

# *Preparation and properties of alkylphosphonium modified montmorillonites*

Asmadi Ali\*, Nor Shalihan Mohamed, Mohamad Awang, Nur `Alyaa Mohd Sani  
School of Ocean Engineering  
Universiti Malaysia Terengganu  
21030 Kuala Terengganu, Terengganu, Malaysia  
\*corresponding author: asmadi@umt.edu.my

Mohd Aidil Adhha Abdullah  
School of Fundamental and Liberal Studies  
Universiti Malaysia Terengganu  
21030 Kuala Terengganu, Terengganu, Malaysia

**Abstract** - Sodium montmorillonite (MMT) was modified with four types of alkylphosphonium surfactants such as tetraoctylphosphonium bromide, tetrabutylphosphonium chloride, triisobutylmethylphosphonium tosylate and tributylmethylphosphonium methyl sulfate. Those types of modified montmorillonite were prepared by cation ion exchange reaction method to obtain high level of intercalation in the montmorillonite. The effect of chemical composition of the alkylphosphonium MMT on the basal spacing, thermal stability, surface area and porosity were evaluated. The highest basal spacing expanded from 1.25 to 2.36 nm from tetraoctylphosphonium bromide MMT, showed the intercalation of the surfactants ion into the intergallery sodium montmorillonite clay layers which caused the increasing of the surface area and porosity by allowing more alkylphosphonium ion passed through the surface and dispersed into clay layer. The confirmations of the intercalated surfactants into layers and fractionated plate-like structures surface morphology of alkylphosphonium modified montmorillonites were revealed by using Scanning Electron Microscope (SEM). Higher thermal stability values for alkylphosphonium MMT compared to alkyl ammonium MMT were found in thermal gravimetric analysis (TGA) in range greater than 200°C. Thus, these properties provide a good potential for the use of alkylphosphonium MMT for the synthesis of polymer/clay nanocomposites.

**Keywords**— *Montmorillonite, Alkylphosphonium surfactants, Intercalation, Nanocomposite*

## I. INTRODUCTION

Sodium montmorillonite is a layered silicate which belongs to the structural family known as the 2:1 phyllosilicate. It is commonly used as a nanofiller in the preparation of polymer nanocomposites because these materials can exhibit by enhancing mechanical properties, improved barrier properties and it is also said to have high thermal stability of polymer nanocomposites [3]. In order to attain the compatibility of the hydrophilic montmorillonite surface with the hydrophobic polymers, the cations were exchanged with long chain of alkyl ammonium

ions by providing intermixing between the organic and inorganic phases [11].

Although these modifications by alkyl ammonium agents have gaining significant success in the preparation polymer clay based nanocomposite but it was presented a problem in these engineering processing because of their low thermal stability properties are not exceed to 200°C [16]. The observed low thermal stability of ammonium surfactants represented a problem for melt compounding and processing of polymer nanocomposites, where high processing temperatures exceeding 200°C were commonly encountered. Thermal degradation during processing could initiate, in addition causing a variety of undesirable effects during processing and the final product.

To overcome this problem, sodium montmorillonite was modified with other group compounds with higher thermal stability such as phosphonium surfactants [11]. Studies by Mittal, (2012) found the thermal stability of phosphonium MMT were superior compared to ammonium MMT.

The main goal of the present study is to characterize the properties of alkylphosphonium MMT on the intercalation process, its surface area and porosity, thermal stability and final structure of the montmorillonite.

## II. METHODOLOGY

### A. Experimental Procedure

Sodium MMT, with cation exchange capacity of CEC 119 meq/100g, was purchased from Kunimine Industries, Japan. Alkylphosphonium modified MMT was prepared by cation ion exchange between sodium ion of Na<sup>+</sup> MMT and phosphonium surfactants ions. Further, 20 g of sodium MMT were dispersed into 1000 ml of water at 80°C and stirred continuously for an hour. The solution of diethyl ether containing phosphonium surfactants then were poured into the suspensions and stirred vigorously for 12 hour to flocculate MMT. The solution was warmed to 60°C to evaporate the

diethyl ether. The resulting solution was filtered and the precipitated of alkylphosphonium modified MMT was washed in hot water (80°C). The resulting alkylphosphonium modified MMT paste was mixed with petroleum ether, dried, ground and sieved to obtain the final products with particle sizes of less than 100µm.

