

Thermal and Rheological Properties of Polyethylene Composites Based on Poly(diphenylsiloxanes)/Organoclay Hybrids Obtained from Two Different Silanes

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Summary: Poly(diphenylsiloxanes) (PDPhS) were synthesized in presence of organophilic clay in order to modify its nanostructure. Two silane monomers were used: dimethoxydiphenylsilane and dichlorodiphenylsilane. The following characterizations were performed for all clays: XRD, FTIR, TG/DTG and SEM. These siloxane-modified clays were more hydrophobic and had enhanced thermal stability. Solvent extraction was carried out in the siloxane-modified clays and the PDPhS soluble fraction analyzed according the molecular weight via GPC. The presence of free and grafted oligomers on clay surface was identified. The modified clays were added to high density polyethylene (HDPE) by melt processing to obtain HDPE/hybrid clay composites which exhibited marked differences on macroscopic properties when compared with neat HDPE.

Keywords: clay; HDPE; inorganic/organic hybrids; oligomers; poly(diphenylsiloxane)

Introduction

The use of compatibilizers is a widespread technique used to modify the interfacial properties of fillers in order to modify polymer properties.^[1–3] Many examples of compatibilized nano- or microfilled composites are reported in the scientific literature.^[4–12]

In the case of hydrocarbon polymers (with apolar nature) the use of clays as inorganic fillers implies the modification of their polar nature by the introduction of organic groups to give them an apolar surface.^[13–15] In general silicate lamellae are modified with ammonium ions or silanes; with copolymers^[16] or oligomers^[17] and in some cases they are pretreated with

monomers that will serve as precursors of the polymer matrix.^[7–9,18,19]

The aim of this work is to use these concepts to obtain a hybrid nanomaterial from a sodium montmorillonite to modify HDPE properties. This clay was modified with ammonium ions and subsequently treated with difunctional silanes aiming to generate a hybrid clay by the synthesis of siloxanes oligomers by hydrolysis/condensation reactions.

In this case a polysiloxane is proposed as compatibilizer because they have an inorganic skeleton (of the same nature of clays) with organic side groups, which provide great versatility to these molecules.^[20]

On the other hand, polysiloxanes with identical side groups can be prepared from different silanes and for that reason it is important to study the effect of silane leaving groups during the preparation of modified clays. These hybrid materials, which will function as filler of hydrocarbon polymer, were prepared from two silane precursors following the same method and

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they were characterized before being introduced into HDPE.

In particular, this work analyzes whether the use of these two different silanes precursors on montmorillonite affects the thermal and rheological behavior of HDPE/hybrid clay composites. The interest in studying these properties is because they determine further material applications besides, they influence on polymer processing conditions.^[19,21,22]

Experimental Part

Materials

The sodium montmorillonite (MNa) was supplied by MINARMCO S.A. (CEC = 70 mEq/100 g, particle size <325 M). The chemical composition of MNa^[23] is (wt%): SiO₂ = 62.0; Al₂O₃ = 18.0; MgO = 3.0; Na₂O = 3.5; CaO = 2.0; K₂O = 1.0; Fe₂O₃ = 7.0; others = 3.5. Hexadecyltrimethylammonium chloride (HDTMA-Cl) GENAMIN CTAC provided by PharmaSpecial. Diphenyl-dichlorosilane (DPhS_{Cl}) and diphenyl dimethoxisilane (DPhS_{OCH₃}) were purchased from SIGMA ALDRICH. HDPE with a MFI = 0.41 g/10 min and a density of 0.9530 g/cm³ was obtained from POLISUR (trade name, 40055L).

Preparation of Organophilic Clay

A 5% wt/v water dispersion of MNa clay was prepared and mixed with HDTMA during 2 h at 80 °C. Then it was filtered and washed until the complete Cl⁻ elimination. The organophilic clay (MC₁₆) was dried at 80 °C for 48 h.^[7]

Preparation of Siloxane Modified Organoclay Hybrids

Silanes were mixed with MC₁₆ in a ratio of 1 to 1 in weight and were maintained in contact for 5 days at room temperature. Distilled water was then added on a H₂O/Si = 20 molar ratio and the mixture kept in contact for another 5 days. Samples were washed until the complete elimination of HCl and CH₃OH. The final intercalated nanomaterials obtained after drying were

named: MC₁₆-PDPhS(Cl) and MC₁₆-PDPPhS(OCH₃).

Preparation of HDPE/PDPPhS/

Clay Composites

HDPE pellets (97 wt%) and modified clays (3 wt%) were mixed using a Haake torque rheometer Rheocord 9000 equipped with a mix chamber and roller rotors at 100 rpm and 190 °C.

