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Surface modification of montmorillonite by the use of organic cations via conventional ion exchange method

Johannes Chanra^{1,*}, Emil Budianto², Bambang Soegijono¹

¹ Material Science Program, Department of Physics, Universitas Indonesia, Depok, Indonesia

² Department of Chemistry, Universitas Indonesia, Depok, Indonesia

* Corresponding author e-mail: johannes.tjong@gmail.com

Abstract. The main problems in synthesis polymer clay nanocomposites (PCNs) with nanoclay filler is the nanoclay was not compatible to most of polymer matrix due to its hydrophilicity which is often causes agglomeration of the nanoclay in the polymer matrix. Surface modification of nanoclay for a good compatibility with polymer matrix is the most important step to achieve homogenous dispersion of clay platelets in polymers. Modification of nanoclay montmorillonite (MMT) can be done through conventional ion exchange method using cationic surfactants. Montmorillonite (MMT) was modified with several cationic surfactants based on its cationic exchange capacity (CEC). The effect of chemical composition of modified MMT on the basal spacing were evaluated by small angle x-ray diffraction (SAXS), the highest basal spacing expanded from 1.21 nm to 2.00 nm showed the intercalation of the surfactant ion into the intergallery of sodium montmorillonite clay layers which caused increasing of surface area and porosity. FTIR spectra shows the successful of inserting alkyl groups from cationic surfactant in interlayer space of montmorillonite. Organophilization reduces the energy of sodium montmorillonite and improves its compatibility with organic polymer. Dispersion analysis and contact angle results shown the surface wettability of montmorillonite was enhanced from hydrophilic to organophilic and resulting good solubility in monomer phase.

Keyword: sodium montmorillonite, surface modification, hydrophilic, organophilic, cationic surfactants

1. Introduction

Sodium montmorillonite (Na-MMT) is a layered silicate which is belong to the 2:1 phyllosilicate structural family smectite clay, it is commonly used as a nanofiller in the synthesis of polymer clay nanocomposites (PCNs) because this type material exhibit by enhance mechanical properties, heat resistance and improved barrier properties [1]. Organo-montmorillonite (OMMT) are synthesized by conventional ion exchange method with cationic surfactants such as quaternary alkylammonium compounds [2]. The intergallery distance of d (001) plane of the clay which has not been modified is relatively small, has hydrophilic environment. Intercalation of organic surfactant between the clay layers can change the surface properties from hydrophilic to hydrophobic, also increase the basal spacing of the layers. Intercalation of layers at a given temperature depends on the organic chain length and cationic exchange capacity (CEC) of layered silicate. CEC is the characteristic property of soil provided by clay and organic matter, it is expressed as meq/100 g [3]. Individual montmorillonite (MMT) layers are about 0.96 nm thick with lateral dimensions that are more than two orders of magnitude larger or “platey” structure with 200 to 600 nm, these layers organize themselves to form stalks by Van Der Waals force



of attraction between them, the attraction force between them is relatively weak so polymer molecules can be intercalated [4]. MMT clay in its natural can be dispersed only in hydrophilic polymers such as poly (ethylene oxide) or poly (vinyl alcohol). In order to render the surface more organophilic, hydrated cations on clay surface are replaced by cationic surfactants.

The high aspect ratio of MMT clay particles is an important factor in polymer property enhancement. Exfoliation of MMT layers in polymer matrix leads to form large interfacial surface area in order to interact with polymer chains, delamination of individual clay mineral layers into polymer matrix only happened in theoretical [5], however exfoliation can lead to form uniform dispersion, this is the main key to enhance mechanical property and barrier properties of polymer clay nanocomposite [6].

The basal spacing of organo-montmorillonite (OMMT) increased with surfactant loading, while the maximum basal spacing increased as the alkyl chain length of the surfactant increased [7]. The level of surfactant loading required to achieve the maximum basal spacing depend on the CEC, previous research reported more than $1.0 \times \text{CEC}$ required to achieve maximum basal spacing [8, 9]. The surfactant can be loaded by two different ways: surfactant cations and surfactant molecules (ionic-pairs) [10], both of them occupied the interlayer spaces formed “*house of card*” structure [7, 11, 12]. In thermal stability analysis, the mass loss at the evaporation temperature was attributed to surfactant loaded in the pores within “*house of card*” structure while mass loss at higher temperature due to decomposition of intercalated surfactants [13, 14].

