

# Composites of High Density Polyethylene and Different Grades of Calcium Carbonate: Mechanical, Rheological, Thermal, and Morphological Properties

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**ABSTRACT:** Calcium carbonate (CaCO<sub>3</sub>)/high density polyethylene (HDPE) composites were prepared in a HAAKE twin screw extruder, using the experimental conditions defined by the factorial experimental design presented in a prior study. In this study, the effect of different grades (Ca<sub>1</sub> and Ca<sub>2</sub>) and CaCO<sub>3</sub> content (varying from 0 to 15 wt %) on the mechanical, rheological, thermal, and morphological properties was evaluated. The results showed that the addition of the filler provoked a decrease on the impact strength, stress at break, and yield stress properties in relation to the pure HDPE. A consequent increase on the modulus of elasticity, indicating an increase on the rigidity

of the composite, was observed. It was also verified a tendency to increase the toughness and the viscosity of the composites as CaCO<sub>3</sub> was added. Scanning electron micrographs showed that as the filler was incorporated to HDPE matrix, CaCO<sub>3</sub> particles tended to agglomerate, especially that grade constituted of particles of smaller size. The thermal analysis showed that the addition of mineral filler caused a decrease on the crystallinity degree. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2559–2564, 2006

**Key words:** HDPE; calcium carbonate; composites; properties

## INTRODUCTION

Calcium carbonate (CaCO<sub>3</sub>) is one of the most abundant minerals found in the Earth's crust. It is available globally in a variety of particle sizes and purities and may be used with or without organic coatings. For this reason, CaCO<sub>3</sub> is the largest volume mineral used in many polymer systems.<sup>1</sup>

Over the last few years, the development of new materials has been oriented toward composites, because they are very attractive systems, with great significance for research and industrial application. Composites based on polyolefins and mineral fillers have been extensively studied, specifically those ones based on polyethylene and inorganic fillers are of great research interest.<sup>2–8</sup>

The main purpose of incorporating fillers, such as CaCO<sub>3</sub>, into polyolefins is to decrease costs and change properties. It is known that fillers often increase the performance of polymeric products and the degree of the improvement of the properties will de-

pend on the judicious choice of filler origin, particle size and shape, the proportion of filler, and the surface treatment to promote the interaction between the polymer matrix and filler. The particle dispersion is also an important factor that determines yield and tensile strength.<sup>6,9–11</sup>

In this article, we report the mechanical, rheological, thermal, and morphological properties of high density polyethylene (HDPE) composites, using nonmodified calcium carbonates. The aim of this work was to study the influence of the addition of different grades and contents of CaCO<sub>3</sub> on the HDPE properties.

## EXPERIMENTAL

### Materials and composite preparation

The material specifications are listed in Tables I and II. The virgin polymer and HDPE/CaCO<sub>3</sub> composites were processed in a HAAKE twin screw extruder. The temperature profile was 190/200/220/220°C and the rotor rate was set at 40 rpm. The compositions analyzed were 0, 5, 10, and 15 wt % of the mineral fillers, which were supplied by Imerys. Irganox was also added in the proportion of 0.10 w/w to stabilize the composites during their processing.

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**TABLE I**  
Specifications of HDPE

HDPE	
Manufacturer	Ipiranga Petroquímica (Brazil)
Designation	HD 7255
Melt index (g/10 min) ASTM D 1238	4.5
Shore hardness ASTM D 2240	63
Vicat softening point at 9.8N ASTM D 1525	127

### Mechanical analysis

The tensile tests were carried out at room temperature in an Instron Tester (model 4202), according to ASTM D 882, using samples obtained by injection molding at 200°C in the barrel and 50°C in the mold. The tensile characteristics were measured at 500 mm/min cross-head speed.

To evaluate the impact strength of the composites, impact tests were conducted according to ASTM D 256 (V-notched), using a TMI Izod Impact, Model 43-0A-01.

The average values of seven repeated tests were taken for each composition.

### Rheological analysis

Complex viscosity ( $\eta^*$ ), storage shear modulus ( $G'$ ), and loss modulus ( $G''$ ) at 200°C were measured using a plate-plate type rheometer (TA Instruments oscillatory rheometer, Model AR 2000) in the angular frequency range of 0.01–628 rad/s, under nitrogen atmosphere.

