

Effect of the organic groups of difunctional silanes on the preparation of coated clays for olefin polymer modification

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ABSTRACT: Sodium montmorillonite (MMT) was organically modified with hexadecyltrimethylammonium ions and subsequently treated with dichlorosilanes and water, aimed at *in situ* silane condensation polymerization and modification of clay platelets by polysiloxane coatings. Dimethyldichlorosilane, methylphenyldichlorosilane, and diphenyldichlorosilane were used to produce three siloxane-modified organoclays. The structure and morphology of the clay materials were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermal gravimetric studies (TG) and scanning electron microscopy (SEM). XRD results showed that the silanes were effectively polymerized in the clay galleries, forming a nanocomposite of intercalated particles. A fraction of the siloxane formed is bonded to the clay surface by covalent siloxane bonds. Strong structural differences in both morphology and thermal stability of the materials may occur when changing methyl or phenyl groups in the siloxane structure. The formation mechanism of these intercalated nanocomposite particles is considered. Finally, these modified clays were incorporated in an olefin polymer and morphological analyses using transmission electron microscope (TEM) images were carried out.

KEYWORDS: oligo-siloxanes, montmorillonite, organophilic clay, hybridized clay, HDPE/coated clay composites, clay/olefin composites, nanocomposites.

Clay science has a long history but in the last decade it has gained in importance due to nanotechnology advances, in particular because clays can be used as polymeric nanocomposites fillers (He *et al.*, 2005; Vaia & Giannelis, 1997a,b). Several studies have been published proving that the incorporation of inorganic nanolayers inside the

polymeric matrix can effectively improve protection against corrosion (Yeh *et al.*, 2006) as well as a variety of other polymeric properties (Alexandre & Dubois, 2000; Tjong, 2006; Lyatskaya & Balazs, 1998).

In every case, the incorporation of a suitable organic species inside the clay galleries (interlayer space) is a key factor for obtaining the best results. Such modification is intended to give these particles excellent dispersion in the polymer phase and also appropriate functional properties such as radiation shielding, or catalytic, optical and barrier properties (Ke & Stroeve, 2005).

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Various methods have been developed to obtain chemical compatibility between clays and polymeric materials. All have taken into account (1) the chemical nature of the host polymer in relation to that of the clay and (2) the modification that is intended to be achieved in the polymer, whether the intention is to produce a new property or to improve an existing one. The application of clays to obtain nanostructured polymeric materials is based on their property of expansion and ionic exchange (Annabi-Bergaya, 2008). These properties allow the incorporation into the clay structure of amphiphilic organic molecules, such as alkylammonium or alkylphosphonium cations by ionic exchange with metallic ions that are found in the interlayer spaces (Alexandre & Dubois, 2000).

The incorporation of these molecules in the interlayer generates an organophilic environment which allows the incorporation of a great variety of hydrophobic molecules at the same time. Within a wide range of possibilities, it is important to obtain a chemical affinity between the inorganic and organic phases by the incorporation of specific monomers (which may be of similar chemistry to the target polymeric matrix) and, obviously, their subsequent *in situ* polymerization.

Several cases in which the monomer used as modifier is of the same chemistry as the polymeric matrix have been reported (Jin *et al.*, 2002; Yu *et al.*, 2003). In some other cases, copolymers have been employed as compatibilizers (Lotti *et al.*, 2008; Saminathan *et al.*, 2008). Another option is to use coupling agents which, most often, are trifunctional silylating agents (Negrete-Herrera *et al.*, 2006; He *et al.*, 2005; Bauer *et al.*, 2003; Park & Kwon, 2004; Beigbeder *et al.*, 2005; Daniel *et al.*, 2008; Frost *et al.*, 2008).

These compounds belong to the particular and interesting family of 'silanes'. When they react with the clay under suitable conditions, they generate polysiloxanes whose main chain is of the same nature as the clays, with organic groups of diverse chemical nature united at a central Si by Si-C

bonds. It is feasible to select silanes of different functionality whose nature gives them chemical affinity with a given polymeric matrix.

This paper proposes the incorporation of oligosiloxanes into organophilic clay by treatment with difunctional silanes and subsequent *in situ* oligomerization, with the aim of obtaining improved hydrophobic behaviour of the organophilic clay for its application in the modification of the properties of hydrocarbon (polyolefin) polymers.

The effect of the organic group during silane incorporation in the clay and also its effect on the compatibilization of the clay with the hydrocarbon polymeric matrix were both studied. Preparative methods were studied, as were comparative analyses of the influence of the methyl and phenyl groups on the incorporation of oligosiloxanes generated by *in situ* oligomerization of the dichlorosilanes [(CH₃)₂SiCl₂, (CH₃)(C₆H₅)SiCl₂, and (C₆H₅)₂SiCl₂] on a MMT previously exchanged with ions of quaternary ammonium salts. Not only are the analyses of structural, thermal and morphological properties of the clays presented but also the results of the morphological study of the incorporation of the modified clays into HDPE with the aim of verifying if the treatment with the different silanes provides an improvement in the compatibilization of the clay with the hydrocarbon polymeric matrix.

EXPERIMENTAL METHODS

Materials

Sodium montmorillonite (MNa) clay supplied by MINARMCO (CEC = 70 meq/100g and particle size <325 Mesh) was used in this work. Its chemical composition is given in Table 1. The MNa clay was modified with hexadecyl trimethylammonium chloride (HDTMA) provided by PharmaSpecial (GENAMIN). Dimethyldichloro silane (DMS), methylphenyldichloro silane

TABLE 1. Composition of natural clay.

