

# Analysis results and modification of Na<sup>+</sup>-montmorillonite with quarterner ammonium salt

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**Abstract:** In this study, preliminary data are reported on the modification of sodium montmorillonite modified with tetra butyl ammonium succinimide as quarterner ammonium salt. The modified material was characterized by FTIR, SEM and WXRD analysis. The analysis results show an overall increase in interlamellar spacing as a result of sodium cation exchange with the cations of long chain quaternary ammonium salt. Synthesized organoclay can be used in food and food packaging field and in column chromatography as fillers.

**Keywords:** Na<sup>+</sup>-Montmorillonite, Organoclays, Modification, Quaternary ammonium salt.



## 1. Introduction

Clays are used in various scientific and industrial applications because they are present in nature, and they can be modified both chemically and physically. The difference between the natural and synthetic materials lies in their surface areas, which are proportional to the degree of delamination or exfoliation of the clay layers. Generally, smectite clay is modified organically via organo-cation exchange [1].

The modified clay minerals, organo- montmorillonites, represent a family of materials which have a lot of applications in a range of key areas, such as rheological control agents [2, 3], reinforcing fillers for plastics and electric materials, particularly adsorbents for organic pollutants [4, 5, 6].

The synthesis of organoclays with quaternary ammonium compounds has been limited. It is probable that increased adsorption may occur with increased number of alkyl chains [7].

## 2. Materials and methods

### 2.1. Materials

Montmorillonite, Mt-Na<sup>+</sup>, a hydrated aluminum silicate with sodium as the predominant exchangeable cation (trade name: Cloisite-Na<sup>+</sup>, CAS# 1318 -93 -0, Southern Clay Products Inc.) is a powder with typical particle size less than 2 µm. Specific gravity of Na<sup>+</sup>-Mt is between 2. 8 and 2. 9, pH value of a 10 % suspension is 10 and its cation exchange capacity (CEC) as reported

by the supplier is 92.6 meq /100 g clay. The physical and chemical properties of Na<sup>+</sup>-Mt are included in Table 1. Modifier, tetrabutyl ammonium succinimide (QAS1) was purchased.

**Table 1**

The physical and chemical properties of Na<sup>+</sup>-Mt.

Molecule formula	(Na, Ca) <sub>0.33</sub> (Al, Mg) <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> ·6H <sub>2</sub> O
The density (g / cm <sup>3</sup> )	2.86
pH (%3 çözelti)	8
The surface area (m <sup>2</sup> /g)	750
CEC (meg / 100 g)	92
The percent of composition (%)	1.40 Na, 2.44 Ca, 9.99 Al, 8.88 Mg, 20.7 Si, 35.53 O, 0.37 H

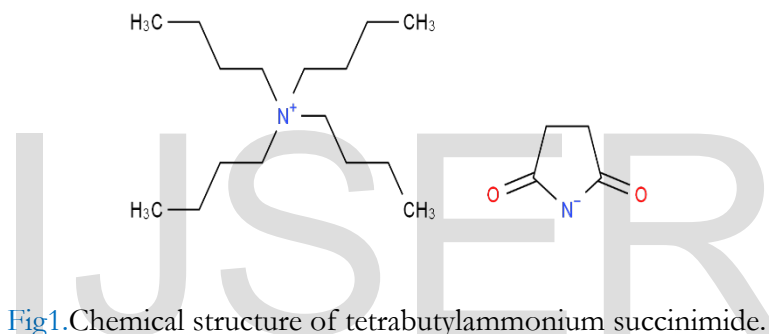


Fig1. Chemical structure of tetrabutylammonium succinimide.

## 2.2. Preparation of the organoclay

The organo montmorillonite (Mt-QAS<sup>+</sup>) was prepared by a cation-exchange method, which is a displacement of the sodium cations of montmorillonite-Na<sup>+</sup> with the QAS<sup>+</sup>. Typically, 1.0 g of Mt-Na<sup>+</sup> was mechanically stirred with 100 mL of deionized water– ethanol v/v(1:1) at 25°C for 1 h to swell the layered silicates. The aqueous solution of the QAS-I was prepared separately by dissolving it (1.5 times of the CEC of clay) in 50 mL deionized water–ethanol at 25°C. Then the dispersed clay was added to this solution and the mixture was stirred at 25°C for 24 h under mechanical stirring. The precipitates of modified filtered using disc filter funnel. Mt-QAS<sup>+</sup> was washed several times with about 100 mL of deionized water–ethanol until no iodide ions was detected by AgNO<sub>3</sub> solution. The final product obtained by filtration was dried at 70°C for 8 h. The dried cake was ground and screened with a 100-mesh sieve to obtain the novel organoclay [8].

**Table 2**

Experimental description and abbreviations of Mts modified with ionic liquids.

