

## ***Investigation of Intercalation of Sodium-Montmorillonite with Octadecyl Trimethyl Ammonium Bromide Surfactant***

Chanra J. Soegijono. B

Material Science, Department of Physic, Universitas Indonesia  
Email: Johannes.Chandra@yahoo.com.sg

Diterima : 15 Februari 2017  
Layak Terbit : 19 Juni 2017

### **Abstract**

*Sodium-montmorillonite (Na<sup>+</sup>-MMT) was intercalation modified with octadecyl trimethyl ammonium bromide (OTAB) in aqueous suspension via an ion exchange mechanism. Fourier transform infrared spectroscopy (FTIR) study indicates that OTAB is successfully intercalated into Na<sup>+</sup>-MMT layers and/or adsorbed on the surface of Na<sup>+</sup>-MMT. X-ray diffraction (XRD) analysis revealed that the interlayer spacing of the Na<sup>+</sup>-MMT was extended with the content of OTAB increasing, and the maximum spacing can reach about 3.80 nm. Results of scanning electron microscopy (SEM) analysis reveals the morphologies change from spherical-like particles to high-aspect ratio flakes after modification. Different configurations of OTAB chains within MMT interlayer are proposed based on the above analysis. The results of contact angle and the dispersion analysis show that the surface wettability of Na<sup>+</sup>-MMT is converted from hydrophilic to organophilic.*

**Keywords:** *montmorillonite; intercalation modification; microstructure; surface property; nanomaterials*

### **Abstrak**

**Investigasi Interkalasi Sodium-Montmorillonit dengan Octadecyl Trimethyl Ammonium Bromide Surfactant.** Sodium-montmorillonit (Na<sup>+</sup> -MMT) adalah interkalasi yang dimodifikasi dengan oktadecil trimetil amonium bromida (OTAB) dalam suspensi air melalui mekanisme pertukaran ion. Penelitian spektroskopi inframerah Fourier (FTIR) menunjukkan bahwa OTAB berhasil diselengi lapisan Na<sup>+</sup> -MMT dan / atau teradsorpsi pada permukaan Na<sup>+</sup> -MMT. Analisis difraksi sinar-X (XRD) menunjukkan bahwa jarak interlayer Na<sup>+</sup> -MMT diperpanjang dengan kandungan OTAB meningkat, dan jarak maksimum bisa mencapai sekitar 3,80 nm. Hasil analisis mikroskop elektron scanning (SEM) menunjukkan perubahan morfologi dari partikel mirip bola hingga flut rasio aspek tinggi setelah modifikasi. Berbagai konfigurasi rantai OTAB + dalam interlayer MMT diusulkan berdasarkan analisis di atas. Hasil sudut kontak dan analisis dispersi menunjukkan bahwa kesetimbangan permukaan Na<sup>+</sup> -MMT diubah dari hidrofilik menjadi organofilik.

**Kata Kunci:** montmorillonit; modifikasi interkalasi; struktur mikro; properti permukaan; Nanomaterials

### **INTRODUCTION**

Montmorillonite (MMT) particularly Na-MMT type is one of the 2:1 layered silicate is commonly use as nanofiller to prepare polymer nanocomposite. Organophilic MMT was prepared by using reactive cationic surfactants, where sodium ions in the MMT were exchange by surfactant's cations in aqueous medium. Cationic surfactants commonly used such as quarternary ammonium compound were intercalated into the interlayer space through ion exchange. By exchanging of sodium cations for surfactant cations, the interlayer of organoclays will increase as the surfactant loading increases and will reach the saturation limit, the surface energy of MMT will decreases and the interlayer spacing will expand, it is correspond to clay cation exchange capacity (CEC) [5,6].

Modification of MMT clay will change the character of MMT from hydrophilic to organophilic.

Organoclays that were synthesise by grafting of cationic surfactants have been widely studied fundamentally and in practical application area, long chain alkylammonium cations can forms a space through ion exchange. The interlayer distance of the d(001) plane of the clay, which has not been been modified is relatively small and the clay have hydrophilic properties, intercalation of cationic surfactant between the layers of MMT not only changes the surface properties from hydrophilic to hydrophobic, but also increase the basal space of the clay layers.

