

# Comparative study of different initiation methods in the functionalization of low-density polyethylene with diethyl maleate: Gamma radiation and ultrasound

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## Abstract

This work unfolds a comparative study of the grafting of a low-density polyethylene with diethyl maleate (DEM) using gamma irradiation and ultrasound as means of initiating the grafting reactions. The grafting degree was determined by FTIR using a reported calibration curve. The efficiency of both functionalization methodologies was calculated and the polymers were characterized by differential scanning calorimetry (DSC) and gel permeation chromatography (GPC). The results showed that the grafting degree increases with the radiation dose when the monomer is inserted by gamma radiation. When the ultrasound methodology was used, an additional initiator such as dicumyl peroxide had to be used in order for the grafting to take place. In this last case, changing the time of exposure to the ultrasound source did not induce significant changes in the obtained grafted degree. The use of ultrasonic radiation plus dicumyl peroxide as grafting initiators promoted more insertion than that when gamma radiation was employed.

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## 1. Introduction

The study of grafting systems for polyolefins gained importance due to their potential applications [1–3]. As it is well known, the grafting mechanism requires a radical initiator, able to promote the insertion of the functional monomer [4]. In this sense, the use of radiation sources could be a good alternative, considering that they can produce macroradicals when the polymeric chains are exposed to them [5], with the additional advantage of the exclusion of a chemical initiator [6–8].

Gamma radiation has been used to graft functional monomers. Bucio et al. [6], have reported that polyolefins films can be grafted with poly(acrylic esters) by either a direct or a vapor phase irradiation method, observing that the grafting degree increases with the monomer concentration and the radiation dose. Grafting of diethylmaleate onto polyethylenes in a decalin solution using gamma rays as initiator has also been studied. The grafting degree was reported to increase as a consequence of an increase of the absorbed dose, evidencing that at high radiation dose the grafting competed with secondary reactions such as long-chain branching and crosslinking [9,10].

On the other hand, the use of ultrasound for grafting monomers onto polymers has been reported. Polypropylene and polyethylene have been grafted with maleic anhydride (MAH) [11,12]. These studies showed that the

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ultrasonic energy can be used as chemical initiator. In the case of polypropylene [11], the grafting degree obtained was higher (4.65%) when lower MAH and chemical initiator (benzoyl peroxide) concentrations were used at higher power levels. However, additional degradation induced by ultrasound was observed. A significant increase in the grafting degree was reached in polyethylene [12] (about 0.6%), when the ultrasound intensity was increased from 60 to 280 W.

Based on those reported works, the aim of this study was to analyze the feasibility of grafting diethyl maleate (DEM) onto a low-density polyethylene (LDPE) using gamma rays and ultrasound as initiators, to propose an alternative grafting methodology that avoids the use of chemical initiators and decreases the effects of secondary reactions.

## 2. Experimental

A commercial low-density polyethylene (LDPE) with a MFI of 4.06 dg/min, supplied by Polynter, C.A. (Venezuela) was used. Solutions of the LDPE were prepared at 10% wt/vol using a blend of *cis* and *trans* decahydronaphthalene (decalin) 99%, supplied by Riedel de Haën, as solvent. Ethanol and *n*-hexane were employed as washing solvents. Diethylmaleate (DEM), manufactured by Aldrich Chemical Company Inc. was used as the functionalization monomer.

Solutions of LDPE and DEM in decalin were prepared, heating and keeping a continuous agitation, as follows: DEM (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  $\gamma$ -rays from a  $^{60}\text{Co}$  source in air atmosphere at room temperature, at a dose rate of 4.8 kGy/h and integral doses ranging from 15 to 400 kGy.

Similar samples were exposed to ultrasonic energy from an Ultrasonic Processor (130 W – 20 kHz). First of all, the horn was immersed into the solution until a complete polymer melt was observed (10 min approximately). Then, the selected dicumyl peroxide (DCP) concentration was added (0.2% and 2%). The exposition time was varied between 10 and 30 min.

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 approximately 18 h.

