Grafting of 3 mercaptopropyl triethoxysilane onto dodecylamuonium intercaled Algerian montmorillonite; characterizations and application for synthesis of polystyrene/organoclay hybrid material by radical polymerization

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Abstract

High grafting efficiency (98%) of 3-mercaptopropyl triethoxysilane (MPTES) onto Algerian montmorillonite was achieved. Before grafting process, the Algerian montmorillonite was sodified, fractionated (<2µm) and intercaled with dodecylamine (DDA) salts. The obtained grafted clay was used to prepare polystyrene/organoclay hybrid material by radical polymerization of styrene monomer. X-ray Fluorescence (XRF) results showed a successful homoionisation of clay and insersion of DDA salts onto montmorillonite. CHN micro-analysis was revealed evolution of the carbon ratio during modification of clay by DDA, grafting and polymerization reactions.

Fourier transform infrared (FTIR) spectrums were mainly confirmed the presence of DDA salts, the grafting of MPTES and polystyrene polymer and increasing of hydrophobicity of clay during modifications process (intercalation, grafting and polymerization). The characterization (XRD) was revealed that DDA salts, 3-mercaptopropyl triethoxysilane molecules and polystyrene polymer were respectively intercaled, grafted and polymerized onto montmorillonite galleries by increasing of d_{001} from 12.69 Å for homoionisated clay to 15.33 Å for intercaled clay and to 21.47 Å for grafted clay and to 25.08 Å for polystyrene/organoclay hybrid material. Thermogravimetic analysis (TGA) showed High grafting efficiency (98%) of MPTES. It showed also that the grafted clay sample have higher thermal stability than intercaled sample and that the thermal stability of prepared organoclay hybrid material is greatly higher than pur polystyrene polymer and that hydrophobicity $_{hybrid\ organoclay} \approx$ hydrophobicity $_{grafted\ clay} >$ hydrophobicity $_{intercaled\ clay} >$ hydrophobicity $_{fractinated\ sodic\ clay}$. The polymer was recovered by hydrofluoric acid attack, analyzed by FTIR and compared to hybrid organoclay FTIR spectra.

Keywords: 3-mercaptopropyl triethoxysilane , Hybrid materials, Silanes, Grafting, Radical polymerization

1. Introduction

Organoclays have been obtained by modifying the surface of clay minerals by organic compounds. They have different applications in sciences and industries [1]. For example they are used for water treatment [2,3] and polymers additives to prepare polymers/organoclays hybrid materials [4]. Among these clays; montmorillonite is one of the most common-type clays that used to prepare the organoclays and organoclays/polymers hybrid materials, because this type of clays is universally abundant in nature and can be obtained in pure form at low cost [5]. The Montmorillonite is clay that belongs to the family of dioctahedral smectites. It consists of a stack of layers. Each layer consists of octahedral alumina sheet trapped between two sheets of tetrahedral silica. The isomorphic substitution of Al(III) by Mg(II) in the octahedral sheet gives it a permanent negative charge [6], where cations can be easily adsorbed. It has several special properties: lamellar structure, swelling ability, special capacity of hydration, adsorption and the possibility of interlayer ion exchange. This latter property makes montmorillonite suitable and ready for possible modifications by cationic organics compounds such as cationic surfactants [7-9]. The montmorillonite is hydrophilic in nature and can only interact with hydrophilic polymers such as poly (ethylene oxide) or poly (vinyl alcohol). So it would be very difficult to mix these kinds of minerals with hydrophobic polymers. To overcome this obstacle and make possible organo-mineral interactions, hydrophobic groups should be introduced on the surfaces of the layers [10].A previous study has shown that the modifications by quaternary alkylammonium ions onto clay have been developed to improve the compatibility of clay minerals with less polar matrices [11]. Previous Studies have shown that the insertion of organic complexes between the layers of a montmorillonite changed the hydrophilic property of its surface making it hydrophobic [12].This modification method may be possible by reacting silanes onto silanol groups Si-OH (which can be quantified by Gran method [13]) located on the sheets edges of this type of clay [14,15] and on structural defects located on the external surfaces of

the layers [16]. In previous study; the modification of montmorillonite by aminosilane reveals that the silane was intercaled in the interlayer spacing of montmorillonite due to the increase in the basal spacing, the high value of the latter can only be explained by the presence of a double layer of molecules of this silane connecting the two layers of clay [17].

In the same context, studies have shown that the grafting of aminopropyltrimethoxysilane onto montmorillonite caused the interlayer space to be inserted, increasing its d_{001}, [18], this confirms the possibility of having a grafting in the galleries of montmorillonite following a reaction between the silanol groups of the edges of the sheets and the alkoxy functions carried by the silicon of the silane, giving rise to bonds with covalent characters (Si-O-Si). It has also been shown that the montmorillonites having undergone surface modifications by silanes are thermally stable compared to montmorillonites having undergone conventional ion exchanges [19]. Studies have shown that the silane when added in high concentrations acts simultaneously on the silanols at the edges of the sheets and on the interlayer Si-O- [20]. These silanes, also called coupling agents, are polyvalent compounds. They represent an easy way to bond chemically polymers to silicas [21]. They can exist in the form of bifunctional monomers: an alkoxy upstream which can react with the silicic surface of clay and a function (vinyl, amine or thiol) downstream suitable for polymerization with another vinyl monomer resulting in the synthesis of an organoclay hybrid material.

