

# Ultraviolet Preirradiation of High-Density Polyethylene for the Grafting of Maleic Anhydride During Reactive Extrusion

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**ABSTRACT:** High-density polyethylene was irradiated with ultraviolet light for various exposure times, as a prestep for hydroperoxide production, before a bulk grafting reaction with maleic anhydride in the melt phase by reactive extrusion. This method was compared with a traditional grafting procedure using peroxides optimized by an evaluation of the grafting level versus the screw speed; the highest speed showed the greatest grafting value. The reaction was followed by Fourier transform infrared, the gel percentage, and the grafting degree, which was evaluated by titration. The effect of grafting for both methods under the established processing

conditions on the thermal properties was observed with differential scanning calorimetry via their heating and cooling thermograms; there were notorious changes in the fusion peak temperatures, indicating differences in the crystallization process after the grafting reaction. The latter was confirmed by NMR spectroscopy, which showed succinic anhydride rings attached to the polyethylene chains. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2882–2888, 2006

**Key words:** functionalization of polymers; polyethylene (PE); radiation; reactive extrusion

## INTRODUCTION

Reactive extrusion has been known since the 1950s and at present is a main process for obtaining modified polymers for which the reaction is carried out in a molten phase. This processing method is helping the development of polymers with new and specific characteristics because of its versatility under control conditions and is economically attractive because materials can be obtained in a continuous way.<sup>1–15</sup> The modification of polyolefins, mainly high-density polyethylene (HDPE), by reactive extrusion has been widely studied,<sup>4,8,10,11,15</sup> and it is common to use free-radical precursors such as organic peroxides to initiate the grafting reactions of specific monomers, such as acrylic acid, glycidyl acrylate and methacrylate, and maleic anhydride (MAH), to increase the properties of adhesion, wetting, and compatibility with other polymers.<sup>2,10</sup> Free-radical generation in molten, solid, and solution phases by nonperoxide methods such as ultrasound, pulverization, and ultraviolet (UV) radiation has been fairly well studied;<sup>15–20</sup> these methods are usually applied or used in reactive extrusion; for example, Zhang and Li<sup>15</sup> grafted MAH onto HDPE

through ultrasonic initiation. We previously reported the UV sensitization of polyethylenes for the grafting of MAH in the molten phase with a bambury-type mixer,<sup>16</sup> demonstrating that UV light is powerful enough to produce the necessary free radicals to attach MAH to the polyethylene polymer chains.

This work shows the performance of UV-preirradiated HDPE for grafting MAH during reactive extrusion with different doses of UV radiation under specific processing conditions. The results are compared with a typical grafting process using peroxides. The grafted HDPE was characterized with several methods, such as titration (to obtain the grafting percentage), the gel percentage, Fourier transform infrared (FTIR) and NMR spectroscopy, differential scanning calorimetry (DSC), and the melt flow index.

## EXPERIMENTAL

### Materials

HDPE 60003 from Pemex (Cuatzacoahuac, Veracruz, Mexico) and MAH from Hoechst Chemicals were used (Frankfurt, Germany). The latter (5% w/w) was added to each sample of preirradiated HDPE. To samples that were not preirradiated, 0.7% (w/w) dicumyl peroxide (DCP; Aldrich Chemicals, Milwaukee, Wisconsin) was added at 98% for comparison.

