EFFECTS OF ORGANOCLAYS ON THE THERMAL PROCESSING OF PE/CLAY NANOCOMPOSITES

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Nanocomposites containing both polyethylene and montmorillonite clay organically modified with four different types of quaternary ammonium salts were obtained via direct melt intercalation. Thus, the main purpose of this work was to evaluate the effect of the organoclay on the thermal stability of polyethylene. The organoclays were characterized by XRD, FTIR, DSC and TG. The polyethylene/organoclay nanocomposites were studied by XRD, TEM, TG, besides an evaluation of their mechanical properties. The results showed that the salts were incorporated by intercalation between the layers of the organoclay and, apparently that the nanocomposites were more thermally stable than pure polyethylene.

Keywords: nanocomposite, organoclay, polyethylene, thermal stability

Introduction

Smectite is the name of a sodium, magnesium, calcium, iron, potassium and lithium aluminosilicate group that presents as main clay mineral the montmorillonite. The clay minerals of this group present $(Si_2O_5)_n$ layers of SiO_4 tetrahedra both above and below a central $AlO(OH)_2$ layer [1].

In these three layer silicates, the isomorphous substitutions require cations, exchange cations, to compensate for the negative charges in their laminar edges [2, 3]. Sodium smectites, those containing sodium as the prevailing interlayer cation are the ones of highest industrial production. These clays can interact with organic compounds to form complexes of varying stabilities and properties. The organoclays have been obtained by the addition of quaternary ammonium salts, of at least 12 carbons atoms, to aqueous dispersions of sodium smectite clays. In these dispersions, the clay particles or layers must be separated of one another and not be stacked, in order to facilitate the introduction of the organic compounds. As a result, the clay exchange cations are replaced by the organic cations of the quaternary ammonium salts that were adsorbed on the negative sites of the clay surfaces.

This exchange is important to increase the basal spacing of the clay and to equal the clay surface polarity with the polymer polarity [4]. So, the clay obtained, known as organophilic or organoclay, is no more soluble in water and it will be compatible with polymer matrices, if the organic quaternary ammonium ions were properly chosen [5, 6]. Organoclays have been used in nanostructured polymer-clay composites and hence they have received special attention.

The advantages of these systems in relation to the traditional systems are the small amounts of organoclay used (<10 mass%) in the polymer matrices and the enhancement of several properties. Significant improvements in mechanical, thermal, optical, electric, dimensional, flammability and barrier properties are due to the large nanoscale contact area between the polymer and the clay. In the polymer/clay nanocomposites, the dispersed phase, i.e., the clay is present in the form of layers, of about 10 Å in thickness and hundreds of nanometers in width and length [2, 5, 7–14].

The careful study of the thermal stability of these systems is very important, since some species of clay have been shown to catalyze the degradation reactions of the nanocomposites [15].

The objective of this work was to prepare and characterize organophilic clays using four different types of quaternary ammonium salts and later add 3 mass% of organoclay in a polyethylene matrix in order to evaluate the thermal stability. The organoclays were characterized by XRD, FTIR, DSC and TG, and the nanocomposites were studied by XRD, TEM and TG, besides an evaluation of their mechanical properties.

Experimental

Materials

A sample of Brasgel PA, a trademark of an industrial montmorillonite (MMT) was used in this work. It is a

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Na$^+$-montmorillonite from Boa Vista, PB state, in Northeastern Brazil and it was supplied by Bentonit União do Nordeste, Brazil.

The quaternary ammonium salts used were: alkyldimethylbenzylammonium chloride (Dodigen 1611), cetyltrimethylammonium chloride (Genamin CTAC-50ET), stearyldimethylammonium chloride (Praepagen WB), all of these supplied by Clariant/Brazil and cetyltrimethylammonium bromide (Cetremide) from Vetec/Brazil. The high density polyethylene (HDPE), JV060, supplied by Braskem/Brazil, was used as the matrix.

Preparation of the organophilic montmorillonite and nanocomposites

An aqueous solution containing about 20.0 g of a quaternary ammonium salt was added to a 2000 mL glass flask containing 32 g of the Na$^+$-montmorillonite (MMT), passing a 200 mesh sieve, and 768 mL of distilled water. The contents were mechanically stirred for 20 min. The stirring was stopped and the resulting organo-montmorillonite (OMMT) was washed with distilled water for several times to remove excess salts, dried at 60°C for 48 h, and finally ground to pass through a 200 mesh sieve, according to the procedure described by Araújo *et al.* [2, 6].

