Melt Grafting of *N*-Carbamyl Maleamic Acid onto Linear Low-Density Polyethylene

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ABSTRACT: The grafting of *N*-carbamyl maleamic acid (NCMA) onto linear low-density polyethylene (LLDPE) was carried out with different concentrations of 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane (DBPH) as an initiator. The modification process was performed in the molten state with a Brabender mixer. All the materials were characterized with Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry, and melt rheology. The analysis of the FTIR spectra indicated that the grafting efficiency increased with the concentration of both NCMA and DBPH. The calorimetric experiments showed that the modification process did not noticeably alter the enthalpy of fusion of LLDPE, whereas the melting temperature of the modified polymers was slightly lower than that corresponding to the original LLDPE. The rheological response of the molten polymers, determined under dynamic shear flow at small-amplitude oscillations, indicated that the modification process induced crosslinking of the chains. Both the dynamic viscosity and elastic modulus of the modified LLDPE increased with the concentration of NCMA and DBPH, showing that larger molecules were generated during the modification process. © 2002 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 40: 3950–3958, 2002

Keywords: linear low-density polyethylene; polyolefins; modification; functionalization of polymers; reactive processing; *N*-carbamyl maleamic acid; organic peroxides; rheological properties

INTRODUCTION
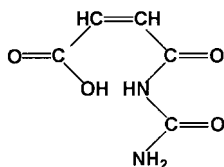
The chemical modification of polyolefins has become a commercially viable approach to produce new materials with improved properties.[1–5] One of the most common methods of modification is the use of controlled free-radical reactions, such as the thermal decomposition of the RO—OR′ bond of different organic peroxides. This induces the formation of RO• free radicals, which attack the molecules of the polymer, subtracting hydrogen atoms and producing reactive macroradicals.

Then, the macroradicals can follow different chemical reactions such as combination (which results in chemical crosslinking), bond scission (obtaining molecules shorter than the original ones), and grafting (if an additive or monomer is present in the medium). All these reactions change the molecular structure of the original polymer, altering its physical and chemical properties.

Polyethylene (PE) is one of the most important commercial polyolefins used today. It has poor compatibility and adherence with other materials because of its nonpolar character, which limits its use. To improve these properties, it has been chemically modified with a vast variety of polar monomers. Some of the most commonly used modifiers are

Scheme 1.   Chemical structure of NCMA.

acrylic acid and esters; maleic anhydride and its analogues, such as fumaric acid and itaconic acid; and dimethylaminoethyl methacrylate and diethyl maleate.[1–11]

In this work, the grafting of *N*-carbamyl maleamic acid (NCMA) onto linear low-density polyethylene (LLDPE) was carried out with 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane (DBPH) as an initiator. To our knowledge, this type of monomer has not been used to modify polyolefins. The chemical structure of NCMA is presented in Scheme 1.

The modification was performed in the molten state. The molecular structure of the modified polymers was characterized with infrared spectroscopy and titration techniques. The thermal behavior was analyzed with differential scanning calorimetry (DSC). The dynamic rheological properties of the molten polymers were measured over an ample range of frequencies at 160 °C.

EXPERIMENTAL

Materials

LLDPE, in a powder form and without additives, was provided by Polisur-Dow S.A. (Argentina). The polymer had a weight-average molecular weight of 70,000 and a polydispersity (weight-average molecular weight/number-average molecular weight) of 2.1, as determined by gel permeation chromatography according to standard procedures.

The organic peroxide used as an initiator was DBPH, which was provided by Akzo Nobel Química (Argentina). The peroxide had a half-life of 1 min at 180 °C according to the information supplied by the manufacturer. It was used diluted in hexane.

NCMA (molecular weight = 158.12) was synthesized in our laboratories with maleic anhydride and urea supplied by Anedra. The synthesis was carried out according to the experimental procedures reported in the literature.[12] The

NCMA is a white but slightly yellow solid and melts at 155–156 °C. It is barely soluble in water but dissolves in hot ethanol and dimethylformamide (DMF).

