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Synthesis and Characterization of Vinyltrimethoxysilane-Grafted Non-Swelling Clay

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Abstract

The structural characteristics as well as the binding capacity of the functionalized halloysite/kaolinite from north Patagonia, Argentina were investigated. The sample was modified by immobilization of ligands containing vinyl (C=C) groups by covalent grafting with surface silanol groups.

Silane grafted non swelling clays were synthesized by using vinyltrimethoxysilane (VTMS) via two different grafting reaction systems: (a) ethanol-water mixture and (b) xylene mixture. The resulting products were investigated using Infrared Spectroscopy (IR), X-ray diffraction (XRD), Thermogravimetric analysis (TGA-DTA), Microanalysis by dispersive energy (EDX) and Contact Angle for water (ϕ). The results indicate that the vinyl groups grafted at the mineral edges changed the hydrophilic nature of the clay mineral into hydrophobic. X-ray diffraction showed that their original structure had been preserved.

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1. Introduction

Areas polluted by organic compounds are of great concern in terms of environmental control. Several types of materials have been studied to remediate these areas.

Smectite clays are the most interesting group of clay minerals used as a sorbent material and the most widely utilized as well. The application of layered silicates relies on the ion exchange properties and swelling ability.

Several organoclays have proved highly efficient in removing neutral organic contaminants from water and can be used, for example, to treat contaminated water, line waste reservoirs, and industrial wastes, to adsorb oil and fuel spills. Most organo-clay complexes are obtained using bentonites, especially the American Wyoming bentonite.

Minerals of the kaolin group (kaolinite, dicrite, nacrite and halloysite) are 1:1 dioctahedral aluminosilicates that have two different basal cleavage faces, Hurlbut (1971). One basal face consists of a tetrahedral siloxane surface with very inert -Si-O-Si links. The other basal surface consists of an octahedral, gibbsite ($\text{Al}(\text{OH})_3$) sheet. Both of these surfaces are electrically neutral in theory. In kaolinite, at the edge of a 1:1 layer, the structure is disrupted and broken bonds occur that are accommodated as OH groups. These edges are estimated to occupy approximately 10 % of the whole kaolinite surface, Williams and Williams (1978); Wierer and Dobias (1988). The potential adsorption sites on kaolinite include the silanol ($\equiv\text{SiOH}$) and aluminol ($\equiv\text{AlOH}$), hydroxyl groups on the mineral edges and the permanently charged sites ($\equiv\text{X}^-$) on the basal surfaces. The hydroxyl groups at the plate edges are considered to be the major reactive sites, Morris et al. (1990). Gu and Evans (2008) determined by optimization of batch titration experiments that the ratio of the edge sites to the basal surface sites was the 6:1 for kaolinite. Halloysite has the same structure and chemical composition of kaolinite, dickite or nacrite but the unit layers in halloysite are separated by a monolayer of water molecules, Joussein et al. (2005). However, their real potentialities can only be developed by subjecting them to chemical treatments.

In north Patagonia, Argentina, a halloysite deposit is currently exploited for ceramic ware purposes. The main mineral in the deposit is halloysite with variable amounts of kaolinite (75% halloysite-25% kaolinite mineral), Cravero et al. (2009). Because of the special characteristics of this clay, new applications are extensively seeking.

The aim of this work is to modify the argentine non swelling halloysitic clays for in the future use it to remove emulsified petroleum from water and to make mixed matrix membranes.

There are several chemical strategies to modify the clay minerals, such as adsorption, ion exchange with organic / inorganic compounds and organic compounds graft, Tuesta et al. (2005); Dai and Huang (1999). The usual modification by ion exchange due to electrostatic interaction with surfactants has the disadvantage that the modifying agent may be released to the aqueous medium, resulting in secondary contamination. By contrast, by grafting a silane onto the surface of the clay, the organic molecule is strongly bound by covalent bonds, preventing its release.

