Synthesis and Characterization of Organoclay from Sodium Montmorillonite and Fatty Hydroxamic Acids

Wisam H. Hoidy, Mansor B. Ahmad, Emad A. Jaffar Al Mulla and Nor Azowa Bt Ibrahim
Department of Chemistry, Faculty of Science, University Putra Malaysia,
43400 UPM, Serdang, Selangor, Malaysia

Abstract: Problem statement: Sodium Montmorillonite (Na-MMT) has been modified via cation exchange reaction using Fatty Hydroxamic Acids (FHAs) synthesized from palm oil as a surfactant to produce organoclay which is used to prepare polymer nanocomposites. **Approach:** Basal spacing, functional groups identification and thermal stability of this Organo-Montmorillonite (OMMT) were characterized using X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy and Thermogravimetric Analysis (TGA) respectively. Elemental analysis was also used to know the composition of OMMT. Cation Exchange Capacity (CEC) was also investigated in this study. **Results:** The (XRD) results showed that the basal spacing of the treated clay with FHA increased to 31Å. The highest d-spacing was observed at 1.8 CEC. FTIR spectra illustrate that FHA compound was successfully intercalated into the clay layers. Tthermogravimetric analysis showed that the thermal decomposition of organoclay occurs in four steps. **Conclusion:** The new organic cation (FHA) was used to modify montmorollonite clay in an attempt to create susceptible clay to polymers. In future, we may predict any derivative of fatty nitrogen compounds can be used as a surfactant for clay modification.

Key words: Sodium montmorillonite, fatty hydroxamic acids, cation exchange capacity, surfactants

INTRODUCTION

Due to their natural availability and the capacity for the chemical and physical modifications, clays are used in many scientific applications. The high cation exchange capacity. Swelling ability and the high platelet aspect ratio are some features that make clays very desirable in the industrial and scientific applications[1].

Clays are hydrophilic in nature because of the presence of inorganic cations on the basal planar of montmorillite rendering the clay ineffective for absorption of aliphatic and relatively hydrophobic compounds[2].

Inorganic ions in the clay can be effectively replaced by organic cationic surfactant molecules through cation-exchange reactions. These result in expansion of the interlayer spacing which leads to an increase in the basal spacing. As a result, the wettability and the thermodynamical interactions increase significantly. For the purpose of industrial applications, either modified or unmodified clay can be chemically remodified. Some of these applications are rheological additives, as thickeners in coating products, glues,

platisols, drilling fluids[3] and for wastewater treatment[4] organoclays are used as thickeners in paints, greases, oil-base drilling muds and for the purpose of gelling various organic liquids[5,6]. Na-montmorillonite is used as carriers for agricultural insecticides to increase production of grains used for food supply[7]. Additionally, Clay mineralscan be used in various paints and varnishes where they act as filler, stable against weathering, to provide and improve abrasion and scratch resistance[8]. Recently, clays have become used in the field of materials science such as solid phase polymeric nanocomposites[9]. The interest in the use of orginacaly modified clays for polymer clays nanocomposite has started at early 90's[10,11]. Organic amine salts were ion exchanged with sodium montmorillonite to form organoclays varying in amine structure or exchange level relative to the clay[12]. Various researches were performed about the applications of OMMT in the area of organic-inorganic hybrids, composites and nano-scale composites[13,14]. The compatibility of clays with polymers can be achieved through the organic modification of clay minerals which leads to a decrease in the surface energy. Contact angle measurements can be used to

Corresponding Author: Wisam H. Hoidy, Department of Chemistry, Faculty of Science, University of Putra Malaysia,
43400 UPM, Serdang, Selangor, Malaysia

determine the surface energy of clays and polymers. The selection of the proper organic modifier ca plays the important role in controlling the surface energy of montmorolinite[15,16]. Sodium montmorillonite was modified via cation exchange reaction using β-dimethyl-aminopropiophenone ammonium, N-phenyldiethanolammonium and glycine-n-hexylester ammonium. Basal spacing up to 13, 15 and 13 Å, respectively. The modification of sodium montmorillonite through the incorporation of amphiphilic octadecylammonium cation in various concentration (10-200% CEC) into the clay's interlayer spaces has been studied, the complete bilayer arrangement requires a higher amount of octadecylammonium than the clay CEC and up to 175% CEC coverage. Additional increase of octadecylammonium to 200% CEC gives rise to a paraffin complex arrangement of alkylammonium cations inside the galleries[17].

