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Modification of montmorillonite by Difattyacyl thiourea using cation exchange process

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ABSTRACT

Cation exchange process was used to modify for montmorillonite (Na-MMT) by difatty acyl thiourea (DFAT). 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. The (XRD) results showed that the basal spacing of the treated clay with DFAT increased from 1.23 nm to 3.05 nm. The highest d-spacing was observed at 2.00 CEC. FTIR spectra illustrate that DFAT compound was successfully intercalated into the clay layers. Thermogravimetric analysis shows that the thermal decomposition of organoclay occurs with higher temperature than pure DFAT.

Key word: Sodium montmorillonite, difatty acyl thiourea, Cation exchange process, Surfactant.

INTRODUCTION

Na-montmorillonite is used as carriers for agricultural insecticides to increase production of grains used for food supply[1]. Additionally, clay mineralscan can be used in various paints and varnishes where they act as filler, stable against weathering, to provide and improve abrasion and scratch resistance[2]. Recently, clays have become used in the field of materials science such as solid phase polymeric nanocomposites[3]. The interest in the use of orginacaly modified clays for polymer clays nanocomposite has started at early 90's[4,5]. 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[6-9].

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.[10].

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[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[12,13]. 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 determine the surface energy of clays and polymers. The selection of the proper organic modifier plays the important role in controlling the surface energy of montmorolinite[14,15]. Sodium montmorillonite was modified via cation exchange reaction using â-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[16].

In this paper, Na-MMT was modified by using difatty acyl thiourea which was synthesized from palm oil with thiourea by reflux method. Optimum conditions of Cationic Exchange Capacity (CEC) percentages are investigated in order to optimize amount of DFAT used for montmorillite modification. Our literature search shows that there is no information was found regarding applying DFAT for clay modify.

MATERIAL AND METHODS

Materials

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

Preparation of Organoclays (OMMTs)

Designate amount of concentrated HCl and DFAT 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 DFAT synthesized according to our recent paper[17], were used at 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 organoclay suspension was filtered and washed with distilled water until no chloride was detected with 1 M silver nitrate solution and 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 a 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 AND DISCUSSION

The presence of DFAT chain in the galleries clay transformation the originally hydrophilic to organophilic silicate and thus significantly increases the basal spacing of the clay layers[18]. The obtained DFAT -MMT was studied by using X-ray diffraction. Na-MMT shows a d001 diffraction peak at 2q = 7.35° which assigns to the interlayer distance of the natural montmorillonite with a basal spacing of 1.23 nm and the basal spacing of modified clay by DFAT increases to 3.05as shown in Table 1.

Table 2 shows the percentage of carbon and nitrogen for modified clay from the elemental 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 DFAT was successful. During the clay modification, sodium ion is replaced by DFAT ions via cation exchange reaction

The FTIR spectra of the Na-MMT is shown in Fig 1a, The peak at 1115 cm^{-1} correspond to Si-O stretching and interlayer water deformation vibrations at 1638 cm^{-1}. The band at 3622 cm^{-1} results from the O-H stretching vibration[19,20].

FTIR spectra of DFAT are shown in Fig. 1b. The peaks observed at wave number of 3416