The polyethylene (PE)/organoclay nanocomposites, containing 3 mass% clay, were prepared in a Torque Rheometer Haake with a counter-rotating twin-screw extruder, at 170–200°C and 60 rpm. In order to assure a better dispersion of the fine clay powder in the high viscosity PE polymer, a 1:1 PE/organoclay master was previously produced in a Torque Rheometer Haake with internal mixer, at 190°C and 60 rpm for 7 min.

Methods

Thermal analyses

The thermal stability was investigated by DSC, using a DSC10 Thermal Analyst 200-TA Instruments equipment. The heating rate was 10°C min^{-1}, from 20 to 350°C, in an air atmosphere. The thermogravimetry (TG) technique was also used, by means of a TGA S1H Shimadzu equipment, operating at a heating rate of 12.5°C min^{-1}, from room temperature up to 900°C under a nitrogen atmosphere with a flow rate of 50 mL min^{-1}. The sample mass was 5.0±0.5 mg. The TG curves were analyzed with the aid of the TASYS software from Shimadzu.

Infrared spectroscopy

The infrared spectroscopy measurements were obtained at room temperature using an Avatar TM 360

instrument, using the standard KBr disk method at the 4000 to 400 cm^{-1} wavelength range. The data acquisition and processing were carried out with a Spectralink interface connected to a microcomputer.

Other measurements

X-ray diffraction (XRD) measurements were performed at room temperature by a XRD-6000 Shimadzu diffractometer (40 kV, 30 mA) using the CuK$_\alpha$ radiation (wavelength of 0.154 nm) at the rate of 2° min^{-1}, in the range from 2 to 30°. The degree of crystallinity of the samples was calculated by the Crystallinity Program of Shimadzu.

Ultra thin films of the nanocomposites, displaying a thickness of about 50 nm, were sliced up with a diamond knife using a Leica Ultracut UCT. These films were observed in a Jeol JEM 1200 EXII transmission electron microscope (TEM). This technique was used to observe the structure and morphology of the nanocomposites, since it shows a more direct evidence of the nanoscale dispersion of organoclay within the PE matrix.

Tensile tests were conducted using a LLoyd LR/10KN Universal Machine at room temperature and crosshead speed of 50 mm min^{-1} for the determination of tensile modulus (TM), yield strength (YS) and elongation at yield (EY) measurements, according to the standard ASTM D638. Izod impact tests were carried out on notched specimens at room temperature using a Ceast Resil 5.5 equipment, according to the standard ASTM D256. Typically, five or more samples were used for each determination.
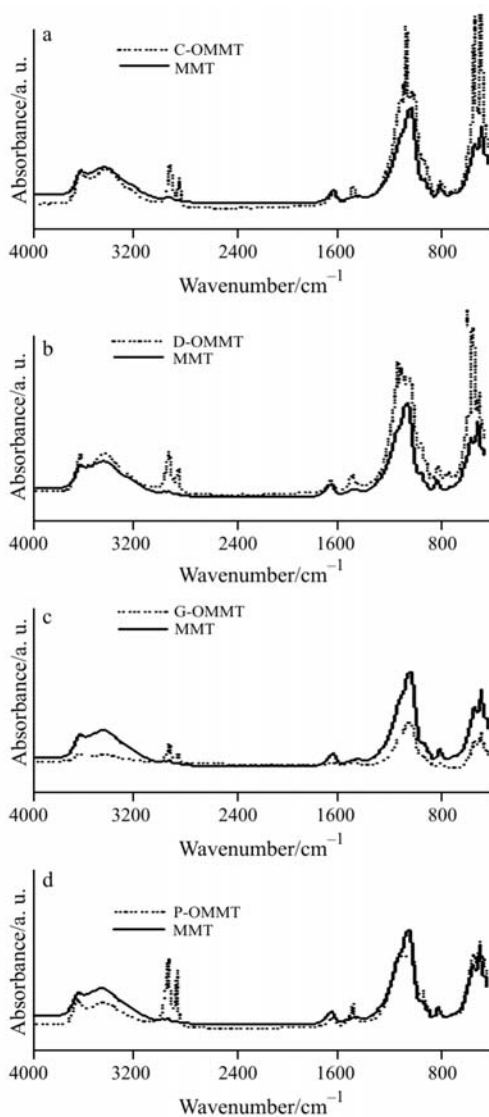
Results and discussion

