

GLOBAL JOURNAL OF ENGINEERING SCIENCE AND RESEARCHES CHARACTERIZATION AND GRAFTING OF ORGANOSILANE IN SWELLING CLAY MATERIALS FROM NADOR

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ABSTRACT

Understanding the structure-property relations in polymer/clay nanocomposites is of great importance in designing materials with desired properties. Along these lines, a critical overview is attempted on the physical and molecular origins of material properties in polymer/clay hybrid nanocomposites. In general, such properties originate from the nature of the layered inorganic fillers and from their nano-dispersion in a polymer. In contrast, other properties are determined by the particular/distinctive interactions between specific polymers with the filler such attributes can not be transferred from one polymer system to another.

Fictionalizations of montmorillonite clay were carried out using 3-aminopropyltrimethoxysilane in toluene media. The organosilane attached to the clay platelets have been identified using Fourier transform infrared spectroscopy (FTIR). Grafting yield has been calculated using thermo gravimetric analysis. X-ray diffraction studies showed that the functionalized montmorillonite clay exhibits intercalation structure and surface interaction of the silane with the broken edge platelets

Keywords: *Montmorillonite, clay, Characterization, Grafting.*

I. INTRODUCTION

Nanocomposites of polymers and inorganic nanoparticles have attracted more and more attention, not only because they combine the advantageous properties of conductive polymer and inorganic particles, but also new type of composite materials with synergistic or complementary behaviors that have interesting physical properties and many potential applications [1-2].

Polymer-layered silicate nanocomposite is a promising class of materials that offers the possibility of developing new hybrid materials with a desired set of properties. The presence of two-dimensional plate like silicate layers in the matrix of a polymer leads to significant gains in the mechanical and barrier properties of the resulting nanocomposite [3]. The properties of polymer-clay nanocomposites are generally determined by their morphologies, the shape of the clay, the size of the clay particles, and the degree of dispersion in the polymer [4]. Layered silicates exhibit many interesting structural features: active sites such as hydroxyl groups, Lewis and Brønsted acidity, and exchangeable interlayer cations [5].

The influence of alkyl ammonium cations in the interlayer swelling of montmorillonite, has been extensively studied [5-6]. The extent of swelling depends on the length and molecular dynamics of the alkyl chain and the cation-exchange capacity (CEC) of the clay [7]. Herrera et al. [8-9] reported the influence of silane coupling agent on the interlayer swelling of the laponite and montmorillonite clays, using toluene as a dispersing medium. The average d-spacing is high with the solvents having low surface energy and high surface energy (toluene) in comparison to the surface energy of the montmorillonite, which indicates that both the dispersive and polar components of surface energy influence the average d-spacing. Influence of dispersing medium on grafting of amino propyltriethoxysilane

in swelling clay materials [10]. In this paper, we report the chemical functionalization of montmorillonite with 3-aminopropyltrimethoxysilane. The functionalized clay has been characterized with different techniques such as Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray diffraction

II. METHOD & MATERIAL.

1. Materials

Clay row materials is a bentonite layered silicate which was obtained from the north eastern region of Morocco (Nador). Fine particles of purified clay were obtained by successive sedimentation and drying procedure. The cation exchange capacity (CEC) of the clay is determined by methylene blue adsorption procedure. The montmorillonite type (Na-MMT) was prepared by stirring 10% of clay suspension with 1N NaCl solution at room temperature for 48 h. The resulting Na-MMT was washed with distilled water and then centrifuged and dried. All chemicals (Aniline, (NH₄)₂S₂O₈, methylene blue) were of analytical grade and were used without further purification.

The raw clay from Nador Carrere was washed five times with desionized water and exchanged with saturated solution of sodium chloride. 3-Aminopropyltriethoxysilane was obtained from Aldrich Chemical Company Inc., USA. Toluene (analytic grade) was supplied from Aldrich Chemical Inc.

2. Determination of Cation exchange capacity (CEC)

A known amount (0.886g) of clay is dried overnight at 200 ° C and then mixed to distilled water to prepare a fine suspension which is stirred for 12 hours. 5 ml of this suspension are placed in a container of 50 ml and 20ml of aqueous solution of methylene blue (MB) with a concentration of 10⁻⁶ mol/dm³ are added. The resulting solution is stirred overnight, then centrifuged for 15 min and the solid is separated from the solution .The remaining amount of MB in solution is determined by UV-visible spectrophotometry.