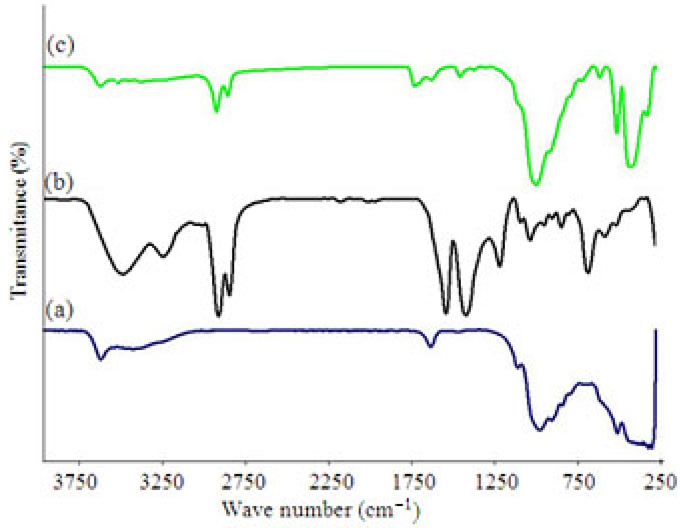

Fig. 1: FTIR spectra of (a) Na-MMT, (b) DFAT and (c) DFAT -MMT

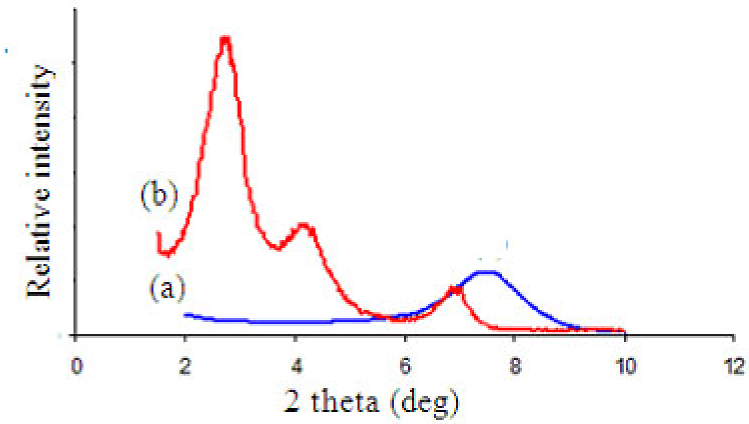

Fig. 2: XRD patterns of (a) Na-MMT and (b) DFAT -MMT

and 3212 cm^{-1} which corresponds to N-H and O-H stretching, at 2856 and 2919 cm^{-1} which corresponds to C-H stretch of alkyl chain, at 1640 cm^{-1} which correspond to C = O for secondary amide and at 1045 and 1112 cm^{-1} which corresponds to C-N stretch respectively.

FTIR spectra of DFAT-MMT are shown in Fig. 1c. The peaks observed at wave number of 3674 cm^{-1} which corresponds to O-H stretching, at 3232 cm^{-1} which correspond to N-H amide, at 2921 cm^{-1} which correspond to C-H asymmetric stretching, at 2856 cm^{-1} which correspond to C-H symmetric stretching and at 1662 cm^{-1} interlayer water deformation vibrations.

Na-MMT was surface treated with DFAT 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

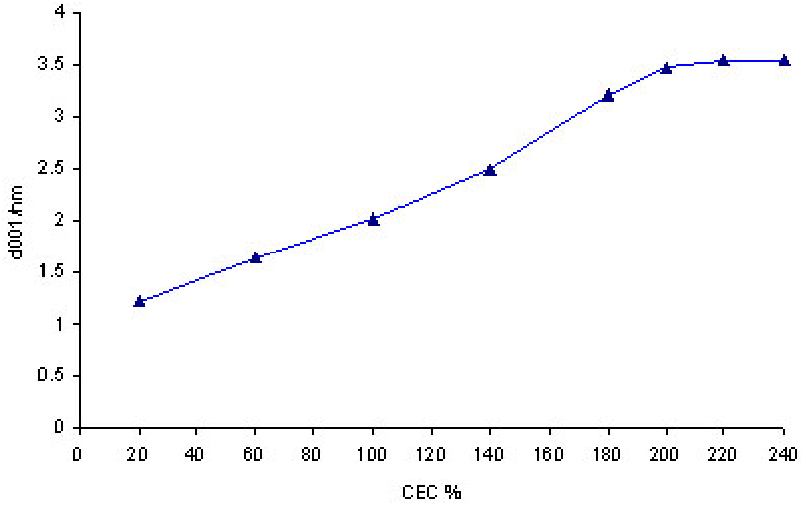

Fig. 3: The basal distance (d001) of pristine (MMT) and Organomodified Montmorillonites (OMMT)

