Grafting of Polyethylenes by Reactive Extrusion. I. Influence on the Molecular Structure

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ABSTRACT: Grafting of polyethylenes is an important method used in the modification of polyolefins with functional groups. Lately, the use of extruders as polymerization reactors has increased considerably. However, knowledge of the details of the reaction in the extruder is still limited. In this investigation, the grafting of various commercial polyethylenes, high-density polyethylenes (HDPEs), and linear low-density polyethylenes (LLDPEs) with diethyl maleate (DEM) was carried out in two corotating twin-screw extruders with different screw configurations and extrusion conditions. Two initiators at different concentrations were used. It was found that when the initiator level was raised in the LLDPEs the grafting degree increased and the molecular weight distribution of the grafted LLDPE2 did not show appreciable differences when they were compared to the virgin resin. On the other hand, the terminal vinyl group concentrations decreased at the expense of increasing the *trans* unsaturation concentrations. This last result is consistent with the formation of long-chain branching. Additionally, the weight-average molecular weight of grafted high-density polyethylene (HDPE1-*g*-DEM) decreased. The grafting efficiencies were consistent with the attained residence times and also with the kinetics of the decomposition of the peroxides. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 161–176, 1998

Key words: reactive extrusion; molecular structure; polyolefins; FTIR; grafting degree

INTRODUCTION

The chemical modification of thermoplastics in twin-screw extruders is an area of growing interest. However, few systematic studies on this type of reaction have been conducted and problems such as low reaction efficiencies and grafting degrees, changes in polymer processability, competition between monomer grafting versus homopolymerization, and crosslinking or even degradation of polymer chains, arising from the complex coupling variables, are still unsolved.

The grafting of maleic anhydride (MAH), diethyl maleate (DEM), and dimethylaminoethyl methacrylate (DMAEMA) on polyolefins has been studied.[1–6] Such reactions have traditionally been carried out in solution where a relatively homogeneous chemical environment is possible because the reactants are more easily mixed.[1,2] However, reactions carried out via reactive extrusion have several economic advantages, such as that functional polymers are produced without the construction of an entirely new facility, the process time is shortened, and the cost of solvent recovery is avoided. To successfully use extruders in reactive processing, some important character-

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Table I Material Properties[a]

Material	Density (kg/L)	Additives (ppm)	MFI × 10^3 (kg/10 min)	T_m (±1°C)
HDPE1	958	Antioxidant (350)	0.40	131
HDPE2	960	Antioxidant (350) + UV stabilizer (1500)	7.3	134
LLDPE1	919	Antioxidant (550)	0.6	125
LLDPE2	924	Antioxidant	5.1	123
LLDPE3	931	Antioxidant	4.6	120
LLDPE4	932	Antioxidant	42	125

[a] As reported by the commercial producers.

istics such as the residence time distribution, mixing, and self-cleaning effects should be accurately controlled according to the polymer properties and usage. Consequently, it would be of high interest to know the influence of the temperature, mass flow rate, screw speed, and screw configurations on the residence time distribution.[7–9] Besides, there are some important factors controlling the dispersion of chemical reactants such as diffusion and compatibility that should be taken into account as well.[10]

To establish the mechanism of free-radical grafting reactions on high molecular weight polyolefins, small molecules have been grafted in order to use them as models. The free-radical bromine graft reactions on squalane, methylhexane, and nonane were studied by Jois and Bronk.[11] On the other hand, the free-radical grafting of maleic anhydride (MA) on polyolefins was studied by Heinen et al.[12] using ^{13}C-NMR spectroscopy and specific isotope labeling of the MA. They found that grafting occurred on secondary and tertiary carbons depending on the composition of the polyolefin. When long methylene sequences were present (>3), grafting occurred mainly on secondary carbons. Otherwise, grafting also occurred on tertiary carbons. Usually, saturated monomeric MA-grafted structures were formed, but it was also found that MA dimers and trimers were grafted on HDPE in the melt. Aglietto et al.[2] showed that solution DEM-grafted polyolefins contained mostly only one unit of DEM. Bremner and Rudin[13] proposed a mechanism by which allylic hydrogens in terminal vinyl groups were preferentially abstracted in peroxide-modified HDPE. A combination of allylic radicals, which gave a crosslink, took place after rearrangement of the terminal vinyl group into a *trans*-vinylene group. Similar results were reported by Lachtermacher and Rudin in their peroxide-modified LLDPEs.[14]

In this article, the effects of screw configuration, extrusion conditions, and initiator concentrations on the grafting degree were studied. The grafting of high-density polyethylenes (HDPEs) and linear low-density polyethylenes (LLDPEs) was carried out in two corotating twin-screw extruders. The grafting degree and the molecular weight distributions were measured and the extent of the effects of the grafting degree on the molecular characteristics was determined.

EXPERIMENTAL

Materials

The properties of the commercial polyethylenes (PEs) used, such as melt flow index (MFI) values, melting temperatures, and molecular characteristics given by the producers are shown in Table I. Two initiators (*I*), Interox [a 90% solution of 2,5-dimethyl 2,5 di(*tert*-butyl peroxyhexane) (DBPH)] supplied by Peroxid–Chemie GmbH and dicumyl peroxide (DP) supplied by Aldrich were used as received. Diethyl maleate (DEM) and dibutyl maleate (DBM) supplied by Aldrich were employed as the functional monomer and tracer agent, respectively, and used as received (the latter has a higher boiling point). The solvents *n*-heptane, acetone, and dichlorobenzene (DCB) were laboratory reagent grade.

Reactive Extrusion

The grafting reactions and DEM premix were carried out in two corotating intermeshing twin-screw extruders, one of them made by Werner &

Table II Screw Elements of the Extruders

	W&P Extruder Configurations A and B		Berstorff Extruder Configuration C	
Item	Quantity	Description	Quantity	Description
A	2	28/14	4	E25/1/2
B	4	42/42	12	37.5/1/2
C	2	42/21	1	KB37.5/5/45LI
D	7	28/28	1	KB37.5/5/45RE
E	3	KB28/5/45RE	3	ZB37.5/5/10RE
F	1	KB20/7/30RE	5	25/1/2
G	1	KB28/5/90	1	KB37.5/5/90
H	1	KB28/7/30RE	1	BLISTER24.5
I	1	KB14/5/45RE	—	—
J	5	20/20	—	—
K	8	GME[a]	—	—

[a] Conveying elements 42/42 in configuration A were substituted by gear mixing elements in configuration B.

Pfleiderer (W&P, ZSK-30), extruder 1 (Ex. 1), and the other one by Berstorff (ECS-2E25), extruder 2 (Ex. 2). The screws of the extruders were assembled from individual screw elements (Table II). The screw of the W&P extruder was configured with different mixing elements after an additional feed zone downstream from the initial feed port. The first screw configuration (configuration A) had four kneading mixing elements after the vent section. The second screw configuration (configuration B) had one block containing mixing gears just below the second feed port followed by kneading elements. The initial section of the screws was for solids conveying and polymer melting and was the same for both configurations. Such a section was configured with conveying elements followed by kneading disks to ensure complete melting before the liquid addition zone. The screw configuration of the Berstorff extruder (configuration C) had a longer effective length without mixing elements beyond the peroxide feed port and the vacuum vent port was used in order to eliminate the unreacted monomer. The screw configurations and type of elements used are shown in Figures 1–3 and Table II.