In the current study, Na-MMT was modified for preparation and characterization organoclay by using fatty hydroxamic acids which were prepared from palm oil with hydroxylmine by reflux method. Although, fatty hydroxamic acids molecular able to replace with Na+ in montmorolinite by ion exchange. Optimum conditions of Cationic Exchange Capacity (CEC) percentages are investigated in order to optimize amount of FHAs used for modification of clay. No information was found in the accessible literature about using fatty hydroxamic acid for clay modification.

MATERIALS AND METHODS

Materials: Sodium montmorillonite used in this study was obtained from Kunimine Ind. Co. Japan. The hydroxylamine hydrochloride used in this study was provided by Fluka, Switzerland. Palm oil was obtained from Ngo Chew Hong oils and fats (M) Sdn. Bhd. Malaysia. Hexane from T.J. Baker, USA.

Synthesis of (FHAs): Palm oil was dissolved in hexane with Hydroxylamine hydrochloride and the mixture was refluxed at 69°C for 10 h using a thermo stated round bottom flask equipped with water-cooled condenser and mechanical stirrer. After the reaction had finished, the product was dissolved in hot hexane and separated from bottom layer by separating funnel. The hexane phase was cooled in an ice bath for 4 h to obtain Fatty Hydroxamic Acids (FHAs) and then, filtered and washed by hexane for three times and dried at 60°C for 2 h.

Preparation of Organoclays (OMMTs): Designate amount of concentrated HCl and FHAs in 800 mL were heated at 80°C distilled water for 1 h, Na^+-MMT was dispersed in 600 mL hot water for 1 h. The first solution was poured in MMT-water and vigorously stirred for 1 h. The precipitation was filtered in a suction filtration and washed several times with distilled hot water till chloride ions completely removed. Then, the precipitation was dried in a vacuum oven at 80°C for 24 h.

The concentrations of FHA used were 20, 60, 100, 140, 180 and 220% CEC of the MMT, respectively. The reaction mixtures were stirred vigorously for 1 h at 80°C. The organoclays suspension was filtered and washed with distilled water until no chloride was detected with 1 M silver nitrate solution. It was then dried at 60°C for 48 h.

Characterizations: 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}.

CHNS analyser (LECO CHNS-932) was used for quantitative analysis of amount of intercalation agent present in the organoclay. A sample of approximately 2 mg of organocly burned at 1000°C under oxygen gaseous flow was used for this test. The sulfamethazine was used as standard.

X-ray Diffraction (XRD) study was carried out using shimadzu XRD 6000 diffractometer with Cu-K α radiation (λ = 0, 15406 nm). The diffractogram was scanned in the ranges from 2-10° at a scan rate of 1° min^{-1}.

TG analysis using Perkin Elmer model TGA 7 Thermalgravimtry analyzer was used to measure the weight loss of the samples. The samples were heated from 30-800°C with the heating rate of 10°C min^{-1} under nitrogen atmosphere with a nitrogen flow rate of 20 mL min^{-1}.

RESULTS

The presence of FHA chain in the galleries makes the originally hydrophilic silicate to organophilic and thus increases the layer-to-layer spacing of Na-MMT[18]. The obtained FHA-MMT was studied by using X-ray diffraction. Na-MMT shows a d001 diffraction peak at 2θ = 7.21° which assigns to the interlayer distance of the natural montmorillonite with a basal spacing of 1.23 nm as known in Table 1[19].

