Front. Chem. China 2011, 6(2): 153–158
DOI 10.1007/s11458-011-0239-4

RESEARCH ARTICLE

Synthesis and characterization of organomodified Na-MMT using cation and anion surfactants

K. R. Vishnu MAHESH[1], H. N. Narasimha MURTHY (✉)[2], B. E. KUMARASWAMY[1], N. RAGHAVENDRA[2], R. SRIDHAR[2], M. KRISHNA[2], Niranjan PATTAR[2], Ratna PAL[2] and B. S. Sherigara[1]

The Sodium Montmorillonite (Na-MMT) is not susceptible to polymer due to its organophilic character and low basal spacing. The primary objective of this study was to improve Na-MMT platelets separation by organically modifying it with cation and anion exchanges using Cetyl trimethyl ammonium bromide (CTAB) and Sodium dodecyl sulfate (SDS) respectively. Basal spacing, presence of functional groups, Zeta-potential with particle size analysis and thermal stability of the Organomodified Na-MMT (OMMT) were characterized using XRD, FTIR, zeta-potential analyzer and TGA respectively. The basal spacing of CTAB modified OMMT increased to 19.5 Å from 11.0 Å which corresponds to the basal spacing of Na-MMT. The SDS modified OMMT did not show any increase in the basal spacing. FTIR spectra of CTAB modified Na-MMT illustrated the attachment of CTAB functional groups to Na-MMT, while the same was absent in the case of SDS modified Na-MMT. The zeta-potential of Na-MMT shifted from −24.88 mV to 15.66 mV in the case of CTAB modified Na-MMT and 12.49 mV for SDS modified Na-MMT, indicating a greater surface potential of the modified nanoclay. The TGA showed greater weight loss for CTAB modified Na-MMT than that for Na-MMT, indicating the effective Na^+ ion exchange with alkyl amines.

Received March 25, 2011; accepted April 5, 2011

1. Department of P.G Studies and Research in Industrial Chemistry, Kuvempu University, Shankaraghatta, Shimoga 577451, India
2. Department of Mechanical Engineering, R V College of Engineering, Bangalore 560059, India
E-mail: hnmdatta@yahoo.com

Keywords Na-MMT, CTAB, SDS, XRD, FTIR, zeta-potential

1 Introduction

Montmorillonite (MMT) is widely used in various scientific fields due to its high cation exchange capacity, large specific surface area, good swelling capacity, high platelet aspect ratio and ease of surface modification [1]. It possesses a 2:1 layered structure with an octahedral alumina layer located between two silicon tetrahedral layers (Fig. 1). Its particles are essentially bundles of nanoclay sheets that are roughly 1 nm in thickness and 100–1000 nm in breadth. For example, an 8 μm clay particle has approximately 3000 nanoclay sheets of 1 nm thick and 20–200 nm in diameter [2]. Layered Smectite-type MMT possesses a negative surface charge which is compensated by exchange of cations, such as Na^+ or Ca^{2+}. As organic cations exchange for exchangeable ions on the mineral surfaces, the cations are released into the solution. The organic cations may also enter into ion-exchange reactions with exchangeable cations between the layer surfaces of the clay and hence may be modified to make the clay strongly organophilic [3].