Based on the modification of the oxide surfaces by silylation, Yoshida et al. (2001) and considering the background on the silylation of inorganic porous membranes, Fernández et al. (2004), silicon wafers, Fernández et al. (2006a) and γ -alumina nanoparticles Fernández et al. (2006b), Fernández et al. (2008), the vinyltrimethoxysilane (VTMS) was selected as silylating agents onto halloysite.

This paper focuses its interest in analyzing the effect of grafting reaction solvents, anhydrous or aqueous, about changes in the material investigated by characterization techniques such as infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (DTA-TG), X-Ray Spectroscopy Energy dispersive (EDX) and water contact angles (θ).

With a view to a technological approach the natural clay was used as received without any further purification.

2. Materials and Methods

The non swelling clay used in this work is a kaolin provided by Minera Lozano-Argentina. The mineral comes from a deposit located in Río Negro Province, (Choique area) Argentina. It is composed of halloysite with variable amounts of kaolinite and minor cristobalite, Cravero et al. (2009). The natural clay was used as received without any further purification.

Chemical analysis, IR, XRD, TGA, DTA were used to characterize the raw material.

The silane coupling agent used was vinyltrimethoxysilane (VTMS) (Fluka, 95095) and the reaction solvents were a mixture of isomeric xylenes (Fluka, 95690), ethanol (Porta, CB139189) and distillate water.

X-ray powder diffraction (XRD) analysis was performed with a Rigaku D-Max III – C diffractometer, with Cu K α radiation, graphite monochromator at 35 kV and 15 mA. To enhance basal diffractions, oriented samples were prepared from suspensions, either on water or alcohol media depending on the grade of hydrophilic or hydrophobic clay behaviour. Halloysite positive identification was obtained with Formamide intercalation, Churchman et al. (1984). The relation between halloysite and kaolinite were obtained as I10/I10+I7 x 100 after Formamide intercalation.

The chemical composition for the natural mineral was determined by X-ray fluorescence analysis (XRF), using an EDX-800 HS spectrometer (Shimadzu).

Infrared spectra using the KBr pressed disk technique were performed on a Back 500 infrared spectrometer. The spectra were collected for each measurement over the spectral range 400–4000 cm⁻¹.

Thermogravimetric analysis (TGA-DTA) was performed on a Rigaku- Denki thermobalance. Samples were heated from room temperature to 1000 °C at a heating rate of 10 °C/min (under air atmosphere) in order to quantify and distinguish the amount of silane in the resultant products of grafting reaction. Previous to thermal analysis a vacuum oven O.R.L – Industria Argentina was used to remove physically adsorbed water of grafted products. Alumina was the inert reference material used in the DTA technique.

The Si/Al mass ratio to natural and modified mineral were obtained by scanning electron microscopy (SEM) using a JEOL 35 CF with a microanalysis by dispersive energy system (EDX) from EDAX DX-4.

The contact angles of water for natural and modify clay mineral were evaluated from photographs using video enhanced image processing. The natural clays and modified clays pellets (diameter = 13 mm; thickness= 1.5 mm) were prepared under a press of 5 Tn. Measurements were conducted with distillate water by use of the sessile drop method. Due to limitations in the technique, angles less than 10 degrees cannot be determined ($\phi < 10^\circ$). Because of this method is approximated in addition to the modification of halloysite/kaolinite surfaces, identical procedure of silylation in dry environment was also performed with oxide (100) silicon wafers (646687-5EA, ALDRICH) as surrogate surfaces for subsequent contact angle measurements. For this surfaces measurements were conducted at a relative humidity of 33 % and 21 °C with MilliQ water by use of the sessile drop method with a FTA200 (Icar) contact angle instrument at SMAP Laboratory (Spain). Before the measurements, each wafer was cleaned according to the sequence followed by Nguyen et al. (2003).

The chemical reactions were conducted in a Velp Scientífica heated and stirred device with a control temperature interface. A rotary evaporator Senco W2-100SP was used for complete solvent elimination.

2.1. Grafting process

The introduction of reactive groups onto the halloysite/kaolinite surfaces was achieved by the reaction of silane with hydroxyl groups of the mineral. In the present study, two different grafting solvents were used.