Table 1: Diffraction angle and basal spacing of montmorillonite and modified montmorillonite with FHA

Sample	2θ (°)	d (001) spacing (Å)
Montmorillonite	7.35	12.2
FHA modified	2.89	31.0

Table 2: C, N and alkylammonium groups contents of the FHA modified montmorillonite

Alkylammonium groups modified montmorillonite	C (%)	N (%)	m mol of alkylammonium groups/1 g montmorillonite	
			Based on C calculation	Based on N calculation
FHA	29.5	2.10	1.53	1.50

Table 2 shows the percentage of carbon and nitrogen from the analysis. The results clearly reveal that the percentage of carbon and nitrogen content of clay increase after modification. This indicates that the replacement of Na+ with FHA was successful. The amount of surfactant intercalated in the organoclay based on carbon and nitrogen content are shown in Table 2. During the clay modification, sodium ion is replaced with FHA ions via cation exchange reaction. Amount of intercalated FHA in the clay interlayer spacing can be measured using elemental analysis.

DISCUSSION

In Fig. 1a, the infrared spectra of the Na-MMT show tow peaks, which correspond to Si-O stretching at 1112 cm^{-1} and interlayer water deformation vibrations at 1636 cm^{-1}. The band at 3620 cm^{-1} results from the O-H stretching vibration[20,21].

FTIR spectra of FHAs are shown in Fig. 1b. Peaks observed at wave number of 3413 and 3210 cm^{-1} which corresponds to N-H and O-H stretching, at 2854 and 2917 cm^{-1} which corresponds to C-H stretch of alkyl chain, at 1641 cm^{-1} which correspond to C = O for secondary amide and at 1044 and 1113 cm^{-1} which corresponds to C-N stretch respectively.

FTIR spectra of FHA-MMT are shown in Fig. 1c. Peaks observed at wave number of 3672 cm^{-1} which corresponds to O-H stretching, at 3230 cm^{-1} which correspond to N-H amide, at 2920 cm^{-1} which correspond to C-H asymmetric stretching, at 2855 cm^{-1} which correspond to C-H symmetric stretching and at 1661 cm^{-1} interlayer water deformation vibrations.

Na-MMT was surface treated with FHA as intercalation agent through 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 a ways from the surface. After the ion exchange reaction, the basal spacing increases from 1.22 nm (Fig. 2a) to 2.89 nm (Fig. 2b) indicating that the FHA was successfully intercalated into the Na-MMT galleries.
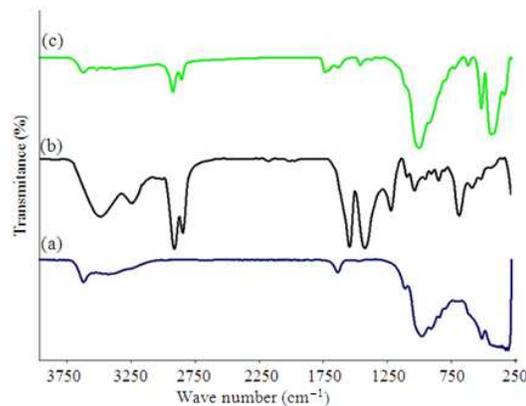

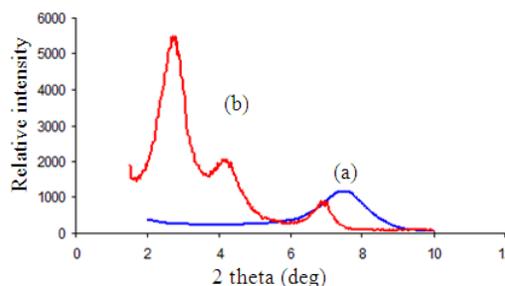Fig. 1: FTIR spectra of (a) Na-MMT, (b) FHAs and (c) FHA-MMT