Melt Grafting Procedure

The PE/NCMA/DBPH reactive mixtures were prepared on the basis of 100 g of PE. The studied concentrations of NCMA were 0.8, 1.6, and 3.2% (w/w), and for each of these concentrations, 0.05, 0.1, and 0.2% (w/w) peroxide was used. The NCMA, PE, and an aliquot of the peroxide solution were put into contact by being poured into a beaker in such proportions so as to give the desired concentrations of the components after solvent (ethanol and hexane) evaporation.

The grafting reactions were carried out in the mixing head of a Brabender Plastograph mixer with a 50-cm^3 capacity. The temperature of the mixer chamber was set to 180 °C, and the screw speed rotation was 20 rpm. The evolution of the torque with time was followed for each reactive mixture. It was assumed that the modification reaction was completed when the torque of the mixing head reached a constant value. The total time of the reaction, counted from the moment that the material was poured into the chamber, was approximately 20 min.

Characterization of the Materials

The nonreacted DBPH and NCMA and their by-products were separated from the modified polymer by the dissolution of the material obtained from the mixer in xylene at 130 °C. Then, the hot solution was precipitated into cold methanol, and this yielded the polymer as a very fine powder after filtration. The grafted polymers were washed repeatedly with DMF and ethanol. All the washed materials were dried *in vacuo* for 48 h before their analysis. From now on, the materials that were obtained directly from the mixer will be called *crude material*, whereas those obtained after washing will be named *PE-g-NCMA*.

The evidence of grafting, as well as its extent, was determined by an analysis of the Fourier transform infrared (FTIR) spectra of the PE and PE-*g*-NCMA specimens with a Nicolet FTIR 520 spectrometer. Films about 0.10 ± 0.01 mm thick were prepared by the melt pressing of the materials at 150 °C between the plates of a hydraulic press. The extension of grafting was estimated from a comparison of the absorbency of the band

centered at about 1718 cm^{-1} normalized by the film thickness of the PE-*g*-NCMA and crude material. This band is typically assigned to carbonyl group vibrations ($\nu >$C$=$O) from carboxylic acid derivatives.[13]

The FTIR spectra of films obtained from simple physical mixtures of LLDPE and NCMA were also studied to assist with the interpretation of the results. These films were prepared by the press molding of a homogeneous mixture of LL-DPE powder and NCMA at 130 °C.

To further explore the nature of the grafting reaction, we studied the presence of carboxyl groups (—COOH) in the grafted polymers with conventional titration methods reported in the literature.[14,15] For this purpose, about 0.3–0.5 g of PE-*g*-NCMA were dissolved in 80 mL of water-saturated xylene at 100 °C. The system was refluxed for 1 h and then was hot-titrated with 0.02 N ethanolic KOH, with a 1% methanolic solution of phenolphthalein as an indicator.

The thermal behavior of LLDPE and PE-*g*-NCMA was determined by DSC with a PerkinElmer Pyris 1 calorimeter calibrated with an Indium standard. To ensure the same thermal history for all samples, we melted each sample in the calorimeter at 150 °C and then cooled it down to 30 °C at the fastest cooling rate allowed by the calorimeter. After this treatment, the melting en-

Table 1. Final Melt Torque Measured for the LLDPE/NCMA/DBPH Reactive Mixtures

DBPH (%, w/w)	NCMA (%, w/w)	Final Torque (Nm)
0.0	0.0	4.3
0.05	0.0	4.9
	0.8	6.9
	1.6	7.1
	3.2	7.3
0.1	0.0	6.6
	0.8	8.0
	1.6	7.6
	3.2	8.2
0.2	0.0	8.7
	0.8	10.5
	1.6	10.7
	3.2	11.4

dotherm was recorded between 30 and 150 °C at a heating rate of 10 °C/min. The melting peak and the area of the thermogram were determined to give both the temperature (T_f) and enthalpy (ΔH_f) of fusion. The values reported for those properties are an average from three to four samples of each material.

The dynamic properties of the molten specimens were studied on a rotational rheometer from Rheometrics RDA-II in the parallel-plate mode. For this purpose, the LLDPE and PE-*g*-NCMA polymers were molded into discs 25 ± 0.01 mm in diameter and about 1 mm thick with a hydraulic press set at 150 °C. The rheological characterization was performed in small-amplitude oscillatory shear flow. The dynamic elastic moduli, $G'(\omega)$, and viscosity, $\eta'(\omega)$, were determined in the linear viscoelastic range of strain at 160 °C and at frequencies (ω) ranging from 0.1 to 500 s^{-1}.