In this study we attempt to prepare a new hybrid organoclay material using a local (Algerian) montmorillonite for the first time. The organo-montmorillonite was prepared successively by the intercalation of dodecylamine (DDA) salts and grafting of 3-mercaptopropyl triethoxysilane (MPTES) on fractionated sodic montmorillonite.

The obtained organoclay which ported SH group was dispersed in styrene monomer to prepare polystyrene/organoclay hybrid material via radical polymerization.

2. Materials and methods

2.1. Materials

The raw clay was purchased from the Maghnia deposit (West of Algeria).The 3-mercaptopropyl triethoxysilane MPTES (M= 238 g/mol, d=0.98), styrene monomer and dodecylamine DDA were purchased from Aldrich product. The experimental protocol focused on preparation of different samples, namely: purification of raw clay, exchange of clay by sodium cations and fractionation, intercalation of DDA onto fractionated sodic clay, grafting of MPTES onto intercalated sample, the radical polymerization to synthesis hybrid material sample and the dissolution of the latter by hydrofluoric acid in order to recover the organic part.

2.2. Purification of raw clay

The raw clay was washed with hydrogen peroxide to remove all organic matter followed by drying in an oven set at 80 °C for 24 h. The purified clay was milled in a mortar, in order to obtain homogeneous particles sizes. The obtained sample was denoted as raw Mt and characterized by: Elemental analysis XRF, TGA, XRD and FTIR.

2.3. Sodification and fractionation of montmorillonite

The raw Mt sample was immersed into NaCl (1M) solution. The contact was repeated 3 to 4 times for a better ion exchange. The mixture was stirred for 20 minutes. It was filtered on a sintered glass and washed with distilled water using the centrifugation method (4000 rpm, for 20 min) until no chloride ion was detected with silver nitrate (AgNO₃) solution. The absence of the white precipitate is the confirmation of this. The mineral part was dried in oven at 80 °C for 24 hours, milled with mortar and sieved (<2 μm). The recovered powder is sodic montmorillonite (Mt-Na), which characterized by: XRF, XRD, FTIR and TGA.

2.4. Mt-Na modified by DDA salts

30 g of Mt-Na was dispersed in 500 ml of hot water (80 °C) and stirred for 1 h (mixture A).
10 g of DDA was dissolved in a mixture of distilled water and hydrochloric acid (36%) at 80 °C for 3 h with stirring (mixture B). The obtained mixture (mixture A+B) was left at room temperature without stirring for about 24 hours. The product was washed with distilled water at 80 °C until a negative chlorine test with AgNO₃. The precipitate was then centrifuged (4000 rpm, 20 min) and dried in an oven (80 °C, 24 hours) to obtain the modified montmorillonite (Mt-DDA), which was characterized by microanalysis (CHN), XRF, XRD, FTIR and TGA.

2.5. Grafting of MPTES onto Mt-DDA

10 g of the Mt-DDA was introduced into a two-pipe flask, immersed in an oil bath, equipped with a nitrogen inlet and a cooler equipped with a bubbler. 50 ml of freshly distilled Toluene (T$_{eb}$ = 110 °C) and 10 mg of hydroquinone (Polymerization inhibitor) were added via a syringe via a capillary.
The suspension was stirred for 15 min. Then 8 ml (≈ 8g) of MPTES (M= 238 g/mol, d=0.98) was added. The suspension was brought to reflux for 12 h under nitrogen sweeping at the temperature of 100 °C. Once this period was complete, the sample was cooled, filtered in a large sinter and then washed with dichloroethane (3 times, 15 min) to eliminate the ungrafted monomer. The recovered sample was dried with a water pump for 6 hours before putting in the oven (80 °C, 24 h) (*Sheme. 1.a*). This sample denoted as Mt-SH, which characterized by microanalysis tests (CHN), XRD, FTIR and TGA.

2.6. Polymerization of styrene onto Mt-SH

5 g of Mt-SH, dried under vacuum were introduced in a 50 ml flask with two tubes.

A determined amount of toluene (freshly distilled solvent) and styrene monomer were introduced using a syringe and a capillary. The suspension was stirred, degassed by bubbling nitrogen for 30 minutes and heated at the polymerization temperature (65 °C). The appropriate amount of azo initiator such as azobisisobutyronitrile (AIBN) was dissolved in 3 ml of toluene was then added, with the ratio [styrene]/[AIBN] = 100.

The polymerization reaction was maintained for 24 h under inert atmosphere.

The suspension was then filtered and the support was placed in a soxhlet for extraction of the ungrafted polymer. The solvent used for the extraction is toluene, which solubilizes the ungrafted polymer and removes it from the surface of the support. Only the grafted polymer remains attached to the surface (*Sheme. 1.b*). The recovered sample is HM, oven-dried (80 °C, 24 h) and characterized by microanalysis CHN, XRD, TGA and FTIR.
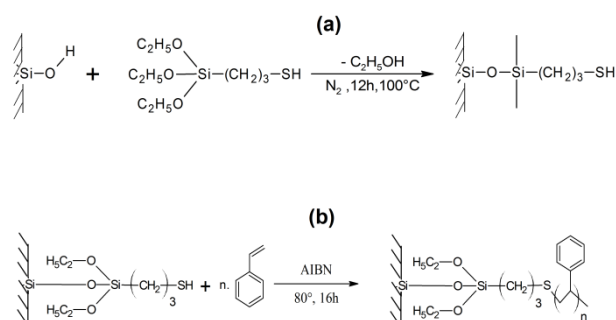
Sheme.1 Schematic illustration of grafting (a) and polymerization (b) equations

2.7. Dissolution of HM by hydrofluoric acid

1g of HM was placed in a Teflon container fitted with an airtight cap. 10 ml of a hydrofluoric acid solution (HF, 40%) was added. The time of contact was 24 h in an oven at 50 °C.