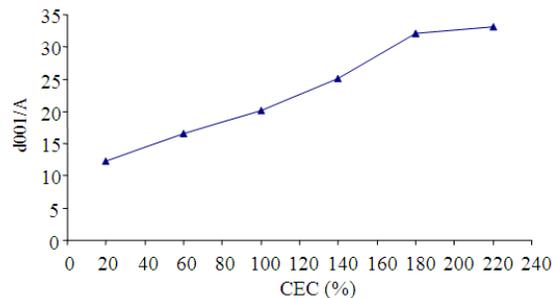Fig. 2: XRD patterns of (a) Na-MMT and (b) FHA-MMT

Fig. 3: The basal distance (d001) of pristine (MMT) and Organomodified Montmorillonites (OMMT)

Cationic Exchange Capacity (CEC) was investigated to determine the optimum amount of FHA as modifier agent to get maximum d-spacing with lower angle-value. Figure 3 shows that the better angle value at 1.8 CEC.

Figure 4 shows the XRD curves for the various amounts of FHAs. The angle values increase as FHAs increase adding up to 1.8 CEC. Beyond which no increase in the CEC was observed.
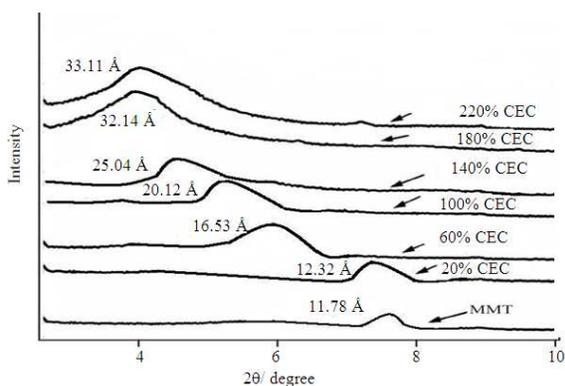
Fig. 4: XRD patterns of pristine and organomodified montmorillonite with various concentrations of FHAs (related to clay CEC)
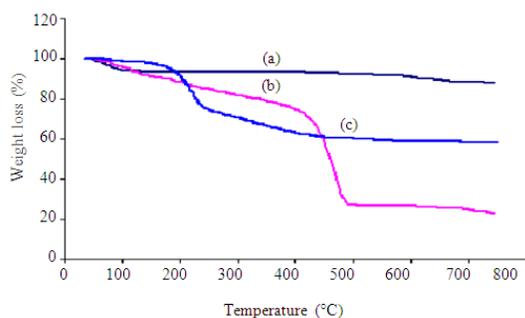

Fig. 5: TGA thermograms of (a) Na-MMT, (b) FHAs and (c) FHA-MMT

Thermal stability plays an essential role in determining both technological applications and processing conditions of OMMT. At a given temperature the OMMT weight loss is directly related to the rate of the OMMT decomposition process.

The thermal decomposition expressed in terms of weight loss as a function of temperature of both pristine clay (Na-MMT) and organoclays are shown in Fig. 5a. Magaraphan et al.[22] divided the Na-MMT differential thermal curve in tow parts; (a) the free water and interlayer water reign in the temperature range 100-200°C (b) the structural water (bonded OH that undergoes dehydroxylation) region in the temperature range 500-1000°C[22]. However, Xie et al.[23] divided the decomposition of the organoclay into four parts; (a) the free water region in the temperature below 200°C (b) the region where organic substances evolve in the temperature range 200-500°C (c) the structural water region in the temperature range 500-800°C and (d) the region between 800-1000°C[23]. Where organic carbon reacts with inorganic oxygen (combustion reaction) the

temperature 800°C[21]. Na-MMT is usually highly hydrated due to its large hydrophilic internal surface[23]. Hence, free water (water between particles and sorbed on the external surfaces of crystals) are released at the temperature of below 100°C[22] as shown in Fig. 5a. The total weight loss of Na-MMT at this region is 11.17%. The second step of decomposition occurs at the temperature range of 400-700°C. This is due to the structure water in the clay; bonded OH that undergoes dehydroxylation[23]. The total weight loss at this region is 3.94%. According to Arroyo et al.[21] water in the interlayer space usually is removed at the temperature of around 350°C. This was proved by Arroyo et al. using X-ray measurement, where at that over this temperature range. The (001) spacing decrease from 11-12.5 Å for Na-MMT to 9.6 Å and no further decrease occurred at higher temperature.