In an anhydrous environment (method 1), we have following the route showed by Fernández et al. (2009), applied to alumina nanoparticles. The silylation reactor system consisted of a 500 ml glass reaction flask that was heated and stirred using a heating/magnetic stirring device positioned into an oil bath. The clay loading of the solution was approximately 80 g/l. Silylation was carried out by using a 10 % (v/v) VTMS solution in xylene. The reaction proceeded for a period of 5 hours at 130 °C. The temperature of the condenser was kept at 75 °C to reflux the solvent back to the reactor while allowing passage of the methanol by-product (bp 65 °C) formed during the silylation reaction. The suspension of clays was rinsed with pure xylene to remove un-reacted silane. Subsequently, the silylated material was dried under vacuum in a rotary evaporator.

On the other hand, in an aqueous environment (method 2) the grafting reaction was carried out in a mixture of water/ethanol (25/75 by volume). The clay loading of the solution was the same that method 1. Silylation was carried out by using a 10 % (v/v) VTMS solution in water/ethanol. The reaction proceeded for a period of 5 hours at 80°C. The temperature of the condenser was kept at 70 °C to reflux the solvent back to the reactor.

After silylation, the particles were washed with pure xylene and with a mixture of water/ethanol for method 1 and method 2 respectively, to remove adsorbed silane molecules by stirring for 12 hours. After this period, the

suspension was maintained without stirring until sedimentation was observed. This washing-step was repeated for 3 times. Finally, particles were dried in a rotary evaporator to remove the remaining solvent.

The grafted products prepared by method 1 and method 2 were denoted as O-HKo and W- HKo, respectively.

3. Results and Discussion

3.1. Clay characterization

The used clay is composed of a mixture of halloysite 10 Å and kaolinite in a 75:25 proportion (Fig. 1 a and b) with traces of opal C-T and quartz. Kaolinite, halloysite proportions were calculated after Formamide intercalation, Churchman et al. (1984).

The formamide test allows estimating the proportion of halloysite in the mixture by computing the $I_{10} / (I_7 + I_{10})$ ratio where I_{10} and I_7 denote the intensity of the XRD peaks near 10 and 7 Å, respectively.

Chemical analysis shows highly pure clay, Table 1. Considering that halloysite has the same theoretical chemical composition as kaolinite except for its higher water content, $(Al_2Si_2O_5(OH)_4 \cdot nH_2O)$, the amount of free silica is about 3%, what is in agreement with the presence of opal C-T and quartz.