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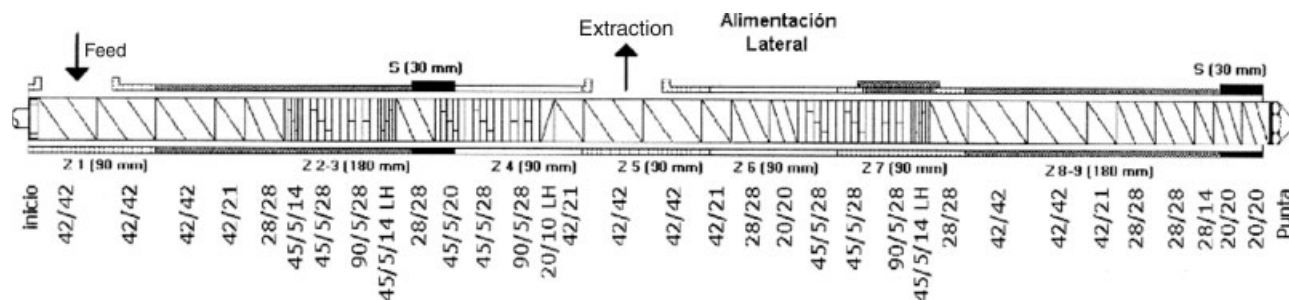


Figure 1 Extruder screw configuration.

## UV radiation

HDPE pellets were exposed to UV radiation in a homemade chamber for 12, 24 and 48 h; this included a manual mixing procedure four times during each exposure to obtain the most homogeneous irradiation possible before the MAH grafting procedure. The irradiation chamber consisted of a UV source (a 40-W fluorescent lamp) with an emission range of 290–390 nm and a maximum peak at 313 nm.

## Grafting reaction

The grafting reaction using peroxide was carried out with a W&F ZSK-30 (Ramsey, New Jersey) twin-screw extruder with at a constant processing temperature of 190°C and screw speeds of 50, 100, 200, 300, and 400 rpm to obtain the best conditions for maximum grafting. Pellets were finally obtained from the filament. The grafting reaction of MAH onto UV-preirradiated HDPE was carried out in the same extruder at the same temperature but with only the 400 rpm screw speed (best condition). The screw configuration used in this work is shown in Figure 1.

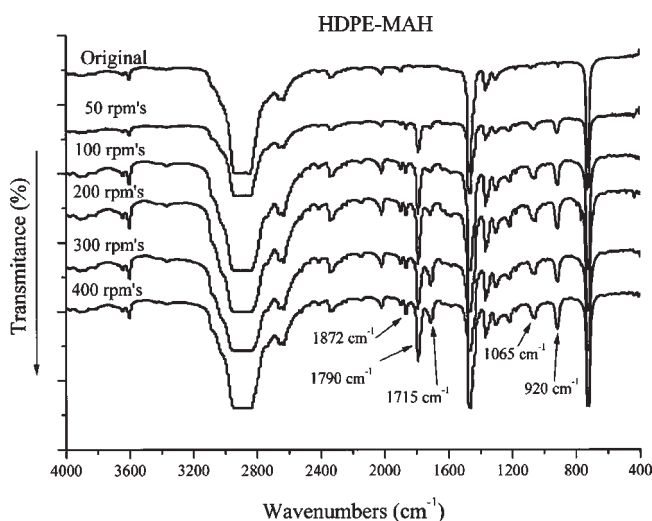


Figure 2 FTIR spectra of polyethylene modified with MAH with peroxide as the initiator at different screw speeds.

## Sample evaluations

### Grafting and gel content

The unreacted MAH was removed by the extraction of 1 g of MAH-grafted HDPE under 250 mL of hot xylene for 8 h according to the apparatus described in ASTM D 2765. The xylene-insoluble portion corresponded to the gel percentage, whereas the soluble part was precipitated and washed with acetone and was finally dried at room temperature. The grafting percentage was determined by the acid number according to a literature-reported procedure.<sup>21</sup>

### FTIR spectroscopy

The precipitated material was used to obtain a film by heating and compression, which was subjected to FTIR transmission spectroscopy with a Nicolet Magna 550C instrument (Madison, Wisconsin). The carbonyl and OH indices were calculated with the bands at 1720 and 3370  $\text{cm}^{-1}$ , respectively, with the 1365- $\text{cm}^{-1}$  band as a reference. The film thickness was approximately 150  $\mu$ .

