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Synthesis of Additives from Montmorillonite to Modify High Density Polyethylene Final Properties

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Summary: This work brings about the modification of sodium montmorillonite clay (MNa) by the cationic exchange with hexadecyltrimethylammonium to turn it into organophilic clay (MC_{16}). Subsequently, MC_{16} was treated with silanes. Three silanes with functional groups of different chemical nature were used. The objective was to determine if the clay could affect high density polyethylene (HDPE) final behavior after being modified with each silane. The following silanes were used: $Cl_2Si(CH_3)_2$, $Cl_2Si(CH_3)(C_6H_5)$ and $Cl_2Si(C_6H_5)_2$. Finally, in situ hydrolysis was carried out to generate the respective siloxanes. These materials were characterized by XRD, FTIR and GPC analyses. Each one of these additives was mixed using melt compounding processing in a Haake torque rheometer Rheocord 9000 equipped with a mix chamber and roller rotors at 100 rpm and 190 °C. All hybrids were characterized by XRD, SEM and thermogravimetric analyses. Barrier properties to cyclohexane were also determined by pervaporation experiments. Results from all studies showed that the addition of approximately 3 wt% of clay has changed the macroscopic properties of the above-mentioned composites, as compared with pure HDPE. This can be explained considering the different polymer/filler interactions which take place in each system.

Keywords: clay; compatibilization; HDPE; organic polymer/inorganic filler hybrids; siloxane

Introduction

Thermoplastics comprise a group of polymers that offers many advantages and which has throughout time replaced other materials in more than a few applications.[1–3] These polymers are liable to changes that allow improving their performance. Nowadays, environment-friendly ways of material modification are pursued, e.g. by adding inorganic natural fillers.[4]

Polymers modified by the addition of inorganic species have been intensely studied, especially over the last years thanks to the development of polymer nanocomposites that in general show enhanced properties.[5–7]

Nevertheless, filler addition does not generally affect just one polymer property but leads to awkward situations.[7] Some of them are: resistance to apolar solvents, mechanical properties, polymer thermal resistance, processability, etc.[8,9]

In this article, sodium montmorillonite clay (MNa) was used as precursor of high density polyethylene (HDPE) additives. This clay was superficially modified and later added to the polymer in order to analyze the effects of each treatment on final organic polymer/inorganic filler hybrid behaviors. In particular, two properties were evaluated: thermal stability and transport properties. As filler addition can influence polymer response to apolar solvents, changing barrier properties of materials, hybrids were evaluated by cyclohexane pervaporation.

Polymer thermal stability is important for the processing stage and for determining the material properties for further applications. Onset temperature provides valuable information to determine manufacture and processability temperatures

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without starting material degradation process.[1,10]

It should be noted that superficial modifications in MNa were carried out aiming to improve the chemical affinity to HDPE.

A wide range of options can be explored seeking polymer/filler compatibility. In the case of mineral clays used as polyolefins modifiers, the selection of an appropriate compatibilizer is of crucial importance since laminar silicates can be partially or totally delaminated in order to obtain polymer nanocomposites.[11–13] In particular, compatibilization treatments have been suggested for polyethylene (PE) or polypropylene (PP), but always by using copolymers with the main chain of the same nature of the matrix and with side groups similar to clay (PE or PP grafted with maleic anhydride).[14,15] However, in this work, enhanced compatibility is proposed by using siloxanes as superficial modifiers of clays, which are afterwards mixed with the melted polymer. In this case, the modifier has the main chain of the same chemical nature of clay and of organic side groups which are compatible with HDPE hydrocarbon macromolecules.

Experimental Part

An Argentinean MNa clay kindly supplied by MINARMCO (cation exchange capacity = 70 mEq/100 g and particle size less than 325 Mesh) was used in this work. The chemical composition of this MNa is given in Table 1.

The MNa clay was modified with hexadecyl trimethylammonium chloride (HDTMA) provided by PharmaSpecial (GENAMIN CTAC). Dimethyldichlorosilane (DMS), methylphenyldichlorosilane (MPhS) and diphenyldichlorosilane (DPhS) were purchased from Sigma Aldrich.