Component	SiO ₂	Al ₂ O ₃	MgO	Na ₂ O	CaO	K ₂ O	Fe ₂ O ₃	Others
Wt.%	62.0	18.0	3.0	3.5	2.0	1.0	7.0	3.5

(MPhS) and diphenyldichloro silane (DPhS) were purchased from Sigma Aldrich.

Preparation of organophilic clay

A 5 wt./v% distilled water dispersion of untreated MNa clay was prepared and the quaternary ammonium salt HDTMA solution was added to the dispersion. The mixture was stirred for 2 h at 80°C and filtered. Several washes were carried out to ensure the complete elimination of chloride ion. After a negative test of the filtrate with 0.1 N AgNO₃ solution, the organophilic montmorillonite clay (HM) was dried at 80°C for 48 h (Yeh *et al.*, 2006).

Preparation of siloxane modified organoclays.

Silanes were mixed with HM in a ratio of 1:1 by weight and were maintained in contact for 5 days at room temperature. Distilled water was then added at a H₂O/Si = 20 molar ratio. During the clay preparation procedure, the presence of HCl was observed, providing evidence of the occurrence of hydrolysis. After 5 days, the treated clays were washed until complete elimination of Cl⁻ ion was achieved. Finally, the following materials were prepared: HM-PDMS, HM-PMPPhS and HM-PDPhS (Monasterio *et al.*, 2010).

Preparation of HDPE/siloxane modified organoclays

HDPE pellets (97 wt.%) and modified clays (3 wt.%) were mixed using melt compounding processing in a Haake torque rheometer Rheocord 9000 equipped with a mixing chamber and roller rotors at 100 r.p.m. and 190°C.

Characterization

X-ray diffraction analyses (XRD) were carried out in an X-ray diffractometer (Rigaku Miniflex) using Ni-filtered Cu-K α radiation, at 30 kV and 15 mA. The data were recorded at 2 $^{\circ}$ 2 θ /min.

FTIR spectra were recorded in a Perkin Elmer FTIR 1720x using pressed KBr disks, at 2 cm⁻¹ of frequency resolution.

The thermal gravimetric (TG) analyses were carried out using a TA Instruments TGA Q500 from 25 to 700°C with a heating rate of 10°C min⁻¹, operating under 60 ml min⁻¹ N₂ flow.

Scanning electron microscopy (SEM) was carried out using a JEOL JSM-5610 LV instrument with an accelerating voltage of 15 kV. Samples were coated with gold in order to study the surface morphology. Transmission electron microscopy (TEM) was carried out in a JEOL100 CX II electron microscope using an accelerating voltage of 100 kV. Ultrathin sections of the composites with a thickness of ~60 nm were prepared using an ultracryomicrotome equipped with a diamond knife. Images were taken at different magnifications (10000 \times , 40000 \times and 50000 \times).

The molecular weight of the siloxane oligomers was determined by gel permeation chromatography (GPC) in an Agilent D2400 system equipped with differential refractive index detector and a linear Phenogel column. Monodisperse polystyrenes were used as calibration standards and chloroform (1 ml min⁻¹) as eluent. Siloxane oligomers were isolated from modified clays via 12 h soxhlet extraction with cyclohexane. Cleaned clays were dried until complete solvent elimination had been achieved prior to further analysis.

RESULTS AND DISCUSSION

XRD analyses

XRD patterns of MNa, HM and the siloxane-modified organoclays are given in Fig. 1. The increase in *d* spacing from 11.85 Å for MNa to 18.20 Å for the ammonium-salt-modified clay (HM) shows that interlayer ion exchange by

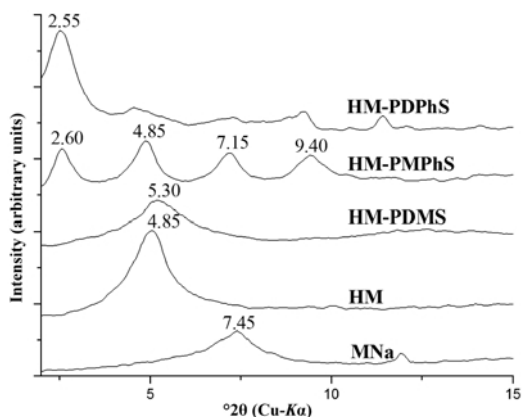


FIG. 1. X-ray diffraction patterns of MNa, HM and the siloxane modified-organoclays.

HDTMA ions took place. The value obtained for HM is equivalent to the sum of two diameters of the HDTMA ion, indicating the existence of a bilayer structure inside the clay galleries (Vaia *et al.*, 1994).

After adding water to and incorporating silanes in HM, *in situ* condensation polymerization occurs and siloxane species are generated. As a result, the patterns of these siloxane-modified phyllosilicates reveal important structural changes.

New peaks at $2\theta = 2.60, 4.85, 7.15$ and 9.40° are seen for HM-PMPHS, showing the existence of structures with different d spacings and an intercalation of the siloxane species generated *in situ*. In the MPhS structure (Fig. 2), the presence of $-\text{C}_6\text{H}_5$ rings increases the rigidity of Si-C groups due to the presence of a $\text{sp}^3\text{-sp}^2$ bond; consequently, siloxane oligomers will take up more space. The increase in the interlamellar spacing evident from the peak at 2.60° is a good indication of the existence of these larger species inside the clay galleries.

HM-PDPhS shows also four peaks at low angles ($<10^\circ 2\theta$) with an intense peak at $2\theta = 2.55^\circ$ as a result of the presence of siloxane species containing two aromatic rings inside the galleries. The d spacing in this case reached 34.6 \AA .