A premix of 8 phr DEM in the PEs was made in each extruder. A maximum of 10 phr of DEM was used in the grafting due to the migration effect that arises from the PE/DEM incompatibility. The DEM was fed through the second port of the extruders (2nd). The experimental conditions used in the DEM premix preparation are shown in Tables III and IV.

By an additional extrusion process, the grafting was carried out and the initiator was then added with the small amount of DEM remaining (2 phr of DEM). The solid materials (pellets of polymer and DEM premix) were starve-fed to the

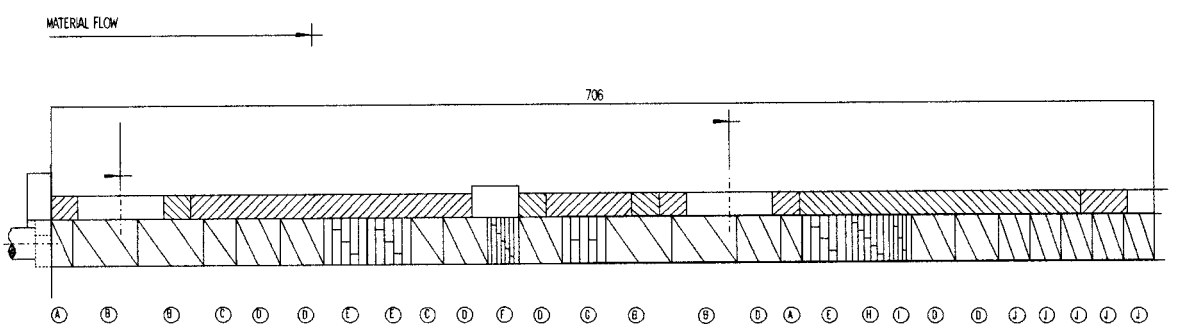

Figure 1 Screw configuration A of the W&P extruder.

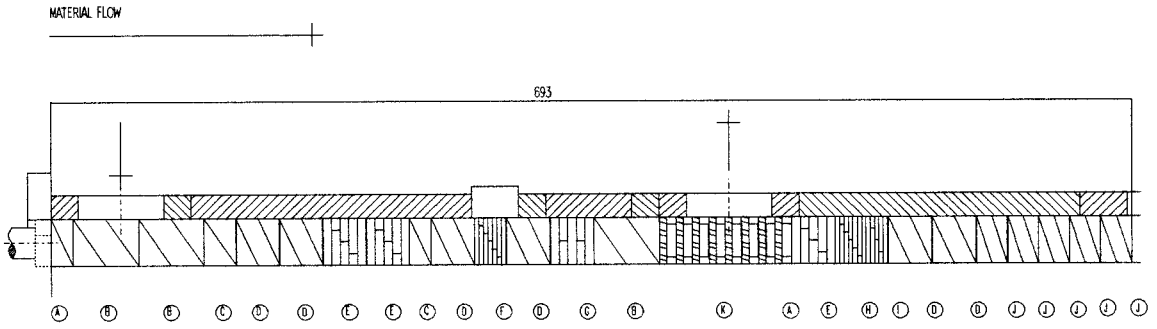

Figure 2 Screw configuration B of the W&P extruder.

extruders by solid feeders and the extrudates were cooled in a water bath and pelletized afterward. The liquid additives were introduced by a liquid injection pump. The initiator was fed through a liquid addition zone shown in Figures 1–3 for the three configurations used. The extrusion conditions of the processes are shown in Tables III and IV.

The influence of initiator concentration, the screw configurations employed, the types of peroxides and PEs (HDPEs and LLDPEs) used, the effect of adding the reactants separately, and the effect of diluting the peroxide with a paraffin oil on the grafting degree were established using the experimental conditions shown in Table V. When experimental conditions 1 and 2 were used, the functionalization via solution and extrusion were compared. The influence of the screw configuration and the type of peroxide employed, at different initiator concentrations, were studied in experimental conditions 3–6, 8–10, and 14–16, respectively.

The effects of adding the initiator with paraffin oil, using a higher temperature in the final section of the extruder and a higher residence time of the initiator (it was added in different feed ports), were studied in experimental conditions 3 and 7 and 11–13, respectively. The experimental conditions 16–19 were designed in order to study the influence of the type of PE (HDPE and LLDPE) and their melt viscosities on the grafting degrees. In previous work,[15] the effect of adding the monomer and initiator together was studied.

Residence Time Distribution (RTD)

In residence time distribution (RTD) experiments, the LLDPE2 was starve-fed to the extruders at 35 rpm by solid feeders. Once the steady state was reached, the mass flow rate of the polymer, the temperature, and the pressure at the die were measured. DBM was used as the tracer (its boiling point is higher than that of DEM, so evaporation losses were minimized) and it was added as a pulse through the liquid injection zone (Figs. 1–3). The temperature profile employed was the same previously mentioned in the grafting reactions. Extrudate samples were collected at several intervals of time and analyzed by Fourier transformed infrared spectroscopy (FTIR), using a Nicolet Magna 550 spectrophotometer. Each experiment was repeated twice.

The RTD function [$E(t)$] is found by the expression

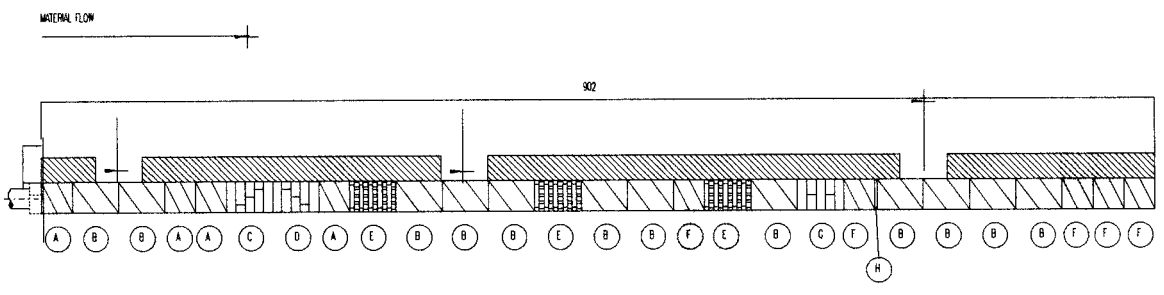

Figure 3 Screw configuration C of the Berstorff extruder.