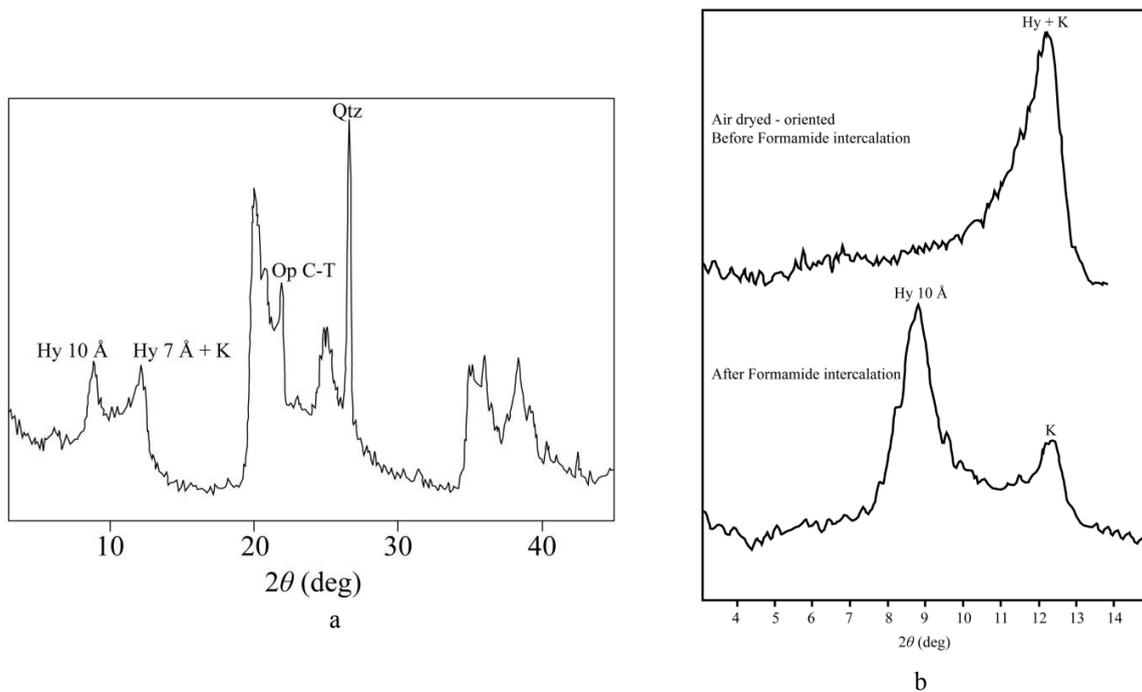


Fig. 1: XRD of natural clay (HKo). a) Whole rock, b) Before and after formamide intercalation

Table 1: Chemical Composition of natural clay (HKo)

(wt. %)	HKo Sample
L.O.I ¹	11.770
SiO ₂	48.078
Al ₂ O ₃	37.730
TiO ₂	1.366
Fe ₂ O ₃	0.594
K ₂ O	0.176
CaO	0.160
V ₂ O ₅	0.046
ZrO ₂	0.027
SO ₃	0.026
ZnO	0.009
CuO	0.008
Ga ₂ O ₃	0.007
SrO	0.002

¹L.O.I: loss on ignition 900 °C

3.2. Elemental surface analysis

After VTMS grafting the EDX analysis shows an increase in the Si/Al mass ratio attributed to the incorporation of Si as silane component.

As demonstrated in Fig. 2, the grafting reaction solvents affect these results, implying an increase of the grafted VTMS from O-HKo to W-HKo, (52 and 98 % respectively).

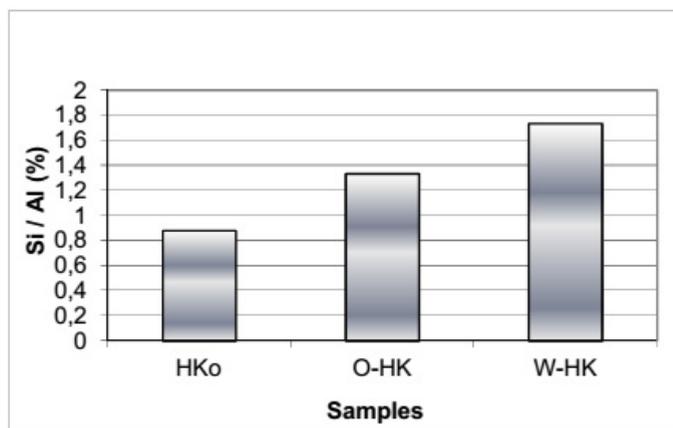


Fig. 2: Si/Al mass ratio of HKo, O-HKo and W-HKo

Infrared spectroscopy is very sensitive to modification of the clay mineral structure by functionalization. The characteristic peaks corresponding to the HKo are listed in Table 2. The presence of surface-grafted VTMS is evident in the infrared spectra as shown in Fig. 3.

The spectrums for both W-HKo and O-HKo reveal peaks at 1617 and 1422 cm⁻¹, which are characteristics of the C=C bond introduced by the covalently bonded VTMS molecules. Further, a series of small peaks near 3000 cm⁻¹ (between 2968 and 3073 cm⁻¹) corresponding to the C-H bond stretching of the vinyl and methyl groups, are also features that are foreign to the halloysite/kaolinite mineral and attributed to VTMS.

As we know, in the solution of ethanol/water mixture, silane is easy to hydrolyze and condense among silane molecules. After hydrolysis, the configuration of silane will be change with polymerization. For the method 2, the hydrolysis of the methoxy group seems to be complete since the band assigned to the unhydrolyzed methoxy group

(ν -O-CH₃ at 2850 cm⁻¹) was not observed. This band is evident for the method 1 indicating the existence of unhydrolyzed methoxy for this product.