### Calorimetric analysis

To investigate the thermal properties of HDPE and its composites, a calorimetric analysis was carried out. A Perkin-Elmer DSC-7 differential scanning calorimeter was used to analyze samples cut from the extrudate. All measurements were performed under nitrogen

flow. The mass of the samples used varied between 4 and 7 mg. The samples were first heated at a rate of 10°C/min from 30°C to above 200°C and kept at that temperature for about 5 min. The samples were then cooled to room temperature at 10°C/min. A second heating run was performed at the same rate through the full melting range. Indium was employed as a standard for temperature and enthalpy calibration of DSC.

The melting temperature ( $T_m$ ) and the crystallization temperature ( $T_c$ ) of polymer were taken at the maximum of the melting peak and at the minimum of the crystallization peak, respectively. The onset crystallization temperature ( $T_o$ ) was determined at the beginning of the crystallization (at the intersection of the peak slope with the baseline). The heats of melting ( $\Delta H_m$ ) and crystallization ( $\Delta H_c$ ) were determined from the corresponding peak areas in the heating and cooling DSC curves.

The percent crystallinity of HDPE in the composites were calculated as follows:

$$\chi_c(\text{HDPE}) = \frac{\Delta H(\text{composite})}{\Delta H^0} \quad (1)$$

where  $\Delta H(\text{composite})$  is the apparent enthalpy of fusion per gram of composite, and  $\Delta H^0(\text{HDPE})$  is the heat of fusion of 100% crystalline HDPE, taken as 293 J/g.<sup>3</sup>

### Morphological analysis

The morphology of the composites was examined in a Jeol scanning electron microscope (SEM), Model JSM-6460 LV. The samples were cryogenically fractured in liquid nitrogen and then coated with an Au/Pd alloy. The dispersion of the filler on the HDPE matrix was observed at accelerating voltage of 20 kV.

## RESULTS AND DISCUSSION

### Mechanical properties

Figures 1(a–e) show the mechanical properties of the pure HDPE and HDPE/CaCO<sub>3</sub> composites. It has

**TABLE II**  
Physical Characteristics of the Mineral Fillers

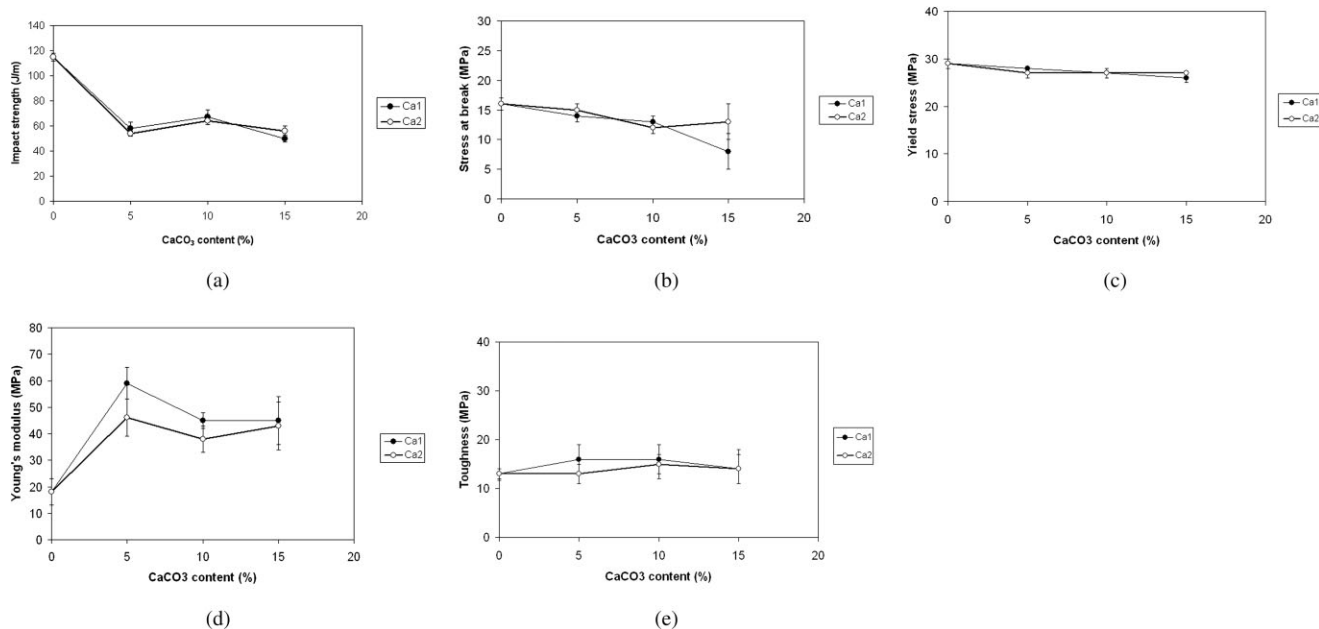
Material	Particle diameter <sup>a</sup> (D-50; $\mu\text{m}$ )	Apparent density <sup>b</sup> (g/cm <sup>3</sup> )	DOP absorption <sup>c</sup> (%)	Brightness <sup>d</sup> (%)	Particle size % below 1 $\mu\text{m}$
Ca <sub>1</sub>	4.0	1.03	38.3	95.7	10
Ca <sub>2</sub>	2.5	1.00	33.3	79.2	18–20