Table III Experimental Conditions Used in the Reactive Extrusion of LLDPE2 in the W&P Extruder at 35 rpm

Condition	Temperature Profile (°C)	Mass Flow Rate (kg/h)
DEM premix	110/135/145/145/150	0.9–1.2
Grafting [1]	160/175/175/180/180	0.4–0.6
Grafting [2][a]	160/175/175/180/180	0.4–0.6

[a] Initiator + paraffin oil (2 phr).

$$E(t) = \frac{C(\mathrm{t})}{\int_0^\infty C(t)\,dt} \tag{1}$$

where $C(t)$ is the tracer concentration. From the RTD function, the mean residence time (t_m) is calculated via the first moment of the distribution:

$$t_m = \int_0^\infty t\,E(t)\,dt \tag{2}$$

The cumulative distribution function, $F(t)$, can be defined as

$$F(t) = \int_0^{t_m} E(t)\,dt \tag{3}$$

The residence time dispersion is important for extruder performance. It can be evaluated by the holdback value [$H(t_m)$]:

$$H(t_m) = 1 - F(t) \tag{4}$$

The average degree of fill (DF_a) in the extruder is calculated by

$$DF_a = H_a \div V_e \tag{5}$$

where H_a is the average holdup value, and V_e, the free volume downstream from the tracer feed port in the extruder (cm^3). The average holdup value is defined as

$$H_a = M\,t_m \div \rho(T) \tag{6}$$

where M is the mass-flow rate (g/s); t_m, the mean residence time (s); and ρ, the density of the molten PE (g/cm^3).

A zero holdback value describes the plug flow and a value of 0.368 describes the ideal mixer. The holdback values could reflect dual behavior, that is, high holdback values could describe either good longitudinal mixing or high stagnancy and channeling. The transport delay time is the min-

Table IV Experimental Conditions Used in the Reactive Extrusion of the Materials in the Berstorff Extruder at 35 rpm

Condition and Feed Port of Additives	Materials	Temperature Profile (°C)	Mass Flow Rate (kg/h)
DEM premix [1, 2nd]	LLDPE3 LLDPE4	110/135/145/145/145/145/150	1.1–1.3
DEM premix [2, 2nd]	LLDPE1 HDPEs	160/175/175/175/175/180/180	1.1–1.3
Grafting [1, 3rd]	LLDPE3	160/175/175/175/180/180/180	0.4–0.6
Grafting [2, 3rd]	LLDPE3	165/185/185/185/200/200/200	1.1–1.3
Grafting [3, 2nd]	LLDPE3	165/185/185/185/200/200/200	1.1–1.3
Grafting [4, 2nd]	LLDPE1 LLDPE3 LLDPE4 HDPEs	160/175/175/175/180/180/180	0.4–0.6

Table V Experimental Conditions of the Grafting Reactions of the Materials at 180°C

Run	Name Codes	DEM[a]	Initiator [*I*] (phr)	Feed Port	Extruder and Configuration
1	LLDPE1-*g*-DEM[e] (solution)	20	DBPH[b] (2.00)	—	—
2	LLDPE1-*g*-DEM (extrusion)	10	DP[c] (0.20)	2nd	Berstorff, C
	LLDPE2-*g*-DEM				
3	(1)	8	DBPH[b] (0.10)	2nd	W&P, A
4	(2)	8	DBPH[b] (0.15)	2nd	W&P, A
5	(3)	8	DBPH[b] (0.20)	2nd	W&P, A
6	(4)	8	DBPH[b] (0.25)	2nd	W&P, A
7	(5)[d]	6	DBPH[b] (0.10)	2nd	W&P, A
8	(6)	8	DBPH[b] (0.10)	2nd	W&P, B
9	(7)	8	DBPH[b] (0.20)	2nd	W&P, B
10	(9)	8	DBPH[b] (0.25)	2nd	W&P, B
	LLDPE3-*g*-DEM				
11	(1)	8	DBPH[b] (0.25)	3rd	Berstorff, C
12	(2)[f]	8	DBPH[b] (0.25)	3rd	Berstorff, C
13	(3)[f]	8	DBPH[b] (0.25)	2nd	Berstorff, C
14	(4)	10	DP[c] (0.20)	2nd	Berstorff, C
15	(5)	10	DP[c] (0.30)	2nd	Berstorff, C
16	(6)	10	DP[c] (0.50)	2nd	Berstorff, C
17	LLDPE4-*g*-DEM	10	DP[c] (0.20)	2nd	Berstorff, C
18–19	HDPEs-*g*-DEM	10	DP[c] (0.50)	2nd	Berstorff, C

[a] Reference DEM concentration to PEs.
[b] 2,5-Dimethyl-2,5-di(*tert*-butyl peroxy-hexane).
[c] Dicumyl peroxide.
[d] Initiator + paraffin oil (2 phr).
[e] At 160°C.
[f] At 200°C.

imum residence time characterizing the plug flow component of RTD in the extruder.[8,9]

Analysis

To eliminate the residual monomer, the functionalization product was dissolved in DCB, washed with acetone, and then dried in a vacuum oven at 60°C for 16 h. The resultant material was dissolved in *n*-heptane at 120°C and the insoluble polymer fractions were isolated. A dissolution of these fractions in DCB at 120°C was also carried out to verify the absence of crosslinked material by visual examination.[4,5,7] The degree of functionalization or grafting degree (GD) was determined by FTIR and ^{1}H-NMR calibration curves.

IR spectra of the functionalized products were obtained using a Nicolet Magna 750 FTIR spectrophotometer. Press molded films were analyzed in the range 4000 to 500 cm^{-1} at a resolution of 4 cm^{-1}. The absorbances at 1740 cm^{-1}, characteristic of carbonyl groups, at 909 and 965 cm^{-1}, characteristics of terminal vinyl and *trans*-vinyl unsaturation groups, respectively, and at 1460, 720, and 730 cm^{-1}, characteristics of the CH_2 groups of PE, were determined. The peak area ratios of 1740/1460, 1740/(720 + 730), 965/1460, and 909 cm^{-1}/1460 cm^{-1} were analyzed to eliminate the dependence of the carbonyl peak area on the film thickness.

^{1}H-NMR spectra of pure and functionalized polymers were examined using a JEOL Eclipse 270 NMR spectrophotometer. Solutions of the polymers in DCB (10% w/w) were prepared. The solvent signal was filtered automatically. The spectra were obtained at 120°C, between 6 and −2 ppm. In the analysis, the signal of the protons attached to the oxygen of the ester group located near 4 ppm and the signal of the protons of the methylene groups located around 1 ppm were considered. The evaluation of the integrals relative to the grafted monomer and the polymer chain proton signals allowed one to determine the function-

alization degree. Two correlations were found between the grafting degree determined via ^{1}H-NMR and the ones obtained via absorbance ratios at 1740/(720 + 730) and 1740 cm^{-1}/1460 cm^{-1} from the FTIR spectra.

Molecular weight distributions of the LLDPE2 and HDPE1, before and after the functionalization reactions, were measured by a Waters 150 GPC equipped with a differential refractometer detector and Styragel packing columns, at 135°C and at a flow rate of 1 mL/min in DCB. Samples were previously dissolved in DCB and filtered. Solution concentrations were 0.1% w/v. A calibration curve was made with monodisperse polystyrene samples and the molecular weights were calculated using the universal calibration curve and the Mark–Houwink constants of polystyrene and lineal PEs.[16]

To measure the shear viscosity of the virgin materials at the peroxide feed port, the steady-state capillary flow properties were determined using a Göttfert capillary rheometer Rheograph, Model 2000, at several crosshead speeds and 175°C. Two capillaries with length-to-diameter ratios of 30 mm/1 mm and 10 mm/2 mm were used. The last ratio was employed for the material with a very high viscosity and sensitivity to melt fracture (LLDPE1). The standard Rabinowitsch corrections were made.