It is important to note that XRD traces of HM-PMPHS and HM-PDPhS show one peak with a 2θ angle greater than that of the MNa (001) plane at 9.4° . This peak cannot be associated with a decrease in the d spacing because the smaller distance between platelets must be that observed when the clay negative charges are offset by Na ions. Therefore the peak was attributed to (002) clay planes (Sinha Ray & Okamoto, 2003).

In the system HM-PDMS (modified with DMS), the peak related to the clay (001) plane remains near the 2θ angle of HM, which suggests that no siloxane intercalation has taken place. However, during the addition of the silanes to the HM clay, a large absorption of the silane by the clay is observed in all silanes, with generation of a paste that becomes a powder after washing and drying. This behaviour is an indication that all silanes employed here have the same diffusion behaviour, penetrating into the galleries and subsequently polymerizing inside them.

Figure 2 indicates the structures of the chlorosilanes used in this work (Chemdraw 5.1). The silanes have smaller dimensions than the basal space reached by HM and the DMS dimensions are the lowest. Thus, one explanation for the absence of change in the position of the clay plane (001) in HM-PDMS might be the high flexibility of the short PDMS chains. It is possible that oligomeric species have been formed inside the galleries in the free volume left by the alkyl ammonium chains.

FTIR analyses

FTIR analyses (Fig. 3) were carried out on clay powders showing the characteristic absorptions of the organic groups in the silanes. The spectra of MNa and HM were added for comparison. The MNa spectrum shows the characteristic peak of structural $-\text{OH}$ stretching vibrations at 3630 cm^{-1} (Lv *et al.*, 2008; Yürüdü *et al.*, 2005). According to the Schultz criterion, the clay used was a non-ideal montmorillonite. Thus its structure may correspond to that of the Hofmann-Endell-Wilm-Marshall-Maegdefrau-Hendricks or the Edelman-Favejee

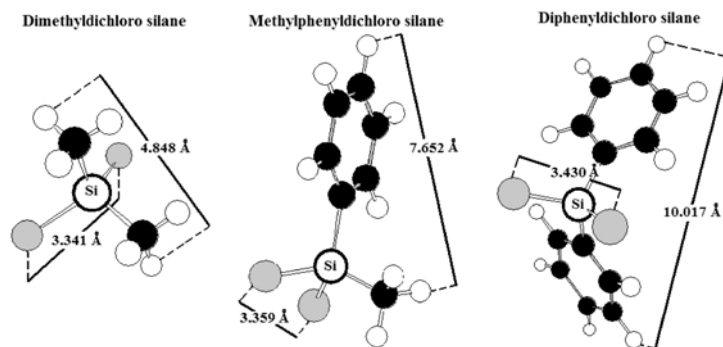


FIG. 2. Simulated molecular structures of chlorosilanes.

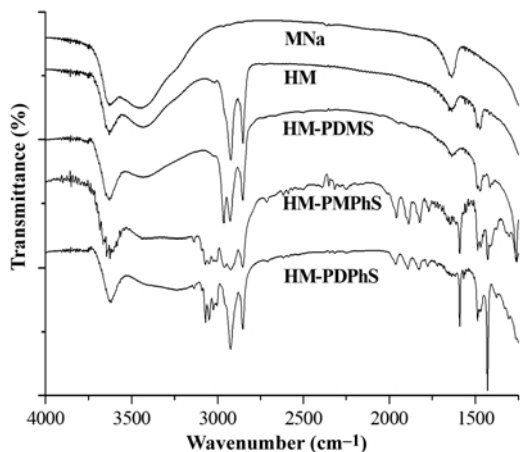


FIG. 3. FTIR spectra of MNa and modified clays.

structure. Consequently, $-\text{OH}$ groups could be bonded to a Si or Al atom (Theng, 1974). Also, MNa shows a broad absorption at 3450 cm^{-1} corresponding to $-\text{OH}$ vibrations of adsorbed water. The intensity of the 3450 cm^{-1} absorption decreases in the silane treated-clays, indicating a decrease of water absorption, which is confirmed by TG-DTG analyses (Fig. 6). Another indication of the presence of moisture is the weak broad peak at 1637 cm^{-1} observed in the MNa, HM and HM-PDMS spectra.

For HM-PMPHS and HM-PDPhS, a sharp medium-intensity peak at 1429 cm^{-1} is seen, due

to the presence of Si bonded with an aromatic carbon.

In all spectra, except for MNa, there are absorptions at 2926 cm^{-1} , corresponding to the asymmetrical stretching of methylene groups, and its symmetrical stretching at 2853 cm^{-1} . There is also an absorption band at 2965 cm^{-1} , corresponding to the asymmetrical stretching of methyl groups of HM-PDMS and HM-PMPHS. Low-intensity combination bands between 1765 cm^{-1} and 1965 cm^{-1} are observed in HM-PMPHS and HM-PDPhS, proving the presence of phenyl groups in these materials. Stretching bands of C-H aromatic bonds at 3000 and 3100 cm^{-1} , and C-C bending of aromatic rings at 1591 cm^{-1} are also identified, confirming the presence of aromatic groups in these two modified clays.

These results do not necessarily prove the existence of siloxane oligomers. For this reason, soxhlet extractions of silane-treated clays were carried out. During this process only siloxane species were lixiviated while HDTMA ions remained in the structure, keeping the system electrically neutral. The lixiviated siloxanes were also analysed by GPC. Table 2 summarizes the results.

