# Grafting of Polyethylenes by Reactive Extrusion. II. Influence on Rheological and Thermal Properties

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**ABSTRACT:** In this article, the effects of the grafting degree and the processing conditions employed to prepare LLDPEs-*g*-DEM and HDPEs-*g*-DEM via reactive extrusion on their rheological and thermal properties were studied. The rheological properties of the virgin samples of LLDPEs, HDPEs, and their functionalized products were determined using capillary and dynamic rheometry. The thermal behavior of the virgin materials and their grafted products was examined by differential scanning calorimetry (DSC). It was found that the rheological properties are more sensitive than are the molecular structure characteristics to the changes produced by the grafting reactions with DEM, under the employed experimental conditions. There is an increase in the dynamic viscosity at low frequencies, in the storage modulus, and in the shear-thinning behavior when the grafting degree increases. The crossover between G'' and G' moves to lower frequencies and the relaxation time spectrum functions are broader in the grafted materials. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2549–2567, 1999

**Keywords:** reactive extrusion; rheological properties; polyolefins; thermal properties; grafting degree

## INTRODUCTION

The rheology of polyethylene (PE) melts has been extensively studied.<sup>1–5</sup> The correlations between rheological functions and molecular parameters such as weight-average molecular weight ( $M_w$ ), molecular weight distribution (MWD), short- and long-chain branching (SCB and LCB), and comonomer content have been reported.<sup>1–4</sup> Linear low-density PEs (LLDPEs) exhibit lower extensional viscosity, lower melt strength, and a lower propensity for strain hardening, as reflected in poorer bubble stability than that of low-density PEs (LDPEs) of the same melt flow index (MFI).<sup>4</sup>

The low-frequency rheological response of melted polymers is extremely sensitive to the molecular structure. For linear polymers, the values of the storage modulus (G') and loss modulus (G'')in the low-frequency range are proportional to the squared frequency  $(\omega)$  and to the frequency, respectively  $(G' \alpha \omega^2 \text{ and } G'' \alpha \omega)$ , otherwise known as the terminal zone. A decrease in the molecular weight and/or in the MWD tends to shift the terminal zone to higher frequencies,<sup>6</sup> whereas the addition of chemical crosslinks results in significant changes in the Newtonian viscosity  $(\eta_0)$  and in the storage modulus. In the studies carried out by Lachtermacher and Rudin,<sup>7,8</sup> Bremner and Rudin,<sup>9</sup> and Smedberg et al.,<sup>10</sup> the effects of crosslinking PE using various reactive ingredients on the terminal vinyl unsaturations were found. On the other hand, Kim and Kim<sup>11</sup> found that at certain peroxide concentrations G' was higher than was G'' in PEs, over the frequency range examined, indicating the existence of a

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three-dimensional network. However, in the peroxide low-concentration range, higher elasticities and viscosities were obtained without gel generation in the products. Similar results were found by Wong and Baker<sup>12</sup> for graft-modified polypropylene (PP).

The grafting of PEs in twin-screw extruders is an area of growing interest. However, few systematic studies on the consequences of this type of reaction on the rheological and thermal behavior have been conducted and problems such as changes in polymer processability and thermal properties, competition between monomer grafting and homopolymerization, and crosslinking or degradation of polymer chains, arising from the complex coupling variables, are still unsolved.

In this article, the effects of the grafting degree and the processing conditions employed to prepare the functionalized materials on the rheological and thermal properties were studied. In previous work,<sup>13</sup> the grafting of various commercial PEs, high-density PEs (HDPEs), and LLDPEs with diethylmaleate (DEM) was carried out in two corotating twin-screw extruders with different screw configurations and extrusion conditions.

It was demonstrated then that the functionalization reaction via extrusion did not significantly change the MWD when an initiator was added into the molten polymer. There was a slight shift in the MWD curves toward the high molecular weight end for the LLDPE2-g-DEM and a slight enhancement in the  $M_w$ ,  $M_z$ , and  $M_{z+1}$  average molecular weights. The reduction in the amount of terminal unsaturation

$$(A_{909cm^{-1}}/A_{1460cm^{-1}})$$

and the slight increase in trans-vinyl unsaturations

$$(A_{965 \mathrm{cm}^{-1}}/A_{1460 \mathrm{cm}^{-1}})$$

in the LLDPEs-g-DEM and HDPE2-g-DEM are in agreement with the mechanism proposed by Lachtermacher and Rudin<sup>7</sup> for long-chain branch formation. However, in HDPE1, there is an increase in the terminal unsaturation and a reduction in the weight-average molecular weight of the grafted products due probably to chain-scission reactions which are competing with the longchain branch formation reactions. Although there is an increase in the long-branch concentrations in all grafted materials, they are materials free of gel as determined by Soxhlet extraction with dichlorobenzene.

## **EXPERIMENTAL**

## Materials

The same materials described in a previous  $study^{13}$  were used in this investigation. The molecular characteristics and the grafting degrees of the LLDPEs and HDPEs are shown in Tables I and II.

## **Reactive Extrusion**

The reactive extrusion conditions are the same as detailed in a previous study.<sup>13</sup> The grafting reactions and DEM premix were carried out in two corotating intermeshing twin-screw extruders, one of them made by Werner & Pfleiderer (W&P) (ZSK-30), and the other, by Berstorff (ECS-2E25). The screws of the extruders were assembled from individual screw elements. 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. A conventional LDPE was included in the present study for comparison purposes.

## **Rheological Tests**

The rheological properties of virgin samples and their functionalized products were determined using capillary and dynamic rheometers.