RESULTS AND DISCUSSION

Residence Time Distribution (RTD)

Reactive extrusion is a process where extruders are used as chemical reactors for the purpose of chemical modification of existing polymers or the synthesis of new ones. The mean residence time of the reactants inside the extruder is a very important process variable because it is considered, to a first approximation, as the reaction time. The RTD function describes the history of the polymer inside the extruder and it is reflected in the efficiency or yield of a chemical reaction and in the extent of degradation. When the RTD is determined, the fact that the reactant molecules enter the extruder at different times must be taken into consideration. For this reason, tracers should be used.[8,9]

Another variable to be considered in reactive extrusion is the difficulty of mixing two dissimilar materials, which is subject, among other things, to the difference in their viscosities and lack of chemical compatibility. One example of this is the compounding of low-viscosity polar liquids like DBM and DEM, usually used as functional monomers in the grafting reactions of polyolefins, with high-viscosity polymers. The standard mixing elements (kneading blocks) employed in twin-screw extruders may not generate enough surface renewal to produce the desired loading and distribution of the liquids. Hence, the use of different types of elements such as gear mixing elements is strongly advised. These elements furnish a suitable diffusion of liquids like oils and silicones when they are located just below the liquid feeding port.[10]

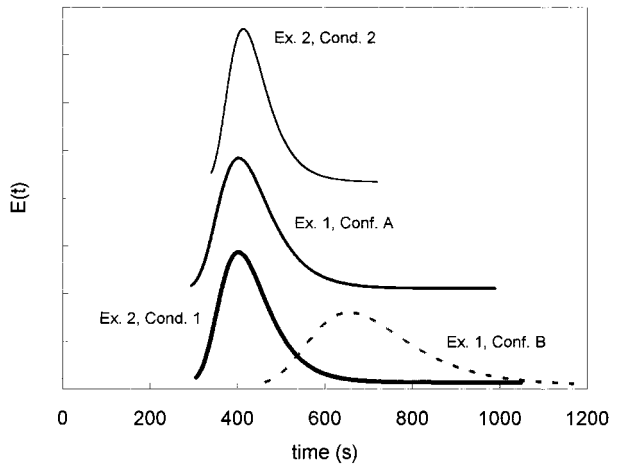

Figure 4 RTD curves, $E(t)$: Ex. 1, configuration A (35 rpm, 0.4 kg/h, and 180°C); Ex. 1, Configuration B (35 rpm, 0.4 kg/h, and 180°C); Ex. 2, condition 1 (35 rpm, 0.4 kg/h, and 180°C); Ex. 2, condition 2 (35 rpm, 1.0 kg/h and 200°C).

DBM was chosen as the tracer because its concentration at any time can be measured by FTIR. It has similar flow characteristics to DEM, which is the functionalization agent used in this study and has a higher boiling point (281°C); consequently, evaporation losses must be lower. The tracer was added through an additional feed port located downstream from the initial feed port so that the polymer is melted and at a constant temperature by then.

The RTD curves for both extruders at 35 rpm and different mass flow rates are shown in Figure 4. The shape of the RTD curve is of great importance for the information it gives about the residence time of the material inside the extruder. LLDPE3 was used in the Berstorff extruder. LLDPE2 and LLDPE3 had very similar flow properties. The screw configuration A of the W&P ex-

Table VI RTD Parameters for the Dibutylmaleate Tracer at 35 rpm

Extruder and Configuration	W&P A	W&P B	Berstorff C	Berstorff C
Mass flow rate (±0.08 kg/h)	0.40	0.40	0.40	1.00
Conditions and DBM feed port	1, 180°C, 2nd	1, 180°C, 2nd	1, 180°C, 3rd	2, 200°C, 2nd
Mean residence time t_m (s)	466	725	484	462
Holdback value $H(t_m)$	0.35	0.43	0.31	0.38
Transport delay time (TDT) (s)	295	463	306	340
Average degree of fill (%)	58	90	99	98

truder had conveying elements just below the second feed port. The screw configuration B had gear mixing elements. The initial and final sections were the same for both configurations (Figs. 1–3). However, their RTD distribution curves were very different. The W&P extruder with the gear mixing elements had an RTD curve that shifts in the direction of longer residence times. There was more spread, and a higher transport delay time was achieved, with screw configuration B as expected. Similar results were found in the Berstorff extruder, condition 2. Although a higher mass flow rate was used in the last one, the material was fed in a feed port close to the hopper. Consequently, the flow length and, hence, the transport delay time were increased (Table VI).

The corresponding values of the experimental mean residence time (t_m), the holdback values [$H(t_m)$], the transport delay time, and the average degree of fill at the experimental conditions are shown in Table VI. An increase in the mean residence time, in the transport delay time, in the average degree of fill, and in the holdback value was observed when extruder 1 configuration B was used. This is because gear mixing elements that withhold the flow for a longer period of time were placed in the screw just below the feeding port. Similar RTD curves were obtained for both extruders at similar experimental conditions (Fig. 4). However, the transport delay time in the Berstorff extruder at higher mass flow rates was slightly higher due to the higher flow length (tracer was added in the second port of the extruder). The average degree of the fill was higher in the Berstorff extruder due to its lower screw diameter and, hence, a lower volume of material was transported. Configuration B of the W&P extruder delayed the flow and consequently gave a higher degree of fill.

Grafting Degree

The ^{1}H-NMR spectra of both LLDPE2 and its grafted product were made. A new resonance was found in the grafted product, that is, the resonance of the proton attached to the carbon adjacent to the carbonyl carbon at 4.14 ppm. The integral of this resonance was compared to that of backbone carbons from about 1.1 to 1.4 ppm and the grafting degree (*GD*), expressed as diethylsuccinate moles per 100 ethylene moles, was calculated.

FTIR spectra of virgin and functionalized PEs are shown in Figures 5 and 6. At 1740 cm^{-1}, there is a clear signal in the functionalized products that is absent in the virgin materials and that is ascribed to the stretching of C═O bonds from ester groups of the DEM molecules attached to the PEs. At 720 and 1460 cm^{-1}, there are two more bands that correspond to the rocking of $(CH_2)_n$ for n equal or higher than 4, characteristics of PEs.

