



Influence of octadecylammonium, *N,N*-dimethylhexadecylammonium, and 1-hexadecyltrimethylammonium chloride upon the fractionated montmorillonite

Thermal stability

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Abstract

Various alkyl-amines (ammoniums) salts were reacted with fractionated sodic montmorillonite (FNa-MMT) to prepare the organomontmorillonites. The interlayer d-spacing obtained by X-ray diffraction analysis of FNa-MMT was increased after the alkylammonium cations intercalation. The FTIR spectrograms indicate the presence of the different surfactant agents in the montmorillonite interlayer space. High-resolution thermogravimetric analysis reveals that the thermal decomposition of the modified montmorillonite occurs in three steps. For the surface morphologies examined by atomic force microscopy, the measured root-mean-square roughness was increased after the reaction of the FNa-MMT ($< 2 \mu\text{m}$) with the different surfactants.

Keywords Montmorillonite · Intercalation · Alkylammonium · X-ray diffraction · Interlayer space

Introduction

During the past 50 years, there has been increased interest in the synthesis of nanocomposites materials by embedding nanosized inorganic particles into polymers [1]. Since the optical, thermal, rheological, and mechanical properties of these materials strongly depend on the techniques used for their elaboration, a variety of synthesis strategies have been reported, with the aim of controlling the dispersion of the inorganic component within the polymer matrix on the nanoscale [2]. Among these inorganic components, montmorillonite is one of the most common-type clays and widely distributed on the earth surface. Due to its nanomicrosize, high surface area, and cationic exchangeable capacity, reagents with special function groups can be intercalated into/or grafted onto the clay interlayer species

or external surfaces to modify and adjust the surface performance of the resultant clay surfaces [1].

Access of guest molecules to host matrix could be a rate-limiting step in the intercalation reaction of swelling clays. Especially when guest molecules are highly hydrophobic and bulky, they would have a low possibility of approaching hydrophilic reaction sites. This kind of organic molecules is difficult to be intercalated into hydrophilic clays by conventional ion exchange methods, which employ clay suspensions with single-solution phases. Recently, their potentials have been tremendously expanded by the intercalation of a variety of biologically active organic substances [3–5].

In order to obtain a better dispersion of clay within the polymer matrix, another approach is to use the clays which are organically modified prior to the synthesis. The modification is usually made by substitution of the cations (Na^+ , K^+ , and Li^+) on the surface of clay layers with cationic surfactants including primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium cations. These surfactants change the nature of the clay surface from hydrophilic to hydrophobic as well as increasing the

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interlayer spacing of the clay, and accordingly, they promote more affinity and space for the polymers [6].

The elaboration of nanocomposite is conditioned by a complete dispersion of the silicates plaquette in the polymer matrix in order to increase the interactions between these two phases. The sodic clay is processed by alkylammonium salt, which gives an organophilic character with the ions cationic exchange (Na^+) with the ammoniums cations [7].

We attempt to introduce two new sites of clay to be studied for the first time (Maadid and Chaaba Hamra M'sila, Algeria). The rest of our study is focused on Maghnia montmorillonite due to its high interlayer spacing. As agents of organophilization available, we have used octadecylamine (ODA), 1-hexadecyltrimethylammonium chloride (HDTACl), and *N,N*-dimethylhexadecylamine (DHDA) as cationic surface active agents. X-ray diffraction is used to study the changes in the organoclay basal spacing depending on the content of the surfactant. The confirmation of the presence of the different types of surfactants in mineral interlayer was investigated by Fourier transform infrared spectroscopy (FTIR). The thermal properties were determined by thermal gravimetric analysis (TG) and differential thermal analysis (DTA). Atomic force microscopy (AFM) was used in tapping mode for morphological characterization.

Experimental

Materials

Three kinds of swelling clay materials, Maghnia, Maadid, and Chaaba El-Hamra obtained from different regions in Algeria were studied. Three surfactant agents octadecylamine (ODA), 1-hexadecyltrimethylammonium chloride (HDTACl), and *N,N*-dimethylhexadecylamine (DHDA) were purchased from Aldrich, Alfa Aesar, and Fluka, respectively.

