Investigation Analysis Results and Modification of Na^+-Montmorillonite With Quaternary Ammonium Salt and Ionic Liquid

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Abstract

Organically modified montmorillonites have attracted a great deal of interest because of their wide applications in industry and environmental protection. We have synthesized organomontmorillonites using montmorillonites with different cation exchange capacities (CEC) and surfactants with different alkyl chain number and chain length. Commercially available unmodified clay was treated under different conditions with aqueous solutions of quaternary ammonium salt; N-N dimethyl-dodecyl amine (QASI) and ionic liquid; 1-hexhyl-3-methyl imidazolium tetrafloroborat (IL1). The modified materials were characterized qualitatively 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 the long chain quaternary ammonium salt and ionic liquid. Synthesized organoclays can be used in food and chemical packaging field.

Keywords: *Food packaging, organoclays, modification, quaternary ammonium salt, ionic liquid.*

1. Introductıon

Organo-montmorillonites are montmorillonites that have been modified with organic surfactants. These hydrophobic materials have attracted much interest because they have found wide applications as adsorbents of organic pollutants, as components in the synthesis of clay-based polymer nanocomposites, and as precursors in the preparation of mesoporous materials [1]

Many practical applications are based on the properties of dispersed bentonites [2]. Organo clay minerals (also called bentones) were initially used for their rheolohical properties, but their most recent application is as filler for a polymer, in order to modify its mechanical, thermal or barrier properties [3, 4].

In the modification of montmorillonites based on ion exchange, the interlayer accessible compensating cations can be exchanged with a wide variety of hydrated inorganic cations or organic cations including those of amines or quaternary ammonium salts [5], and also oxonium, sulfonium, phosphonium and more complex cationic species such as methylene blue and cationic dyestuffs. Hydrophilicity of the modified mineral decreases and basal spacing of the alkyl ammonium derivatives increases with increasing of the alkyl chain's length of the ammonium salts [6]. They have

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surfaceactive properties, possess anti-microbial activity and are known to be bioactive [7, 8]. Quaternary ammonium salts (QASs) are an economically advantageous class of industrial compounds, and cationic surfactants. The quaternary alkylammonium salts (QACs) are cationic surfactants [9].

There are a large number of imidazolium-based ILs [6] and quaternary ammonium salts. The purpose of this study is to compare the results of organoclays's analysis according to the difference between ionic liquid and quaternary ammonium salt.

2.Experimental

2.1.Materials

Chemicals of high purity were obtained from various commercial sources, which consisted of N-N dimethyl-dodecyl amine (Aldrich), 1-hexhyl-3-methyl imidazolium tetrafloroborat (Aldrich) and silver nitrate (Merck), hydrochloric acid (Merck).

Montmorillonite, Na^+-Mt, a hydrated aluminum silicate with sodium as the predominant exchangeable cation (trade name: Cloisite-Na^+, CAS# 1318 -93 -0, Southern Clay Products Inc.) is a powder with typical particle size less than 2 µm. Specific gravity of Na^+-Mt is between 2. 8 and 2.9, pH value of a 10% dispersion 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^+-Mt are included in Table 1.

2.2. Method

2.2.1. Preparation of the organoclay

The organo montmorillonite (Mt-QAS^+) was prepared by a cation-exchange method, which is a displacement of the sodium cations of montmorillonite-Na^+ with the QAS^+ [10]. Typically, 1.0 g of Mt-Na^+ 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 QASI 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 mechanically stirred. The precipitates of modified filtered using disc fitler funnel. Mt-QAS^+ was washed several times with about 100 mL of deionized water–ethanol until no iodide ions was detected by $AgNO_3$ 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.