20 ml of toluene was then added and the suspension was stirred for 1 hour at room temperature. Finally, 50 ml of boric acid (H_3BO_3, 4%) was added to neutralize the remaining HF [22]. The polymer was recovered by precipitation in methanol, analyzed by FTIR and compared to the FTIR spectra of HM.

2.8. Characterizations

X-ray Fluorescence; the chemical compositions are determined by X-Ray Fluorescence (XRF) spectrometry Philips PW 2400 XRF. The samples were prepared by the method of fusion with LiB_4O_7.

CHN; Elements C and N were determined by thermal conductivity through combustion in oxygen at 1050 °C under a stream of helium with formation of CO_2 and NO_2.

The separation of the two species is done on a chromatographic column

The XRD measurements were carried out using a diffractometer (Philips diffractometer X'Pert Software) using Cu-K$_\alpha$ radiation (λ = 0.1540 nm) which includes: An X tube with Cu anode powered by high frequency. A goniometer equipped with a detector. A monochromator located on the diffracted beam used to select the average wavelength of Cu. A computer equipped with software for piloting the goniometer and counting and recording the results. We used a step of 0.02 ° and a counting time of 1.05 second /step, for a 2 θ interval between 3 and 80 °. The corresponding basal space was calculated by application of Bragg's law.

TGA; The analyzes were carried out under a nitrogen flow at 10 ml/min, for a heating rate of 10 °C/min and a temperature interval of 30 to 800 °C, using a thermogravimetric analyzer of the SHIMADZU TGA brand. -51

The grafted amount was determined from TG results according to [10] using eq (1) from the weight loss, $W_{200-600}$, between 200 and 600 °C corresponding to silane degradation.

Grafted amount (m_{equiv}/g)=$10^3 \times W_{200-600}/(100- W_{200-600})M$　　　(1)

Where M (g/mol) is the molecular weight of the grafted silane molecule.

$W_{200-600}= W_{Mt-SH(200-600)}- W_{Mt-DDA(200-600)}$　　　(2)

The grafting yield, which corresponds to the percentage of silane molecules which effectively participated in the coupling reaction, was calculated as follows:

Grafting yield (%)=grafted amount×100/[silane]　　　(3)

Where [silane]=3.36 meq / g

FTIR; The Fourier transform infrared FTIR spectra are recorded on a branded device (Shimadzu FTIR 830 spectrophotometer) with a spectral range of 4000 and 400 cm^{-1}. 297 mg of pure and dry KBr are mixed with 3 mg of solid product. The pellet is obtained by compression of the mixture under vacuum (8 tonnes/cm^2).

3. Results and discussion

3.1. Analysis of Elements by XRF

The compositions of raw Mt, Mt-Na and Mt-DDA were determined by XRF technique.
The results of elements analysis by XRF are grouped in the *Table. 1*

Table 1: XRF results of raw Mt, Mt-Na and Mt-DDA samples.

Mass ratio (%)	Raw Mt	Mt-Na	Mt-DDA
SiO_2	54.13	55.28	55.20
Al_2O_3	17.74	18.20	18.00
Fe_2O_3	3.51	3.14	2.15
CaO	1.24	0.60	0.08
MgO	5.03	3.10	2.32
SO_3	0.42	0.38	0.39
K_2O	1.17	0.78	0.76
Na_2O	1.96	3.75	0.42
L.F	13.61	15.36	09.43
Σ	99.58	100.59	88.75

In order to better evaluate the cations exchanged with sodium cations in Mt-Na and nitrogen in Mt-DDA, to know the nature of the cations replaced during the exchanges, the ratios [Cation / Si] were calculated before and after both exchanges. The obtained results were mentioned in the *Table. 2.*

Table 2: Atomics reports [Cation / Si], before and after exchange by DDA salt.

[Catio/Si]%	Al/Si	Fe/Si	Ca/Si	Mg/Si	S/Si	K/Si	Na/Si
Mt-Na	37.34	8.53	1.62	7.25	0.58	2.48	10.77
Mt-DDA	36.99	5.82	0.19	5.43	0.58	1.40	1.20

The comparison between raw clay and sodic montmorillonite showed a decrease in Ca, K and Mg ratios after sodification of clay. But an increase in Na ratio was observed.

The composition of the **Mt-DDA** showed clearly that the Na^+ cations were replaced by the $-NH_3^+$ cations of DDA salt during the modification (nitrogen ratio = 1.74%). These results were confirmed by the calculation of the [Cation / Si] ratios where a clear decrease in the [Na /Si] ratio from 10.77 to 1.20% after modification. The other [Cation/Si] ratios have kept approximately constant values, so; these cations did not represent exchange sites.

3.2. Elements analysis by CHN method

The results obtained by this technique were for Mt-DDA, Mt-SH and HM and were grouped in the Table 3

Table 3: CHN results of Mt-DDA, Mt-SH and H M samples

Sample	Mt-DDA	Mt-SH	HM
% C	5.30	12.42	31.05
N %	1.74	----	-------

The results obtained by CHN showed clearly a nitrogen rate of 1.74%, which confirms the exchange of Na^+ cations by NH_3^+ cations.