Table 2: List of the Wave-number of Infrared Absorption Spectra in Fig. 3 for natural clay (HKo)

Peak	Wave number (cm ⁻¹)	Assignment
3699		OH stretching of inner-surface hydroxyl groups
3622		OH stretching of inner hydroxyl groups
1640		OH deformation of water
1101		perpendicular Si-O stretching
1056		in -plane Si-O stretching
925		OH deformation of inner hydroxyl groups
784		Si-O
765		Si-O perpendicular
684		Si-O perpendicular

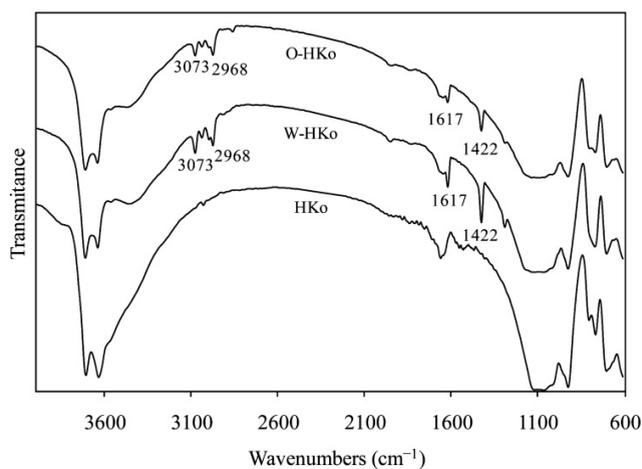


Fig. 3 : IR spectra of HKo, W-HKo and O-HKo

3.3. X-ray diffraction

With grafting silane onto halloysite/kaolinite, the non expansion of the mineral layers was demonstrated by X-ray diffraction. The XRD patterns of the halloysite/kaolinite before and after grafting are shown in Fig. 4. The basal spacing was 7.20; 7.20 and 7.13 Å for HKo, W-HKo and O-HKo respectively.

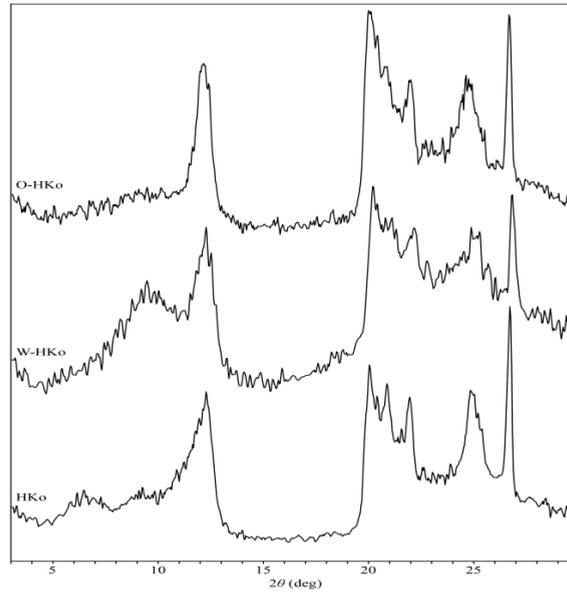


Fig. 4: XRD patterns of HKo, W-HKo and O-HKo

3.4. Thermal analysis of grafted halloysite/kaolinite

To gain more insight into the grafting process thermal analyses were used to determine the amount of silane molecules chemically anchored on the clay edges after extensive washing of the non-reacted coupling agent. In addition, the samples of modified clays were dried at 130 °C in a vacuum oven for 24 hours previous of thermal analyses.

Thermogravimetric analysis (TGA) was provided as a simple method to measure the content of silane and physisorbed water, Shen et al. (2007). This method is based on the assumption that the dehydration and dehydroxylation reactions correspond to the two discrete mass loss steps in TG curves and they do not overlap each other.