### B. Materials

Sodium MMT and Cloisite 20A with cation exchange capacity of CEC 119 meq/100g, was purchased from Kunimine Industries, Japan. Surface modification of modified montmorillonite were performed by four types of alkylphosphonium surfactants: tetrabutylphosphonium chloride, triisobutyl(methyl)phosphonium tosylate, tributylmethylphosphonium methyl sulfate and tetraoctylphosphonium bromide.

### C. Characterization of modified montmorillonites

#### • X-ray Diffraction (XRD)

Sodium MMT and phosphonium MMT (3g) was compressed to tablets in a stainless steel sample holder for several minutes under 5 ton loads. A Shimadzu XRD6000 X-ray Diffractometer with CuK $\alpha$  radiation ( $\lambda=0.154$  nm) located in UMT was used to measure the basal spacing. The scanning range ( $2\theta$ ) was from 3° to 15° at 0.1°/ min at room temperature, using 40 kV and 70 mA.

#### • Thermogravimetric analysis (TGA)

The alkylphosphonium MMT together with alkyl ammonium MMT and sodium MMT were characterized by thermogravimetric analysis and the samples were heated over temperature range of 25-800°C at scanning rate of 10°C/min under nitrogen atmosphere with a gas flow rate of 40mL/min using Perkin-Elmer Pyris1 TGA instrument. All the samples were dried at 110° C in vacuum during 48h before the analysis. All the data were recorded in Table 2.

#### • Analysis of surface area and porosity (ASAP)

The surface area of montmorillonite played important role to show the interaction between alkylphosphonium ions with sodium ion in the clay gallery. The specific surface area and pore size distribution characteristic of MMT were analyzed using the nitrogen adsorption-desorption isotherm properties. This analysis was carried out by using Micromeritics ASAP 2000. The data analysis of Brunauer Emmet and Teller (BET) surface area and Barrett Joyner and Halenda (BJH) desorption average pore size diameter were summarized in Table 3.

#### • Scanning electron microscopy (SEM)

The samples were examined to evaluate the surface morphology and composition of the montmorillonite after the intercalation of the alkylphosphonium surfactant by using scanning electron microscope JEOL-JSM-6360L (SEM).

## III. RESULTS AND DISCUSSION

### A. X-ray diffraction analysis

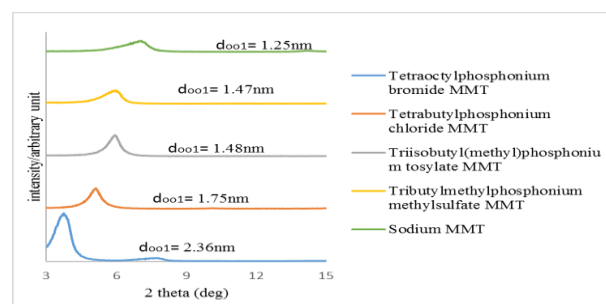
XRD analysis was carried out in order to determine the basal spacing or interlayer distance ( $d_{001}$ ) of alkylphosphonium MMT. Increasing the interlayer distance is important in order to be successful at nanocomposite processing, because the intercalation of the polymer chains with organically layered silicate are more probable with a higher interlayer distance. This is important to determine the exfoliated or intercalated of nanocomposite because it can improve the properties of nanocomposite product [8]. Results of these analyses are recorded in Table 1 and the diffractograms of all alkylphosphonium MMT are plotted in Figure 1.

Sodium montmorillonite (Na-MMT) exhibited a basal reflection or interlayer distance ( $d_{001}$ ) at 7.082°, which, according to the Bragg's law ( $n\lambda = 2d \sin \theta$ ), implied an interlayer spacing of 1.25 nm. After the organic modification of the clay, the basal reflection was displaced to lower angles for every type of alkylphosphonium MMT which meant the interlayer distance was increased due to the intercalation of the surfactant between the silicate layers [11].

TABLE 1 XRD ANALYSIS OF MONTMORILLONITES

Samples	$d_{001}$ (nm)	Interlayer spacing (nm)	Interlayer arrangement
Tributylmethylphosphonium methylsulfate MMT	1.47	0.51	Monolayer
Triisobutyl(methyl)phosphonium tosylate MMT	1.48	0.52	Monolayer
Tetrabutylphosphonium chloride MMT	1.75	0.79	Bilayer
Tetraoctylphosphonium bromide MMT	2.36	1.4	Paraffin

Fig. 1. XRD diffractograms samples analysis of unmodified clay (Na-MMT) and 4 types of alkylphosphonium MMT.