RESULTS AND DISCUSSION

Melt Reaction Behavior

The chemical modification of LLDPE with different concentrations of NCMA and DBPH was carried out in the molten state as described in the Experimental section. Figure 1 shows the evolution of the torque in the Brabender mixer with the reaction time for LLDPE modified with 0.2% peroxide and reacting mixtures containing PE, 0.2% DBPH, and different concentrations of NCMA.
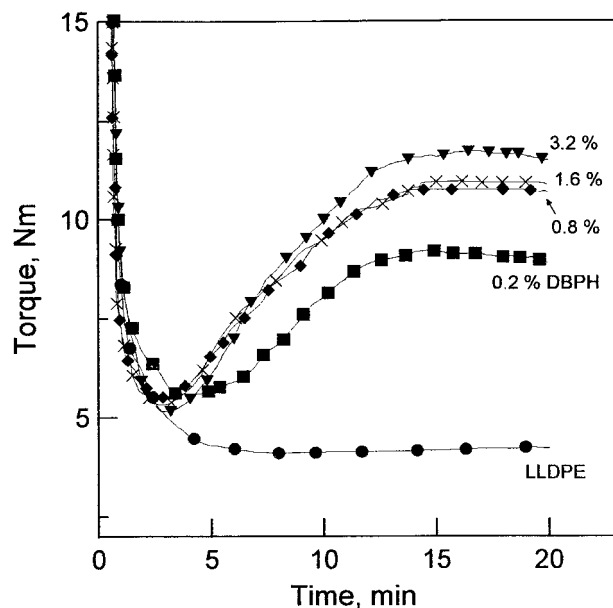

Figure 1. Evolution of the torque with time for the following materials: (●) PE, (■) PE/0.2DBPH, (♦) PE/0.2DBPH/0.8NCMA, (×) PE/0.2DBPH/1.6NCMA, and (▼) PE/0.2DBPH/3.2NCMA.

The evolution of the torque for pure LLDPE is also shown for comparison. The values of the torque measured at the end of the process are summarized in Table 1.

We observe that the curve describing the flow behavior of LLDPE has a characteristic initial decrease of the torque up to a constant value, which is due to the melting process. The chemical modification of LLDPE with DBPH produces an increase in the value of the final torque of the melt with respect to the original ones. Moreover, the value of the torque for every LLDPE sample treated with DBPH increases with the concentration of peroxide, as shown in the data presented in Table 1. This can be associated with the changes in the molecular structure of the polymer induced by the peroxide attack. Under the experimental conditions followed here, the crosslinking of the LLDPE molecules is expected to be the main reaction that takes place in the mixer chamber.[16,17] For the reactive mixtures containing NCMA, the value of the torque at the end of the process is even higher than the corresponding values of the LLDPE/DBPH reactive mixture. The results presented in Table 1 seem to indicate that, with equivalent DBPH contents, the torque increases slightly with the concentration of NCMA. This is an indication that the presence of NCMA enhances the linkage between the molecules of the polymer, producing an additional rise in the viscosity of the medium in comparison with that of the LLDPE modified solely with peroxide. The additional crosslinking of ethylene polymers to that produced by the peroxide attack has also been observed during the melt grafting of the polymer with other different polar monomers such as maleic anhydride[18] and acrylic acid and its ester derivatives.[19]

