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Characterization of Gamma Irradiated PEs using ESR, FTIR and DSC Techniques

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Summary

We study the effects of γ-rays on different PEs using the ESR, FTIR and DSC. The changes in the ESR and FTIR spectra after irradiation is studied. We found that the chemical reactions produced during radiation as well as during the storage time are mainly scission and crosslinking and/or branching. The percentage of each of these reactions was determined by the Charlesby-Pinner equation and we concluded that they depend on the linearity of the PE.

Introduction

The effect of ionizing radiation on polymers is of great interest and has been studied intensively (1-10). The physical and chemical modifications induced by effects of the radiation in these materials limit their use in environments where they are subjected to the action of such ionizing radiations. Nonetheless sometimes, it is required that polymers resist the ionizing radiations without suffering any change or degradation that modifies their properties.

The effects of ionizing radiation on polymers include: i) crosslinking and chain scission, ii) formation of small molecular fragments, and iii) modification of the molecular structure. Molecular weight changes resulting from (i) can markedly influence the material properties (1,3).

Therefore, the present work studied the change caused by γ-radiation on different PEs. The structure and property changes induced by γ-irradiation and the aging effect after irradiation in different samples were characterized using ESR (Electron paramagnetic resonance), FTIR (Fourier transform infrared spectroscopy) and DSC (Differential scanning calorimetry) techniques.

Experimental

The materials used in this study were a high-density polyethylene (HDPE; MFI of 0.10 dg/min at 190°C, 2.16 Kg), a low-density polyethylene (LDPE; MFI of 0.19 dg/min at 190°C, 2.16 Kg) and a linear low-density polyethylene (LLDPE; MFI of 0.52 dg/min at 190°C, 2.16 Kg). The samples were cut in pellet form (small cylinders of approximately 2 mm of diameter for 4 mm long). Films of all specimens were compression molded (1.5-2 mm of thickness). Films and pellets were irradiated with γ-rays from a ^{60}Cobalt source in air at a dose rate of 4.8 kGy/h. Radiation doses were in the range 0-1000 kGy. The samples analyzed were pellets, for all experimental techniques, except for FTIR.

The ESR spectra were obtained in the X band EMX BRUKER spectrometer, at room temperature. The total free radical concentration of the samples was obtained using the 4-(2-iodoacetamide)-2,2,6,6-tetramethylpiperidinoxyl radical as standard of comparison. The experimental conditions (microwave power and the modulation field) were adjusted to avoid effects of saturation in the ESR spectrum. FTIR spectra were taken from the films already irradiated in a Nicolet Magna-IR 750 spectrometer, in the 4000-400 cm^{-1} interval, at a resolution of 4 cm^{-1}.

To study the influence of the irradiation process in the thermal properties of the PEs, differential scanning calorimetry thermograms were taken using a Mettler Toledo (DSC 821e). The first cooling and second heating (after a common thermal history) thermograms were recorded from samples cut out from the already mentioned pellets, at 10 °C/min. These studies were carried out on the samples after 30 days of storage.

The degree of crosslinking of the unirradiated and irradiated samples (after one month) was assessed by degree of gelation (wt%) (4).

Results and Discussion

1.- Analysis of the ESR spectra

Figure 1a shows the ESR spectrum of the HDPE, irradiated at 900 kGy. A multiple peak spectrum is observed due to the different free radicals present in the sample. This spectrum can be interpreted like an overlapping of several spectra belonging to different paramagnetic structures and is a typical spectrum for a mixture of alkyl ($- CH_2 -\dot{C}H-CH_2 -$), allyl ($- CH_2 - \dot{C}H-CH=CH-CH_2 -$) and polyenyl ($- CH_2 -\dot{C}H-(-CH=CH -)_n-CH_2 -$) radicals (5-6). The hyperfine splitting constant of the alkyl radical a_1 was determined to be 17.5 Gauss and that of the allyl radical, a_2 = 11.3 Gauss, which are in accordance with the values reported in the literature (6-8). The peaks corresponding to the alkyl radical are marked with the number "1", those corresponding to the allyl radical with the number "2" and the central and very intense peak is attributed to the polyenyl radical. The effect of storage over thirty days is shown in Figure 1b; a single and symmetrical signal centered in g=2.003 is observed in the spectrum and it can be attributed to the polyenyl radical (7). This fact is an indication that the allyl and alkyl radicals have reacted with the environment producing more stable species. All the samples show qualitatively the same spectrum. Figure 1c displays an interesting behavior in the HDPE irradiated at doses $\leq$ 150 kGy. The relative intensity of the alkyl radical increases in respect to the signal of the allyl radical, thus leading to a best definition of the peaks for the latter.