To determine the grafting or functionalization degree (*GD*), expressed as diethylsuccinate moles per 100 ethylene moles in LLDPEs (Table VII), calibration curves were used. Those curves were obtained from peak area ratios $A_{1740\text{cm}^{-1}}/A_{1460\text{cm}^{-1}}$ and $A_{1740\text{cm}^{-1}}/A_{(720+730)\text{cm}^{-1}}$, and the grafting degree, from ^{1}H-NMR (Fig. 7). The latter measurement was taken as the absolute value of GD and FTIR ratios were referred to them. Figure 7 is the result of these IR–NMR calibrations. In the experimental range of error, both of them give almost the same value of the *GD*. The use of these curves allows one to determine quantitatively the functionalization degree in a simpler, more rapid and exact way than by means of any other method of analysis described in the literature.[1,2,7] Also, the grafting degree was expressed as the weight

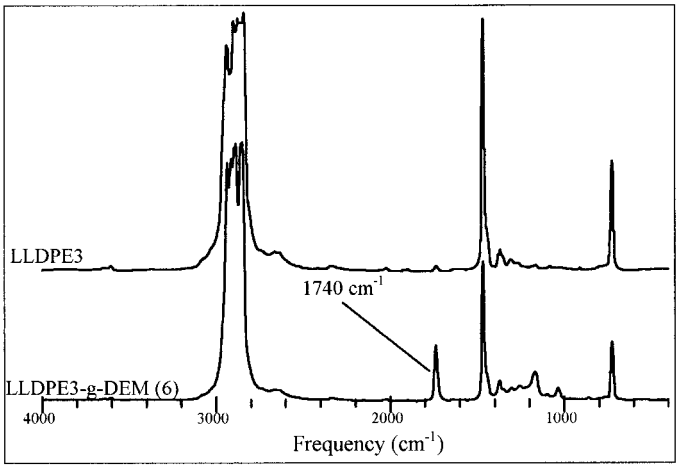

Figure 5 FTIR spectra of LLDPE3 and LLDPE3-*g*-DEM(6).

of DEM units per 100 g of ethylene, weight percent (Table VII).

Another technique found in the literature is the Fodor et al.[17] method for determining the grafting degree. It was followed by Aglietto et al.[2] and by us[15] in our preliminary studies. That method overestimates the grafting degree values, probably due to a low compatibility between polyolefins and poly(diethyl fumarate). On the other hand, the calibration curve obtained from DEM solutions in octane underestimates those grafting degree values due to the difference between the extinction coefficients of the compression-molded films and those of the solutions. The grafting degrees of the materials are reported in Table VII. Moreover, the grafting efficiency is defined as the ratio of the grafting degree to the amount of DEM used. When the same amount of DEM is used, the grafting efficiency is proportional to the grafting degree.

Effects of Screw Configuration, Initiator Concentration, and Extrusion Conditions

In reactive extrusion, the process variable interactions must be known in order to study and fully understand it. These variables are mainly the screw speed, the mass flow rate, and the temperature profile. Except for the material temperature, the other two variables influence the RTD.[8,9] The mean residence time was considered as a first approximation, as the time required for the decomposition of 95% of the Interox peroxide (DBPH). In Table VIII, the times required to dissociate the 90 and 95% of the employed peroxides at 180 and 200°C are reported. The thermal de-

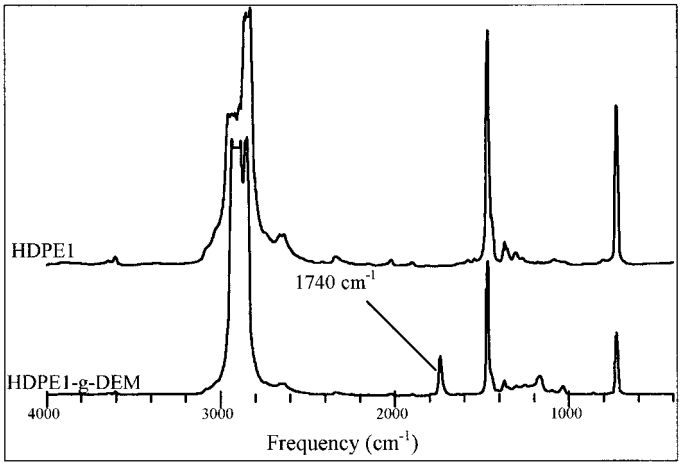

Figure 6 FTIR spectra of HDPE1 and HDPE1-*g*-DEM.

Table VII Grafting Degrees of the Materials and Their Absorbance Ratios ($A_{965cm^{-1}}/A_{1460cm^{-1}}$, $A_{909cm^{-1}}/A_{1460cm^{-1}}$)

Name Codes	Grafting Degree (mol %)	Grafting Degree (wt %)	$[A_{965cm^{-1}}/A_{1460cm^{-1}}] \times 10^3$	$[A_{909cm^{-1}}/A_{1460cm^{-1}}] \times 10^3$
LLDPE1	—	—	0.00	3.7 ± 0.3
LLDPE1-*g*-DEM (solution)	0.92	5.7	—	—
LLDPE1-*g*-DEM (extrusion)	0.05	0.3	0.77 ± 0.04	2.9 ± 0.1
LLDPE2	—	—	1.6 ± 0.2	7.4 ± 0.4
LLDPE2-*g*-DEM				
(1)	0.35	2.2	2.4 ± 0.1	3.7 ± 0.1
(2)	0.40	2.5	2.3 ± 0.2	2.8 ± 0.3
(3)	0.42	2.6	2.4 ± 0.1	3.0 ± 0.3
(4)	0.59	3.6	2.5 ± 0.1	2.2 ± 0.1
(5)	0.36	2.2	—	—
(6)	0.10	0.6	1.5 ± 0.1	5.7 ± 0.6
(7)	0.21	1.3	1.6 ± 0.1	4.1 ± 0.5
(8)	0.37	2.3	2.1 ± 0.2	2.5 ± 0.1
LLDPE3	—	—	1.8 ± 0.1	7.4 ± 0.1
LLDPE3-*g*-DEM				
(1)	0.62	3.8	2.9 ± 0.1	1.5 ± 0.1
(2)	0.55	3.4	2.5 ± 0.1	1.5 ± 0.2
(3)	0.47	2.9	2.0 ± 0.1	1.8 ± 0.1
(4)	0.37	2.3	—	—
(5)	0.40	2.5	—	—
(6)	0.62	3.8	2.0 ± 0.1	2.0 ± 0.1
LLDPE4-*g*-DEM	0.10	0.6	2.0 ± 0.1	2.1 ± 0.1
HDPE1	—	—	0.00	0.80 ± 0.02
HDPE1-*g*-DEM	0.29	1.8	1.6 ± 0.1	2.0 ± 0.3
HDPE2	—	—	0.41 ± 0.01	8.3 ± 0.4
HDPE2-*g*-DEM	0.20	1.3	0.71 ± 0.02	7.3 ± 0.6

composition of these materials is conformed by a series of chemical reactions of first-order kinetics and the environment in which the peroxide is immersed affects its decomposition rate. Therefore, the Arrhenius parameters of Interox in dodecane, PE, and polypropylene and of DP in dodecane and PE were used.[18,19] Interox was employed as an initiator in preliminary studies, but because of its longer decomposition times in PE, DE was used instead.[19]

In a previous study,[15] the influence of the initiator, functionalization agent concentration, temperature, and reaction time on the grafting degree via a solution was established. It was found that the grafting degree is a function of the percentage of the dissociated initiator, calculated from the Interox decomposition constants in mineral oil. When the functionalization monomer concentration was kept constant, an increase in the dissociated initiator concentration produced an increase in the grafting degree up to a limit, because a higher concentration of free radicals made them recombine among themselves at higher rates. On the other hand, an increase in DEM concentration produced an increase in the grafting degree. Some authors have proposed that the peroxide concentration reaches a limit because higher concentrations promote termination reactions by combination and/or disproportion that compete with the insertion of DEM in LLDPE and aid the formation of unsaturation, crosslinking, and/or long-chain branching.[11,12,20]