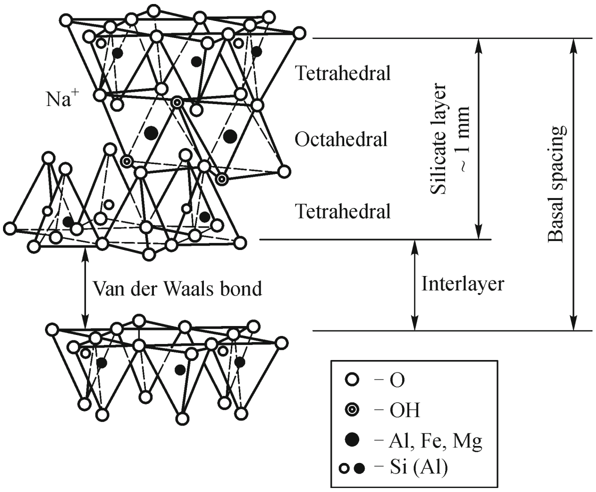


Figure 1 Layered structure of Montmorillonite

The organophilic clays are not compatible with hydrophobic organic matrices as the spacing between the clay sheets is extremely narrow, and hence diffusion of polymer chains in the clay galleries is not possible. This often leads to aggregation of clay particles, and the aggregated clay sheets act as stress-concentration sites in the polymer matrix. When the clay sheets exist in such bundles and the original interlayer spacing of clay sheets is unaltered in polymer matrix, the composite is referred to as a tactoid nanocomposites structure. If the interlayer spacing of clay sheets is increased and the clay sheets are poorly dispersed, the composite is referred to as intercalated nanocomposites. If the clay sheets are well dispersed and distributed, the composite is referred to as exfoliated nanocomposites. Generally, an exfoliated morphology of clay platelets is sought with the expectation that it would improve the properties of the nanocomposites [4–7].

The inorganic ions in the clay can be effectively replaced with organic cationic surfactant molecules through cation-exchange reactions. This result in the expansion of the interlayer spacing, which leads to an increase in the basal spacing, is shown in Fig. 2. As a result, the wettability and the thermodynamical interactions increase significantly [8,9]. Organo modified MMT has been widely used as a filler in many thermoplastic and thermoset polymers as rheological additives, thickeners in coating products, glues, etc. [10–12]. Improvements in mechanical, thermal, barrier and fire properties of the polymer nanocomposites due to the use of organomodified MMT have been reported [13–23]. Anionic surfactants are difficult to intercalate into layer galleries of Na-MMT because it is anionic in nature and it requires some other sophisticated techniques [24], hence a cationic critical alkyl length of 12 carbons or more was found necessary for promoting exfoliation [9].

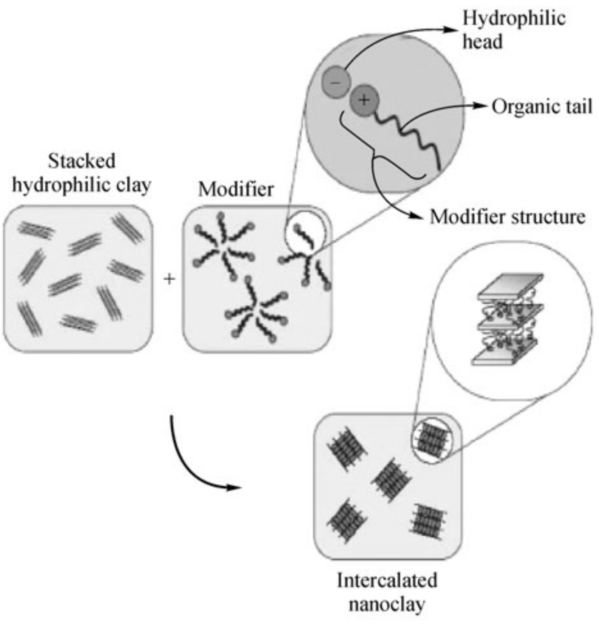


Figure 2 Clay modification process [27]

The selection of proper organic modifier plays an important role in controlling the surface energy of MMT. Cetyl trimethyl ammonium bromide (CTAB) is a cationic surfactant consisting of a cationic organoamine with a 19-carbon tail attached to the amine group. A few authors [25] studied CTAB modification of Na-MMT and reported an increase in basal spacing based on XRD [25]. However, the improvements due to such modifications depend upon the ion exchange process parameters such as time, speed and temperature. Duration of 1 to 5 h has been reported for the process. The improvements have been studied mostly using XRD and FTIR [26,27].

The present research is an attempt to study the effect of CTAB and SDS modifications of Na-MMT to achieve greater basal spacing. The effect of modification was studied using XRD, FTIR, particle size analysis with zeta-potential and TGA. The modification would help achieving compatibility with polymers through the incorporation of cation and anion into the clay's interlayer spaces.

2 Experimental

2.1 Materials and modification of Na-MMT

The Na-MMT was procured from Southern Clay Product, USA. The two modifiers, namely, CTAB and sodium dodecyl sulfate (SDS) were procured from Sigma-Aldrich, India. $AgNO_3$ was procured from Sigma-Aldrich, India. to examine the presence of chlorine in the precipitate.