FTIR spectra were taken from compression-molded films of the functionalized polymers and their grafting degrees were determined by means of a reported  $^{13}\text{C}$  NMR-FTIR calibration curve [13]. These spectra were recorded in a NICOLET Magna-IR 560 E.S.P. Spectrometer after 32 scans and at 2  $\text{cm}^{-1}$  of resolution. The peak area ratios ( $1740\text{ cm}^{-1}/1460\text{ cm}^{-1}$ ) were estimated, considering the characteristic bands of DEM at  $1740\text{ cm}^{-1}$  and of polyethylene at about  $1460\text{ cm}^{-1}$ , corresponding to the

C=O stretching vibration and C–H bending vibration of  $\text{CH}_2$ , respectively. The grafting degree 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 calculated through the ratio of the initial monomer moles added into the solution and the grafting degree obtained for each sample, calculated as mol percent 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 Mettler Toledo DSC822 calorimeter. Samples were heated under nitrogen atmosphere from 25 to 170 °C at  $20\text{ }^\circ\text{C min}^{-1}$  and kept at 170 °C for 3 min, in order to erase all previous thermal history. Then, the sample was cooled at  $10\text{ }^\circ\text{C min}^{-1}$  from 170 to 25 °C. Finally, a second heating was performed from 25 to 170 °C at  $10\text{ }^\circ\text{C min}^{-1}$ . The crystallinity degree ( $X_c$ ) was calculated using the enthalpy of a perfect crystal as reference (293.6 J/g).

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 an calibration curve based on standard polystyrenes.

## 3. Results and discussion

The low-density polyethylenes grafted using the proposed initiating methods (gamma rays and ultrasound) showed the characteristic band related with DEM insertion at  $1740\text{ cm}^{-1}$ , according to the expected grafting mechanism, which in both cases occurs in a similar way, considering that the nature of the generated macroradicals is the same as that obtained by other grafting methodologies [4]. Additionally, the obtained spectra are similar to those reported in the literature [9–14], which allowed to evidence that the functionalization indeed took place and to calculate the grafting degree by the calibration curve reported by Rosales et al. [13].

When gamma radiation was employed, the grafting degree values did not show significant variations at low irradiation doses (15, 30 kGy), as it is displayed in Fig. 1. However, when higher doses were applied, a considerable increase was noticed as the absorbed dose increased, achieving the maximum grafting degree (0.52% molar) at 400 kGy and 30 DEM%. This means that the polymer needs higher radiation energies in order to produce enough number of radicals that can induce the insertion of the functional monomer, which besides, improves the efficiency of the grafting process (Table 1). The influence of DEM concentration can only be ascertained from 50 kGy, where the increase of the amount of the functional monomer allowed obtaining higher grafting degrees values. However, the efficiency of this system is lower, evidencing that the monomer can not be totally consumed. This was attributed to the low DEM insertion achieved and diffusion problems inherent to this initiation method.

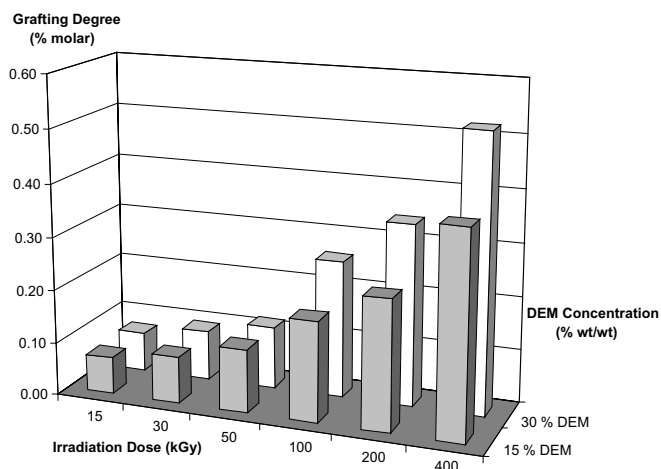


Fig. 1. Grafting degree of LDPE functionalized with DEM (15 and 30 wt.% in solution) at different gamma irradiation doses.

On the other hand, when ultrasound was tested to induce the DEM insertion, the first fact observed was that it is also necessary the addition of dicumyl peroxide as chemical initiator, because no insertion was observed when the samples were exposed to ultrasound alone. Even at low peroxide concentration (0.2%), no grafting was obtained. Significant grafting degree values were obtained at 2% of dicumyl peroxide.