The FTIR analyses carried on each soluble fraction sample obtained from extraction of the treated clays confirm the formation of siloxanes into HM lamellae. After solvent extraction the clays were also analysed by FTIR. Figure 4a and b shows the presence of characteristic groups of silanes used

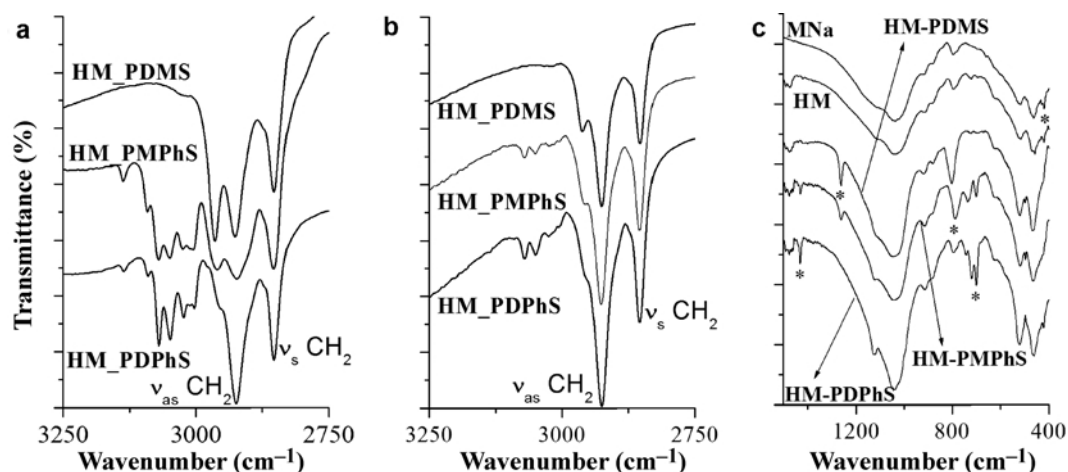
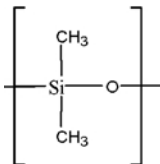
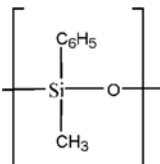
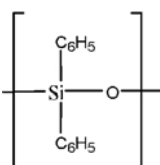
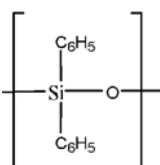


FIG. 4. FTIR spectra of siloxane modified clay from 3250 to 2750 cm^{-1} (a) before and (b) after solvent extraction; (c) FTIR spectra of siloxane modified clays after solvent extraction from 1500 to 400 cm^{-1} .

TABLE 2. Data obtained from GPC analyses.

Smallest basic unit	m ^a	Mn	Polydispersity ^b	DP ^c
	74	375	1.10	~5
	136	392	1.32	~3
	198	73·100	2.37	~537
	198	331	1.26	~2

^a m= Repeating unit molar mass (g mol⁻¹)

^b Polydispersity (Mw/Mn)

^c DP= Degree of polymerization (=Mn/m)

in this work before and after extraction. Methylene characteristic peaks are identified as references; they belong to HDTMA chains. Peaks with lower intensity can be seen at the same position after the extraction process.

The results indicate that oligomeric species are formed in both states, free and covalently bonded to clay surfaces states. To confirm silane-clay grafting, FTIR spectra of the extracted clays were evaluated between 1500 and 400 cm⁻¹ (Fig. 4c). Grafted oligomers have been identified by the peak at 1430 cm⁻¹ (phenyl ring) and by the bands between 750 and 650 cm⁻¹ (out of plane bending aromatic C-H) for HM-PMPHS and HM-PDPhS; also by the peak at 1260 cm⁻¹ (symmetric deformation of the methyl groups, Si-CH₃) and the band near to 800 cm⁻¹ (stretching of the Si-C link) for HM-PMPHS and HM-PDMS. The last peak is typical for the Si-CH₃ group, but it exhibits shifts according to the nature of the substituting groups (Fujii *et al.*, 1999; Silverstein & Webster, 2004; Smith *et al.*, 1991).

Following Dai & Huang (1999), FTIR spectra of clays treated with coupling agents will show changes if there is a chemical link between them as a consequence of chemical environment modification; but if interactions are weak (molecules coating on or adsorbing to the clay surface) FTIR spectra should be invariant. In Fig. 4c, changes were noticed at 520 cm⁻¹ and 460 cm⁻¹ corresponding to Si-O-Mg and Si-O-Fe groups, respectively (Yürüdü *et al.*, 2005).

Other changes were noticed in the intensities of the 1050 cm⁻¹ band in the FTIR spectra (Fig. 5). In order to avoid the effect of concentration on sample preparation, the -CH₂ symmetrical stretching peak (2853 cm⁻¹) from HDTMA ions was used as a reference. As has been mentioned above, these species will not be removed by the solvent because they maintain the electroneutrality of clay lamellae, which can be considered as macroanions with alkylammonium ions as compensating cations (Annabi-Bergaya, 2008). The species affected by

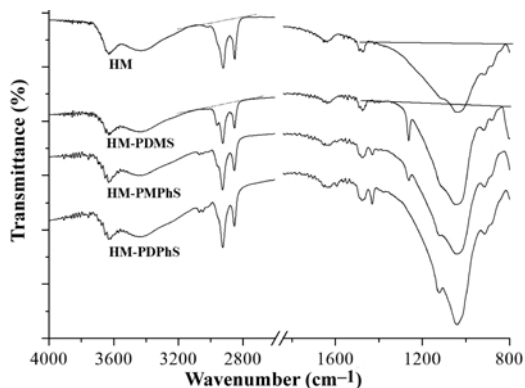


FIG. 5. Comparison of FTIR spectra of siloxane-modified clays after solvent extraction.

cyclohexane (solvent) are those of free or grafted oligo-siloxanes.