Infrared spectroscopy and X-ray diffraction results

Infrared spectroscopy and X-ray diffraction were respectively used to confirm the presence of the quaternary ammonium salt and its intercalation in between the clay layers. Figure 1 illustrates the infrared spectroscopy results for the industrial clay and the clays treated with the quaternary ammonium salts. Observing the infrared spectra of industrial and treated clays, a peak at 3632 cm^{-1} can be observed, which is ascribed to the vibration of OH groups from MMT. The peak at 3435 cm^{-1} is related to water and the peak at 1048 cm^{-1} is related to the Si–O groups. Peaks at 920, 800 and 525 cm^{-1}, related to the Al octahedral layers, and are noticed in the untreated and salt-modified clays. Also, for the quaternary ammonium salt-treated samples, bands at 3629 cm^{-1} can be observed, which are related to the vibration from NH groups. In these salt-modified samples are also observed bands

at 2846 and 2918 cm^{-1} that are related to the symmetric and asymmetric vibrations from CH$_2$ groups, respectively, and bands at 3001 cm^{-1}, corresponding to asymmetric vibrations of the CH$_3$ groups. The band at 1459 cm^{-1} indicates the flexural vibration from CH$_2$ groups. These observations agree with the literature [16, 17]. The bands due to NH, CH$_2$ and CH$_3$ groups in the infrared spectra of treated montmorillonite samples evidence the presence of the quaternary ammonium salts in the structure of these clay samples.
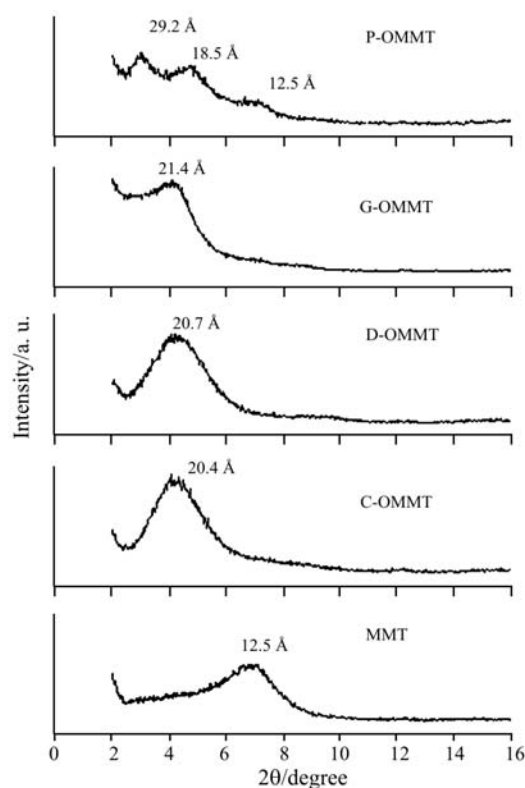
Figure 2 shows the XRD patterns for the commercial Brasgel PA clay, either unmodified or modified with the quaternary ammonium salts Dodigen, Genamin, Praepagen and Cetremide. It can be observed that the unmodified clay (MMT) has a peak

corresponding to an interlayer spacing d_{001}=12.5 Å. These interlayer spacings for the samples treated with quaternary ammonium salts, obtained from the corresponding XRD patterns, are 20.4 Å for cetremide (C-OMMT), 20.7 Å for dodigen (D-OMMT) and 21.4 Å for genamin (G-OMMT). In the case of the montmorillonite treated with praepagen (P-OMMT) two peaks were observed, ascribed to the interlayer spacings d_{001}=29.2 Å and d_{002}=18.5 Å, in which occurred the intercalation of the salt between the layers of organoclay. Another peak corresponding to interlayer spacings of 12.5 Å is probably due to an incomplete ion exchange, with some residual Na-MMT remaining in the material. The results indicated that all the quaternary ammonium salts were intercalated between two basal planes of MMT, leading to an expansion of the interlayer spacing. As a matter of fact, all the d_{001} spacings had raised upon the treatment with the quaternary ammonium salts.