Sodium montmorillonite preparation

The raw clays (Maghnia, Maadid, and Chaaba El-Hamra) were first washed with distilled water and hydrogen peroxide (H_2O_2) 30% using a stirring process for 48 h in order to eliminate the organic materials. The suspensions were then washed several times in distilled water at room temperature and dried in the oven at 50 °C for 1 week. Only Maghnia montmorillonite (MMT) solution was added into NaCl solution with a mass ratio of Clay/NaCl = 100/5.55 and stirred for 8 h at (70 °C). The suspension was washed several times with distilled water using the centrifugation method until no chloride ion was detected with silver nitrate (AgNO_3) solution (0.1 N) test. The precipitate was then dried at 80 °C for 24 h in the vacuum oven. The product was

ground and sieved through 90 μm for further use. The treated sodium montmorillonite is designed as (Na-MMT).

Fractionated montmorillonite preparation

The montmorillonite suspension was placed into centrifuge tubes, and then the suspension was siphoned off by suction using a syringe in order to recover the montmorillonite fraction whose particle size is $< 2\mu\text{m}$. The discards were collected and stocked for other applications. For each sampling, the procedure was repeated many times to collect an adequate amount of fractionated montmorillonite. The recovered suspension was then dried at 80 °C and crushed with a mortar. The fractionated montmorillonite was designed as FNa-MMT (Fig. 1).

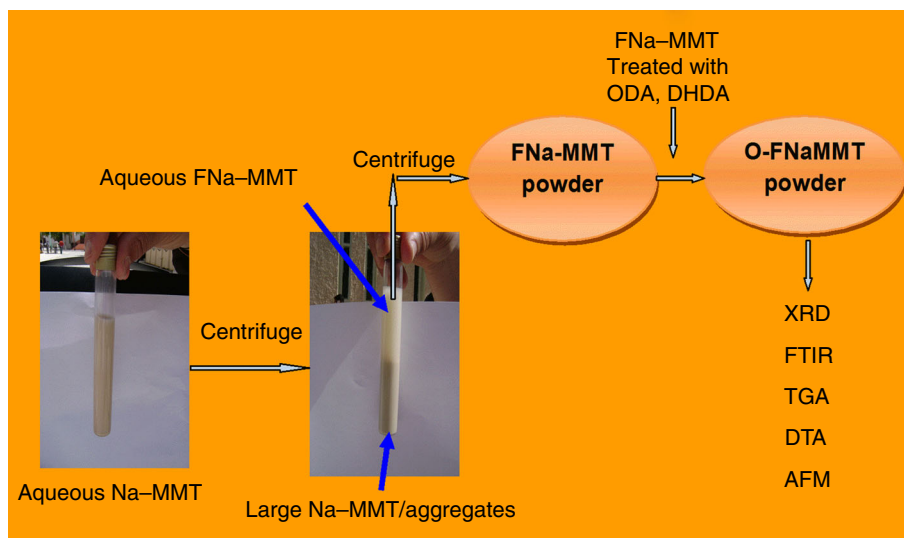
Organomontmorillonites preparation

The organic montmorillonite was prepared by cationic exchange between the fractionated sodium montmorillonite and modifying agents: ODA, DHDA, and HDTACl in an aqueous solution. 30 g of fractionated sodium montmorillonite was dispersed into 500 mL of hot water (80 °C) and stirred for 1 h. 7.68 g, 7.68 g, and 9.12 g of ODA, DHDA, and HDTACl, respectively, were dissolved in a mixture of distilled water and hydrochloric acid (36%) at 80 °C during 3 h with stirring. The obtained mixtures were let to themselves at ambient temperature without stirring for approximately 24 h. All organomontmorillonites products were washed free of chloride anions with distilled water at 80 °C using AgNO_3 tests. The precipitates were then dried to obtain organomontmorillonites with octadecylammonium (ODA-MMT), *N,N*-dimethylhexadecylammonium (DHDA-MMT), and 1-hexadecyltrimethylammonium chloride (HDTACl-MMT).

Methods

X-ray diffraction patterns were followed up by a Philips diffractometer X'Pert Software, with CuK_α ($\lambda = 1.54 \text{ \AA}$) radiation source at room temperature. Bragg's law $d_{(hkl)} = \lambda / 2 \sin\theta_{\text{max}}$ was used to calculate the basal spacing (d_{001}) of the montmorillonite layers. All scans were performed in 2θ range between 2.5 and 50 degrees. The infrared spectroscopy, FTIR, was recorded on a Shimadzu FTIR 8300 spectrophotometer, using the KBr pressed disc method. Thermal gravimetric (TG) and DTA analysis were performed using DW5470H63 STA analyser under a flowing nitrogen atmosphere, and heated from room ambient temperature to 700 °C, with a heating rate of 10 °C min^{-1} . The atomic force microscopy (AFM) images of the organomontmorillonites were obtained with an Asylum Research an Oxford Instruments company type: MFP-3D.

