Changes in Structural Characteristics of LLDPE Functionalized with DEM Using Gamma-Irradiation

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ABSTRACT: This work studies the structural changes produced by gamma-radiation as a source of free radicals for functionalizing linear low-density polyethylene (LLDPE) with diethyl maleate (DEM). The grafting of the DEM onto the LLDPE was carried out in solution using gamma-rays from a ^{60}Co source in air at room temperature, at a dose rate of 4.8 kGy/h and absorbed doses ranging from 15 to 400 kGy. The increase in the dose produced a higher concentration of free radicals and hence a higher grafting degree. The effects of DEM concentration are only perceptible at absorbed doses higher than 50 kGy. For a concentration of 30% DEM, the functionalization degrees ranged from 0.04 to 0.44 mol%. The use of gamma radiation modifies the structural and physical characteristics of the functionalized polyethylene with respect to the unmodified one, because, depending on the dose, the effects of gamma-rays can lead to crosslinking of materials with decreased flowability. The effects of gamma-radiation onto the molecular structure and molecular weight distribution of LLDPE are mitigated by the presence of DEM, due to the competition with the chain scission, branching and crosslinking reactions, for the consumption of the free radicals. The results provided by applying the successive self-nucleation and annealing technique allow reaching an unequivocal conclusion: that the free radicals formed by gamma radiation for the DEM insertion and main chain modifications are preferentially generated in the secondary carbons of the more regular —CH_2— sequences. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1106–1116, 2012

Key words: activation energy; crystallization; degradation; differential scanning calorimeter

INTRODUCTION

Functionalization is one of the methods more commonly used for the modification of the chemical structure of polymers. This method consists of inserting or grafting a monomer with functional groups into the main chain to generate interaction sites that allow improving compatibility with other materials through hydrogen bonding, covalent bonds or ionic interactions.[1–3] In most cases, this insertion is achieved by introducing unsaturated polar monomers by means of grafting reactions via free radicals in the presence of an initiator.

There are numerous studies[1–18] that have shown that polyolefin functionalization particularly that of polyethylene is one of the most promising alternates to increase chain polarity and achieve greater adhesion onto other materials. Pioneers in this area were Gaylord et al.,[7,8] who functionalized polyolefins with maleic anhydride at concentrations lower than 2 wt % in the presence of initiators of the peroxide type, obtaining a degree of insertion between 0.2 and 1.7 wt %.

Aglietto et al.[14,19] used diethyl maleate (DEM) for the functionalization of high-density and linear low-density polyethylenes (LLDPE) in solution. They used dicumyl peroxide as an initiator agent and DEM concentrations varying between 5 and 100 wt %. Functionalization degrees between 2 and 5 mol % were reported.

Rosales et al.,[5] Perera et al.,[9] Márquez et al.,[15] and Villarreal et al.[16] also studied the functionalization of LLDPE with DEM by means of reactive extrusion and observed that the grafting degree (GD) ranged between 0.1 and 0.6 mol %, which was attributed to the large amount of tertiary hydrogens in the LLDPE main chain. As these hydrogens are more labile, they favor the formation of a higher number of active sites at which DEM insertion could take place. They also determined that while tertiary hydrogens are more reactive, DEM is preferably inserted into

secondary carbons, due to the occurrence of two effects: a statistical factor that gives rise to a greater production of secondary radicals because chains have a lower quantity of tertiary carbons and a steric hindrance of the DEM molecule, which, due to its size, makes tertiary radicals' access more difficult.

Gamma radiation has been used as a precursor source of free radicals required to functionalize polymer chains because its high penetration power favors the formation of a large number of active sites, not only on the surface, but also throughout the entire polymer matrix.[20,21] When exposed to radioactive sources, polyethylenes may experience structural changes, including those in molecular weight and molecular weight distribution, crystallinity degree, unsaturations and branching, etc.[22,23] These changes, like in the case of thermal degradation, are the result of collateral reactions that take place as a consequence of the formation of free radicals.[21,24–26] The most important collateral reactions are those that directly affect molecular weight, such as chain scissions and crosslinking, which, even in low proportion, have a significant impact on the polymer's structure and properties.

Therefore, this work studies the structural changes produced in the polymer by γ-radiation as a source of free radicals for functionalizing LLDPE with DEM. The functionalization is carried out to increase its chain polarity, thereby improving its compatibility and surface adhesion onto other more polar polymers and fillers.

EXPERIMENTAL

A commercial LLDPE with a melt flow index (MFI) of 3.9–4.2 dg/min, supplied by Polynter, C. A. (Venezuela) was used. Solutions of the LLDPE were prepared at 10% wt/vol using a blend of *cis* and *trans* decahydronaphtalene (decalin) 99%, supplied by Riedel de Haën, as solvent. Ethanol and *n*-hexane were used as washing solvents. DEM, manufactured by Aldrich Chemical Company Sigma Aldrich (USA), was used as the functionalization monomer.

Functionalization of LLDPE

Solutions of LLDPE and DEM in decalin were prepared, under heating and continuous agitation, as follows: DEM (5, 10, 15, and 30 wt %) was added to the solution at 100°C and then the polymer was dissolved at 120°C.

Samples of these solutions were irradiated with γ-rays from a ^{60}Co source in air atmosphere at room temperature, at a dose rate of 4.8 kGy/h and absorbed doses ranging from 15 to 400 kGy.

After the exposure to the radiation source, ethanol was added to precipitate the functionalized polymer.

The extracted polymer was filtered and washed several times with *n*-hexane and dried in a vacuum oven at 60°C for ∼ 18 h.