Figure 3 presents the X-ray diffraction patterns for the PE/unmodified clay and PE/modified clay composites. The diffractogram of the PE/unmodified clay composite has a peak corresponding to an interlayer spacing of 13.3 Å, which is close to the distance of 12.5 Å (Fig. 2) of the unmodified clay, indicating that the increase of the basal spacing did not

Fig. 1 Infrared spectra of montmorillonite (MMT) and montmorillonite treated with the quaternary ammonium salts
a – cetremide (C-OMMT), b – dodigen (D-OMMT),
c – genamin (G-OMMT) and d – praepagen (P-OMMT)

Fig. 2 XRD patterns of montmorillonite (MMT) and montmorillonite modified with the quaternary ammonium salts cetremide (C-OMMT), dodigen (D-OMMT), genamin (G-OMMT) and praepagen (P-OMMT)

occur. On the other hand, the sample of the nano-composite of PE with the clay modified with Cetremide, PE/C-OMMT, presents the displacement of the XRD peak toward a lower angle values, what represents an increase to 30.02 Å in the basal spacing. It was thus noticed that with the presence of the organoclay, the peak related to the original PE/un-modified clay interlayer spacing disappeared, and two new peaks appeared, related to the distances of 30.02 and 15.57 Å. The first figure can be due to the interca-lation of the polymer between the layers of organo-clay and the second figure can be attributed to a small amount of montmorillonite layers that were not intercalated by PE molecules.

The X-ray diffraction pattern for the sample of the nanocomposite of PE with the clay modified with dodigen, PE/D-OMMT is almost the same as the one of montmorillonite treated with dodigen (Fig. 2), but it presents a broader peak. This may be due to a poor compatibility between the organoclay and PE, what was insufficient to form a nanocomposite. In other words, this can evidence the presence of residual lay-ered clay tactoids in this sample.

The X-ray diffraction pattern for the sample of the nanocomposite of PE with the clay modified with genamin, PE/G-OMMT, shows that the intercalation of the polymer chains increases the interlayer spacing to 34.61 Å, leading to a shift of the diffraction peak to-wards lower angles. A second peak, corresponding to an interlayer spacing of 19.53 Å, which is close to the distance of 21.4 Å of the clay modified with genamin, can be ascribed to a small amount of montmorillonite layers that were not intercalated by PE molecules.

For the X-ray diffraction pattern for the sample of the nanocomposite of PE with the clay modified with praepagen, PE/P-OMMT, the main diffraction peak points out to an interlayer spacing of 36.12 Å, due to the intercalation of the polymer chains between the layers of the organoclay. A second peak, related to a distance of 19.41 Å, similarly to the case of genamin, can be attributed to a small part of montmo-rillonite layers that were not intercalated by PE mole-cules. A third diffraction peak conforms to an interlayer spacing of 12.5 Å and it is probably due to an incomplete ion exchange, with the presence of some residual MMT.

TEM images of selected PE/clay nanocomposites are provided in Fig. 4. It can be seen that the tactoids of MMT layers are dispersed within the PE matrix (Fig. 4a). In Fig. 4b it can be seen that some C-OMMT layers were intercalated and dispersed within the PE matrix, however, a certain amount of unexfoliated C-OMMT layers existed as clusters. Therefore, the ob-tained PE/C-OMMT composites are partially interca-
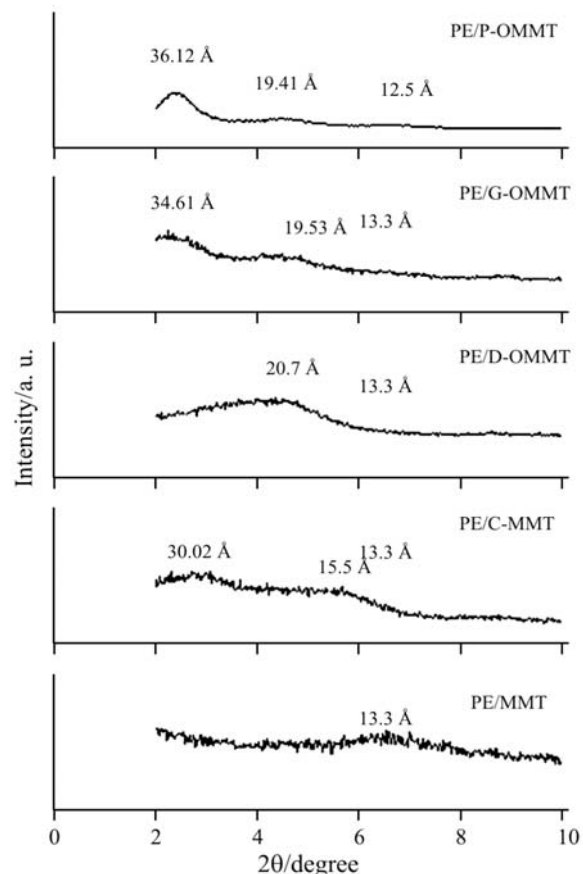