Characterization

X-ray diffraction analyses (XRD) were performed at 2°/min in a Rigaku Miniflex DRX600 diffractometer using Ni filtered CuK α radiation at 30 kV and 15 mA. HDPE composites samples (thickness ~2 mm) were prepared by compression molding at 190 °C and cooled under pressure by water circulation. Measures were performed in duplicate.

Clay samples were evaluated by infrared spectroscopy in a Perkin Elmer FTIR 1720x using pressed KBr disks, at 2 cm⁻¹ of frequency resolution.

The thermal gravimetric studies (TG/DTG) were performed in a TA TGA Q500 from 25 to 700 °C (heating rate = 10°/min, nitrogen flow = 60 mL/min).

Scanning electron microscopy (SEM) of clays was carried out in a JEOL JSM-5610 LV microscope at 15 kV. SEM microphotographs of HDPE/hybrid clay composites were carried out in a JEOL JSM-6480 LV at 20 kV and 30 kV. Samples were immersed in liquid N₂, then fractured and Au-coated. Several images at various magnifications were studied.

Transmission electron microscopy (TEM) was carried out in JEOL100 CX II electron microscope at 100 kV. Ultrathin sections of the composites (thickness ~60 nm) were prepared by ultracryomicrotomy. Images were taken at different magnifications.

Siloxanes oligomers molecular weights were determined by gel permeation chromatography (GPC) in an Agilent system equipped with differential refractive index detector and a linear Phenogel column (calibration standards = monodisperse PS, solvent = CHCl₃, 1 mL/min). Oligomers

were isolated from the modified clays via soxhlet extraction with C_6H_{12} . Extracted clays were dried until complete solvent elimination.

Composites rheological behavior was evaluated at $200^\circ C$ using a parallel disks rheometer TA AR2000 ($D=25$ mm, $h=1$ mm, N_2 atmosphere). The range studied was between $0.1 \leq \omega \leq 100 \text{ rad s}^{-1}$. A strain sweep experiment was performed at a fixed frequency of 5 rad/s.

Results and Discussion

Analyses of Siloxane Modified Clay

GPC Analysis

GPC results from the soluble fraction of clays modified by DPhS-Cl and DPhS- OCH_3 are presented in Table 1. Both monomers produced cyclohexane soluble siloxanes species with similar features, i.e., considering the PS used as GPC calibration standards, only dimers were obtained. The mentioned soluble fraction was analyzed by FTIR confirming the synthesis of PDPHS on treated clays.

Thermogravimetric Analyses

Figure 1 shows the curves obtained from the thermogravimetric analyses of all clays.

MC_{16} shows a lower weight loss than MNa under $100^\circ C$. A similar behavior has been observed by Picard et al. [13] after clay modification with organic cations. This weight loss is related with water moisture and it almost disappears for PDPHS treated clays.

MC_{16} -PDPHS(Cl) and MC_{16} -PDPHS(OCH_3) have higher final weight losses because the amount of organic components is higher. Authors such as Shen et al. [24], Camino et al. [25] and Zhu et al. [26] explained that several DTG peaks are observed on silane treated clays due to different bonding environment, and especially chemically bonded species are those who degrade at higher temperatures (400 – $500^\circ C$). From siloxane organoclay hybrids it can be seen that weight losses take place at higher temperatures than for MC_{16} . Thus it is inferred the existence of more stable species indicating improvement in the thermal stability. This may be an advantage because during processing the

Table 1.

GPC analyses of modified clays

Modified clay	Smallest basic unit	m ^{a)}	Mn	Polydispersity ^{b)}	DP ^{c)}
MC_{16} -PDPHS (Cl)	$[-Si(C_6H_5)_2-O-]$	198	331	1.26	~ 2
MC_{16} -PDPHS (OCH_3)	$[-Si(C_6H_5)_2-O-]$	198	361	1.08	~ 2

^{a)}m = repeating unit molar mass [g/mol] ^{b)}Polydispersity (Mw/Mn) ^{c)}DP = Degree of polymerization (=Mn/m)

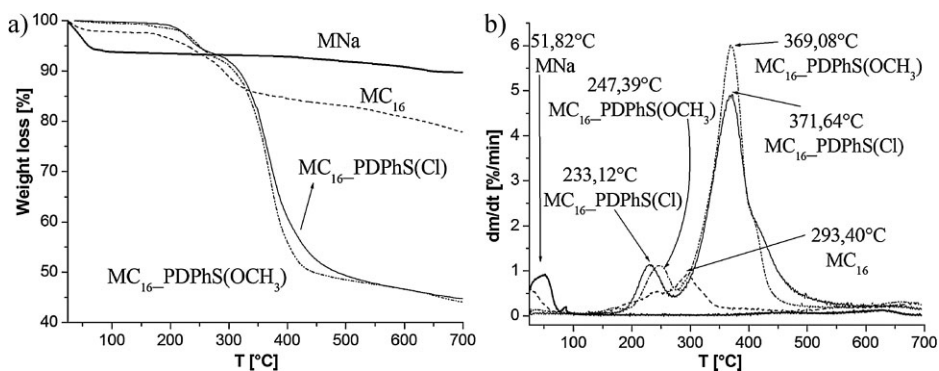


Figure 1.

a) TG and b) DTG curves of MNa, MC_{16} and silanes treated clays.