The same results revealed the presence of carbon with a rate of 5.30% in Mt-DDA sample and which increased to 12.42% in Mt-SH sample. This increase is quite logical because the used silane in grafting contains the organic functions in its structure (ethoxy and propyl) which were added to the intercalated surfactant (DDA) which also contains a long chain alkyl (dodecyl) in its structure. This proves that the modification by DDA and the grafting were real.

These same results also showed an increase in carbon content in the HM, from 12.42 for Mt-SH to 31.05% for HM. This is in favour of a significant presence of other organic compounds which could be the macromolecular chains, resulting from the reactions of polymerization of styrene. This hypothesis should be confirmed by other characterization tests such as FTIR and XRD.

3.3. FTIR results

The FTIR spectra of five samples (raw Mt, Mt-Na, Mt-DDA, Mt-SH and HM) were regrouped in *Figure 1.*
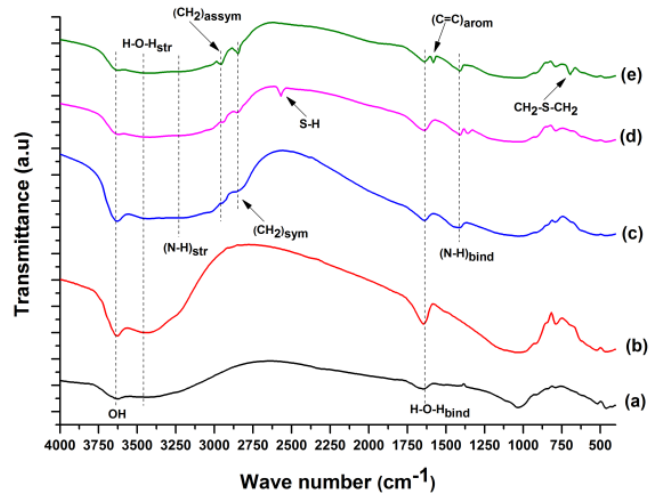

Figure 1. FTIR spectra of raw Mt (a), Mt-Na (b), Mt-DDA (c), Mt-SH (d) and H M

The characteristic bands of raw Mt (*Figure 1.a*) with their respective attributions are grouped in the *Table. 4.*

Table 4: Mains bands appeared in raw Mt FTIR spectra with their attributions

	ν (cm^{-1})	Attributions
Raw Mt	3625.90	Stretching vibrations of O-H layers
	3440.70	H-O-H Stretching vibrations of physorbed water
	1650.90	H-O-H Binding of physorbed water
	1033.70	Si-O Binding
	925.76	Al-Al-OH Vibrations
	840.90	Mg-Al-OH Vibrations
	786.90	Mg-Fe-OH Vibrations
	617.17	Al-O-H Vibrations
	524.60	Si-O-Al Vibrations
	462.88	Si-O Vibrations
	424.31	Si-O-Si Vibrations

For Mt-Na spectra (*Figure 1.b*), the intensity of OH bands (OH of water) was increased to a large extent due to the intercalation of Na^+ cations, leading to the formation of more hydrophilic surface.

In the Mt-DDA spectra (*Figure 1.c*), the majority of the raw Mt bands were preserved, but new bands located at 2954.7 cm^{-1} and 2854.4 cm^{-1} were appeared attributed to stretching vibrations of CH and CH$_2$ from the alkyl chain, respectively [23]. The bands located at 3201 cm^{-1} and 1420 cm^{-1} can be assigned respectively to the N-H stretching and binding of ammonium [24].

In comparison with the Mt-Na spectra (*Figure 1.b*), the decrease in intensities of the bands at 3440 cm^{-1} and 1635.5 cm^{-1} related to OH hydration water was noticed, because the hydrated cations initially present in the interlayer space (Na^+) were substituted by DDA cations during the cation exchange process, which transform the surface of clay from hydrophilic to hydrophobic state, this means that the intercalation of montmorillonite by the alkyammonium

produces less space available for adsorption of water molecules, so the intercalation by DDA has taken place.

The spectra of Mt-SH sample was represented in (*Figure 1.d*). In addition to the characteristic bands of the mentioned samples (raw Mt, Mt-Na and Mt-DDA), the spectra of grafted clay showed new band located at 2569 cm^{-1}, assigned to: S-H group of the silane molecules [25].

The higher intensities of the absorption bands at 2947 and 2854.4 cm^{-1} compared to Mt-DDA sample were also observed, which confirmed that the silane was successfully grafted onto the silanol of montmorillonite sheets.

The significant decrease in band intensity located at 3624 cm^{-1} which attributed to OH of the silanols Si-OH and the aluminols Al-OH located at the tetrahedral and octahedral montmorillonite sheets in the Mt-SH sample compared to that in the Mt-DDA, can be explained by the conversion of the silanol Si-OH to Si-O-Si during grafting process with the silane (*Sheme. 1.a*), The significant decrease in band intensity located at 1635.5 cm^{-1} was also observed, which implies a decrease in the water content and a more change of the montmorillonite surface from its hydrophilic state to a hydrophobic one.

In the HM spectra (*Figure 1.e*), a band at 1581 cm^{-1} attributed to aromatic C=C of styrene was appeared.