A particular characteristic of the crude materials is their color, which has a red tint and whose intensity increases with the concentration of NCMA for each DBPH concentration. PE-*g*-NCMA is also colored, but the intensity of the color is much lighter than that presented by the crude material. This characteristic of the modified materials could be explained if the extremely reactive groups present in NCMA suffer some kind of chemical transformation during the melt reaction process. There are several studies reporting the formations of red materials in systems based on copolymers of maleimides and/or *N*-alkylmaleimides.[20,21] We take advantage of the arguments presented in those studies, which were stated to explain the generation of color in such systems,
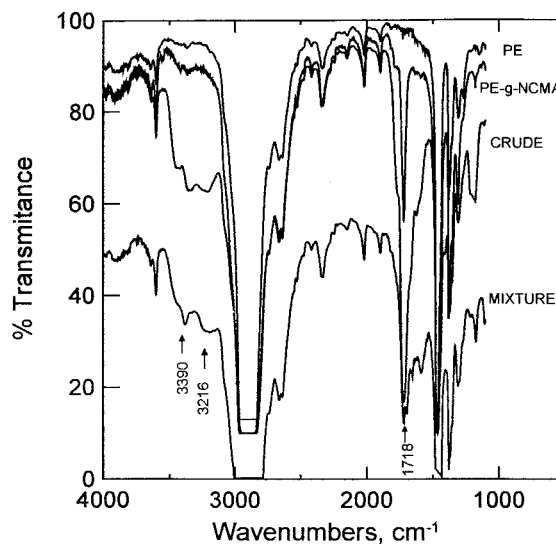

Figure 2. FTIR spectra in the $4000-1000$-cm^{-1} wave-number range. The legend beside each curve identifies the material. The spectra were shifted along the transmittance axis to distinguish their differences.

and of our FTIR and titration results to suggest a plausible chemical reaction that can occur in the grafting process, as we discuss later.

FTIR Characterization

FTIR spectroscopy was used to verify the grafting of NCMA onto the LLDPE molecules. Figure 2 displays the FTIR spectra of LLDPE and the crude material and PE-*g*-NCMA obtained with 3.2% NCMA and 0.2% peroxide. These spectra have been chosen as examples to illustrate the changes in the molecular structure of LLDPE that occur after its modification. As a reference, the spectrum corresponding to a physical mixture of LLDPE and 3% NCMA is also included.

The spectrum of LLDPE modified with 0.2% peroxide, which is not shown in Figure 2, displays the typical bands of PE. The modified LLDPE shows no evidence of the incorporation of new chemical groups. Carbonyl and hydroxyl structures that display characteristic absorption bands in the range of 1700–1750 and at 3000 cm^{-1}, respectively,[13] do not seem to be present in detectable concentrations.

The spectrum of the physical mixture displays absorption bands associated with the chemical groups present in NCMA as well as those characteristics of PE. The broad band between 3400 and 3300 cm^{-1}, which is not present in the spectra
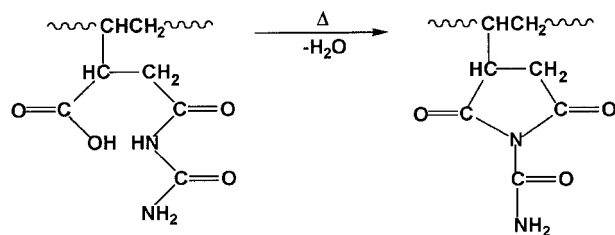
Scheme 2. Intramolecular condensation reaction.

corresponding to LLDPE, can be associated with the vibration of the amine group (ν —NH_2).[13] Another band centered at about 3200 cm^{-1} can be attributed to the vibration of the hydroxyl of the acid group.[13] In addition, there are other bands between 1750 and 1600 cm^{-1} that can be related to the absorption of carbonyl groups from urea derivatives and carboxyl acids.[13] The crude material also shows absorption bands that can be associated with NCMA. However, when the material was washed to obtain the PE-*g*-NCMA polymer, some of them were no longer distinguished in the spectrum.

In the spectra of the PE-*g*-NCMA samples, a band corresponding to the amine groups can be slightly distinguished in the region between 3400 and 3300 cm^{-1}. Also, a strong absorption band, which can be associated with carbonyl groups, is clearly centered at 1718 cm^{-1}. These bands are not present in the peroxide-modified PE spectra. As anticipated before as a result of the coloring observed after grafting, these observations indicate that NCMA suffers some kind of chemical transformation in the grafting reaction. The comparison of the spectrum of the physical mixture with the corresponding spectrum of PE-*g*-NCMA supports this observation. Only the amine band and the band centered at 1718 cm^{-1}, within the carbonyl region, appear in the spectra of the grafted material; the hydroxyl band is no longer noticeable. The titration experiments performed gave no evidence of the presence of carboxyl acid groups in the grafted material. Therefore, the carbonyl and amine groups observed in the FTIR spectra should come from chemical groups that originated in the transformation of NCMA during the grafting reaction.