## **Capillary Flow**

The steady-state capillary flow properties were measured using a Göttfert capillary rheometer,

Name Codes	Grafting Degree (mol %)	Grafting Degree (wt %)	$rac{A_{ m 965\ cm^{-1}}}{A_{ m 1460\ cm^{-1}}}  imes 10^3$	$rac{A_{ m 909~cm^{-1}}}{A_{ m 1460~cm^{-1}}}  imes 10^3$
LLDPE1	_	_	0.00	$3.7\pm0.3$
LLDPE1-g-DEM				
(solution)	0.92	5.7	_	_
LLDPE1-g-DEM				
(extrusion)	0.05	0.3	$0.77\pm0.04$	$2.9\pm0.1$
LLDPE2	_	_	$1.6\pm0.2$	$7.4\pm0.4$
LLDPE2-g-DEM				
(1)	0.35	2.2	$2.4\pm0.1$	$3.7\pm0.1$
(2)	0.40	2.5	$2.3\pm0.2$	$2.8\pm0.3$
(3)	0.42	2.6	$2.4\pm0.1$	$3.0\pm0.3$
(4)	0.59	3.6	$2.5\pm0.1$	$2.2\pm0.1$
(5)	0.36	2.2		_
(6)	0.10	0.6	$1.5\pm0.1$	$5.7\pm0.6$
(7)	0.21	1.3	$1.6\pm0.1$	$4.1\pm0.5$
(8)	0.37	2.3	$2.1\pm0.2$	$2.5\pm0.1$
LLDPE3	_	_	$1.8\pm0.1$	$7.4\pm0.1$
LLDPE3-g-DEM				
(1)	0.62	3.8	$2.9\pm0.1$	$1.5\pm0.1$
(2)	0.55	3.4	$2.5\pm0.1$	$1.5\pm0.2$
(3)	0.47	2.9	$2.0\pm0.1$	$1.8\pm0.1$
(4)	0.37	2.3		_
(5)	0.40	2.5		_
(6)	0.62	3.8	$2.0\pm0.1$	$2.0\pm0.1$
HDPE1	_	_	0.0	$0.8\pm0.08$
HDPE1-g-DEM	0.29	1.8	$1.57\pm0.05$	$2.0\pm0.3$
HDPE2	—	—	$0.41\pm0.01$	$8.3\pm0.4$
HDPE2-g-DEM	0.20	1.3	$0.71\pm0.02$	$7.3\pm0.6$
LLDPE4-g-DEM	0.10	0.6	$2.0\pm0.1$	$2.1\pm0.1$

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

Rheograph Model 2000, at several crosshead speeds. Seven capillaries with diameters (D) of 1 and 2 mm and several length-to-diameter ratios (L/D) were used. The onset of melt fracture or flow unstability was determined by visual inspec-

tion of the extrudate strands and several duplicate measurements were carried out at 200°C. The Bagley and the standard Rabinowitsch corrections were made. The MFI values of the extrudates were obtained at 190°C, 2.16 and 5 kg of

 Table II
 Molecular Characteristics of the Materials and Their Grafted Products

Material	Grafting Degree (mol %)	$\begin{array}{c} M_n \times \ 10^{-4} \\ (\text{g/mol}) \end{array}$	$M_w  imes 10^{-4} \ ( m g/mol)$	$M_z  imes 10^{-4}$ (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
LLDPE1	_	2.90	13.5	36.5	4.70
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
LDPE	_	2.67	19.0	61.3	7.37



**Figure 1** Loss modulus (G'') as a function of time for the PEs and their grafted products at 200°C and 0.1 rad/s of frequency.

load, using a Davenport Melt Index in agreement with ASTM D 1238.

#### **Dynamic Flow**

The viscoelastic properties of the materials were measured on Rheometrics RDA-II equipment using 25-mm-diameter parallel plates. Strain sweeps were made at frequencies of 1 and 10 rad/s in order to fix the limits of the linear viscoelastic range. The shear storage modulus (G') and the shear loss modulus (G''), as well as the dynamic viscosity  $(\eta')$  were determined by small-amplitude oscillatory shear experiments in the linear viscoelastic range of strain, at 160, 180, and 200°C except for the LLDPE1 and its grafted products, LLDPE2-g-DEM(1) and LLDPE2-g-DEM(6), which were determined only at 200°C. To examine the thermal stability of the samples, time sweeps were performed at a fixed strain, 200°C, and three different frequencies of 0.1, 0.5, and 1 rad/s.

The frequency sweeps were conducted from 1 to 100 rad/s. Except for the lowest decade of frequency, all data points for each material were determined within a time span of t < 5 min. The total time for loading, trimming, and relaxing never exceeded 5 min.

#### **Thermal Behavior**

The thermal behavior of the virgin materials and their grafted products was examined by DSC on a Perkin–Elmer DSC-2. Samples were first heated from room temperature to 170°C, held there for 5 min, and then cooled to room temperature at 10°C/min. To eliminate the different thermal histories of the materials, the melting thermograms were obtained during the second heating cycle at 10°C/min.

## **RESULTS AND DISCUSSION**

#### **Dynamic Flow**

Strain sweeps at fixed frequencies of 1 and 10 rad/s were carried out with all the samples, that is, virgin materials and their functionalized products, in order to fix the limits of the linear viscoelastic range of strain. As a result, linear viscoelastic behavior was achieved in the whole strain range at frequencies of 0.1 and 0.5 rad/s and up to a value between 10 and 20% of strain for frequencies in the range of 1–100 rad/s.

Isothermal time scans were performed for up to 20 min at a fixed strain, a temperature of 200°C, and frequencies of 0.1, 0.5, and 1 rad/s. The results are illustrated in Figures 1–4 where the dynamic storage modulus (G') and the loss modulus (G'') are plotted as a function of time (t). The thermooxidative degradation in air was observed to become noticeable after 5 min at 0.5 rad/s and 10 min at 1 rad/s. It was also noted that the storage modulus (G'') to this type of degradation. During thermooxidative degradation of polyolefins, chain scission and grafting may lead to branching and partial crosslinking.<sup>7</sup> Harrel and



**Figure 2** Storage modulus (G') as a function of time for the PEs and their grafted products at 200°C and 0.1 rad/s of frequency.

Nakajima<sup>14</sup> examined the effects of oxidation, shear, and thermally induced reactions in LLDPE resins during the mixing process on their rheological properties. These authors concluded that the formation of long-chain branches and the increase of molecular weight produce low-frequency complex viscosity and storage modulus enhancements. However, in the higher-frequency range, the complex viscosity and the storage modulus are not significantly affected.

A similar trend is revealed for all samples in this study: virgin resins and their grafted products (Figs. 1–4). The error introduced by thermooxidative degradation on the measurement of viscoelastic properties was relatively small at  $200^{\circ}$ C and times lower than 6 and 10 min for time sweeps at 0.5 and 1–100 rad/s, respectively. However, it was worthy of attention at the lowest frequency (0.1 rad/s). The shear storage and loss modulus values were extrapolated to zero time (-300 s), which was the time before the trimming and relaxing operations, when the sample was loaded into the rheometer.