After drawing baselines (Fig.5), an increase in the 1050 cm^{-1} band intensity was observed; this can only be explained by an increase in Si–O–Si bonds. Intensity changes were as follows:

HM-PDPhS > HM-PMPPhS > HM-PDMS, which indicates that the amount of covalently bonded species differs for each clay.

This experimental fact is associated with the solvolysis process during soxhlet extraction, which is governed by oligomer chain flexibility and length and by the stability of the cyclic species that form during silicone decomposition. The nature and size of the hydrocarbon groups bonded to the Si atom (Fig. 2) will determine the stability of cyclic species (trimers and tetramers). Thus the solvolysis mechanism is different for each siloxane. In Fig. 6 a bond-breaking process for oligosiloxanes is proposed.

The mechanisms outlined in Fig. 6b and c can take place in the three clays studied. However, according to the GPC results and R–Si–R' bond flexibility, it is expected that cyclization (Fig. 6b) occurs in HM-PDMS. The mechanism in Fig. 6c is more feasible for HM-PDPhS due to the presence of the phenyl group which makes the ring more unstable. HM-PMPPhS shows an intermediate behaviour.

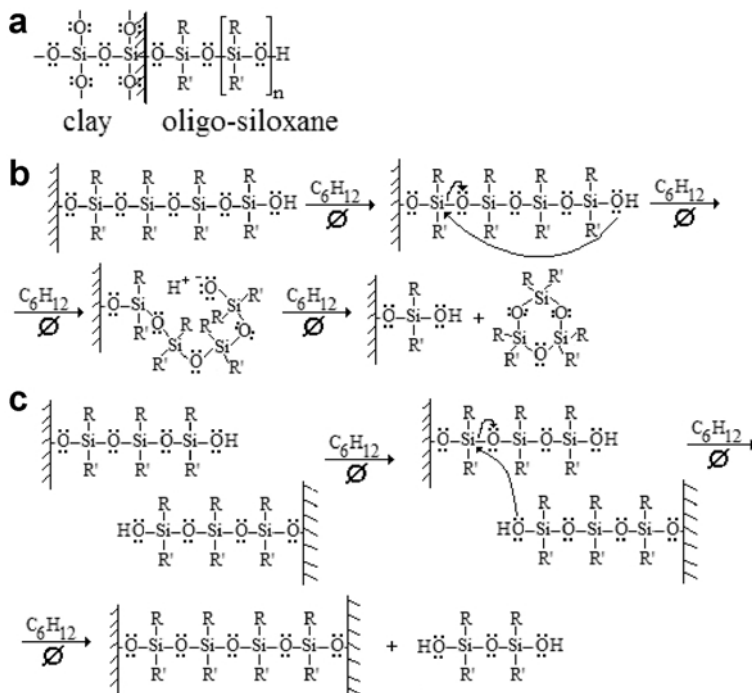


FIG. 6. (a) Representation of Si-O-Si bonds that are present in grafted oligo-siloxanes; (b) and (c) mechanisms proposed for the reactions that may take place during solvolysis. (For clarity, HDTMA ions were omitted from Fig. 6). (R, R' = -CH₃, -C₆H₅).

Consequently, HM-PDMS after extraction would have fewer Si-O-Si bonds, but HM-PDPhS will retain a large concentration of those bonds, which matches the tendency observed for the 1050 cm^{-1} band in Fig. 5.

Thermogravimetric analyses

Figure 7 shows the TG and DTG curves of the clay materials. The final weight loss increases in treated clays because the organic content also increases. Nanoplatelets coated with PDMS and PDPhS siloxanes show higher degradation temperatures than the others organophilic clays.

Figure 7b shows a peak at 52°C for MNa, indicating the presence of water in this material. This peak decreases for HM and tends to disappear in materials treated with siloxanes. The thermal behaviours observed for MNa and HM match those described by Picard *et al.* (2007), Shen *et al.* (2007) and Song *et al.* (2002). They reported a decrease in clay water content after cationic exchange and a weight loss between 3 and 5 wt.% of structural $-\text{OH}$ for pristine montmorillonite. These results confirm that the $-\text{OH}$ peak (3630 cm^{-1}) observed in the FTIR spectra of silane-modified clays corresponds to the Si-OH bond in siloxane end groups (Fig. 3).

Degradation products arise from the homolytic rupture of HDTMA alkyl chains, cyclic compounds that are generated when clays are modified by siloxanes, and other organic products from methyl or phenyl groups, such as benzene (Camino *et al.*, 2002; Jovanovic *et al.*, 1998). From TG analysis of

pure siloxanes, it is possible to determine the products obtained by non-oxidizing degradation (Camino *et al.*, 2002; Tiwari *et al.*, 2004; Zulfiqar & Ahmad, 1999). Usually, silicones start to depolymerize above 200°C (Kricheldorf, 1996) which agrees with the curves observed in Fig. 7b. However, these species can be coatings on the external surfaces of the sheets, or may be intercalated or grafted into the clays analysed in this work. Therefore several stages have been observed during degradation.

It can be seen (Fig. 7b) that HM has two degradation steps between 150 and 350°C , whereas HM-PDMS shows a peak between 170 and 280°C and a higher degree of degradation in the range 400 – 550°C . HM-PMPHS has an important weight loss between 200 and 350°C , followed by other degradation step up to 500°C . Finally, HM-PDPhS shows a first degradation in the range 200 – 270°C and a second step with a maximum at 371°C that ends at $\sim 550^\circ\text{C}$. According to Shen *et al.* (2007), He *et al.* (2005) and Park & Kwon (2004), the intercalated species and organic moieties will degrade up to $\sim 400^\circ\text{C}$, while grafted compounds will decompose above that temperature range. This indicates the presence of oligomers grafted into siloxane-treated clays.