A plausible explanation of the chemical transformation suffered by NCMA is that the high temperature used to carry out the grafting reaction may induce intermolecular or intramolecular condensation reactions between the amine (—NH_2) and carboxyl (—COOH) groups of that

molecule. The literature contains references to the intramolecular condensation of maleamic acid to form amides; this reaction is promoted at temperatures above 170–180 °C.[22] Therefore, the grafted NCMA could generate a new imide–amide compound by intramolecular condensation, as presented in Scheme 2.

The *N*-carbamyl succinimide so generated is a urea derivative whose FTIR spectra should display absorption bands in the carbonyl region similar to those presented by NCMA. To verify this hypothesis, we hydrolyzed about 0.5–1 g of PE-*g*-NCMA for 2 h with a 0.05 N hydroalcoholic NaOH solution. After this treatment, it was expected that the amide groups (—$CONH_2$) would turn into carboxylate groups (—COO^-).[23] This last chemical unit displays an absorption band in the region between 1650 and 1550 cm^{-1} in the FTIR spectrum. Figure 3 shows the FTIR spectra corresponding to the grafted material and hydrolyzed PE-*g*-NCMA in the wave-number region ranging from 2000 to 1200 cm^{-1}. There is practically no difference between the two spectra within this region, except for the band at 1550–1680 cm^{-1}, which appears only in the spectra of the hydrolyzed polymer. This band has a maximum absorption at 1620 cm^{-1} that can be associated with a carboxylate group.[13]
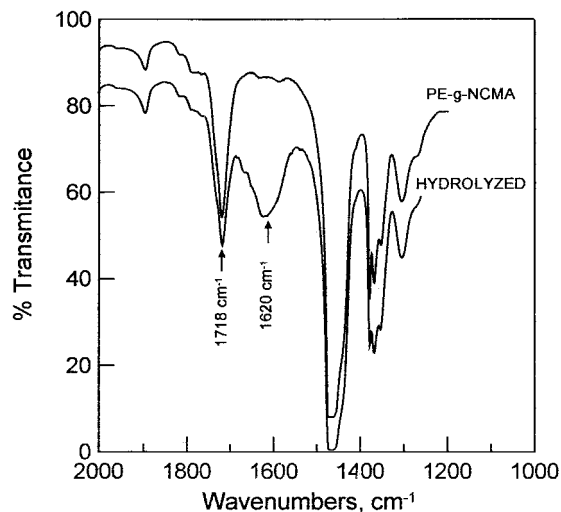

Figure 3. FTIR spectra in the 2000–1200-cm^{-1} wave-number range of PE-*g*-NCMA obtained with 3.2% NCMA and 0.2% DBPH and the corresponding hydrolyzed material. The marked bands correspond to carbonyl (>C—O) and carboxylate (—COO^-) groups. The legend beside each curve identifies the material. The spectra were shifted along the transmittance axis to distinguish their differences.
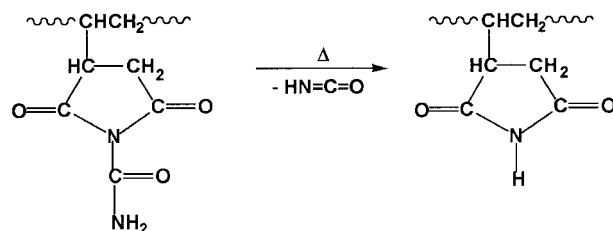
Scheme 3. Thermal decomposition of *N*-carbamyl succinimide.

The experimental conditions adopted for the modification of PE in the mixing chamber may also promote other chemical reactions such as the thermal decomposition of *N*-carbamyl succinimide. This reaction could generate succinimide, as displayed in Scheme 3.[24] This derivative would also show typical absorption bands in the carbonyl zone of NCMA.