A simple generalization of the Carreau–Yasuda model, a relationship between viscosity and rate of strain, was used.<sup>15</sup> This model was employed to describe the dynamic viscosity ( $\eta'$ ) as a function of frequency ( $\omega$ ) in the form

$$\eta' = \eta_{0c} [1 + (\omega\tau)^{\beta}]^{\alpha} \tag{1}$$

where  $\eta_{0c}$  is the Newtonian viscosity and  $\tau$ ,  $\alpha$ , and  $\beta$  are equation parameters. For large deformation rates ( $\omega \tau >>> 1$ ) a "power law" is recovered, with its exponent



**Figure 3** Loss modulus (G'') as a function of time for the PEs and their grafted products at 200°C and 0.5 rad/s of frequency.



**Figure 4** Storage modulus (G') as a function of time for the PEs and their grafted products at 200°C and 0.5 rad/s of frequency.

$$n_1 = 1 - \alpha \beta \tag{2}$$

Since  $0 \le n_1 \le 1$ , the values of the product  $\alpha \beta$  should also be within these limits.

Figures 5 and 6 show the dynamic viscosity data  $(\eta')$  and storage modulus (G') as a function of frequency at different temperatures for the LLDPE2 and LLDPE3. It is seen in all cases that the dynamic viscosity decreases and the storage modulus increases as the frequency increases, that the dynamic viscosity and storage modulus decrease as the melt temperature increases,<sup>1,6</sup> and that both materials have very similar rheological behavior. The data obtained between the frequency limits of 0.5–100 rad/s and the extrapolated data at 0.1 rad/s were fitted to eq. (1) in order to obtain the four constants listed in Table III at 200°C. The fit between the experimental and theoretical curves was excellent with a reduced standard error of measurements of less than 0.42%. The activation energy of flow  $(E_a)$  was calculated and also is presented in Table III. The values found are in good agreement with the literature values: E = 29 to 34 kJ/mol for the LLDPEs and 22–29 kJ/mol for HDPEs.<sup>1,2,4</sup>

The contribution of the viscous component to the viscoelastic behavior is given by the loss modulus (G'') or the dynamic viscosity ( $\eta'$ ), while the elastic behavior is represented by the storage modulus (G'). The plots Log G' versus Log G'' illustrate the relative contribution of the G' response to that of G''. This mode of presentation was suggested by Han<sup>6</sup> because it was found to be independent of the temperature and molecular weight for monodisperse materials and it is very sensitive to LCB and the MWD



**Figure 5** Dynamic viscosity  $(\eta')$  as a function of frequency  $(\omega)$  for LLDPE2 at different temperatures and LLDPE3 at 200°C.



**Figure 6** Storage modulus (G') as a function of frequency ( $\omega$ ) of LLDPE2 at different temperatures and LLDPE3 at 200°C.

for commercial polymers in the low-frequency range.

Figure 7 shows the dynamic viscosity data and storage modulus as a function of the frequency for the LLDPE1 and HDPE1 at 200°C. The high viscosity at low frequencies of LLDPE1 and HDPE1 is a direct result of the high weight-average molecular weight of these linear polymers. However, the viscosity at high frequencies is affected by the weight-average molecular weight as well as by the MWD. The LLDPEs are materials with a narrower MWD than that of the HDPEs and show less sensitivity to shear rate and a lower storage modulus at low frequencies.<sup>1-4</sup> In other words, the melt viscosity at high shear rates is lower for samples having a broad MWD than for samples having a narrow MWD when the weight-average molecular weight is the same for both samples.

Figures 8–10 show the dynamic viscosity data  $(\eta')$  and the storage modulus (G') as a function of frequency for the LLDPE1, LLDPE2, HDPE1, and their grafted products. Figure 8 illustrates the plots of dynamic viscosity versus the frequency of the LLDPE1, solution-functionalized LLDPE1 with a grafting degree of 0.92 mol DES/100 mol LLDPE1, and the extrusion-functionalized LLDPE1 with a grafting degree of 0.05 mol DES/100 mol LLDPE1. The low-frequency viscosities of the LLDPE1 and the solution-functionalized LLDPE1 (LLDPE1 and the solution-functionalized LLDPE1 (LLDPE1-g-DEM) are almost the same, while at higher frequencies, the LLDPE1-g-DEM is less viscous. However, the extrusion-

Material	$G_x  imes 10^{-4} \ { m (Pa)}$	$\omega_x$ (rad/s)	Ea (kJ/mol)	n	$rac{ au_c  imes 10^{-5}}{ ext{(Pa)}}$
	0.50	00.0		0.50	2.0
	8.79	88.9		0.59	2.0
LLDPE1-g-DEM (solution)	2.90	18.7	—	—	—
LLDPE1-g-DEM (extrusion)	2.24	2.36	—	0.49	1.8
LLDPE2	26.0	> 100	31	0.62	2.4
LLDPE2-g-DEM (1)	13.5	> 100	_	_	_
LLDPE2-g-DEM (4)	2.67	12.6	37	_	_
LLDPE2-g-DEM (6)	21.5	> 100	_	_	
LLDPE3	27.5	> 100	29	0.64	2.4
LLDPE3-g-DEM (6)	1.92	4.00	35	0.48	1.8
HDPE1	3.18	7.59	23	0.37	2.3
HDPE1-g-DEM	0.56	0.25	27	0.39	4.2
LDPE	0.84	1.08	51	0.36	1.0

Table III Rheological Characteristics of the Materials at 200°C



**Figure 7** Dynamic viscosity  $(\eta')$  and storage modulus (G') as a function of frequency  $(\omega)$  of LLDPE1 and HDPE1 at 200°C.

functionalized LLDPE1 shows the highest dynamic viscosity curve although it has the lower grafting degree. The size exclusion chromatography (GPC) measurements of the MWD did not reveal pronounced changes between the MWDs of the virgin LLDPE1 and the LLDPE1-functionalized with DEM via a solution (LLDPE1-g-DEM) as reported earlier.<sup>16</sup> Similar results were found by Aglietto et al.<sup>17</sup> for their LLDPE functionalized with DEM via a solution. GPC measurements are not very sensitive to changes in higher moments of the MWD ( $M > 5 \times 10^6$ ), which affect the  $M_z$ and higher molecular averages, while rheological properties are more sensitive to those changes.<sup>3</sup>

The behavior found in the LLDPE1 functionalized by solution is attributed to the formation of a low level of LCB and/or the presence of polar groups inserted on the chain. Long branching in polymers is thought to give a more pseudoplastic or shear-thinning characteristic to the material<sup>18</sup> compared to the linear analogs. The increase of viscosity is a direct result of the enlargement of the molecular weight, which can be increased as a result of chain branching, chain extension, and, most significantly, crosslinking.