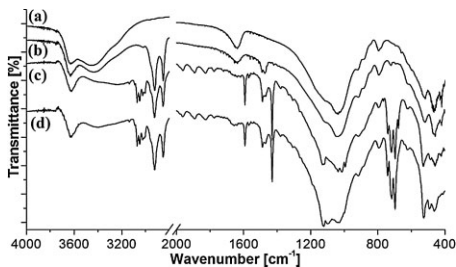


Figure 2.

Infrared spectra of (a) MNa, (b) MC_{16} , (c) MC_{16} -PDPhS(Cl) and (d) MC_{16} -PDPhS(OCH_3).

interlamellar structure of clays modified with alkyl ammonium chains does not stay intact.^[21,22]

In the silane modified clays, it is expected that intergallery spaces remain the same during HDPE mixing ($T_{\text{processing}} \sim 200^\circ\text{C}$), which could facilitate intercalation and/or delamination.

Infrared Spectroscopy Analyses

Characteristic bands of the clays used in the preparation of HDPE/hybrid clay composites are observed on Figure 2. The presence of HDTMA ions is evidenced due to bands at 2926 cm^{-1} (CH_2 asymmetrical stretching), 2853 cm^{-1} (CH_2 symmetrical stretching) and 1480 cm^{-1} (CH_2 in-plane bending).^[24,27] The 3400 and 1640 cm^{-1} bands are related to $-\text{OH}$ groups on the phyllosilicates.^[28] A decrease in the $\text{H}-\text{O}-\text{H}$ deformation peak (1640 cm^{-1}) is noted in the DPhS modified

clays, indicating that these materials become less hygroscopic as it was confirmed by TG/DTG data (Figure 1).

The characteristic peaks of Si-OH stretching vibrations (3630 cm^{-1}) and Si-O-Si (1050 cm^{-1}) are observed for all samples.^[29] On the other hand, the presence of aromatic species is detected by the set of bands from 1720 to 2020 cm^{-1} (monosubstituted aromatic), the peaks corresponding to aromatic C-C stretching within the ring (1590 cm^{-1} , 1430 cm^{-1}), and the out of plane bending aromatic C-H (750 to 650 cm^{-1}).^[30] Considering these results, it seems that no significant differences could exist between clays modified by the two diphenylsilanes. However, vibrational changes under 1300 cm^{-1} were noticed when compared with those of MC_{16} (Figure 2). In order to have more insights on the nature of the species trapped in the clay, IR spectra of MC_{16} modified with both diphenylsiloxanes were compared to clays before hydrolysis (Figure 3a). Another comparison was carried out between spectra of MC_{16} -PDPhS(OCH_3) and MC_{16} -PDPhS(Cl) after soxhlet extraction and MC_{16} (Figure 3b). Both comparisons would provide information about species covalently bonded to the clay. According to Dai et al.^[31], molecules of the coupling agent fixed on the clay mineral surface by chemical bonding change the IR spectra.

As CH_2 symmetrical and asymmetrical stretching bands are present in all modified clays (Figure 3a), they were used as reference

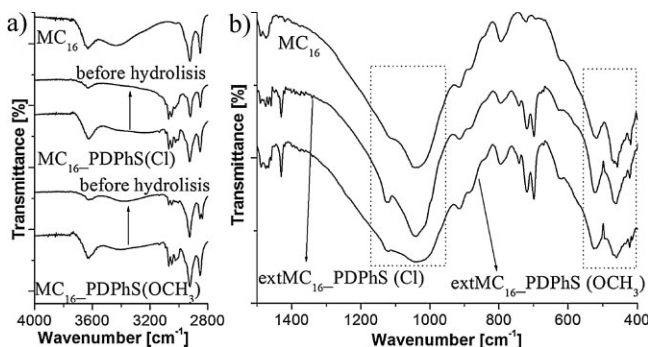


Figure 3.