As Fig. 2 shows, the time of exposure has no influence on the grafting degree when 15 DEM% was used. However, the increase on DEM concentration not only produced a higher monomer insertion but also allowed to evidence the effect of the time of exposure. This was expected because the probability of dicumyl peroxide decomposition into radicals increases when higher exposure times are elapsed, increasing the insertion of the functional monomer, which is more suitable when more DEM is present into the reaction medium. In this case, the maximum grafting degree achieved was 0.6% molar, when 30% DEM and 30 min of exposure time were employed.

It is noteworthy that the results presented above are comparable with those obtained using other functionalization methodologies, such as reactive extrusion, where DEM and dicumyl peroxide were been employed, e.g. Rosales et al. [13], that reported grafting degrees between 0.2 and 0.6 mol%. In this sense, gamma radiation offers an alternative method when the final use of the grafted polymer requires low chemical levels such as in food packaging, biomedical articles, etc.

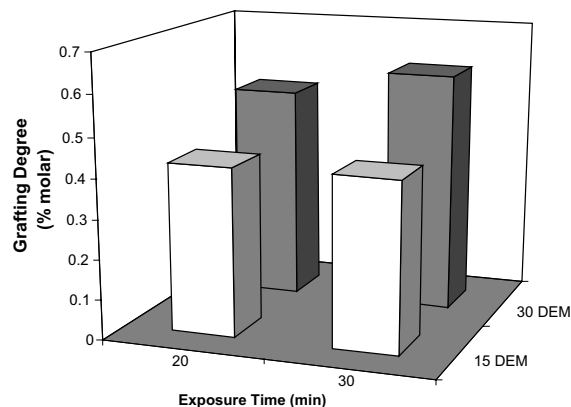


Fig. 2. Grafting degree of LDPE functionalized with DEM (15 and 30 wt.% in solution) at different ultrasound exposure times using 2 wt.% of dicumyl peroxide.

Comparing both irradiation sources, the obtained results showed that ultrasound plus dicumyl peroxide used as initiation method not only provided higher grafting degree values than those obtained with gamma radiation, but also that it was more effective according to the efficiency values (Table 1). The presence of the dicumyl peroxide allowed for an additional radical generation into the system, with a lower energy requirement to promote the scission of the polymer C–H bond without a chemical initiator as in the gamma radiation case. Additionally, ultrasound waves were able to increase the temperature of the system, melting the polymer and making more favorable the diffusion of the monomer toward the macroradicals, which therefore improved the efficiency of the system.

The thermal properties did not evidence structural changes as a consequence of the type of radiation source and the variation of the radiation conditions. All samples displayed melting temperatures between 109 and 110 °C and crystallinity contents between 35 and 40%. This fact can be attributed to the low grafting degrees obtained, meaning that the DEM insertion did not produce significant variations on the linear chain sequences.

The molecular weight distributions showed no appreciable differences when the polymer without DEM was exposed to ultrasound at the different exposure times (Fig. 3(a)). When gamma radiation was used, a significant curve displacement toward the fractions of higher molecular weights was observed as the radiation dose increase (Fig. 3(b)). This fact demonstrates that ultrasound is not able to modify significantly the molecular weight distribu-

Table 1  
Grafting efficiency of LDPE functionalized with DEM by gamma rays and ultrasound as initiators

% DEM	Gamma irradiation Integral dose (kGy)						Ultrasound <sup>a</sup> Exposure time (min)	
	15	30	50	100	200	400	20	30
15 DEM	10.0	12.5	17.0	27.0	35.1	55.1	45.5	45.9
30 DEM	5.3	6.7	8.4	18.5	24.5	37.3	57.7	64.6

<sup>a</sup> 2% dicumyl peroxide was added.

