Exxon. Characteristics of the LLDPE samples have been described later.⁷ These samples have a Melt Index (g/10 min) ranging from 0.7 to 2.8, a density (g/cm³) ranging from 0.917 to 0.926, and an oxygen permeability (L m⁻² atm⁻¹(24 h)⁻¹) varying from 0.52 to 1.26. The samples contained a processing antioxidant partially extracted by acetone in 48-h Soxhlet washing.

Degradation conditions

Specimens were irradiated at room temperature with γ -rays from ⁶⁰Co source at the Hahn-Meitner Institute, Berlin. Irradiations were performed both under vacuum and in the presence of air, since it has been established that the efficiency of crosslinking increases in vacuum, while the radiative oxidation and subsequent destruction of macromolecules is intensified when polyethylene is irradiated in the presence of oxygen.⁸ For the series under vacuum, the samples were placed in glass ampoules that were subsequently evacuated and sealed off from the vacuum line. A brief exposure to air was inevitable for the specimens irradiated in vacuum when transferred to TGA and FTIR equipment. For the sake of uniformity, samples

irradiated in air were also placed in glass ampoules with an open top. Two irradiation dose rates were used: 1.98 and 0.15 KGy/h. Films of 100 μ m thickness were used since our earlier studies, dealing with the γ - and photo-oxidation of these films, did not show any oxygen control process. This means that no oxygen starvation occurred during the oxidation.

Analytical procedure

FTIR spectroscopy was obtained using a Nicolet instrument 560 Magna instrument at a 4 cm⁻¹ resolution. The absorbance at 1715 cm⁻¹ was used to evaluate the level of oxidation after γ -irradiation in terms of accumulation of carbonyl groups (ketone and carboxylic acid).⁴ TGA was performed using an Omni-therm 1000 unit under a flowing nitrogen atmosphere at a scan rate of 10°C per minute between 20°C and 600°C. DSC runs were performed with the aid of a Seiko DSC 220C in nitrogen atmosphere; samples were heated from 20°C to 200°C at a heating rate of 10°C/min and then cooled at the same rate. The reproducibility of temperature measurement on both the TGA and the DSC was $\pm 3^\circ\text{C}$. TGA/FTIR experiments were performed using a TGA/SDTA 851 (Mettler/Toledo) coupled with a FTIR-spectrometer Nexus 470 (Nicolet). Samples of 15–20 mg were heated at 10°C/min to a maximum temperature of 600°C in a flowing air atmosphere to evaluate the thermal oxidation, and the infrared spectra of the volatile products of decomposition were recorded in the 400–4000 cm⁻¹ range.

TABLE I
Effect of Dose and Dose Rate on DSC Properties of Polyethylene

γ -Dose/dose rate (K Gy)/(K Gy/h)	$T_{\text{onset of melting}}$ (°C)	T_m (°C)	ΔH_m (J/g)	X (%)	$T_{\text{onset of cooling}}$ (°C)	$T_{\text{peak of cooling}}$ (°C)	ΔH_c (J/g)
Irradiation in air							
0/0, 1st	120.3	126	151.6	52.3	113.6	73.2/113.6	-130.3
0/0, 2nd	120.4	127.5	149	51.4	—	—	—
25/0.15, 1st	120.4	126	155.5	53.6	114.3	73.6/112.3	-131.8
25/0.15, 2nd	120	127.1	151.7	57.3	—	—	—
25/1.98, 1st	121	127.6	138	47.6	113.2	72.6/111	-118.9
25/1.98, 2nd	120.2	128.6	134.1	46.2	—	—	—
100/0.15, 1st	120.5	126.3	157.3	54.2	113.7	72.6/111.7	-134.1
100/0.15, 2nd	120.9	127.4	153.2	52.8	—	—	—
100/1.98, 1st	121.1	126.9	155.2	53.5	113.7	71.5/110.7	-137.6
100/1.98, 2nd	120.2	128	152.3	52.5	—	—	—
Irradiation under vacuum							
25/0.15, 1st	120.4	127	145.1	50.1	114.1	71.7/111.8	-119
25/0.15, 2nd	121.7	128.3	135.2	46.6	—	—	—
25/1.98, 1st	121.3	126.1	147.5	50.9	114.1	73.3/112.4	-127.3
25/1.98, 2nd	119.7	127.3	143.4	49.5	—	—	—
100/0.15, 1st	120.5	126.4	157	54.1	114.3	71.7/111.5	-138.3
100/0.15, 2nd	121.3	127.5	154	53.1	—	—	—
100/1.98, 1st	120	127.2	133.3	46	113.4	75.2/111.1	-109.3
100/1.98, 2nd	115.5	125.9	123.2	42.5	—	—	—