The LLDPE1-g-DEM(1), functionalized via solution, was prepared with a higher monomer concentration and at a lower temperature than was the LLDPE1-g-DEM(2) functionalized via extrusion. These conditions reduced the probability of LCB in this material and, consequently, the enhancement in the low-frequency dynamic viscosity is lower when compared to the LLDPE1-g-DEM(2) (Fig. 8).



**Figure 8** Dynamic viscosity  $(\eta')$  and storage modulus (G') as a function of frequency  $(\omega)$  of LLDPE1 and its grafted products at 200°C.



**Figure 9** Dynamic viscosity  $(\eta')$  and storage modulus (G') as a function of frequency  $(\omega)$  of HDPE1 and its grafted products at 200°C.

On the other hand, the HDPE1 resins showed no detectable *trans* unsaturations by FTIR analysis, but upon a grafting reaction with peroxide, significant concentrations were seen for the HDPE1-g-DEM (Table I). At the same time, comparisons of the weight-average molecular weight and terminal unsaturations of the virgin resin and the HDPE1-g-DEM show a decrease in the former and an enhancement in the second one, which indicates that chain-scission processes are occurring at the experimental conditions in the functionalization via extrusion of the HDPE1. However, the Newtonian viscosity and the storage modulus at a constant frequency are higher in the HDPE1-g-DEM (Fig. 9). These results suggest that there are, in fact, two simultaneous competing mechanisms in this system: chain scission and LCB formation. Similar results were found by

Wong and Baker in their PP-g-styrene copolymers.<sup>12</sup> The amount of terminal unsaturations is higher in the LLDPE1 than in the HDPE1 and the grafting reaction in the former material decreases the terminal unsaturations and increases the *trans*-vinyl unsaturations, which supports the idea that terminal vinyl coupling is occurring in the LLDPE1-g-DEM material, which is the reason for the very high Newtonian viscosity found. The same results were obtained for the HDPE2 (this material was produced by the same manufacturer as that of the LLDPEs). Lachtermacher and Rudin<sup>7,8</sup> and Bremner and Rudin<sup>9</sup> reported similar results in their peroxide-modified resins.

The dynamic viscosities of the LLDPE2 and its grafted products as a function of the frequency are shown in Figure 10. The increase of the Newtonian dynamic viscosities of extrusion-function-



**Figure 10** Dynamic viscosity  $(\eta')$  as a function of frequency  $(\omega)$  for LLDPE2, LLDPE3, and their grafted products at 200°C.



**Figure 11** Ratio of storage modulus and ratio of loss modulus as a function of grafting degree of LLDPE2 at 200°C and 0.1 rad/s.

alized products compared to those of the unreacted resins is consistent with the formation of a low level of LCB in the LLDPE2 resins during the grafting process (Table I) or with an enlargement in the MWD. There was no evidence of gel in any of the products. The comparisons are in agreement with the measured changes in the MWD as reported earlier.<sup>13</sup> The MWDs of the LLDPE2-g-DEM(4) and LLDPE2-g-DEM(6) with grafting degrees of 0.59 and 0.10 mol %, respectively, did not show appreciable differences when compared to those of the virgin resin. There is a slight shift of the molecular weight on the side of higher molecular weights and a slight enhancement in the  $M_w$ ,  $M_z$ , and  $M_{z+1}$  average molecular weights.

A Newtonian region is observed for the low molecular weight LLDPE2, LLDPE3, and LLDPE2-g-DEM<sup>6</sup> materials. However, for the highest grafted LLDPE2 material, the Newtonian region in an oscillatory flow was not observed even at the highest experimental temperature as a consequence of the branch formation in the LLDPE2-g-DEM materials. At higher frequencies, the differences among the dynamic viscosities of the products functionalized by extrusion with differents amounts of an initiator in the W&P extruder are lower. Figure 11 shows the influence of the grafting degree on the ratio of the loss modulus and the ratio of the storage modulus of the LLDPE2-g-DEM and the virgin LLDPE2  $(G''_{\text{LLDPE2-g-DEM}}/G''_{\text{LLDPE2}}$  and  $G'_{\text{LLDPE2-g-DEM}}/G'_{\text{LLDPE2}}$  at 0.1 rad/s of frequency and 200°C.

It is well known that peroxide-initiated chain extension and branching reactions in PE result in higher melt viscosities. The low-frequency dy-

namic viscosity and the storage modulus increase as the grafting degree is increased for LLDPE2g-DEM (Fig. 11). This behavior is in agreement with the measured changes in the MWDs, as reported earlier. The functionalized material with the higher grafting degree (LLDPE2-g-DEM(4)) did not reveal pronounced changes in the MWDs. On the other hand, the reduction in the amount of terminal unsaturations  $(A_{909cm^{-1}}/A_{1460cm^{-1}})$  and the slight increase of *trans*-vinyl unsaturations (Table I) are consistent with the mechanism proposed by Bremmer and Rudin.<sup>9</sup> Long-branch formation is apparent primarily by coupling allylic radicals. Interconnection of such long branches would lead to crosslinking for the PEs modified with peroxides. However, there was no evidence of gels in any of the functionalized LLDPE2 materials.

Harrel and Nakajima<sup>14</sup> examined the effects of oxidation, shear, and thermally induced reactions in LLDPE during the mixing process without peroxide. Lachtermarcher and Rudin<sup>8</sup> reported the effects of peroxide modification in LLDPEs on the rheological properties. These authors concluded that the formation of long-chain branches and the increase of molecular weight produce a low-frequency viscosity enhancement. However, in the higher-frequency range, the viscosity is not significantly affected. A similar trend is revealed for the LLDPE1-g-DEM and LLDPE2-g-DEM.

The plots of the storage modulus (G') as a function of loss modulus (G'') of the materials and their grafted products are shown in Figures 12 and 13. These curves are independent of the melt temperature and weight-average molecular weight for monodisperse polymers. However, ma-



**Figure 12** Storage modulus (G') as a function of loss modulus (G'') of LLDPE2 and its grafted products at 200°C.

terials with broader MWDs and with LCB have a higher storage modulus.<sup>6</sup> This latter behavior is displayed by the grafted materials and is in agreement with the mechanism proposed before.