Clay	Modifiers	QAS <sup>+</sup>	Exchange temp./time/CEC amount used (C/h/stoichiometry)
Mt	-	-	-
Mt-2	[C <sub>20</sub> H <sub>40</sub> N <sub>2</sub> O <sub>2</sub> ]	QAS-1	25 / 24/ 1 gr
Mt-6	[C <sub>20</sub> H <sub>40</sub> N <sub>2</sub> O <sub>2</sub> ]	QAS-1	25 / 24/ 2 gr

### 2.3. Methods

Infrared spectra were recorded using KBr pellets in the range 4000–400 cm<sup>-1</sup> on an ATI UNICAM system 2000 Fourier transform spectrometer. The samples were characterized by XRD for crystal structure, average particle size, and concentration of existing impurities. A Rigaku Rad B-Dmax II powder X-ray diffractometer was used to obtain diffraction patterns of these samples. Morphology of the organoclays was examined by a JEOL JSM 5600 LV scanning electron microscopy (SEM).

## 3. Results And Discussion

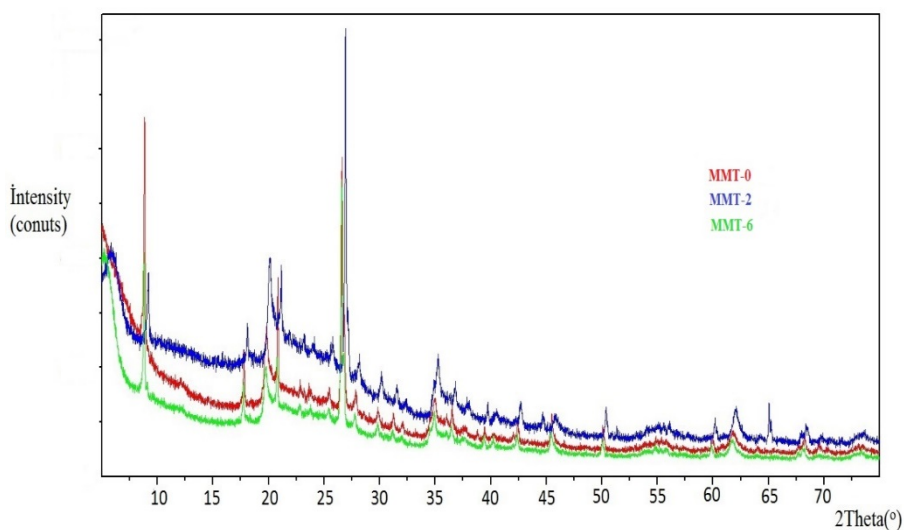
### 3.1. Characterization of PU nanocomposite films

XRD is powerful technique used to characterize the extent of silicate dispersion. One-dimensional X-ray diffraction patterns of Mt and O-Mt are shown in Figure. 2. The d<sub>0 0 1</sub> spacing was calculated and is listed in Table 3 from peak positions using Bragg's law  $d = \lambda / 2 \sin \theta$ . It is clear that the d-spacing observed for Na<sup>+</sup>-Mt (7.27 Å) increased to values ranging from 9.681 Å to 10.06 Å because the small inorganic Na<sup>+</sup> cation was exchanged by quaternary ammonium salt.[9]. The peaks are shifted toward lower 2θ by this modification, showing the larger interlayer spacing in comparing organoclays made with Mt and O-Mt [10].

**Table 3**

X-ray diffraction data for organoclays

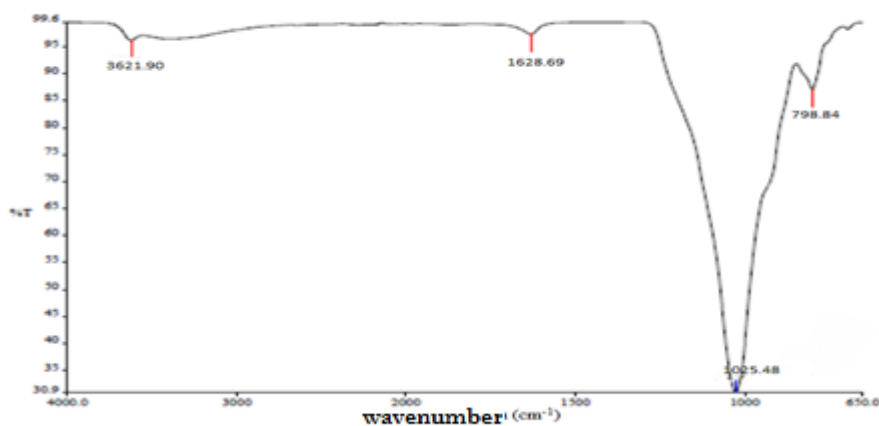
Sample	2θ	d-spacing
MMt-0	8.814	7.227
MMt-2	8.130	9.681
MMt-6	7.7810.06	