Characterization of functionalized LLDPE

Fourier transform infrared spectroscopy (FTIR) spectra were taken from compression-molded films of the functionalized polymers and their GDs were determined by means of a reported ^{13}C NMR-FTIR calibration curve.[3] These spectra were recorded in a NICOLET Magna-IR 560 E.S.P. Spectrometer after 32 scans and at 2 cm^{-1} of nominal resolution. The peak area ratios (1740 cm^{-1}/1460 cm^{-1}) were estimated, considering the characteristic bands of DEM at 1740 cm^{-1} and that of polyethylene at about 1460 cm^{-1}, corresponding to the C=O stretching vibration and C—H bending vibration of CH_2, respectively. The GD was calculated from the results of three FTIR spectra of two different samples with a standard deviation of ∼2%. The efficiency of the monomer insertion was also calculated through the ratio of the initial monomer moles added into the solution and the GD obtained for each sample, calculated as mol percentage of DEM inserted into the polymer chains.

The characterization of the functionalized polymer was carried out as follows. Differential scanning calorimetry (DSC) was performed on a Metter Toledo DSC822 calorimeter. Samples were heated under nitrogen atmosphere from 25 to 170°C at 20°C/min and kept at 170°C for 3 min, in order to erase all previous thermal history. Then, the sample was cooled at 10°C/min from 170 to 25°C. Finally, a second heating was performed from 25 to 170°C at 10°C/min. The crystallinity degree (X_c) was calculated using the enthalpy of a perfect polyethylene crystal as a reference (293.6 J/g).

The same DSC calorimeter was used to carry out the successive self-nucleation and annealing (SSA) technique.[27] Once the thermal history of the sample was erased, it was heated at 10°C/min up to a selected self-seeding and annealing temperature (T_s), where it was isothermally kept for 5 min and then cooled down to 25°C. Then, the sample was heated again to a new self-seeding and annealing temperature, which was 3°C lower than the previous Ts and held there for 5 min before cooling it to 25°C at 10°C/min. This thermal treatment was repeated, being each T_s 3°C lower than the previous one, until the minimum temperature selected was reached. Finally, the sample was heated at 10°C/min up to 170°C and its thermogram was recorded.

Weight-average molecular weight and molecular weight distributions were determined by gel permeation chromatography (WATERS Alliance GPCV 2000) at 135°C with 1,2,4-trichlorobenzene as mobile

phase, using a calibration curve based on standard polystyrenes.

MFI measurements were taken from the irradiated and non-irradiated samples. A Ray Ran Advanced Melt Flow System with a weight of 2.16 kg was used at 190°C, according to ASTM D-1238 standard procedure.

Thermogravimetric analyses (Mettler Toledo TGA851) were carried out, using a heating rate of 20°C/min up to 700°C under N_2. The activation energy (E_a) and initial decomposition temperatures (T_{id}) were calculated from the data obtained, using the McCallum-Tanner method.[28]

Gel content of irradiated samples (ca. 1 g) was determined by Soxhlet reflux experiments after 72 h of extraction, using xylene as a solvent and cellulose extraction filters. After drying, the sample was weighed again and the gel content was calculated as a relative difference between the initial and final masses of the samples, as shown in eq. (1):

$$GC = \left[\frac{W_f - W_d}{W_i - W_d} \right] \times 100 \qquad (1)$$

where GC is the percentage of gel content, W_i is the initial total weight of the extraction filter plus the sample, W_f is the final total weight of the extraction filter plus the sample, and W_d is the weight of the filter.

The electron paramagnetic resonance (EPR) spectra were obtained in an X-Band EMX BRUKER spectrometer at room temperature. The total number of spins per gram total free radical concentration (TFRC) of the samples was obtained by performing, with the ORIGIN software, the second integral of the recorded spectrum and comparing it with that of the 4-(2-iodoacetamide)-2,2,6,6-tetramethylpiperidinoxyl radical, which was used as a comparison standard. The experimental conditions (microwave power and modulation field) were adjusted to avoid the effects of saturation in the EPR spectrum. No EPR signal could be obtained at zero doses, because of the detection limits of the spectrometer.

RESULTS AND DISCUSSION

Functionalization of LLDPE

Figure 1 shows that the concentration of radicals increases with the absorbed dose, because an energy increase implies that more active species are formed.[29] This study also included the evaluation of the decline of the concentration of radicals over time, after one month of storage, with a fast and remarkable consumption of active species after irradiation being observed.

The consumption of radicals basically involves two processes: a faster one in which radical species
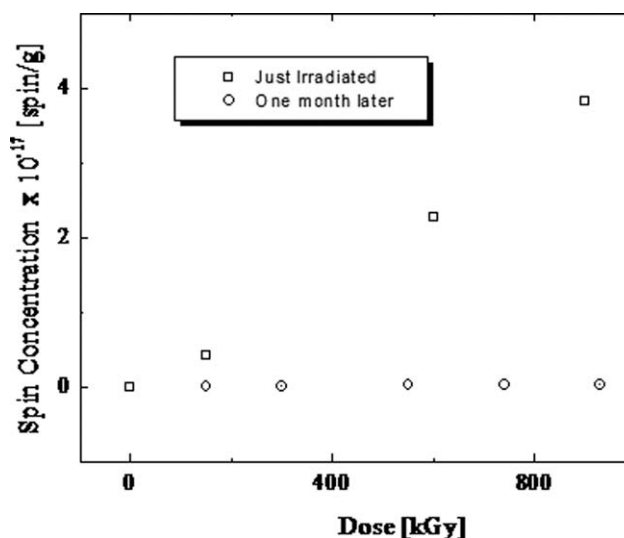

Figure 1 Free radical concentration in LLDPE at different doses.