The G'-G'' crossovers,  $G_x$  and  $\omega_x$ , of the materials and their functionalized products are shown in Table III. Zeichner and Patel<sup>19</sup> reported that, for PP,  $G_x$  is related to the MWD, and  $\omega_x$ , to the zero-shear viscosity. A similar behavior was reported by Utracki and Schlund<sup>1</sup> for LLDPEs. The  $G_x$  and  $\omega_x$  values found for the LLDPE1 are in agreement with the results presented by Utracki and Schlund.<sup>1</sup> However, the G'-G'' crossovers for the grafted materials are lower than those found for the virgin materials.

Graessley and Roovers<sup>20</sup> reported that, in star polystyrenes, the crossover of G' and G'' occurs at a lower frequency as compared to that in linear polystyrene, suggesting a broader relaxation spectrum for the former polymer. These authors observed that the crosspoint moves to lower frequency as the molecular weight of the arms increases. These same trends found for the grafted resins are presented in Figures 14 and 15. The relaxation spectrum was established using the method proposed by Ramkumar et al.<sup>21</sup> The longer relaxation times found for the LLDPEgrafted materials could be explained by the presence of a transient network structure produced by mechanical entanglement of polymeric chain as a result of the presence of Y-type branches also noted by Lachtermarcher and Rudin<sup>8</sup> in their peroxide-modified PEs.

The storage modulus (G') and loss modulus (G'') values were recalculated from the relaxation



**Figure 13** Storage modulus (G') as a function of loss modulus (G'') for LLDPE1, HDPE1, their grafted products, and LDPE at 200°C.



**Figure 14** Relaxation time spectrum (*H*) as a function of relaxation time ( $\lambda$ ) of LLDPE2 and their grafted products at 200°C.

time spectrum function  $H(\lambda)$  with the following equations:

$$G'(\omega) = \int_{-\infty}^{\infty} \frac{\omega^2 \lambda^2}{(1+\omega^2 \lambda^2)} H(\lambda) \ d \ln \lambda \qquad (3)$$

$$G''(\omega) = \int_{-\infty}^{\infty} \frac{\omega\lambda}{(1+\omega^2\lambda^2)} H(\lambda) \ d \ln \lambda \qquad (4)$$

where  $\lambda$  is the relaxation time, and  $\omega$ , the oscillatory frequency.

The maximum errors found in the storage modulus (G') and in the loss modulus (G'') calculated from the relaxation spectrum function  $H(\lambda)$  were



$$G''_{\rm error} = \frac{\sqrt{\sum_{i=1}^{N} \left(\frac{G''_{\rm cal}}{G''_{\rm exp}} - 1\right)^2}}{\sqrt{(N-1)}}$$
(5)

$$G'_{\text{error}} = \frac{\sqrt{\sum_{i=1}^{N} \left(\frac{G'_{\text{cal}}}{G'_{\text{exp}}} - 1\right)^2}}{\sqrt{(N-1)}} \tag{6}$$

where  $G''_{exp}$  is the experimental loss modulus values;  $G''_{cal}$ , the loss modulus values calculated



**Figure 15** Relaxation time spectrum (*H*) as a function of relaxation time ( $\lambda$ ) of LLDPE1, HDPE1, their grafted products, and LDPE at 200°C.

Material	$\begin{array}{c} \eta_{0\tau} \\ (\text{kPa s}) \end{array}$	η <sub>0c</sub> (kPa s)	$ au\left(\mathrm{s} ight)$	$\lambda_{\max} \atop { m (s)}$	$n_1$	$Je^0 imes 10^4 \ ({ m Pa}^{-1})$
LLDPE1	13.9	13.5	1.4	1.56	0.47	1.13
LLDPE1-g-DEM (solution)	22.4	22.3	4.8	5.31	0.44	2.37
LLDPE1-g-DEM (extrusion)	125	110	32.3	76.5	0.43	6.12
LLDPE2	1.8	1.7	0.17	0.11	0.64	0.60
LLDPE2-g-DEM (6)	2.5	2.1	0.23	0.27	0.58	1.10
LLDPE2-g-DEM (1)	4.9	5.0	0.84	0.45	0.50	0.91
LLDPE2-g-DEM (4)	30.9	30.8	15.0	27.2	0.49	8.82
LLDPE3	1.8	1.8	0.19	0.11	0.66	0.60
LLDPE3-g-DEM (6)	56.8	53.0	24.5	65.0	0.45	11.4
HDPE1	27.0	27.5	7.9	13.9	0.38	5.16
HDPE1-g-DEM	85.3	80.0	80.0	61.1	0.39	7.13
LDPE	104	101	53.9	145	0.37	14.0

Table IV Rheological Parameters of the Materials at 200°C

from  $H(\lambda)$ ;  $G'_{exp}$ , the experimental storage modulus values;  $G'_{cal}$ , the storage modulus values calculated from  $H(\lambda)$ ; and N, the number of data points.

The Newtonian or zero-shear viscosity  $(\eta_{0\tau})$ , the equilibrium shear compliance  $(Je^0)$ , and the maximum relaxation time or terminal relaxation time  $(\lambda_{\max})$  were calculated from the relaxation time spectrum function  $H(\lambda)$  with the following equations:

$$\eta_{0\tau} = \int_{-\infty}^{\infty} \lambda H(\lambda) \ d \ \ln(\lambda) \tag{7}$$

$$Je^{0} = \int_{-\infty}^{\infty} \frac{\lambda^{2}}{\eta_{0}^{2}} H(\lambda) \ d \ln(\lambda)$$
 (8)

$$\lambda_{\max} = \eta_0 J e^0 \tag{9}$$

where  $\lambda$  is the relaxation time;  $\lambda_{\text{max}}$ , the maximum or terminal relaxation time; and  $H(\lambda)$ , the relaxation time spectrum function.

From the relaxation spectrum time data, the zero-shear viscosity (Newtonian viscosity  $\eta_{0\tau}$ ), and the equilibrium shear compliance  $(Je^0)$  were evaluated by eqs. (7) and (8). The Newtonian viscosity found with this method and that found with the extrapolated values of the Carreau–Yasuda equation  $(\eta_{0c})$  were almost the same for the virgin materials and their grafted products. The Newtonian viscosity  $(\eta_{0\tau})$  and the equilibrium compli-

ance  $(Je^0)$  of the materials and their grafted products are reported in Table IV. The ratio between the Newtonian viscosity  $(\eta_{0LLDPE2-g-DEM})$  and the equilibrium compliance  $(Je^0_{LLDPE2-g-DEM})$  of the LLDPE2-g-DEM materials compared to the Newtonian viscosity  $(\eta_{0LLDPE2})$  and equilibrium compliance  $(Je^0_{LLDPE2})$  of the virgin resin LLDPE2 are shown in Figure 16. The addition of random branching into a sample increases the relaxation time spectrum in the terminal region and raises both  $\eta_0$  and  $Je^0$  as was observed in Figures 14–16 and Table IV for the grafted materials and the LDPE.

