



## Studies on Preparation and analysis of Organoclay Nano Particles

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### Abstract

*This study deals with conversion of clay to Organoclay with the help of surfactant called CTAB and evaluated for its properties. The prepared organoclay was analyzed by SEM, XRD and FTIR techniques. X-Ray diffractograms indicate the intercalation of organic moiety between the layers of montmorillonite. The thermal properties were analyzed using thermogravimetry, shows that the incorporation of organic cation alters the thermal stability of the Na-MMT.*

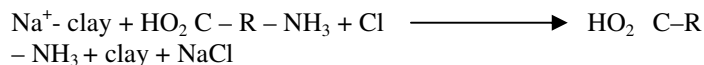
**Keywords:** Basal spacing, montmorillonite, organoclay, thermal stability.

### Introduction

Clay is a naturally occurring material formed by breaking and chemical decomposition of igneous rocks with fine texture of particle size less than 0.002 mm (2 micron). Finest part of clay is similar to colloid with fine grain size, stickiness and plasticity characteristics when wet<sup>1</sup>. Clay can be grouped depending on the way that the tetrahedral and octahedral sheets are packed into layers. If there is only one tetrahedral and one octahedral group in each layer, the clay is known as 1:1 clay e.g. Kaolinite and 2:1 clay has two tetrahedral sheets with the unshared vertex of each other and forming each side of the octahedral sheet as known as layer silicates. The 2:1 layer silicates include mica, smectite, vermiculite and chlorite. Smectite group is further divided into montmorillonite (MMT), nontronite, saponite and hectorite species<sup>2,3,4</sup>. Among these layered silicates, MMT is widely used as reinforcement for the polymer-clay nanocomposites because it is environmental friendly, readily available in large quantities at relatively low cost and its intercalation chemistry is good and well understood<sup>5</sup>.

Montmorillonite type of clay is extremely fine grained; it swells if water or organic solvent is added as well as it does not form macroscopic crystals<sup>6,7</sup>. Montmorillonite is a 2:1 type consisting of two silicon oxygen sheets held together by intervening cations with water molecules in the interlayer spaces<sup>1</sup>. Two outer tetrahedral layers which contains Si and O atoms are fused with an inner octahedral layer containing Al and Mg atoms which are bonded to oxygen or hydroxyl group. Individual clay particle has “platey” structure with lateral dimension of 200 to 600 nanometers and thickness of only 0.96 nm<sup>8,9</sup>. These layers organize themselves to form stalks by vanderwalls force of attraction between them. The attraction force between layers is relatively weak so polymer molecules can be intercalated between them<sup>5,10,11</sup>. So in pristine form, clay is hydrophilic (platelets contain Na<sup>+</sup> or k<sup>+</sup> ions)<sup>12</sup>.

Clay in its natural form can be dispersed only in hydrophilic polymers like Poly (ethylene oxide) and poly (vinyl alcohol)<sup>13,14</sup>. In order to render the surface more organophilic, hydrated cations of clay surface are replaced by cationic surfactants (alkylammonium or alkylphosphonium / onium) to lower the surface energy. Sodium ions in natural clay are exchanged with an amino acid such as 12-aminododecanoic. Schematic of reaction is shown in equation 1<sup>15</sup>.



The cations receding between the layers cause the organic molecules to radiate away and increase the interlayer spacing between platelets. So modified clay is more compatible and facilitates the intercalation of polymer chain between the clay galleries. At a given temperature, layer spacing depends on the organic chain length and CEC of layered silicate.

Cation exchange capacity (CEC) is the characteristic property of soil provided by clay and organic matter. It is expressed as meq/100g<sup>16</sup>. It is the capacity of the soil to hold cations, like Al<sup>3+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup> and H<sup>+</sup><sup>14</sup>. It is understood as the quantity of positively charged ions held by the negatively charged surface of clay mineral. But in general most of the clay minerals tend to have a negative charge, due to substitution of silica cation (Si<sup>4+</sup>), by aluminum cation (Al<sup>3+</sup>) in the clay sheet structure. This phenomenon, referred to as isomorphous substitution produces the capacity in clay sheets to hold positive charges.