15 g of the Na-MMT was dissolved in 500 mL hot water to obtain a uniform dispersion. 6.2 g of CTAB was dissolved in 500 mL double distilled water. The two solutions were mixed together and stirred vigorously for 6 h at 60°C using a hot plate magnetic stirrer. The solution was centrifuged using high speed REMI C 24 centrifuge at 8000 r/min for 3 min. The modified MMT suspension was washed repeatedly using distilled water and filtrated until no precipitate appeared when the filtrate was titrated with a 0.1 mol/L $AgNO_3$ solution. The filtered cakes were dried in a vacuum oven at 80°C for 12 h, and ground using ball mill to obtain fine powder of the organo-modified nanoclay. The same procedure was used to modify the Na-MMT with SDS as modifier.

2.2 Structure and chemistry of the modifiers

CTAB is a cationic surfactant consisting of a cationic organoamine with a 19-carbon tail attached to the amine group. It bears chemical formula: $(C_{16}H_{33})N(CH_3)_3Br$, the IUPAC name being hexadecyl-trimethyl-ammonium.

The Cation exchange of CTAB with Na-MMT due to the modification can be represented as:

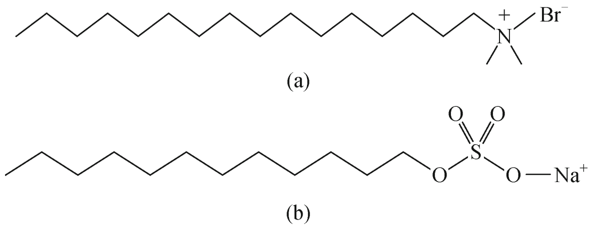
$$\begin{aligned}&\text{MMT-Na}^+ + (C_{16}H_{33})N(CH_3)_3Br\\&\quad\rightarrow \text{MMT-}(C_{16}H_{33})N(CH_3)_3 + \text{NaBr}\end{aligned} \tag{1}$$

SDS is an anionic surfactant of an anionic organo sulfate consisting of a 12-carbon tail attached to a sulfate group. It bears chemical formula: ($C_{12}H_{25}SO_4Na$), the IUPAC name being sodium dodecyl sulfate.

The anion exchange of SDS with Na-MMT due to the modification can be represented as:

$$\begin{aligned} &\text{MMT-Na}^+ + (C_{12}H_{25}SO_4Na) \\ &\quad \rightarrow \text{MMT-}(C_{12}H_{25}SO_4) + 2\text{Na} \end{aligned} \tag{2}$$

The structure and the properties are shown in Fig. 3 and Table 1 respectively.


(a)

(b)

Figure 3 Chemical structure of (a) CTAB and (b) SDS

Table 1 Properties of CTAB and SDS

Properties	CTAB	SDS
Molecular formula	$C_{19}H_{42}BrN$	$NaC_{12}H_{25}SO_4$
Molar mass	364.45 g/mol	288.38 g/mol
Appearance	White powder	White powder
Melting point	237°C–243°C	206°C
Density	1 g/cm^3	1.01 g/cm^3

3 Characterization of modified Na-MMT

XRD, FTIR, zeta-potential analysis and TGA

X-Ray diffraction studies of the unmodified and modified Na-MMT were carried out using a high resolution X-ray diffractometer (X'Pert PRO) at a scanning rate of 2°/min using Cu Kα radiation operating at 45 kV and 40 mA. XRD was aimed at studying the dispersion of MMT in vinylester based on the levels of d-spacing which indicates the exfoliation. The FTIR spectrum was recorded on Perkin Elmer FTIR 1650 spectrophotometer at ambient temperature using a KBr disk method. The disk containing 0.0010 g of the sample and 0.3000 g of fine grade KBr was scanned at 16 scans at wave number range of 400–4000 cm^{-1}. Zeta-potential and particle size analysis was performed using Model NPA152–31A Zetatrac supplied by Microtrac, USA. Light scattering particle size technology measurement ranges from 0.8 to 65 microns; measurement angle is 180 degrees; Zeta-potential ranges from -125 to $+125$ mV. Thermogravimetric analysis (TGA) was carried out using Universal V4.5A TA Instrument by measuring the weight loss of the samples as a function of temperature. The samples were heated from 25°C to 800°C at a heating rate of 10°C/min in Nitrogen atmosphere with a Nitrogen flow rate of 20 mL/min.