### Melt flow index

The product obtained from reactive extrusion was used to determine the melt flow at 190°C and a 21,600-g load

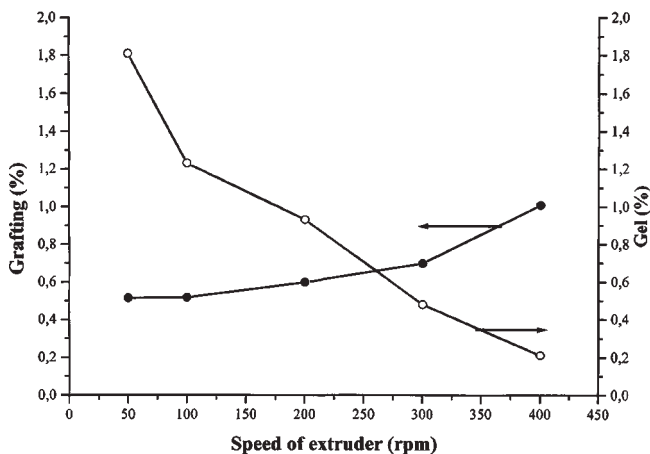
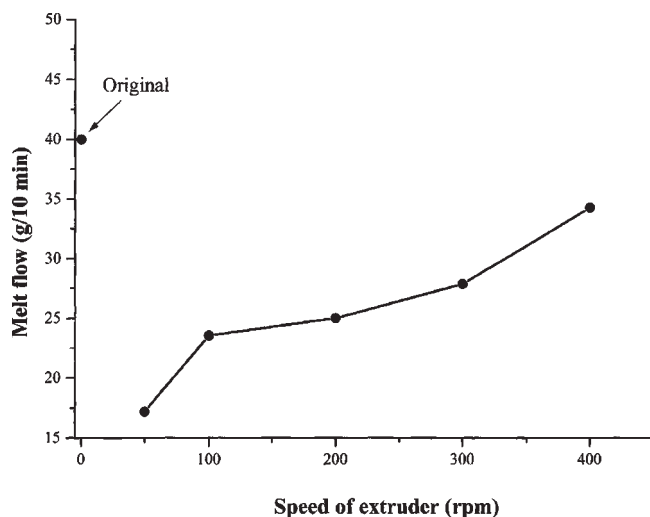


Figure 3 Grafting of MAH and gel content of polyethylene modified with MAH with peroxide as the initiator at different screw speeds.



**Figure 4** Melt flow index of polyethylene modified with MAH with peroxide as the initiator at different screw speeds.

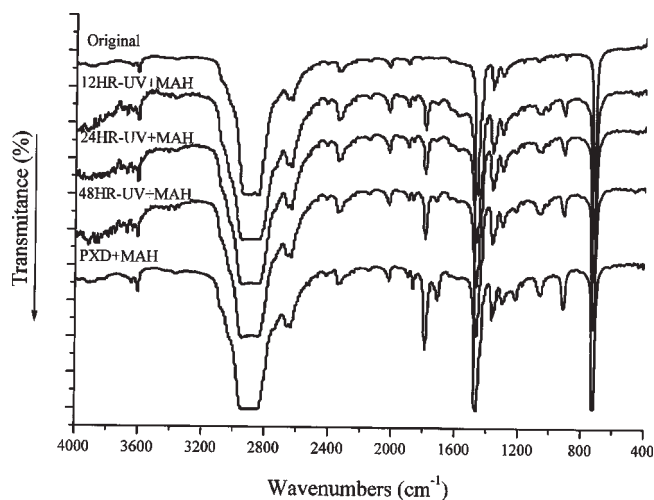
with a Kayeness model 7053 instrument. The evaluation was carried out according to ASTM D 1238 (Morgantown, Pennsylvania).