Comparison among infrared spectra of: a) MC_{16} -PDPhS(Cl) and MC_{16} -PDPhS(OCH_3) with MC_{16} modified with silanes before hydrolysis and b) MC_{16} with MC_{16} -PDPhS(Cl) and MC_{16} -PDPhS(OCH_3) after solvent extraction.

for comparison between spectra. Figure 3a shows that Si–OH and –OH bands decreased in MC₁₆ after silane addition, which indicated silane grafting on the clay surface.^[24]

On Figure 3b it is noticed that certain amount of siloxane species remains covalently bonded to clay layer surfaces (after cyclohexane extraction) as can be inferred by the presence of bands from PDPHS corresponding to phenyl ring (1430 cm⁻¹), and changes on the Si–O–Si (1050 cm⁻¹), Si–O–Mg (520 cm⁻¹) and Si–O–Fe (460 cm⁻¹) bands.^[32]

The extracted MC₁₆_PDPHS(Cl) presents a sharper Si–O–Si band evidencing different clay remaining structures. When MNa is modified by HDTMA ions, Si–O–Si band observed on FTIR spectra correspond only to clay sheet structure (Figure 4a) and for that reason MC₁₆ has the same shape. But after silane hydrolysis, the Si–O–Si band exhibit vibrational changes caused by the presence of siloxane species of Figure 4b.

The differences in the spectra of MC₁₆_PDPHS(OCH₃) and MC₁₆_PDPHS(Cl)

have suggested that the polymerization of the two silanes have generated different distributions of siloxanes inside the clays which could be related with the diffusion of the monomers. To justify this hypothesis, molecular structures of each species were analyzed by Chem3D Ultra software (Figures 4c and 4d).^[33]

The phenomenon of liquid-phase diffusion is very complex to describe. However many correlations (e.g.: Stokes-Einstein theory) depicts the diffusion coefficient as inversely proportional to the size of the solute molecules.^[34] Regarding silane-MC₁₆ system, solutes (silanes) will diffuse through the organic environment provided by alkyl chains in MC₁₆.

Considering the values on Table 2, DPhS_Cl can diffuse more easily than DPhS_OCH₃ due to its lower size. Consequently, MC₁₆ galleries will retain more DPhS_Cl monomers.

Siloxane Modified Organoclay Synthesis

When silane is put in contact with MC₁₆, an equilibrium takes place (Scheme 1),

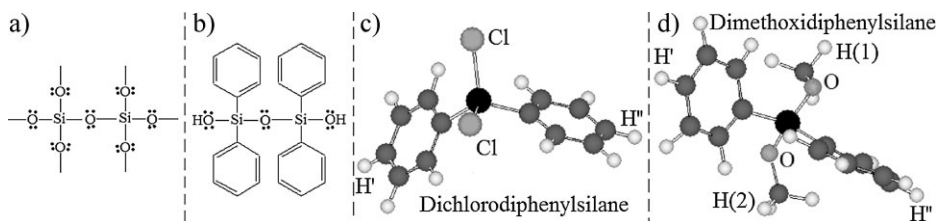


Figure 4.

a) Characteristic Si–O bonds present into clay sheets; b) characteristic Si–O bonds present into PDPHS dimers. 3D molecular structures of c) DPhS_Cl and d) DPhS_OCH₃.

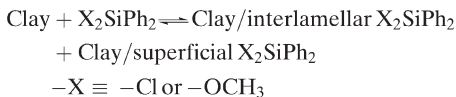
Table 2.

Data extracted from molecular simulation (Figure 4c and 4) and XRD patterns of clays modified with each species after hydrolysis

Silane	Area ^{a)} [Å ²]	Volume ^{b)} [Å ³]	Dipole Moment [Debye]	Distance between atoms [Å]	Interlayer distance ^{c)} [Å]
Cl ₂ Si (C ₆ H ₅) ₂	252	377	3.015	Cl–Cl = 2.108 H'–H'' = 8.770	25.1
(OCH ₃) ₂ Si (C ₆ H ₅) ₂	287	457	0.891	H(1)–H(2) = 6.215 H'–H'' = 9.865	22.0

^{a)}Connolly molecular area ^{b)}Volume was calculated from Connolly molecular area assuming spherical geometry.

^{c)}From XRD analysis assuming a lamella thickness = 9.5 Å

**Scheme 1.**

Equilibrium proposed for the process of diffusion during preparation of siloxane modified organoclay hybrids.

where the predominant interaction will depend on $-\text{X}$ group nature.