Alkylphosphonium MMT, tributylmethylphosphonium methyl sulfate MMT implied basal spacing of 1.47nm at 5.987° whereas, triisobutyl(methyl)phosphonium tosylate MMT exhibited the basal reflection angle at 5.94° and the basal spacing increased 1.25nm to 1.48nm. The basal spaces equivalent both of tributylmethylphosphonium methyl sulfate MMT and triisobutylmethylphosphonium tosylate MMT are consistence with a monolayer arrangement of the quaternary

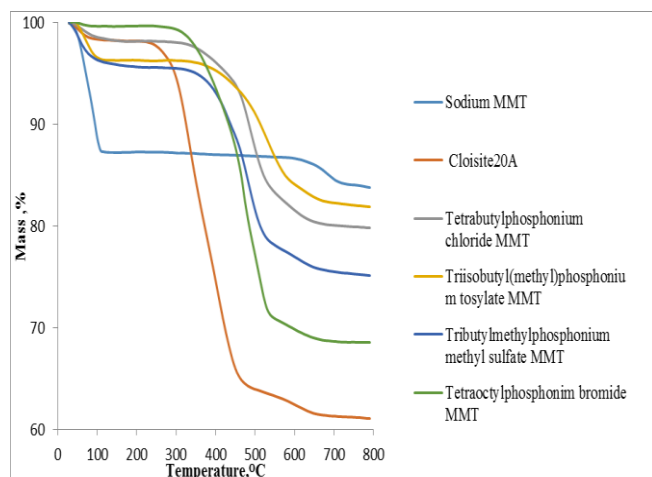
alkylphosphonium ion in the interlayer space. The third surfactant which is tetrabutylphosphonium chloride also increased the interlayer distance between layers of montmorillonite with the basal spacing obtained about 1.25nm to 1.75nm as well increased the clay surface thickness. The basal spacing value obtained by this modified MMT is consistence with a bilayer arrangement of intercalated surfactants while the maximum of basal space at 2.36nm obtained from tetraoctylphosphonium bromide MMT, it would indicate a paraffin-type arrangement of intercalated surfactants [10].

From this study, it proved the presence of alkylphosphonium group in the silicate layered interlayer space were increased basal spacing of MMT due to the intercalation of the surfactant ions and it is possible to be used in nanocomposite processing layer silicate.

### B. Thermal analysis

Figure 2 showed the thermogravimetric analysis (TGA) curves from 25 to 800 °C for the sodium, alkylammonium and alkylphosphonium montmorillonite. TGA analysis for alkyl ammonium MMT was measured in order to compare the thermal stability with alkylphosphonium MMT. The thermal stability of alkylphosphonium MMT was expected to have higher value than alkylammonium MMT which exceed 200°C so that it can be used in engineer polymer processing.

**Fig. 2.** TGA curve of natural clay, alkyl ammonium and 4 types alkylphosphonium MMT.



For sodium MMT, the weight loss in the TGA curve in Figure 2, and the prominent endotherms peaking near 100 °C in the curves, may be ascribed to interlayer water associated with the exchangeable Na<sup>+</sup> ions with a minor contribution from

physisorbed ('free') water held in interparticle pores and the highest percentage of water content is obtained about 11.83%. The weight loss at the endothermic peaks (650–750°C) is associated the lowest organic content (2.03%) with the loss of structural water through dehydroxylation of montmorillonite layers. At weight lose between 750-800°C, carbonaceous residues were released about 0.29%.

In discussing the thermal characteristics of the modified montmorillonites, Xie et al., (2002) have separated the curves into four districts regions: i) evaluation of free water and gases below 150°C; ii) evaluation of organic substances between 150 and 500°C; iii) dehydroxylation of the montmorillonite between 550 and 700°C; and iv) evaluation of carbonaceous residues between 700 and 1000°C.

First region of free water and gases also occurred in MMT of alkylphosphonium and alkyl ammonium at 50-150°C when the water and other gaseous species are absorbed to the interparticles pores. Water content for all modified montmorillonite is lower than unmodified clay due to the high hydrophobicity of the surfactant agent of alkylammonium and alkylphosphonium in range 0.34-3.65% compared to sodium MMT with 11.82%. From TGA curves, tetraoctylphosphonium bromide MMT has revealed only 0.35% of water content, it is smaller than Cloisite 20A (1.27%) by keeping the degree of high hydrophobicity between alkylphosphonium and alkyl ammonium ions [11].

The thermal behaviour of modified montmorillonites in region ii is very important since in this temperature range the surfactant in interlayer clay begin to decompose. It was revealed the thermal stability increased as the intercalated surfactant or basal spacing decreased.