It was noticed, the absence of band related to S-H of silane and appearance of new band located at 694 cm^{-1} attributed to CH_2-S-CH_2 [26]. The increase in the bands intensities which located at 2954 and 2846 cm^{-1} in HM compared to Mt-SH allow us to confirm the radical polymerization reaction by transfer of hydrogen between the styrene and the thiol function of the silane. The decrease in the intensity of the 1635 cm^{-1} band attributed to water promotes the hydrophobic character of HM.

3.4. XRD results

The XRD spectra of the five samples are represented in *Figure 2*. It clearly showed the disappearance of some peaks presented in raw Mt related to impurities after the first modifications process. This is due to a successful washing and purification process of the raw clay was achieved. Despite the various treatments of raw Mt (purification, exchange with Na^{+}, modification by DDA, grafting and polymerization), the main peaks were not modified. Therefore, these treatment can not leading to a significant change in the structure of clay.

These various treatments have changed only the interlayer spacing d_{001} of clay platelets (*Table. 5* and the *Figure 2*).
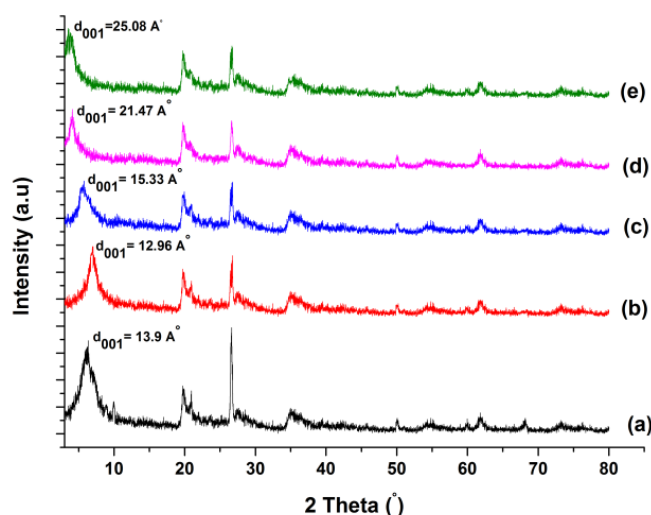

Figure 2. XRD patterns of raw Mt (a), Mt-Na (b), Mt-DDA (c), Mt-SH (d) and H M.

Table 5: values of 2θ (001 reflexion) and d_{001} of five samples

Samples	raw Mt	Mt-Na	Mt-DDA	Mt-SH	H M
2Θ (°)	6.35	6.96	5.76	4.11	3.52
d_{001} (Å)	13.90	12.69	15.33	21.47	25.08
Spectra	(a)	(b)	(c)	(d)	(e)

The raw clay showed several reflections in the angular range 2 θ (2 - 10 °) indicating the presence of various mono and bihydrated cations and a predominance of montmorillonite with small amounts of impurities such as Quartz, Feldspat and traces of Cristobalites [27].

The characteristic peak of montmorillonite displays a diffraction at 2 θ = 6.35 °, corresponding to a basal spacing d_{001} = 13.90 Å. This spacing represented the sum of the thickness of the TOT layer of montmorillonite (9.50 Å) [28] and the interlayer spacing which depends on the size of the cations and the interlayer water whose mass content was determined by TGA. The Mt-Na showed a peak located at 2 θ = 6.96 ° (d_{001} = 12.69 Å), this decreasing in spacing value is mainly due to the substitution of the exchangeable cations K^{+}, Ca^{2+} and Mg^{2+} which were exchanged by the monovalent cations Na^{+}.

The increase in spacing d_{001} to 15.33 Å (2 θ = 5.76 °) displayed by Mt-DDA confirms the intercalation of alkylammonium cations between sheets of the montmorillonite.

It should be remembered that the possible arrangements of the alkylammonium ions intercalated in the interlayer spaces of the smectites, can be in monolayer, in bilayer, in pseudo-trilayer and in paraffin structure arrangements [29].

The length of DDA molecule was approximately 16.73 Å and a thickness about 2.809 Å (values determined by the Chemsketch software, *Sheme. 2*).
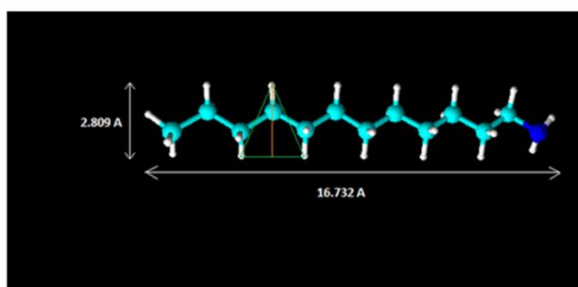
Sheme 2. Representation of DDA molecule size determined by the Chemsketch software.

The interlayer space available is 5.83 Å, (15.33 Å– 9.50 Å).The cations adsorbed could therefore be intercaled in the galleries of montmorillonite in two layers horizontally superimposed (2×2.809≈5.83 Å).

The functionalization of Mt-DDA was carried out by grafting of MPTES molecules carrying ethoxy –OC_2H_5 groups as a hydrolyzable alkoxy group and the thiol function as a functional group.

If the MPTES silane were interacted with the clay mineral surface, forming chemical bonds at the interface, it must be first converted to reactive silanol by hydrolysis. This hydrolysis can occur directly on the surface of the substrate by reaction with the surface water (direct hydrolysis) or during a previous step of preparation of the aqueous silane solution (prehydrolysis).