Fig. 1 Schematic illustration of fractionated montmorillonite preparation



Results and discussion

XRD results

In this study, Maghnia montmorillonite was selected according to its high interlayer space $d_{001} = 15.24 \text{ \AA}$. This allows an adequate amount of surfactant agents to intercalate within the interlayer galleries space (Fig. 2).

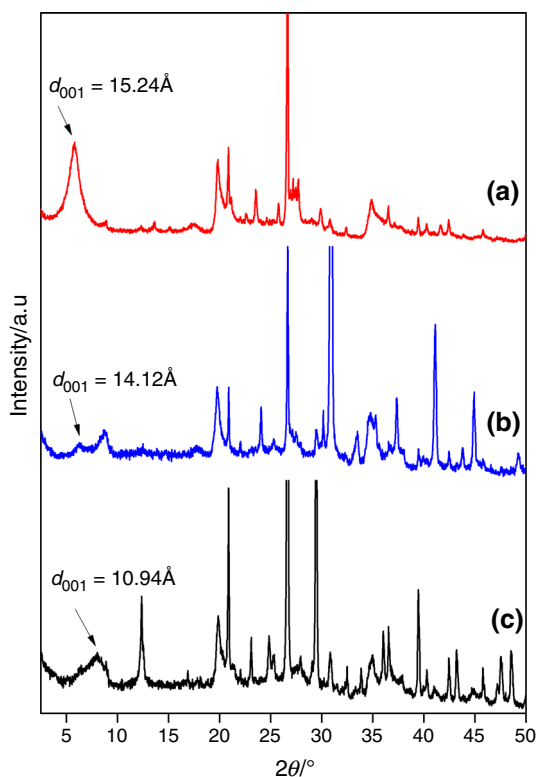


Fig. 2 XRD patterns of Maghnia (a), Chaaba Hamra (b), and Maadid (c) montmorillonites

Figure 3 reveals the X-ray spectra for MMT, FNa-MMT, and organomontmorillonites (ODA-MMT, DHDA-MMT, and HDTACI-MMT). Bragg's equation was used to calculate the basal spacing of the fractionated and the organomontmorillonites. The d_{001} diffraction peak for FNa-MMT in the 2θ region is located at 5.83° , corresponding to $d_{001} = 15.24 \text{ \AA}$. Xiang Wang [8] has reported

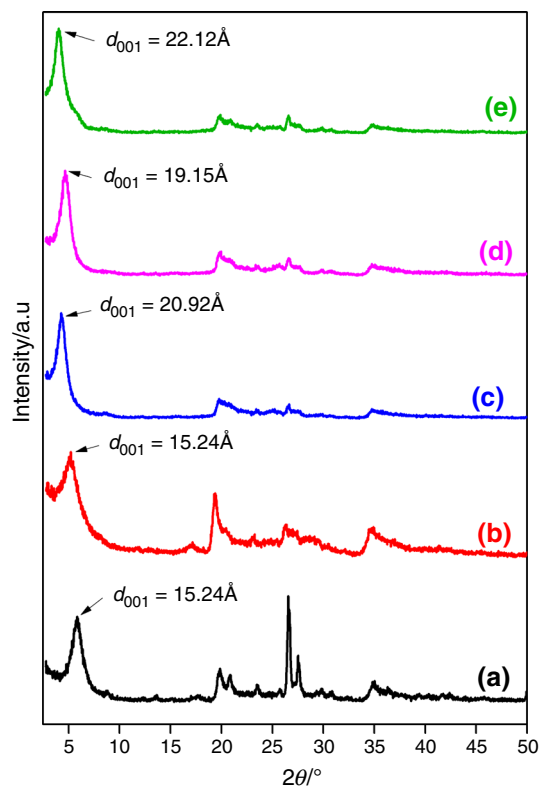


Fig. 3 XRD patterns of virgin (MMT) (a), fractionated (FNa-MMT) (b), and organomontmorillonites modified by different alkylammoniums (ODA-MMT) (c), (DHDA-MMT) (d), and (HDTACI-MMT) (e)