Silylation yields were determined by thermogravimetric analysis (TGA). Each sample was heated at 10 °C/min up to 1000 °C to eliminate all the organosilanes bonded on the surface, Zubakova et al. (1987). All runs were performed in an air atmosphere.

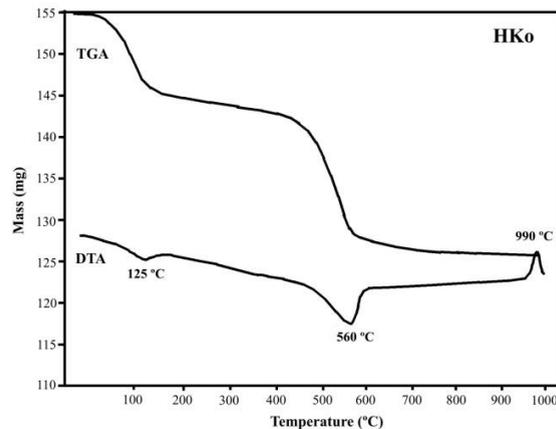


Fig. 5: TGA and DTA curves of HKo run in an air atmosphere

The thermogravimetric analysis of the pure halloysite/kaolinite is shown in Fig. 5. The DTA curve of HKo displays two peaks at ca. 120 y 560 °C, assigned to the loss of physically adsorbed water (5.36 %) and the dehydroxylation of halloysite/kaolinite (13.4 %). For HKo there is a small mass loss (ca. 1.6 %) in the range 200-410 °C attributed to the loss of the organic matter due to the natural clay was used as received without any purification or cleaning pre-treatment. Therefore, a greater mass loss than expected should be attributed to evaporation and/or decomposition of silane.

Both of the DTA curves of W-HKo and O-HKo display two peaks at 375 and 610 °C for W-HKo and at 385 and 608 °C for O-HKo corresponding to the decomposition of the grafted silane, Fig. 6 and Fig. 7. In addition, the peak at 208°C for W-HKo and 250 °C for O-HKo corresponds to the physically adsorbed VTMS. Due to the modified clays were dried in a vacuum oven, it is noted that the peak corresponding to the loss of physically adsorbed water disappear after grafting with VTMS.

The TGA curves of the clays used before and after grafting indicate that there are 6.22 and 4.20 % (wt %) VTMS grafted of W-HKo and O-HKo, respectively.

The mass quantity of grafted VTMS was evaluated as the difference between the weight loss for silylated clays and for unmodified ones at 1000°C without consider the amount of water adsorbed.

The grafting reaction in an aqueous environment (method 2) has improved the immobilization capacities of the organic content by 48 %. These results are in agreement with the increase of Si/Al mass ratio for this method.

This reflects that the grafting method has an important influence on the amount of the grafted silanes, i.e., the grafting reaction conducted in an aqueous environment favours silane molecules chemically anchored on the clay edges for the mineral selected in this work. This result is different from ones expected for inorganic oxides substrates.