It is accepted that in the process of reactive extrusion PE degradation as well as crosslinking could occur simultaneously, but because of the stability of the formed polymeric radical, crosslinking seems to be the dominant reaction at ordinary conditions for the LLDPEs.<sup>7-11</sup> Therefore, the effects of thermal processing on the chemical and physical properties of PE are strongly dependent on the oxygen present in the mixer. When air is accessible to the molten polymer, the weight-average molecular weight decreases. The grafting via solution was made in an inert atmosphere. However, in the functionalization via extrusion, the peroxide was added to the extruder in an open feed port when the monomer was well mixed in the molten polymer. With these conditions, secondary reactions such as thermaloxidation and radical termination could be taking place just in the element below the feed port. The formation of LCB in the grafted products, which



**Figure 16** Newtonian viscosity and compliance as a function of the grafting degree of LLDPE2 at 200°C.

gives rise to spectacular differences in the rheological behavior, cannot readily be detected by means of molecular weight determinations.<sup>8</sup>

There is a slight increase in the weight-average molecular weight for the LLDPE2-g-DEM(4) and a slight enhancement in its activation energy (Tables II and III). The activation energy  $(E_a)$ , or the temperature dependence of the viscosity, is also expected to be a function of the branching level. An Arrhenius dependence of the Newtonian viscosity was used to estimate  $E_a$  for the materials and their grafted products. The relative proportions of branched and linear species and the rheological behavior, at a given branching level, will depend on the branching mechanism. LCB formation as a result of peroxide degradation will affect both the proportion of branched species and the rheological behavior more than it will the equivalent branching levels as a result of thermal or mechanical degradation.<sup>7</sup> The enhancements of the viscosity and storage modulus at 0.1 rad/s frequency and 200°C of LLDPE1 due to thermooxidative degradation inside the rheometer chamber can be seen in Figures 1 and 2.

Another way to present the viscoelastic behavior of polymers is to plot the data of the phase angle  $[(\delta(\omega)]$  versus the logarithmic dynamic shear modulus  $[\text{Log}(G^*)]$ , both measured at various angular frequencies and temperatures. The function  $\delta(\omega)$  is very characteristic of the structure parameters of the material, such as the MWD, network structures due to crosslinking, and reinforcement with fine fillers.<sup>22,23</sup> The  $\delta(\omega)$ versus  $\text{Log}(G^*)$  results for the virgin resins and their grafted products are reported in Figures 17 and 18. These curves are independent of the tem-



**Figure 17** Phase angle ( $\delta$ ) as a function of complex modulus ( $G^*$ ) of LLDPE2, LLDPE3, their grafted products, and LDPE.



**Figure 18** Phase angle ( $\delta$ ) as a function of complex modulus ( $G^*$ ) of the LLDPE1, HDPE1, and their grafted products at 200°C.

perature for the LLDPE2 and LLDPE3. At low frequencies, the viscoelastic behavior tends toward that of a simple liquid  $(\delta \rightarrow \pi/2)$ , and at high frequencies, toward that of an elastic rubber  $(\delta \rightarrow 0)$ . For the grafted products, a vertical shift can be seen and the viscoelastic behavior tends toward that of an elastic rubber when the grafting degree is increased.

The rheological behavior at a high shear rate can be represented by a power-law model. All materials used have non-Newtonian characteristics, as indicated by the power-law index (n < 1). The power-law index at 200°C is shown in Table III for the virgin resins and their grafted materials are more pseudoplastic and their sensitivity to melt fracture is higher, except for the HDPE1-g-DEM. The critical shear stress  $(\tau_c)$  is lower for the grafted material than for the virgin resin (Table III). These results are consistent with the longbranching formation. The effects of LCB on the rheological properties are similar to those of crosslinking, and it is difficult to separate the two contributions. However, all functionalized materials are gel-free. Hence, the crosslinking density may have been too low, resulting in LCB rather than the formation of a three-dimensional, insoluble network.

The MFI expressed in g/10 min, which is widely used by industry to specify the processing behavior of polymers, is the flow rate measured at a specific temperature of 190°C and a low shear stress of  $1.97 \times 10^4$  Pa using a 2.16 kg of load, a very short capillary with a length-to-diameter of 3.8, and a flat entry according to ASTM D 1238, condition E. The MFI values are presented in Tables V and VI for the materials used and then functionalized. Also, the MFI were determined at different residence times in the channel at 5 kg of load due to the very low values at 2.16 kg of load for the functionalized resins (Table VI).

Although the MFI value is supposed to represent the reciprocal of the particular viscosity measured at the MFI condition of temperature and shear stress, it is strongly influenced by the elasticity of the polymer because of the short L/Dratio and the flat entry of the capillary. The highest MFI values found for the resins extruded once (Table VI) are due probably to the effect of shear modification.<sup>5</sup> The influence of the grafting degree, screw configurations, grafting temperature, and type of peroxide on the MFI value is consistent with the mean residence time in the extruder and the kinetics of the peroxide decomposition as was found in previous work.<sup>13</sup> For the LLDPEs, higher residence times and transport delay times in the extruder produced lower MFI values. When configuration B was used, a lower grafting degree was obtained at the same initiator concentration. The transport delay time and mean residence time in the extruder were higher when they were compared to configuration A in the W&P extruder. The free radicals formed could be lost in secondary reactions such as radical termination reactions and thermal-oxidation or through devolatilization of the reactives. These secondary reactions could be taking place just in the liquid mixing elements. The long-branching reactions could be also taking place because of the higher transport delay time and mean residence time for configuration B.