the following values ($2\theta = 7.06^\circ$, $d_{001} = 12.5 \text{ \AA}$). The intercalated clay FNa-MMT by ODA and DHDA leads to an increase in d_{001} distances, where the 2θ values are located at 4.22 and 4.61° corresponding to $d_{001} = 20.92$ and 19.15 \AA , respectively. These modifications suggest an increase in the basal spacing of the silicate layers. The increase in the basal spacing was due to the intercalation of the alkylammonium in the clay platelets by ion exchange mechanism. The intercalation of the clay FNa-MMT with HDTACl increases the d_{001} spacing (2θ located at lower values 3.99°) corresponding to $d_{001} = 22.12 \text{ \AA}$. This was about twice the distance to the van der Waals diameter of the trimethyl group [9–11]. When the carbon number of the main chain of alkyl-amine (ammonium) increases, the intergallery distance of the organoclay increases [12]. These results showed that the interlayer space of the clay intercalated by quaternary alkylammonium (HDTACl-MMT) is bigger than that intercalated by ternary and primary alkyl-amines.

FTIR results

FTIR spectra of FNa-MMT and those organically modified clays are shown in Fig. 4. For FNa-MMT sample, bands at

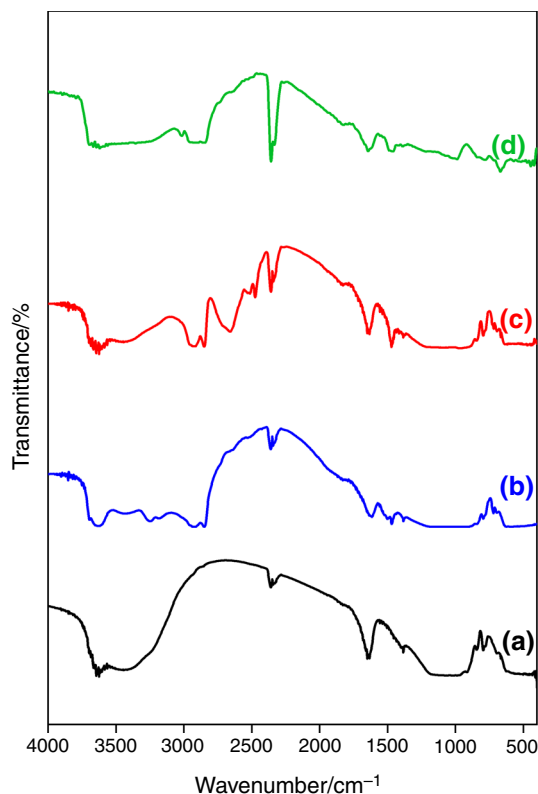


Fig. 4 FTIR spectra of FNa-MMT (a) before and after alkylammonium intercalation (ODA-MMT (b), DHDA-MMT (c), and HDTACl-MMT (d))

1040 cm^{-1} (owing to stretching vibration of Si–O–Si from silicate), 910 cm^{-1} (from Al–OH–Al deformation of aluminates), 860 , and 432 cm^{-1} (Si–O–Al stretching and Si–O bending vibrations of montmorillonite, respectively) were observed [13]. Antisymmetric stretching vibrations of structural –OH groups in FNa-MMT sheets at 3625 cm^{-1} , symmetric stretching vibrations from water molecule observed at 3416 cm^{-1} , and in-plane bending vibrations of H–O–H at 1636 cm^{-1} are very sensitive and respond to changes in the structure of montmorillonite were also observed [14–17]. For organoclays, interaction of FNa-MMT with surfactants cations (ODA, DHDA, and HDTACl) caused appearance of new bands at 2957 and 2834 cm^{-1} , assigned to antisymmetric and symmetric stretching vibration of CH_2 from the alkyl chain, respectively. Also, the intensity of –OH bands (–OH of water) was reduced to a large extent due to the intercalation of surfactants as a result of the removal of interlayer hydrated cations by alkylammonium groups on ion exchange, leading to the formation of hydrophobic surface. The intercalated montmorillonites surface populated with bulky alkyl chains produces less space available for adsorption of water molecules. The intensity of these bands was reduced to a large extent. All these changes indicate intercalation of FNa-MMT by the surfactants.