H, specific enthalpy; X, the crystallinity calculated assuming the heating of fusion of perfectly crystalline PE to be 290 J/kg.

RESULTS AND DISCUSSION

Differential scanning calorimetry

The results obtained from DSC measurements are summarized in Table I. There is some tendency for increasing the melting temperature with radiation dose in all experimental conditions. This tendency is relatively obvious for high dose rate and vacuum atmosphere irradiation. Two peaks are observed in the cooling curves with the one at higher temperature being much larger than the lower temperature peak. The presence of two exotherms indicates a multiphase-system that is not affected by the γ -irradiation. A small decrease of crystallinity with the dose rate is observed for samples irradiated under vacuum with a dose rate of 1.98 K Gy/h. This observation may be explained by increased hindrance of segment mobility due to crosslinking reactions that prevents crystal growth. It has been reported that, since crosslinking occurs predominantly in the amorphous or fold-surface regions of polyethylene crystal rather than the crystalline phase, a large relative decrease in crystallinity is not expected in irradiated PE,⁹ if crosslinking reactions occur: this is the case here-in. On the other hand, for samples irradiated in air at low dose, an increase of crystallinity is first noticed, followed by a decrease. An opposite situation is observed during irradiation under air at high dose rate and under vacuum at low dose rate. Comprehensive explanation of these observations is difficult with the results in hand; additional experiments are necessary to elucidate these points.

In brief, our DSC results contradict earlier works^{10,11} that found a significant influence of γ -irradiation on DSC data of LLDPE irradiated till 2×10^3 K Gy dose. The low-integrated dose used in our study could be the main reason for this discrepancy.

Thermogravimetric analysis

The thermal stability of different LLDPEs has been studied by TGA. Classical one-step degradation curves were obtained. The onset temperature of the degradation, as measured by the temperature at which 10 and 50% mass loss occur - T_{10} and T_{50} , respectively-, are plotted in Figures 2 and 3. An increase of T_{10} and T_{50} , with γ dose for samples irradiated under vacuum at a dose rate of 1.98 K Gy/h, is observed. At the lowest dose rate, the corresponding temperatures increase first then decrease. This is not an artifact, since it has been observed on several samples tested in this study. These results indicate that the thermal stability of LLDPE samples γ -irradiated under vacuum is enhanced relative to the virgin material; this is understandable because under these conditions no oxidation can occur. This was confirmed from FTIR analysis by the absence of the 1720 cm^{-1} band corresponding to the production of carbonyl compounds (primarily carboxylic acids and ketones). Consequently, crosslinking reactions of radicals produced must be the major process that may lead to an improvement of the thermal stability of polymer through the formation of more compact three-dimensional structures. There is a significant difference between the two dose rates:

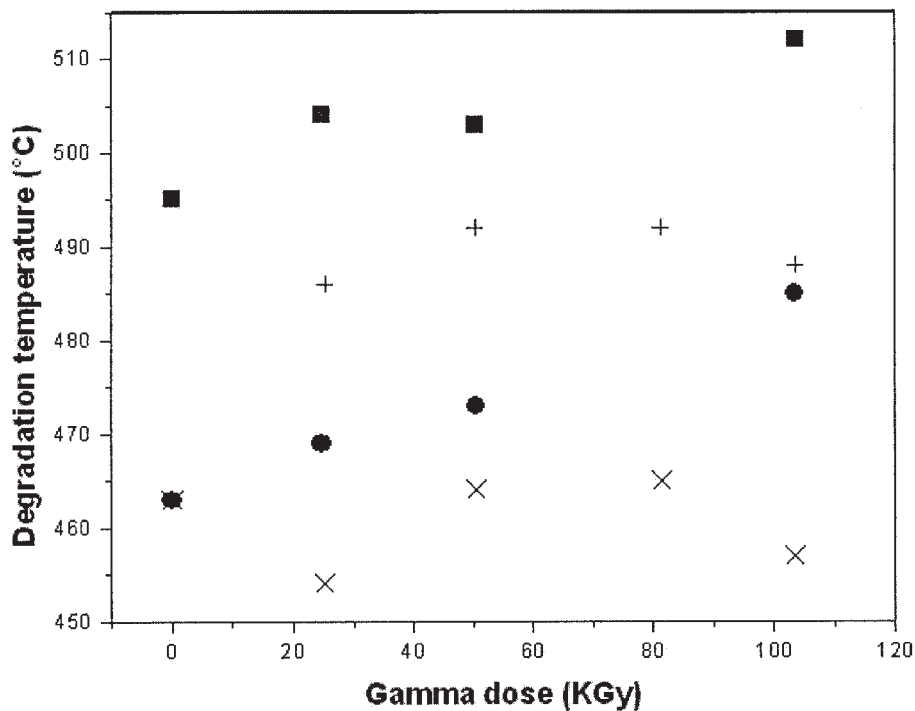


Figure 2 The onset temperatures of LLDPE γ -irradiated under vacuum or in air with a dose rate of 1.98 KGy/h: (■) T₅₀/vacuum, (+) T₅₀/air, (●) T₁₀/vacuum, (×) T₁₀/air.

at the low dose rate, the cross-linked structure does not persist, whereas at the higher dose rate it is persistent. Additional experiments are required to validate this assumption.

A decrease in thermal stability of samples γ -irradiated under air was observed whatever the dose rate. In air, the polymer undergoes oxidation according to a well-known mechanism.¹² Crosslinking reactions

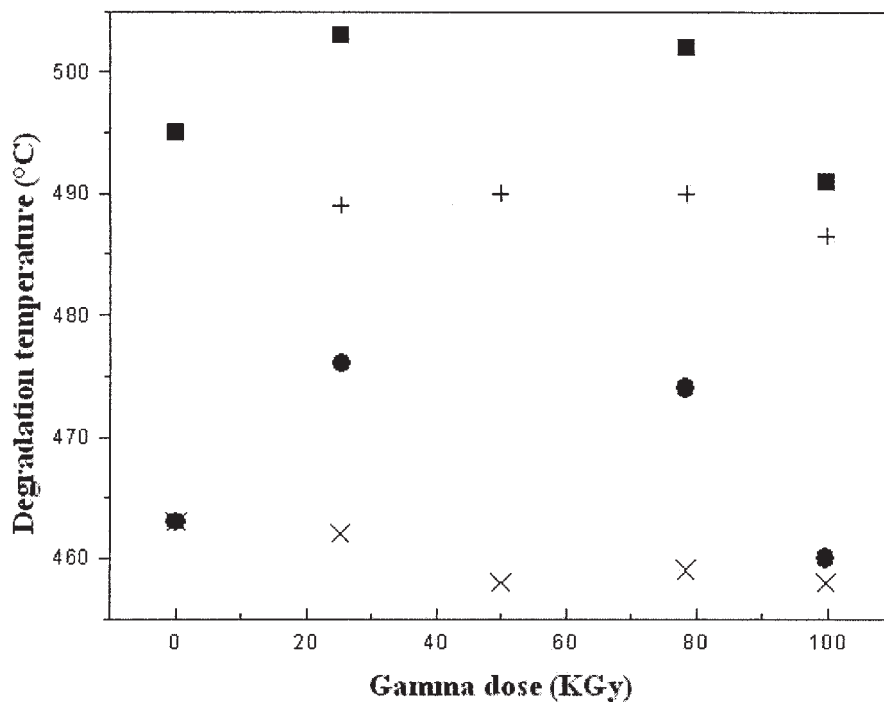


Figure 3 The onset temperatures of LLDPE γ -irradiated under vacuum or in air with a dose rate of 0.15 KGy/h: (■) T₅₀/vacuum, (+) T₅₀/air, (●) T₁₀/vacuum, (×) T₁₀/air.