#### Thermal analysis

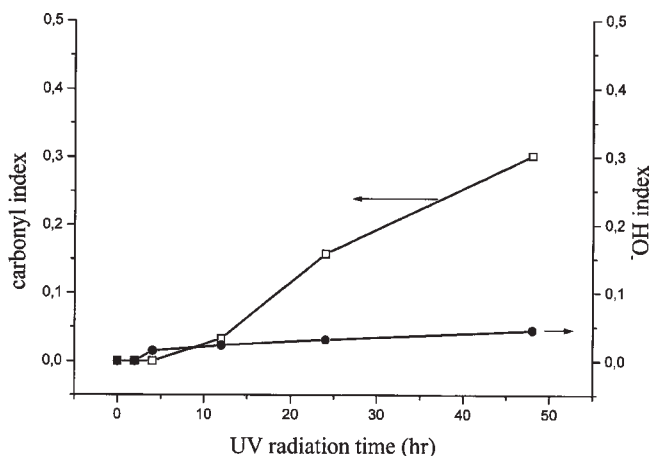
To evaluate the thermal properties, a TA Instruments 2920 differential scanning calorimeter (New Castle, Delaware) was used with a heating and cooling ramp of 5°C/min and a nearly 10-mg sample. To obtain the crystallinity percentage ( $1 - \lambda$ ) [ $\lambda$  = Fraction of amorphous state], the following equation was applied:

$$(1 - \lambda)(\%) = \Delta H_F \times (100/\Delta H_{Feq})$$

where  $\Delta H_F$  is the enthalpy of fusion and  $\Delta H_{Feq}$  is the enthalpy of fusion at equilibrium when the polymer is totally crystalline ( $\Delta H_{Feq} = 288.8 \text{ J/g}$ ).<sup>22</sup>



**Figure 5** FTIR spectra of polyethylene treated with UV light and MAH at different exposure times and with peroxide (PXD) and MAH.



**Figure 6** Carbonyl and OH groups produced at different exposure times.

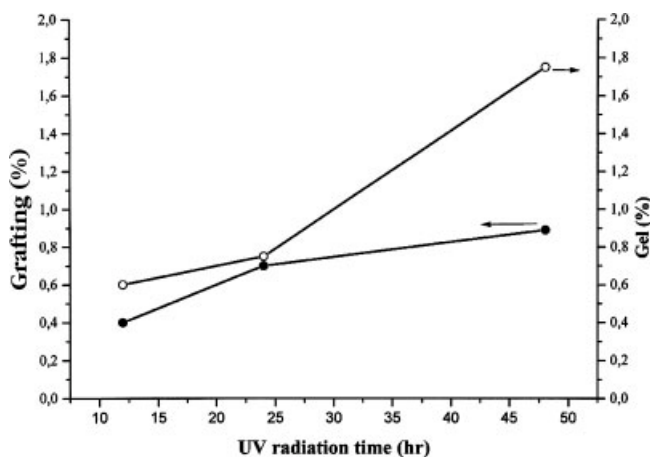
#### NMR spectroscopy

The <sup>1</sup>H-NMR spectra of grafted polyethylene were obtained with a JEOL Eclipse-300 spectrometer (Tokyo, Japan) at 110°C; the samples were dissolved in tetrachloroethane and deuterated chloroform.