In addition to intramolecular condensation reactions, several intermolecular reactions are possible. The intermolecular condensation between grafted NCMA groups may form different kinds of urea derivatives, whose chemical structures would be similar to allophanates or biurets. These particular urea derivatives have typical carbonyl vibration absorption bands in the 1720–1690-cm^{-1} zone.[13]

Because of their particular chemical structure, these types of compounds have a large amount of conjugated double bonds, unshared pairs of electrons from nitrogen atoms and carbonyl groups, whose presence can favor color development, probably because of resonance structures. The occurrence of an intermolecular reaction may explain not only the color formation in the PE/NCMA/DBPH mixtures but also the difference of behavior observed in the evolution of the torque of the mixing chamber between these materials and the LLDPE modified only with peroxide, as mentioned earlier.

We have tried to quantify the amount of NCMA that is effectively incorporated into LLDPE using the FTIR results albeit the chemical changes already having been described. Table 2 shows the absorbance of the 1718-cm^{-1} band normalized by the thickness of the film for all the crude material and PE-*g*-NCMA. The table also includes an index, I_g, that can only be considered an indication of the grafting efficiency of NCMA onto LLDPE. The index is expressed as a percentage, and it was obtained from the relationship between the normalized intensity of the 1718-cm^{-1} absorption band of the PE-*g*-NCMA polymer and that corresponding to the crude material. We do not make the distinction here whether NCMA is incorporated as single units or as oligomeric sequences.

The data presented in Table 2 suggest that the amount of NCMA incorporated to the polyethylene augments with the concentration of NCMA for a given peroxide concentration. However, I_g takes lower values as the concentration of NCMA increases. This means that the process becomes less efficient when higher amounts of NCMA are added to the mixing chamber.

The amount of peroxide seems to increase the efficiency of the process when the lowest concentration (0.8%) of NCMA is used. However, the efficiency does not show a well-defined trend when higher concentrations of NCMA are employed. According to these results, the grafting process is more dependent on the concentration of NCMA and DBPH in the initial reaction mixture when low concentrations of both reagents are employed.

Table 2. Normalized Absorbance and Relative Grafting Efficiency (I_g)

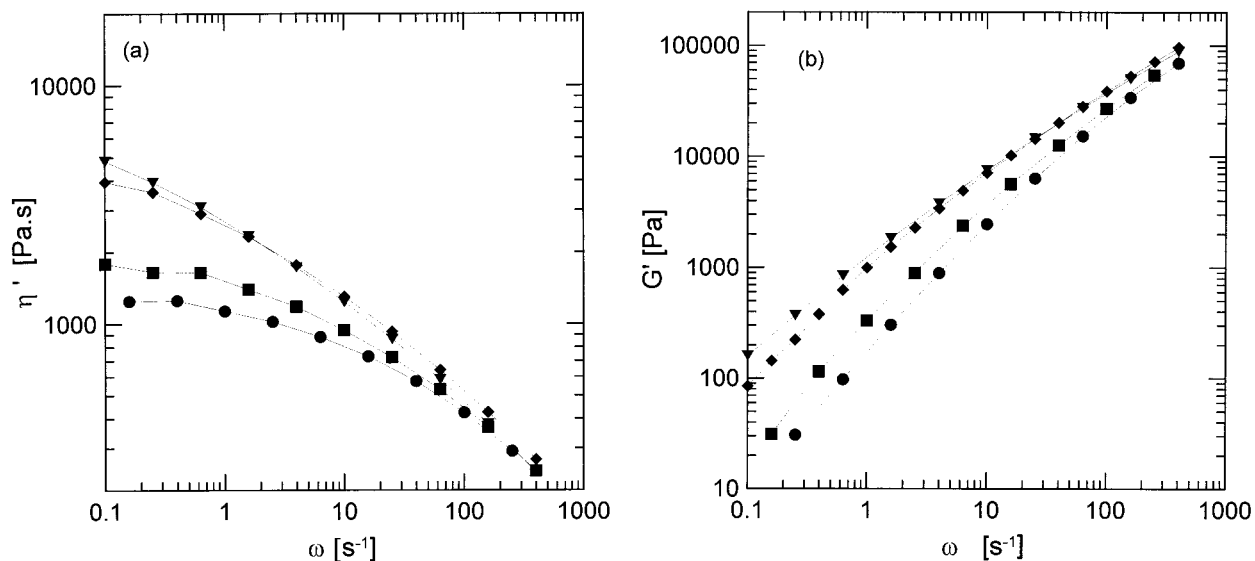| DBPH (%, w/w)	NCMA (%, w/w)	A_{1718} (mm)		l_g
		Crude	LLDPE-*g*-NCMA	
0.05	0.8	3.0 ± 0.1	1.0 ± 0.1	~33
	1.6	4.5 ± 0.6	1.4 ± 0.2	~31
	3.2	9.4 ± 0.7	2.0 ± 0.1	~21
0.1	0.8	2.9 ± 0.1	1.7 ± 0.1	~58
	1.6	4.8 ± 0.1	1.9 ± 0.1	~39
	3.2	8.4 ± 0.2	1.8 ± 0.3	~21
0.2	0.8	2.1 ± 0.1	1.3 ± 0.1	~62
	1.6	3.6 ± 0.7	1.4 ± 0.2	~39
	3.2	7.7 ± 0.4	2.1 ± 0.1	~27