Figure 2 shows the total free radical concentration (radicals/g) of the studied polymers (HDPE, LDPE, LLDPE) unirradiated, irradiated and post-irradiated after a storage time of one month. Figure 2a unfolds that the formation of radicals is small for small doses of radiation, the HDPE having the greatest concentration. Upon increasing the amount of radiation, an increase in the concentration of radicals is observed, this phenomenon being most noticeable as said, in the HDPE.

After storage (Figure 2b), a decrease in the radical concentration in the PEs is obtained. However, a still rather high concentration is observed in the HDPE due to its higher degree of crystallinity, because of the fact that the radicals remain trapped in the crystalline regions. In LDPE and LLDPE, a very low radical concentration is observed due to very high reaction rates among themselves. Hence, it can be concluded that the radicals decay considerable more quickly in branched polyethylenes than in linear PE. In summary, in all the homopolymers, the decrease in the radical concentration can be attributed to the easier recombination of those formed in the amorphous regions due to the higher chain mobility.

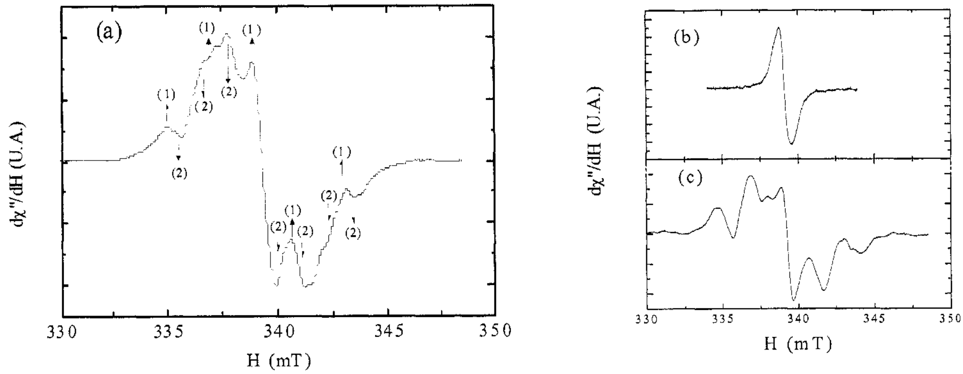

Figure 1: EPR spectra of: a) HDPE irradiated at 900 kGy. b) 900kGy, 30 days after irradiation. c) Irradiated at 150 kGy (recently irradiated).