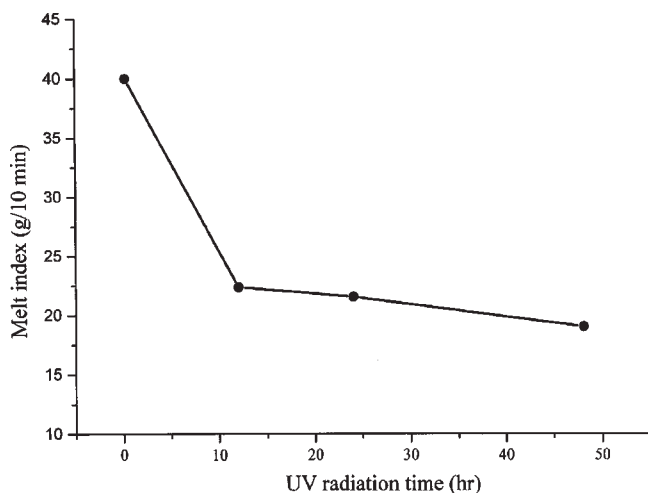
## RESULTS AND DISCUSSION

### Grafting reaction with peroxide

With a common procedure for polymer modification with a free-radical initiator (peroxide) and with the variation of the speed of a twin-screw extruder, HDPE materials were obtained with different grafting grades of MAH. Figure 2 shows FTIR spectra in which peaks at 1790 and 1872  $\text{cm}^{-1}$  can be seen, indicating the presence of the carbonyl succinic ring from the anhydride group; they also show the carbonyl acid group at 1715  $\text{cm}^{-1}$ , the double bonding of carbon with carbon ( $\text{C}=\text{C}$ ) at 920  $\text{cm}^{-1}$ , and the simple bond of carbon



**Figure 7** Grafting of MAH and gel content of polyethylene treated with UV light and MAH at different exposure times.



**Figure 8** Melt flow index of polyethylene treated with UV light and MAH at different exposure times.

with oxygen of five-member rings at  $1065\text{ cm}^{-1}$ .<sup>16,23,24</sup> All these peaks increase notoriously with the speed of extrusion.

The grafting and gel percentages are shown in Figure 3; the xylene-insoluble material, corresponding to the crosslinked polymer produced during reactive extrusion, was inversely proportional to the speed of extrusion. The highest concentration of the gel obtained was around 1.8%, corresponding to the lowest speed. This behavior indicated that the residence time of the polymer inside the extruder was determinant for the more efficient crosslinking process. Such results were confirmed with the melt flow data shown in Figure 4 because the melt flew faster when the speed screw was increased. On the other hand, the grafting grade was proportional with the speed extrusion; the highest value was 1.05%, which corresponded to the maximum speed of extrusion.

The observed grafting and gel behavior was related to the competition between the polymer grafting reaction and crosslinking. In our particular case, when the extruder screw speed was increased for the grafting reaction, apparently grafting was the dominant process, as we observed less crosslinking; these results are in agreement with those reported by Genzebeld and Janssen.<sup>4</sup> They observed that with an increase in the screw speed, component mixing was favored. This increased the probability that the MAH monomer would found an active site in the polymer by the action of peroxide. When the residence time was reduced, the

polymer degradation process by the temperature was reduced; this was another factor producing crosslinking. At a slow extruder screw speed, the dominant reaction was crosslinking, mainly because of the high residence time and the peroxide action, which could promote the thermal degradation of the polymer. This behavior is in agreement with some authors such as Genzebeld and Janssen<sup>4</sup> and Kustadinova et al.<sup>25</sup>

These results were used for setting up the next experimental step: using UV-preirradiated HDPE, with different times of radiation exposure, with the same MAH to carry out the grafting reaction in the extruder without the addition of any peroxide.

