

Modification of montmorillonite, Using different phosphonium salts, study their effect upon the structure .

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Abstract:-

In this study, sodium montmorillonite was modified using three organic phosphonium salts triphenylphosphonium chloride (Tpp-Cl), octyl triphenylphosphonium bromide (C8tpp-Br) and hexadecyl triphenylphosphonium bromide (C16 tpp-Br). Fourier transform infrared (FTIR) spectroscopy was used to identify the functional groups of organo-montmorillonites (OMMTs). Basal spacing and thermal stability of OMMTs were investigated by X-ray diffraction (XRD) and thermogravimetric analysis (TGA) respectively. Elemental analysis was used to identify the composition of modified sodium montmorillonites. Optimum conditions of cationic exchange capacity (CEC) were studied in order to determine the optimum amount of phosphonium salt used for modification of clay. The X-ray diffraction results show that the basal spacing of the treated clay with Tpp-Cl, C8tpp-Br and C16 tpp-Br increased to 1.51, 1.91 and 2.42 nm, respectively. FTIR spectra illustrate that phosphonium salts were intercalated into the clay layers. Elemental analysis results indicate that phosphonium cations were successfully exchanged with Na present in the clay layers. Thermal analysis provides an indication of the stability of the OMMTs.

I. Introduction:-

Clays (Na-MMTs) are widely used in various areas of science as carriers for agricultural insecticides, thickeners in coating products, drilling fluids and in wastewater treatment applications because of their availability as a natural material and their ability to be modified with organic molecules [1]. This modification may be carried out via exchanging the original inter-layer cations by organic cations where transform from organophobic to organophilic materials and significantly increase the basal spacing of the clay layers [2]. It is generally accepted that the extent of swelling depends on the length of the alkyl chain and the cation exchange capacity of the clay [3]. By exchanging cations in the clay minerals which contain hydrated Na⁺ ions with alkyl ammonium [4] or phosphonium salts [5], organo-montmorillonites (OMMTs) are mainly obtained.

The use of OMMT in polymer nanocomposite has attracted considerable attention in this field of materials science and technology [2,6]. The incorporation of OMMTs in polymers offers diversified applications because of the improvement of barrier and flame retardant properties, the enhancement of physical, thermal and mechanical properties, the increase of dimensional stability, and the high heat distortion temperature of the OMMT-incorporated polymer.

Many studies were conducted on the modification of Na-MMT by different organic compounds such as quaternary ammonium salts [7,8] and phosphonium cations [5,9]. The modification of sodium montmorillonite through the incorporation of

octadecylammonium [3] and octadecyltrimethylammonium cations into the clay's interlayer spaces were investigated [10]. They reported that the maximum amount of cations were at 2 and 1.5 CEC respectively. Triphenyl vinylbenzyl phosphonium chloride and tetraoctyl phosphonium bromide salts were used as intercalate agents for Na-montmorillonite [11]. The basal spacing of these phosphonium montmorillonites was 1.85 and 2.12 nm respectively. Phosphonium montmorillonite were also synthesized and characterized with enhanced thermal stability by A. Patel et al. (2007) [9]. It is found that the basal spacing of tetrabutylphosphonium, hexadecyl tributylphosphonium and tetradecyl tributylphosphonium montmorillonites was 1.4, 2.32 and 219 nm, respectively. Thermal degradation behavior of organoclays using TGA, and TG/FTIR in order to understand the process of thermal degradation, and determined various degradation products were reported by Xie et al.(2001) [7]. They observed that the thermal stability of alky phosphonium-MMT is higher than that of ammonium-MMT indicates that alkylphosphonium salts offer unique opportunities for melting processing polymer layered silicate nanocomposites.

In this study, the modification of sodium montmorillonite through incorporation of triphenylphosphonium chloride, octyl triphenylphosphonium bromide and hexadecyl triphenylphosphonium bromide into the clay's interlayer spaces were investigated. . In addition to thermal stability, basal spacing and function groups identification of phosphonium-montmorillonite, the optimum conditions of CEC are investigated in order to optimize the amount of phosphonium salt used for modification of clay. These OMMTs could have enormous potential for various applications in research and industrial fields.

II. Experimental

Materials: Triphenylphosphine and xylene were purchased by T.J.Baker (USA). Sodium montmorillonite (Kunipia F) was obtained from Kunimine Ind. Co. Japan. 1-bromooctane and 1-bromohexadecane were obtained from Fluka (Switzerland).