TG results

Both thermogravimetric (TG) and its derivative (DTG) curves, in inert atmosphere, of FNa-MMT (Fig. 5) show two degradation steps with maxima at 114 and $650 \text{ }^\circ\text{C}$ related to the following mass losses: first (7%) observed in the temperature range from 61 to $185 \text{ }^\circ\text{C}$ and second (1.40%) between 560 and $695 \text{ }^\circ\text{C}$. These mass loss steps were attributed to desorption of adsorbed water from the particle surfaces and dehydration of the hydrated Na^+ cations in the interlayer space [18–20] and loss of OH units through dehydroxylation of the montmorillonite (560 – $695 \text{ }^\circ\text{C}$) [21]. On the other hand, organically montmorillonite undergoes four-step decomposition process. The vaporization of free water takes place at temperatures below $200 \text{ }^\circ\text{C}$ (mass loss 0.9%). This low mass loss is an indication of a decrease in adsorbed water and water content in interlayer space and refers to exchange of hydrated Na^+ cations with surfactants cations [22, 23]. The surfactant's decomposition happens in the temperature range 200 – $500 \text{ }^\circ\text{C}$. Dehydroxylation of the aluminosilicates occurs between 560 and $695 \text{ }^\circ\text{C}$. The last step is associated with the combustion reaction between organic carbon and inorganic oxygen substances (combustion of the charcoal) at temperatures higher than $700 \text{ }^\circ\text{C}$ [24]. For the intercalated organomontmorillonite layers (ODA-MMT Fig. 6, DHDA-MMT Fig. 7, and HDTACl-MMT Fig. 8), the

Fig. 5 TG, DTG, and DTA curves of fractionated montmorillonite

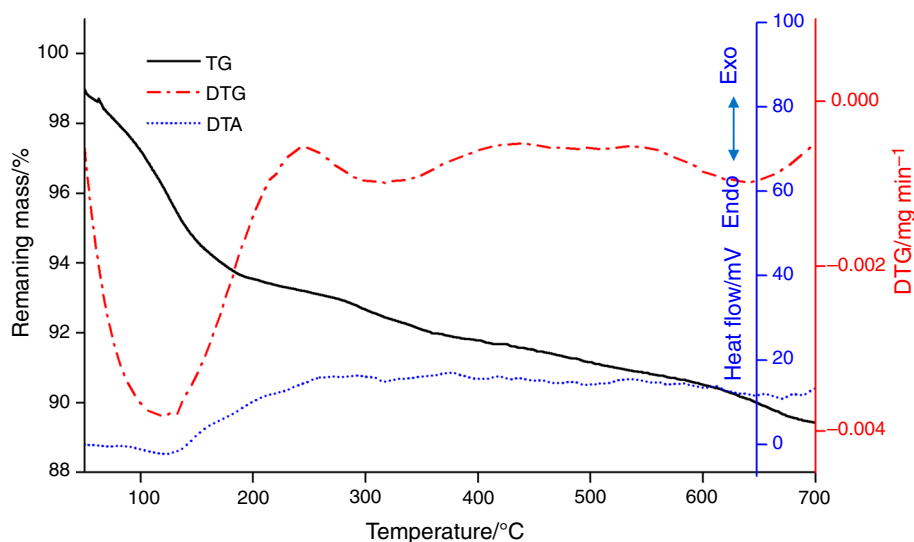
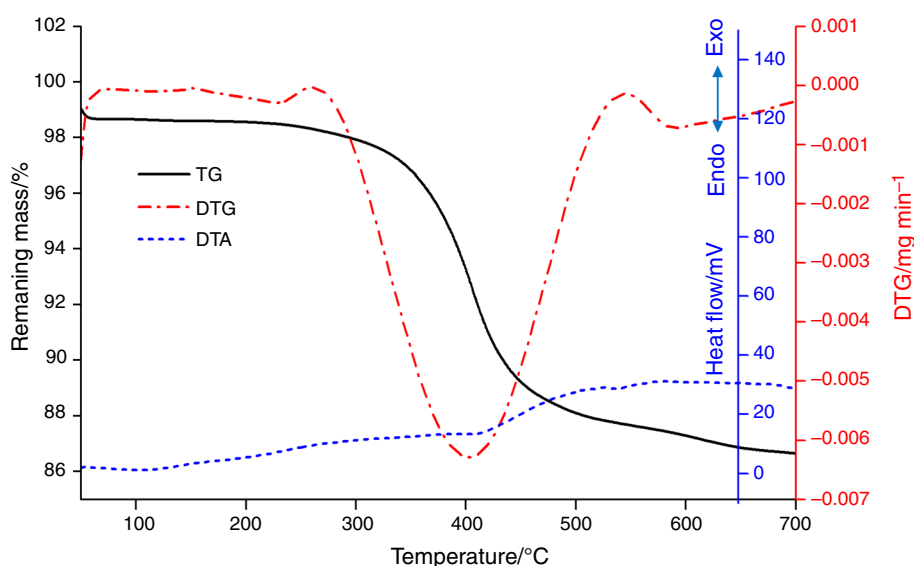