The grafting degrees of the products, the absorbance ratios $A_{965cm^{-1}}/A_{1460cm^{-1}}$ (proportional to the concentration of *trans*-vinyl unsaturations), and the absorbance ratios $A_{909cm^{-1}}/A_{1460cm^{-1}}$ (proportional to the concentration of terminal vinyl unsaturations) are reported in Table VII. As de-

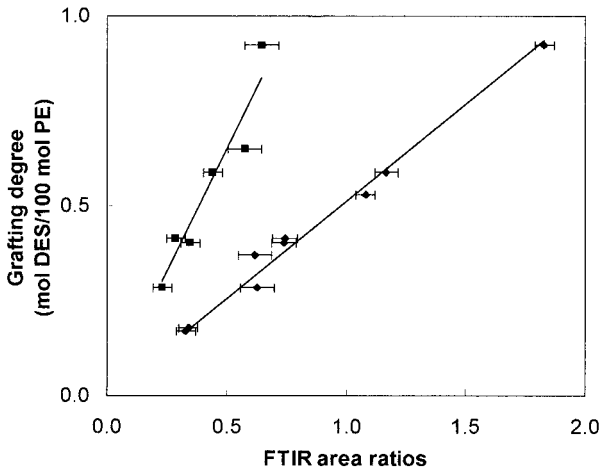

Figure 7 Calibration curves, relations between ^{1}H-NMR (as grafting degree) and FTIR area ratios: (■) $A_{1740cm^{-1}}/A_{1460cm^{-1}}$; (◆) $A_{1740cm^{-1}}/A_{(720+730)cm^{-1}}$.

picted, more DEM was grafted on the LLDPEs when the initiator concentration was increased. This last result does not depend on the extruder type, screw configuration, and peroxide employed (runs 3–10 and 14–16, Table V). The absence of gels in the grafted PEs was demonstrated in qualitative analysis through their complete dissolution in DCB.

In the previous studies of extrusion-grafted LLDPE1,[15] a premix of DEM in the polymer was also made, the initiator was added through the extruder hopper, and a temperature of 200°C in the last zone of the extruder was used. The high melt viscosity of this material and the conditions employed promoted crosslinking reactions that lowered significantly the processability of the functionalized resin. Additionally, the molecular weight distribution curve of LLDPE1-*g*-DEM fell below those of virgin and solution-grafted LLDPE1, probably because the high molecular weight fractions did not dissolve and were lost in the filter prior to the GPC analysis.[14,16] The functionalization variables used in the W&P extruder at 200°C brought about the complete decomposition of DBPH in PE (99% of decomposition). However, the peroxide attack to the polymer in the melting zone of the extruder, the employed temperature, and/or the tails at long residence times in the RTD curves promoted crosslinking reactions that lowered the processability of the functionalized product (LLDPE1-*g*-DEM) and originated the presence of the gels.

The mixing effect and the molecular diffusion in reactive extrusion are important because reactants with a very low viscosity are added to a highly viscous polymer melt. The LLDPE1 and HDPE1 are extrusion-grade materials with the highest viscosity curves at high shear rates and, as will be seen later, the secondary reactions in the LLDPE1 reduced the processability of the extrusion functionalized product. For this reason, a low concentration of initiator (0.2 phr) was employed for this material. Although the grafted product obtained in the functionalization via extrusion [LLDPE1-*g*-DEM (extrusion)] was free of gel, because the peroxide was added when the monomer was well mixed in the melted polymer, the grafting degree obtained was the lowest due to its high melt viscosity and the presence of antioxidants on this material.

The process variables used in the functionalization via solution (160°C and 45 min) ensure the 85% decomposition of the peroxide (1.7 phr) in DCB.[18] Although the viscosity effect as well as the secondary reactions are reduced when compared to functionalization via extrusion, the cage effect[20] in extrusion (melted material) is important and a higher initiator and DEM concentrations must be used in grafting via the solution. Conse-

Table VIII Time Required to Dissociate 90 and 95% of Interox (DBPH) and DP[18,19] as a Function of the Reaction Media

% Dissociation and type of peroxide	Temperature (°C)	Dodecane	PE	Polypropylene
90% of DBPH	180	8.2	12.2	16.8
	200	1.4	1.9	2.7
95% of DBPH	180	10.7	15.8	21.9
	200	1.9	2.5	3.5
95% of DP	180	4.1	5.3	—
	200	0.8	0.9	—

quently, a higher grafting degree was achieved via the solution [LLDPE1-*g*-DEM(1)]. On the other hand, the low compatibility between DEM and PEs promoted monomer migration from the extrudates when a concentration higher than 10 phr of DEM was used in grafting by extrusion.

A high transport delay time in the extruder means high stagnancy and channeling in the elements just below the initiator feed port because the same feed port was used to add the tracer agent in the RTD curves' determination. The temperatures in the extruder zone, downstream from the liquid addition zone, were the same in order to obtain an isothermal flow in the reaction zone of the extruder. When the grafting reactions are promoted due to stagnancy just below the peroxide feed port, secondary reactions such as thermal-oxidation or devolatilization of reactives could take place as well, because the initiator feed port zone is open to the environment. Long tails on the longer time side in the RTD curves could also be promoting secondary reactions such as chain scission, crosslinking, and/or long-chain branching.

The influence of the screw configuration and the initiator concentration on the grafting degree can be seen in Table VII. When configuration B was used in the W&P extruder, a lower grafting degree was achieved, probably due to the long residence times attained and the high transport delay time (Table VI). Although the gear mixing elements incorporate a higher amount of liquids into the mass in nonreactive mixing,[10] they are not that effective in functionalization reactions. The mechanical mixing intensity and the high transport delay time due to the liquid mixing elements in screw configuration B had an adverse effect on the overall grafting yield because the free radicals formed could be lost in secondary reactions such as radical termination reactions, thermal-oxidation, and/or mechanochemical degradation or through reactive devolatilization as was mentioned earlier, which lowered the grafting efficiencies. These secondary reactions could be taking place just in the liquid mixing elements. As a matter of fact, a yellow film on the functionalized products was observed there.

The melt viscosity of the material and the grafting reaction rate are affected by the temperature in the reaction zone of the extruder. High temperatures in the initiator feed port and/or high transport delay times decreased the grafting degree due to thermal-oxidation, mechanochemical degradation reactions, and/or devolatilization of reactives, as was mentioned above. The grafting reactions at the highest temperatures [Table V, LLDPE3-*g*-DEM(2) and LLDPE3-*g*-DEM(3)] were carried out in extrusion conditions where the transport delay time in the extruder was higher than the time required to dissociate 95% of the DBPH (Tables VI and VIII). In these conditions, the free radicals formed could be lost in secondary reactions just below the feed port, which, in turn, lowered the grafting degrees. At the extrusion conditions of LLDPE3-*g*-DEM(3), the transport delay time was higher and a lower grafting degree was obtained when it was compared to LLDPE3-*g*-DEM(2) (Table VI).