formed in the amorphous phase are more easily recombined due to the higher chain mobility[30]; and a slower one according to Dole et al.,[31] in which radicals formed in the crystalline phase slowly migrate to the interface with the amorphous phase, where they finally react. This is why the decline of radicals takes place more rapidly in branched polyethylenes than in the linear ones, as shown by Albano et al.[29]

Therefore, it can be inferred that it is possible to use *in-situ* irradiation as a methodology[24] for the formation of radicals and to functionalize the polymer, because when the polymer and the functional monomer are jointly irradiated, it can be guaranteed that the production of radicals and functionalization reactions happen simultaneously, thereby reducing the possibility of the recombination of radicals. Hence, it could also be inferred that a preirradiation method is less effective.[32]

The solvent (decalin) and the functionalizing agent (DEM) were also evaluated at the same doses to prove whether these reagents are inert to radiation. It was found that EPR spectra did not show any sign indicating the formation of radicals in these compounds. Therefore, it is inferred that radicals involved in functionalization reactions only come from the polymer species under study.

Since the insertion of a functional group into any polymer chain necessarily implies partially modifying its chemical structure, the infrared spectroscopy technique (FTIR) was employed to determine the insertion of DEM into the polyethylene chain, considering that this technique is highly sensitive to the specific presence of functional groups.[5,6] These spectra make it possible to easily identify the characteristic bands of the polymer and the inserted monomer, even at low functionalization percentages.
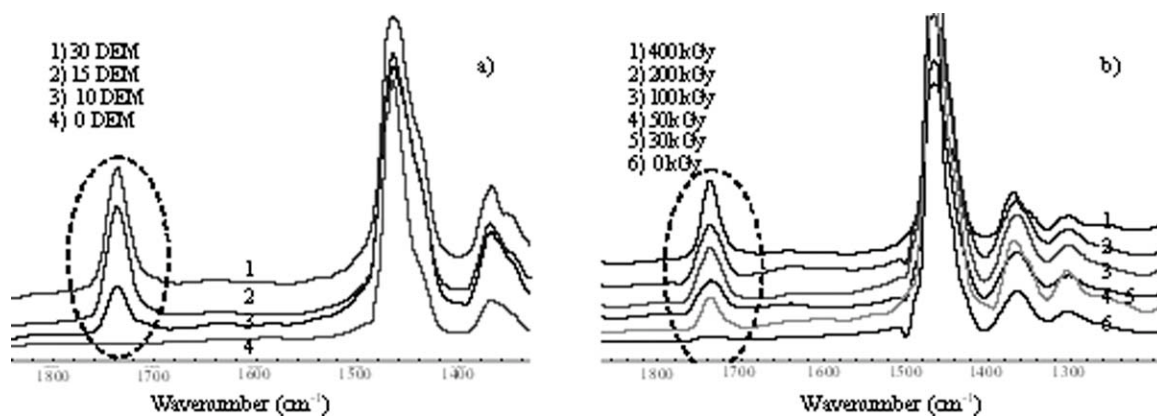
Figure 2 FTIR spectra of grafted LLDPE in the 1200 - 1850 cm^{-1} region: (a) 100 kGy at different DEM concentrations; (b) 30 % DEM at different doses. Band at 1740 cm^{-1} is assigned to the stretching vibration of C=O bonds (coming from DEM), and that at 1460 cm^{-1} to the C—H bending vibration of CH$_2$ sequences.

Figure 2 shows FTIR spectra of LLDPE functionalized with different DEM contents at the same dose (a) and at 30% DEM at different doses (b), with the insertion of the DEM unit into the LLDPE chain being evident. In addition to the characteristic bands of the polyethylenes at 1460 cm^{-1} for C—H deformation and 720 cm^{-1}, which is characteristic of the rocking movement of sequences with a carbon number higher than or equal to four, the appearance of a new band at 1740 cm^{-1} can also be observed. This band can be attributed to the carbonyl group (C=O) stretching, belonging to the DEM structure that is displaced as it is inserted onto the polymer chain. In addition, when the dose was increased, the presence of new bands was not observed [Fig. 2(b)].

Furthermore, in the 1350 and 1000 cm^{-1} region, bands corresponding to the ester group (C—O) that is present in DEM are also observed, which can be seen in more detail in Figure 2b, where the spectrum magnification makes it possible to identify absorbance bands belonging to the deformation of the DEM's C—O bond at 1261 and 1163 cm^{-1}, and the band corresponding to the stretching of the ester C—O—C bond at 1080 cm^{-1}. It is worth noticing that these bands are not present in the LLDPEs or in the irradiated LLDPEs in the absence of the functional monomer, at the same dose used for functionalization.

The spectrum of the functionalized LLDPE (Fig. 2) does not present the band attributed to the C=C stretching at 1645 cm^{-1} observed in the DEM structure. This also shows that the monomer is inserted as a pending diethyl succinate unit (monomer unit equivalent to DEM, but without unsaturation). This structure coincides with the reaction mechanism proposed by Aglietto et al.[14] for the insertion of DEM induced by the use of peroxides.

The functionalization or GDs attained for LLDPE (0.04–0.44 mol %) are shown in Figure 3, where the effects of dose and that of DEM concentration are

shown. It can also be observed that as the dose is increased, the GD also increases, because the higher the energy supplied to the system the higher the likelihood that more active centers are generated, with this implying that a greater number of radical capable of participating in the functionalization reaction would be produced.[33] According to Ganzeveld et al.,[10] the higher the concentration of the functionalizing agent, the higher the probability of macroradicals encountering monomer molecules thereby increasing the insertion probability.

Figure 3 shows that the GD increases with dose (15–400 kGy), independently of the DEM concentration in the reaction blend; this agrees with the reported studies on the formation of radical species as a consequence of the exposure to γ-rays,[29,33] where the concentration of the active species increases with the dose applied.