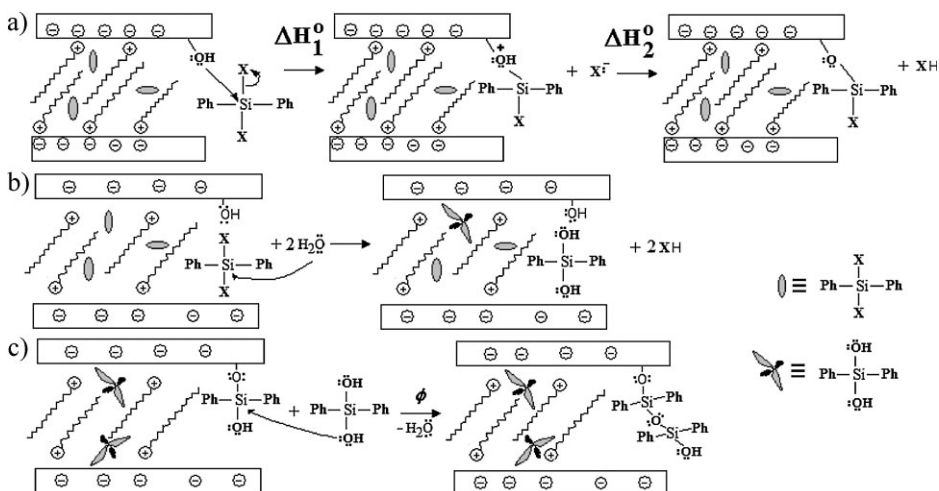
After water addition, the hydrolysis leaves a superficial coverage inside and outside nanoplatelets in both clays, but different amounts of siloxane oligomers will remain on each place according to the silane diffusion. There will be more oligomers outside nanoclay for MC₁₆-PDPHS(OCH₃). For this reason this clay spreads better on molten HDPE, offering a more compatible interface (Figure 9).

After hydrolysis, siloxanes oligomers can remain: i) grafted to clay lamellae, ii) bonded by van der Waals forces with alkyl chains of organophilic clay, or iii) bonded by hydrogen bonds with terminal hydroxyls and oxygen of the tetrahedral sheets.^[24–26,35,36] Global mechanism of modification is described in Figure 5.

In both systems, monomers have two phenyl groups and two leaving groups that allow obtaining PDPHS by hydrolysis and condensation. However, during MC₁₆ impregnation silanes interact in different ways with clay lamella surface (Figure 5a). Different energies are associated with bond scission on 1st stage according to the monomer used. When (C₆H₅)₂SiCl₂ is used, $-\text{OH}$ on clay surface reacts breaking Cl-Si bond (93 kcal/mol); whereas in (C₆H₅)₂Si(OCH₃)₂, it should occur a O-Si rupture (112 kcal/mol).^[20] ΔH_1° represents energy variation on 1st stage due Si-O bond formation between $\equiv\text{Si}-$ from monomer and $-\text{O}-$ from nanoclay; while ΔH_2° corresponds to enthalpy variation of the 2nd stage. Thus, there was a significant difference between these two systems at the 1st stage.

According to the experimental procedure, after water addition, a siloxane formation takes place from grafted silanes and free silanes (in excess) (Figure 5b).

Chemical interaction between (C₆H₅)₂Si(OCH₃)₂ and the phyllosilicate surface implicates breaking a bond of the same nature. Consequently, this will only takes place after water addition, because it

**Figure 5.**

Schematic illustration showing the steps involved on clay impregnation ($\text{X} \equiv -\text{Cl}$ or $-\text{OCH}_3$). a) Grafting of silane onto montmorillonite layer; b) hydrolysis on MC₁₆ impregnated with (C₆H₅)₂SiX₂ after water addition; and c) condensation that may occur during drying. Both, b) and c) reactions can take place with free or grafted molecules.

provides a stronger nucleophile to attack Si-OCH₃ allowing the reaction with clay. In this case, both free and grafted siloxane formation will occur simultaneously in this system. Thus, siloxane treated clay will have some differences due to their unequal genesis, not to mention, the difference in pH of each medium. Both aspects are supported by experimental results.

Morphological Analysis

SEM micrographs of MC₁₆ and siloxanes modified clays are shown on Figure 6.

MC₁₆ on Figure 6a presents stacked aggregates with irregular shapes but after silane hydrolysis the initial sample of MC₁₆ is more disaggregated. In Figure 6b, sheets (~1.3 μm) and agglomerates are found for MC₁₆-PDPhS(Cl). While Figure 6c shows flake-like particles for MC₁₆-PDPhS(OCH₃). The particle size for all clays varies, however siloxanes treated materials exhibit sheet morphologies.

Although MC₁₆-PDPhS(Cl) and MC₁₆-PDPhS(OCH₃) have the same oligomeric species (Table 1); they are not the same as it has been pointed out on the infrared spectra discussion mentioned above. It is evident that differences in the modification mechanism of both materials (Figure 5) lead to different structural modifications as a consequence of the strain extended by the swelling of silane monomers and the hydrolysis.

Analyses of HDPE/PDPhS/Clay Composites

X-Ray Diffraction Analyses

Comparison between XRD patterns of clay and its corresponding HDPE/clay composites are shown in Figure 7. The increase on montmorillonite basal space from $2\theta = 7.4^\circ$ (MNa) to $2\theta = 4.8^\circ$ (MC₁₆) demonstrate an effective cation exchange (Figures 7a and 7b).