Preparation of octyl triphenylphosphonium bromide (C8tpp-Br): A solution of 1-bromooctane (0.02 mole) and triphenylphosphine (0.04 mole) in 200 ml. of xylene was heated under reflux for 12 hours and continuous stirring. The mixture was cooled to about 60°C, and the colourless precipitate product was filtered, washed with 50 ml of xylene, and then dried at 60°C for 24 h. The yield of C8tpp-Br was 91%.

Preparation of hexadecyl triphenylphosphonium bromide (C16 tpp-Br): This compound was prepared by using 0.02 mole of 1-bromohexadecane and 0.04 mole of triphenylphosphine. The resulting colourless precipitate was filtered, washed with xylene and dried at 60°C for 24 h. The yield of C16 tpp-Br was 89%.

Preparation of OMMTs: Modification of the Na- MMT was carried out by replacing its sodium ion with phosphonium groups from triphenylphosphonium chloride Tpp-Cl (prepared from designate amount of Tpp with concentrated hydrochloric acid), C8PPh-Br and C16PPh-Br through an ion-exchange process in an aqueous solution. The Na-montmorillonite was first dispersed in 80 ml of hot distilled water at 80 °C and stirred vigorously for 1 h. A solution containing phosphonium salt with 70 ml distilled water and 30 ml ethanol was then added into the suspension at 80 °C and stirred for another 1 h. The precipitate was filtered and washed with hot distilled water for several times until no halide ion was detected with 0.1M AgNO₃ solution. It was then dried at 60 °C

for 48 h. The organophilic montmorillonite was grinded with a mortar and particles sieved of size less than 100 μm

Characterization: Fourier transform infrared (FTIR) spectra in the range 4000–400 cm^{-1} were obtained using Perkin–Elmer 1650 infrared Fourier transform spectrometer by KBr pellet technique. The weight loss of the samples

was measured through thermogravimetric analysis (TGA) using Perkin Elmer model TGA 7 Thermalgravimetry Analyzer. The samples were heated from 30 to 800°C with a heating rate of 10°C/min under nitrogen atmosphere with a nitrogen flow rate of 20 ml/min.

The clay dispersion was determined by XRD Shimadzu XRD 6000 diffractometer with operating in the theta-to-theta geometry using Cu $\text{K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The scans were performed in 2θ ranges of 2° to 10° at a scanning speed of 1°/min.

III. RESULTS AND DISCUSSION

X-Ray Diffraction (XRD) Analysis: Montmorillonite consists of tetrahedral silica layers and octahedral alumina layers, having negative charges which must be counterbalanced by exchangeable cations in the interlayers [12]. The basal spacing between these layers is dependent on the size of the cation. Ion exchange is dependent on CEC of MMT being used. The degree of ion exchange of the sodium ion by Tpp⁺, C8pph⁺ and C16pph⁺ is affected the basal spacing of OMMT. Figure 1 illustrates the amount of the d (001) spacing for different amounts of phosphonium salt (C16pphBr) intercalated montmorillonite. It can be noticed that upon the exchange of the Na⁺ ion by C16pph⁺ at 0.2 CEC, the basal spacing increased from 1.23 to 1.42 nm. On further increasing of the CEC value, change in the d(001) spacing was observed until approaching to optimum values. The optimum values of basal spacing for C16pph⁺ at 2 CEC level was 2.42 nm. At higher CEC values the C16pphBr does not cause a significant further clay expansion and the phsphonium salt is simply adsorbed on the surface of clay particles.

The increasing of basal distance (d 001) of OMMT against various concentrations of C16pph-Br is depicted in Figure 2 which shows that the Na-MMT modification increased the basal spacing of the clay suggesting that the phosphonium cations were successfully intercalated into the clay. Figure 2 also shows that the intercalation of the phosphonium ion as surfactant cation with the silicate layers increases the silicate interlayer spacing leading to shift of the 001 diffraction peaks to lower angles. X-Ray patterns for Na-MMT and phosphonium modified MMT were compared in order to know the effect of presence and Length of alkyl chain in phosphonim salt of the Na-MMT modification. Figure 3 shows that the optimum basal spacing (d 001) of the natural clay (Na-MMT) increased from 1.23 nm to about 1.51, 1.91 and 2.42 nm at 2 CEC as a response to the exchange of sodium ion in the clay by phosphonium ion of Tpp⁺, C8pph⁺ and C16pph⁺, respectively. Diffraction angle and basal spacing of natural clay (Na-MMT) and modified clays with Tpp-Cl, C8pph-Br and C16pph-Br are summarized in Table 1 which shows that the basal spacing of C8pph-Br is greater than Tpp-Cl due to alkyl chain presence while the optimum basal spacing of the C16PPh-MMT was the greatest compared to those of Tpp-MMT and C8PPh-MMT. The effect can be attributed to the arrangement of phosphonium ion as surfactant molecules type in the interlayer spacing of Na-MMT due to alkyl chain length [13]. Scheme 1 shows schematic drawing the clay modification of organic phosphonium salts.

