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Modification of Montmorillonite by New Surfactants

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Abstract: The sodium Montmorillonite is not susceptible to polymer due to its organophobic character and has low basal spacing. This study reports on the effect of three new organic cations including Triethyl Amine (TEA), Tripropyl Amine (TPA) and Trioctyl Amine (TOA) on the basal spacing of the clay as indictors to the sociability of the clay to the incorporation of polymers. The Fourier Transform Infrared spectroscopy (FTIR) was used to evaluate the incorporation of the three organic cations in the clay. The X-ray diffraction technique was utilized to indicate the basal spacing of the treated clay as a measure of the susceptibility of new organoclays. The FTIR, XRD and CHNS elemental analysis results shown that the three new organic cations acrylonitrile/montmorillonite were successfully incorporated in the Montmorollite clay. X-ray diffraction indicates that the basal spacings in acrylonitrile/montmorillonite of the treated clay with TEA, TPA and TOA individually increased by 14.2, 15.1 and 19.5Å, respectively. FTIR spectra illustrate that amine compounds were successfully intercalated into the clay layers.

Key words: Sodium montmorillonite, triethyl amine, tripropil amine, triocthyl amine, modification, surfactants, organic cations

INTRODUCTION

Sodium Montmorillonite are widely used in various science fields due to their large cation exchange capacity, high specific surface area, good swelling capacity and high platelet aspect ratio and ease with which their surface can be modified (He *et al*., 2007a, b). Presence of inorganic cations such as Na+ and Ca+^{2} on the basal planar surface of montmorillite layers makes it hydrophilic in nature and hence, shows the clay ineffective for absorption of aliphatic and relatively hydrophobic compounds (Kim *et al*., 2003; Xie *et al*., 2001). However, cation-exchange reactions have been traditionally exploited as an effective method to replace these inorganic ions with organic cationic surfactant molecules, which intercalate into the clay gallery, resulting in expansion of the interlayer spacing and leading to an increase in the basal spacing. These organic cations render the surface of the clay mineral hydrophobic, leading to the increase of the clay wettability and providing favourable interactions with organic molecules. Both organic-modified and unmodified clays have been used for different industrial applications such as rheological additives, thickeners in coating products, glues, plastisols, drilling fluids and cosmetics (Jaynes and Boyd, 1991). Recently, clays were used in the field of materials science such as solid phase polymeric nanocomposites. In the 1990's, the use of organically modified clays in the polymer-clay nanocomposites has attracted researchers into this area of materials science and technology (Kojima *et al*., 1993; Zhang and Wilkie, 2003). The organic modification of clay minerals leads to a decrease in surface energy making clays compatible with polymers. The surface energy of clay minerals and polymer can be determined from contact angle measurements (Maiti and Bhowmick, 2005). Stretz *et al*. (2005) reported that melt processed nylon 6-clay nanocomposites was prepared using organoclay, which contains methyl tallow bis 2-hydroxyethyl quaternary ammonium ions. Based on X-ray diffraction analysis, various arrangements of alkyl chains in organoclays had proposed by Lagaly (1986) Novel organo-montmorillonites have been synthesized and characterized using different ammonium compounds (Rajkiran and Kartic, 2008; Arroyo *et al*., 2003). Series of anion-cation surfactants modified organoclays were prepared by incorporating of cationic surfactant hexadecyltrimethyl ammonium bromide and anionic surfactant, sodiumdodecyl sulfonate to montmorillonite (Chen *et al*., 2008; Magaraphan *et al*., 2001). In this study, three different aliphatic ammonium compounds, namely Triethyl Amine (TEA), Tripropyl Amine (TPA) and Trioctyl Amine

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(TOA) were used to modify the compatibility of montmorillonite clay with polymers. These organo-montmorillonites can be used in various research and industrial applications.