Siloxane treatment of MC₁₆ (Figure 7c and 7d) give rise to a disordered system as it

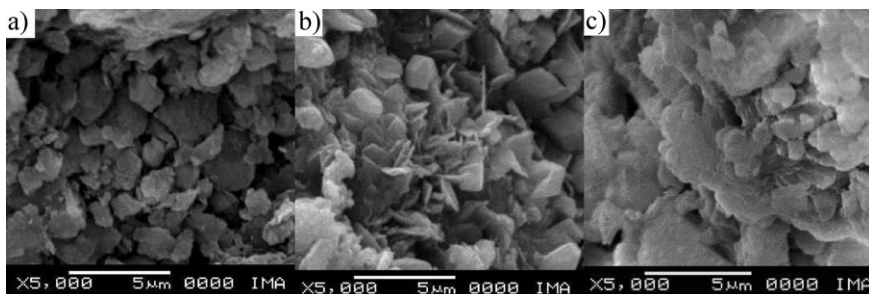


Figure 6.

Scanning electron micrographs of MC₁₆: a) before silane treatment, b) after DPhS(Cl) hydrolysis and c) after DPhS(OCH₃) hydrolysis.

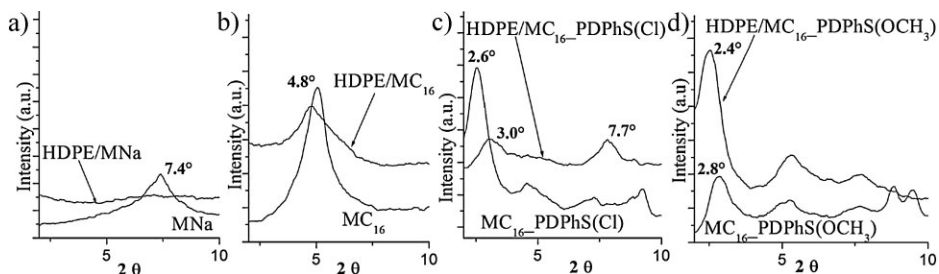


Figure 7.

X-ray diffraction patterns of clays: a) MNa, b) MC₁₆, c) MC₁₆-PDPhS(Cl), d) MC₁₆-PDPhS(OCH₃), and their HDPE / hybrid clay composite.

is appreciate from the presence of several featureless peaks.^[37] Partial intercalation in MC₁₆ is evidenced by the new peak at $2\theta \approx 2.7^\circ$ and the permanence of the peak at $2\theta \approx 5.0^\circ$. The former peak is sharper for MC₁₆-PDPPhS(Cl) which suggests the occurrence of intercalation to a larger extent than MC₁₆-PDPPhS(OCH₃).^[38] These evidences are consistent with: the equilibrium proposed on Scheme 1; the differences observed for Si–O–Si band in Figure 3b, where MC₁₆-PDPPhS(Cl) shows a sharper peak than MC₁₆-PDPPhS(OCH₃); and with the mechanism proposed on Figure 5.

None intercalation is noticed between PE and MNa or MC₁₆ because interlayer spaces are the same (Figures 7a and 7b).^[39] The low intensity of HDPE/MNa is due to dilution effect because no intercalation can take place as it has been confirmed by TEM (Figure 9).

XRD traces show changes on hybrid clays structure after HDPE incorporation (Figure 7c and 7d), although they still remain some peaks indicating that tactoids are present.^[39] The peak intensity at $2\theta = 2.6^\circ$ decreases on HDPE/MC₁₆-PDPPhS(Cl) maybe due to dilution and/or delamination effect. However, it shifts to $2\theta = 3.0^\circ$ and a peak appears at 7.7° suggesting stacking recovery of clays.^[40,41] HDPE/MC₁₆-PDPPhS(OCH₃) reveals a partial intercalation because 2.8° peak shifts to 2.4° but the others peaks do not entirely disappear.

PDPPhS/clay hybrids behavior observed during HDPE composites formation is consistent with their X-ray diffractograms

and IR spectra. For MC₁₆-PDPPhS(Cl) more intercalated and anchored siloxane species occupy interlaminar spaces preventing subsequent intercalation of HDPE. While MC₁₆-PDPPhS(OCH₃) has a lower degree of intercalation and less covalent bonds formation with the clay facilitating HDPE intercalation process.

Rheological Behavior

All HDPE/clay composites present changes in the rheological behavior. In all materials, complex viscosities ($|\eta^*|$) have decreased with increasing oscillation frequency (ω) (pseudoplastic behavior) due to highly entangled molecules which under high shear rate become oriented, leading to a reduction of viscosity.^[42] HDPE/hybrid clay composites present lower $|\eta^*|$ than pure polymer (Figure 8a). In particular, HDPE/MC₁₆-PDPPhS(Cl) shows the lowest $|\eta^*|$ and it can be observed some parallelism with the curve presented for pristine HDPE. HDPE/MC₁₆-PDPPhS(OCH₃) exhibits a similar behavior at low frequencies, but as ω increases the values of $|\eta^*|$ look alike HDPE/MNa and HDPE/MC₁₆.