Preparation of Organophilic Clay

A 5% g/mL distilled water dispersion of untreated MNa clay was prepared and 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 for ensuring complete elimination of chloride ion. After negative test of the filtrate with 0.1N $AgNO_3$ solution, the organophilc montmorillonite clay (MC_{16}) was dried at 80 °C for 48 h.[17]

Preparation of Siloxane Modified Organoclays

Three mixtures were prepared by putting in direct contact 10 g of silane with 10 g of MC_{16} at room temperature and they were maintained in contact for 5 days. Then distilled water was added on a $H_2O/Si = 20$ molar ratio. After 5 days, treated clays were washed until complete elimination of Cl^- ion. According to the silane used, e.g., DMS, MPhS and DPhS, the following materials were prepared: MC_{16}-PDMS, MC_{16}-PMPhS and MC_{16}-PDPhS, respectively.

Preparation of Polymeric Hybrids

HDPE/clay mixing was performed using melt compounding processing in a Haake torque rheometer Rheocord 9000 equipped with a mix chamber and roller rotors at 100 rpm and 190 °C during 10 min. The following hybrids were obtained: HDPE/MNa, HDPE/MC_{16}, HDPE/MC_{16}_PDMS, HDPE/MC_{16}_PMPhS and HDPE/MC_{16}_PDPhS. All these compounds contained 97 wt% of HDPE pellets and ~3 wt% of clay.

Characterization

X-ray diffraction analyses were performed in a Rigaku Miniflex DRX 6000 diffractometer using nickel filtered CuKα radiation

Table 1.
Percentual composition of natural clay.[16]

Component	SiO_2	Al_2O_3	MgO	Na_2O	CaO	K_2O	Fe_2O_3	Others
wt%	62.0	18.0	3.0	3.5	2.0	1.0	7.0	3.5

operating at 30 kV and 15 mA. The data were recorded at 2θ rate of 2° per minute.

The treated clays were evaluated by infrared spectra recorded in a FTIR 1720x-Perkin Elmer spectrometer using pressed KBr disks at 20 scans and 2 cm^{-1} resolution.

Siloxanes oligomers from modified clays were obtained via soxhlet extraction with cyclohexane. The cleaned clays were dried until complete solvent elimination.

Molecular weights and polydispersity indexes were obtained using gel permeation chromatography (GPC) in an Agilent system equipped with differential refractive index detector and a linear Phenogel column. Monodisperse polystyrenes were used as calibration standards and chloroform (1 mL/min) as eluent.

Thermogravimetric characterization (TG/DTG) was performed from 25 to 700 °C at a heating rate of 10K/min, under a N_2 flow (balance purge flow = 40 mL/min and sample purge flow = 60 mL/min), with a thermal analyzer TA Instruments (USA), TGA Q500.

Transport properties were evaluated using standard pervaporation equipment with cyclohexane as solvent. Film behaviors were observed at three temperatures. Vacuum was maintained using liquid N_2.

Scanning electron microscopy (SEM) was carried out in a JEOL JSM-6480 LV. Samples were coated with gold in order to study the surface morphology.

Results and Discussion

XRD Analyses

Figure 1 shows X-ray diffractograms of unmodified and modified clays before and after melt compounding with HDPE. Comparing only clay XRD patterns, it was observed that cation exchange leads to an increase in basal distance (Figure 1b), generating at the same time a lipophilic medium between clay sheets. When silanes were added to MC_{16} a diffusion phenomenon took place. However, after hydrolysis, only clays that were treated using MPhS (Figure 1d) and DPhS (Figure 1e) showed higher intercalation degrees.

While this would suggest that DMS does not intercalate into MC_{16}, it must be pointed out that during the preparation of these materials the same diffusive behavior was observed for the three species. This indicates that the expansive effect of the synthesis of PDMS oligomers is lower than those from the other oligomers, which may be related to the small size of DMS side groups and to the decrease in Si-CH_3 bond rigidity compared with Si−C_6H_5 bond in MPhS or DPhS.