Fig. 3 XRD patterns of PE/unmodified clay (MMT) and PE/modified clay nanocomposites
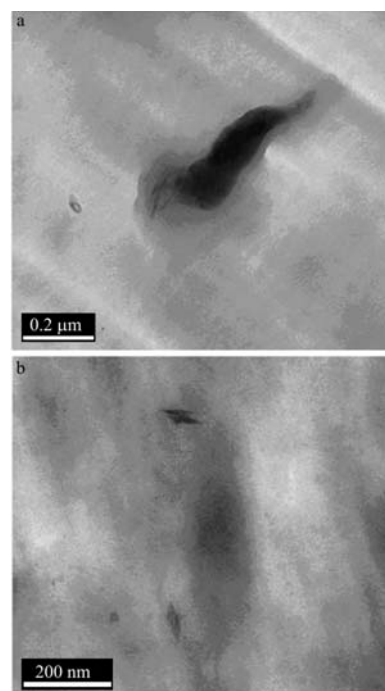

Fig. 4 TEM micrographs of a – PE/3 mass% MMT; b – PE/3 mass% C-OMMT

lated nanocomposites. This agrees with the XRD pattern obtained for the C-OMMT sample.

Thermal behavior

Figures 5a–d present the DSC curve of the four quaternary ammonium salts used. Figure 5a illustrates the DSC curve for the cetremide salt. This salt is solid at room temperature and displays a melting point of 100°C. An exothermic band in the range from 170 to 230°C can also be observed. An endothermic band, peaking at 250°C, was noticed, probably due the salt thermal decomposition.

Figure 5b shows the DSC curve for the dodigen salt. This salt is liquid at room temperature and it presents an endothermic peak at about 80°C, probably due to its volatilization. Another endothermic band is also observed with a peak temperature of 200°C, which is probably due to the salt decomposition.

Figure 5c presents the DSC curve for the genamin salt. It is also liquid at room temperature and the endothermic peak at about 110°C is probably due to its volatilization. The peak observed at 250°C is probably attributed to its decomposition.

The DSC curve for the praepagen salt can be seen in Fig. 5d. Two endothermic peaks are noticed at 33 and 70°C, apparently ascribed to its primary and secondary volatilizations, respectively. It is probable that the salt decomposition begins at 200°C with a maximum at 270°C.

The results of DSC indicate possible preliminary decomposition temperatures of the salts. This study is very important contribution to the knowledge of the performance and thermal stability of these salts at the processing temperatures of these polymeric materials.

Figure 6 shows the DSC curves PE (PE), PE/unmodified clay nanocomposite (PE/MMT) and the nanocomposites of PE/clay modified with the quaternary ammonium salts: cetremide (PE/C-OMMT), dodigen (PE/D-OMMT), genamin (PE/G-OMMT) and praepagen (CE/P-OMMT).

Table 1 presents the thermal properties of PE and its nanocomposites. The properties studied were the melting temperature taken at the melting peak, T_m, the heat of fusion due to the PE melting, measured by the melting peak, ΔH_m, the degree of crystallinity, X_c, and the maximum decomposition temperature, TG, taken from the DTG curves. Two values of degree of crystallinity are presented, the values obtained from XRD and the values obtained by DSC, in which the degree of crystallinity is taken as the ratio $\Delta H_m/\Delta H_{mo}$. The value of ΔH_m was previously defined and ΔH_{mo} is the heat of fusion for 100% crystalline PE, 293 J g^{-1}.