Figure 4. Frequency dependence of (a) the dynamic viscosity and (b) the elastic modulus at 160 °C for the following materials: (●) PE, (■) PE/0.05DBPH, (♦) PE/0.05DBPH/0.8NCMA, and (▼) PE/0.05DBPH/3.2NACM.

The effect of the monomer and peroxide initiator concentrations on the grafting process qualitatively agrees with that observed in other systems. For example, when the concentration of both the peroxide initiator and monomer increases, the amount of the grafted polar monomer increases, whereas the grafting efficiency slightly decreases during the modification of PE with

acrylic acid (and its ester derivatives)[19] and 2-(dimethylamino)ethyl methacrylate.[10]

Rheological Characterization

Rheological analyses were performed to determine differences in the flow behavior of the reacted mixtures with respect to the original LLDPE. Figures 4 and 5 compare the melt behavior
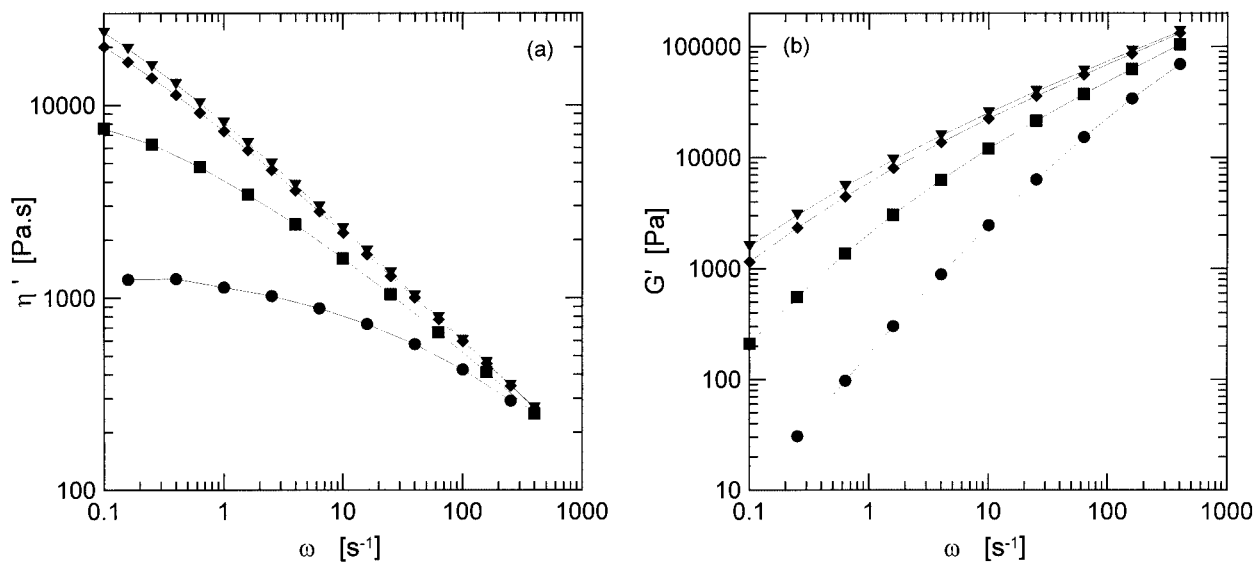

Figure 5. Frequency dependence of (a) the dynamic viscosity and (b) the elastic modulus at 160 °C for the following materials: (●) PE, (■) PE/0.2DBPH, (♦) PE/0.2DBPH/0.8NCMA, and (▼) PE/0.2DBPH/3.2NACM.