Fig. 6 TG, DTG, and DTA curves of organomontmorillonite (ODA-MMT)



corresponding first derivative DTG curve shows three mass losses. The first mass loss of 0.9% (between 75 and 136 °C) with maxima at 105 °C is assigned to the dehydration of free and interlayer water, and the second mass loss of 0.17% at a pick temperature of 264 °C for ODA-MMT, 2.6% at a pick temperature of 260 °C for DHDA-MMT, and 6.9% at a pick temperature of 290 °C for HDTACI-MMT. This peak was associated with the surfactant adsorbed to the external surfaces of the montmorillonite. The third peak temperature approaches 400 °C corresponding to a mass loss of 11% ODA-MMT 6.3% DHDA-MMT, and 6.3% HDTACI-MMT assigned to the intercalated alkylammonium between the layers.

Xi et al. [25] distinguished three different molecular environments for surfactants in montmorillonite-ammonium organoclays: (1) surfactant cations intercalated into the interlayer spaces through cation exchange and bound to

surface sites via electrostatic interaction; (2) surfactant (cations and/or molecules) physically adsorbed on the external surface of the particles, and (3) surfactant molecules located within the interlayer spaces. Xi et al. [26] indicated that the molecules of surfactant exceeding the CEC adhere to the clay mineral surface by van der Waals forces and their properties are very similar to those of pure surfactant. The surfactant, physically adsorbed on the external surface, can be removed after washing, resulting in an increase in thermal stability and a decrease in surface energy of the resulting organoclay [27].

DTA results

Differential thermal analysis (DTA) curves of FNa-MMT (Fig. 5) and the corresponding organoclays (ODA-MMT Fig. 6, DHDA-MMT Fig. 7, and HDTACI-MMT Fig. 8)

Fig. 7 TG, DTG, and DTA curves of organomontmorillonite (DHDA-MMT)