The silanol form of the silane can be grafted onto clay mineral by reaction of condensation with the hydroxyl groups on the montmorillonite surface. In this case the S-H functions will be found between sheets of the clay. This would increase the hydrophobicity of the montmorillonite.

The XRD spectra of Mt-SH revealed a basal spacing d_{001} = 21.47 Å (2θ = 4.11 °) greater than 15.33 Å displayed by the Mt-DDA. In addition to grafting reaction of silane molecules on silanol Si-OH of the sheets edges of montmorillonite, this increase in d_{001} is an advance of another hypothesis for reaction type that is the condensation of the hydroxyl groups of surface with silane molecules whose alkoxy groups are hydrolyzed by interlamellar hydration water. This deduction is in perfect agreement with the results study realisead by [30] wich concluded that the grafting reactions of silanes on montmorillonites was strongly depend on its concentration.

This study showed that grafting can occured on the silanols of sheets edges and those on the hydroxylated surfaces, for silanes concentration ≥3 mmol /g of montmorillonite.

This exactly coincides with an amount 8 ml (3.26 mmol/gg) of MPTES (M = 238 g / mol and a density = 0.98 g/ml) added to 10 g of clay.

On the XRD spectra of hybrid material H M, a first peak located at 2θ = 3.52 ° (d_{001} = 25.08 Å) was observed. An increase of 3.61 Å compared to d_{001} of the Mt-SH was observed, which can only be explained by the presence of macromolecular chains of the polymer (the polymerized styrene with the thiol function by transfer of hydrogen between the styrene and the thiol function of the silane MPTES) onto clay galleries.

In addition; the peak intensity related to 001 reflexion is unchanged, this is indicated that the majority of polymer is intercaled in clay galleries (intercalated structure).

3.5. TG results

The Both thermogravimetric (TG) and its derivative (DTG) curves, in inert atmosphere, of five samples were represented in Figure 3.

The (TGA and DTG) curves of raw Mt sample (Figure 3.a,a) were revealed two degradations steps. The first mass loss is located at the temperature range (30 - 250 °C) with a maxima at 133 °C evaluated at 09.54% attributed to the desorption of physically adsorbed water and to dehydration of interlayer hydrated cations. The second range (600 - 750 °C) with a maxima at 700 °C displayed the mass loss of 03.29%, attributed to dehydroxylation of the aluminosilicate sheets [31].

The (TGA and DTG) curves of Mt-Na sample (Figure 3.b,b) were also revealed two degradations steps. The first mass loss is located at the same temperature range (30 - 250 °C) with a maxima at 128 °C evaluated at 11.46% attributed to the desorption of physically adsorbed water and to dehydration of interlayer hydrated cations. The second range (600 - 750 °C) with a maxima at 675 °C displayed the same mass loss of 03.84%, attributed to dehydroxylation of the aluminosilicate sheets. These results correspond to those found by the elements analysis (losses on fire).

The mass loss displayed by Mt-Na in the range (30 - 250 °C) was higher than raw Mt, this can be explained by the high number of water molecules entoured the Na^+ ions compared to other cations (Ca^{2+}, Mg^{2+} and K^+) because Na^+ is more hydrated.

The (TG and DTG) curves of the Mt-DDA (Figure 3.c,c) presented three degradations steps. The first mass loss in the ranges (30 - 210 °C) with a maxima at 113 °C, the second (210 - 450 °C) with a maxima at 290 °C and the last (500 - 700 °C) with a maxima at 600 °C, evaluated at 07.14%, 09.15% and 02.29% respectively, which correspond to release of physisorbed water, to decomposition of DDA and to dehydroxylation phenomenon, respectively.

The mass loss 07.14% is lower than the values displayed by the first two samples in the same temperature range, this is an indication of a decrease in the water molecules adsorbed in the interlayer of montmorillonite and confirms the exchange of hydrated cations Na^+ by DDA cations. [32].

In previous study; a pure HDTMA which having more number of carbon then DDA, the decomposition of this surfactant was occurred in the range of temperature (200-350 °C) with a maxima at 269 °C [12] , whereas the decomposition of DDA intercaled clay over on large temperature range (210 - 450 °C), with a maxima at 290 °C, passed 30 minutes, taking into account the heating rate of 10 °C/min (TGA operating conditions), this slow decomposition proves that the intercalation of alkylammonium molecules in gallery of clay retards their decompositions, this is indirectly a favour of intercalation efficiency process. The last degradation step located in the range (500 - 700 °C) with a maxima at 600 °C displayed the

mass loss of 2.29 %, attributed to dehydroxylation of the aluminosilicate sheets.

The (TG and DTG) curves of Mt-SH sample (*Figure. 3.d,d'*) were showed only two degradations steps; the first (250 - 620 ◦C) with two maximas ; at 370 ◦C (in the range 250 - 510 ◦C estimated at 46.5 %) and 550◦C (in the range 510 -620 ◦C estimated at 4.5 %) attributed to the decomposition of DDA and M PTES and the second step (620 - 750 ◦C) with a maxima at 720 ◦C estimated at 3.25% attributed to dehydroxylation of the aluminosilicate sheets.

Furthermore, the decomposition process of the Mt-SH was slower than that of the Mt-DDA (more large temperature range than Mt-DDA), and a higher mass loss, which can be attributed to the grafting of silane molecules, with higher thermal stability based on the Mt-DDA. Results on the thermal stability of materials provided additional evidence that the grafting of TMSPM at montmorillonite layers was successful.