As regards XRD of clay/polymer hybrids, peak intensity decreases may be due to the dilution of additives when added to HDPE matrix, or can reflect the decrease on tactoid size.[4] Peaks have almost disappeared on Figure 1d for HDPE/MC_{16}_PMPhS hybrid, which indicates that the filler was dispersed in HDPE matrix. Figures 1c and 1e show HDPE/MC_{16}_PDMS and HDPE/MC_{16}_PDPhS patterns, respectively. A partial stacking recovery[18] was noticed as interlayer distances decreased, if they are compared with those of modified clays. These different behaviors can be associated with siloxane oligomeric species generated among clay platelets during hydrolysis. Two aspects must be taken into account when analyzing silane treated clays: 1) although reaction conditions were the same, each monomer generates chains of different lengths (Table 2); and 2) the chemical nature of organic groups attached to the silicon atom is different. Both factors can affect subsequent clay/polyolefin interactions.

Finally, it is necessary to point out that the absence of peaks in HDPE/MNa pattern (Figure 1a) is due not to an exfoliation, but to a dilution effect. This material has been previously studied by TEM[16] proving that no intercalation and/or exfoliation took place owing to the poor compatibility between pristine clay and HDPE.

FT-IR Spectra Analyses

Table 3 shows the peaks observed for the additives obtained from MNa clay. Pristine

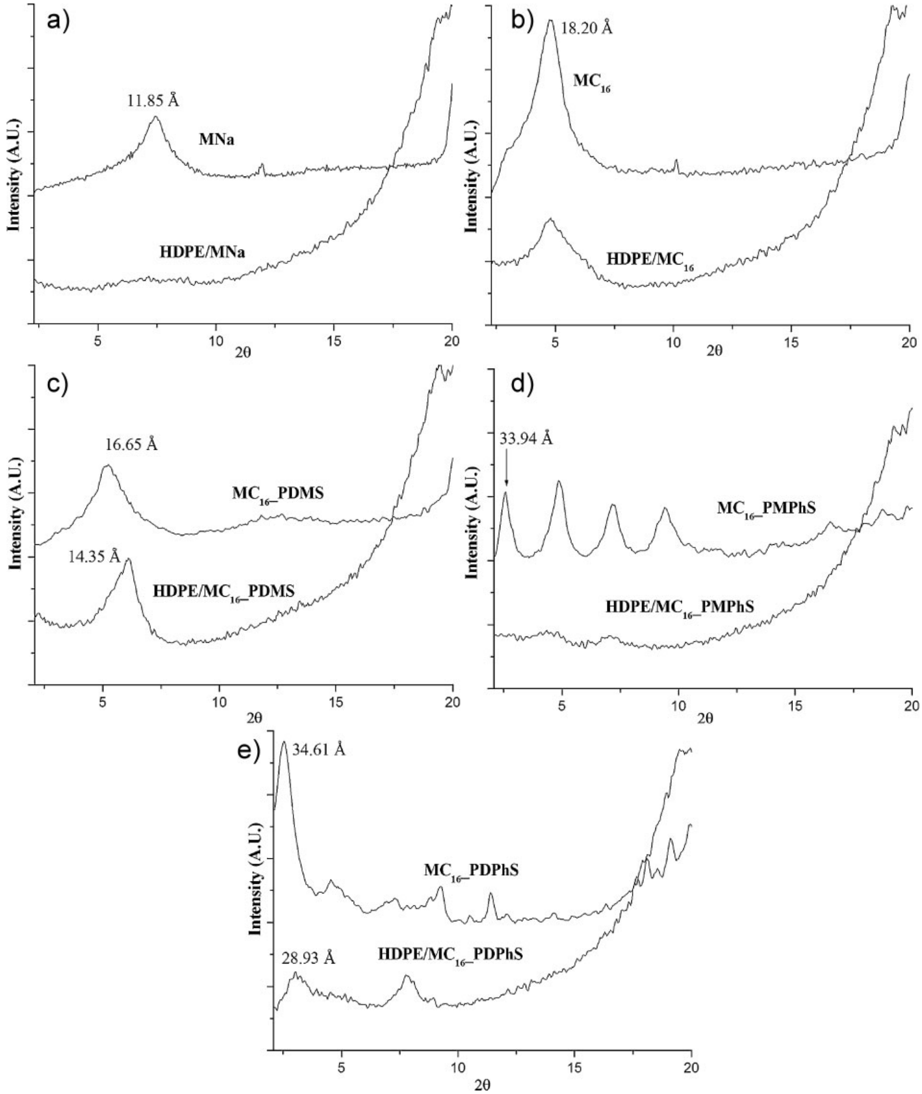


Figure 1.