Some of the novel applications of Organoclay are mentioned here<sup>17-28</sup>. It is used in the ink formulation to help and adjust the consistency of printing inks to the desired value. By incorporation of small amount of organically modified layered silicate, good colour distribution, desired film thickness, etc. are obtained. AS organoclay gives good working stability, water resistance and high temperature resistant features, it is widely

used as thickening for lubricating oils and greases used for foundries, mills, high-speed conveyors, etc. Areas like medicine, cosmetic and waste water treatment also use organoclay in their various applications. It is used to have good colour retention and coverage for nail lacquers, lipsticks and eye shadows in cosmetic industry. Organoclay exhibits a synergistic effect with many commonly utilized water treatment unit processes including granular activated charcoal, reverse osmosis and air strippers. Thus clay is being used widely used in various industries.

Clay was also used as filler material in textile industry since long, for giving temporary finish or gloss to the material but now a day much literature is available on incorporation of organoclay within the filament to enhance its properties which can be further improved if structural aspects of organoclay are more systematically studied. So in the work, we have made an attempt to covert bulk clay to organoclay using CTAB as surfactant and systematically analyzed with the help of SEM, FTIR, TGA and XRD pattern.

### Material and Methods

**Materials:** Montmorillonite clay with cation exchange capacity of 60 meq/100 gm was taken as the starting material. All the chemicals mentioned in table 1 were used without any further purification.

**Equipments:** List of equipments used: i. SEM/EDX Model JSM-5610 LV Japan, with oxford Inca Software for characterizing surface morphology and elemental analysis of nano particles. ii. FTIR spectroscopy (FT-IR was carried out on Shimadzu FT-IR 8400S spectro photometer using the Kbr pellet method). iii. Thermogravimetry (TGA) was carried out using a Shimadzu TGA-50 thermal analyzer. iv. X-ray Diffraction (XRD) was carried out using D8 advance with CuK  $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ).

**Methods: Preparation of Organoclay nano particles:** Sodium Montmorillonite (Na-MMT) clay (5 gms) was dispersed in 500 ml of distilled water. The suspension was vigorously stirred for 24 hrs at room temperature using magnetic stirrer. An aqueous solution of 0.03M (1.09 gm in 100 ml distilled water) CTAB (Cetyl Trimethyl Ammonium Bromide) was gradually added to the Na-MMT dispersion. The resulting Organoclay suspension

was further stirred for 12 hours at room temperature. The suspended product was filtered under vacuum, using whatman paper no. 1. The resulting product was further dispersed into 50 ml fresh distilled water and stirred again for another 4 hours.


Resultant modified clay was washed thoroughly to remove chloride. The product was washed repeatedly till it become free from the chloride which was confirmed by checking against  $\text{AgNO}_3$  solution. The final Organoclay which was free from chloride was dried at  $60^\circ\text{C}$  for 24 hours and finally ground using a Pestle Mortar in order to obtain fine powder. The experiments were carried out with different molarities of CTAB. The resultant product was characterized by FTIR, TGA and SEM.

**Characterization of Organoclay nano particles: Scanning Electron Microscopy (SEM):** Scanning Electron Microscopy was used to characterize the nano particles shape and size. SEM image was formed using transmitted electrons (instead of the visible light) which can produce magnification up to 1, 00,000 X with resolution up to  $100\text{ \AA}$ . Organoclay nano deposited aluminum sheet was dried and illuminated under scanning electron microscope. Scanned images with different magnification and resolution were recorded on computer.

**Elemental analysis by Oxford-Inca software on SEM:** The elemental analysis of the prepared modified clay nano particles was performed on scanning electron microscope (SEM) using Oxford Inca Software. The Organoclay nano particles were deposited on carbon coated aluminum sheet. EDX analysis of these samples was carried out using Oxford-Inca software on scanning electron microscope. The instrument reports the presence of elements in pure and oxide state qualitatively.

**FT-IR Spectroscopy:** The technique is based on the fact that a chemical substance shows marked selective absorption in the infrared (IR) region. After absorption of IR radiation, the molecules of a chemical substance vibrate at many rates of vibration giving rise to close packed absorption bands called IR absorption spectrum which will correspond to the characteristic functional group and bands present in a chemical substance. Thus an IR spectrum of a chemical substance is a finger print for its identification. FT-IR was carried out on Shimadzu FT-IR 8400S spectro photometer using the Kbr pellet method.