Fourier Transform Infrared (FTIR) Spectroscopy: The FTIR spectra of Tpp-Cl, C8pph-Br and C16pph-Br are illustrated in Figure 3. The spectra of Tpp-Cl exhibit bands 3054 and 3000 cm^{-1} which can be assigned to C—H of aromatic stretching. The bands at 1610 cm^{-1} , 1080 cm^{-1} and 710 cm^{-1} correspond to C=C-C of aromatic ring stretch, C-H of aromatic CH in-plane bend and C-H of aromatic CH out-of-bend, respectively. The band at around 1434 cm^{-1} is corresponding to C-P [14]. In addition of these bands, C8pph-Br and C16pph-Br spectra show bands at around 2916 and 2848 cm^{-1} are attributed to the C-H asymmetric stretching and symmetric stretching vibration [15].

The presence of phosphonium ion in the clay was determined by FTIR spectroscopy. The FTIR spectra of Na-MMT, Tpp-MMT, C8pph-MMT and C16pph-MMT are shown in Figure 4. In the spectra of Na-MMT, the peaks at 3618, 1625 and 1010 cm^{-1} are due to the O-H stretching, nterlayer water deformation and the Si-O stretching vibration, respectively. The other strong bands absorption at 512 cm^{-1} and 440 cm^{-1} indicate the presence of Al-O stretching and Si-O bending, respectively in the clay. The Tpp-MMT, C8pph-MMT and C16pph-MMT spectra show the major bands of Tpp-Cl, C8pph-Br and C16pph-Br spectra in addition to the bands of the original Na-MMT. These results suggest the Tpp⁺, C8pph⁺ and C16pph⁺ are intercalated in the silicate layers.

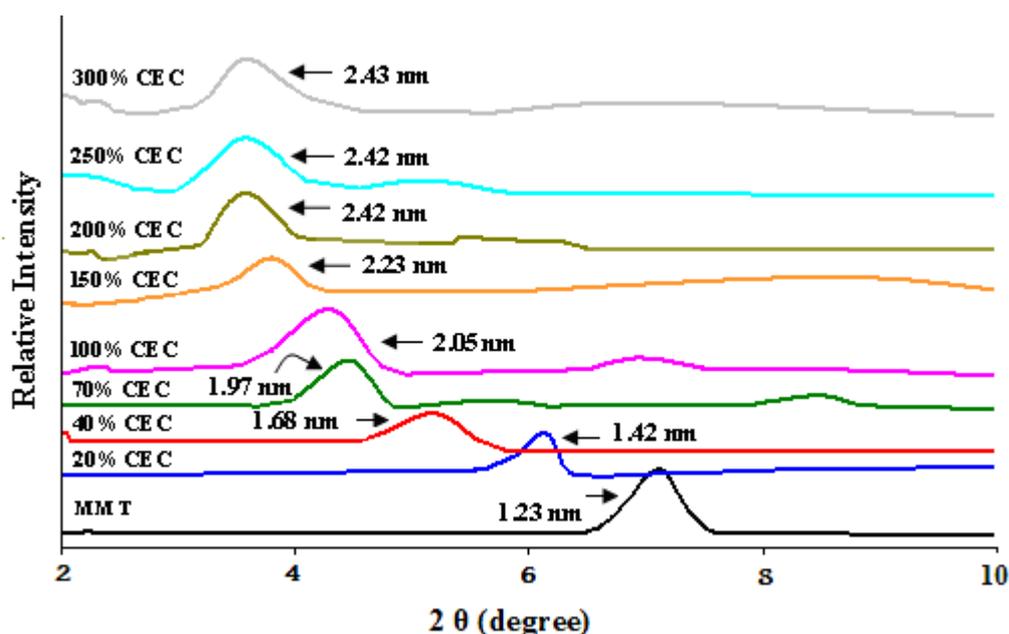


FIG. 1: XRD diffraction patterns of pristine MMT and OMMT with various concentrations of C16pphBr surfactant (related to clay CEC)