The (TG and DTG) curves of HM sample (*Figure 3.e,e'*) were showed two degradations steps; the first (300 - 600 ◦C) with a maxima; at 426 ◦C estimated at 60 % attributed to the decomposition of DDA , MPTES and grafted polystyrene polymer and the second step (600 - 750 ◦C) with a maxima at 720 ◦C estimated at 10 % attributed to dehydroxylation of the aluminosilicate sheets.

The almost total absence of water loss recorded at low temperatures (<250 ° C) in Mt-SH and HM confirms the very pronounced hydrophobic character of these two types of materials.
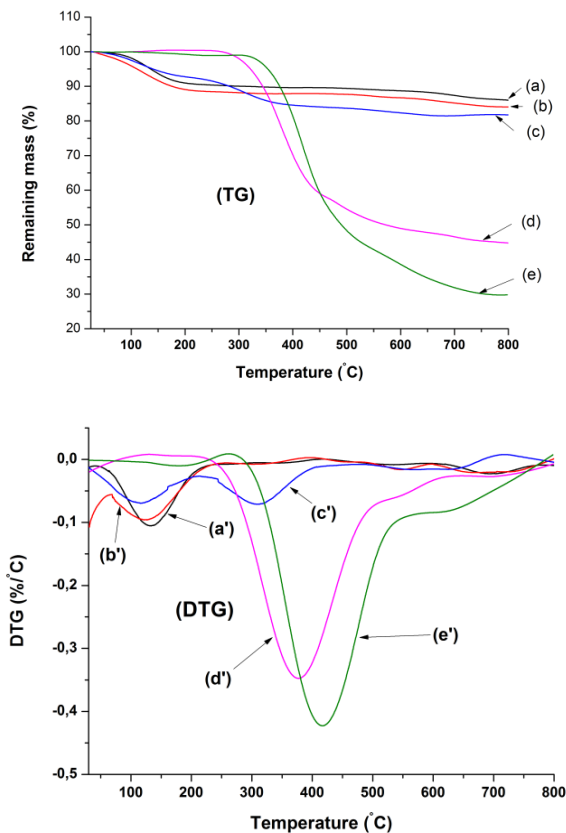

Figure 3. TG, DTG curves of raw Mt (a, a'), Mt-Na (b,b'), Mt-DDA (c,c'), Mt-SH (d,d') and HM hybrid material (e,e')

The TG results showed also a high grafting efficiency of silane onto Mt-DDA which represented in *Table. 6*

Table 6: Grafting yield determination from TG results

Sample	weight loss (%)[a]	grafted amount (mequiv/g)[b]	grafting yield (%)[c]
Mt-DDA	50	--------------------------	--------------------
Mt-SH	11	3.31	98

[a]Weight loss between 200 and 600 °C. [b] Determined using eq (1). [c] Determined using eq (3).

3.6. Thermal stability of hybrid material

The thermal stability of the HM hybrid material and pure Polystyrene polymer [33] were studied.

The onset decomposition temperatures ($T_{5\%}$) (5% mass loss temperature), ($T_{10\%}$) (10% mass loss temperature), ($T_{20\%}$) (20% mass loss temperature), the mid-point decomposition temperature ($T_{50}\%$) (50% mass loss temperature) and the finally mass loss temperature (T_f obtained from DTG) of two materials are listed in *Table. 7*.

At ($T_{5\%}$); The onset decomposition temperatures ($T_{5\%}$) for both materials have occurred in the same temperature.

In TG/DTG curves of Mt-SH ; the onset decomposition of this material was started in lower temperature (250 ◦C) value compared to HM, this indicated that the grafted polymer retards the decomposition of both silanes and DDA molecules.

At $T_{10\%}$ (C); the $T_{10\%}$ was 6 °C higher for the HM than that observed for the pure Ps.

At $T_{20\%}$ (C); the $T_{50\%}$ was 11 °C higher for the HM than that observed for the pure Ps.

At $T_{50\%}$ (C); the $T_{50\%}$ was 88 °C higher for the HM than that observed for the pure Ps.

At the end of decomposition process, the T_f of H M was 150 °C higher than pure Ps.

These indicated that Mt-SH sample exhibited a beneficial effect on the improving of the thermal stability of polystyrene.

This great enhancement of thermal stability may be that the amount of intercalated Ps is high enough to promote high thermal stability of polymer, which acts as a physical barrier preventing the heat to propagate quickly and delaying its decomposition. The TG analysis confirms the result obtained by XRD that showed the majority intercaled polymer in the clay galleries. Samakande et al. [34] observed similar results with Ps/clay nanocomposites prepared by free-radical polymerization in bulk. In their work it is clear that a higher degree of intercalation of polystyrene polymer in clay galleries, led to the improvement of the Ps/clay nanocomposites thermal stability.

Greesh et al [35] were compared thermal stabilities of intercaled and exfoliated Ps/ MPTMS grafted Na-MMT nanocomposites who found higher thermal stabilities for intercalated structures relative to the exfoliated morphologies.