Table-1  
 Chemical specifications

Sr no	Name	Formula	Grade	Mol.wt. gm/mol	Supplier
1	CTAB Cetyl trimethyl ammonium bromine		AR	364.45	Sd Fine chemicals.
2	Silver nitrate	$\text{Ag NO}_3$	AR	311.80	Sd Fine chemicals.

**Thermogravimetric analysis (TGA):** Thermogravimetry (TGA) was carried out for Na-MMT and Organoclay samples by using a Shimadzu TGA-50 thermal analyzer. The samples were heated from ambient temperature to 700°C with 10°C/min temperature in normal atmosphere. The thermograms associated with TG for control and treated sample were obtained from the instrument output. Detailed information with respect to mass loss degradation onset temperature were obtained from these thermograms for both the samples.

**X-Ray Diffraction (XRD):** Understanding the initial basal spacing in the prepared organoclay is very important for determining the potential for polymer intercalation. This is determined by X-ray diffractometer. X-ray diffraction was performed on dried powder sample. The Organoclay was grounded into a fine power prior to XRD measurements using a Pestle Mortar with sufficient pressure. The scans were performed for each sample and the values are reported for the basal spacing. The X-ray diffraction patterns were obtained using diffractometer D8 advance with CuK  $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ )

## Results and Discussion

Na-MMT clay was converted to Organoclay by using CTAB as surfactant. The morphological, structural and thermal characteristics were recorded and are discussed in this chapter.

**Formation of Organoclay particles:** The Na-MMT clay has been converted into Organoclay nano particle by a simple swelling technique using de-ionized water. The prepared Organoclay was tested against  $\text{AgNO}_3$  solution to ensure removal of chloride content. SEM micrographs technique has been used to observe morphology of prepared material and FT-IR spectra of the Organoclay was recorded for the confirmation of chemical compounds.

It has been observed from the experimental work (schematically presented in figure 2) as well as from the literature that the clay exhibits expansion in water due to ingress of free water and also due to the presence of minerals with predominantly expands the lattice.