In this research, sodium-montmorillonites were modified with three type of surfactants; alkylammonium with different alkyl chain length (C14 (MTAB); C16(CTAB) and C18(OTAB)). The amount of surfactant cations in the interlayer space was 2 times the CEC of Na-MMT (110 meq/100g); this amount was confirmed by previous research [15]. Organo-montmorillonites were characterized by small angle x-ray scattering (SAXS) to obtained the basal spacing of OMMTs and FTIR.

This paper reports the changes in the structure of a montmorillonite clay intercalated with a long chain organic surfactant, to compare the results of OMMT’s analysis according to the difference surfactants. It is important to know the structure and properties of OMMT clays and their application.

2. Experimental

2.1. Materials

Unmodified montmorillonite clay with cation exchange capacity, CEC 110 meq/100 g, supplied from ECC Hangzhou, China, MMT was used as without any further purification. Alkyl ammonium surfactant, MTAB, CTAB, and OTAB were purchased from Pioneer Chemicals China and used as received. Silver nitrate solution, purchased from Sigma-Aldrich.

2.2. Organoclay Preparation.

MMT (20 g) was dispersed in 1500 mL distilled water, the solution was stirred with high speed stirrer for 2 hours until a clear solution was obtained. The organic modifier was weighed (based on MMT clay’s $2.0 \times \text{CEC}$) and dissolved in 500 mL distilled water until all organic modifier dissolved in water. Amount of surfactant used were calculated based on CEC of MMT as following:

$$\text{Weight of surfactant (g)} = n \times \text{CEC} \times A \times B \quad (1)$$

where A = weight of MMT (g) and B = is molecular weight of surfactant (g/mol); n = ratio to be used. Based on equation 1.1, the amount of surfactant needed for surface modification of MMT can be tabulated as following:

Table 1. Amount of cationic surfactant's calculated for MMT modification.

Surfactant type	Molecular weight (B) (g/mol)	Ratio used (n)	MMT CEC (meq/100 g)	Weight of MMT (A) in grams	Amount of surfactant required (g)
MTAB	336.39	2.0	110	20.00	14.79
CTAB	364.45	2.0	110	20.00	16.03
OTAB	392.50	2.0	110	20.00	17.27

Mixed the two solution and stirred under mechanical stirrer for 24 hours at room temperature. The mixed solution then precipitated with high speed centrifugal (3500-4000 rpm), several washing were done until the solution free of bromide ions (test with silver nitrate 0.1M solution). Keep the precipitated in constant temperature oven at 60°C for 1 night. Finally ground the resulting organoclay with Pestle Mortar for 30 second and stored in desiccator.

2.3. Characterization

2.3.1. SAXS Diffraction. X-ray diffraction (SAXS, Philips binary scan, RD) was performed on dried powder samples. The scans were performed for each samples with starting $2\theta = 3.00^\circ$ to $2\theta = 30.00^\circ$ at room temperature. Anode material Cu with $K-\alpha_1 = 1.54060 \text{ \AA}$ and $K-\alpha_2 = 1.54443 \text{ \AA}$, ratio = 0.50000, diffractometer type, XPERT MPD. The machine was operated at 30 mA, 40 kV.

2.3.2. FTIR Analysis. FTIR spectra for all samples were run on a Perkin Elmer Model 1600 Spectrophotometer using KBr pellets.

3. Results and discussions

3.1. X-ray diffraction with SAXS.

X-ray diffraction patterns (Fig. 1) of different organoclays showed value of the diffraction peak corresponding to d(001) distance that increased from 1.21 nm for the unmodified MMT to 2.0 nm for the nanoclay modified with alkylammonium surfactants with 2.0 CEC level. Results on Table 2, indicated that at least a fraction of the cationic surfactants has replaced the hydrated interlayer cations of MMT [16].