The representation of $|G^*|$ (complex modulus) vs δ (phase angle) (Figure 8b) allows to identify the rheological percolation threshold.^[43] According to these curves none of the HDPE/hybrid clay composites present this structure. However, there are significant differences which are evidenced by this figure. All composites containing organically modified clays present values between those of pristine HDPE and HDPE/MNa. In particular

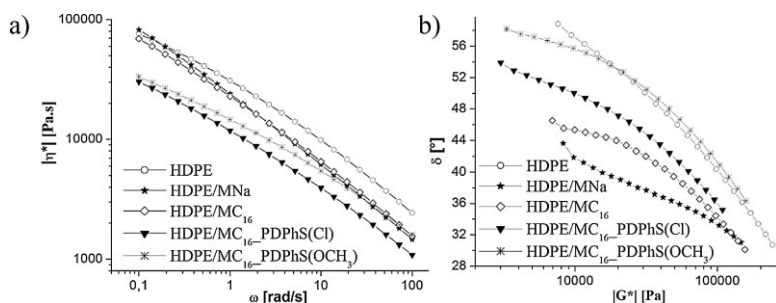


Figure 8.

Rheological properties of HDPE/clay composites: a) $|\eta^*|$ vs ω , b) δ vs $|G^*|$.

HDPE/MC₁₆_PDPHS(OCH₃) has almost the same behavior than pure polyolefin.

As mentioned above, better dispersion seems to have been attained for HDPE/MC₁₆_PDPHS(OCH₃) composite (Figure 9) and this is evidenced by the rheological data, where this material shows a similar behavior with HDPE.

Thermal Degradation Properties

Results from thermogravimetric analyses of polymer composites are summarized in Table 3. TG/DTG curves show that thermal degradation took place in one stage.

Since the polymer matrix is the same for all the material prepared, it can be concluded that clay sheets, alkyl chains from HDTMA and siloxane oligomers used as clay modifiers (in spite of being in low percentage) exert changes in the polyolefin decomposition mechanism and for that reason different behaviors are observed.

HDPE composites leave the same amount of residue corresponding to the inorganic part of the organoclay added. Except for HDPE/MC₁₆_PDPHS(Cl) that shows a slight difference on the values of weight loss, probably due to the higher

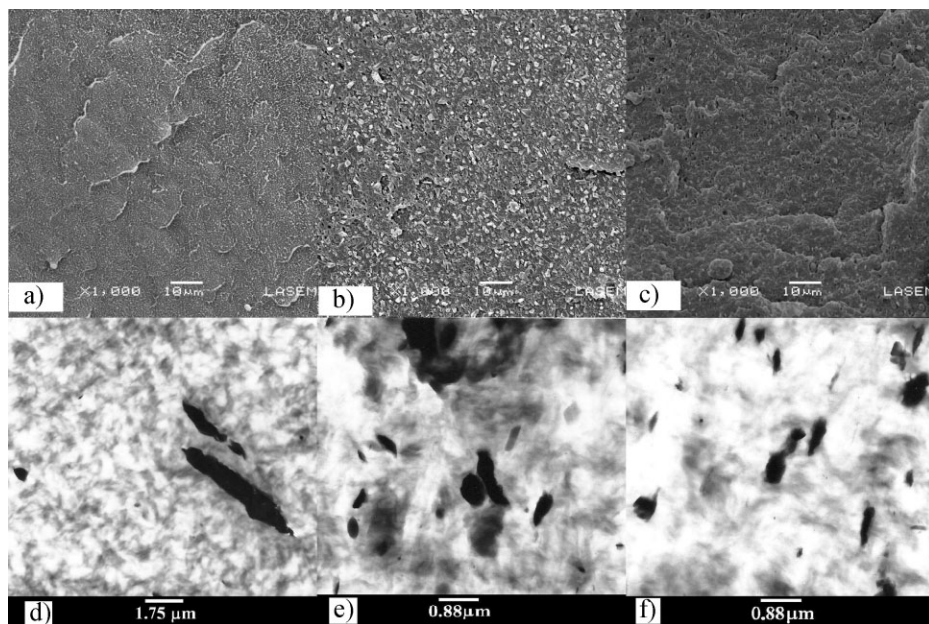


Figure 9.

Scanning electron micrographs of a) pure HDPE, b) HDPE/MC₁₆-PDPHS(Cl), c) HDPE/MC₁₆-PDPHS(OCH₃). Transmission electron micrographs of: d) HDPE/MNa, e) HDPE/MC₁₆-PDPHS(Cl), f) HDPE/MC₁₆-PDPHS(OCH₃).

Table 3.