Based on the results obtained in other research works on functionalization,[2,6] the behavior expected
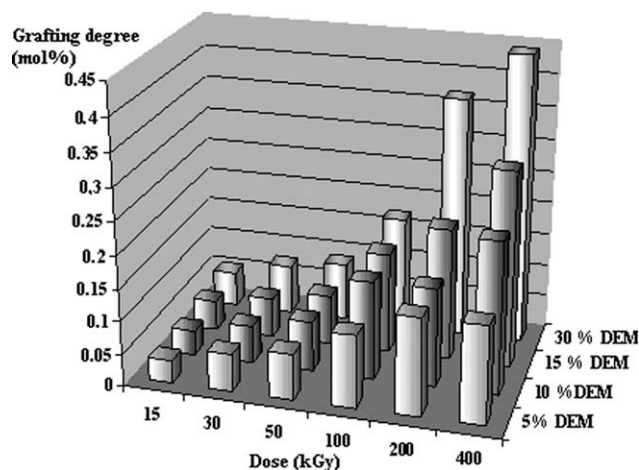
Figure 3 Effect of the dose and DEM concentration on the GD of LLDPE.
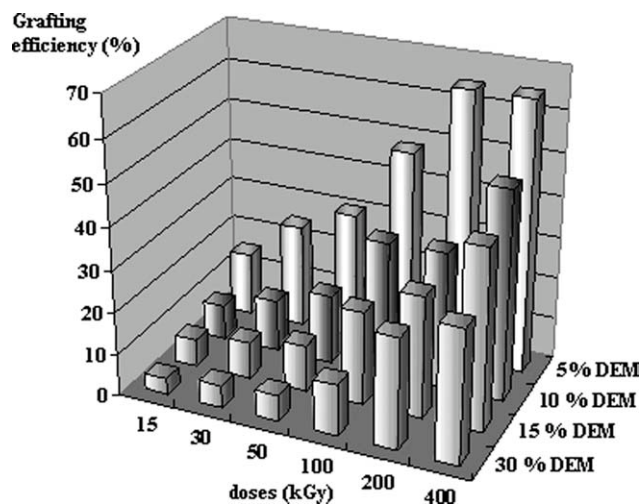
Figure 4 Grafting efficiency (%) in LLDPE at different DEM concentrations and doses.

is for the GD to increase as a consequence of a higher content of functionalizing agent; however, this trend could only be observed at doses over 50 kGy, which seems to indicate that at lower doses no remarkable differences in the quantity of radicals are produced, thus meaning that a lower content of DEM is enough to consume up the active species. It is worth mentioning that the functionalization degrees obtained (0.04–0.44 mol %) are within the range of values reported for functionalized LLDPEs using thermal decomposition initiators, like in the work by Rosales et al.,[6] where GDs between 0.05 and 0.64 mol % were obtained when LLDPE was functionalized with DEM in a dichlorobenzene solution using a peroxide as an initiator.

A relevant aspect to be considered in this type of systems is the efficiency of functionalization, which is expressed as the ratio between the degree of functionalization and the percentage of DEM used. Efficiency depends on numerous parameters, including irradiation conditions, the composition of the functionalization media, temperature, the polymer chemical nature and, especially, the reactivity of the functionalizing agent. It is also worth highlighting that, like in other functionalization methods, there is a competition between the functional monomer insertion and the collateral reactions resulting from the reaction between radicals, which include chain scissions, branching, and crosslinking.

According to Figure 4, the highest efficiencies correspond to the lowest concentration of DEM (5%), thereby meaning that for a number approximately equal of radicals generated at a given dose, the probability of total consumption of DEM molecules present in the media is higher when the proportion of molecules is lower. Therefore, although the insertion degree is low, its efficiency will be higher. Moreover, this effect increases as more radicals are produced in the media; therefore the efficiency for low DEM contents is even higher when the dose is increased.

Characterization of functionalized LLDPE

As observed in Figure 5, MFI progressively declines as the dose is increased for the same DEM concentration. This responds to the increase in production of free radicals when energy supplied to molecules is higher. These radicals, besides inducing insertion, participate in crosslinking and chain coupling reactions that restrict molecular mobility. As a consequence, the polymer loses its flowing capability and therefore presents a lower MFI. The occurrence of chain scissions as the main mechanism of modification due to the secondary reactions can be ruled out, because otherwise MFI values would have increased. It can also be observed that for the same dose, MFI values remain almost constant, independently of the DEM concentration used. Therefore, these results allow estimating the influence of the DEM molecule insertion on flow properties, because a further decrease was expected as a consequence of the increase in chain polarity.[34] Furthermore, exposure of the LLDPE to γ-rays at the conditions herein tested results in increased average molecular weights, because radicals produced in this case lead to crosslinking and long-chain branching as preferential secondary reactions. These reactions occur at a larger scale as the dose is increased.[34]