GPC results (Table 2) show a unimodal distribution in the siloxane-treated clays, except for HM-PMPHS. This would explain why DTG curves (Fig. 7b) show peaks at certain ranges of temperature; the synthesized oligomeric species have a characteristic average molecular weight, so they degrade at specific temperatures.

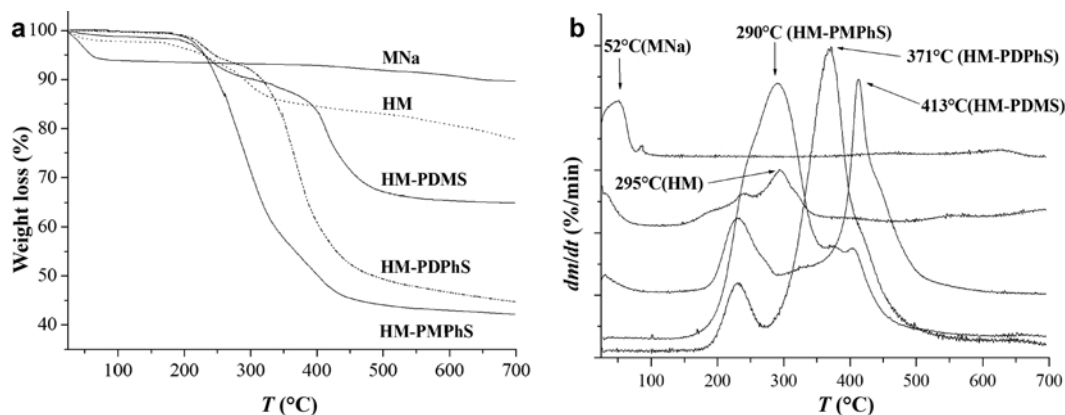
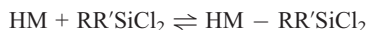


FIG. 7. (a) TG and (b) DTG curves of MNa and modified clays.

Mechanism proposed

All this experimental evidence for siloxane formation enables us to propose a clay-silane interaction mechanism which takes into account the nature of both components and the preparation method.

The first step to be considered is the HM-silane equilibrium when contact occurs:



Organosilanes have a low polarity and diffuse into the interlamellar spaces of HM as was confirmed by XRD (Fig. 1). Between clay platelets there are alkyl chains of ammonium ions saturated with chlorosilanes until equilibrium concentration is reached.

Schemes describing the possible HM-organo-silane interactions are presented in Fig. 8. In this figure, reactions are shown based on HM function-

ality, the presence of $-\text{OH}$ groups and the equilibrium between negative clay charges and R_4N^+ .

Figure 8a shows nucleophilic reaction of $-\text{OH}$ groups on the silicon, generating a covalent bond between HM and silane. This new species reacts with $-\text{OH}$ groups in montmorillonite platelets as shown in Fig. 8b. HCl is eliminated, connecting the clay with silane by $-\text{O}-\text{Si}-\text{O}-$ interactions which have the same nature of the existing bonds on clay nanoplatelets. Reactions outlined in Fig. 8a and b correspond to a species that remains covalently bonded to the nanoplatelets, while reactions in Fig. 8c and d may also take place on free silane molecules.

Figure 8c presents the reaction between water and the species generated in Fig. 8a, forming a silanol group. Siloxane chains bonded to HM are generated when silanol groups react with silane monomers as shown in Fig. 8d.

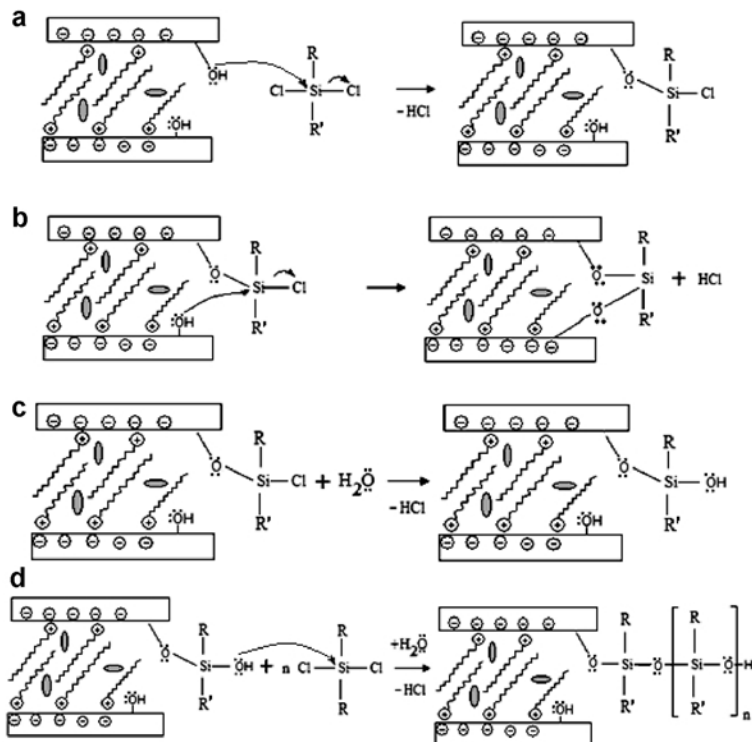


FIG. 8. Schemes of possible reactions that take place when HM is treated with chlorosilanes. Grey ovals represent silane molecules dispersed between clay platelets. One of these molecules of monomer was amplified to show what may occur during clay treatment. PDMS: $\text{R} = \text{R}' = (-\text{CH}_3)$; PMPHS: $\text{R} = (-\text{CH}_3)$; $\text{R}' = (-\text{C}_6\text{H}_5)$ and PDPHS: $\text{R} = \text{R}' = (-\text{C}_6\text{H}_5)$.