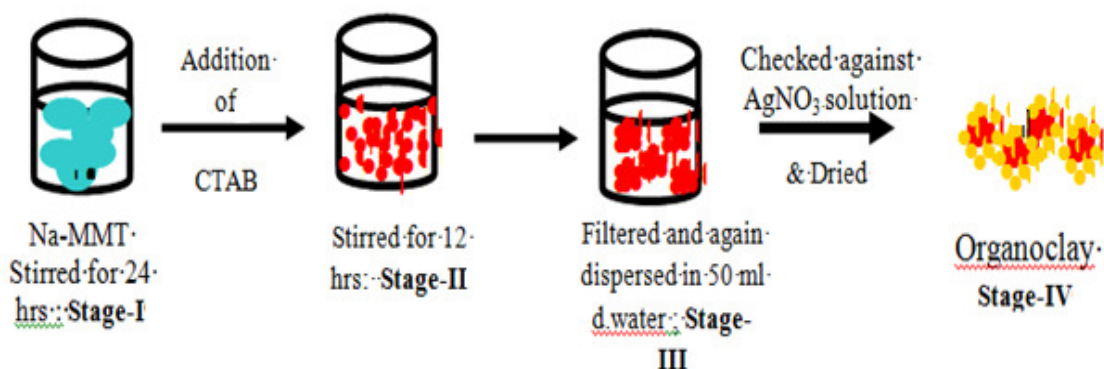


Figure-1  
 Schematic process diagram of Organoclay preparation

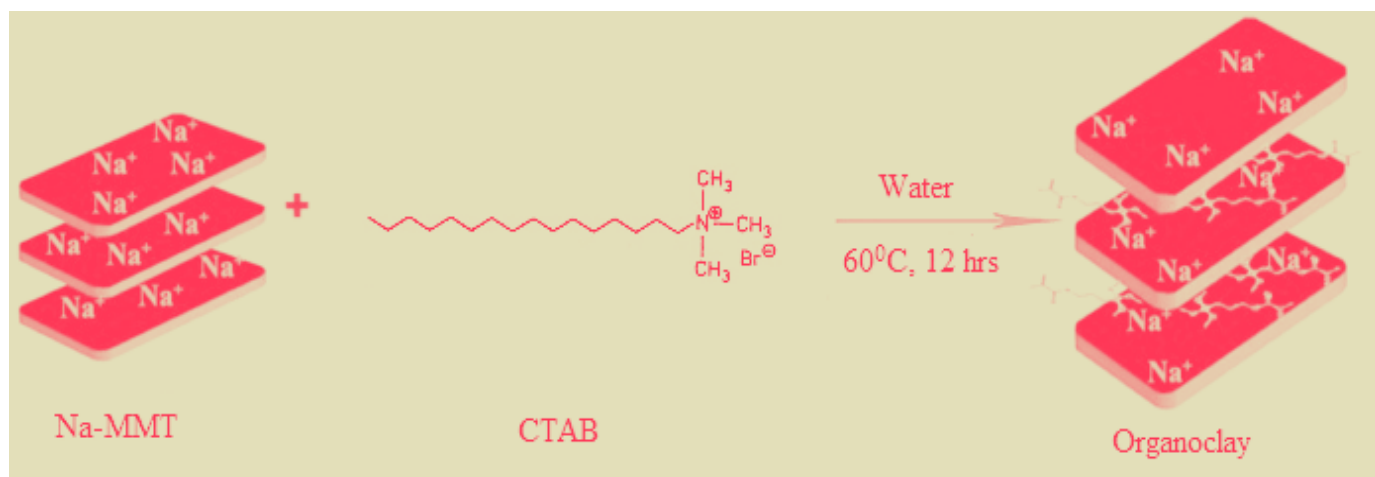
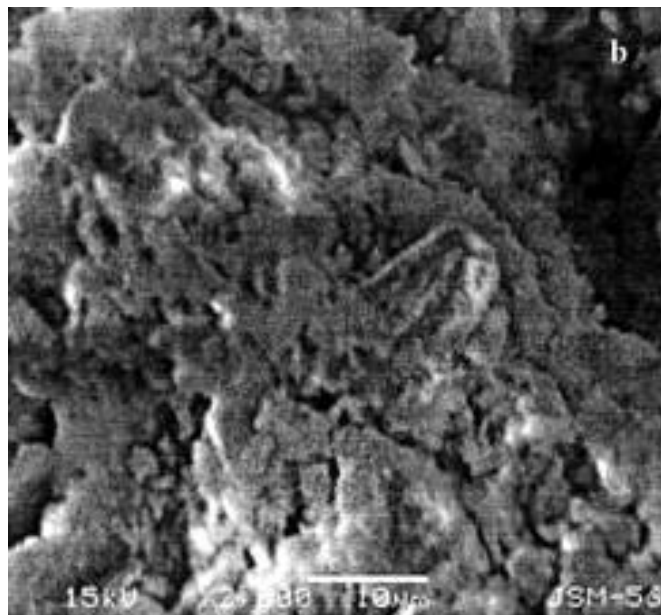


Figure-2  
 Conversion of Organoclay nano particles from Na-MMT clay

**Analysis:** Montmorillonite is among the most widely known clay minerals, and is extensively tried by various researchers across the world in adsorption applications because of its large surface area and relatively wide interlayer space being expandable in aqueous media. In this study, montmorillonite were converted to Organoclay had a dominant opaque-brownish black appearance. The morphology of powder was studied by SEM, the chemical composition and structure was confirmed by FT-IR spectroscopy and XRD pattern respectively. Finally the thermal behavior was studied by Thermogravimetric analysis (TGA). Discussions upon characterizations of MMT Organoclay are provided in the following subsections.

**SEM Analysis:** Figure 3 shows the scanning electron microphotographs of prepared MMT Organoclay nanoparticles deposited on carbon coated aluminum sheet. The average size as seen from the scale of the photograph is ranging between 50 – 90 nm. Figure 3 (a) shows aggregates of Na-MMT clay where as 3(b) shows uniform dispersion of the Organoclay nanoparticles.

Surface morphology of Na-MMT clay Figure 3(a) clearly indicates that the particles in Na-MMT clay before the treatment was in closely attached or in aggregates form due to the intermolecular forces. The surface morphology can be supported by various reports available in literature that aluminosilicates type clay consists of silica SiO<sub>4</sub> tetrahedra bonded to alumina AlO<sub>6</sub> octahedra in a variety of ways, which have a sheet-like (layered) structure. A 2:1 ratio of the tetrahedra to the octahedra results in smectite clays, montmorillonite; which we have used in this study. It has been observed from Figure 3b represent surface morphology of modified or swollen Na-MMT Organoclay particles with cationic surfactant CTAB.