### Grafting reaction with UV preirradiation

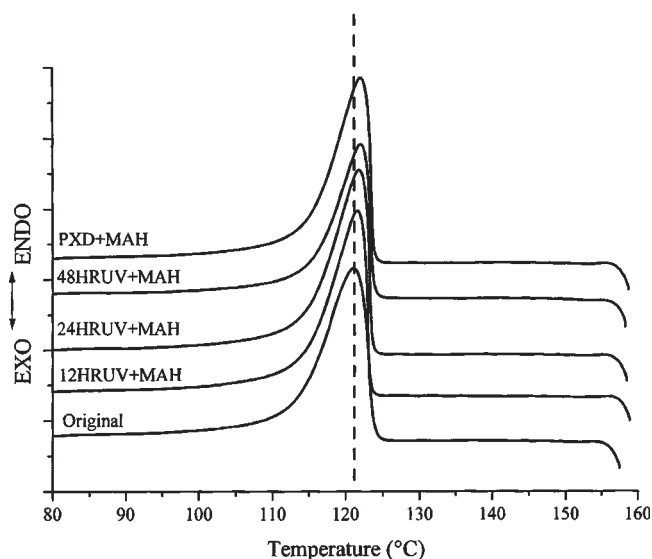
#### FTIR spectroscopy

There were visible changes for all preirradiated polyethylenes after the grafting reaction with UV exposure for times of 12, 24, and 48 h; this was due to hydroperoxide formation during the irradiation time.<sup>16</sup> Such oxidized structures reacted during the high-temperature processing. The FTIR spectra of these samples are shown in Figure 5, along with the same development of bands observed in the spectra of HDPE grafted with peroxide (under the same processing conditions); in this case, the bands increased with the UV exposure time of HDPE. This behavior, observed along with the irradiation, was due to the progress of the oxidation, which initially only oxidized the surface, whereas at longer times, this effect penetrated the polymer matrix, apart from the obvious extensive effect on the surface.<sup>26</sup>

To explain the oxidation development before the grafting reaction, an evaluation of carbonyl and OH group formation was carried out by FTIR for the UV-preirradiated materials; this is shown in Figure 6. The materials with 2 and 4 h of UV exposure did not produce carbonyl groups, but OH ones appeared at 4 h of treatment (slightly seen); this development was in agreement with the oxidation mechanism reported in our previous article,<sup>16</sup> in which the OH groups were consumed to produce the carbonyl species. It was also supported by the low number of OH groups through the treatment time. The materials with longer UV exposure times produced more carbonyl and OH groups, corroborating the increase in the grafting observed in Figure 7.

**TABLE I**  
Crystallization and Fusion Temperatures Before and After Grafting with UV Preirradiation and Peroxide

Material	Original	12 h of UV and MAH	24 h of UV and MAH	48 h of UV and MAH	Peroxide and MAH
Crystallization temperature (°C)	121.1	121.5	121.9	122.1	122.2
Fusion temperature (°C)	133.7	130.3	130.5	130.4	131.0



**Figure 9** Crystallization peaks of polyethylene treated with UV light and MAH at different exposure times and with peroxide (PXD) and MAH.

#### Grafting and gel content

The grafting degree and gel content are shown in Figure 7, and they are in perfect agreement with the results observed in the FTIR spectra in Figure 5: the grafting of MAH onto UV-preirradiated HDPE increased with the exposure time to reach a maximum at 48 h. On the other hand, the gel content also increased with the UV exposure time (Fig. 8). This development occurred because with the UV exposure time, the reactive structures increased and therefore could produce more free radicals.

Such behavior was similar to that observed when peroxide was used as the initiator along with the screw speed.<sup>4,11,25,27</sup> Figure 3 shows that the maximum grafting percentage obtained at 400 rpm and 190°C was around 1%, whereas UV irradiation (Fig. 7) showed 0.8% under the same processing conditions, indicating that the exposure to UV light developed active sites that increased with time, producing more activity in the same way as it was increased with the peroxide content.

#### Thermal analysis

The HDPE grafted by UV preirradiation or peroxide (under the same processing conditions), showed an increment in the crystallization temperatures, as shown in Table I. This effect, also shown in Figure 9, was basically due to the grafting of MAH onto the polymer matrix; this produced changes in the forms of the crystals, producing less perfection in the structure by disturbing the chain movements as a result of the functional group presence.<sup>8,16,26,28,29</sup> The latter was clear when we evaluated the crystallization percentage (Table II); grafted MAH could act as a nucleating agent.

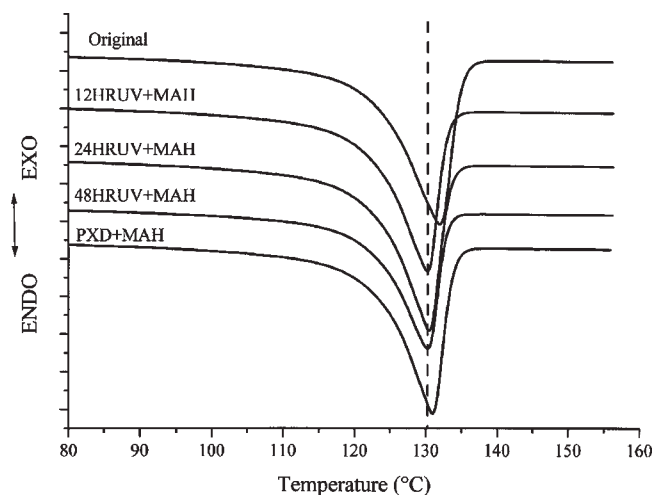
**TABLE II**  
Crystallization Percentage Before and After Grafting with UV Preirradiation and Peroxide