MATERIALS AND METHODS

Materials: Sodium montmorillonite (Kunipia F) used in this study was obtained from Kunimine Ind. Co. Japan. The triethylamine, tripropylamine and trioctylamine, (Sigma-Aldrich), Germany. Hydrochloric acid from J.T. Baker, USA.

Preparation of organoclays (OMMTs): The OMMTs were prepared by dissolving 2.2 mL of concentrated HCl and amine compound in 800 mL of 80°C distilled water and Na^+-MMT was dispersed in 600 mL hot water. The first solution was poured in MMT-water and vigorously stirred for 1 h. The white 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. Table 1 shows, the structures of the three organoclays.

Ionization of TEA:

$$N\,(C_2H_5)_3 + HCl \rightarrow N\,(C_2H_5)_3.HCl \rightarrow (C_2H_5)_3NH^+Cl^-$$

Cation exchange:

$$MMT\text{-}Na^+ + (C_2H_5)_3\,NH^+ \rightarrow MMT\text{ - }{}^+NH\,(C_2H_5)_3 + Na^+$$

where, $(C_2H_5)_3N^+$ and MMT-$^+$NH $(C_2H_5)_3$ are TEA and TEA-MMT, respectively.

Ionization of TPA:

$$N\,(C_3H_7)_3 + HCl \rightarrow N(C_3H_7)_3\,HCl \rightarrow (C_3H_7)_3NH^+Cl^-$$

Cation exchange:

$$MMT\text{-}Na^+ + (C_3H_7)_3NH^+ \rightarrow MMT\text{ - }{}^+NH\,(C_3H_7)_3 + Na^+$$

where, $(C_3H_7)_3N^+$ and MMT-$^+$NH $(C_3H_7)_3$ are TPA and TPA-MMT, respectively.

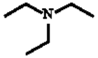
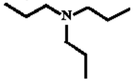
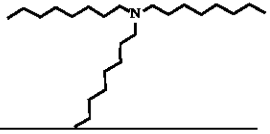
Ionization of TOA

$$N\,(C_8H_{17})_3 + HCl \rightarrow N\,(C_8H_{17})_3.\,Hcl \rightarrow (C_8H_{17})_3NH^+Cl^-$$

Cation exchange

$$MMT\text{-}Na^+ + (C_8H_{17})_3NH^+ \rightarrow MMT\text{-}{}^+NH\,(C_8H_{17})_3 + Na^+$$

Table 1: The structures of the three organoclays

Name of organoclay	The structure
Triethylamine (TEA)	
Tripropylamine (TPA)	
Trioctylamine (TOA)	

where, $(C_8H_{17})_3N^+$ and MMT-$^+$NH $(C_8H_{17})_3$ are TOA and TOA-MMT, respectively.

Characterizations: Organoclay were characterized using three different techniques including Fourier Transform Infrared spectroscopy (FTIR), (CHNS analyzer) and X-Ray Diffraction (XRD).

Fourier transform infrared spectroscopy: 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 analysis: CHNS analyzer (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): X-Ray Diffraction (XRD) study was carried out using Shimadzu XRD 6000 diffractometer with Cu-K θ-radiation (λ = 0.15406 nm). The diffractogram was scanned in the ranges from 2-10°C at a scan rate of 1°C min^{-1}.

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy: Fourier Transform Infrared (FTIR) spectroscopy is a useful technique to verify the presence of TOA+, TPA+ and TEA+ in the clay, respectively. Figure 1a-c show, the FTIR spectra of Na-MMT, pure TOA and TOA-MMT, Fig. 2a-c show, the FTIR spectra of Na-MMT pure TPA and TPA-MMT, pure TPA and TPA-MMT and Fig. 3a-c show, the FTIR spectra of Na-MMT, pure TEA and TEA-MMT, respectively. The infrared spectrum of the Na-MMT shows two peaks, which correspond to Si-O stretching at 1040 cm^{-1} and interlayer water deformation vibrations at 1642 cm^{-1} (Guo *et al.*, 2006). The band at