<sup>a</sup> Measured in Imerys laboratory, using SEDIGRAPH, model 5100.

<sup>b</sup> Measured in Imerys laboratory by ISO/R787/11-1970.

<sup>c</sup> Measured in Imerys laboratory based on ASTM D 281-31.

<sup>d</sup> Measured in Imerys laboratory, using a Brightness Tester, model S4BL, based on TAPPI.



**Figure 1** Mechanical behavior of HDPE and HDPE/CaCO<sub>3</sub> composites versus CaCO<sub>3</sub> content (a) impact strength, (b) stress at break, (c) yield stress, (d) Young’s modulus, and (e) toughness.

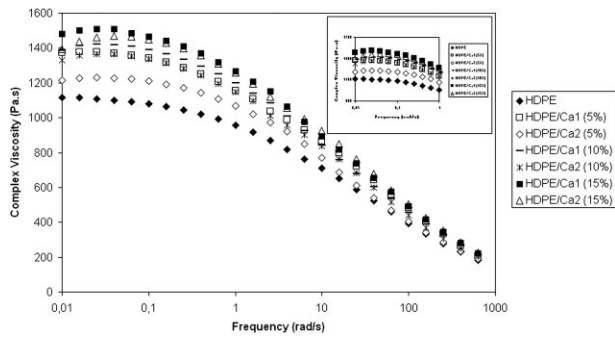
been reported<sup>12</sup> that the mechanical properties of composites depend on the characteristics and interaction between the composition components.

The figures show that the addition of CaCO<sub>3</sub> provoked a decrease on the impact strength of the composites. In the range of 5–15 wt % of filler, it was not observed a significant variation of that property. It was also verified an increase in Young’s modulus for the composites when compared with pure HDPE, indicating an increase in the rigidity of the materials; in other words, the fillers used presented a reinforcing effect on the HDPE matrix. The addition of Ca<sub>2</sub> filler produced materials with lower values of elasticity modulus. Probably, this behavior is related to a poorer particle distribution caused by Ca<sub>2</sub> filler because of its tendency to produce agglomeration. The higher tendency to form clusters observed in Ca<sub>2</sub> composites is due to the higher percent of fines (below 1 μm) of Ca<sub>2</sub> filler. Those fines tend to produce agglomerates.

The stress at break tended to decrease and this behavior was more evidenced with the filler with the higher particle size. The yield stress of the composites shows similar values within the range of experimental error. The addition of both fillers in the HDPE matrix did not provoke a significant variation in toughness in relation to the pure HDPE. It is known that to improve toughness, it is necessary to obtain a low particle matrix adhesion (to favor debonding) but at the same time, it is also necessary to prevent particle agglomeration and void coalescence.<sup>12</sup> It was also reported that the dispersion quality of CaCO<sub>3</sub> particles plays a crucial role in toughening efficiency and that stearic acid coated particles present a large positive effect on that property.<sup>13</sup> Probably, the behavior observed in this work is due to the presence of agglomerates, which tend to form when mineral filler is incorporated into HDPE matrix, avoiding an increase in the composite toughness. Both fillers analyzed in this work were uncoated.