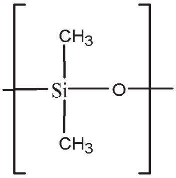
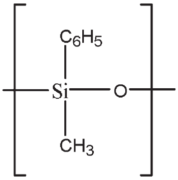
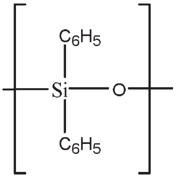
XRD patterns of clays and their corresponding HDPE hybrid.

clay presents the typical bands observed for montmorillonite clay.[19] The peaks corresponding to methylene group ($\sim$2920 cm^{-1}, $\sim$2850 cm^{-1}, $\sim$1475 cm^{-1}) evidence the presence of alkyl chains on MC_{16} and siloxane treated clays.[20]

In particular, MC_{16}_PDMS and MC_{16}_PMPhS spectra exhibit absorption bands corresponding to methyl group near to 2960 cm^{-1} and 1260 cm^{-1}. While MC_{16}_PMPhS and MC_{16}_PDPhS spectra showed peaks corresponding to phenyl group in the 3100-3000 cm^{-1} region. This group has also presented absorption bands at 1591 cm^{-1}, 1429 cm^{-1}, and between 2000 and 1700 cm^{-1}. From these data, it was confirmed the presence of the siloxanes oligomeric species described on Table 2.

No bands near 3440 cm^{-1} and 1640 cm^{-1} were detected for MC_{16}_PMPhS and MC_{16}_PDPhS, evidencing their high hydrophobicity. It is important to state that –OH stretching belongs only to absorptions on the clay sheet for MNa and MC_{16}. How-

Table 2.
Data obtained from GPC analyses.

Smallest basic unit	m [a)]	Mn [b)]	Polydispersity [c)]	DP [d)]
 $\left[-\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}-O-\right]$	74	375	1.10	~5
 $\left[-\underset{CH_3}{\overset{C_6H_5}{\mathrm{Si}}}-O-\right]$	136	392	1.32	~3
		73,100	2.37	~537
 $\left[-\underset{C_6H_5}{\overset{C_6H_5}{\mathrm{Si}}}-O-\right]$	198	331	1.26	~2

[a)] m = repeating unit molar mass [g/mol]
[b)] Mn = number average molecular weight
[c)] Polydispersity = weight average molecular weight/ number average molecular weight (Mw/Mn)
[d)] DP = degree of polymerization (Mn/m)

ever, they also may correspond to terminal silanol groups in the case of MC_{16}_PDMS, MC_{16}_PMPhS and MC_{16}_PDPhS.

Thermal Properties

Table 4 summarizes the information extracted from TG thermograms on the final weight losses and the typical temperatures for thermal decomposition process.

In all cases, additives caused a delay on the onset compared with HDPE thermal degradation. Specifically, the hybrid containing MC_{16}_PMPhS presents the lowest temperature to T(1%) while the Tonset is

Table 3.
Infrared Absorption for MNa, MC_{16} and siloxanes-treated clays (Frequencies in cm^{-1})

	MNa	MC_{16}	MC_{16}_PDMS	MC_{16}_PMPhS	MC_{16}_PDPhS
−OH stretching	3621	3621	3622	3626	3620
−OH stretching	3448	3434	3437		
aromatic C−H stretching				3100 to 3000	3100 to 3000
CH_3 asymmetrical stretching			2966	2960	
CH_2 asymmetrical stretching		2922	2926	2922	2924
CH_2 symmetrical stretching		2850	2852	2852	2852
Combination bands				2000 to 1700	2000 to 1700
H−O−H deformation	1636	1637	1637		
C−C stretching within the ring				1591	1591
CH_2 scissoring band		1473	1473	1473	1475
C−C stretching within the ring				1429	1429
Si−CH_3 symmetric deformation			1263	1259	
Si−O in plane stretching	1035	1036	1033	1039	1035
C−H out of plane bending				729	740

Table 4.
Information obtained from TG curves.

