

## Effect of aging in HDPE blended with DEM in decalin

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Electron paramagnetic resonance (EPR) was used to study the effect of aging on irradiated samples of high-density polyethylene (HDPE) blended with diethyl maleate (DEM) in different proportions. Initially, we synthesize the HDPE using bis-(cyclopentadienyl) zirconium dichloride and P-MAO. The functionalization of the synthesized HDPE was carried out in a 10% weight/vol of polyethylene in decalin solution using different percentages of diethyl maleate (5, 10, 15 and 30% in weight). The samples were irradiated at 5, 15 and 30 kGy. An exponential decay in the total free radicals concentration was observed in the pure HDPE sample at the 15 and 30 kGy irradiation doses, as it was expected. For the 15 and 30 kGy irradiation doses the HDPE blended with 15 and 30% of DEM in decalin shows an increase in the total free radical concentrations as the storage time is increased. This behavior has been interpreted in terms of trapped free radicals.

*Keywords:* Paramagnetic resonance; polyethylene; free radicals; irradiation.

Usando resonancia paramagnética electrónica (RPE), se estudia el efecto del envejecimiento sobre muestras irradiadas de polietileno de alta densidad (PEAD) mezclado con dietil maleato (DEM) en distintas proporciones. Inicialmente, se sintetizó el PEAD utilizando dicloruro de bis-(ciclopentadienil) zirconio y P-MAO. La funcionalización del PEAD sintetizado se realizó en una solución de 10% peso/volumen de polietileno en decalina, utilizando diferentes porcentajes de dietil maleato (5, 10, 15 y 30% en peso). Las muestras fueron irradiadas a 5, 15 y 30 kGy. El PEAD puro muestra un decaimiento de primer orden de la concentración total de radicales libres para 15 y 30 kGy, como es de esperarse. El PEAD mezclado con DEM y decalina a 15 y 30% de DEM y para las dosis de 15 y 30 kGy muestra, al transcurrir el tiempo, un incremento en la concentración de radicales libres totales. Este comportamiento lo hemos interpretado en términos de radicales libres atrapados.

*Descriptores:* Resonancia paramagnética; polietileno; radicales libres; irradiación.

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### 1. Introduction

The polyolefines are the most important polymers in the international market thanks to their low cost, good handling, and a wide range of physical-chemical properties. However, the lack of polarity in their structure limits their use in certain commercial areas. The poor capacity to adhere to, or to blend with other polymers, has inspired studies that permit the chemical modification of the polyolefines, especially in polyethylene. This change in the structure would improve the miscibility in the mixtures with polar polymers, and would increase the applications of these materials in the world trade. The grafting of functional groups (functionalization) in the polymeric chains confers them some polarity, improving their properties and favoring the adherence or compatibility with other materials. These functionalization reactions can be carried out in a solution or in the melt through reactive extrusion [3,4]. In general, the initiation of the functionalization takes place through decomposition of organic compounds called initiators, such as the dicumyl peroxide. Nowadays, a tendency to use gamma radiation as initiator and generator of free radicals is growing [6,7]. In this work, we studied the behavior of radicals in the process of functionalization of high-density polyethylene synthesized in our laboratory with

diethyl maleate in decalin irradiated with gamma radiation. EPR was used to observe the variation of the total free radicals concentration as a function of aging.

### 2. Materials and Methods

The materials used in this study were HDPE, decalin and diethyl maleate. The synthesis of the high-density polyethylene (HDPE) was carried out using bis-(cyclopentadienyl) zirconium dichloride and P-MAO. The functionalization was carried out in solutions of 10% weight/vol of polyethylene in decalin, and 10% weight/vol of polyethylene in nonane, using different diethyl maleate concentrations (5, 10, 15 and 30%), and different radiation doses (5, 15 and 30 kGy) with a dose rate of 5 kGy/h. Small volumes (500 mm<sup>3</sup>) of the samples were used for EPR measurements. The EPR spectra were obtained in an X band EMX BRUKER spectrometer, at room temperature. The total number of spins per gram of sample was obtained using the 4-(2-iodoacetamide)-2,2,6,6-tetramethylpiperidinoxyl radical as standard of comparison. The experimental conditions (microwave power and modulation field) were adjusted to avoid saturation effects in the EPR spectrum.