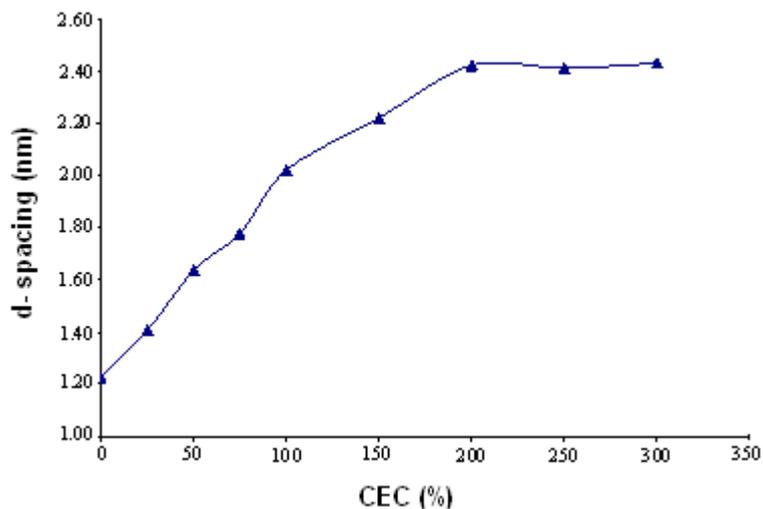


FIG. 2: The basal distance (d001) of OMMT vs. C16pph concentration (CEC%)