Samples	T (1%) [°C]	T (10%) [°C]	Tonset	T (50%) [°C]	T (90%) [°C]	Char Yield[a)] [%]
HDPE	295.11	422.75	429.58	450.56	467.55	0.32
HDPE/MNa	382.94	443.54	451.60	465.49	477.21	2.42
HDPE/MC_{16}	356.88	445.00	450.46	459.93	467.83	2.50
HDPE/MC_{16}_PDMS	301.55	420.41	442.95	465.39	483.72	2.26
HDPE/MC_{16}_PMPhS	270.22	451.74	463.68	477.41	489.79	1.69
HDPE/MC_{16}_PDPhS	315.31	450.27	457.00	469.10	479.48	1.96

[a)] Values differ from those expected evidencing dispersión defects.[21]

the highest. These results can be associated with the bimodal behavior of oligomers extracted from this modified clay. At the beginning there is a weight loss even lower than HDPE which matches the existence of species with a lower molecular weight. Then PMPhS oligomers with higher molecular weights participate later reaching the highest onset temperature for this material which is Tonset.

When 10% of weight loss is reached, HDPE/MC_{16}_PDMS exhibits similar values of temperature close to pure polymer. HDPE/MC_{16}_PMPhS and HDPE/MC_{16}_PDPhS show the highest temperatures if compared with the rest of hybrids. Mixtures containing MNa and MC_{16} show similar values between them.

While weigh loss increases HDPE/MC_{16}_PMPhS hybrid presents the highest temperature values. At 90% weight loss, composites containing additives modified by siloxanes show the highest temperatures.

Table 4 presents values obtained from TGA and DTG curves. According to Van Krevelen, the ratio $T_{max} \sim T_{50\%}$ is applicable to these results.[22] However, the other ratios proposed by this author referred to activation energy and initial weight loss temperatures are not kept.

Activation energy values were calculated by taking into account first-order kinetics. Arrhenius equation was used:

$$\ln\left(-\frac{1}{m}\cdot\frac{dm}{dt}\right) = \ln A - \frac{E_a}{RT}$$

Although HDPE shows first-order kinetics, it exhibits two activation energies.[24] This is associated with the fact that for low weight losses, the degradation is related to imperfections on polymer chains and the elimination of high volatile products. But the second degradation stage involves C–C bond ruptures that implicate more energy.[25,23] Several authors have researched on this polymer and report different energy values and reaction orders.[23]

In this work, the introduction of modifiers to polymer matrix in all cases causes changes on activation energy values evidencing alterations on the degradation process, compared with pure polyolefin.

It is well known that polyolefin decomposition process mainly occurs through a random chain rupture, and not by depolymerization. The activation energy calculated involves a complex mechanism which should consider two aspects: i) typical reaction characteristics of solid-gas systems via free radical, and ii) chain reactions. The first ones are affected by the spreading of the reaction volatile products, which is related to the nanoplatelet dispersion within the HDPE, and the latter are affected by the chain reaction mechanisms.[26,10] As studied hybrids have had the same polymer matrix, it can be concluded that additives used have caused different effects on this mechanism, and for that reason different behaviors had been observed. Although nanoclay effect was mentioned, it is obvious that is not the only factor that affects these behaviors.

DTG curves (Figure 2), activation energies and maximum mass loss rate (Table 5) exhibit similar tendencies among some materials. In the first stage of degradation, hybrids modified by sodium clay and MC_{16} have higher thermal stabilities as

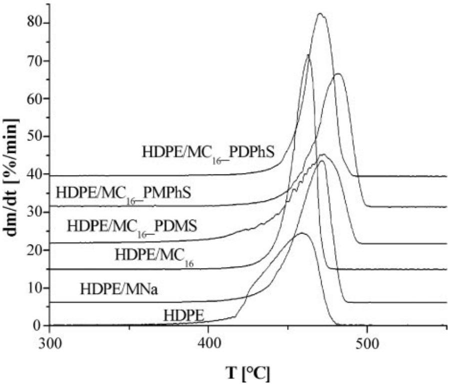


Figure 2.
DTG curves of prepared materials.

they presented an increase on Ea[23] compared with pure HDPE values, but composites modified by siloxanes presented lower Ea values. This is probably due to the fact that siloxane systems contain oligomeric species (verified by GPC), which may be eliminated from each system more easily during heating. As regards the second stage, activation energies were higher which means that fillers have had a stabilization effect, except for HDPE/MC_{16}_PDMS.