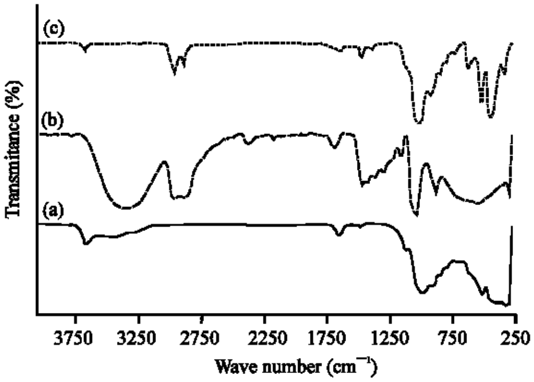


Fig. 1: FTIR Spectra of (a) Na-MMT; (b) TOA and (c) TOA-MMT

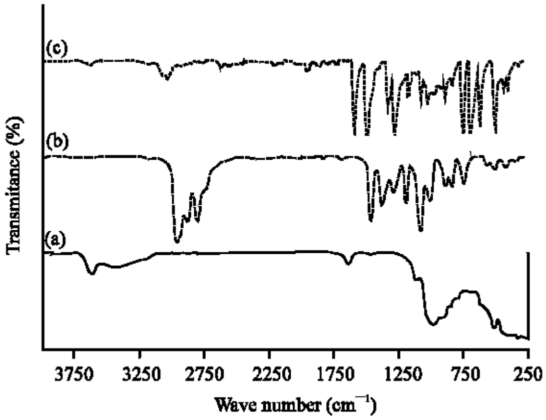


Fig. 2: FTIR spectra of (a) Na-MMT; (b) TPA and (c) TPA-MMT

3630 cm^{-1} results from the O-H stretching vibration. The peaks observed in the TOA-MMT (2926 and 2856 cm^{-1}), TPA-MMT (2923-2851 cm^{-1}) and TEA-MMT (2928 and 2854 cm^{-1}) infrared spectra correspond to the presence of the C-H asymmetric and symmetric stretching vibration, respectively.

In the spectra of TOA-MMT, TPA-MMT and TEA-MMT, The absorption bands at 3628, 3624, 3619 cm^{-1} indicate the presence of the free O-H stretching and at 1077, 1074 and 1071 cm^{-1} corresponded to C-N stretching, respectively (Shalaby *et al*., 2000; Ramachandranl *et al*., 2007). This suggests that TOA, TPA and TEA are sorbed into the silicate layers of Na-MMT.

X-Ray diffraction analysis: The alkyl ammonium cation exchange enables the conversion of the hydrophilic interior clay surface into the hydrophobic surface and consequently increase the layer distance as well (Liu and Wu, 2001). In this study, Na-MMT was surface treated with TOA, TPA and TEA 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. The presence of these aliphatic chains in the galleries makes the originally hydrophilic silicate to organophilic and thus, increases the layer-to-layer spacing of Na-MMT (Huang *et al*., 2001). The obtained TOA-MMT, TPA-MMT and TEA-MMT were studied by using X-ray diffraction measurements in the 2θ ranges from 2°-10°. Na-MMT shows a d001 diffraction peak at 2θ = 7.35° which, assigns to the interlayer distance of the natural montmorillonite with a basal spacing of 12.2Å as known in Fig. 4 (Agag and Takeichi, 2001). After the ion exchange reaction, the basal spacing (d001value) increases from 12.2-14.2 Å (Fig. 4a), 15.1 and 19.5Å (Fig. 4b-d) for TEP-MMT, TPA-MMT and TOA-MMT,