Pure FHA started to decompose at 113.08°C and ended at 468.54°C as shown in Fig. 5b. The major difference between the thermal decomposition of Na-MMT and the thermal decomposition of the organically modified clay is in the range of 57.35-325.91°C. The thermogram of FHA-MMT shows that the thermal decomposition of FHA-MMT occurs in four steps as shown in Fig. 5c. The first step is due to the releasing of free water between particles and water sorbed on the external surfaces of crystals[23]. The decomposition of organic constituent in FHA-MMT occurs in second step where it started to decompose from 223.04-325.91°C. The weight loss at this step was 18%. The last two steps, which occurs at the range 400-810°C was due to the dehydration of structural water in the clay[23].

CONCLUSION

The new organic cation (FHA) was used to modify montmorollonite clay in an attempt to create susceptible clay to polymers. FHA-MMT was characterized using FTIR, XRD, TGA and CHNS.

Based on results of this study, the following conclusions can be drawn:

- FHA was successfully incorporated in the montmorollite clay
- The basal spacing of the montmorrlite clay was increased as a result of incorporating FHA
- Basal spacing was increased to 31 nm by the incorporation of FHAs
- An optimum angle value was obtained as 1.8 CEC
- The TGA curves for these organoclays show four-step degradation which corresponds to degradation due to residual water desorption, dehydration, followed by decomposition of the organic modifier

and the dehydroxylation of the organo-montmorillonite

FTIR spectra show that the FHA was successfully intercalation in the MMT.

REFRENCES

1. Xi, Y., R.L. Frost, H. He, T. Kloprogge and T. Bostrom, 2005. Modification of Wyoming montmorillonite surfaces using acationic surfactant. Langmuir, 21: 8675-8680.
http://www.ncbi.nlm.nih.gov/pubmed/16142947

2. Giannelis, E.P., 1996. Polymer layered silicate nanocomposites. Adv. Mater., 8: 29-35. DOI: 10.1002/adma.19960080104

3. Lan, T., P.D. Kaviratna and T.J. Pinnavaia, 1995. Mechanism of clay tactoid exfoliation in epoxy-clay nanocomposites. Chem. Mater., 7: 2144-2150. http://pubs.acs.org/doi/abs/10.1021/cm00059a023

4. Beall, G.W., 2003. The use of organoclays in water treatment. Applied Clay Sci., 24: 11-20. DOI: 10.1016/j.clay.2003.07.006

5. Zadaka, D., Y.G. Mishael, T. Polubesova, C. Serban and S. Nir, 2007. Modified silicates and porous glass as adsorbents for removal of organic pollutants from water and comparison with activated carbons. Applied Clay Sci., 36: 174-181. DOI: 10.1016/j.clay.2006.04.012

6. Lagaly, G., 1986. Interaction of alkylamines with different types of layered compounds. Solid State Ion., 22: 43-51.
http://cat.inist.fr/?aModele=afficheN&cpsidt=8306182

7. Konta, J., 1995. Clay and man: Clay raw materials in the service of man. Applied Clay Sci., 10: 275-335. DOI: 10.1016/0169-1317(95)00029-4

8. Murray, H.H., 2000. Traditional and new applications for kaolin, smectite and palygorskite: A general overview. Applied Clay Sci., 17: 207-221. http://cat.inist.fr/?aModele=afficheN&cpsidt=1525490

9. Ruiz-Hitzky, E. and A. van Meerbeek, 2006. Clay Mineral and Organoclay-Polymer Nanocomposites. In: Handbook of Clay Science, Bergaya, F., B.K.G. Theng and G. Lagaly (Eds.), Vol. 1, Elsevier, Amsterdam, ISBN: 0080441831, pp: 583-621.