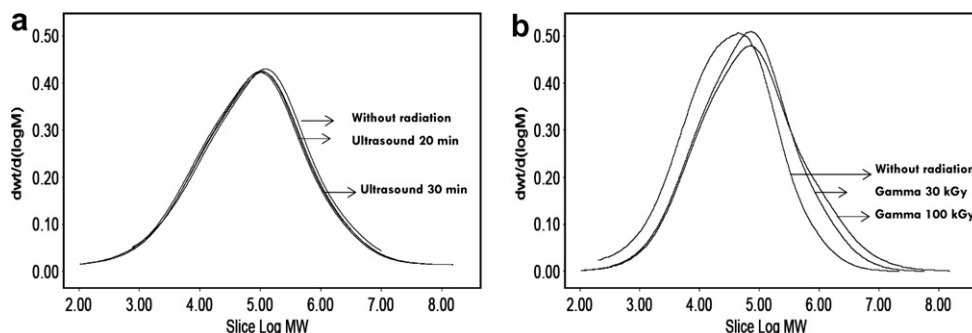


Fig. 3. Molecular weight distribution curves of LDPE without DEM, exposed to irradiation sources: (a) ultrasound at different exposure times; (b) gamma irradiation at different integral doses.

Table 2

Average molecular weights ( $M_n$  and  $M_w$ ) and polydispersities of LDPE functionalized with 30 wt.% DEM by gamma rays and ultrasound as initiators

Radiation source	Sample	$M_n$	$M_w$	Polydispersity
Without radiation	0% DEM-0 kGy	6552	143247	21.9
Gamma rays	30% DEM-30 kGy	13099	239267	18.3
	30% DEM-50 kGy	20109	387837	19.3
	30% DEM-100 kGy	28982	410477	14.2
Ultrasound	30% DEM-2pdc-20 min	10047	191301	19.0
	30 % DEM-2pdc-30 min	9762	211887	21.7

Table 3

Average molecular weights ( $M_n$  and  $M_w$ ) and polydispersities of LDPE irradiated with gamma rays and ultrasound without DEM

Radiation source	Sample	$M_n$	$M_w$	Polydispersity
Without radiation	0% DEM-0 kGy	6552	143247	21.9
Gamma rays	0% DEM-30 kGy	10892	331932	19.3
	0% DEM-50 kGy	11098	419507	30.5
	0% DEM-100 kGy	11591	631580	37.8
	0% DEM-20 min	11286	224980	19.9
Ultrasound	0% DEM-30 min	11230	223886	19.9

tion, because its energy is insufficient to produce significant molecular changes, while the energy induced by gamma irradiation is higher and able to produce a higher number of radicals in the medium and induce long-chain branching and crosslinking [5,15,16].

This effect also can be noticed when the changes in the molecular weights of the functionalized LDPEs obtained by both radiation sources (Table 2) are compared. Such changes are more pronounced when gamma irradiation was used as initiator. An important increase in the molecular weight with the raise of gamma radiation dose can be noticed due to the fact that when the supplied energy is increased the competition of secondary reactions such as long-chain branching and crosslinking [15,16] becomes predominant. Additionally, it is important to consider that the radiation with gamma rays was performed without stirring, hence the poor diffusion makes the radicals coupling more favorable. More significant changes were produced in the molecular weight of LDPE when it was irradiated without the grafting monomer at different doses (Table 3). The values shown in this table corroborate that the effect of ultrasound in the LDPE's molecular weight is not important.

This last fact is an important advantage, because the grafting can be achieved without significant changes in the polymer's final properties, especially in the mechanical properties, which depend on the molecular structure [16]. Gamma radiation also produced a decrease in the polydispersity as a consequence of structural molecular changes that seems to homogenize the population of polymer chains.

The results showed a slight increase in the molecular weights of the ultrasound treated materials, evidencing that secondary reactions could also have been occurring due to the presence of the dicumyl peroxide, but the better diffusion of DEM as a consequence of the vortex originated by the ultrasound waves makes the monomer insertion reactions more favorable. The polydispersity in these last cases did not show significant changes.

#### 4. Conclusions

Both Gamma radiation and ultrasound were able to promote the DEM insertion into the polymeric chains, achieving the maximum grafting degree values of 0.52%

and 0.60%, respectively, at the better setting conditions. The ultrasound exposure seems to be more efficient, when an additional chemical initiator is added (dicumyl peroxide). Ultrasound did not produce significant changes on the molecular structure of LDPE. On the contrary, changes in the molecular weight distribution curves were ascertained when gamma radiation was employed. This result is important, when the final application demands for keeping the original polymer properties after the grafting.

The grafted products obtained by gamma radiation seem to be a good alternative to manufacture food packaging, biomedical articles or other applications that require low levels of structural changes from the starting polymer.

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