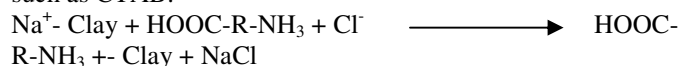


(b)

**Figure-3**

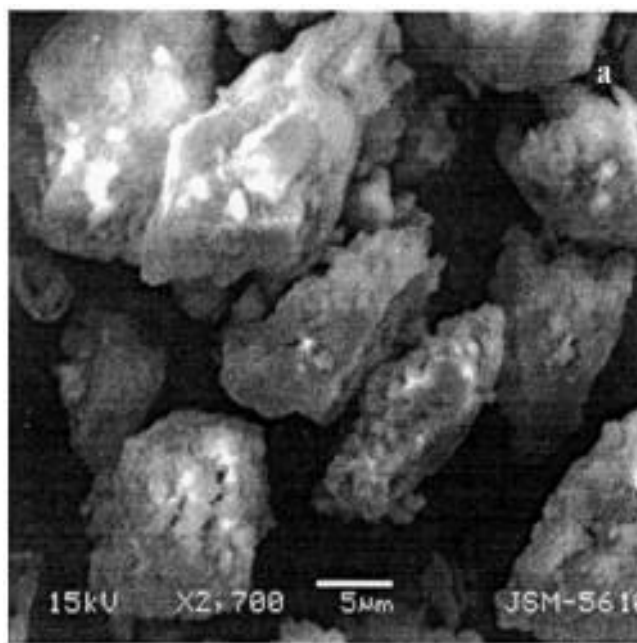
**Scanning electron microphotographs of (a) Na-MMT clay particles and (b) Organoclay nanoparticles deposited on carbon coated aluminum sheet**

Uniformly dispersed small particles have been observed, compared to the Na-MMT particles. The sizes of the particles were also clearly fall in nano scale. This may be due to the sodium ions in the clay can be exchanged for an amino acid such as CTAB:

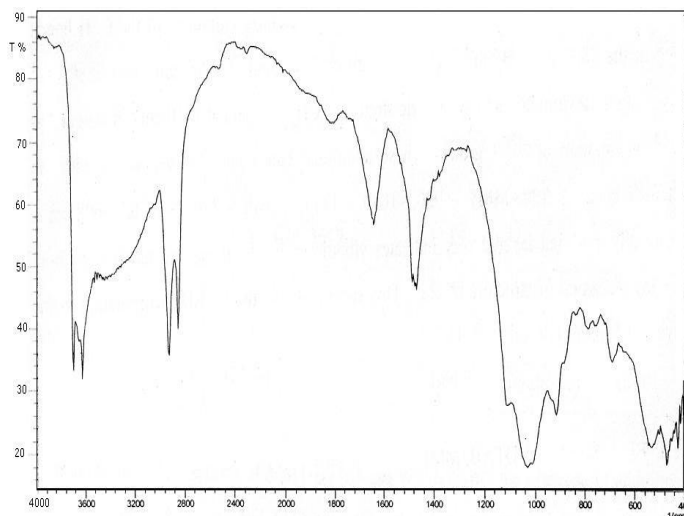


**FTIR spectral analysis:** Analysis depends upon the fact that a chemical substance shows marked selective absorption in the infrared (IR) region. After absorption of IR radiation, the molecules of a chemical substance vibrates giving rise to close packed absorption bands called IR absorption spectrum which will correspond to the characteristic functional group and bands present in a chemical substance. Thus an IR spectrum of a chemical substance is a finger print for its identification. FT-IR spectra of Na-MMT clay recorded on Shimadzu FT-IR 8400S spectrophotometer using the Kbr pellet method is shown in figure 4

From figure 4 IR spectra peaks for Na-MMT clay of montmorillonites located near 1030 cm<sup>-1</sup> belongs to the Si-O stretching vibrations. OH bending modes of structural hydroxyl groups and water molecules lie in the spectral region of 3400 cm<sup>-1</sup>. The position of the hydroxyl stretching band of Al-OH and Si-OH lies at 3620 cm<sup>-1</sup> and 3690 cm<sup>-1</sup> respectively in IR spectrum of Na-MMT. A weak absorption at 920 cm<sup>-1</sup> confirms of Al-Al-OH bending vibrations. A peak at 1640 cm<sup>-1</sup> is observed which shows the bending mode in water.