Cationic exchange of Na^+-Mt (Mt) was carried out with 1-hexyl-3-methyl imidazolium tetrafluoroborate (IL_1) and aqueous solutions stirring at 60 °C for 2 h and at 1X1 concentrations of the clay based on CEC. After filtration, all modified clays were repeatedly (more than 15 times) washed with distilled water. For clays modified with IL_1 washing was continued until no residual halogen anion was detected

Table 1. *The Physical And Chemical Properties of Na^+-Mt.*

Molecule formula	$(Na, Ca)_{0.33}(Al, Mg)_2 Si_4O_{10}(OH)_2 6H_2O$
The density (g / cm^3)	2.86
pH (%3 çözelti)	8
The surface area (m^2/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

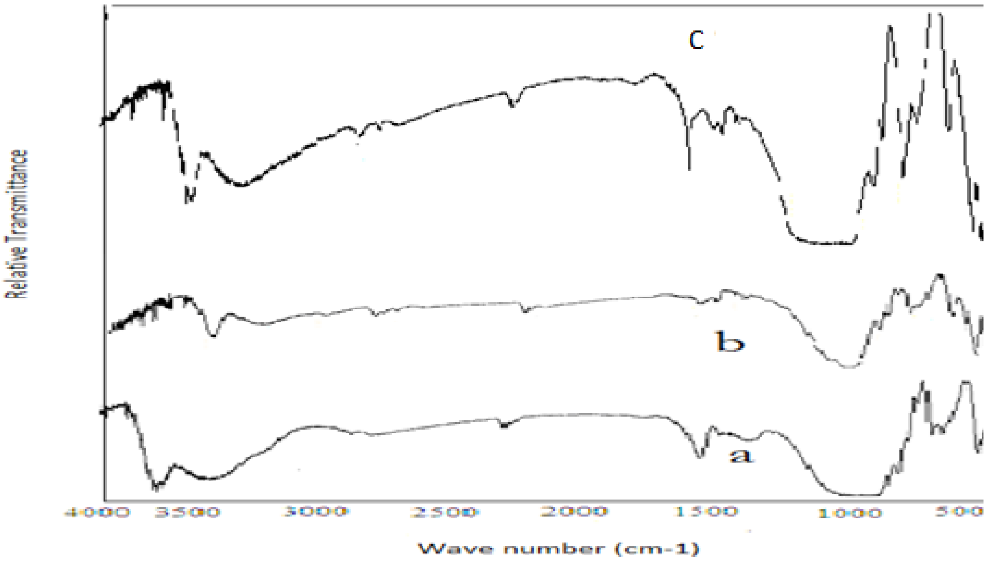

Fig. 1. *FTIR spectra of (a) Mt, (b) Mt1 and (c) Mt2.*

by adding 0.1 M silver nitrate solution in the filtrate. It is to be noted that filtration time for all treated clays was significantly shorter than that for the unmodified one. After 24 h at room temperature, drying continued at 80 ^{o}C for 12 h under vacuum [11].

2.3.Measurements

Infrared spectra were recorded as KBr pellets in the range 4000 - 400 cm^{-1} on an ATI UNICAM systems 2000 Fourier transform spectrometer. The samples were characterized by X-ray diffraction (XRD) for the crystal structure, average particle size and the concentration of impurity compounds present. Rigaku Rad B-Dmax II powder X-ray diffractometer was used for X-ray diffraction patterns of these samples. The 2θ values were taken from 20° to 110° with a step size of 0.04° using CuKα radiation (λ value of 2. 2897 Å). The dried samples were dusted onto plates with low background. A small quantity of 30(±2) mg spread over 5 cm^2 area used to minimize error in peak location and also the broadening of peaks is reduced due to thickness of the sample. This data illustrate the crystal structure of the particles and also provides the inter-planar space, *d*.

Morphology of the organoclays was examined by a JEOL JSM 5600 LV scanning electron microscopy (SEM).

3.Results And Discussion

FT-IR spectroscopy

Figs.1. compares FT-IR spectra of unmodified Mt, clays modified Mt-1 and Mt-2. The clay 's CEC concentration with IL1 (Mt-1) and QAS1 (Mt-2). All spectra of the modified clays contain characteristic peaks of the respective modifier, an indication of their presence. In the spectrum of Mt shown in Fig.1, the silicon-oxygen and aluminum-oxygen bonds are respectively observed at 1044 cm^{-1} and 620 cm^{-1},and the magne- sium-oxygen is assigned to a band between 470 and 530 cm^{-1}. The strong peak at 1650 cm^{-1} and the broad band at 3440 cm^{-1} have been assigned to the bending and stretching modes of absorbed water. Sharp peaks around 3600 cm^{-1} are assigned to the hydroxyl group.