10. Kojima, Y., A. Usuki, M. Kawasumi, A. Okada, T. Kurauchi and O. Kamigaito, 1993. One-pot synthesis of nylon 6-clay hybrid. J. Polymer Sci., Part A: Polymer Chem., 31: 1755-1758. DOI: 10.1002/pola.1993.080310714

11. Alexandre, M. and P. Dubois, 2000. Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class ofmaterials. Mater. Sci. Eng., 28: 1-63. DOI: 10.1016/S0927-796X(00)00012-7

12. Fornes, T.D., P.J. Yoon, D.L. Hunter, H. Keskkula and D.R. Paul, 2002. Effect of organoclay structure on nylon 6 nanocomposite morphology and properties. Polymer, 43: 5915-5933. DOI: 10.1016/S0032-3861(02)00400-7

13. Stretz, H.A., D.R. Paul, R. Li, H. Keskkula and P.E. Cassidy, 2005. Intercalation and exfoliation relationships in melt-processed poly (styrene-co acrylonitrile)/montmorillonite nanocomposites. Polymer, 46: 2621-2637. DOI: 10.1016/j.polymer.2005.01.063

14. Shah, R.K., D.H. Kim and D.R. Paul, 2007. Morphology and properties of nanocomposites formed from ethylene/methacrylic acid copolymers and organoclays. Polymer, 48: 1047-1057. DOI: 10.1016/j.polymer.2007.01.002

15. Maiti, M. and A.K. Bhowmick, 2005. Structure and properties of some novel fluoroelastomer/clay nanocomposites with special reference to their interaction. J. Applied Polymer Sci., 44: 162-176. http://cat.inist.fr/?aModele=afficheN&cpsidt=17469140

16. Dharaiya, D. and S.C. Jana, 2005. Thermal decomposition of alkyl ammonium ions and its effects on surface polarity of organically treated nanoclay. Polymer, 46: 10139-10147. DOI: 10.1016/j.polymer.2005.08.027

17. Zidelkheir, B. and M. Abdelgoad, 2008. Effect of surfactant agent upon the structure of montmorillonite X-ray diffraction and thermal analysis. J. Therm. Anal. Calorimetry, 94: 181-187. DOI: 10.1007/s10973-008-9053-8

18. Huang, J.C., Z.K. Zhu, J. Yin, X.F. Qian and Y.Y. Sun, 2001. Poly (etherimide) montmorillonite nanocomposites prepared by melt intercalation: Morphology, solvent resistance properties and thermal properties. Polymer, 42: 873-877. DOI: 10.1016/S0032-3861(00)00411-0

19. Agag, T. and T. Takeichi, 2000. Polybenzoxazine-montmorillonite hybrid nanocomposites: Synthesis and characterization. Polymer, 41: 7083-7090. http://cat.inist.fr/?aModele=afficheN&cpsidt=1387574

20. Zhang, J. and C.A. Wilkie, 2003. Preparation and flammability properties of polyethylene-clay nanocomposites. Polymer Degradat. Stab., 80: 163-169.
http://cat.inist.fr/?aModele=afficheN&cpsidt=14642116

21. Arroyo, M., M.A. Lopez-Manchado and B. Herrero, 2003. Organo-montmorillonite as substitute of carbon black in natural rubber compounds. Polymer, 44: 2447-2453. DOI: 10.1016/S0032-3861(03)00090-9

22. Magaraphan, R. and W. Lilayuthalert, 2001. Preparation, structure, properties and thermal behavior of rigid-rod polyimide/MMT nanocomposites. Compos Sci. Technol., 61: 1253-1264.

23. Xie, W., Z. Gao, K. Liu, W.P. Pan and R. Vaia *et al.*, 2001. Thermal characteristic of organomodified montmorillonite. Thermochimica Acta, 367-68: 339-350. DOI: 10.1016/S0040-6031(00)00690-0