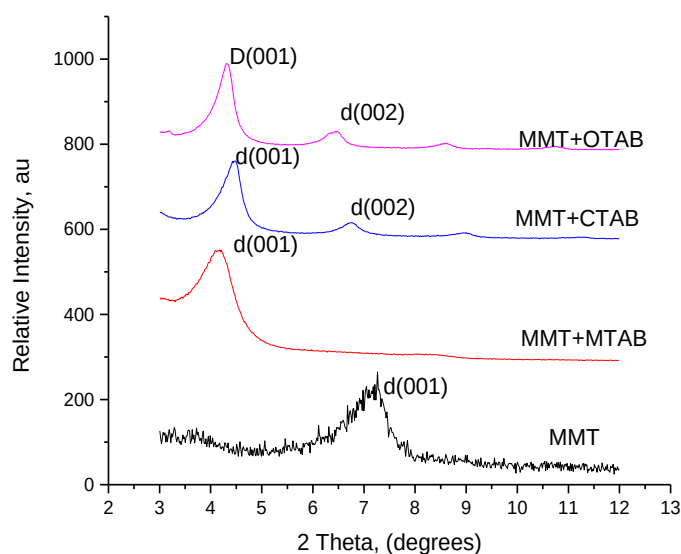


Figure 1. X-ray diffraction pattern of unmodified MMT and modified MMT with different cationic surfactants.

From these distance, the basal spacing was calculated using Bragg's law. Taking into account the thickness of the layer 0.95 nm. In the cases for CTAB and OTAB, which is more than one $d(001)$ line, the percentage of the area of each one of them in respect to total area were considered and calculated. The pristine MMT showed basal reflection at $2\theta = 7.2^\circ$ corresponding to $d(001) = 1.21$ nm, this value are within the range of expected values for typical smectite clays (1.2 to 1.6 nm) under ambient temperature and humidity [17]. Montmorillonite was identified by the $d(001)$ value coupled with $d(060) = 0.15$ nm and Greene-Kelly test. According to this test, MMT with consisted of Li-saturation and glycolation were heated up to 300°C , and basal spacing of MMT will collapsed to 0.96 nm, it is indication of MMT specific characteristics [18]. The linear alkyl substituents of the intercalated ammonium ions may formed paraffin-like formation, the expected basal spacing for monolayer intercalation and bilayer intercalation are given by models from Kopka *et al.* [19] and Lagaly and Weiss [20] as following [19, 20]:

Monolayer

$$dL = 1.18 + 0.127 nC \sin \alpha \quad (2)$$

Bilayer

$$dL = 1.66 + 0.254 nC \sin \alpha \quad (3)$$

Where dL is the basal spacing, nC is the number of carbon atoms in the alkyl chain and α is the tilt angle. The α value calculated based on equation (1.3) using the information of Table 2 as following: MMT+MTAB = 5.74° , MMT+CTAB = 4.01° and MMT+OTAB = 4.01° .

Table 2. Basal Spacing of MMT and modified MMT with various type of surfactants

Sample	Pos, 2θ	Interlayer spacing	Basal spacing (nm)	Interlayer	Structure
MMT	7.26	$d(001)$	1.21	0.26	
MMT+MTAB	4.20	$d(001)$	2.09	1.14	Bilayer/ pseudotrilayer
MMT+CTAB	4.46	$d(001)$	2.00	1.05	Bilayer/ pseudotrilayer
	6.74	$d(002)$	1.31	0.36	Monolayer
MMT+OTAB	4.35	$d(001)$	2.03	1.08	Bilayer/ pseudotrilayer
	6.30	$d(002)$	1.40	0.55	Monolayer

These angle values are not equivalent to bilayer or typical paraffin-type tilt angle; it must be noted that the interlayer conformation still assumed by intense debate. The formation of intercalated still in the form of disordered chain with a lot of gauche conformers.