**TABLE III**  
Calorimetric Data for HDPE/CaCO<sub>3</sub> Composites

Composite	$\Delta H_{m_{II}}$ (J/g)	$-\Delta H_c$ (J/g)	$\chi_c$ (HDPE)	$T_{m_{II}}$ (°C)	$T_c$ (°C)
HDPE	194.71	184.26	0.58	130.53	113.30
HDPE/Ca <sub>1</sub> (5 wt %)	188.57	178.20	0.56	131.37	114.80
HDPE/Ca <sub>2</sub> (5 wt %)	187.70	173.99	0.55	132.03	113.30
HDPE/Ca <sub>1</sub> (10 wt %)	178.82	166.64	0.54	132.53	114.63
HDPE/Ca <sub>2</sub> (10 wt %)	182.52	170.72	0.56	131.70	113.13
HDPE/Ca <sub>1</sub> (15 wt %)	167.63	157.73	0.52	131.87	115.13
HDPE/Ca <sub>2</sub> (15 wt %)	167.78	156.94	0.53	131.37	113.47



**Figure 2** Complex viscosity versus frequency of pure HDPE and HDPE/CaCO<sub>3</sub> composites.

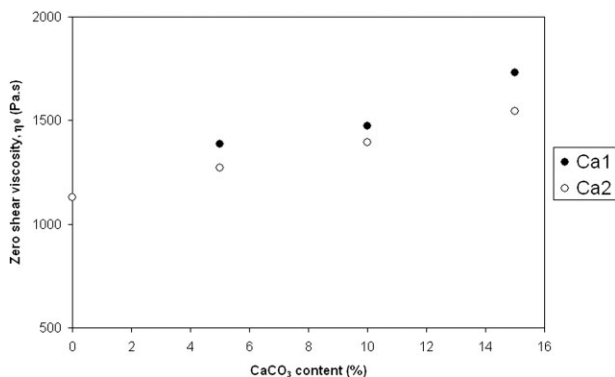
### Thermal properties

The values of the thermal parameters are summarized in Table III.

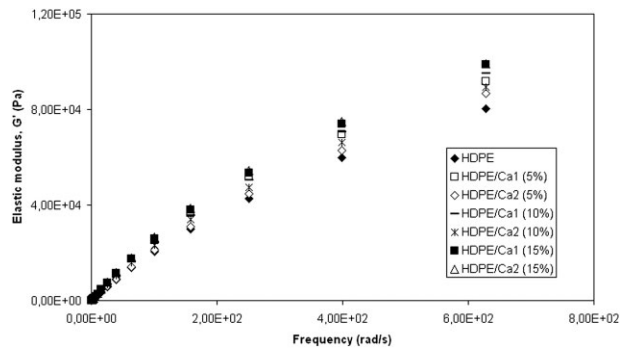
Table III also shows that the values of  $\Delta H_m$  during the second heating runs, tended to present a slight decrease in relation to the pure HDPE, resulting in a decrease in the crystallinity degree ( $\chi_c$ ) when calcium carbonate was added. As expected, this occurred because of the reduction of the crystalline portion in the material (polymeric portion). Those quantities do not show substantial changes between the composites analyzed—HDPE/Ca<sub>1</sub> and HDPE/Ca<sub>2</sub>. Probably, it occurred because of the fact that the difference in particle sizes of the two calcium carbonate grades studied was not enough to change the thermal behavior of the systems.

### Rheological analysis

Figure 2 shows the dependence of complex viscosity on the frequency range analyzed for HDPE and HDPE composites. As it can be seen, both pure HDPE and HDPE composites showed a shear thinning behavior, i.e., the viscosity decreased with increasing frequency. As expected, the addition of mineral filler caused a



**Figure 3** Zero shear viscosity versus CaCO<sub>3</sub> content.



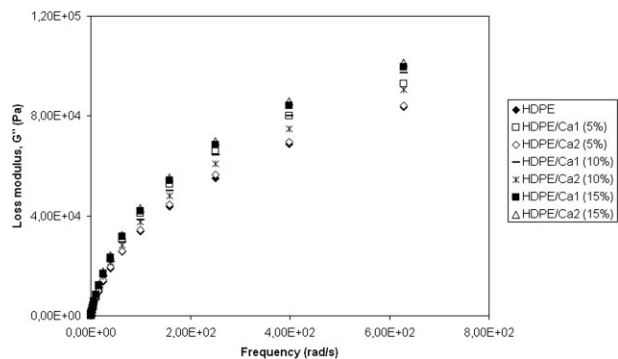
**Figure 4** Elastic modulus ( $G'$ ) versus frequency for HDPE and HDPE/CaCO<sub>3</sub> composites.

rise in viscosity relative to pure HDPE because of a larger interference with the polymer flow.