It is important to mention that the hydroxyl groups represented in Fig. 8 may correspond to either Si–OH or Al–OH bonds according to the theoretical structure accepted (Hofmann or Edelman structures). In addition, according to He *et al.* (2005) and Shanmugaraj *et al.* (2006), the presence of –OH groups can be due to structural defects in the Si–O tetrahedral sheet and the layer edges with ‘broken’ bonds that will be active, similar to the Si atom environment in silica. If they react with silane during grafting, interlayer, external surface and ‘broken’ edge grafting will be allowed.

Morphology of siloxane-modified clays

SEM micrographs of MNa and modified clays are shown in Fig. 9. These clays exhibited different morphologies. Differences between MNa and HM are quite important. The incorporation of HDTMA causes a disintegration of the initial particle of clay due to interlamellar stress resulting from the entrance of the organic phase into the galleries. X-ray results are consistent with this gradual modification of the montmorillonite structure (Fig. 1).

Silane *in situ* polymerization has changed the final aspect of organophilic clays. In the SEM images in Fig. 9c and d (HM-PDMS and HM-PMPHS), the particle sizes seem to be similar to that of HM (Fig. 9b), but these particles are covered with polymeric material. In the case of HM-PMPHS (Fig. 9d), although the siloxane-modified clay resembles the material in Fig. 9c, a higher state of disintegration is clearly observed. This might result from the greater rigidity and size of the chains of PMPHS species. This effect is even more accentuated in the image in Fig. 9e, corresponding to the sample treated with DPhS. The two phenyl groups give more rigidity to the siloxane chains of PDPhS.

Finally, in Fig. 9e ‘laminar groups’ can be observed. This explains what happens in (d) because only a few ‘laminar groups’ can be present in HM-PMPHS, due to the shape and molecular size of MPhS.

Morphological analyses of HDPE modified with siloxane-treated clays

Aiming to verify whether silane-clay treatments contribute to compatibilization of phyllosilicates

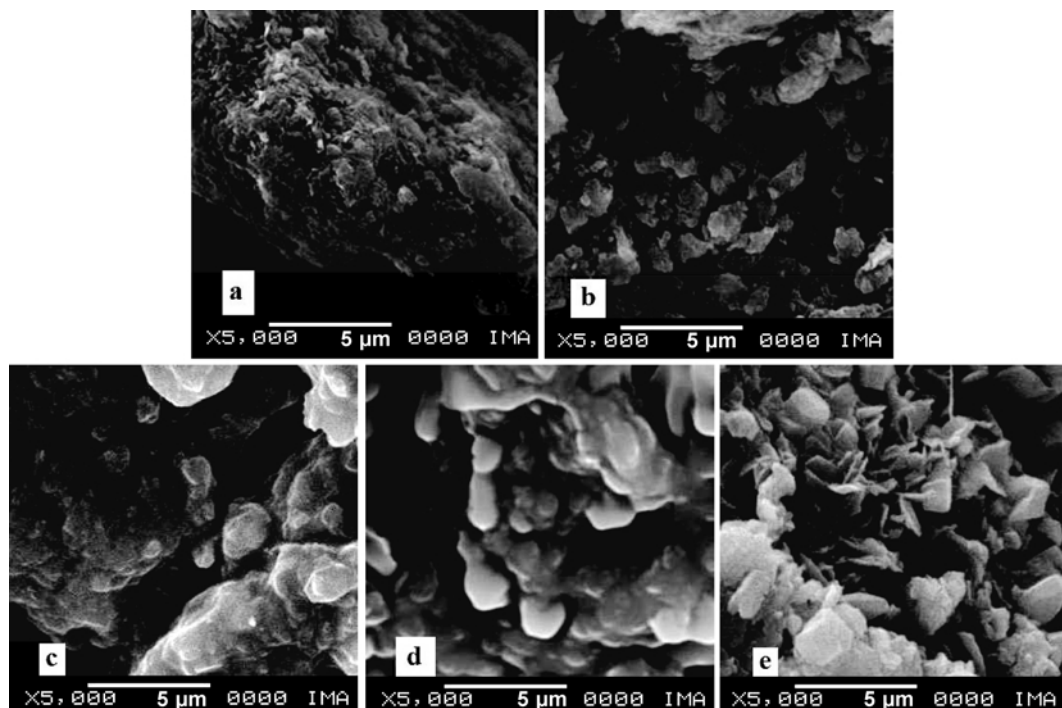


Fig. 9. SEM micrographs of clays (a) MNa, (b) HM, (c) HM-PDMS, (d) HM-PMPHS and (e) HM-PDPhS.