In this stage, it is known as first exothermic point which indicated the point at which the intercalated surfactant begins to decompose in the layer of nanoparticles. The onset temperatures for the quaternary ammonium and phosphonium modified montmorillonites are recorded in Table 2 below. The alkylammonium MMT (Cloisite 20A) showed the lower onset temperature  $T_{onset} = 173^{\circ}\text{C}$  than all the modified MMT from quaternary alkylphosphonium agent showed the value of  $T_{onset}$  exceed 200°C. The highest value obtained from tributylmethylphosphonium methyl sulfate MMT with  $T_{onset} = 370^{\circ}\text{C}$  and it can be classified as the nanoclay. that has high thermal stability and high hydrophilicity with the 3.05% of water content in this organic clay. Tetraoctylphosphonium bromide surfactant has low thermal stability with value about  $T_{onset} = 313^{\circ}\text{C}$  due to high degree of hydrophobicity of the montmorillonite properties [11]

The low onset temperature of tetraoctylphosphonium bromide compared with other alkylphosphonium (tetrabutylphosphonium chloride MMT, triisobutyl(methyl)phosphonium tosylate MMT and tributylmethylphosphonium methyl sulfate MMT) appears to

TABLE 2 TGA RESULTS OF MONTMORILLONITES

Samples	Water content (%)	Onset temperature of Decomposition (°C)	Organic Content (%)	Residual organics (%)
Sodium MMT	11.82	NA	2.03	0.29
Cloisite20A	1.27	173	33.66	0.95
Tributylmethylphosphonium methyl sulfate MMT	3.05	370	17.02	0.16
Triisobutyl(methyl)phosphonium tosylate MMT	3.65	368	10.9	0.17
Tetrabutylphosphonium chloride MMT	1.45	346	14.9	0.10
Tetraoctylphosphonium bromide MMT	0.34	313	35.9	0.06

NA-not available

be related to the looser arrangement of this surfactant in the interlayer space compared with the monolayer and bilayer arrangement of other alkylphosphonium MMT. The percent of organic content in modified montmorillonites was estimated by subtracting with the weight loss of unmodified montmorillonite between temperature 200-750°C due to dehydroxylation. It showed the montmorillonite with lower water content contained more organic content due to chemical structures of the surfactants presented in montmorillonite [9].

It also noted that all samples showed a flat plateau between 750-800°C to retain residual organic in the montmorillonite

### C. Surface area and porosity

Table 3 showed surface area and porosity properties for the montmorillonite. It clearly indicates that all the montmorillonite exhibit Type IV isotherm, attributed to the mesoporous-type of absorbent with pores in the range 2.0-50nm, associated with aggregates of plate-like particles giving rise to slit-shaped pores. The BET surface area increased as the basal spacing of the surfactant increased in silicate layers. Unmodified montmorillonite (sodium MMT) has smallest BET surface area with large value of BJH desorption average pore diameter of the surface of montmorillonite and tend to form big agglomerates with a layer disposition. Tributylmethylphosphonium methyl sulfate MMT and triisobutyl(methyl)phosphonium tosylate MMT have obtained smaller surface area compared to alkyl ammonium and other alkylphosphonium MMT and it ascribed formation of less fractionated lamellas. Larger surface area was measured from tetraoctylphosphonium bromide MMT and more fractionated plate-like structure on the surface. With the smaller value BJH desorption average pore diameter, it showed the good dispersion occurred as substance or particle of alkylphosphonium cation intercalated in the interlayer space of clay minerals instead of sticking onto the surface. These data are interrelated with SEM micrographs for montmorillonite which confirmed the formation of plate like structure.