4 Results and discussion

4.1 XRD studies

The alkyl ammonium cation exchange enables the conversion of the hydrophilic interior nanoclay surface into the hydrophobic surface, which consequently increases the interlayer distance as well. In the present research Na-MMT was modified with CTAB and SDS as intercalation agents through the cation exchange process. The cationic head groups of the intercalation agent molecule would preferentially reside at the layer surface and the aliphatic tail will radiate away from the surface. The presence of these aliphatic chains in the galleries makes the organically hydrophilic silicate modified to organophobic and thus increases the layer basal spacing of Na-MMT [1].

The organo modified CTAB-MMT and SDS-MMT were studied by using XRD (Fig. 4) in the 2θ range at a scanning rate of 2°/min. The basal spacing of Na-MMT is 11.0 Å as calculated using the Bragg's Equation:

$$2d \cdot \sin\theta = \lambda \tag{3}$$

where d is the basal spacing; θ is the Bragg peak angle; $\lambda = 0.154$ nm, the X-ray wavelength.

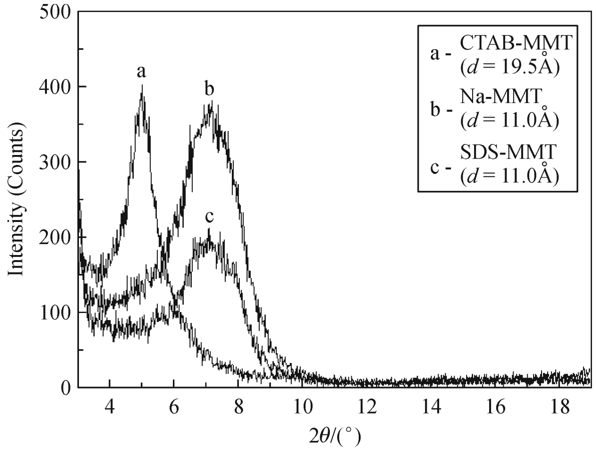


Figure 4 XRD of Na-MMT and modified MMT

After the ionization reaction the basal spacing of CTAB-MMT increased from 11.0 to 19.5 Å, compared to that of Na-MMT, but no such increase was observed in the case of SDS modification. This is also supported by XRD and FTIR results.

4.2 FTIR spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a useful technique to examine the presence of CTAB and SDS functional groups in the nanoclay. The FTIR spectra in Fig. 5 show the chemical structures of Na-MMT and the organo modified nanoclays. The absorption bands at 3714 and 3496 cm^{-1} are ascribed to the free-OH stretching and the hydrogen-bonded-OH stretching respectively. Compared with that of Na-MMT, the bands area of CTAB-MMT increases, demonstrating the increase in the –OH content caused by the introduction of CTAB. The 1648 and 1496 cm^{-1} bands peaks are associated with the $-CH_3$ group in CTAB. At the same time, the bands peak at 1648 cm^{-1} is also associated with the $RN(CH_3)^{3+}$ ion in CTAB. Besides, the bands at 2820 cm^{-1} and 2950 cm^{-1} are caused by the stretching of $-CH_2$ group, which comes from CTAB with long aliphatic tail in their molecules [9].

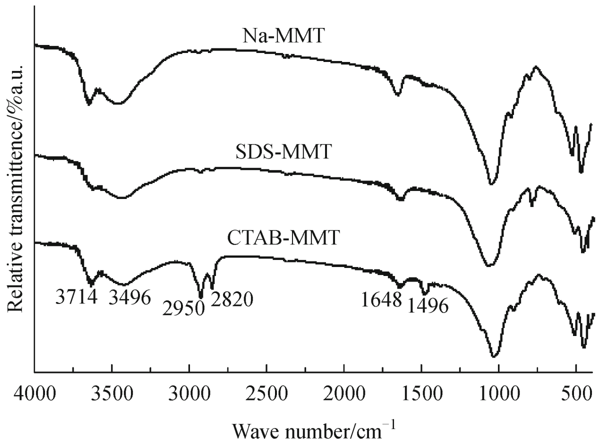


Figure 5 FTIR of Na-MMT and modified MMT

SDS modified Na-MMT does not show any bands peak, which may be because SDS functional group and Na-MMT are both anionic and repel with each other. The functional group is not intercalated in the layer galleries of Na-MMT. The visual observation of significant swelling when CTAB was added to Na-MMT indicated intercalation. But, such an effect was not observed when SDS was added to Na-MMT.