As shown in Table 1, the DSC technique was used to evaluate the thermal stability of the polymer matrix in
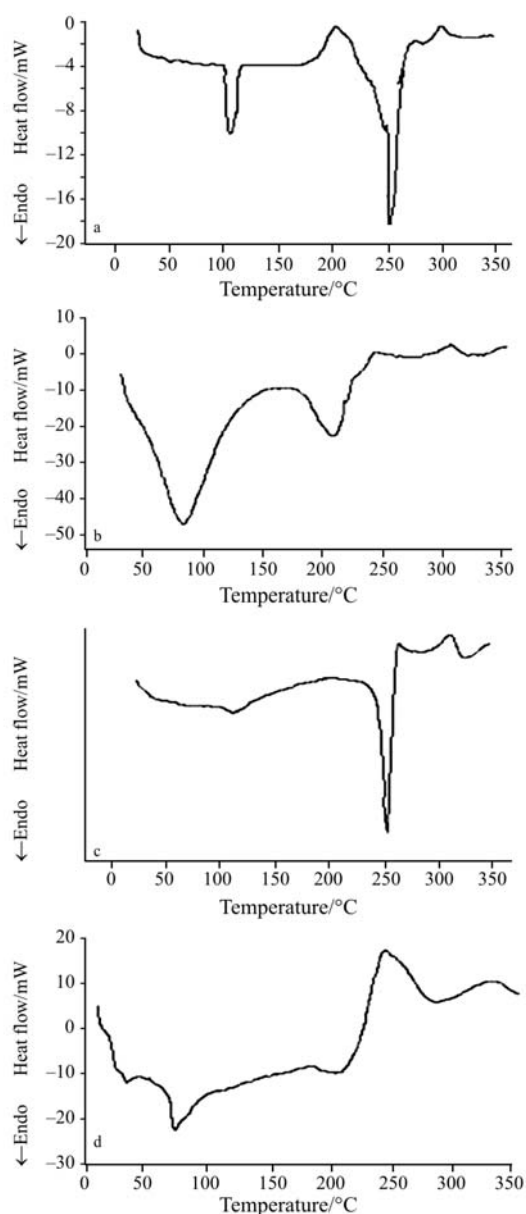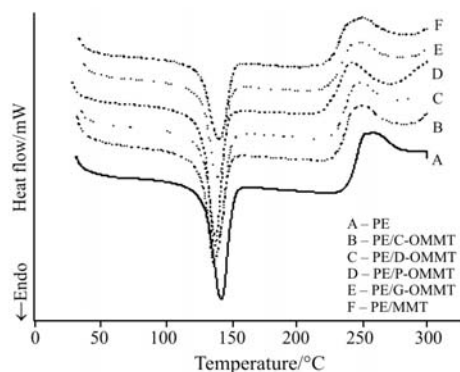

Fig. 5 DSC curve for the quaternary ammonium salts
a – cetremide, b – dodigen, c – genamin and d – praepagen

the presence of the organoclay. No meaningful difference was observed in the melting temperatures of the PE matrix for the different samples studied. Moreover, the shape of the melting peaks of the PE/organoclay composites is practically identical to the ones of the PE matrix. This indicates that the presence of clay did not influence the size and the crystal ordering.

A similar trend can be observed for the PE degradation, i.e., apparently no significative change was observed in the degradation temperatures. It seems that the presence of the organoclay does not modify or alter the matrix degradation and that the quaternary ammonium salts are stable at the processing temperatures used. On the other hand, the presence of the

Fig. 6 DSC curves for PE (PE), PE/unmodified clay
    nanocomposite (PE/MMT) and the nanocomposites of
    PE/clay modified with the quaternary ammonium salts:
    cetremide (PE/C-OMMT), dodigen (PE/D-OMMT),
    genamin (PE/G-OMMT) and praepagen (PE/P-OMMT)

organoclay had a nucleating effect, because the degree of crystallinity was bigger than for pure PE. Some authors explain that the clay can act as nucleating agent, increasing the crystallization temperature of the samples [18, 19]. Therefore, this study on the thermal stability, besides using DSC, must be completed by other analysis techniques such as TG.

The thermal properties of the commercial clay, the organoclays, PE/unmodified clay composite and the composites of PE/clay modified with the four different quaternary ammonium salts were studied by thermogravimetry. The clay layers display a high barrier action and the large thermal stability is related to the lowering of the diffusion of oxygen molecules into the nanocomposites, due to barrier property of the clay. So, at a lower level of oxygen, which is main factor for the deterioration of the polymer, the nanocomposite is more strong toward the oxidative decomposition.