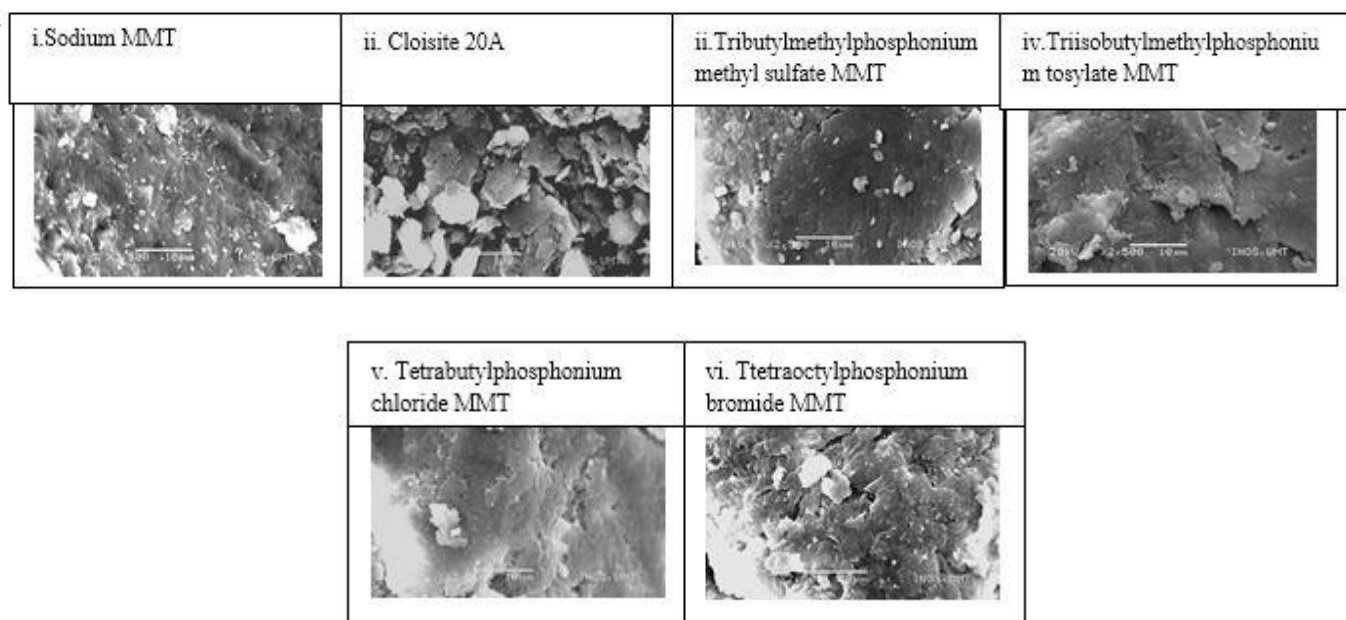
TABLE 3 SURFACE PROPERTIES OF MONTMORILLONITES

Samples	BET surface area (m <sup>2</sup> /g)	BJH desorption average pore diameter (nm)
Sodium MMT	10.5192	18.8113
Cloisite20A	17.6443	16.0649
Tributylmethylphosphonium methylsulfate MMT	22.0428	11.5914
Triisobutyl(methyl)phosphonium tosylate MMT	24.7454	10.4676
Tetrabutylphosphonium chloride MMT	28.4205	10.6767
Tetraoctylphosphonium bromide MMT	35.0781	7.4225

### D. SEM analysis

From the SEM images for the i, ii, iii, iv, v and vi in Figure 5, all samples are confirmed the morphology of the montmorillonite clay platelets. In the pristine state, Na-MMT soft surface where large lamellas tend to form big agglomerates with a layer disposition. After the modification with alkylphosphonium montmorillonite (APMMT): tetraoctylphosphonium bromide, tetrabutylphosphonium chloride, triisobutylmethylphosphonium tosylate and tributylmethylphosphonium methyl sulfate, the surface of the montmorillonite turned rougher than in Na-MMT with more fractionated lamellas and particles with the form of flakes. These plate-like structures did not group in an oriented disposition, such as in sodium MMT, and formed a mass of particles in a disordered way. The modification of alkylammonium MMT also showed the rough surface same as the modified APMMT. The hybrid systems developed in this study could be applied then as reinforcements of polymer matrices for the development of polymer/layered silicate nanocomposites with improved thermal or mechanical properties. Intercalation or well dispersed of alkylphosphonium MMT between the silicate layers also may improve the pore size and hydrophilicity of the polymer matrix samples.

**Fig.3.** SEM images of sodium MMT (i), alkyl ammonium MMT (ii) and 4 types alkyphosphonium MMT (iii,iv,v and vi)



#### IV. CONCLUSION

Several techniques were used to characterize the properties of MMT. Montmorillonites modified with quaternary phosphonium ions have the larger basal spacing compared to their pristine state which promoted the intercalation of the surfactant ion into silicate layers. In addition, the modifications of montmorillonites with alkyphosphonium ions have showed a greater thermal stability than alkyl ammonium MMT would be suitable for processing polymer nanocomposites at high temperature. The morphology structure of these alkyphosphonium and alkyl ammonium MMT were assessed by SEM microscopy which confirming the formation the plate-like structure and the average pore diameter in range 2.0-50nm (mesoporous type) obtained from surface area and porosity analysis. Thus, these properties provide a good potential for the use of alkyphosphonium MMT for the synthesis of polymer/clay nanocomposites.

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