4.3 Zeta-potential analysis and particle size analysis

Zeta-potential is the electrical potential developed at the solid–liquid interface in response to the relative movement of the nanoparticle and the solvent. The zeta-potential of Na-MMT and modified Na-MMT was studied by dispersing the nanoclay in double distilled water. The zeta-potential of particles is a good indicator of their electrical potentials: the higher the zeta potential is, the greater the surface potential of charged clay particles will be. For clayey soils, it is usually negative (resulting from the charge on the particle surfaces), but it is strongly dependent upon the pore fluid chemistry. The results of zeta-potential of clay minerals reported by different authors are varied because of the variations in the source of clay, the experimental technique, and the method of converting electrophoretic mobility to the zeta-potential in different solutions [26]. The particle size increased from 1.946 μm (Na-MMT) to 2.465 μm for CTAB-MMT. But, there was no change in the particle size in the case of SDS-MMT, indicating no improvement due to SDS modification. The zeta potential of CTAB-MMT was + 15.66 mV, whereas that of Na-MMT was only − 24.88 mV, which means an increase of 162.54%. Surprisingly, SDS-MMT also showed considerably good value of zeta-potential though it is less than that of CTAB-MMT. Detailed output of the zeta-potential and particle size analyzer is shown in Table 2 and the particle size distribution is shown in Figs. 6–8.

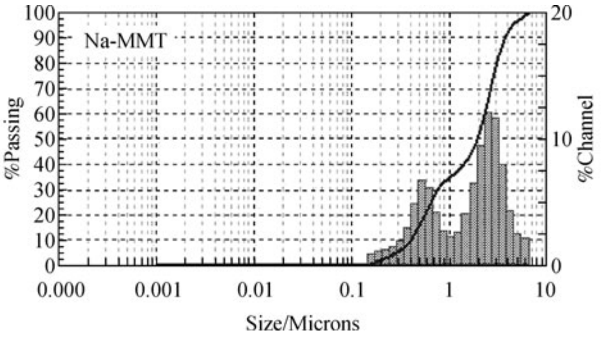


Figure 6 Zeta particle analysis of Na-MMT

4.4 Thermogravimetric analysis (TGA)

TGA of Na-MMT and CTAB-MMT was performed to study the thermal stability of the nanoclay. Such a study was not performed on SDS-MMT based on the discouraging XRD and FTIR results. Thermal stability plays a vital role in determining the engineering applications and processing conditions of OMMT. At a given temperature, the OMMT

Table 2 Zeta-otential analysis and particle analysis of unmodified and modified nanoclays

Material	Average particle size	Mobility	Zeta potential	Charge	Polarity	Conductivity
Na-MMT	1.946 μm	− 2.09μ/s/v/cm	− 24.88 mV	− 0.341 fc	Negative	658 μs/cm
CTAB-MMT	2.465 μm	+ 1.32μ/s/v/cm	+ 14.66 mV	+ 0.281 fc	Positive	264 μs/cm
SDS-MMT	1.966 μm	+ 1.87μ/s/v/cm	+ 12.47 mV	+ 0.156 fc	Positive	159 μs/cm