Table 3. T_f and ΔH_f Values of Selected Samples of LLDPE-*g*-NCMA

DBPH (%, w/w)	NCMA (%, w/w)	T_f (°C)	ΔH_f (J/g)
0.0	0.0	127 ± 0.8	137 ± 0.6
0.05	0.8	126 ± 0.4	136 ± 1.6
	3.2	125 ± 0.2	135 ± 0.8
0.2	0.8	124 ± 0.1	136 ± 0.3
	3.2	124 ± 0.2	135 ± 0.4

at 160 °C of the original LLDPE, the LLDPE modified with DBPH, and the PE-*g*-NCMA materials obtained with two concentrations of NCMA, 0.8 and 3.2%. The material functions studied were $\eta'(\omega)$, and $G'(\omega)$. The LLDPE modified exclusively with peroxide shows a progressive increase in both dynamic functions as the amount of peroxide increases, in agreement with the results of the evolution of torque and also with the observations of other authors.[17,19,25–27] These effects are the result of the increasing amount of larger and more complex macromolecules formed by the chain-linking reactions. The PE-*g*-NCMA materials exhibit larger values of both the viscosity and elastic moduli than those corresponding to the PE modified only with the same amount of peroxide. Moreover, the values of those dynamic properties at a low frequency seem to increase slightly with the concentration of NCMA at a given concentration of peroxide. These results suggest that NCMA promotes additional chain-linking reactions and that there is a combined effect between DBPH and NCMA favoring crosslinking reactions and molecular weight enhancement.

Thermal Characterization

The thermal properties of LLDPE and selected samples of PE-*g*-NCMA were studied by DSC. Table 3 summarizes the T_f and ΔH_f values for some of the materials. ΔH_f of LLDPE seems not to be noticeably affected by the modification process. However, the melting temperatures display a slight decreasing trend with the amount of NCMA at a given peroxide concentration. The melting point drops almost 3 °C when LLDPE is modified with the highest amount of peroxide and NCMA. The molecular weight increase due to crosslinking reactions and the generation of new branching points on the molecular chains of LLDPE may explain these observations.[28]

CONCLUSIONS

The melt grafting of NCMA onto LLDPE was successfully carried out in the melt with DBPH as an initiator. This modification of the original PE resin introduces both carbonyl and imide groups that provide additional functional groups than the most common functionalization with maleic anhydride. The compatibility of these modified polymers with other materials is under study. The FTIR spectroscopy characterization of the grafted materials reveals the presence of carbonyl groups in the polymer chains, but these carbonyl groups are not the same as those in the original NCMA. This is attributed to intermolecular or intramolecular condensation reactions occurring in addition to the grafting process between amine (—NH$_2$) and carboxyl (—COOH) groups of NCMA.

The efficiency of grafting decreases as the concentration of NCMA increases for all the peroxide concentrations used. In all cases studied, the final torque of the materials modified with NCMA is higher than that corresponding to the LLDPE/DBPH mixture. In addition, the final torque increases with the NCMA concentrations, indicating variations in the flow properties of the materials. The values of the viscosity and elastic moduli of the LLDPE-*g*-NCMA material are larger than those of the LLDPE modified only with peroxide, and this indicates that NCMA promotes the generation of larger macromolecules through intermolecular reactions.

PE-*g*-NCMA displays a thermal behavior that is very similar to that of the original LLDPE, as revealed by DSC analysis. The melting temperatures of selected samples are slightly lower than those of the original LLDPE. These results are clear evidence that grafting occurs without major changes in the thermal behavior of the original resin.

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