Also, enhancement in the peroxide concentration and in the temperature increases the proba-

	Extruder Configuration,		$\mathrm{MFI}  imes 10^3 \ \mathrm{(kg/10\ min)}\ \mathrm{Residence}$ Time Before Test (min)		
Material	Condition (Type of Peroxide)	Grafting Degree <sup>a</sup>	5	10	
LLDPE2-g-DEM		0.00	$4.3 \hspace{0.2cm} \pm \hspace{0.2cm} 0.1 \hspace{0.2cm}$	$4.4 \hspace{0.2cm} \pm \hspace{0.2cm} 0.1 \hspace{0.2cm}$	
(1)	A (DBPH <sup>b</sup> )	0.35	$1.7 ext{ }\pm ext{ }0.1 ext{ }$	$1.7 \pm 0.1$	
(2)	A (DBPH <sup>b</sup> )	0.40			
(3)		0.42			
(4)	A (DBPH <sup>b</sup> )	0.59	$0.80\pm0.08$	$0.66\pm0.05$	
(5)	A (DBPH <sup>b</sup> )	0.36	$1.2 \pm 0.2$	$1.0 \pm 0.1$	
(6)	A (DBPH <sup>b</sup> )	0.10			
(7)	B (DBPH <sup>b</sup> )	0.21	$2.7 ext{ }\pm ext{ }0.1 ext{ }$	$2.5 ext{ }\pm ext{ }0.2 ext{ }$	
(8)	B (DBPH <sup>b</sup> )	0.37	$0.56\pm0.05$	$0.54\pm0.02$	
LLDPE3-g-DEM		0.00	$3.9 \pm 0.1$	$3.8 \pm 0.1$	
(1)	C, 3 (DBPH <sup>b</sup> )	0.62	$0.36\pm0.01$	$0.33\pm0.02$	
(2)	C, 1 $(DBPH^b)$	0.55	$0.66\pm0.03$	$0.64\pm0.02$	
(3)	C, 2 $(DBPH^b)$	0.47	$0.34\pm0.01$	$0.33\pm0.02$	
(4)	$C, 4 (DP^c)$	0.37	$0.66\pm0.03$	$0.63\pm0.02$	
(5)	$C, 4 (DP^c)$	0.40	$0.40\pm 0.01$	$0.38\pm0.02$	
(6)	C, 4 (DP <sup>c</sup> )	0.62	$0.11\pm0.01$	$0.09\pm0.02$	

Table V Influence of Grafting Degree and Residence Time Before Test on the MFI of the Materials at 2.16 kg of Load and 190°C

<sup>a</sup> mol DES/100 mol PE. <sup>b</sup> 2,5-Dimethyl-2,5-di(*tert*-butyl peroxyhexane).

<sup>c</sup> Dicumyl peroxide.

bility of LCB reactions and reduces the MFI of the LLDPEs (conditions 1 and 4 for the LLDPE2-g-DEM and conditions 2 and 3 for the LLDPE3-gDEM). The lower efficiency of the dicumyl peroxide was attributed to a higher probability of radical breakdown and the generation of aceto-

	Grafting Degree (mol	$\mathrm{MFI} imes10^3$
Material	DES/100 mol PE)	(kg/10 min)
HDPE1	0.00	$0.95\pm0.02$
HDPE1 <sup>a</sup>	0.00	$1.7\pm0.1$
HDPE1-g-DEM	0.29	$1.4\pm0.1$
C C		$(1.4 \pm 0.1)^{ m b}$
HDPE2	0.00	$18.0\pm0.6$
HDPE2 <sup>a</sup>	0.00	$16.7\pm0.4$
HDPE2-g-DEM	0.21	$7.2\pm0.1$
		$(6.3 \pm 0.2)^{\rm b}$
LLDPE1	0.00	$1.8\pm0.1$
LLDPE1 <sup>a</sup>	0.00	$3.3\pm0.2$
LLDPE1-g-DEM	0.05	$0.73\pm0.04$
(extrusion)		$(0.73 \pm 0.01)^{ m b}$
LLDPE3	0.00	$8.1\pm0.2$
LLDPE3 <sup>a</sup>	0.00	$10.9\pm0.3$
LLDPE3-g-DEM (6)	0.62	$1.39\pm0.04$
		$(1.31 \pm 0.04)^{ m b}$

Table VI Influence of Grafting Degree on the MFI of the Materials Functionalized with Dicumyl Peroxide at 5 kg of Load and 190°C

<sup>a</sup> Extruded once.

<sup>b</sup> Residence time before test: 10 min.

phenone as a by-product.<sup>11</sup> For these reasons, a higher concentration of dicumyl peroxide was employed, the MFI of the LLDPE3-g-DEM(6) was lower than that of the LLDPE3-g-DEM(1), and the secondary reactions such as long-chain branch formation increased.

The low MFI values found for the LLDPE1-g-DEM, LLDPE2-g-DEM, LLDPE3-g-DEM, and HDPE2-g-DEM, when they were compared to those of virgin resins, are consistent with the LCB formation. However, the HDPE1-g-DEM has a slight reduction in MFI. This result is also consistent with the two competing reactions, chain scission and LCB, for this material.

Adding the peroxide with a paraffin oil did not change the grafting degrees<sup>13</sup> of LLDPE2-g-DEM(1) and LLDPE2-g-DEM(5). However, the MFI values are lower than for the LLDPE2-g-DEM(1), due probably to the higher concentration of DEM used in the latter. The MFI values for the HDPE1-g-DEM, HDPE2-g-DEM, and the LDPE3g-DEM (Table VI) are influenced by the elasticities and the MWDs of these materials, the weightaverage molecular weight, and the branching index.

The structures of polyolefins grafted with DEM by solution have been elucidated using <sup>13</sup>C-NMR spectroscopy by Aglietto et al.<sup>17</sup> They demonstrated that the side chains in the final product contained mostly only one unit of DEM. On the other hand, in the grafting reactions with MA, grafting mainly occurred on secondary carbons when long methylene sequences were present (>3). Otherwise, grafting also occurred on tertiary carbons.<sup>24</sup> The studies of free-radical grafting reactions on model compounds onto polyolefins showed the presence of 8–40 species, depending on the reaction conditions and how enormously complicated the radical grafting reactions in polyolefins could be.<sup>25</sup>

Secondary reactions, such as chain scission and crosslinking, could take place simultaneously with the grafting reactions. Depending on the structure of the macroradicals, the formed crosslink could be either tetrafunctional (X-point) or trifunctional (Y-point). An X-point is formed when two secondary radicals combine, and a Ypoint, when a secondary and a primary combine as was shown by Bremner and Rudin.<sup>9</sup> The slight enhancement in the weight-average molecular weight found in the LLDPE2-g-DEM(4) could be due to the former crosslinking reactions in a very small proportion, since the grafted products are gel-free materials, but the higher increase of the Newtonian viscosity  $(\eta_0)$  and the storage modulus in the LLDPEs-g-DEM compared to their virgin resins are due to the second type of crosslinking reactions. In functionalization by extrusion, the crosslinking reactions could be taking place due to the cage effect<sup>12</sup> and the presence of vinyl unsaturations in the LLDPEs, but in grafting by solution, this type of reaction was reduced.