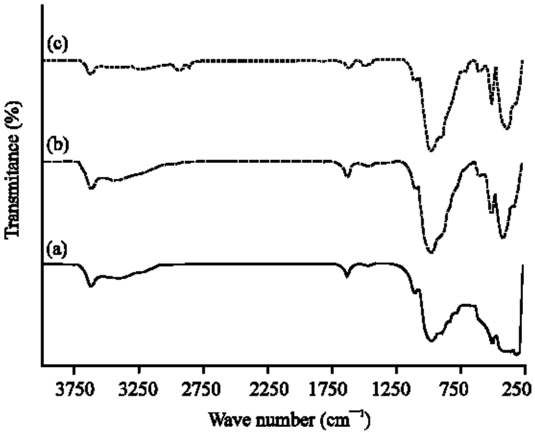


Fig. 3: FTIR spectra of (a) Na-MMT; (b) TEA and (c) TEA-MMT

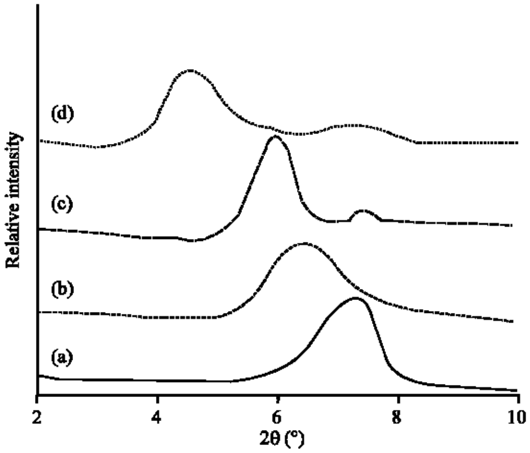


Fig. 4: The XRD patterns of (a) Na-MMT; (b) TEA-MMT, (c) TPA-MMT and (d) TOA-MMT

Table 2: Diffraction angle and basal spacing of montmorillonite and modified montmorillonite with different organic cations

Samples	Exchanged cation	2θ(°)	d(001) spacing (A)
Montmorillonite	Na^+	7.35	12.2
TEA modified	$(C_2H_5)_3NH^+$	6.31	14.2
TPA modified	$(C_3H_7)_3NH^+$	5.93	15.1
TOP modified	$(C_8H_{17})_3NH^+$	4.59	19.5

Table 3: C, N and alkylammonium groups contents of the TEA, TPA and TOA modified Montmorillonite

Alkylammonium/ groups modified/ montmorillonite	C (%)	N (%)	Mmol of alkylammonium/ groups/1 g montmorillonite	
			Calculation based on C	Calculation based on N
TEA	20.36	3.96	2.827	2.823
TPA	21.57	2.799	1.997	1.999
TOA	23.34	1.133	0.810	0.809

respectively, suggesting that the TEP^+, TPA^+ and TOA^+ have been intercalated into the Na-MMT galleries. These results were summarized in Table 2. Thus, X-ray diffraction results indicate that TEA, TPA and TOA are successfully intercalated into the silicate layer.

CHNS analysis: Table 3 shows, the results of C and N analysis of the TEA, TPA and TOA modified Montmorillonite. The high contents of C and N in all samples indicate that TEA, TPA and TOA cations were successfully exchanged into the clay. It also shows that 2.827 mol of TEA, 1.997 mol of TPA and 0.810 mol of TOA are sorbet by 1 g of the clay based on C calculations and 2.823, 1.999 and 0.809 mol TEA, TPA and TOA, respectively, based on N calculations. Satisfactory cation exchange of Na+ ion in clay with amines was reported by Takeichi *et al.* (2002).

CONCLUSION

Three new organic cations including TEA, TPA and TOA were used to modify Montmorollonite clay in an attempt to create susceptible clay to polymers. The organoclays were characterized using FTIR, XRD and CHNS.

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

- The three organic cations can be successfully incorporated in the montmorollite clay
- The basal spacing of the montmorrlite clay increases as a result of incorporating TEA, TPA and TOA
- The incorporation of TEA, TPA and TOA increases the basal spacing by 14.2, 15.1 and 19.5, respectively
- The new organoclay can be susceptible to polymers

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