Influence of the Type of PE

The LLDPEs-*g*-DEM should have the highest grafting degrees when compared to the HDPEs-*g*-DEM, probably due to the higher amount of tertiary hydrogens per chain length, which are more labile and, hence, more easily extractable, leaving active sites where the insertion of DEM can take place. However, the presence of antioxidants and other stabilizers can affect the insertion process because their specific function is to entrap free radicals, consequently decreasing the grafting degree.[20] On the other hand, in commercial HDPE polymerization, a comonomer is generally used to reduce the crystallinity, and short-chain branches (SCB) are introduced on the polymer chain. Also, the α-olefin comonomers in LLDPE or the SCB are distributed nonuniformly at different intervals along some molecules and heterogeneously at different concentrations in different molecules. The low molecular weight chains are more branched than are the high molecular weight ones for the LLDPEs.[14]

Additionally, as the grafting reaction is diffusion-limited, high-viscosity materials could lower the functionalization degrees.[7] The viscosity of a fluid describes the ratio between the shear stress and the shear rate. Generally, polymer melts are non-Newtonian fluids. This means that the ratio of the shear stress and shear rate is not constant, but dependent on the shear rate. This ratio is called the apparent viscosity (η_a). The average shear rates in the extruders downstream from the initiator feed port were calculated following the method reported by Michaeli et al.[21] The shear viscosity of the virgin materials at these shear rates and 180°C are shown in Table IX. The materials with very similar high viscosities are HDPE1 and LLDPE1, with similar medium vis-

Table IX Apparent Shear Viscosity of the Virgin Materials at 175°C and Two Shear Rates

Material	$\eta_a \times 10^{-3}$ (Pa s) at 10 s^{-1}	$\eta_a \times 10^{-3}$ (Pa s) at 30 s^{-1}
HDPE1	7.76	3.95
HDPE2	1.67	1.09
LLDPE1	6.82	4.07
LLDPE2	2.65	1.64
LLDPE3	2.54	1.69
LLDPE4	0.43	0.32

cosities are the LLDPE2 and LLDPE3, and with low viscosities are LLDPE4 and HDPE2.

When the HDPEs are compared between themselves, HDPE1 has a higher functionalization degree than that of HDPE2, even though the latter has a lower viscosity. This fact can be attributed probably to the presence of a UV stabilizer that entraps the free radicals and, consequently, diminishes the number of sites where the DEM molecules can be inserted.[11,12,20]

The LLDPE3-*g*-DEM[4] had a higher grafting degree than that of the LLDPE1-*g*-DEM because the last one also has an antioxidant in a higher proportion and, as mentioned before, it diminishes the grafting degree by about 26%.[15] Additionally, due to its high viscosity, there is some difficulty in the access of functional groups to its active sites, giving rise to other reactions such as the increased formation of long-chain branching without crosslinking. This last fact was demonstrated in the qualitative analysis from the absence of gels. When LLDPE1-*g*-DEM(2) and LLDPE4-*g*-DEM are compared, a higher grafting degree is achieved in the latter under similar grafting conditions, probably due to its lower viscosity, even though the grafting reaction is affected by the stabilizer type and concentration and other additives that can entrap free radicals.[11,12,20]

The role of terminal unsaturations in increasing the crosslinking efficiency or coupling reactions was studied previously in peroxide-modified PEs,[13,14,20] although the exact mechanism is not always agreed on. Bremner and Rudin[13] reported the major contributing reactions of terminal vinyl in a free-radical scheme that accounts for the changes in vinyl group concentrations in PE. The reduction in the amount of terminal unsaturation ($A_{909cm^{-1}}/A_{1460cm^{-1}}$) with the grafting degree for the LLDPEs-*g*-DEM (Table VII) is in agreement with the mechanism proposed by them.[13] These conclusions also fit in the work done by Lachtermacher and Rudin,[14] that is, chain-extension reactions account for a decrease in the amount of terminal vinyls upon the peroxide reaction.

Allylic radicals are intermediate species in chain-coupling reactions involved in peroxide modification and/or grafting reactions of LLDPE, yielding *trans* or *cis* unsaturations. This is demonstrated by a shift in the molecular weight distribution curves of the modified polymers toward the high molecular weight end compared to the virgin resins, as will be mentioned later. Simultaneously, the number of *trans* unsaturations ($A_{965cm^{-1}}/A_{1460cm^{-1}}$) tends to increase slightly with the grafting degree. Apparently, long-branch formation is due mainly to coupling allylic radicals. Such reactions cause a decrease in terminal unsaturations and an increase in internal unsaturations, as observed in Table VII. Interconnection of such long branches would lead to crosslinking in the peroxide-modified PEs. However, there was no evidence of gels in any of the functionalized materials. The exclusive production of Y-type branches noted by Lachtermacher and Rudin[14] in their work may not persist in other PE resins that have much lower unsaturation levels such as HDPE1.

The proportion of terminal vinyl groups [$(A_{909cm^{-1}}/A_{1460cm^{-1}})_{LLDPE2\text{-}g\text{-}DEM}/(A_{909cm^{-1}}/A_{1460cm^{-1}})_{LLDPE2}$] and the proportion of *trans*-vinylene groups [$(A_{965cm^{-1}}/A_{1460cm^{-1}})_{LLDPE2\text{-}g\text{-}DEM}/(A_{965cm^{-1}}/A_{1460cm^{-1}})_{LLDPE2}$] as a function of the grafting degree are given in Figure 8. This figure shows that vinyl groups are consumed in the grafting reaction. On the other hand, the proportion of *trans*-vinylene groups increase to a minor extent during the LLDPE2 grafting reactions. The same result was also found in all LLDPE and in HDPE2. This last polymer was produced with the same technology as that of the LLDPEs. An increase in the terminal vinyl group and in the *trans*-vinylene group concentrations are observed in HDPE1-*g*-DEM (Table VII). The virgin resin showed no detectable *trans* unsaturations by FTIR analysis, but upon the grafting reaction, there is an slight enhancement. This trend is in agreement with a mechanism of chain scission. New terminal vinyls are produced by either a beta scission of a secondary polymeric radical or by a disproportionation of two terminating primary polymeric radicals. The first of these two mechanisms contributes to a decrease in the molecular weight, while the second one has no noticeable effect.