TABLE II
TGA/FTIR Data for Virgin and γ -Irradiated LLDPE

γ -Dose/dose rate (K Gy)/ (K Gy/h)	T ₁₀ (°C)	T ₅₀ (°C)	DTGA (°C)	Absorbance at 1715 cm ⁻¹
Irradiation in air				
0/0	312	391	252, 335, 356, 395	0
25/0.15	314	364	209, 352, 361, 383	0
25/1.98	310	350	267, 334, 401, 452	0
100/0.15	300	420	255, 423	0.45
100/1.98	270	342	263, 325, 398, 429	0.52
Irradiation under vacuum				
25/0.15	385	430	390, 424, 438, 465	0
25/1.98	404	438	430, 441, 455, 516	0
100/0.15	359	422	389, 409, 465, 533	0
100/1.98	362	434	278, 332, 423, 467	0

may occur simultaneously but the chain scission reactions that accompany the oxidation reactions are more important and no improvement of thermal stability is observed.

Comparison of the onset temperature values, obtained for γ -irradiated samples using two different dose rates (1.98 and 0.15 K Gy/h), does not show significant differences except at high γ -dose. Indeed, at 100 K Gy, the onset temperature values in vacuum are much larger for samples irradiated at 1.98 K Gy/h than at 0.15 K Gy/h. These differences range from 13 to 96°C for T₁₀, from 10 to 21°C for T₅₀, and from 5 to 18°C for DTG. This result suggests that crosslinking reactions are more efficient at high dose rate than at low dose rate in vacuum. This effect is not observed for samples irradiated in air, because of the concomitant occurrence of oxidation and crosslinking reactions.

The results of TGA/FTIR in air atmosphere are summarized in Table II. It is worth noting that all samples decompose in a multi-step degradation process. One can also observe, in Table II, that the presence of air enhances the decomposition process with a shift of the onset temperatures toward lower values. Significant improvement in the thermal oxidation was observed for samples γ -degraded under vacuum relative to virgin LLDPE. The degradation of these samples commences at the point where that of virgin LLDPE is complete (this was clearly observed on the Gram-Schmidt reconstructions, not shown here). Samples irradiated at high dose rate present better results. This improvement is not linear, since a decrease of the onset temperatures is observed when the γ -dose is increased. This indicates that formation of weak links takes place simultaneously with crosslinking reactions. At a certain level of formation, these weak links may lower the thermal stability, even though crosslinking reactions have occurred. A detailed examination of the FTIR spectra obtained from the Gram-Schmidt reconstruction of LLDPE samples γ -irradiated under vacuum shows interesting features

(Fig. 4). The gaseous products released are identical during the major weight loss, whatever the dose rate (spectra A and B). The major bands, absorbing at 2361 and 2339 cm⁻¹, may be ascribed to carbon dioxide and carbon monoxide; a strong band at 2934 cm⁻¹, with shoulders around 2860 and 2968 cm⁻¹, indicates that most of the evolved gases are hydrocarbon in nature. In the carbonyl region, a broad band centered at 1731 cm⁻¹ appears; it is ascribed to carbonyl groups, such as carboxylic acid, lactone, and ketone. At the end of the decomposition, for samples γ -irradiated at high dose rate, the FTIR spectrum (D) reveals the formation of unsaturated groups, which are not seen at low dose rate (spectrum C). The major bands that appear can be attributed to vinylidene (878 cm⁻¹) and *cis*-vinylene (1287 cm⁻¹). The presence of unsaturation, in samples γ -irradiated at the high dose rate, could be another consequence of the high production of radicals, with disproportionation of the radicals being the route to explain their formation.⁴ This result suggests that, at the minimal sterilization dose of 25 K Gy, plastic medical devices made from polyethylene are more susceptible to produce unsaturations at high-dose rate than at low one. This could be of importance in many aspects in the choice of the conditions of sterilization of polymeric materials (dose rate, stabilizers, etc.).