Figure 2 also shows that the incorporation of Ca<sub>2</sub> (filler with high percent of fines below 1  $\mu\text{m}$ ) produced composites with lower viscosity values in relation to those with Ca<sub>1</sub>. A zoom of the curves between 0.01 and 1 rad/s is presented to better visualize that behavior. In a general way, particles of small size have a more accentuated tendency to agglomerate, decreasing the dispersion of those particles on the plastic matrix and consequently decreasing the viscosity.

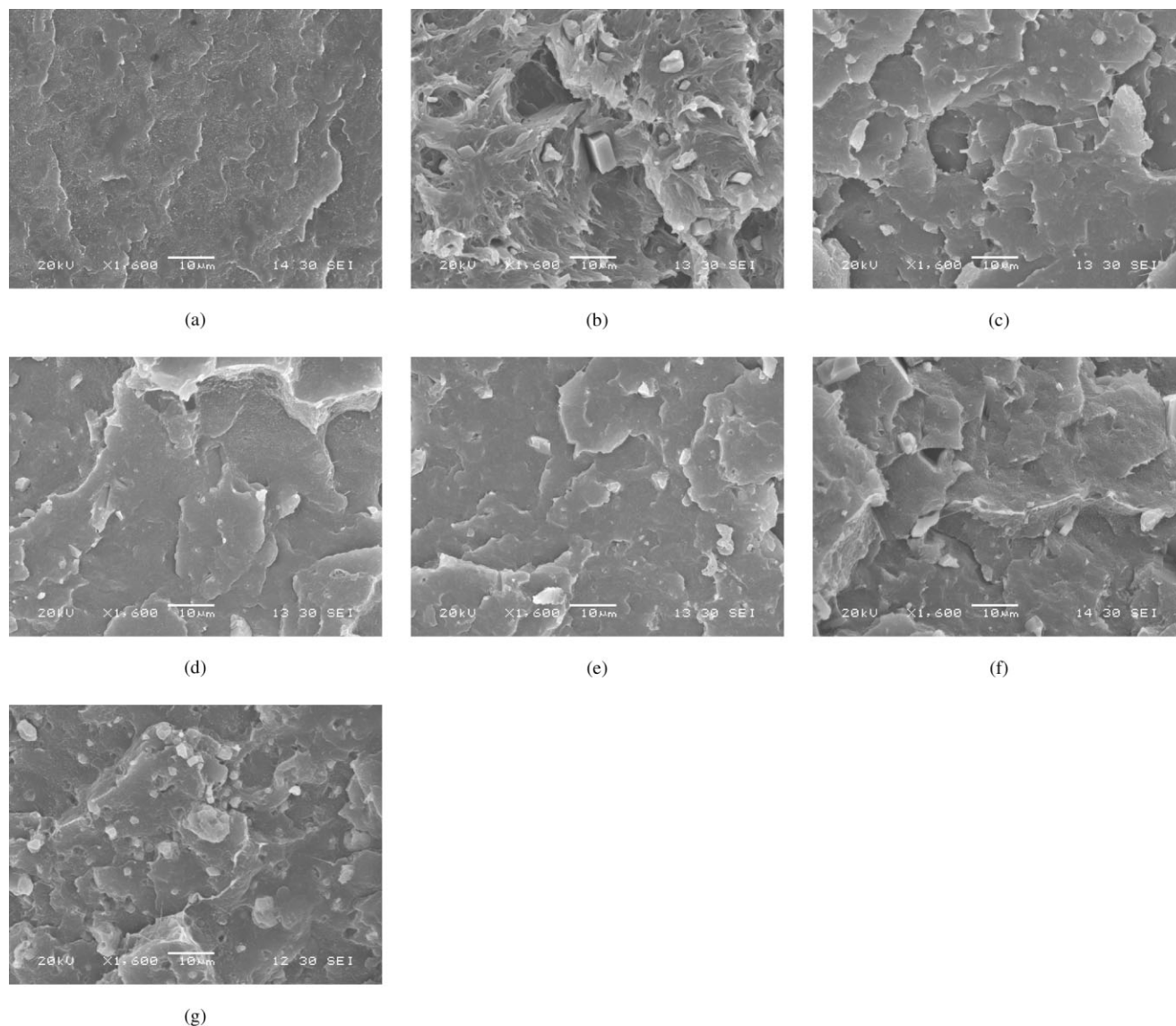
Zero shear viscosity of pure HDPE and composites were obtained from a TA Instruments dynamic stress rheometer at 200°C as shown in Figure 3. This plot shows clearly that the addition of mineral fillers caused an increase on  $\eta_0$  of the HDPE/CaCO<sub>3</sub> composites. It can also be observed that the addition of Ca<sub>2</sub> filler produced materials with lower  $\eta_0$  values.