Finally after analyzing maximum rate of degradation, polymer containing MC_{16}_PMPhS as modifier presents the maximum mass loss rate, at 20 °C over pure HDPE, and HDPE/MC_{16}_PDMS shows the lowest value.

Barrier Properties

Permeability values and the permeation activation energies (EaP) for each HDPE/clay hybrid are described in Table 6. Composites containing MNa and MC_{16}_PDMS show enhanced barrier properties with respect to pure HDPE.

If EaP values are compared to interlamellar spaces (Figure 1) there is no correlation between these factors. This may be inferred after consideration of HDPE/MC_{16} and HDPE/MC_{16}_PDMS values. Even though clay gallery heights are similar, EaP are quite different. Thus, polymer intercalation degree is not the only factor that influences barrier properties.

EaP involves several aspects. On the one hand, it indicates temperature sensibility of each system (membrane). It was observed that permeation process is more influenced by temperature for HDPE/MNa and it is barely affected for HDPE/MC_{16}_PMPhS. On the other hand, EaP involves information about solubility and solvent diffusion through membrane.[27] Then, it is evident that both processes were changed by species used as MNa modifiers.

Although fillers are well dispersed as shown SEM microphotographs (Figure 3),

Table 5.
Data obtained from themogravimetrical analyses.

Samples	Max. Mass loss rate [%/min]	T_{max} [°C]a)	Ea [kJ/mol]b)	ΔT [°C]c)
HDPE	24.52	458.99	71.61 332.32*	315–405 405–480
HDPE/MNa	37.41	471.52	155.84 498.79	390–430 430–480
HDPE/MC_{16}	56.77	462.80	108.02 636.37	360–440 440–465
HDPE/MC_{16}_PDMS	23.57	472.82	64.40 255.66	290–375 375–475
HDPE/MC_{16}_PMPhS	35.17	481.73	62.25 460.56	275–415 415–480
HDPE/MC_{16}_PDPhS	43.21	470.37	40.68 527.71	310–420 420–475

a)Temperature at maximum mass loss rate
b)Activation energy (Ea) calculated according to TGA curves
c)Temperature range for Ea calculations
*Value similar to that reported by Albano et al.[10] and Chrissafis et al.[23]

Table 6.
Results extracted from pervaporation at different temperatures.

Sample	T = 50 °C		T = 60 °C K		T = 70 °C		EaP [kJ/mol]
	P[a)]	P_R[b)]	P	P_R	P	P_R	
HDPE	129.99	1.00	151.12	1.00	221.57	1.00	24.44
HDPE/MNa	77.84	0.60	145.39	0.96	196.05	0.88	42.68
HDPE/MC_{16}	148.13	1.14	154.31	1.02	205.65	0.93	14.99
HDPE/MC_{16}_PDMS	79.35	0.61	124.47	0.82	173.22	0.78	36.00
HDPE/MC_{16}_PMPhS	173.23	1.33	181.36	1.20	185.43	0.84	3.14
HDPE/MC_{16}_PDPhS	131.45	1.01	184.27	1.22	232.57	1.05	26.32

[a)] P in [g.mm/day · m^2 · atm]
[b)] P_R = Relative permeability = P/P_{HDPE}
[c)] e_{sheet} = 9,5 Å

different morphologies are observed according to the additive used. This is intimately related to changes observed on macroscopic properties.

The highest EaP of HDPE/MNa can be associated to the low interaction polymer/clay, which becomes more marked as temperature increases. This will lead to greater mobility of HDPE chains which will promote interface separation and consequently the free volume will increase facilitating cyclohexane diffusion. Temperature sensibility, i.e. EaP, is lower for HDPE/MC_{16}_PDMS, probably due to an improvement of interface contact caused by the presence of $-CH_2$ from alkyl chains and $-CH_3$ groups from PDMS oligomers.