Aminosilane fictionalization of montmorillonite

Four grams of clay was dispersed in 150 ml of solvent at 60 °C using a mechanical stirrer. Four gram of 3-aminopropyltrimethoxysilane dissolved in 100 ml of solvent was added to the clay dispersion under constant stirring and stirring was continued for 24h. The final solid was filtered ; washed with toluene and ethanol. It was then soxhlet extracted with mixture of ethanol and dichloromethane (1:1) for 12h to remove the silylating reagent residue. The immobilized clay (clayNH₂), was dried in vacuum at room temperature for 48h.

3. Characterizations

FTIR characterization

About 0.01 g of clay was mixed with 1 g of potassium bromide (KBr) and pelletized in the hydraulic press at 10 kPa. FTIR spectra were recorded in the range from 4000 to 400 cm⁻¹ using a Shimadzu spectrophotometer operated in the transmission mode. The resolution was kept at 4.0 cm⁻¹ and the number of scans was 32.

Thermogravimetric analyses

Thermogravimetric analyses were carried out using Perkin–Elmer TGA in the temperature range from 25 to 1000°C at a scanning rate of 10 °C. min⁻¹ under nitrogen environment to evaluate the amount of intercalated 3-aminotriethoxysilane.

X-Ray diffraction

X-ray diffraction measurements were performed using a Mac-science X-ray diffractometer equipped with a back monochromator operating at 40 kV and a copper cathode as the X-ray source ($\lambda = 1.54 \text{ \AA}$).

III. RESULT & DISCUSSION

1. FTIR characterization

MMT consists of one AlMg₄OH₂ octahedral sheet binding with two tetrahedral Si–O sheets [11-12]. The FT-IR spectrum of the pure clay (Fig. 1) show a characteristic peak at 3634 cm⁻¹ corresponding to the hydroxyl stretching

that is bonded to the aluminum and magnesium Al (Mg) OH or Al (Al) OH). The peaks at 3400 and 1630 cm^{-1} are due to the $-\text{OH}$ stretching and bending vibrations of the adsorbed water. The broad peak over the range of 1200 to 1000 cm^{-1} with the peak maximum at 1043 cm^{-1} is due to the $\text{Si}-\text{O}$ stretching of silicates present in the clay. The bending vibrations of Al (Al) OH and Mg (Mg) OH in MMT occurs at 918 and 800 cm^{-1} , respectively.

It has been reported that broken edges and structural defects in $\text{Si}-\text{O}$ silicate edges are active and can undergo grafting reactions with multifunctional silanes [12]. It is then expected that a condensation reaction can take place in toluene between the hydroxyl groups of MMT and silanol groups or SiOCH_3 groups of 3-aminopropyltrimethoxysilane. The FT-IR results of functionalized clay support this fact. Indeed, the new peaks observed in functionalized clay spectrum at 2934 and 2850 cm^{-1} are due to the $-\text{CH}$ asymmetric and symmetric stretching of $-\text{CH}_2$ groups. Furthermore, new peaks appear at 1560 , 1506 , and 681 cm^{-1} that correspond to the $-\text{NH}_2$ and $-\text{CH}_2$ bending vibrations and $-\text{CH}$ out-of-plane deformation respectively confirming the condensation of the coupling agent on the clay surface. The broad peak in the range of 1200 to 950 cm^{-1} in MMT is attributed to the overlap of $\text{Si}-\text{O}$ stretching and $\text{Si}-\text{O}$ bending vibrations. However, a significant increase in peak height for the modified clays at 1032 cm^{-1} indicates the interaction of the silane with the platelet face.