Polymeric nanocomposites with small amount of organoclay able to improve mechanical

properties, thermal stabilities and gas barrier properties. However the application of polymeric nanocomposites in the system much depend on the compatibility of organoclay as filler and polymer matrix and homogenous stability of the polymer.

In this paper, we present preparation and characterization of Na-MMT clay by using longest carbon chain octadecyl trimethyl ammonium bromide (OTAB) We report the basal spacing by XRD and thermogravimetric behaviour by TGA.

## MATERIAL AND METHODS

Material, Unmodified sodium montmorillonite clay (Na-MMT) with Cation Exchange Capacity, CEC 92 meq/100g was supplied by Zhejiang Hongyu New Material Technology Company Limited. The quaternary alkyl ammonium surfactant, octadecyl trimethyl ammonium bromide (OTAB), was purchased from Anhui Benma Pioneer Technology Company Limited and used without further purification.

Preparation, Weigh 10 gram of Na-MMT and dispersed into 750 ml distilled water, stirred the solution for 2 hours until clear dispersion was obtained. Weigh 4.25 gram of cationic surfactant, dissolved into 250 mL of distilled water, stirred until all surfactant dissolved in water. Cationic surfactant solution was added into Na-MMT solution by dropwise, the mixture was stirred for 24 hours at room temperature under vigorous stirring. The dispersion was left 24 hours and the excess of water was decanted. The obtained precipitate was recovered by successive centrifugation steps at 3500 relative centrifugal force (RCF) for 5 minutes. Several washing were done on the obtained precipitate with distilled water until no free organic modifier was detectable using silver nitrate test. The obtained organoclay paste was put into sealable container and stored in a fridge. Powder samples were used to evaluate the extend of modifier grafting onto the MMT clay platelets were drying the organoclay overnight at 45 C under vacuum.

Characterization, X-ray diffraction (XRD) analysis was performed using Philips machine at 30 kV by a Cu tube (Cu K $\alpha$  radiation,  $\lambda = 0.154$  nm) at a scanning rate of 2°/min with  $2\theta$  range of 1°–8° for sample pilarized and 1°–50° for Na-MMT. TEM JEOL 1200 to observe morphology.

## RESULT AND DISCUSSION

Figure 1 and Figure 2 show X-ray diffraction pattern of Na-MMT before pillarization, and after pilarization. Na-MMT before intercalation show by the presence of peak at 6.10 which was

basal spacing from Na-MMT with d value of 14.23 Å. The result from diffractogram of intercalated Na-MMT by OTAB show the appearance of new peak which dominant at  $2\theta=2.700$  with d value of 25.95 Å.

Figure 3 show TEM observation on Na-MMT powder before pillarization. It show the particles sphere like.

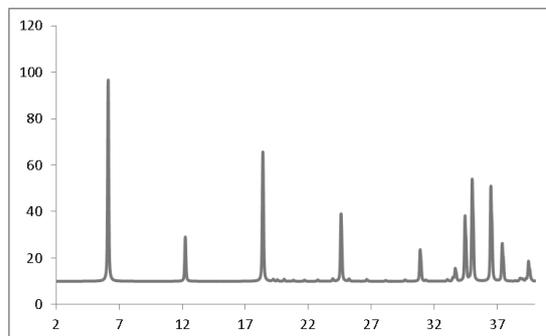


Figure 1 . X-ray diffraction patterns of Na-MMT.