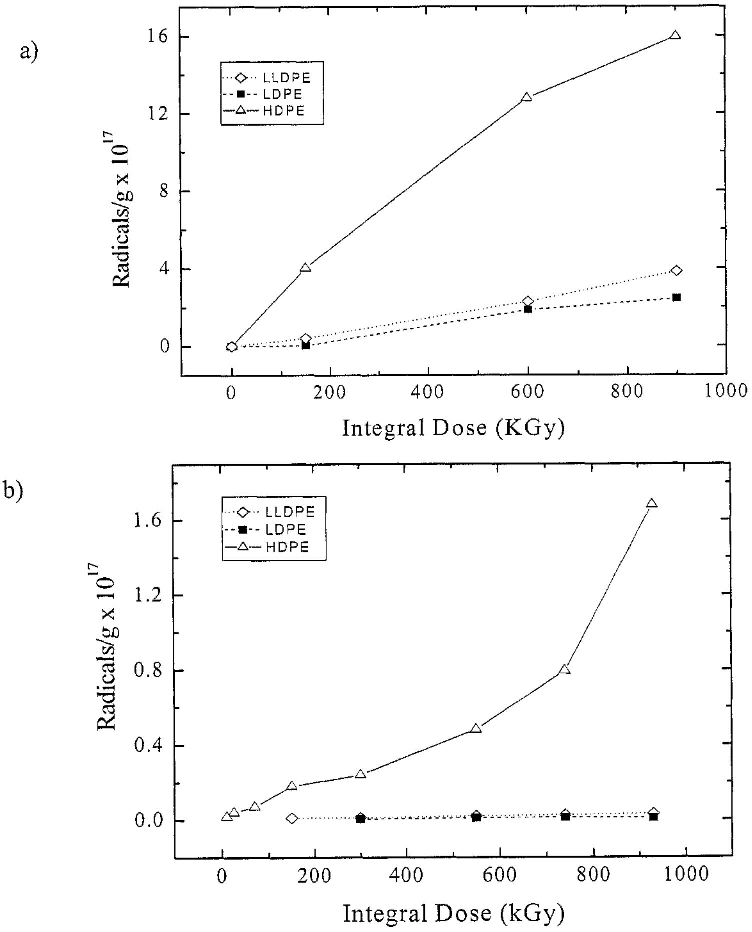

Figure 2: Radicals concentration at different radiation doses (a), and post-irradiated after a storage time of a month (b).[The lines are a guide for the eyes].

The process of radical decay in crystalline polymers, especially in polyethylenes, involves two processes: one rapid (due mainly to the radicals less stable) and another slow (9). According to Dole et al. (10), the rapid decay in the radicals occurs in the non-crystalline phase and generally takes part at the beginning of the experiment. The slow process, on the other hand, is due to the diffusion of the radicals from inside the crystal to its surface to react. That is why, after a month of storage, there is still a noticeable concentration of radicals in the sample of irradiated HDPE.

2) Analysis of the FTIR spectra

The HDPE, LDPE and LLDPE spectra are displayed in Figure 3. In the interval 1600-1800 cm^{-1}, the increase of the band attributed to carbonyl groups (C=O) with the radiation dose can be observed. The degradation products containing the carbonyl group are mainly ketones, carboxylic acids and esters, which show absorbance peaks in the 1650-1850 cm^{-1} range (acid 1713cm^{-1}; ketones 1718cm^{-1}; ester 1741cm^{-1}). Therefore, due to the simultaneous presence of different degradation products, the band attributed to the C=O groups appears broader with an increase in the radiation dose.

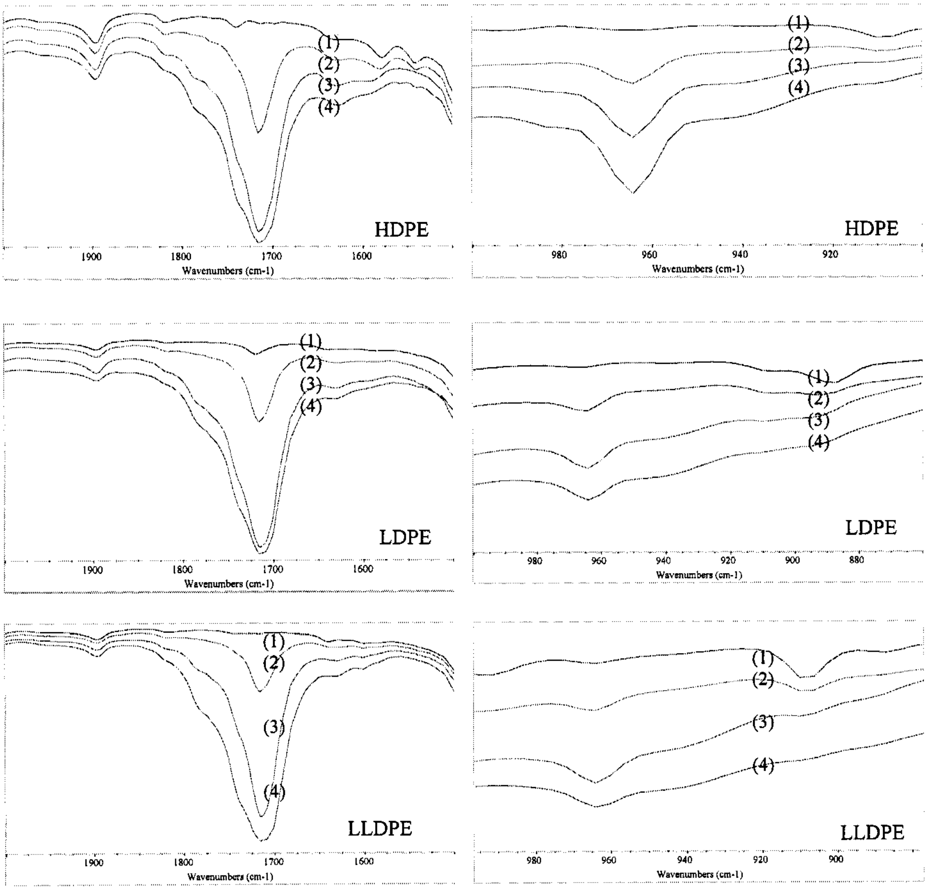

Figure 3: FTIR of HDPE, LDPE and LLDPE irradiated at different doses [1) unirradiated, 2) 150kGy, 3) 550kGy, 4) 930kGy], a) range 1500-2000 cm^{-1}, b) 900-1000 cm^{-1}.