Hence, the crosslink density must have been too low, resulting in LCB rather than in the formation of a three-dimensional, insoluble network. The effects of LCB on the rheological properties are similar to those of crosslinking and it is difficult to separate the two contributions. However, the fact that the HDPE1-g-DEM exhibited an increased storage modulus implies that the HDPE1 was branched to some degree as a result of grafting. Comparison of the storage modulus (G') is a much more sensitive indicator of the presence of branches. Similar results were found by Kasehagen et al.<sup>18</sup> in their branched polybutadiene materials.

## **Thermal Properties**

Processing of pure PEs did not modify significantly their thermal properties, as DSC scans of these materials revealed after treating them at the same conditions of the functionalization process. In comparison with pure materials, DSC scans of grafted ones showed slight changes in their melting peak temperatures. A reduction of about 5°C in its melting peak temperature  $(T_{mpeak})$  was observed in the material with the higher grafting degree LLDPE2-g-DEM(4) (see Tables I and VIII). It can be seen in Table VII that, as the grafting degree increases, the  $T_{mpeak}$ of the materials seems to decrease, which indicates that there is a reduction of the polymer lamellar thickness, probably due to an interruption of the ethylene segments as a consequence of the grafting process in the extruder. The proposed general mechanism for DEM grafting into PE indicates that an active site is first formed by the initiator in a secondary carbon and then DEM inserts itself in this site to form a diethyl succinate (DES) group. It is known that this group is excluded from the lamellar structure, similar to those chain branches which are larger than pendant methyl groups.<sup>27</sup> This fact leads to shorter linear sequences that could then crystallize. Therefore, when the grafting degree is higher, more DEM groups are attached to the molecules and, consequently, shorter linear crystallizable

Grafting Degree <sup>a</sup>	Configuration	$T_c$ Peak (±1°C)	$\begin{array}{c} T_m \; \mathrm{Peak} \\ (\pm 1^{\mathrm{o}}\mathrm{C}) \end{array}$	% C <sup>b</sup>	$Wc^{ m d} imes10^2\ (\pm0.1\ { m m})$
0.0	_	100	122	39	1.9
$0.0^{\rm c}$	А	103	123	39	1.5
0.10	В	103	121	36	1.5
0.21	В	102	121	37	1.7
0.34	А	100	121	37	3.0
0.35	А	104	121	36	3.0
0.36	А	100	119	37	2.4
0.37	В	103	120	36	1.7
0.40	А	105	120	38	3.0
0.42	А	105	120	36	2.7
0.50	Α	103	118	35	3.6

Table VII Thermal Properties of the LLDPE2 and Their Grafted Products

<sup>a</sup> mol DES/100 mol LLDPE.

 $^{\rm b}$  Fusion enthalpy of the PE (100% crystallinity) 293 J/g.  $^{26}$ 

<sup>c</sup> Extruded once.

<sup>d</sup> Peak width at halft-height.

segments are present. On the other hand, a broader lamellar thickness distribution is produced. In fact, as can be seen in Table VII, there is an increase of the half-height width  $(w_{1/2})$  of the exotherm signal of the functionalized polymers as their grafting degree is higher. Similar results were obtained by Lachtermacher and Rudin<sup>8</sup> for their peroxide-modified LLDPE. They observed that the intensity of the peak, pertaining to the linear polymer fraction, decreased with increasing peroxide concentration, while the peak at the lower temperature, belonging to the branched materials, became broader. They attributed these results to an increase of chain irregularities by the formation of branches during reactive extrusion.

As was mentioned before,<sup>13</sup> higher functionalization degrees were obtained, increasing both the DEM and initiator concentrations. Additionally, secondary reactions such as chain scission and/or chain-extension reactions could also promote interruptions of linear crystallizable segments and, consequently, a lower melting peak temperature. However, these effects cannot be separated from those of the grafting reactions by means of DSC heating and cooling scans. Similar results were found for the LLDPE3 and the HDPE1 (Table VIII).

## **CONCLUSIONS**

Rheological properties are more sensitive to the changes produced by grafting reactions with

Material	Grafting Degree <sup>a</sup>	$\begin{array}{c} T_c \; \mathrm{Peak} \\ (\pm 1^{\mathrm{o}}\mathrm{C}) \end{array}$	$\begin{array}{c} T_m \text{ Peak} \\ (\pm 1^\circ \text{C}) \end{array}$	% C <sup>b</sup>
LLDPE3	0.00	100	121	43
LLDPE3 <sup>c</sup>	0.00	103	122	43
LLDPE3-g-DEM (1)	0.62	101	122	37
LLDPE3-g-DEM (2)	0.55	101	122	38
LLDPE3-g-DEM (3)	0.47	101	122	39
HDPE1°	0.00	120	131	61
HDPE1-g-DEM	0.29	124	130	61

Table VIIIThermal Properties of LLDPE3, HDPE1, and Their GraftedProducts

<sup>a</sup> mol DES/100 mol LLDPE.

 $^{\rm b}$  Fusion enthalpy of the PE (100% crystallinity) 293 J/g.  $^{26}$ 

<sup>c</sup> Extruded once.

DEM than are the molecular structure characteristics, under the employed experimental conditions. There is an increase in the dynamic viscosity at low frequencies, in the storage modulus, and in the shear-thinning behavior when the grafting degree increases. The crossover between G'' and G' moves to lower frequencies and the relaxation time spectrum functions are broader in the grafted materials. All these properties indicate a higher degree of LCB and higher melt elasticity without the presence of gel in the products. When LLDPEs are functionalized with DEM, new materials with rheological characteristics very similar to those of LDPEs are obtained, with enhanced bubble stability in a tubular filmextrusion process and without significant changes in the thermal properties. Additionally, improved compatibility in the blends with polar high oxygen permeability polymers, such as polyamides and polyesters, would be expected, making those blends suitable for coextrusion as ionomer substitutes.

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