However, since the *trans*-vinyl unsaturation is also increasing as a result of coupling reactions, it

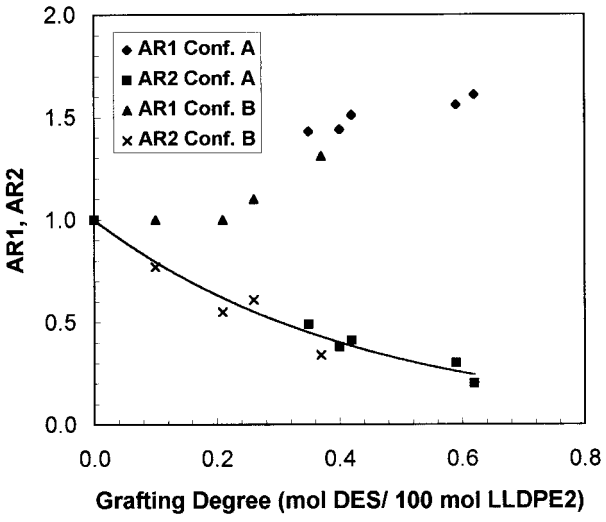

Figure 8 Absorbance ratios as a function of the grafting degree. AR1: $[(A_{965cm^{-1}}/A_{1460cm^{-1}})_{LLDPE2\text{-}g\text{-}DEM}/(A_{965cm^{-1}}/A_{1460cm^{-1}})_{LLDPE2}]$; AR2: $[(A_{909cm^{-1}}/A_{1460cm^{-1}})_{LLDPE2\text{-}g\text{-}DEM}/A_{909cm^{-1}}/A_{1460cm^{-1}})_{LLDPE2}]$.

can be concluded that there are two competing mechanisms of chain growth and chain scission occurring in the melt. Similar results were found by Bremner and Rudin[13] with their dicumyl peroxide-modified HDPEs.

Effect of Type of Peroxide and Its Feeding Conditions

The efficiency of the type of peroxide used was evaluated in experimental conditions 11, 14, 15, and 16 (Table V). The DBPH showed a higher efficiency than that of the DP. This means that a similar grafting degree was obtained for the LLDPE3-*g*-DEM(1) with a lower amount of DBPH (0.25 phr) compared to 0.5 phr of DP used in LLDPE3-*g*-DEM(6). The lower efficiency of the DP could be attributed to a higher probability of radical breakdown and the generation of acetophenone as a by-product. DP decomposes when it is exposed to heat, and two cumyloxy radicals of equal reactivity are formed. Alkoxy radicals are known to be strong hydrogen-abstracting species. The cumyloxy radical can also decompose via a β-scission reaction into acetophenone and a methyl radical. This last radical is very reactive and probably increases the secondary reactions.[20]

The dilution of the peroxide in the paraffin oil or with a small amount of DEM resulted in similar grafting degrees as expected because the dilution of peroxide was anticipated to aid its mixing in the extruder [Table VIII, LLDPE2-*g*-DEM(1) and LLDPE2-*g*-DEM(5)]. However, Oliphant and Baker[7] found lower grafting efficiencies when diluting the peroxide in liquid paraffin, probably due to the higher amount of peroxide used in their experiments.

Molecular Weight Distributions

The molecular characteristics of the virgin materials and their grafted products are reported in Table X and Figures 9 and 10. The molecular weight distribution curves of the LLDPE2-*g*-DEM(4) with the highest grafting degree (Fig. 9) showed no appreciable differences from those of their virgin resin LLDPE2. The same results were found by Aglietto et al.[2] and by us[15] in functionalization via solution. The only difference is a slight shift in the molecular weight distribution curves toward the high molecular weight end for the LLDPE2-*g*-DEM(4) compared to the virgin resin LLDPE2. There was no evidence of gels in any functionalized product. Similar results were found by Lachtermarcher and Rudin[14] in PEs modified with small concentrations of peroxides.

On the other hand, the HDPE1-*g*-DEM grafted by extrusion, whose molecular weight distribution is depicted in Figure 10, had a lower weight-average molecular weight compared to that of

Table X Molecular Characteristics of the Materials and Their Grafted Products

Material	Grafting Degree (mol %)	$M_n \times 10^{-4}$ (g/mol)	$M_w \times 10^{-4}$ (g/mol)	$M_z \times 10^{-4}$ (g/mol)	M_w/M_n
HDPE1	—	1.98	18.2	60.8	9.18
HDPE1-*g*-DEM	0.29	2.19	12.7	41.6	5.83
LLDPE2	—	2.63	7.87	18.2	2.99
LLDPE2-*g*-DEM(4)	0.59	3.06	9.47	24.6	3.09
LLDPE2-*g*-DEM(6)	0.10	2.31	8.83	22.7	3.83

virgin HDPE1. This result could be attributed to chain-scission reactions on the HDPE1 that are competing with the grafting reactions.

These features demonstrated that the functionalization reaction via extrusion did not significantly change the molecular weight distribution, when the initiator was added to the melted polymer. A broader distribution could be attributed to the branching sites in the polymer structure of the LLDPEs. The results suggest that the grafting occurs preferentially on the longer or less substituted methylene sequences as has been reported elsewhere.[12] Additionally, there are several types of competing reactions in the extruder, that is, thermal-oxidation, mechanochemical degradation, grafting, and formation of long-chain branches. However, the actual competing mechanisms contributing to each of these major reactions are not well understood.

CONCLUSIONS

The grafting efficiencies were consistent with the attained residence times. As the transport delay time and mean residence time increased beyond a certain point, the free radicals formed could be lost in secondary reactions such as thermal-oxidation, mechanochemical degradation, and/or chain extension through long branches for the LLDPEs, which, in turn, lowered the grafting degrees. The higher the initiator concentration, the higher the grafting degree of LLDPEs, no matter what screw configuration, peroxide, or extruder was used. DBPH showed a higher efficiency in the grafting reactions. It was also demonstrated that the functionalization reaction via extrusion of LLDPEs did not significantly change the molecular weight distribution when the initiator was added in the melted polymer. There was no evidence of gels in any of the functionalized products.

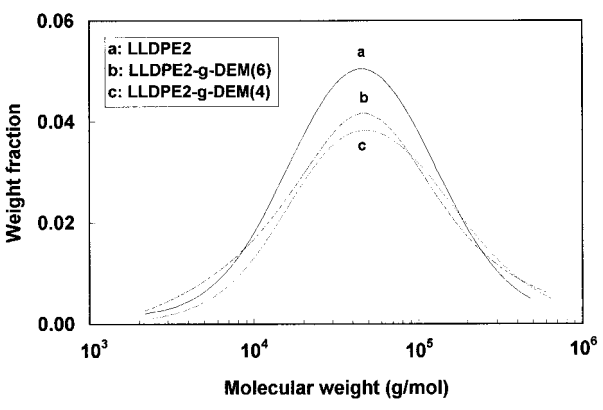

Figure 9 Molecular weight distributions of LLDPE2 and its grafted products.

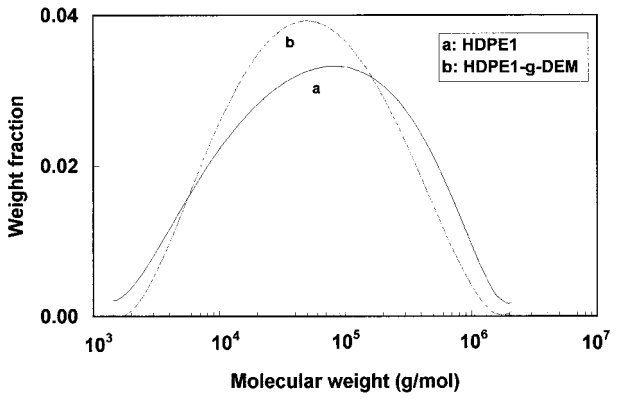

Figure 10 Molecular weight distributions of HDPE1 and its grafted product.

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