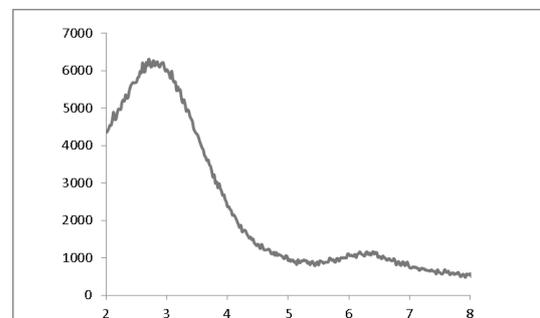


Figure 2 . X-ray diffraction patterns of pillared Na-MMT

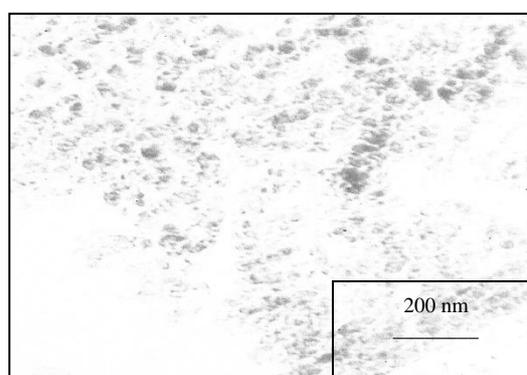


Figure 3 . TEM image of Na-MMT before pillarization

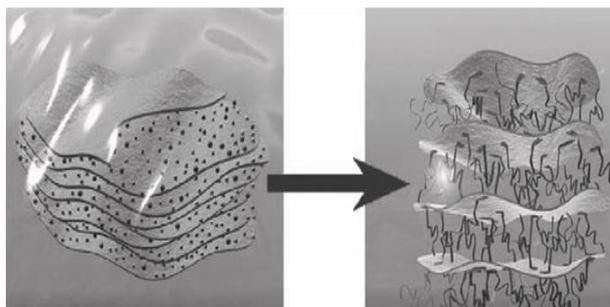


Figure 4. Schematic picture of ion exchange reaction [16]

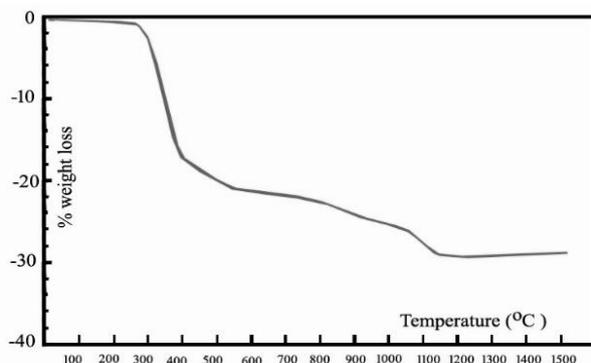


Figure 5. Percent weight loss of pillared Na-MMT

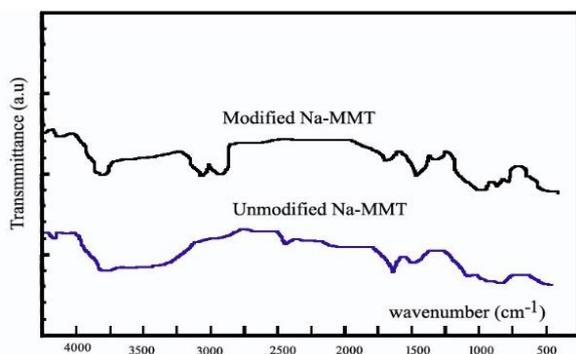


Figure 6. FTIR spectra of Na-MMT and modified MMT

The thermogravimetric analysis showed that the thermal decomposition of pillared Na-MMT on various temperatures. From the thermogram shown in figure 5, there are several mass loss steps observed, one occurring on below 100 Celsius and other starting from 300 Celsius, attributed to loss of water through dehydroxylation of the organoclays. Previous study shown that dehydroxylation occurs from 400 to 650 Celsius,

The percent mass loss depend on amount of concentration of the surfactant and also type of surfactant used, when the concentration of surfactant loading are increased, the percent loss will also increased due to molecules of surfactant desorbed from the layer of silicate.

FTIR spectroscopy able to analyze the changes in the molecular structure by measuring the vibrations, the changes can be observed from the differences in IR spectra.

The bands between 3300-3650  $\text{cm}^{-1}$ , indicated OH stretching region, 1600-1700  $\text{cm}^{-1}$ , indicated HOH bending vibration, 1030-1040  $\text{cm}^{-1}$  indicated Si-O-Si stretching, 460-480  $\text{cm}^{-1}$  Si-O-Si bending and 530-540  $\text{cm}^{-1}$  Al-Si-O bending [19].

From FTIR data spectrum, OTAB can enter the galleries and bond to Na-MMT. The presence of the C-H stretching of OTAB at 3000-2840  $\text{cm}^{-1}$ , and the double bond C=C stretching 1667-1640  $\text{cm}^{-1}$  of OTAB indicates the existence of OTAB in the pretreated montmorillonite samples.