### 3. Experimental Results

The EPR spectra of the HDPE irradiated at 15 and 30 kGy, HDPE (15 and 30% DEM) in decalin irradiated at 15 kGy, HDPE (30% DEM) in decalin irradiated at 30 kGy, HDPE with decalin irradiated at 15 and 30 kGy, HDPE with nonane irradiated at 15 kGy, HDPE (30% DEM) with nonane irradiated at 15 kGy, HDPE (5 and 10% DEM) irradiated at 30 kGy, and decalin (30% DEM) irradiated at 30 kGy were obtained. Blends without decalin and blends with nonane gave us poor spectra, which can be associated with that of the HDPE alone [2]. Nonane and decalin solvents and all the samples irradiated at 5 kGy did not give detectable EPR signals, while the blends with DEM and decalin showed, for a short time interval ( $\sim 100$  hours), a characteristic EPR signal for the polyethylene irradiated with gamma radiation [2]. After this time interval the signal turned into that of a decalin cation radical one.

Figure 1 shows the spectrum for the HDPE just irradiated at 15 kGy. The spectrum shows fourteen absorption lines that are in agreement with the formation of allyl, alkyl and polyenyl radicals [1,2]. The alkyl radical has been marked in the spectrum with the number 1, while the allyl radical has been marked with the number 2. A narrow, very intense, central line is observed, which correspond to the polyenyl radical. In the inset, the spectrum is shown for the same sample eighteen days after the irradiation process. The effect of aging is the recombination of the allyl and the alkyl radicals thus remaining the polyenyl radical. This is in agreement with previously published results [2]. The HDPE irradiated at 30 kGy shows the same behavior, in other words, only an increase in the total free radical concentrations are observed. From the spectrum we obtained the hyperfine coupling constants. For the spectrum signed 1, we obtained  $a_1 = 23$  Gauss and for the spectrum signed 2, we obtained  $a_2 = 28$  Gauss.

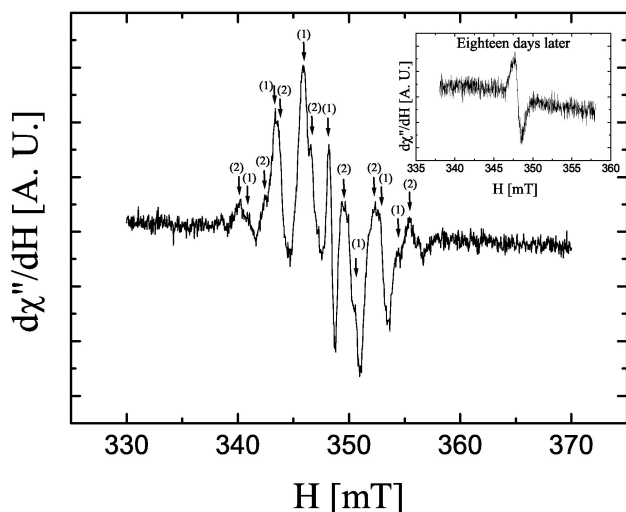


FIGURE 1. EPR spectra of HDPE irradiated at 15 kGy. The inset shows the spectra eighteen days after irradiation.

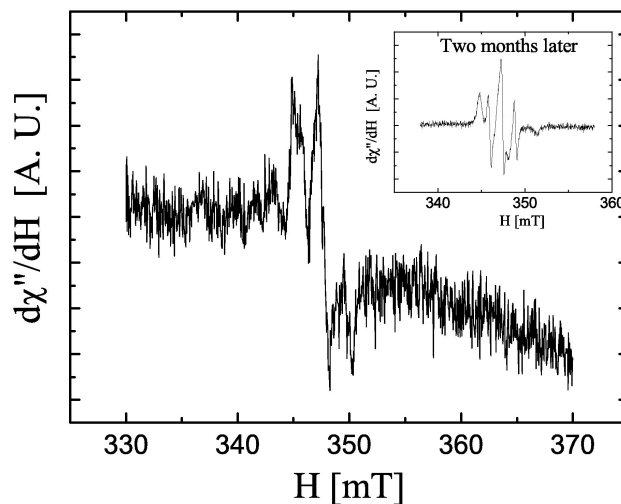


FIGURE 2. EPR spectra of HDPE (15% DEM) irradiated at 15 kGy. The inset shows the spectra two months after irradiation.