Figure 6 presents the molecular weight distribution curves of the functionalized LLDPE with 30% of DEM at different doses, through which the effect of γ radiation on the 30–100 kGy range can be analyzed, because high viscosities and little solubility of functionalized polymers at higher doses did not
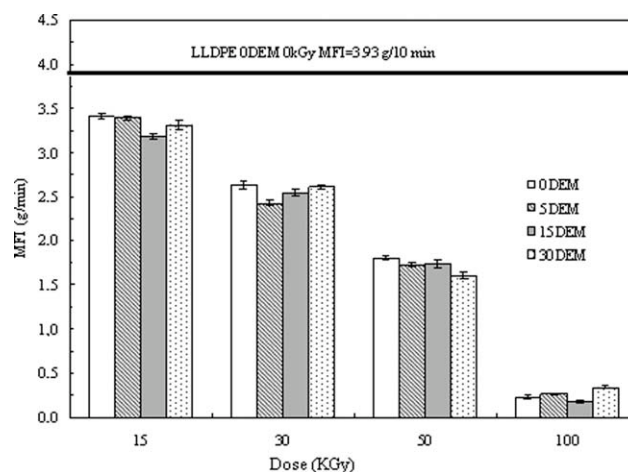
Figure 5 MFI values of grafted LLDPE at different DEM concentrations and doses.
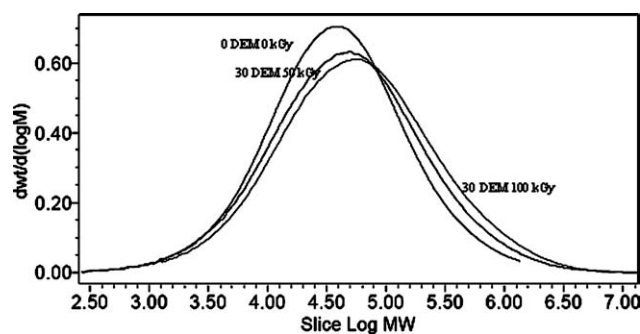
Figure 6 Molecular weight distribution curves of LLDPE grafted with 30% DEM at different doses.

allow the corresponding test to be performed. It can be observed that when the dose is increased, the distribution curves are displaced toward higher molecular weights.

This increase can also be observed by means of a qualitative comparison of the number and weight average molecular weight values (M_n and M_w, respectively) of the LLDPE functionalized with 30% DEM at different doses, reported in Table I. These results let infer that both larger and smaller molecules (M_w and M_n variation, respectively) are involved in the branching and crosslinking reactions already mentioned.

Determining average molecular weights made it possible to demonstrate that exposure to γ-rays effectively brings about molecular weight distribution changes, which are reflected in the increase in the weight average molecular weight values and in the dispersion index at a higher dose. This behavior can be attributed, as mentioned before, to the fact that, in the case of the LLDPE used in this study, radiation predominantly favors long-chain branching and crosslinkings.[25] Furthermore, a remarkable increase in polydispersity is observed, which is also indicative of the generation of new molecular species as a consequence of collateral reactions.

This effect can also be seen in the molecular weight distribution curves (Fig. 6), where an increase in fractions with higher molecular weights can be observed due to the combination of macro-

radicals involved in the crosslinking and branching reactions.

The effects of radiation on polyethylene matrices have been thoroughly studied.[21,24,35,36] These effects have demonstrated that the predominating mechanism is long-chain branching and/or crosslinking. Therefore, gel content was determined. This value is proportional to the formation of three-dimensional networks that make the polymer lose its solubility. When this parameter was evaluated based on the dose, it was found that crosslinking evidence is only observed starting from 100 kGy, because below this dose, polymers evaluated were, apparently, completely soluble.

Figure 7 shows the gel content based on the applied dose, both for functionalized polymers and for those irradiated in the absence of DEM. As it is observed, the gel content increases with the dose, as expected, because when the number of radicals in the medium is higher, it is more likely that secondary reactions occur, which in this case mainly include branching and crosslinking, with this latter being responsible for the increase in insoluble fractions. Concerning the presence of DEM in the medium, this brings about a significant reduction in gel content, which can be understood as an evidence that functionalization strongly competes with secondary reactions, thereby preventing these latter from taking place at a larger scale.

Aglietto et al.[14] report that the high DEM reactivity reduces crosslinking reactions in systems in which they are carried out in solution and peroxide is used as an initiator. This agrees with the results obtained at low doses. However, due to the increased production of radicals at higher doses, the viscosity of the reaction medium and the absence of agitation, a large part of the radicals that are close to each other react before they coincide with the functionalizing agent molecules, with macroradical combination reactions being therefore produced.

Furthermore, to confirm the nature of changes already observed in both the flow index values and the molecular weight distributions of functionalized LLDPE, the number of unsaturations present in these samples was evaluated. Lachtermacher

TABLE I
Number (M_n) and Weight (M_w) Average Molecular Weights and Polydispersity Index (ID) of LLDPE Grafted with 30% of DEM

Dose	30% DEM			0% DEM		
	M_n	M_w	ID	M_n	M_w	ID
0 kGy	–	–	–	17078	90118	5.3
50 kGy	15181	147386	9.7	13292	149609	11.3
100 kGy	16614	174772	10.5	15185	177872	11.7

– Non applicable
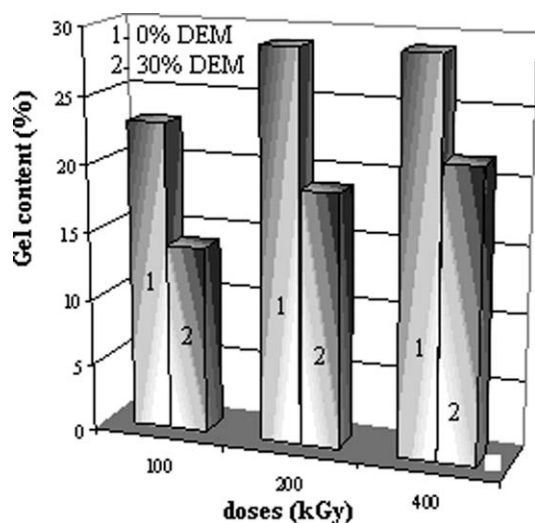
Figure 7 Gel content of LLDPE grafted with 30% DEM at different doses.

et al.[37,38] and Bremmer et al.,[39] among others, demonstrate the importance of the polymer terminal unsaturations in the branching and crosslinking reactions. These studies report that reactions in terminal vinyl groups in the presence of free radicals can explain changes in the concentration of other types of vinyl groups. According to these studies, allylic hydrogens are more active and, therefore, easier to extract. Afterward, molecular changes that may lead to long-chain branching due to the combination with another macroradical may take place and give rise to new internal unsaturations of the *cis* and *trans* vinyl types.