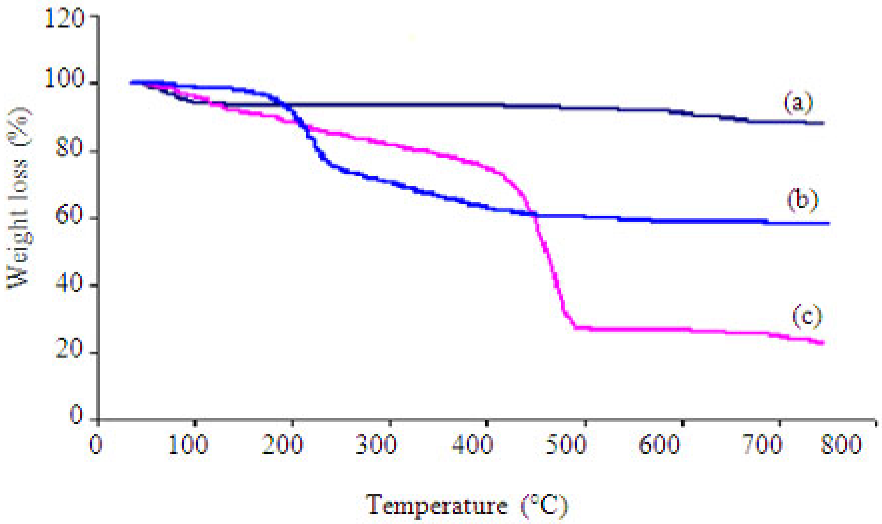

Fig. 4: TGA thermograms of (a) Na-MMT, (b) DFAT -MMT and (c) DFAT

exchange reaction, the basal spacing increases from 1.23 nm (Fig. 2a) to 3.05 nm (Fig. 2b) indicating that the DFAT was successfully intercalated into the Na-MMT galleries.

The Cationic Exchange Capacity (CEC) was investigated to determine the optimum amount of DFAT as modifier agent to get maximum d-spacing with lower angle-value. Figure 3 shows that the better d spacing at 2.0 CEC.

Table 1: Diffraction angle and basal spacing of montmorillonite and modified montmorillonite by DFAT

Sample	2q (°)	d (001) spacing (nm)
Montmorillonite	7.35	1.23
DFAT modified	2.96	3.05

Fig. 4a shows the thermal decomposition expressed in terms of weight loss as a function of temperature of both pristine clay (Na-MMT) and organoclays. The Na-MMT differential thermal curve is divided 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[21]. However, Xie *et al*.[22] 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[22] 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[22]. Hence, free water (water between particles and sorbed on the external surfaces of crystals) are released at the temperature of below 100°C[21] as shown in Fig. 5a. The total weight loss of Na-MMT at this region is 11.51%. 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[22]. The total weight loss at this region is 4.05%. According to Arroyo *et al*.[20] 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.

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

Clay	C(%)	N(%)	m mol of alkylammonium groups/1 g montmorillonite	
			Based on C calculation	Based on N calculation
DFAT-MMT	29.5	2.10	1.53	1.50
Na-MMT	0.46	0.15		

Pure DFAT started to decompose at 114.19 °C and ended at 471.53 °C as shown in Fig. 4c. The major difference between the thermal decomposition of Na-MMT and the thermal decomposition of the organically modified clay is in the range of 58.61-327.82 °C. The thermogram of DFAT -MMT shows that the thermal decomposition of DFAT MMT occurs in four steps as shown in Fig. 4b. The first step is due to the releasing of free water between particles and water sorbed on the external surfaces of crystals[22]. The decomposition of organic constituent in DFAT - MMT occurs in second step where it started to decompose from 226.15-327.97°C. The weight loss at this step was 19%.

The last two steps, which occurs at the range 400-810°C was due to the dehydration of structural water in the clay[22].

CONCLUSION

Difatty acyl thiourea was used to modify Na-MMT by cation exchange process. DFAT was successfully incorporated in the montmorollite clay. Basal spacing was increased to 3.05 nm by the incorporation of DFAT. An optimum angle value was obtained as 2.0 CEC. FTIR spectra show that the DFAT was successfully intercalation in the MMT. This study is attempted to create susceptible clay to polymers.

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