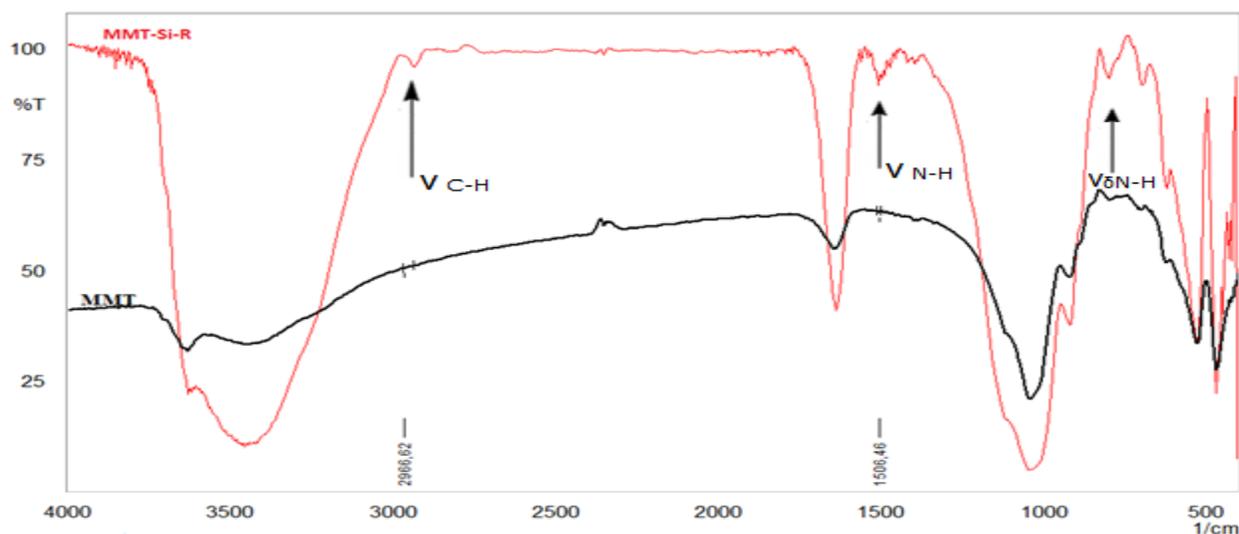


Fig.1 FT-IR spectra of pure and functionalized clay

2. Cation exchange capacity (CEC)

The thickness of the clay sheets is approximately 1 nm while their lateral dimensions may vary from 30 nm to several microns, depending on the type of silicate. The stacking of the layers results in a regular space between Van der Waals layers called the interlayer or the gallery layer. Isomorphous substitution between different cations in the layers (Al^{3+} replaced by Mg^{2+} or Fe^{2+} , and Mg^{2+} replaced by Li^+) generates negative charges that are counterbalanced by alkali cations such as Na^+ and Ca^{2+} located within galleries. This type of silicate is characterized by moderate external load known as the cation exchange capacity (CEC) and generally expressed in milliequivalents per 100 g load. This charge is not locally constant, and may vary from one layer to another layer, and must be regarded as an average value for the whole crystal. In our case cation exchange capacity was measured by adsorption of methylene blue molecules through the recovery of property of this small molecule and charge the results obtained and shown in Fig isothermal adsorption capacity that is the order $de109\text{ meq/g}$ (Fig.2).

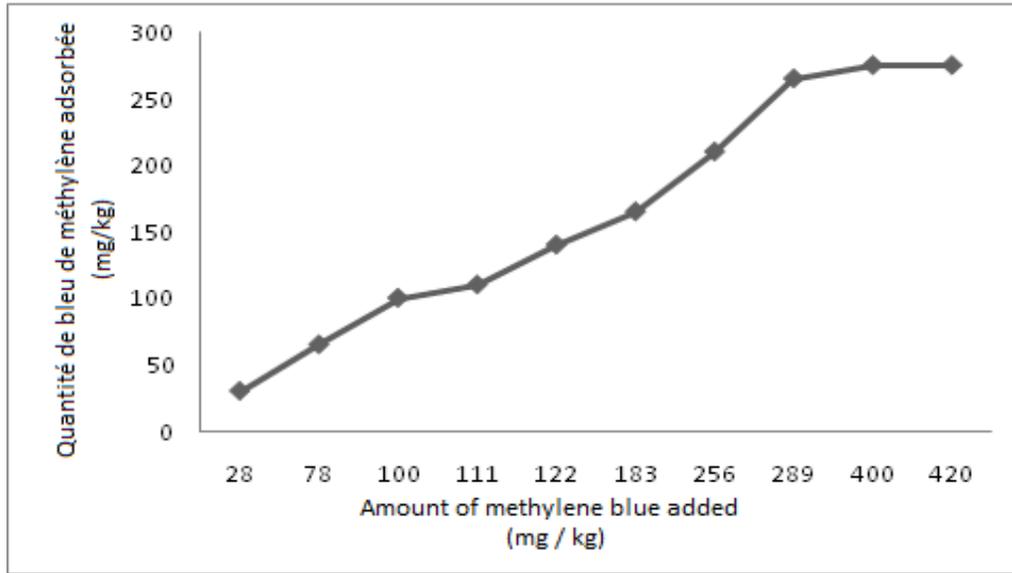


Fig. 2 Adsorption isotherm of clay methylene blue

3. Chemical composition (wt %) of clay

The examination of the results of chemical analysis (table 1) shows that clay layers contains is relatively low in calcium and magnesium compared to the raw samples .This is an indication to these elements mainly from carbonates (calcite, dolomite).Raw clay contain low quantities. This iron element may exist in free forms (oxide, hydroxide) as it may be part of clay network.