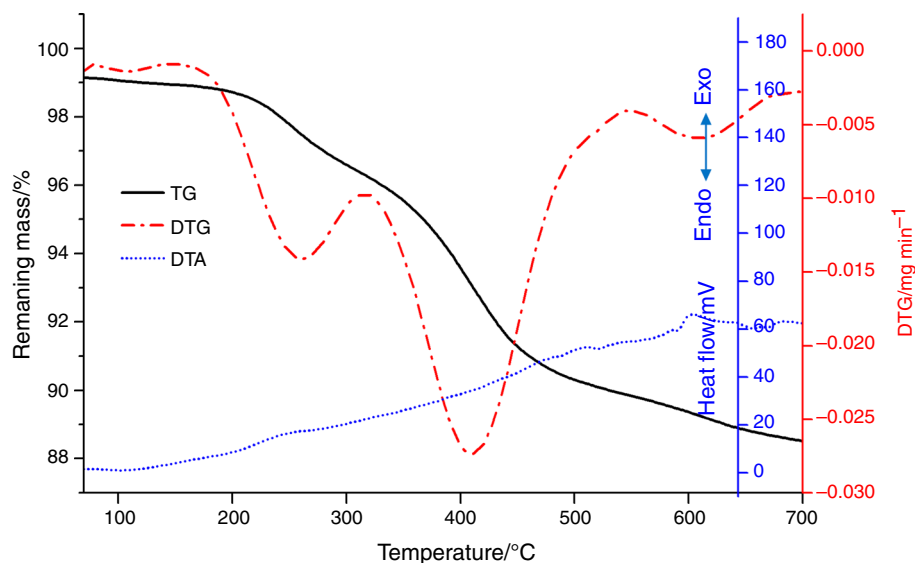
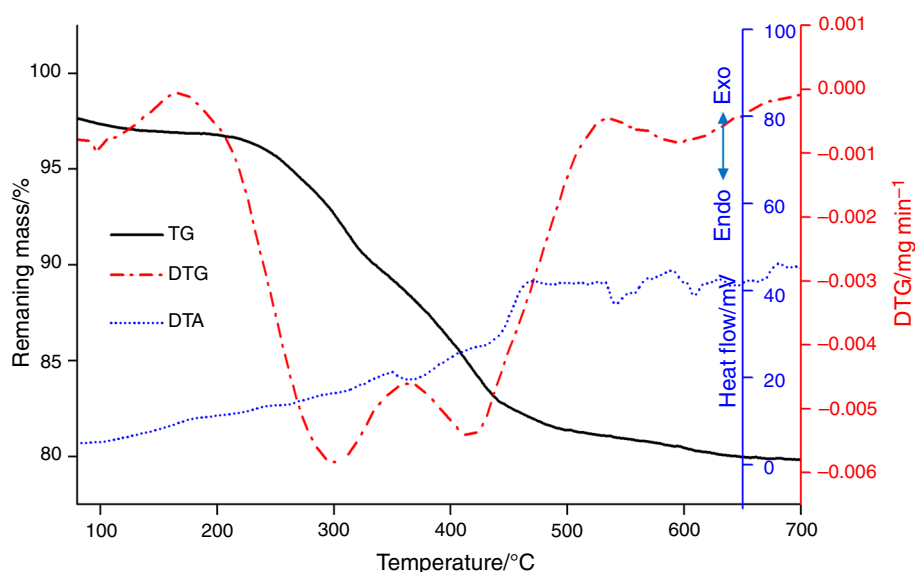


Fig. 8 TG, DTG, and DTA curves of organomontmorillonite (HDTACI-MMT)



were displayed. One significant endothermic change was observed at 122.8 °C due to the volatilization of both the free water (i.e., the water sorbed on the external surfaces of crystals) and the water residing inside the interlayer space, forming hydration spheres around the exchangeable cations. Halim et al. [28] reported a temperature around 70 °C, assigned to the dehydration of interlayer water inside the montmorillonite. One exothermic reaction was detected at near 313.1 °C (ODA-MMT), 251.8 °C (DHDA-MMT), and 349.1 °C (HDTACI-MMT). This change was due to the successive decompositions and oxidation of the free surfactants and those adsorbed to the external surfaces of the montmorillonite. Another change detected at a temperature approaches 410.4 °C (ODA-MMT), 480.1 °C (DHDA-MMT), and 414.6 °C (HDTACI-MMT) which was due to the successive decomposition of the adsorbed

and intercalated alkylammonium cations associated with maximum rate of thermooxidative destruction of the various organic compounds and the deposition of various condensation products formed as the results of a complex series of reactions [29].

AFM results

Figure 9 displays the 3D AFM images (10 $\mu\text{m} \times 10 \mu\text{m}$) of the montmorillonite thin pellets (FNa-MMT, ODA-MMT, DHDA-MMT, and HDTACI-MMT). The measured root-mean-square (RMS) roughness of the FNa-MMT (< 2 μm) sample was 52.7 nm, and it is more smoothness sample. After the reaction with the surfactants, the value of RMS for organo-montmorillonite samples was increased to 101.6, 108.1, and 204.1 nm for ODA-MMT, HDTACI-