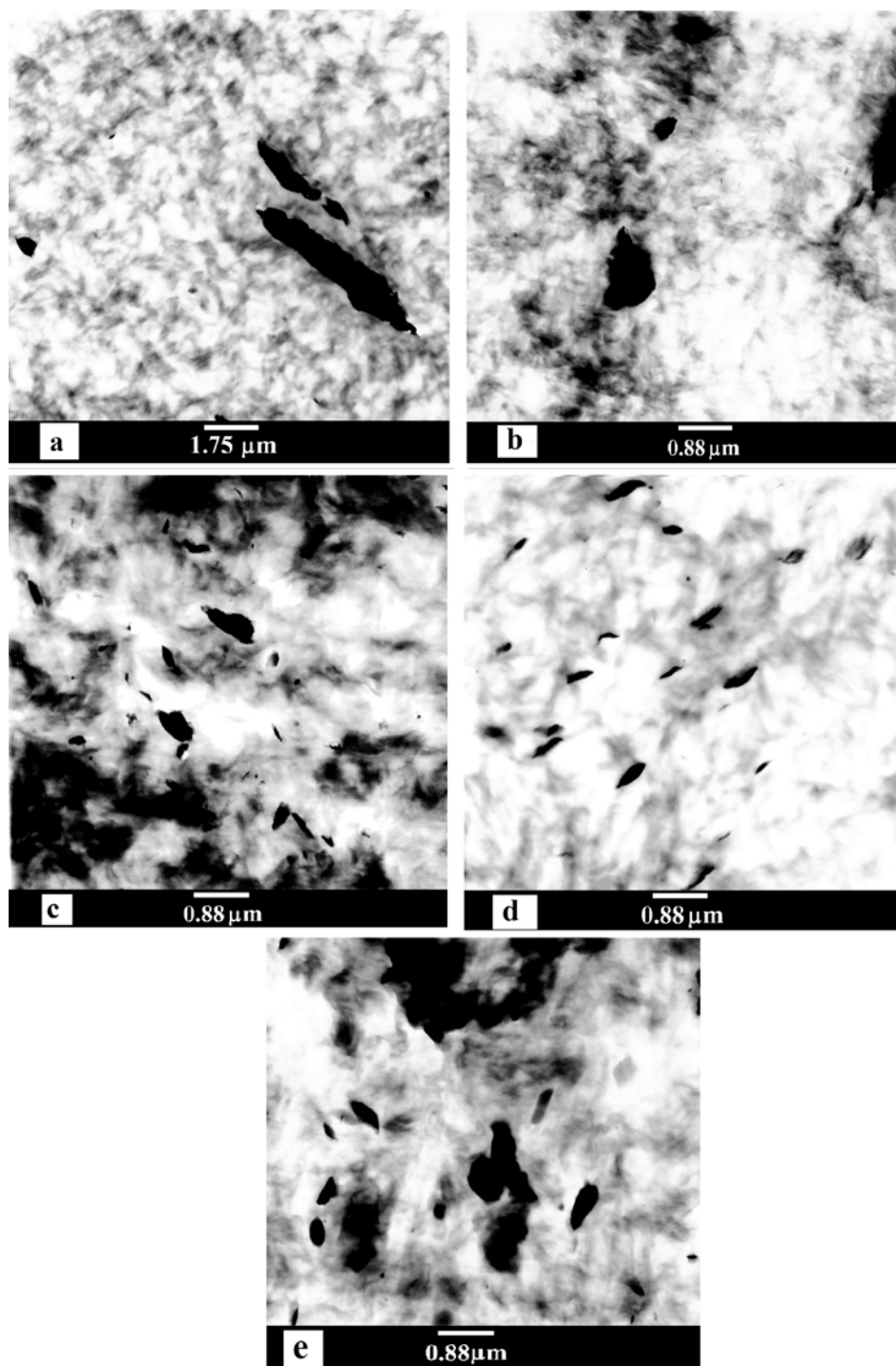


FIG. 10. TEM micrographs of HDPE modified by (a) MNa, (b) HM, (c) HM-PDMS, (d) HM-PMPHS and (e) HM-PDPHS.

with a hydrocarbon polymer matrix, siloxane-treated clays were added to HDPE by melt processing. Figure 10 shows TEM images of HDPE modified by pristine clay, organophilic clay and the organophilic clay modified with the different silanes. The last samples show greater platelet disaggregation, leading to particles of nanometric size. In the case of HM-PMPHS, the dispersion achieved is more homogeneous than the other samples under the conditions evaluated in this work.

When MNa turns into HM, the medium existing between the clay platelets becomes organophilic. However, this primary modification usually is not enough for achieving a good polymer-clay interaction, especially when polyolefins are used as the matrix. Recently, three methods have been suggested for olefin polymers: *in situ* polymerization, the solvothermal method and melt intercalation (Lee *et al.*, 2005). Depending on the technique chosen, different degrees of clay delamination will be achieved. *Via* melt processing, only exfoliated/intercalated structures are obtained when organophilic clay is used with compatibilizers which may commonly be copolymers with the backbone of the same nature of polymer matrix (Lee *et al.*, 2005).

For the systems evaluated on this paper, it has been observed that using siloxane-treated clays leads to an improved organophilic clay dispersion into polyolefin on a nanometric scale, without using a copolymer as compatibilizer.

CONCLUSIONS

Organophilic clay was modified using three different silanes. Results show several differences in final clay properties related to silane functional groups and their diverse oligomer lengths. These modified materials can be used as polyolefin additives, anticipating that the treatment will lead to an improved integration between clay nanoplatelets and the polymeric matrix.

Modifications carried out on montmorillonite change two factors in silane-treated clay. (1) *The internal structure of the additive*: XRD results show new interlamellar distributions for each siloxane. The interlamellar distribution varies according to silane functional groups, promoting different arrangements of HDTMA alkyl chains. (2) *The possible interactions with the polymer matrix*: it has been shown that HM-PMPHS clay achieves a better dispersion than other clays in a hydrocarbonated

polymer such as HDPE. This implies that not only is a large basal spacing important for clay delamination but also for its chemical affinity, as can be seen with HM-PDPHS. This clay shows the greatest XRD shift at lower angles. However HM-PMPHS was better dispersed, probably due to the presence of $-CH_3$ groups. It is to be expected that clay-macromolecule interactions will change due to the different chemical natures of functional groups present in siloxane chains, but further research with these siloxane-coated clays must be carried out.

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