CONCLUSIONS

In this report, changes in the γ -dose rate of irradiation on the thermal properties of LLDPE have been investigated. DSC shows that changes in crystallinity occur as a result of the irradiation. There is a tendency toward a decrease in crystallinity, which may be explained by the formation of a compact structure that prevents crystal growth. This effect is more apparent for samples γ -irradiated under vacuum. TGA investigations indicated an enhancement of the thermal stability for samples irradiated under vacuum, probably due to crosslinking reactions; an observation that is more pronounced at a high-dose rate. For samples

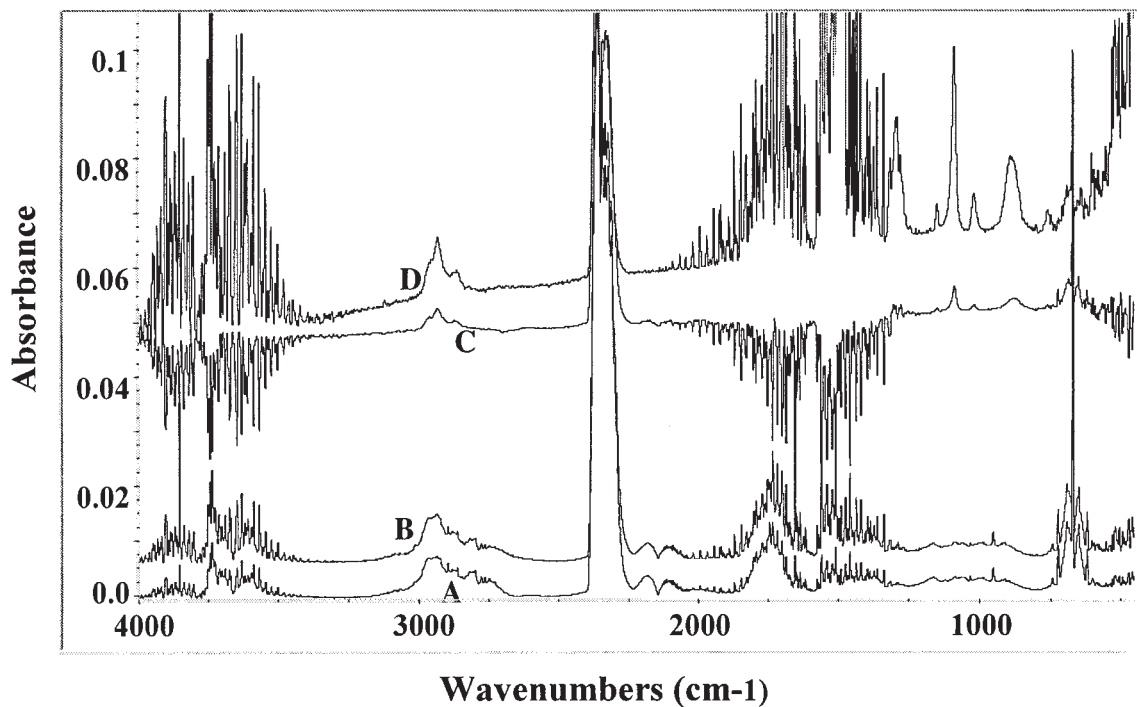


Figure 4 Infrared spectra of gaseous products at two different stages for LLDPE γ -irradiated till 25 KGy dose: at the major weight loss of decomposition, (A) and (B), corresponding to samples irradiated with 0.15 and 1.98 KGy/h, respectively; at the end of decomposition, (C) and (D) for low and high dose rates, respectively.

irradiated in air, crosslinking reactions are less important than chain scission reactions, regardless of the dose rate; the result is a decrease of the thermal stability. To get a better insight in to our results we think that additional experiments, such as ESR measurements, may be useful to validate our explanations.

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