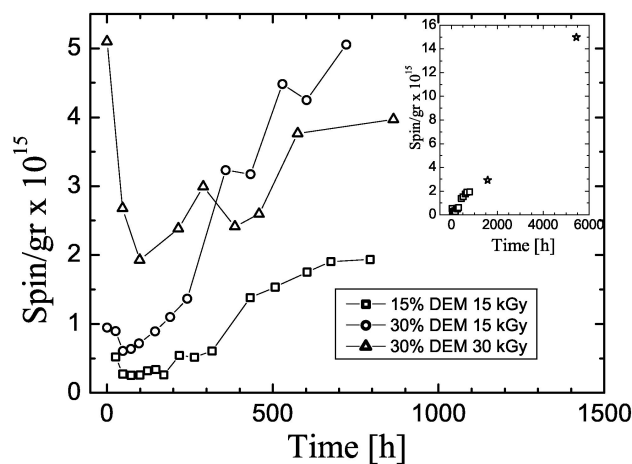


FIGURE 3. Total radical concentration for all the blends studied. The inset shows the behavior of the HDPE (30% DEM) irradiated at 15 kGy after up to 6000 hours.

Figure 2 shows the spectrum obtained for the HDPE (15% DEM) in decalin irradiated at 15 kGy. A very noisy spectrum of six absorption lines is observed. Three of them can be associated with allyl radicals, the very intense central line could be associated to the polyenyl radical, and the other three can be associated with the alkyl radicals. The same spectrum was obtained for every mixture of HDPE-DEM in decalin. The spectra for HDPE (30% DEM) in decalin at 15 kGy and 30 kGy show the same behavior. The inset in the figure shows the effect of aging on the HDPE (15%DEM) in decalin irradiated at 15 kGy; we can see that as time increase, the spectrum is resolved, making possible to separate the absorption lines in it. After a longer period, the spectrum is entirely a  $[(c - DEC)^+]$  spectrum, consisting of two triplets of hyperfine lines each one corresponding to two equivalent hydrogen atoms ( $2H$ ) interacting with the paramagnetic center, resulting in the following two hyperfine coupling constants  $a_1(2H) = 32.8$  Gauss and  $a_2(2H) = 14.93$  Gauss. The first group resonates around  $g = 2.00955$ , and the second

one around  $g = 2.00723$ , in accordance with the parameters obtained for decalin at room temperature onto several matrices [8]. This effect is not present in the same blends without decalin. Decalin alone gives no EPR signal. The short relaxation times of decalin at room temperature are likely to make the spectrum registration impossible [8].

In Fig. 3, the total free radical concentrations are shown as a function the time for all the studied blends. In the period  $0 \leq t \leq 100 h$  we can observe that the total free radical concentrations fall for all the samples studied. After this period, the total free radicals concentration with time increase. This behavior is in disagreement with the results for decalin [8], and for HDPE [2] previously reported, because the total free radical concentrations for both shows an exponential decay with time. Eight months later, the spectrum of the blends was similar to that of decalin. The spectrum for HDPE in decalin, without DEM, and just irradiated, is the same as that for the samples with DEM in decalin eight months after being irradiated. We interpret the increment in the total free radical concentrations as a competition among radicals formed by the polymer degradation and decalin radicals. In a first phase, only the radicals belonging to the polymer are present, decaying quickly ( $\sim 100 h$ ), and in a second phase the decalin radicals are the most important radicals present in the sample. It was demonstrated that the decalin radical cation takes part

in ion-molecular charge transfer to a neutral molecule [8], in our case the HDPE-DEM blend. The increment in the total free radicals concentration supposes that the HDPE-DEM acts as a matrix that slowly exchange charge with decalin, freezing the dynamics of generation of decalin radicals. The inset of the figure shows that the total free radicals concentrations continue increasing 6000 hours after irradiation. Experiments will be continued to observe whether any changes are produced in the behavior of the total free radicals concentration.

#### 4. Summary

The experimental results suggest that allyl, alkyl and polyenyl radicals are generated in the HDPE. In the HDPE (15 and 30%) blends after being irradiated with gamma radiation at 15 and 30 kGy, the polyenyl radical is much more stable. The effect of aging in the blends HDPE-DEM in decalin is the appearance of the  $DEC^+$  radical and a continuous increase of the total free radicals concentration at least until 6000 hours after irradiation. In the HDPE in decalin without DEM sample, this radical can be observed immediately. The HDPE-decalin blend acts as an inhibitor of the  $DEC^+$  radicals reactions.

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