The spectrum of Mt-1 in Fig. 1(b) shows peaks for the imidazolium functional group in the range between 1000 and 1650 cm^{-1}; for example, the peaks in the range of 1320–1600 cm^{-1} are due to carbon–carbon and carbon–nitrogen vibrations; the conjugated strong peaks around 1570 and 1630 cm^{-1} are due to carbon–nitrogen–carbon or carbon–carbon bonds [12].

The FTIR spectrum for Mt modified with quaternary ammonium salts are shown in Fig. 1(c). The spectra of Mt-A shows, peaks at 2800 -2900 cm^{-1} was caused by the stretching of ammonium dodecyl sulphate (aliphatic C–H stretching vibration) [13].

XRD analyses

Fig. 2 shows typical XRD for the clay and organoclays. The *d*001 reflection has sharp intense peak at 2Θ= 9.079, 6.580, 6.690 for Mt, Mt -1 and Mt-2, respectively. The *d*001 spacing was calculated and listed in Table 2 from peak positions using Bragg's law $d = \lambda/2 \sin \theta$. It is clear that the *d*-spacing for Mt (9.08A°) increased to (13.54, 13.10A°) since the small inorganic Na$^+$ cation is exchanged by onium group through an ion exchange process. Fig. 2. presents series of XRD corresponding to clays:

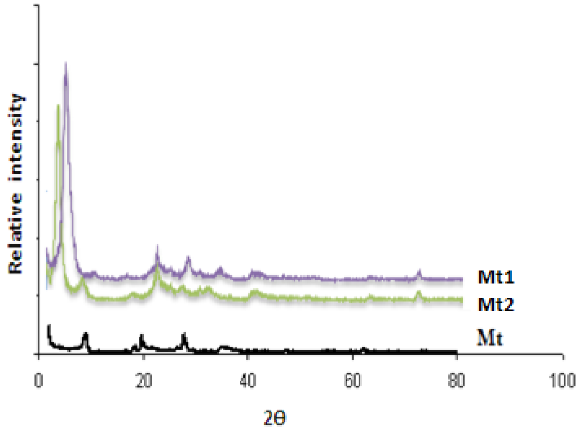

Fig.2. *XRD patterns of clay (Mt) and organoclays (Mt -1, Mt-2).*

This confirmed that the organoclay is intercalated between the layers. Increase in d-spacing vs. the washed unmodified Mt follows the order Mt-1> Mt-2. The higher extent of intercalation corresponding to the largest interlayer distance of 1.354 nm in Mt-1 (compare with 0.973 nm for Mt) is obtained with IL-1.

SEM spectra

The surfaces of Mt and Mt modified samples was observed by using a Jeol JSM-5610 scanning electron microscopy after gold

Table 2. *X-Ray Diffraction and Thermal Analysis Data for The Samples.*

Sample	x-ray data	
	2Θ	d-spacing
Mt	9.079	0.973
Mt-1	6.580	1.354
Mt-2	6.690	1.310