Elemental analysis by X-ray fluorescence spectroscopy (XRF) with the aid of a panlytical Minipal 2 provided with a CrK α radiation ($\lambda = 0.2291$ nm). The measurements were performed at 20 kV and 5 uA. The samples were analyzed in powder form, without any additional preparation. Each powder was put in an XRF sample cup plastic.

Table 1: chemical composition (wt %) of clay

Clay sample	SiO ₂ %	MgO%	CaO%	Fe ppm	Al ₂ O ₃ %
Raw clay	61	5.71	4.1	1.13	15.4
Purified clay	65	5.6	3.3	-----	16.3

4. X-ray diffraction

The x-ray diffraction analysis (Fig.3) shows that the chemical grafting of the MMT with 3-aminomethyltriméthoxysilane moves the line (001) Angle of diffraction from $2\theta = 7^\circ$ ($d = 12.5 \text{ \AA}$ interlayer space) to a $2\theta = 6^\circ$ (interlayer space $d = 15 \text{ \AA}$). The spacing of the clay sheets confirms the intercalation and condensation of the silane groups of 3-aminomethyltriméthoxysilane broken edges with the clay nanoparticles (OH-Al and Mg-OH) .

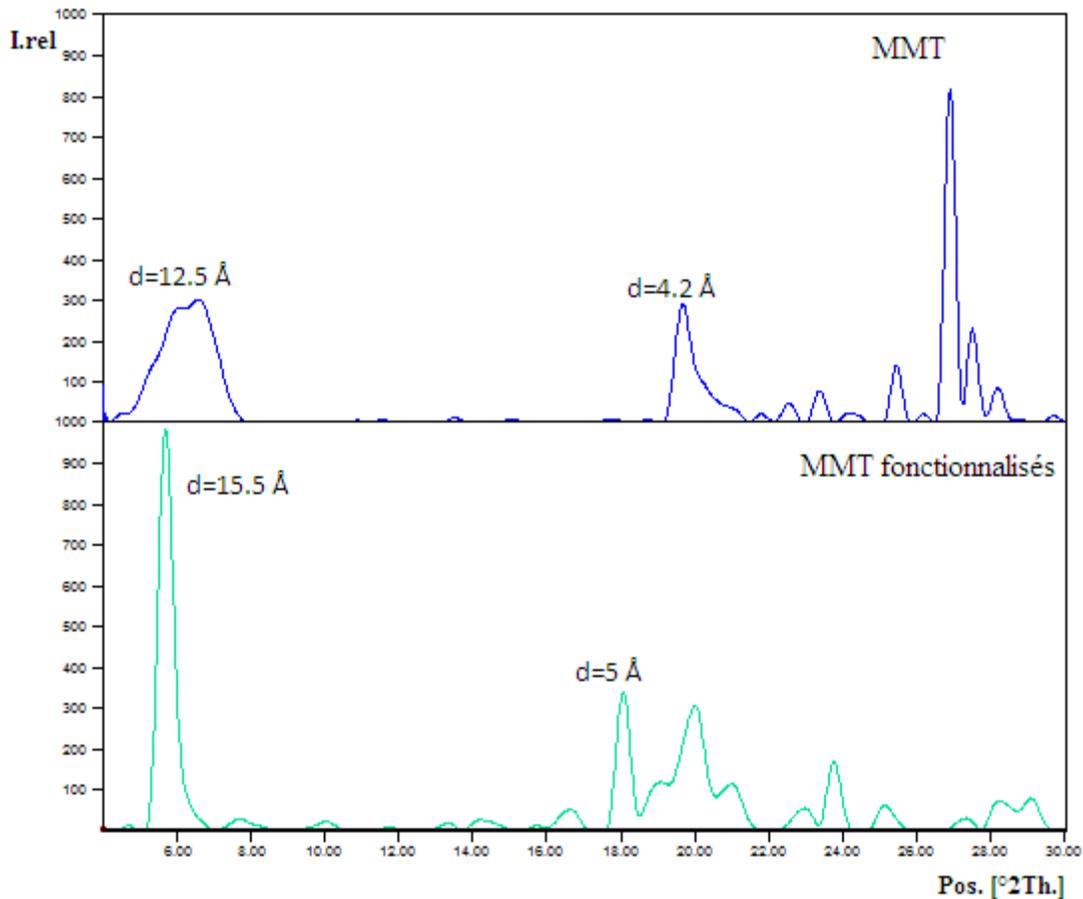


Fig.3 X-ray diffraction patterns of pure and functionalized MMTs.