FTIR spectra of LLDPE showed the vibrational modes corresponding to the unsaturations present, particularly the band at 909 cm^{-1} of the terminal vinyl groups (RCH = CH$_2$) and that at 965 cm^{-1}, with this latter being assigned to the *trans*-vinylene group (RCH = CHR). The presence of these bands proved to be independent of the DEM concentration and the increase in the dose. However, with higher DEM content and at higher doses, these bands are seemingly more defined. The quantification of these bands was performed by calculating their area ratios with the 1460 cm^{-1} band of the polyethylene being selected as an internal standard. Table II shows a decrease in the amount of terminal vinyls (A_{909} cm^{-1}/A_{1460} cm^{-1}) in both irradiated as well as functionalized LLDPEs. This agrees with the fact that the presence of terminal unsaturations in the polymer chains also favors termination reactions due to coupling and/or disproportion, which are responsible for crosslinking and long-chain branching that increase the chains' molecular weight.[37] However, it can be inferred that at high doses ($\geq$100 kGy), chain scission reactions start to gain some significance; therefore, a slight increase in terminal unsaturations

can be observed. This behavior could have been demonstrated through the increase in the populations with a lower molecular weight in the molecular weight distribution curve; however, insolubility of the irradiated samples at higher doses rendered this determination impossible.
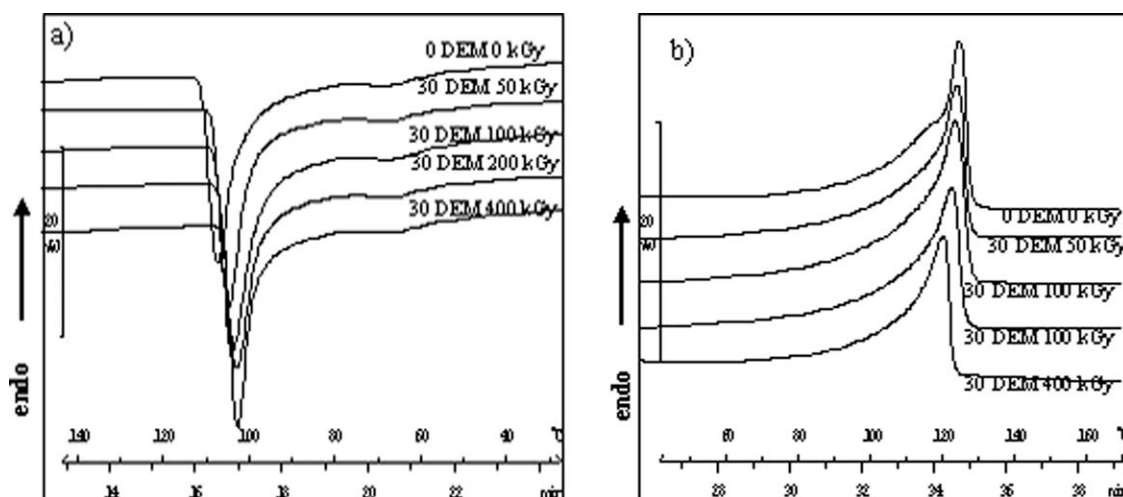
Through the analysis of the band at 965 cm^{-1}, an increase in *trans*-vinyl unsaturations is observed. This coincides with the work by Bremmer and Rudin[39] and Swanda and Balke[40] who evaluated the increase in *trans*-vinyl unsaturations as a consequence of the secondary branching reactions due to the coupling of the allylic radical with other radicals. These unsaturations could also be the result of the scission of C—H bonds in secondary carbons, which are produced due to the effect of γ radiation. This activates β hydrogens and renders them more susceptible to the abstraction by another adjacent radical, thereby giving rise to unsaturations of the *cis* and *trans* types; with the latter being the most favored one in terms of its conformation.[41]

Furthermore, intermediary species in these reactions (allyl radicals) contribute to the formation of internal *cis* or *trans* unsaturations. Therefore, the number of *trans*-vinyl unsaturations (A_{965} cm^{-1}/A_{1460} cm^{-1}) tends to increase. These effects are favored with the increase of the dose, independently of the DEM concentration, the presence of which seemingly reduces the unsaturation variations, in accordance with the competition of the insertion mechanism with collateral reactions.

In the case of the analysis of the thermal properties, Figure 8 shows crystallization exotherms and melting endotherms of the functionalized LLDPE, with peaks presenting a wide crystallization and

TABLE II
Peak Area Ratios of Vinyl Unsaturations of LLDPE Irradiated at Different Doses and Grafted

	Peak area ratios corresponding to unsaturations $\times 10^3$	
	Terminal vinyls 909 cm^{-1}/ 1460 cm^{-1}	*Trans* vinyls 965 cm^{-1}/ 1460 cm^{-1}
0DEM_0kGy	8.08	1.08
0DEM_30kGy	5.95	1.32
0DEM_50kGy	4.96	2.44
0DEM_100kGy	5.44	3.72
0DEM_200kGy	6.11	5.85
0DEM_400kGy	7.16	10.43
30DEM_15kGy	6.02	2.67
30DEM_30kGy	6.78	3.13
30DEM_50kGy	6.52	3.73
5DEM_100kGy	6.81	4.02
15DEM_100kGy	6.07	5.38
30DEM_100kGy	6.05	5.93
30DEM_200kGy	6.35	8.62
30DEM_400kGy	7.62	18.67