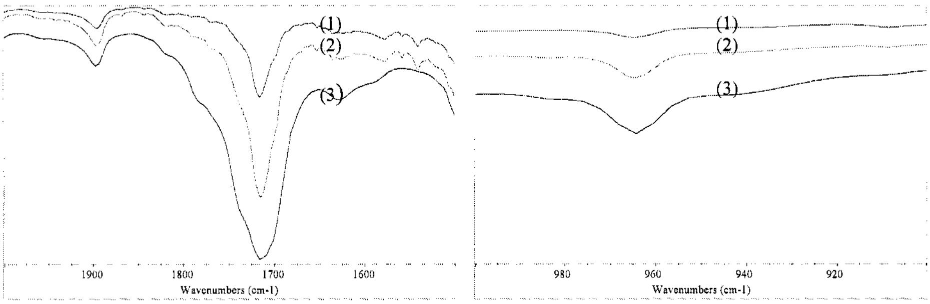

Figure 4: FTIR of irradiated HDPE [1) 150 kGy, 2) 550 kGy, 3) 930 kGy] after a month of storage in air at different doses. a) range 1500-2000 cm^{-1}, b) 900-1000 cm^{-1}.

Additionally, the band at 964 cm^{-1}, which is attributed of the trans-vinylene groups (trans-RCH=CHR), increases linearly with the absorbed dose, as shown in Figure 3. For these polyethylenes, a decrease in the 888 and 909 cm^{-1} bands, corresponding to the vinylidene and terminal vinyl groups, respectively, is observed. This implies the likelihood of crosslinking and/or formation of long chain branching. On the other hand, the FTIR spectrum of LLDPE without irradiation shows bands in 909 and 965 cm^{-1}, and at higher doses, a change in 935 cm^{-1} begins to be noticeable.

Finally, regarding the spectra carried out after 30 days of storage, it may be inferred that time does not appear to have any effect on the analyzed bands. Figure 4 shows the spectra of HDPE after 30 days at different radiation doses.

3) Analysis of the DSC thermograms

The change in melting temperature (T_m), the crystallization temperature (T_c) and the crystallinity of the HDPE, LDPE, LLDPE were plotted as a function of the radiation dose (Figure 5). As it can be seen, the melting and crystallization temperatures and crystallinity decrease with an increase in the radiation dose. The above interpretation is also valid for the variation of the onset temperature with radiation dose.

Because the melting point is an indication of the crystalline size and perfection, a decrease in the melting point implies a smaller and/or a less perfect crystal formed after irradiation. Two possible explanations can be put forward: the first would consider a chain scission mechanism, that is, a decrease of the molecular weight due to the irradiation, and the second argument would imply occurrence of branching and/or possible cross-linking, both producing a decrease in the melting point, due to the fact that the linear sequences capable of crystallization are being interrupted, thereby decreasing the lamellar thickness. These results are in agreement with the analysis of the FTIR spectra. The progressive decrease in the melting point was interpreted assuming a preferential destruction of the large crystals by the radiation. The relationship between crystallization temperature and irradiated dose for the PEs was obtained. The results (Figure 5) showed a non-linear decrease of the crystallization temperature with the increase of the radiation dose. This behavior is ascribed to the fact that crystallization of some parts of the polymer occurs, together with freezing of the reorientation motion of the molecules, which is actually expected to occur while cooling. The above interpretation is also valid for the variation of the onset temperature with radiation dose.

Using the results of average crosslinking measurements, Figure 6 displays that the gel fraction increases with the radiation dose, almost reaching the limit for each polyethylene, at an approximate dose of 150 kGy. This is because a dose rate that caused chain branching, crosslinking and oxidation degradation reactions simultaneously was used. These results agree with those in the literature (11).