5. The thermal analysis

To gain more insight into the grafting reaction between silane and MMT, thermal analysis was carried out to determine the amount of grafted silane. Fig. 4 shows the differential thermogravimetric results of pure and functionalized MMTs. The weight loss of functionalized MMTs is greater than that of pure MMT. The initial degradation of the unmodified and silane-functionalized clay below 100 °C is attributed to the vaporization of adsorbed water and toluene [16]. This is supported by the presence of two peaks in the DTG curves for MMT. In the case of functionalized MMTs, it is interesting to observe new degradation steps in the temperature range from 200 to 600 °C. An earlier report of DTG curves of silane-functionalized clay displays four peaks, which are interpreted as degradation of physically adsorbed, intercalated, and/or grafted silane molecules [10]. In our case, two broad peaks are observed within the temperature range from 200 to 750 °C. The first degradation (200 to 350 °C) is attributed to the adsorbed silanes hydrogenbonded to the surface hydroxyl groups present in the broken edges of the clay platelets. The peaks at around 420–520 °C are attributed to the intercalated silane between the clay platelets and the peaks at around 560 to 680 °C are due to the chemically grafted silane with the clay platelets. The degradation peak to 715 °C is attributed to the degradation of aluminum silicate layers [13] of free water (between pores and aggregates) and water bonded to the cations by hydrogen bonding or free solvents present between the pores [14]. The major weight loss above 600 °C is due to the dehydroxylation of aluminosilicate

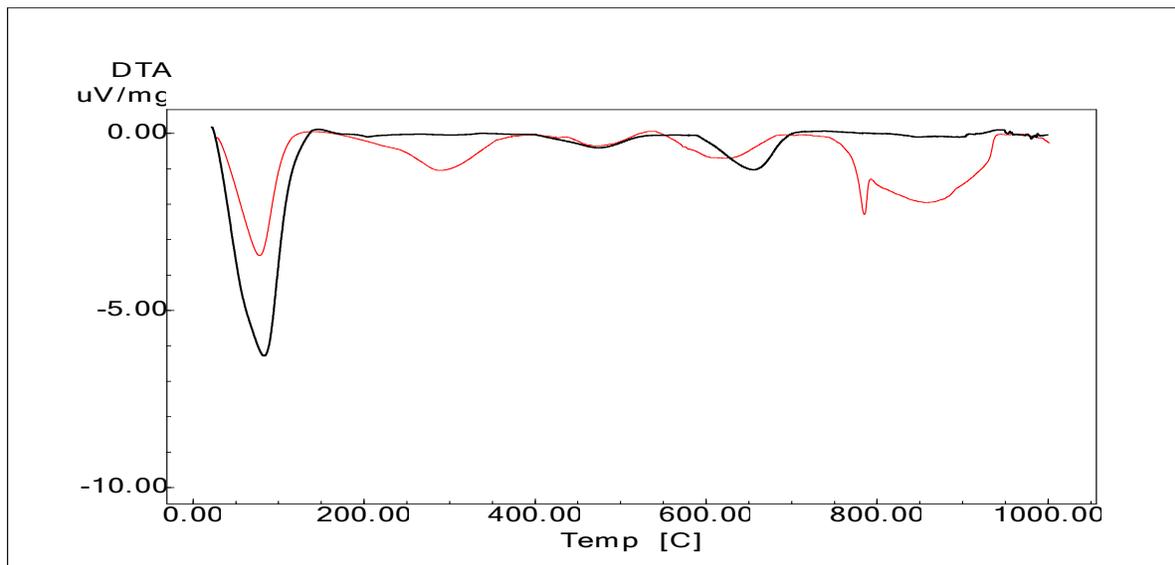


Fig. 4 DTG curves of pure and functionalized MMTs.

IV. CONCLUSION

Examination of the FTIR spectra of montmorillonite and montmorillonite functionalized reveals the appearance of the new heights in 2930 and 2850 cm^{-1} that corresponds to symmetric and asymmetric -CH elongation confirms the presence of the silane to the surface. Comparison of ATD functionalized MMT and pure MMT shows us the emergence of new damage has around 200 ° C and 350 ° C which corresponds to breaking of chemical bonds between the silane and clay nanoparticles according to the method of functionalization. The d-spacing increases from 12.3 Å to 15.3 Å indicating intercalation of aminosilane. The result presented in this work shows us that we can have a better compatibility between the bentonite nanocharges and a polymer matrix polyaniline thanks to the NH₂ function at the end of the counting agents and the crying spacing at the level of the interlayer space Of clay particles this compatibility ensures a synthesis of polymer-clay nanocomposites with remarkable physical and chemical properties

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