On the other hand, the alkylammonium cations in the modified organoclays could suffer decomposition,

Table 1 Thermal properties of the PE matrix and its
    nanocomposites

| Specimen	$T_m/°C$ DSC	$\Delta H_m/J\ g^{-1}$ DSC	$X_c/\%$ XRD	TG/°C
PE	142.5	124.0	42.3	57.4	515
PE/MMT	140.8	100.9	34.4	55.2	520
PE/C-OMMT	136.4	127.1	43.4	65.7	527
PE/G-OMMT	139.7	116.4	39.7	70.7	524
PE/D-OMMT	139.2	116.4	39.7	60.7	527
PE/P-OMMT	135.5	124.2	42.4	80.6	526

T_m – melting temperature taken at the melt peak;
ΔH_m – heat of fusion due to PE melting, measured through
the melting peak; X_c – degree of crystallinity obtained by
DSC, taken from $\Delta H_m/\Delta H_{mo}$; ΔH_{mo} – heat of fusion for PE,
100% crystalline, 293 J g^{-1}; TG – maximum decomposition
temperature taken from DTG curves

following the Hofmann elimination reaction. It should be remarked that the reaction products, as well the clay itself, can catalyze the degradation of the polymer. As pointed out by Ray *et al.* and Zhao *et al.* [20, 21], it is hence very important to analyze the thermal stability of the PE/clay nanocomposites.

Figure 7 shows the TG and DTG curves, in a nitrogen atmosphere, of commercial montmorillonite and montmorillonite treated with the four quaternary ammonium salts. It can be observed that the commercial clay presents the first stage of the degradation at the range from 30 to 170°C, which is due to the loss of adsorbed water. The second stage of degradation takes place in the range from 430 to 630°C and it caused by dehydroxylation, the elimination of hydroxyl groups from the structure of the silicate layers.

For the samples treated with the different quaternary ammonium salts, two new thermal decomposition stages are presented, one due to a mass loss at range from 180 to 400°C, with a maximum at 300°C, ascribed to the initial decomposition of the quaternary ammonium salts and another at the range from 570 to 750°C, attributed to the final decomposition of the organic salt. Also it can be seen that the clay modified with praepagen quaternary ammonium salt displays a higher thermal stability than other salts.

Xie *et al.* [15] studied the thermal and chemical degradation of montmorillonite modified with several quaternary ammonium salts. The authors showed that the initial mass loss was related to a small amount of the organic salt that was not intercalated into the clay, but was associated to the aluminum silicate surface or to small ionic molecules. They claimed also that the second loss can be associated to the high molecular
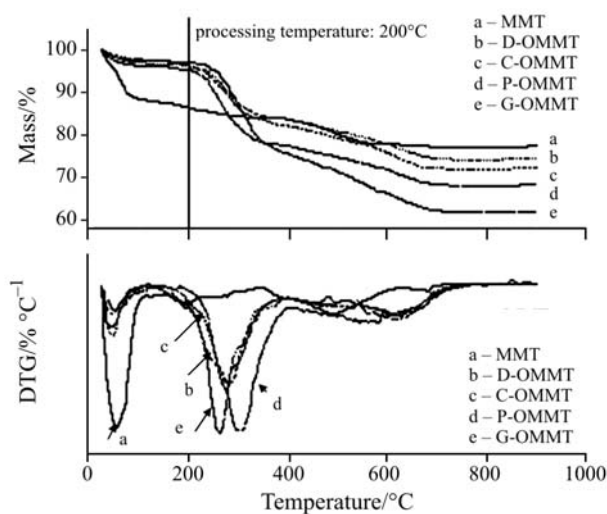
Fig. 7 TG and DTG curves of commercial Brasgel PA clay
    (MMT) and the clay modified with the quaternary ammo-
    nium salts: cetremide (C-OMMT), dodigen (D-OMMT),
    genamin (G-OMMT) and praepagen (P-OMMT)

**Table 2** Mechanical properties of PE and its nanocomposites

Specimen	Tensile modulus/MPa	Yield strength/MPa	Elongation at yield/%	Izod impact strength/J m^{-1}
PE	939.46±77.1	19.28±0.6	7.4±4.3	128.2±5.4
PE/MMT	903.8±110.3	18.8±0.5	8.1±3.0	96.5±13.5
PE/C-OMMT	879.1±78.9	18.7±0.4	10.0±0.2	96.4±6.7
PE/G-OMMT	895.8±44.4	19.1±0.2	10.0±0.4	98.1±5.9
PE/D-OMMT	943.5±92.9	18.9±0.4	8.6±3.5	92.2±5.3
PE/P-OMMT	1011.5±103.2	19.9±0.8	6.7±4.2	99.3±9.9

mass molecules that are within the interlamelar spacing, which volatilize at higher temperatures.