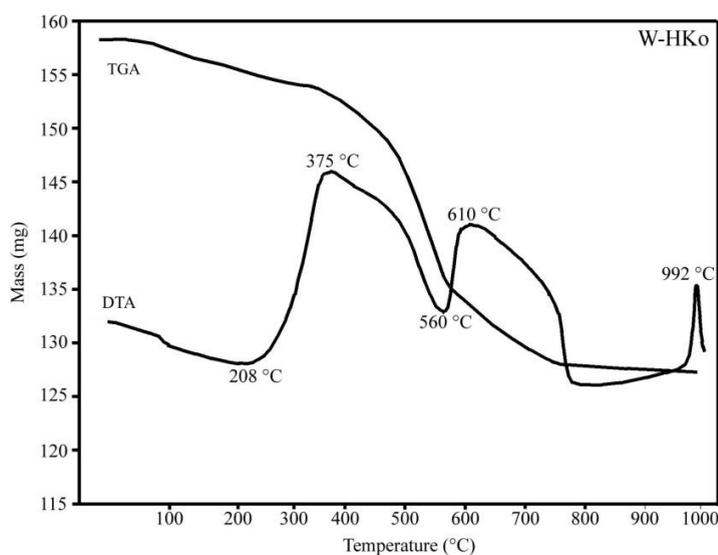


Fig. 6: TGA and DTA curves of W-HKo run in an air atmosphere

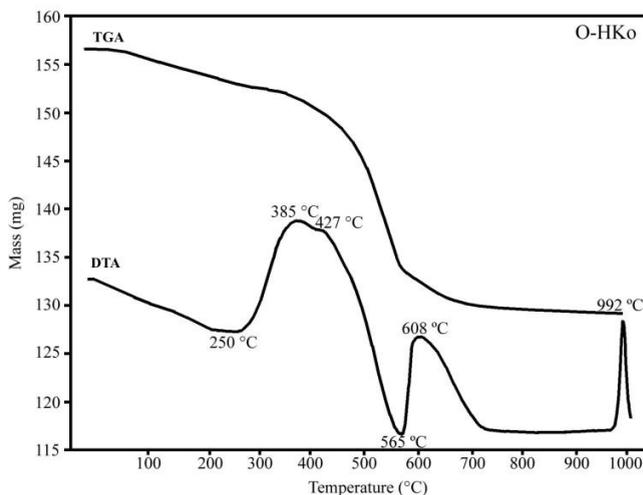


Fig. 7: TGA and DTA curves of O-HKo run in an air atmosphere

3.5. Surface hydrophobicity: Contact angles for water (ϕ)

Natural clays have a hydrophilic character, but depending on the coupling agent selected to carry out the grafting reaction it is possible to change it.

Our previous studies, Fernández et al. (2006a) had demonstrated that hydrophilic oxide silicon wafers after the silylation reaction with VTMS acquire hydrophobic properties.

In this work, identical procedure of silylation was performed in order to modify halloysite/kaolinite surfaces.

One way to estimate substrate hydrophilicity or hydrophobicity is to measure the contact angle. In the case of the oxide silicon wafers, the surfaces are flat and the measurement of the contact angle are more easy and exactly than on clay powder. For this reason, we used the wafer as surrogate surface to compare the tendency with the clays pellets.

The hydrophobicity of the VTMS-grafted surfaces was assessed by contact angle measurements with water as reference for the relative interactions of the modified and natural substrate with a polar solvent. The results reported corresponding to 5 minutes after deposition of water drop on the surfaces, time enough to reach a stable condition to conduce the measurement.

The results are listed in Table 3. The contact angle for the natural clay pellet result less than 10 degrees and cannot be determined.

Beyond a doubt, it was found that the contact angle increased after the grafting reaction for any surfaces. These results demonstrate the extremely hydrophobic nature of W-HKo and O-HKo.

EDX and TGA analysis has demonstrated that the grafting yield for the method 2 greater than method 1. However, method 1 and 2 showed similar contact angle measurement. This result can be explained because of in method 2 the remaining methoxy groups of the silane moieties were hydrolyzed during the chemical reaction.

Table 3: Contact angles of water (ϕ)

Substrate	Contact Angle ϕ °
Oxide silicon wafer	59
Oxide silicon wafer + VTMS	154
KHo pellet	-
O-KHo	150
W-KHo	143

4. Conclusions

The authors are not aware of publications describing the functionalization of a halloysite/kaolinite from north Patagonia, Argentina with organosilanes. We report here the possibility of utilizing these mineral for the preparation of an organic-inorganic hybrid material by grafting an organosilane containing the vinyl group onto the surface of clay. The vinyl group was chosen due its great affinity for hydrocarbons.

The process of synthesis proposed in this paper seems to be adequate in order to obtain functionalized nano-materials. Silane grafted a non swelling clay was synthesized with a trifunctional silane (VTMS).

Grafting of the VTMS onto Halloysite/kaolinite particle was successful achieved by silylation reaction in an anhydrous and aqueous medium. They have been confirmed by an exhaustive analysis of their structure.

The solvent environment impact on the grafting yield but it can be seen that the grafting method has not an important influence on the hydrophobicity character of the modified clays.

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