## CONCLUSION

The results state that OTAB have entered the interlayer space of Na-MMT. During the process surfactants modified Na-MMT by pillarizing basa spacing of Na-MMT.

These findings are important to the preparation of low-cost Na-MMT and relevant to the exfoliation in the synthesis of polymer nanocomposites for industrial applications.

## ACKNOWLEDMENT

This research is supported financially by Hibah Publikasi Internasional Terindeks untuk Tugas Akhir Mahasiswa University of Indonesia through letter of decree No.1997/UN2.R12/HKP.05.00/2016.

## REFERENCES

- Abuja., *Non-metallic mineral endowment in Nigeria: Raw Material Research & Development Council*, Federal Ministry of Science and Technology, (2010).
- D. Chaiko, in *PCT Int. Appl.*, (University of Chicago, USA). Wo, 2002, p. 24 pp. N. M. Soule and S. E. Burns, *Journal of Geotechnical and Geoenvironmental Engineering* 127 (2001) 363
- Gelfer, M.; Burger, C.; Fadeev, A.; Sics, I.; Chu, B.; Hsiao, B.S.; Heintz, A.; Kojo, K.; Hsu, S.; Si, M.; Rafailovich, M.; Langmuir 2004, 20, 3746
- Gilman J W, Jackson C L, Morgan A B, et al. Flammability proper- ties of polymer-layered silicate nanocomposites, propylene and polystyrene nanocomposites. *Chem. Mater.* 2000, 12(7):

- G. R. Alther, *Water Environment & Technology* 13 (2001) 31
- Meincke O, Hoffmann B, Dietrich C, et al. Viscoelastic properties of polystyrene nanocomposites based on layered silicates. *Macro- mol. Chem. Phys.*, 2003, 204(5/6): 823–830.
- Nielsen L E. Models for the permeability of filled polymer systems. *J. Macromol. Sci. Chem.*, 1967, 1(5): 929–942
- Othmani-Assmann, H.; Benna-Zayani, M.; Geiger, S.; Fraisse, B.; Kbir-Arighuib, N.; Trabelsi-Ayadi, M.; Ghermani, N.E.; Grossiord, J.L.; *J. Phys. Chem. C* 2007, 111, 10869.
- Patel H A. Synthesis and Characterization of Nanoclays for polymeric nanocomposites, paints and adsorption applications, Thesis, Central Salt & Marine Chemicals Institute, India, 2008 (11).
- P. Maiti, K. Yamada, M. Okamoto, K. Ueda and K. Okamoto, “New Poly lactide/Layered Silicate Nanocomposites: Role of Organoclays,” *Chemistry of Materials*, Vol. 14, No. 11, 2002, pp. 4654-4661. doi:10.1021/cm020391b
- Tahani, A.; Karroua, M.; Van Damme, H.; Levitz, P.; Bergaya, F.; *J. Colloid Interface Sci* 1999,216,242
- Theresa O E, Grace OBI, Flix EO, Fundatihminoglu., Effect of exchanged surfactant cation on the structure of kaolinitic clay., *J. Mater Sci, Appl.* 2015:1.
- Xi Y, Ding Z, He H, et al. Structure of organoclays—an X-ray diffraction and thermogravimetric analysis study. *J. Colloid. Interface Sci.*, 2004, 277(1): 116–120.
- . Yano K, Usuki A, Okada A, et al. Synthesis and properties of polyimide–clay hybrid. *J. Polym. Sci., Part A: Polym. Chem.*, 1993, 31(10): 2493–2498.
- Y.Park, G.A.Ayoko, J.Kristof, E. Horvath and R.L.Frost: Thermal stability of organolays with mono- and di alkyl cationic surfactant. , *J. Therm Ana. Cal.* 92(1), 129 (2008).
- Zanetti M, Camino G, Thomann R, et al. Synthesis and thermal behavior of layered silicate-EVA nanocomposites. *Polymer*, 2001, 42(10): 4501–4507.
- Zheng H, Zhang Y, Peng Z, et al. Influence of clay modification on the structure and mechanical properties of EPDM/montmorillonite nanocomposites. *Polym. Test.*, 2004, 23(2): 217–223.
- Zhu J, Morgan A B, Lamelas F J, et al. Fire properties of polystyrene–clay nanocomposites. *Chem. Mater.*, 2001, 13(10): 3774–3780