The thermal stability of the PE/clay nanocomposites is improved with the presence of the quaternary ammonium salts, as pointed out in Fig. 8. Before 400°C takes place the initial stage of degradation that can be due to the Hoffman elimination reaction and to the catalyzed degradation of the clay. Pure PE degrades faster than PE/clay nanocomposites, i.e., at temperatures higher than 400°C the PE/clay nanocomposites are more stable than pure PE. Apparently, the nanocomposites in which the organoclay was treated with dodigen (D-OMMT) and genamin (G-OMMT) salts are more stable than the other samples. The maximum decomposition temperature values, obtained from the DTG curves, are 515, 520, 524, 527, 527 and 526°C for pure PE, PE/MMT, PE/G-OMMT, PE/C-OMMT, PE/D-OMMT and PE/P-OMMT, respectively. This suggests that at the range of the processing temperatures the degradation of the system does not occur, i.e., the nanocomposites are stable up to 340°C.

Mechanical properties of the PE/clay nanocomposites

Table 2 shows yield strength, tensile modulus, elongation at yield and Izod impact strength of pure PE
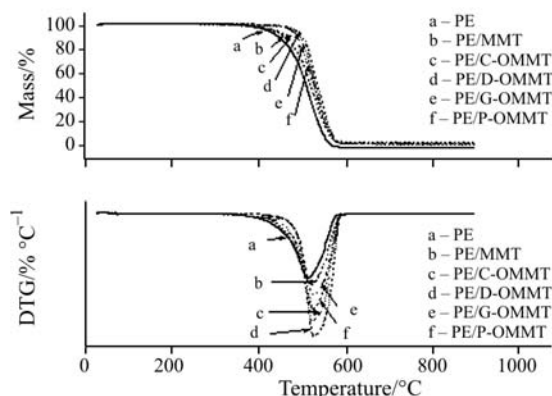
Fig. 8 TG and DTG curves of PE (PE), PE/unmodified clay nanocomposite (PE/MMT) and the nanocomposites of PE/clay modified with the quaternary ammonium salts: cetremide (PE/C-OMMT), dodigen (PE/D-OMMT), genamin (PE/G-OMMT) and praepagen (CE/P-OMMT)

and its nanocomposites. Generally, it can be observed that the mechanical properties of the nanocomposite samples are close to the mechanical properties of pure PE. The samples PE/P-OMMT and PE/C-OMMT present higher values for the tensile modulus when compared with pure PE. Probably, these samples display a higher rigidity than the PE matrix. The yield strength values of the nanocomposites do not change significantly in comparison with pure PE, while the Izod impact strength decreases slightly, what is a typical characteristic of polymer/clay nanocomposites [22].

The organoclays and the quaternary ammonium salts used in this work did not decrease neither the thermal stability nor the mechanical properties of the PE matrix. This is an especially interesting result. The mechanical and flammability properties with different clay contents in the PE nanocomposites will be the object of a further investigation.

Conclusions

Four different types of quaternary ammonium salts were used to modify montmorillonite clay. PE/clay nanocomposites were later prepared by melt intercalation, with the main purpose of studying the effect of organoclay on the thermal stability and mechanical properties of PE. The infrared results showed the presence of the cations from the quaternary ammonium salts in the structure of the treated montmorillonite. The XRD results of the clays indicated that the quaternary ammonium salts were intercalated within the interlayer spacing of MMT and expanded it. All the d_{001} spacing values increased upon the intercalation of the quaternary ammonium salts. By XRD and TEM, the presence of intercalated nanocomposites was clearly observed, at least for most of the material.

The use of organoclays, replacing the untreated montmorillonite clay, improved the thermal stability of the PE/clay nanocomposite. Apparently, the nanocomposites with the organoclay treated with dodigen (D-OMMT) and genamin (G-OMMT) salts are more stable than the other samples. It was also shown that

the samples do not degrade at the processing temperature, i.e., the nanocomposites are stable up to 340°C. In general, the values of the mechanical properties of the nanocomposites are close to the ones of pure PE.

Acknowledgements

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