Table 7: TGA data of pure PS polymer and H M at different decomposition temperatures (T$_{5\%}$, T$_{10\%}$, T$_{20\%}$, T$_{50\%}$, and T$_f$)
**Values are from Wang et al [33]

Sample	T $_{5\%}$ (C)	T$_{10\%}$ (°C)	T$_{20\%}$ (C)	T$_{50\%}$ (C)	T $_f$ (C)
Pure Ps	354**	370**	390**	412**	440**
H M	353	376	401	490	590

3.7. Dissolution hybrid material by HF attack

The attack of H M by hydrofluoric acid, lead to recover the polymer (silane-styrene) initially grafted and to highlight in the FTIR spectra in *Figure 4*.
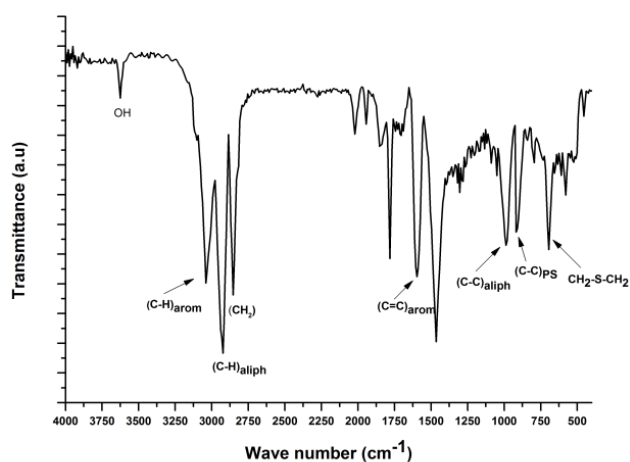

Figure 4. FTIR spectra of recovered polymer by HF attack

The main characteristic bands appeared in recovered polymer spectra (*Figure 4*) with their respective attributions are grouped in the *Table. 8*.

Table 8: Mains bands appeared in recovered polymer FTIR spectra with their attributions

Bands (cm^{-1})	Attributions	Bands (cm^{-1})	Attributions
3625.9	OH	1589.2	(C=C)$_{arom}$
3039.6	(C-H)$_{arom}$	987.4	(C-C)$_{aliph}$
2923.8	(C-H)$_{aliph}$	918	(C-C)$_{PS}$
2854.4	CH$_2$	694.3	CH$_2$-S-CH$_2$

Table.8 includes the main bands appeared in the recovered polymer spectra *Figure.4*, which can be identified as PS bound to the organic part of the silane, this is confirmed by the presence of the band located at 694.3 cm^{-1} attributed to CH$_2$-S-CH$_2$. The occurrence at 3625.9 cm^{-1} attributed to O-H aluminols from the octahedral layers of montmorillonite which HF did not destroy. The superposition of the two spectra (recovered polymer and hybrid material) was represented in *Figure 5*. It was clearly showed common analogous bands designated by (a. a '), (b .b'), (c. c '), (d. d'), (e. e') and (f. f ') attributed respectively to the vibrations of (OH), **(C-H)**$_{arom}$ **(C-H)**$_{aliph}$ **(CH$_2$)**

(C=C)$_{arom}$ (C-C)$_{aliph}$ (*Table.9*). it is important to notice the appearance ;on the spectrum (a) of a series of bands in the interval 1200 - 400 cm^{-1} which were masked by the silicic framework in the H M before the HF attack.
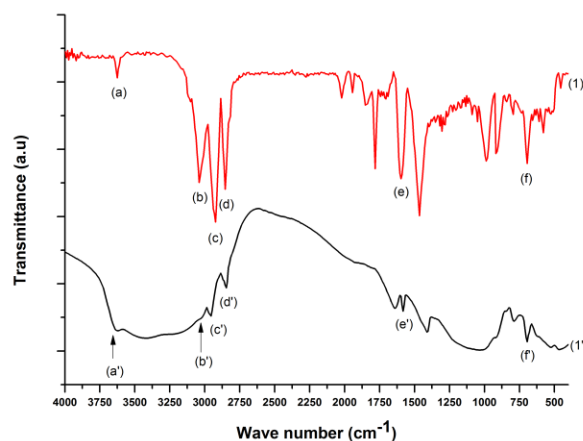

Figure 5. FTIR spectra of recovered polymer by HF attack (1), and hybrid material (HM) (1')

Table 9: Attributions of diffirents bands of FTIR spectra (1) and (1')

Bands of spectra (1) (cm^{-1})		Bands of spectra (1') (cm^{-1})	
(a)	3625.9	(a')	3633.6
(b)	3039.6	(b')	3055.0
(c)	2923.8	(c')	2954.7
(d)	2854.4	(d')	2846.7
(e)	1589.2	(e')	1581.5
(f)	694.3	(f')	694.0

4. Conclusion

To prepare an organoclay hybrid material; the grafting of a functional monomer (styrene) by radical polymerization onto Algerian montmorillonite exchanged by an alkylammonium (DDA salts) and functionalized beforehand by a silane (MPTES) carrying a chemical function (SH) allowing the polymerization of the styrene monomer at the surface of clay by transfer of hydrogen between the styrene and the thiol function of the silane was realized. Various physicochemical characterizations using XRF, CHN, XRD, TGA and FTIR have demonstrated ; the intercalation of DDA salts by enhancement of interlayer space of clay ; the grafting of MPTES by creation of the new covalent bond Si-O-Si between the clay surface and the silane and the grafting of macromolecule polymer with the functionalized silane. These results of characterization revealed also the higher thermal stability of prepared organoclay hybrid material compared to pristine polystyrene polymer and the strong hydrophobicity of its area. We have just exposed a series of original results characterizing the behaviour of organoclay hybrid material manifesting an intercaled structure, very pronounced thermal stability and hydrophobic character.

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