3.2. FTIR spectrum of unmodified and modified MMT.

The full FTIR spectra of OTAB surfactant, MMT, and MMT modified with MTAB and CTAB were recorded in the range of $400\text{--}4000\text{ cm}^{-1}$ as illustrated in Fig. 2. The spectrum of MMT shows specific behavior of unmodified MMT with asymmetric stretching vibrations of --OH groups at 3640 cm^{-1} and the symmetric stretching and in-plane bending vibrations of free hydroxyl groups of interlayer water molecule at 3350 cm^{-1} and 1470 cm^{-1} correspond to the surface changes from hydrophilic to hydrophobic state [21, 22]. Asymmetry CH_2 stretching and symmetry CH_2 stretching peaks were absent in IR spectrum of MMT indicate that inserting of alkyl groups of cationic surfactant in OMMT interlayers. As the peaks was narrow, we can only compare the variation of their intensity instead of peak area. The intensity of these peaks usually increase by increase of surfactant content, indicating the intercalation of higher amount of surfactant in MMT.

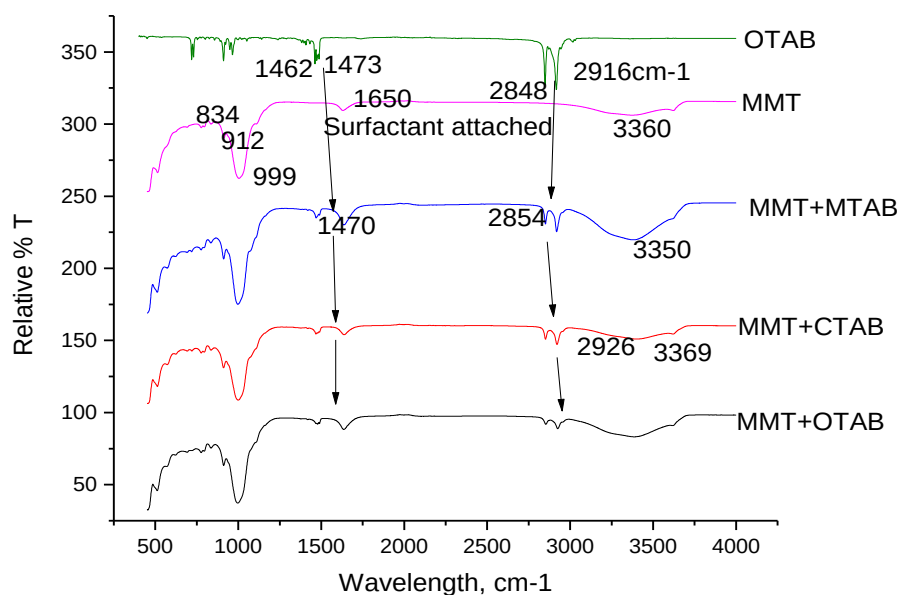


Figure 2. FTIR spectra of unmodified MMT and modified MMT with MTBA, CTAB and OTAB.

Table 3. Positions and assignments of IR vibration observed in the range 400-4000 cm^{-1}

Assignment	Frequency (cm^{-1})			
	MMT	MMT+MTAB	MMT+CTAB	MMT+OTAB
Structural OH stretching	3630	3633	3620	3620
Symmetric OH stretching	3362	3370	3368	3369
Asymmetric CH_2 stretching		2926	2921	2924
Symmetric CH_2 stretching		2854	2851	2852
H-O-H bending	1630	1634	1636	1638
CH_2 scissoring		1476	1468	1478
Si-O stretching	1003	1000	1000	1002
	913	834	830	834
CH_2 rocking	777	775	778	776

When the surfactant intercalated into interlayer space of MMT, the Si-O stretching band in its tetrahedral structure was also changed, as observed from Fig. 2, the unmodified MMT from 910-1003 cm^{-1} which is attributed to Si-O stretching, was changed on OMMT, its frequency decreased to 834 cm^{-1} , however the change depends on surfactant loading. The changes in Si-O stretching bands are attributed to intercalation of surfactant on silicate surface of MMT.

4. Conclusions

Organo-montmorillonites obtained by modifying with organic cations through conventional ion exchange method. Alkylammonium surfactant, MTAB, CTAB and OTAB intercalated the MMT clay was confirmed by X-ray diffractions, small angle X-ray scattering (SAXS). Basal spacing d_{001} of MMT increased from 1.21 nm to 2.0 nm and changes the surface property from hydrophilic to hydrophobic. Organo-montmorillonite (OMMT) clays synthesized, can be used as nanofiller in synthesis of hybrid latex through polymerization or melt blending techniques.

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