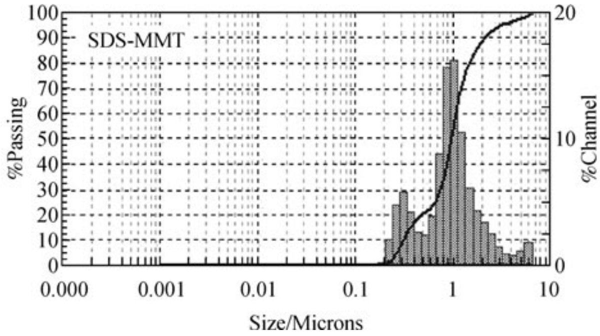


Figure 7 Zeta particle analysis of SDS modified MMT

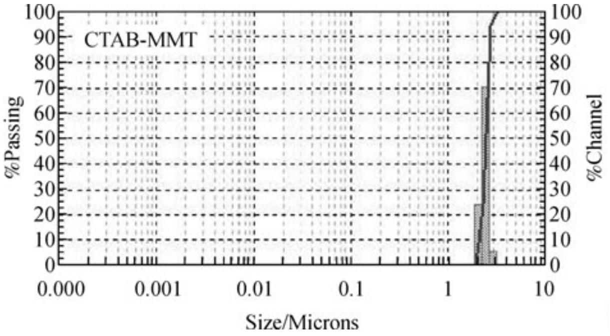


Figure 8 Zeta particle analysis of CTAB modified MMT

weight loss is directly related to the rate of the OMMT decomposition process [8]. The thermal decomposition expressed in weight loss as a function of temperature of both Na-MMT and CTAB-MMT is shown in Fig. 9. The Na-MMT differential thermal curve has two parts, the first being the free water and the interlayer water region in 100°C to 200°C range, and the second the structural water (bonded OH undergoes dehydroxylation) region in 500°C to 800°C range. The TGA pattern of Na-MMT is in concurrence with Magarappan et al. [25].

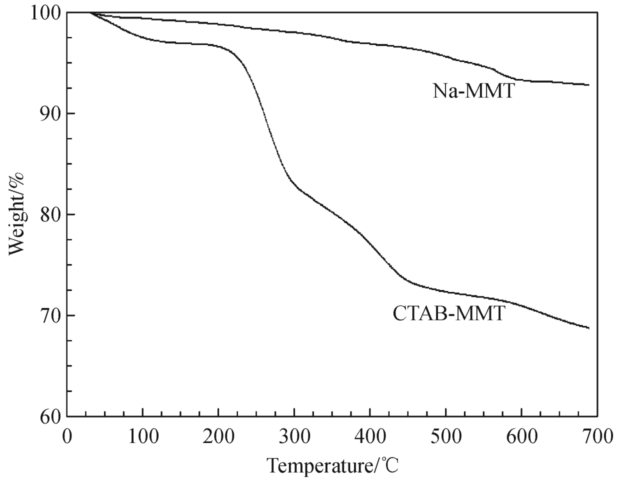


Figure 9 TGA curves of unmodified Na-MMT and modified CTAB-MMT

The CTAB-MMT differential thermal curve showed three parts, the free water region in the temperature below 211.43°C, the region where organic substance evolved between 211.43°C and 413.5°C, and the structural water region between 413.5°C and 800°C. The reason for the relatively low organic content for OMMT is related to the dehydroxylation of the bonded OH group which can be detached during the purification.

5 Conclusions

Na-MMT was modified using CTAB and SDS modifiers using ion exchange method. Based on the experimental results the following conclusions were drawn:

- CTAB modified Na-MMT showed basal spacing of 19.5 Å, which was greater than that of Na-MMT.
- SDS-modified Na-MMT did not show any increase in basal spacing when compared with that of Na-MMT.
- FTIR spectra of CTAB modified Na-MMT illustrated the attachment of CTAB functional groups to Na-MMT, while the same was absent in the case of SDS modified Na-MMT.
- Zeta potential of Na-MMT shifted from −24.88 to 15.66 mV in the case of CTAB modified Na-MMT and to 12.49 mV for SDS modified Na-MMT, indicating greater surface potential of the modified nanoclay. The average particle size increased from 1.946 μm (Na-MMT) to 2.465 μm (CTAB modified Na-MMT). SDS modification did not show increase in the particle size.
- The TGA showed greater weight loss for CTAB modified Na-MMT than that for Na-MMT, indicating effective Na^+ ion exchange with the alkyl amines.
- The CTAB modified Na-MMT synthesized in this research can be used for preparing nanocomposites with polar polymers in order to render good level of dispersion, improved mechanical and other properties.

Acknowledgements The authors thank the authorities of Naval Research Board, New Delhi, India for providing the financial support for this research work. Thanks also go to the St. Joseph College, Bangalore for XRD and FTIR facilities and Polymer Science Department, SK University for TGA and DSC facilities.

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