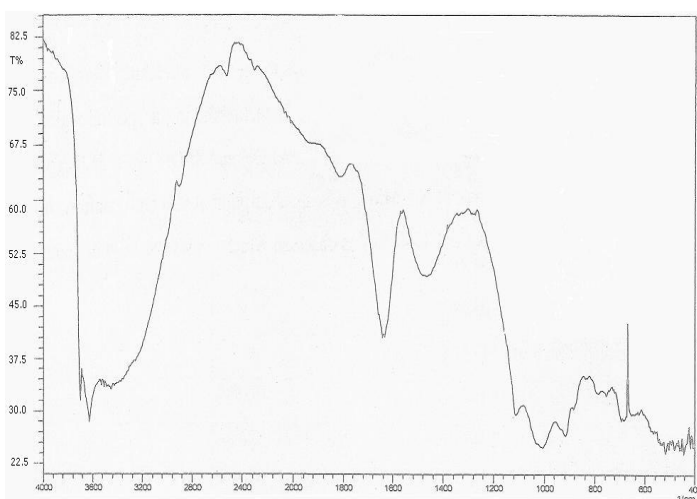


(a)



**Figure-4**  
**FT-IR spectra of Na-MMT clay particles**

Figure 5 shows the FT-IR spectra of MMT-CTAB 0.03M which shows the presence of additional bands at  $2900\text{ cm}^{-1}$  and  $2830\text{ cm}^{-1}$ . The stretching vibrations of the C-H bonds occurring in the  $2800 - 2900\text{ cm}^{-1}$  region, peaks for the same also observed at absorption band  $2900\text{ cm}^{-1}$  and  $2830\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$ . The stretching vibrations of the C-H bonds occurred in the  $2800 - 2900\text{ cm}^{-1}$  region. The absorption band at  $2900\text{ cm}^{-1}$  and  $2830\text{ cm}^{-1}$  corresponding to asymmetric and symmetric stretching -  $\text{CH}_2$ . A band at  $1450\text{ cm}^{-1}$  is assigned to the bending vibration of N-H groups. These additional bands are observed along with the characteristic bands at Na-MMT,  $\sim 920$ ,  $\sim 1030$ ,  $\sim 1115$ ,  $\sim 1640$ ,  $\sim 3400$ ,  $\sim 3620$ ,  $\sim 3698\text{ cm}^{-1}$ . An Organically modified layered clay indicated vibrational bands or organic modifier without causing any distortion of structure of clay. This spectrum shows the CTAB incorporation in the inter layers of Na-MMT clay.

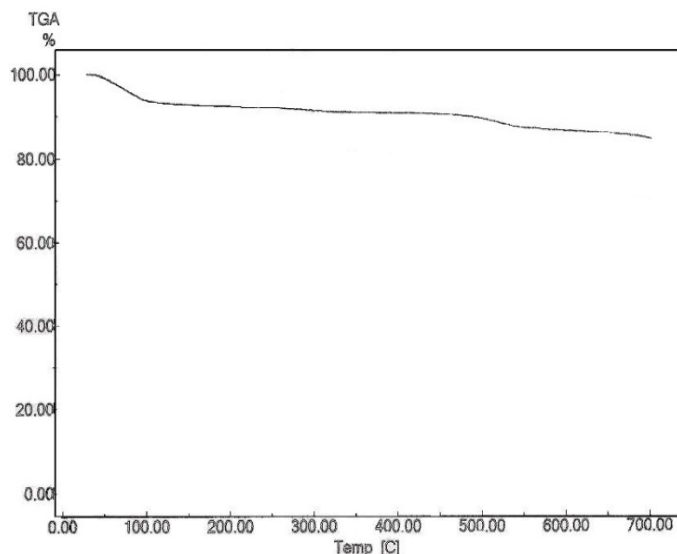


**Figure-5**  
**FT-IR spectra of CTAB MMT clay particles (Organoclay)**

**Thermogravimetric Analysis (TGA):** Thermogravimetric analysis is done to elucidate decomposition behaviour thermally. The weight loss arising from the degradation was studied by thermogravimetry analysis. Data are recorded as thermogram of weight versus temperature weight loss with time at constant temperature called isotherm TGA. A modern TGA instrument allows thermogram to be recorded on microgram quantities of material. Samples of 12 mg were heated till  $700^\circ\text{C}$ . The TGA trace was used to determine the % weight loss at  $700^\circ\text{C}$  which is sufficient temperature to degrade the organic content present in modified Na-MMT clay.