Material	1 - $\lambda$ (%)
Original	74.6
12 h of UV and MAH	72.2
24 h of UV and MAH	69.0
48 h of UV and MAH	53.2
Peroxide and MAH	67.1

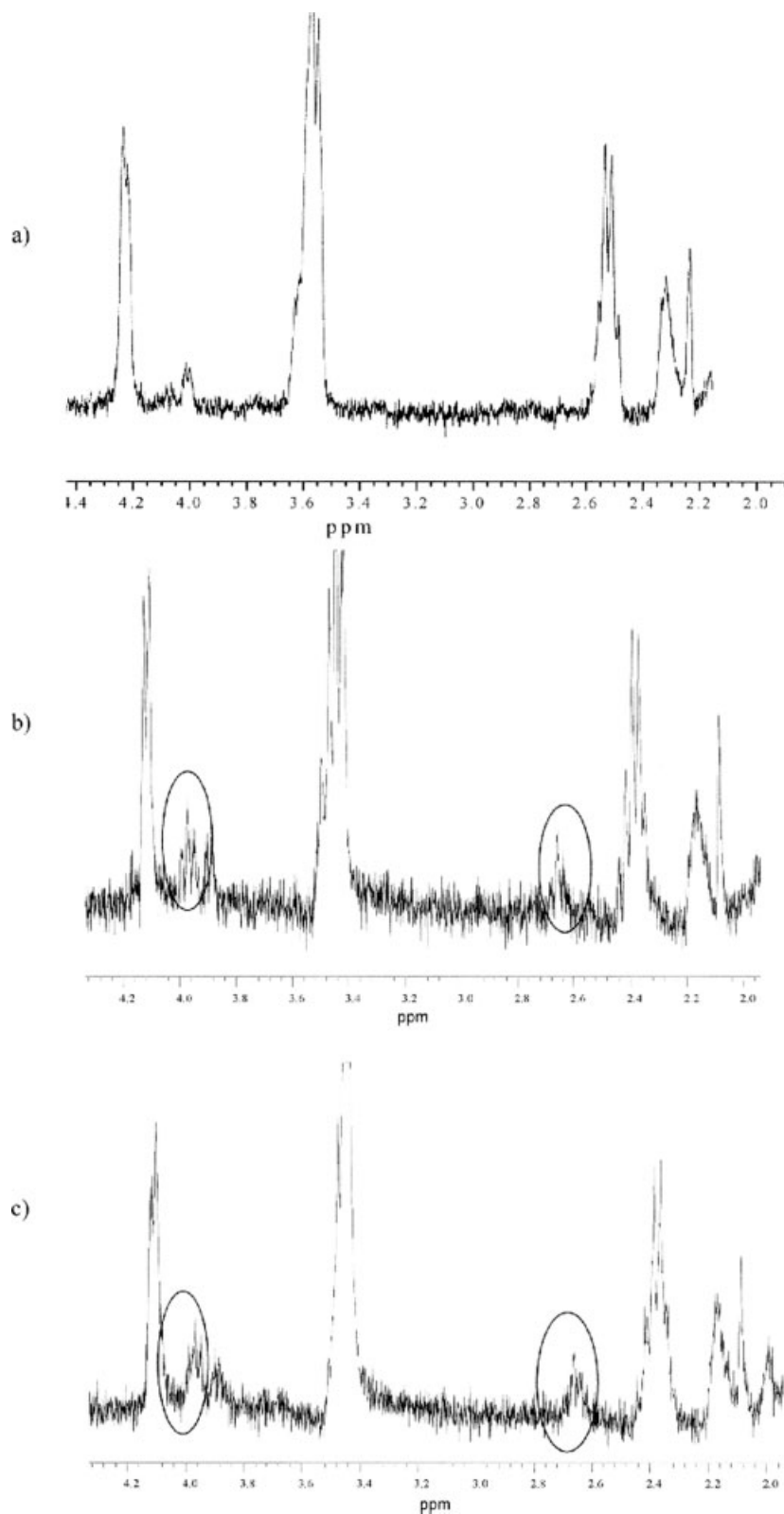
The fusion peaks observed in the DSC thermograms for grafted materials also showed some effects due to the presence of MAH on the polyethylenes; this is shown as a reduction in such peaks, as displayed in Figure 10. The reduction effect for the transition temperatures was a result of the grafted chemical structure, which was voluminous and did not allow the polymer chains to accommodate properly, affecting the perfection of the crystal. Similar effects on transition temperatures (crystallization and fusion temperatures) were observed by Duvall<sup>29</sup> for polypropylene, by Rosales and coworkers<sup>6,8</sup> and Simmons and Baker<sup>30</sup> for polyethylene, and more recently by Zhang and Li.<sup>15</sup> On the other hand, Liu et al.<sup>31</sup> did not observe such changes in the fusion temperatures of polyethylenes grafted with MAH, perhaps because of the use of a high heating speed ( $>10^{\circ}\text{C}/\text{min}$ ) during DSC evaluations, which could hide the fusion temperature reduction.