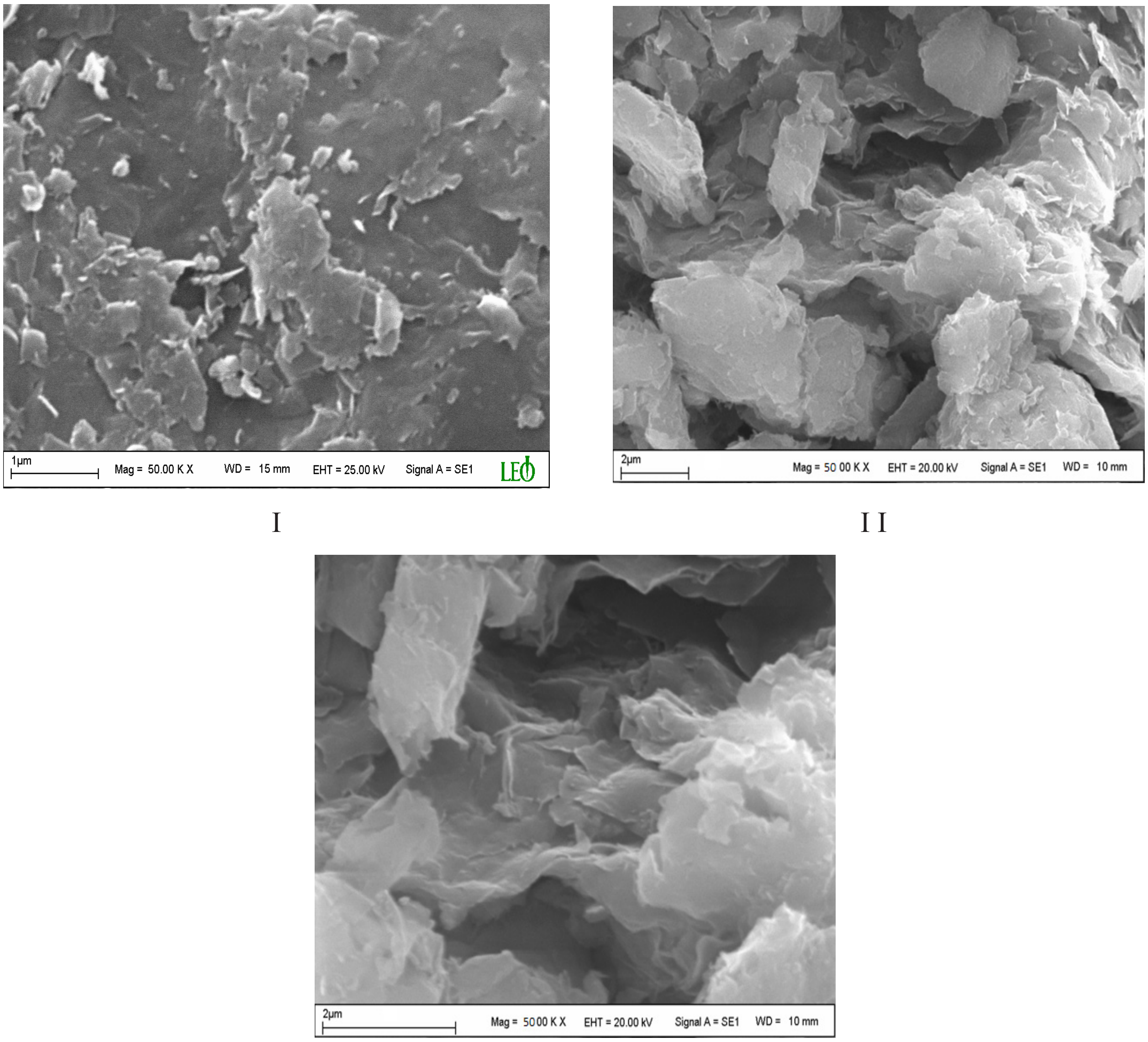

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Fig.3. *SEM images of samples, I) Mt, II) Mt-1 and III) Mt-2*

coating to determine the dispersibility of organoclay. SEM examination of the surfaces samples occured fractures. Fig.3. shows a micrograph of the fracture surface at 50.00 magnifications.

Fig.3 shows SEM images of Mt (unmodified clay) and Mt -1 and Mt-2 (modified clay). 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. These properties may show an increase or a decrease due to restrictions in the mobility of clays during stretching.

4. Conclusion

Organoclays obtained by modifing with organic cations were synthesized and characterized. The intercalation of four modifier in Mt through exchange with interlamellar sodium ions was confirmed by comparing with the results of untreated Mts and modified clays with organic cations by the following results:
A reasonable correlation was obtained between the above methods in determining the amounts of cations present in the modified clays and efficiency of intercalation. Synthesized organoclays can be used in food and chemical packaging field.

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