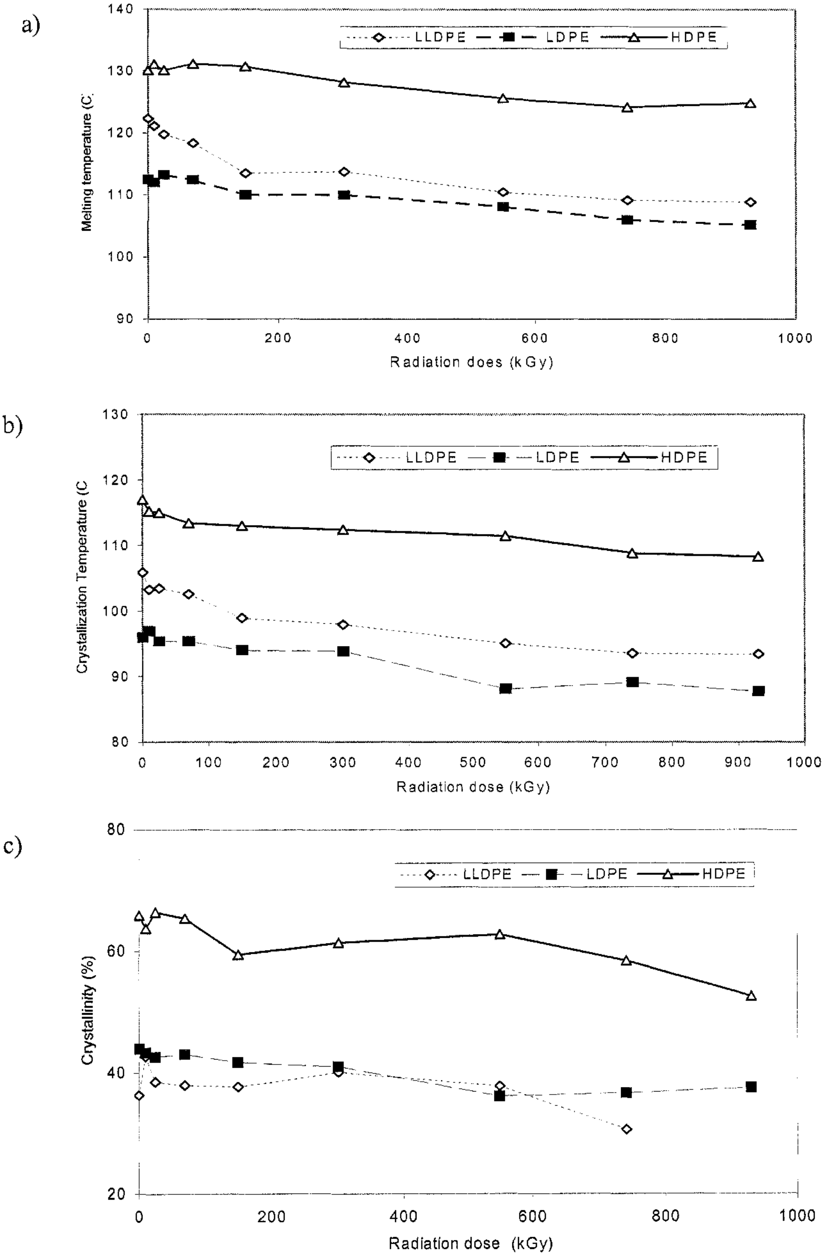

Figure 5: Melting (a) and crystallization (b) temperatures and degree of crystallinity (c) of HDPE, LDPE and LLDPE vs. radiation dose. [The lines are a guide for the eyes].

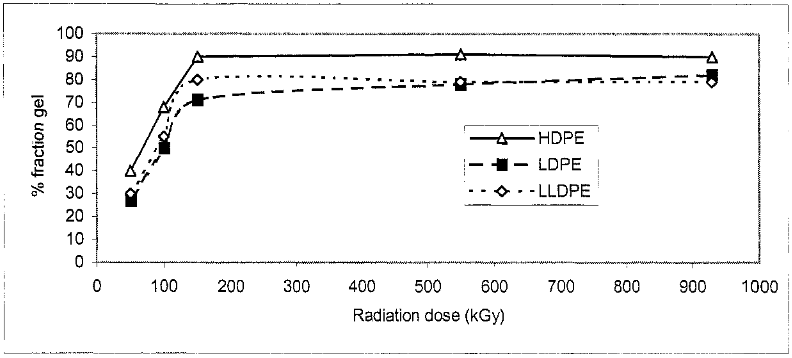

Figure 6: Fraction gel of the different PEs versus radiation dose. [The lines are a guide for the eyes].