TG/DTG data of HDPE and HDPE/clay composites

Sample	T _{onset} ^{a)} [°C]	T _{10%} [°C]	T _{50%} [°C]	T _{90%} [°C]	T _{max} [°C]	Max. Mass loss rate [%/min]	Total weight loss [%]
HDPE	295	422	450	467	459	24.52	100.00
HDPE/MNa	383	443	465	477	472	37.41	97.58
HDPE/MC ₁₆	357	445	460	467	463	56.77	97.50
HDPE/MC ₁₆ -PDPHS (Cl)	315	450	469	479	470	43.21	98.04
HDPE/MC ₁₆ -PDPHS (OCH ₃)	281	402	449	473	460	18.34	97.65

^{a)} Considering T_{1%} as the onset temperature.

portion of oligomers trapped inside clay galleries. Regarding Figure 1b, it is noticed that MC₁₆-PDPHS(Cl) has a larger amount of thermally stable oligomers than MC₁₆-PDPHS(OCH₃) (400 and 500 °C). This also would explain differences between thermal stability of HDPE/MC₁₆-PDPHS(OCH₃) and HDPE/MC₁₆-PDPHS(Cl) due to the restricted thermal motion of intercalated species, an effect that was observed for other intercalated polymer systems.^[44,45]

Comparing the evolution of non-oxidative degradation of these materials, it can be seen that HDPE/MC₁₆-PDPHS(OCH₃) presents similar values of that observed for HDPE in T_{50%} and T_{90%} and T_{max}. Both materials also exhibit similar rheological behaviors as it was observed on Figure 8b. Nonetheless, HDPE/MC₁₆-PDPHS(OCH₃) composite presented the lowest maximum mass loss rate which means it decomposes much slower than neat polymer. HDPE/MC₁₆-PDPHS(OCH₃) has the lowest T_{onset} whereas the rest of the composites present a delay on T_{onset} compared with the unmodified polyolefin.

Analogous improvements on thermal stability were exhibited by HDPE/MNa and HDPE/MC₁₆-PDPHS(Cl), in spite of their different internal structures (Figure 7a and 7c). According to Leszczynska et al.^[44], microcomposites (e.g. HDPE/MNa) show comparable behaviors with polymers where clay layers are partially intercalated and incorrectly dispersed, which would explain these similarities and which matches with the morphologies observed from TEM photographs (Figure 9).

Morphological Analysis

SEM and TEM microphotographs are presented on Figure 9.

HDPE/MC₁₆-PDPHS(OCH₃) and HDPE/MC₁₆-PDPHS(Cl) presented good filler dispersion (Figure 9b and 9c). However better disaggregation was reached by MC₁₆-PDPHS(OCH₃). This behavior has been ascribed to the different superficial coverage attained during silane in situ polymerization (Scheme 1).

Figure 9e shows that there is a clustering of particles for HDPE/MC₁₆-PDPHS(Cl) as it has been pointed out on X-ray patterns of this sample (Figure 7c). The HDPE/PDPHS/clay composite containing PDPHS(OCH₃) was better dispersed but clay sheets still remain trapped into MC₁₆-PDPHS(OCH₃) stacks.

Microphotographs of HDPE/MC₁₆-PDPHS(OCH₃) and HDPE/MC₁₆-PDPHS(Cl) resemble to that observed by Tjong^[46] in a polyamide/montmorillonite system and Sinha Ray and Okamoto^[45] in a polylactide/clay, when the performed procedure do not allow to exfoliate nanoclay into the polymer matrix. The dark entities on Figure 9e and 9f correspond to the PDPHS/montmorillonite intercalated hybrids. Nevertheless, the original size of MNa was diminished to ~300 nm for HDPE/MC₁₆-PDPHS(Cl) and ~200 nm for HDPE/MC₁₆-PDPHS(OCH₃).

Conclusion

In situ hydrolysis of difunctional silanes into organophilic montmorillonite allows obtaining intercalated hybrid nanomaterials according to X-ray results. The advantage of this procedure is that it does not require the use of solvents and it is performed at room temperature. In spite of using diphenylsilanes with different reactive groups, the same oligomeric species were obtained (dimers). Siloxane modified clays have presented higher hydrophobicity and have improved their thermal stability.

Nonetheless, differences between silane leaving groups affect coating distribution in organophilic clay. This has modified the interface interaction with HDPE as it has been exhibited by clay distribution on TEM and SEM images and the rheological changes.

In addition, the improvement of thermal properties was different for HDPE/PDPHS/montmorillonite composites. Although thermal resistance of HDPE/MC₁₆-PDPHS(Cl) increases, this composite showed

larger stacking recovery. On the contrary, HDPE/MC₁₆_PDPhS(OCH₃) showed lower thermal stability but it has improved dispersion of inorganic material under the processing conditions evaluated in this work.

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