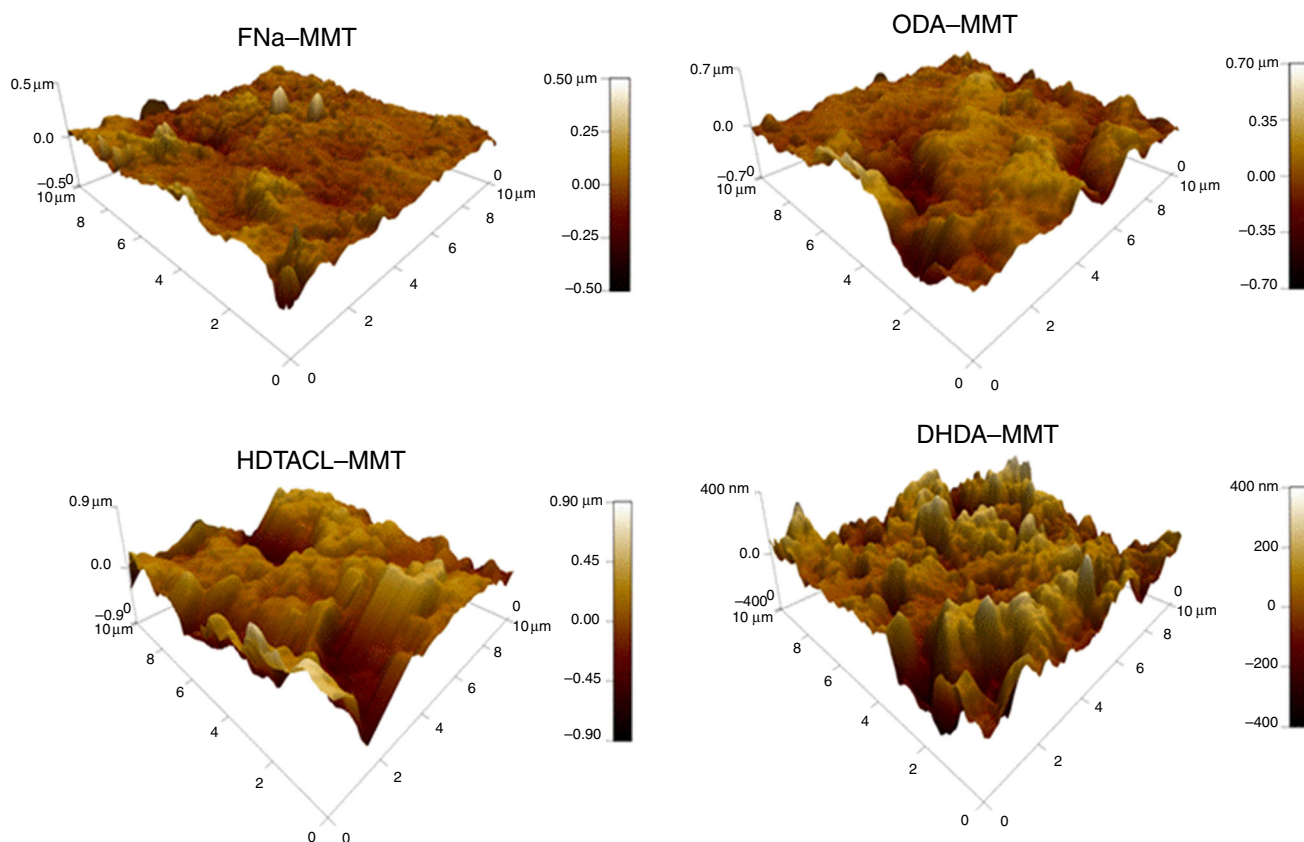


Fig. 9 AFM images of fractionated and organomontmorillonite with various alkylammoniums

MMT, and DHDA-MMT, respectively. The surface protrusions were more pronounced for organomontmorillonite than FNa-MMT. This surface modification can be interpreted by the hydrophobic state of the organomontmorillonite, which leads to a hard and rigid structure.

Conclusions

Three alkyl-amines salts (ammoniums) were reacted with fractionated montmorillonite. The XRD results showed that Maghnia montmorillonite reveals the highest interlayer d-spacing and was used for further studies. The fractionated montmorillonite intercalated with the sus cited surfactants by cationic exchange indicated an increase in the distance inside the reticular in the diffractograms of X-rays (XRD). It was observed that the modified montmorillonite by quaternary alkylammonium (HDTACL-MMT) reveals the highest interlayer distance than that modified by primary alkylammonium (ODA- MMT) and ternary alkylammonium (DHDA-MMT), respectively. TG studies showed a better thermal stability of (HDTACL-MMT) than (ODA-MMT) and (DHDA-MMT).The surface of clay after modification was more protruded having bigger value of RMS, confirmed by AFM. This surface modification can be

interpreted by the hydrophobic state of the organoclays, which leads to a hard and rigid structure. The preceding results accentuate the importance of alkylammonium in the modification process of natural montmorillonite and have important implications for any attempts to incorporate the organomontmorillonite particles in the preparation of polymer nanocomposites.

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