**Fig2.** XRD patterns of clay (Mt) and organoclays.

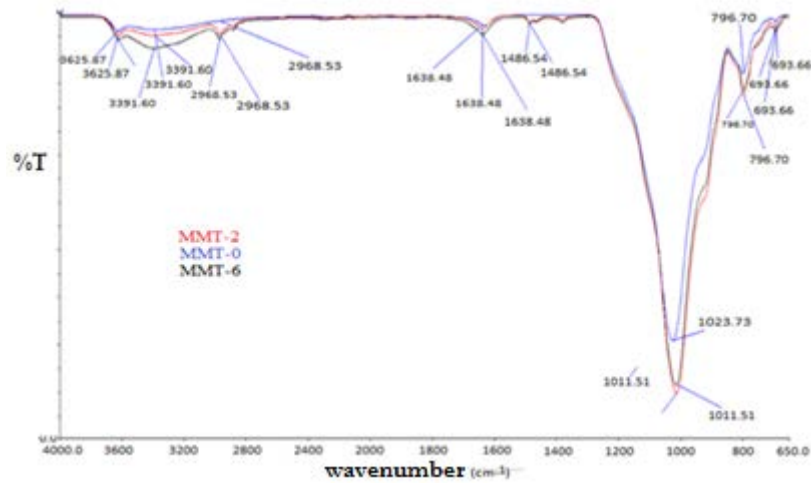
This confirmed that the organo- montmorillonite is intercalated between the layers. Increase in d-spacing vs. the washed unmodified Mt follows the order MMt-6 > MMt-2. Because the amount of clay used in MMt-6 is more than MMt-2, so it leads to an increase in surface area[11].

Figs.3,4 compare FT-IR spectra of unmodified MMt-0, clays modified MMt-2, MMt-6. MMt-0 is shown in Figure. 3. In the spectrum of Mt shown in Fig.3, the silicon-oxygen and aluminum-oxygen bonds are respectively observed at  $1044\text{ cm}^{-1}$  and  $620\text{ cm}^{-1}$ , and the magnesium-oxygen is assigned to a band between  $470$  and  $530\text{ cm}^{-1}$ . The strong peak at  $1650\text{ cm}^{-1}$  and the broad band at  $3440\text{ cm}^{-1}$  have been assigned to the bending and stretching modes of absorbed water. Sharp peaks around  $3600\text{ cm}^{-1}$  are assigned to the hydroxyl group.



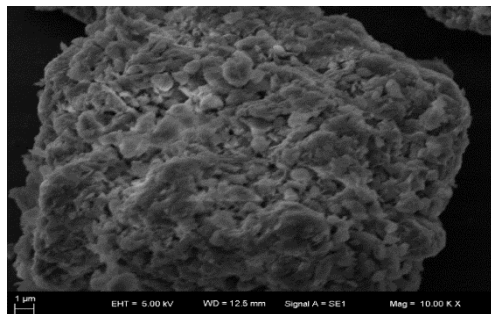
**Fig 3.** FTIR spectra of MMt-0.

A longer hydrocarbon chain in QASs produces significantly stronger peaks in the ranges of 2955–3173  $\text{cm}^{-1}$  and 1472–1645  $\text{cm}^{-1}$ . These peaks occur at 1472  $\text{cm}^{-1}$ , 1645  $\text{cm}^{-1}$ , and in the range 2955–3173  $\text{cm}^{-1}$ , indicating the presence of QASs in the modified MMT-2 and MMT-6.

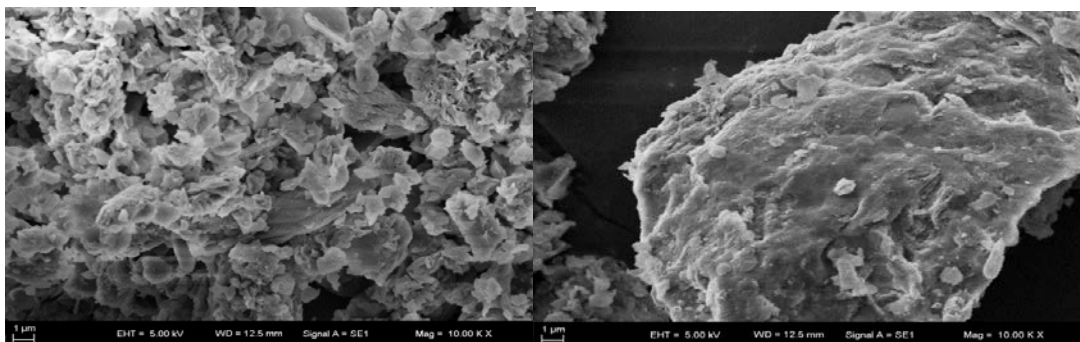


**Fig 4.** FTIR spectra of MMT-0, MMT-2 and MMT-6.

The surfaces of Mt and Mt modified samples was observed by using a Jeol JSM-5610 scanning electron microscopy after gold coating to determine the dispersibility of organoclay. SEM examination of the surfaces samples occurred fractures. Fig.5 shows a micrograph of the fracture surface at 10.00 magnifications.



(a)



(b)

(c)

**Fig 5.** SEM images of samples, a) MMT-0, b) MMT-2 and c) MMT-6

The stress and strain at the breaks at surface of clays increase depending on the state of clay dispersion, concentration and modifiers. The energy values showed a correlation with the stress and strain at break

## Conclusion

In this study, organo- montmorillonites were prepared by using montmorillonite and quarterner ammonium salt [tetrabutyl ammonium succinimide (QAS-1), as an example of a surfactant with a long alkyl chain. The highest extent of intercalation was obtained with MMT-6 according to XRD results. Synthesized organoclay can be used in food packaging field and in column chromatography as fillers.

## References

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