According to the literature,<sup>14</sup> all viscoelastic materials behave more or less solid-like (elastic) or liquid-like (viscous), depending on the rate at which they are deformed. This behavior is related to the fact that strained macromolecules tend to pull back to their original shape. The dynamic storage modulus ( $G'$ ) translates the elastic behavior of the material and may be considered as the amount of the stored energy. The



**Figure 5** Loss modulus ( $G''$ ) versus frequency for HDPE and HDPE/CaCO<sub>3</sub> composites.





**Figure 6** SEM micrographs of samples (a) HDPE, (b) HDPE/Ca<sub>1</sub> (5%), (c) HDPE/Ca<sub>2</sub> (5%), (d) HDPE/Ca<sub>1</sub> (10%), (e) HDPE/Ca<sub>2</sub> (10%), (f) HDPE/Ca<sub>1</sub> (15%), and (g) HDPE/Ca<sub>2</sub> (15%).

dynamic loss modulus ( $G''$ ) represents the amount of dissipated energy. The change of  $G'$  and  $G''$  with the frequency is a measure of the relative motion of all molecules in the bulk and can give important information about the flow behavior of polymer melts.

In Figure 4, the variation of the elastic modulus ( $G'$ ) with the investigated frequencies of HDPE/CaCO<sub>3</sub> composites is compared with that of pure HDPE. A zoom on the elastic behavior of the pure polymer and composites is shown.

Figure 4 shows that as calcium carbonate is added, higher values of  $G'$  were obtained. Accepting that  $G'$  is related to the stored energy, the above findings indicate that the incorporation of mineral filler produced more elastic materials. The addition of Ca<sub>2</sub> filler in HDPE showed a tendency to produce lower values of  $G'$ , indicating that the materials were less elastic in relation to

the Ca<sub>1</sub> composites. This behavior probably is due to the poor particle dispersion on the HDPE matrix.

The dependence of the loss modulus ( $G''$ ) on the investigated frequencies of HDPE/CaCO<sub>3</sub> composites and pure HDPE is shown in Figure 5. As can be seen, for all examined materials,  $G''$  values increased as calcium carbonate was added. Taking into account that the dynamic loss modulus ( $G''$ ) represents the amount of dissipated energy, such results indicate that the addition of CaCO<sub>3</sub> materials with higher energy dissipation were produced. The HDPE/Ca<sub>2</sub> composites tended to present lower  $G''$  values.

### Morphological analysis

Figure 6 shows the SEM of HDPE and HDPE composites.

The analysis of the  $\text{CaCO}_3$  dispersion, carried out by SEM, shows that the addition to HDPE of higher contents of  $\text{Ca}_2$  [Figs. 6(e) and 6(g)] seemed to present a higher number of clusters. This behavior probably means that a poorer particle dispersion in the HDPE matrix has occurred. This result is in accordance with the mechanical and rheological results found in this work.

### CONCLUSIONS

Composites of HDPE and  $\text{CaCO}_3$  were prepared. Even the difference of the particle size between the two grades of this filler analyzed in this work being small, some little differences were observed in the mechanical and rheological properties of the two systems (HDPE/ $\text{Ca}_1$  and HDPE/ $\text{Ca}_2$ ). The elastic modulus presented lower values when  $\text{Ca}_2$  grade was incorporated to the HDPE matrix. Beyond that, HDPE/ $\text{Ca}_2$  composites tended to present lower viscosity values in relation to HDPE/ $\text{Ca}_1$ , indicating that the first systems probably present poorer particle dispersion in the plastic matrix. This result was confirmed by SEM analysis. It seems that  $\text{Ca}_2$  tends to produce agglomerates with higher particle size because of the higher proportion of particles with sizes below  $1 \mu\text{m}$ , beyond that, the addition of  $\text{Ca}_2$  seems to produce a poorer dispersion, resulting in composites with lower viscosity and elastic modulus values. The thermal analysis showed

that the addition of mineral filler to HDPE provoked a slight decrease in the crystallinity degree because of the reduction of the crystalline portion in the material.

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