Figure 8 Normalized thermograms of LLDPE grafted with 30 % DEM at different doses: (a) Crystallization Exotherms; (b) Melting Endotherms.

melting temperature range, respectively, as can be observed. This characteristic is inherent to LLDPEs and reflects the heterogeneous structure of this polymer, which possesses short branching distributed over different intervals along the main chain.[42]

The slight displacement of the curves toward lower temperature values corresponds to the increase in the GD with the dose and also indicates that the presence of DEM interrupts the linear sequences, thereby leading to a decrease in the lamellar thickness, because this group is excluded from the crystalline structure.[43]

On the other hand, the bimodality observed in the LLDPE's melting endotherm is indicative of the presence of more than one crystalline structure, where the highest temperature peak corresponds to the molecules with a higher molecular weight, which proportionally possesses a lower number of branching, whereas the valley observed at lower temperatures is a result of the crystallization of molecules with a lower molecular weight and a higher content of branching.[44] It is also observed that in addition to the displacement of the melting peak toward lower temperatures, this bimodality disappears due to the change in the type of crystalline populations produced by the inclusion of DEM, the possible formation of branching and crosslinking.
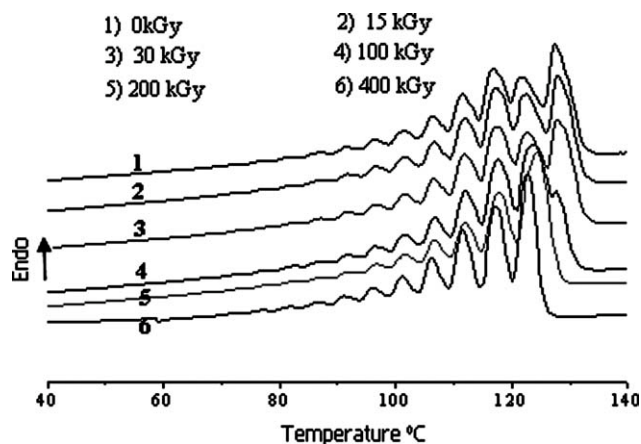
The changes in values of the thermal parameters shown in Table III are within the deviation resulting from the experimental error. Moreover, according to the thermograms, a trend to a decline in melting and crystallization temperatures is seemingly evident when the dose is increased. This change is more evident in the case of the crystallinity degree, which, as may be expected, is slightly lower, not only due to the presence of DEM, but also to branching and crosslinking due to the effect of the exposure to γ-rays.

To gather more information on the thermal behavior of functionalized polymers, they were evaluated by means of the SSA technique.[27] In these thermograms, the peak with the highest melting temperature corresponds to the thickest crystals produced by crystallization of the more linear molecules. This is mainly due to the crystallization of the chain segments that are capable of producing more stable crystals at a determined self-nucleation temperature; whereas the other chains form unstable crystals or remain in molten state, crystallizing during cooling to generate the successive peaks. In addition, further heating allows these crystals to thicken, due to the exclusion of defects and the internal reorganization of chains, which reduces free energy and allow more stable crystals to be created, thereby leading to an

TABLE III
Crystallization Peak Temperature (T_c), Melting Peak Temperature (T_m) and Crystallinity Degree of LLDPE Irradiated At Different Doses (kGy) and Grafted with Different DEM Concentrations

Dose	DEM (wt. %)	T_c ($\pm$ 1°C)	T_m ($\pm$ 1°C)	Crystallinity (%)
0	0	107	124	46
50	0	106	124	44
	10	106	123	43
	15	105	124	44
	30	106	123	45
100	0	106	124	43
	10	106	122	44
	15	106	122	43
	30	105	123	44
200	0	106	123	44
	10	104	123	42
	15	104	123	43
	30	104	122	42
400	30	104	121	41

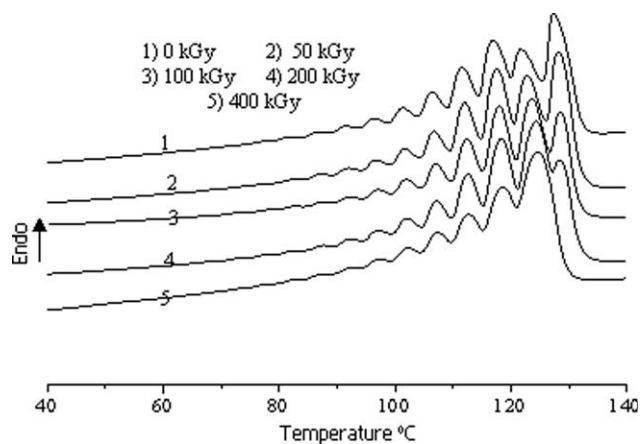**Figure 9** Heating scans after SSA of LLDPE grafted with 30 % DEM at different doses.

Figure 10 Heating scans after SSA of LLDPE irradiated at different doses.

increase in melting temperature. Furthermore, the application of this method makes it possible to obtain information concerning the likely location of units inserted into the polymer main chain.[15]

Figure 9 shows that the endotherm with the highest melting peak progressively decreases with the increase in the dose, until completely disappearing when 200 kGy are applied. At the same time, height and width of the remaining endotherms increase, especially those of the endotherm with the second highest melting temperature. This variation is much more evident when the percentage of the partial areas of each one of the endotherms is compared based on the dose (Table IV). According to the results reported,[15] this implies that DEM insertion and branching or crosslinking are capable of modifying crystalline populations in such a way that when the $-CH_2-$ sequence is interrupted, imperfections are produced inside the chain that make it lose its linearity and thereby lead to a decrease in the melting temperature. A remarkable displacement of this endotherm toward a lower temperature value can also be observed when high doses are applied, thus

suggesting that DEM insertion and the formation of imperfections favor the reduction of the lamellar thickness.