TGA gives the information about the thermal stability of the Organoclay. The TA curves for unmodified Na-MMT clay and organically modified clay are shown in figure 6(a) and figure 6(b). It was noted that the TGA of the Na-MMT occurred in three mass loss steps: Between ambient and  $100^\circ\text{C}$ , at  $480^\circ - 500^\circ\text{C}$  and stable till  $700^\circ\text{C}$ . These mass loss steps occurs may be due to desorption of water from the clay, dehydration of the hydrated cation in the interlayer and the dehydroxylation of the montmorillonite respectively.

From the figure 6(a) and 6(b) it has been observed that the mass loss observed in four steps of steps for the Organoclay. In case of  $\text{MMT-CTAB}_{0.03\text{M}}$ , the first step was from the ambient to  $80^\circ\text{C} - 120^\circ\text{C}$  and was attributed to desorption of water. The second step occurs from  $220^\circ\text{C}$  to  $330^\circ\text{C}$  and was assigned due to decomposition due to organic matter (of surfactant). The third mass loss step till  $700^\circ\text{C}$  was attributed due to the loss of structural hydroxyl group from within the clay. That was an indication of the thermal stability of modified clay. Further, the TGA curve of  $\text{MMT-CTAB}_{0.03\text{M}}$  and clay shows first degradation step from ambient to  $70^\circ\text{C}$  temperature range. The second step occurs from  $200^\circ\text{C}$  to  $260^\circ\text{C}$  and third step occurs at  $300^\circ\text{C}$ .



**Figure-6(a)**  
**Thermo gravimetric curve for Na-MMT clay**

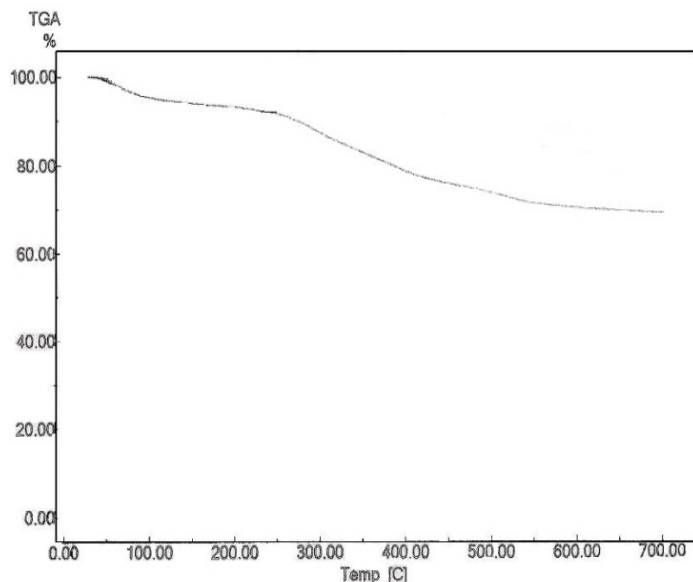


Figure-6(b)

Thermogravimetric curve for CTAB MMT clay

**XRD Pattern Analysis:** Organophilic clay can be produced usually from hydrophilic clay by ion exchange with an organic cation such as an alkylammonium ion. The clay chemical complex, which exhibits definite gallery spacing between the platelets, is called a nano Organoclay

Fine powder of Organoclay was scanned on Diffractometer for the measurement of basal spacing. The recorded values for Na-MMT clay and CTAB- MMT (Organoclay) are reported in table 2.

The basal spacing of Na-MMT and MMT-CTAB<sub>0.03M</sub> are shown in table 2. X-diffractograms of Na-MMT and MMT-CTAB<sub>0.03M</sub> exhibits an increase in d-spacing compared to the original unmodified clay i.e. Na-MMT, indicating the formation of intercalated structures. The high intensity reflection for MMT-CTAB<sub>0.03M</sub> confirms a high degree of order for a lamellar stacking of layers of these organically modified clays.

The increase in the value of basal spacing depends upon two factors. One is the presence of large hydrophobic groups on surfactants and second is the decrease in surface energy of Na-MMT. As the size of hydrophobic groups are increases the basal spacing increases to a large extent as seen from the Table 2 and corresponding X-diffractograms (figure 7).