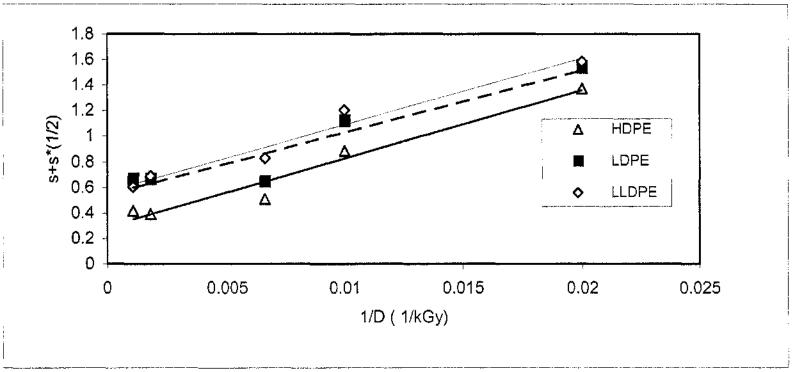

Figure 7: Plot of s+s$^{(1/2)}$ against 1/Di .

Sample	p/q	r_g
HDPE	0.2935	31.03
LDPE	0.5441	33.41
LLDPE	0.5709	36.48

Table 1: Values of the intercept (p/q) from the Charlesby-Pinner equation and radiation dose to Gelation (r_g)

As it can be seen, the gel fraction is higher in the case of the HDPE as that of the low-density sample (LDPE) for the same radiation dose, which can be attributed to the HDPE being more crystalline than the LDPE. The amorphous region includes the interlamellar volume and the defect sites in the lamellae and a higher crystallinity leads to a greater proximity of the crystal lamellae, which also anchor the amorphous segments. The higher proximity of the amorphous segments increases the extent of crosslinking in the HDPE sample.

The gel percentage implies that the degree of crosslinking was significantly increased by irradiation and then it remain constant for radiation dose >200kGy, shown by the 965 cm^{-1} band in the FTIR, since it did not change with the storage time. The gel percentages found in LDPE and LLDPE are lower than that of HDPE, due to a higher oxygen diffusion because of their higher amorphicity.

Figure 7 is the Charlesby-Pinner plot of the different polyethylenes irradiated with gamma rays in air at room temperature. The Charlesby-Pinner equation is given as follows (12): $S+\sqrt{S}=p/q+2/q\mu D$, where s is the sol fraction, Di is the radiation dose expressed in kGy, q is the proportion of units crosslinked, p is the radio of main chain fractures to chain units, and μ is the weight average of initial degree of polymerization. This equation predicts that a plot of $s+s^{(1/2)}$ against 1/Di should be linear. The intercept is the p/q ratio and the slope is $2/q\mu$.

Figure 7 shows that the data are not completely linear. In this study, the linear deviation occurs at doses higher than 200 kGy. Table 1 shows the values of the intercept of the data on the $s+s^{(1/2)}$ axis, which indicates that the probability of scission or crosslinking depends on the structural characteristics of the PEs. It is noteworthy that the HDPE shows that 70% of the formed radicals react via crosslinking and the remaining via chain scission, as indicated by the fact that p/q is equal to 0.2935. On the other hand, in the less crystalline polyethylenes, LDPE and LLDPE, p/q is equal to 0.5441 and 0.5709, respectively, showing that for each crosslinking reaction, a scission in the chain is produced, due to their higher amorphicity, indicating that the diffusion of oxygen and therefore the formation of carbonyl groups are higher

On the other hand, the value of the radiation dose at gelation r_g (that is, the dose at which $s+s^{(1/2)}=2$) is calculated for all polyethylenes and is given in Table 1. The radiation dose at gelation is the dose of irradiation at where the first insoluble residue is detected in the irradiated polyethylene. In the values shown in Table 1, it can be seen that for the polyethylenes used, this value is approximately similar, being in the 30 to 36 kGy range.

Conclusions

The EPR spectra indicate that a mixture of alkyl, allyl and polyenyl radicals is produced after irradiation in all the PEs studied. The spin concentrations in irradiated HDPE, before and after storage, are higher than those found in the other PEs. This is because the concentration of radicals decays more slowly in linear than in branched polymers. The FTIR analysis showed that chain scission, crosslinking and/or branching reactions are produced in the PEs studied. These results are confirmed by the p/q values found in the Charlesby-Pinner equation. The progressive decrease in the melting point was interpreted assuming a preferential destruction of the large crystals by irradiation.

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