The SSA final thermograms in the absence of DEM (Fig. 10) confirm the effect of the formation of new branching and crosslinking as a consequence of the coupling of radicals produced by γ radiation. When these thermograms are compared with those of the functionalized LLDPEs, it can be observed that the inclusion of DEM notably influences the decrease of the highest temperature endotherm, which not only presents a greater reduction in the partial area, but also disappears at lower doses than the one reported for polymers irradiated in the absence of DEM (Tables IV and V). The results provided by applying the SSA technique allow reaching an unequivocal conclusion: that the free radicals formed by γ radiation for the DEM insertion and main chain modifications are preferentially generated in the secondary carbons of the more regular $-CH_2-$ sequences. Hence, modifications of the peaks melting at higher temperatures are the more noticeable.

TABLE IV
Partial areas (%) and Melting Peak Temperatures of the Endotherms Obtained Through SSA of LLDPE Grafted with 30 % DEM as a Function of the Dose and the Self-Seeding Temperature (T_s)

	Dose (kGy)									
	Area (%)					Melting peak temperature (°C)				
T_s	0	30	100	200	400	0	30	100	200	400
127	26.5	21.4	10.3	0.0	0.0	127	128	128	-	-
122	19.5	20.2	27.0	38.4	25.0	122	123	124	124	123
117	19.6	20.4	22.0	22.5	20.7	117	118	118	118	118
112	14.1	14.4	15.4	14.6	16.0	112	112	112	112	112
107	8.2	8.2	10.1	10.1	12.0	106	107	107	107	106
102	5.2	5.7	6.2	7.1	7.5	101	102	102	102	101
97	3.8	3.7	4.4	4.3	6.2	96	97	97	97	96
92	2.0	1.7	2.9	3.0	4.9	92	92	92	92	91
87	0.8	0.9	1.8	1.4	3.0	87	87	87	87	87

TABLE V
Partial Areas (%) of the Endotherms Obtained Through SSA of LLDPE Irradiated at Different Doses as a Function of the Self-Seeding Temperature (T_s)

	Dose (kGy)				
T_s	0	50	100	200	400
127	26.5	21.8	15.6	12.7	0.0
122	19.5	19.1	21.4	24.9	37.4
117	19.6	19.2	18.5	19.9	22.0
112	14.1	13.4	13.5	12.4	14.1
107	8.2	9.3	8.6	10.0	10.8
102	5.2	6.1	6.8	5.4	7.0
97	3.8	4.5	4.5	4.5	4.3
92	2.0	3.2	3.8	3.5	2.6
87	0.8	2.1	2.8	2.7	1.1

Thermogravimetric studies determined that all of the functionalized LLDPEs have a single-step decomposition, like the LLDPE, without appreciable differences being observed among the thermograms obtained. Table VI shows that degradation temperature remains almost constant and activation energy decreases as part of the effects produced by radiation, which is much lower in the case of functionalized polymers. Therefore, it can be inferred that this decrease is a consequence of the increase in crystalline imperfections, similarly to the presence of a higher proportion of internal unsaturations in the LLDPE (Table II). Furthermore, the higher the dose, the lower the decrease in the activation energy with respect to the unmodified LLDPE; this agrees with the fact that crosslinking provides a higher thermal stability. It is also evident that the presence of DEM results in a decrease of activation energy, when it competes with branching and crosslinking reactions for the consumption of radical species.

TABLE VI
Initial decomposition temperature (T_i), Final decomposition temperature (T_f), Activation Energy (E_a) and reaction order (n) in LLDPE irradiated in absence of DEM and grafted with 30 % DEM

Sample	T_i (°C) ± 1	T_f (°C) ± 1	E_a (KJ/mol)	Reaction order (n)
LLDPE 0DEM0_kGy	455	505	452	1
LLDPE 0DEM15_kGy	456	505	403	1
LLDPE 0DEM30_kGy	451	504	390	1
LLDPE 0DEM50_kGy	452	504	397	1
LLDPE 0DEM100_kGy	452	505	406	1
LLDPE 0DEM200_kGy	455	505	415	1
LLDPE 0DEM400_kGy	458	505	423	1
LLDPE 30DEM30_kGy	454	504	379	1
LLDPE 30DEM50_kGy	452	505	380	1
LLDPE 30DEM100_kGy	452	504	400	1
LLDPE 30DEM200_kGy	455	505	405	1
LLDPE 30DEM400_kGy	453	505	408	1

CONCLUSIONS

The results confirmed that γ radiation can be used for the formation of free radicals and LLDPE functionalization. The increase in the absorbed dose favors a higher formation of radical species, thereby obtaining a higher GD. The effects of DEM concentration are only perceptible when doses higher than 50 kGy are used. Independently of the DEM concentration used, efficiency increases with a higher dose. For a concentration of 30% DEM, when the highest dose (400 kGy) is applied, a maximum functionalization degree of 0.44% molar is reached for the polyethylene under study (LLDPE).

In addition to the functionalization process, the exposure to γ-rays brings about changes in the polyethylene structure, due to the secondary reactions in which radical species are also involved. The use of γ radiation modifies the structural and physical characteristics of the functionalized polyethylene with respect to the unmodified one, because, depending on the dose, the effects of γ-rays can lead to crosslinking of materials with decreased flowability.

The effects of γ radiation on the molecular structure and molecular weight distribution are mitigated as a result of the presence of DEM, due to the competition with the chain scission, branching and crosslinking reactions, for the consumption of the free radicals.

The results provided by applying the SSA technique allow reaching an unequivocal conclusion: that the free radicals formed by γ radiation for the DEM insertion and main chain modifications are preferentially generated in the secondary carbons of the more regular ─CH$_2$─ sequences.

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