Table-2

Final basal spacing recorded for Na-MMT and Organoclay

Sr. No.	Sample	Final Basal Spacing	
		Nm	2 Theta
1	Na-MMT	44.689	19.851
2	MMT-CTAB	44.711	19.841

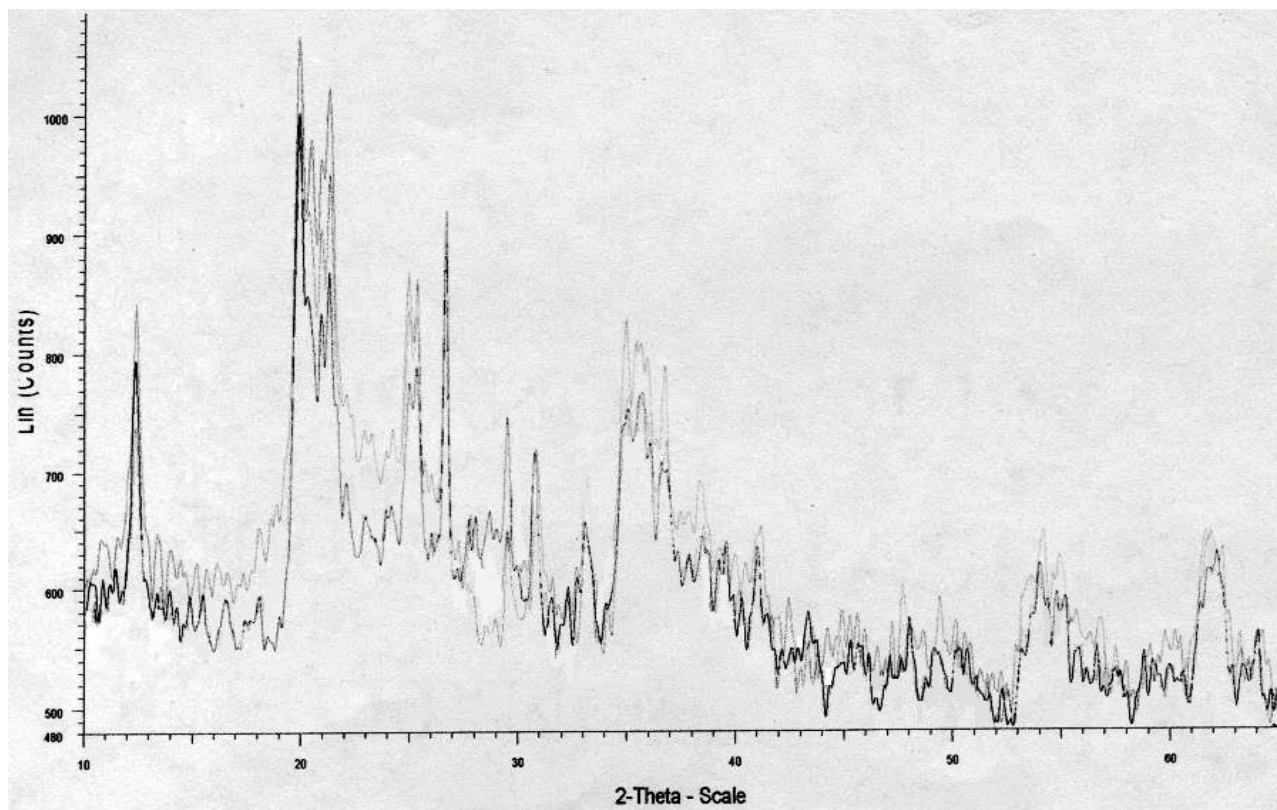


Figure-7

X-ray differection pattern of Na-MMT nad CTAB- MMT clay

## Conclusion

Sodium montmorillonite was successfully modified to Organo montmorillonite using CTAB as surfactant. The surface morphology of the prepared Organoclay was observed by SEM micrographs and its chemical composition was confirmed by FT-IR spectroscopy.

The SEM images as well as increase in basal spacing of MMT-CTAB<sub>0.03M</sub> from X-Ray diffractograms indicate the intercalation of organic moiety between the layers of montmorillonite.

The thermal stability study of Organoclay by TGA shows that the incorporation of organic cation (CTAB; surfactant) alters the thermal stability of the Na-MMT.

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