#### NMR spectroscopy

The  $^1\text{H}$ -NMR spectrum of the original HDPE is shown in Figure 11(a), whereas the grafted HDPE with 12 h of preirradiation time is shown in Figure 11(b), and HDPE grafted with peroxide as the initiator is shown in Figure 11(c). The grafted polymer showed two small



**Figure 10** Fusion peaks of polyethylene treated with UV light and MAH at different exposure times and with peroxide (PXD) and MAH.



**Figure 11** <sup>1</sup>H-NMR spectra of (a) untreated polyethylene, (b) polyethylene treated with UV light and MAH, and (c) polyethylene treated with peroxide and MAH.

resonances at 2.65 and 3.95 ppm, which were evidence that succinic anhydride rings were individually attached to HDPE, as mentioned in the literature,<sup>10,16</sup>

because there was no poly(maleic anhydride), as evidenced by the presence of a broad group of resonances over 4.2 ppm.<sup>26</sup> These results were in agreement with

those reported more recently by Zhu et al.<sup>27</sup> during the grafting of MAH onto LLDPE with a DCP-like initiator, MAH monomers were mainly attached to the polyethylene chain as single MAH groups.

### CONCLUSIONS

The grafting of MAH onto UV-pretreated HDPE in reactive extrusion showed good sensitivity to the exposure or treatment time: the grafting and gel percentages were proportional to this irradiation. The results obtained in this work with UV radiation showed behavior similar to that reported when peroxide was used as an initiator because, for the latter, 1% grafting was obtained, whereas 48-h-UV-irradiated HDPE, under the same processing conditions, had 0.8%. With a high concentration of reactive sites, by either UV light or peroxide addition, not only was a high grafting degree produced, but the gel content was also increased. The presence of MAH in the chains of HDPE produced some changes in the crystallization and fusion temperatures and a notorious reduction in the level of crystallinity. Extruder conditions, such as high-speed screws, were very important factors for obtaining a good grafting degree and less gel content, as shown in the setting experiments with peroxide as the initiator. MAH was attached to the UV-preirradiated HDPE chain by single monomers because evidence of poly(maleic anhydride) was not found. These results clearly indicate that UV-degraded HDPE could replace peroxides for chemical modifications with optimized irradiation conditions.

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