Activation energies for HDPE/MC_{16} and HDPE/MC_{16}_PMPhS have decreased significantly taking pure HDPE as reference. In the first case, it is evident that the hydrophobicity of alkyl chains was not enough to avoid free volume increase during cyclohexane transport. In the second, the

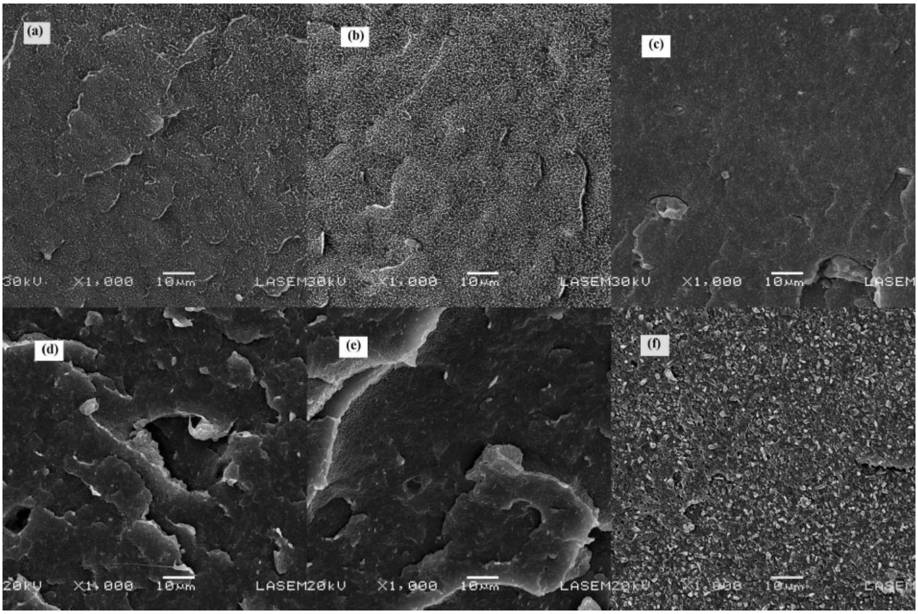


Figure 3.
SEM microphotographs of (a) HDPE,[16] (b) HDPE/MNa, (c) HDPE/MC_{16}, (d) HDPE/MC_{16}_PDMS, (e) HDPE/MC_{16}_PMPhS and (f) HDPE/MC_{16}_PDPhS.[16]

increase in free volume is not due to the lack of compatibility, as can be inferred from XRD patterns (Figure 1d). Nevertheless, PMPhS oligomers (Table 2) have a large length; consequently they can separate HDPE chains.

Finally, HDPE/MC$_{16}$_PDPhS exhibits similar EaP and permeabilities than pure HDPE. By means of Figure 1e, it can be observed that HDPE partially intercalates due to the high distance generated for the presence of the bulky groups from DPhS. However, the dimers obtained (Table 2) seem not to influence the original free volume of HDPE.

Conclusion

In this work, a natural multilayer clay mineral was used as raw material. Hydrophilic clay was modified at nanometric level by the introduction of species with different chemical functionalities, in order to obtain additives for HDPE. Three modified clays were synthesized containing siloxane oligomers with different behaviors.

Macroscopic changes have taken place on HDPE after its hybridization with synthesized nanomaterials. According to XRD results, HDPE/MC$_{16}$_PMPhS exhibited an intercalated/exfoliated structure while others HDPE/clay hybrids have shown microcomposite structure. Nonetheless, after evaluating thermal and barrier properties, their responses did not follow a direct correlation with the degree of intercalation.

Resistance to thermal non-oxidative degradation was improved when siloxane-modified clays or pure clay were used. Concerning barrier properties, HDPE/MNa and HDPE/MC$_{16}$_PDMS have shown better results in terms of cyclohexane permeability al low temperatures. Meanwhile, HDPE/MC$_{16}$_PMPhS was the hybrid with the lowest EaP.

Thus, it was concluded that HDPE macroscopic properties were mainly influenced by the interactions existing between the polyolefin and clay surface modifiers.

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