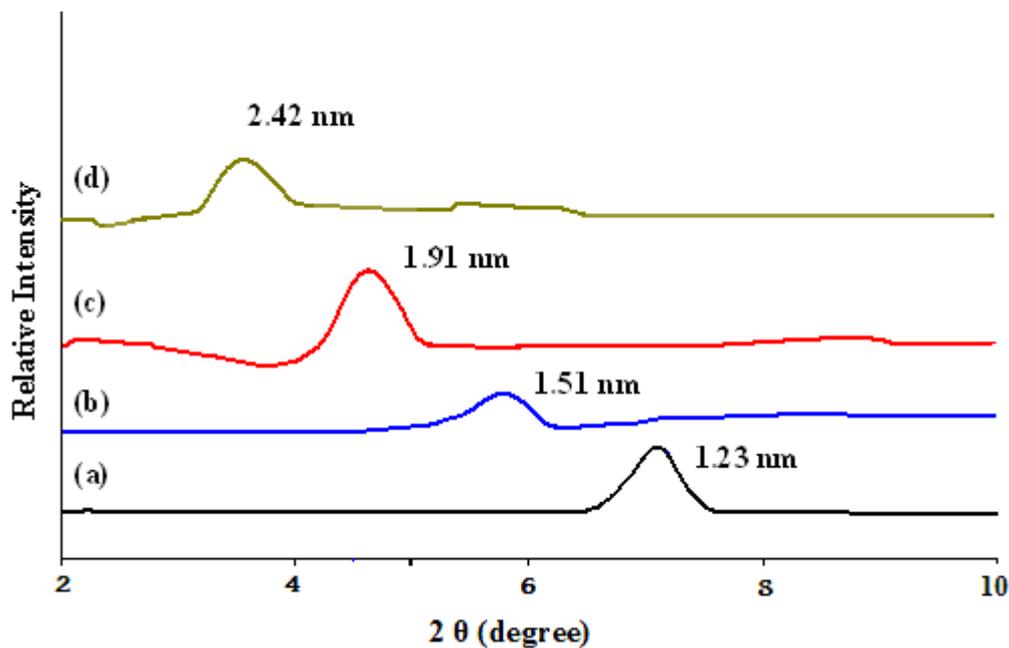
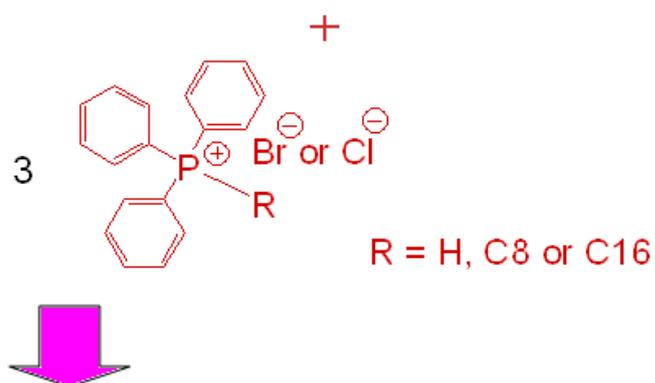
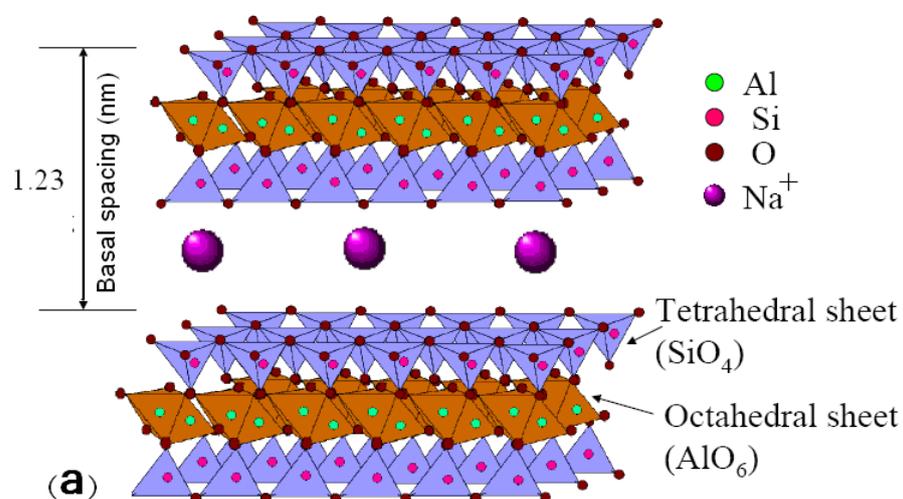
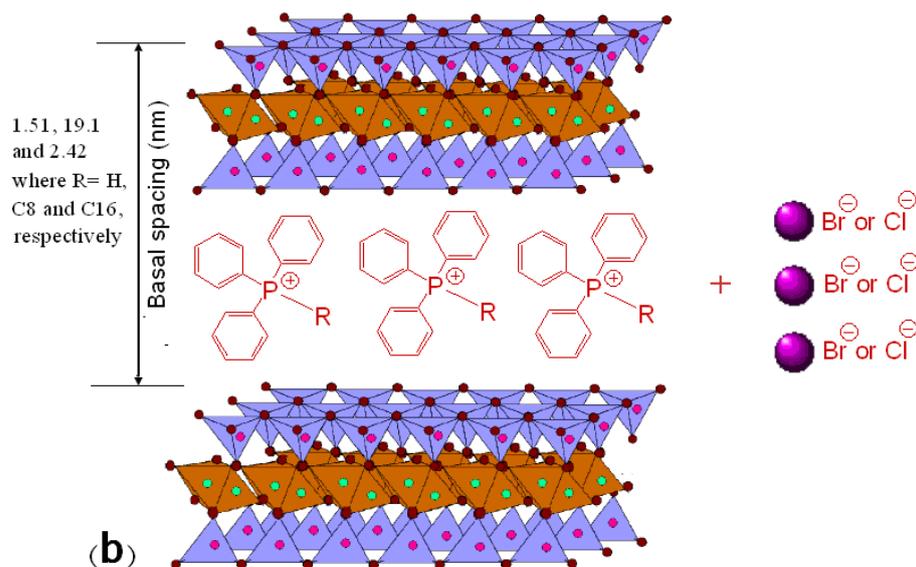


FIG. 3: XRD patterns of (a) Na-MMT, (b) Tpp-MMT, (c) C8pph-MMT and (d) C16pph-MMT.

Table I: Diffraction angle and basal spacing of natural clay
 (Na-MMT) and Na-MMT modified with phosphonium salts
 (Tpp-MMT, C8pph-MMT and C16pph-MMT)

Type of clay	Exchanged Cation	2θ (degree)	d -spacing (nm)
Na-MMT	Na ⁺	7.13	1.23
Tpp-MMT	(Ph) ₃ -P ⁺ -H	5.80	1.51
C8pph-MMT	(Ph) ₃ -P ⁺ -C ₈ H ₁₇	4.59	1.91
C16pph-MMT	(Ph) ₃ -P ⁺ -C ₁₆ H ₃₃	3.62	2.42





SCHEME 1: Layered Silicate: (a) Unmodified sodium montmorillonite (b) Sodium montmorillonite modified by phosphonium salts

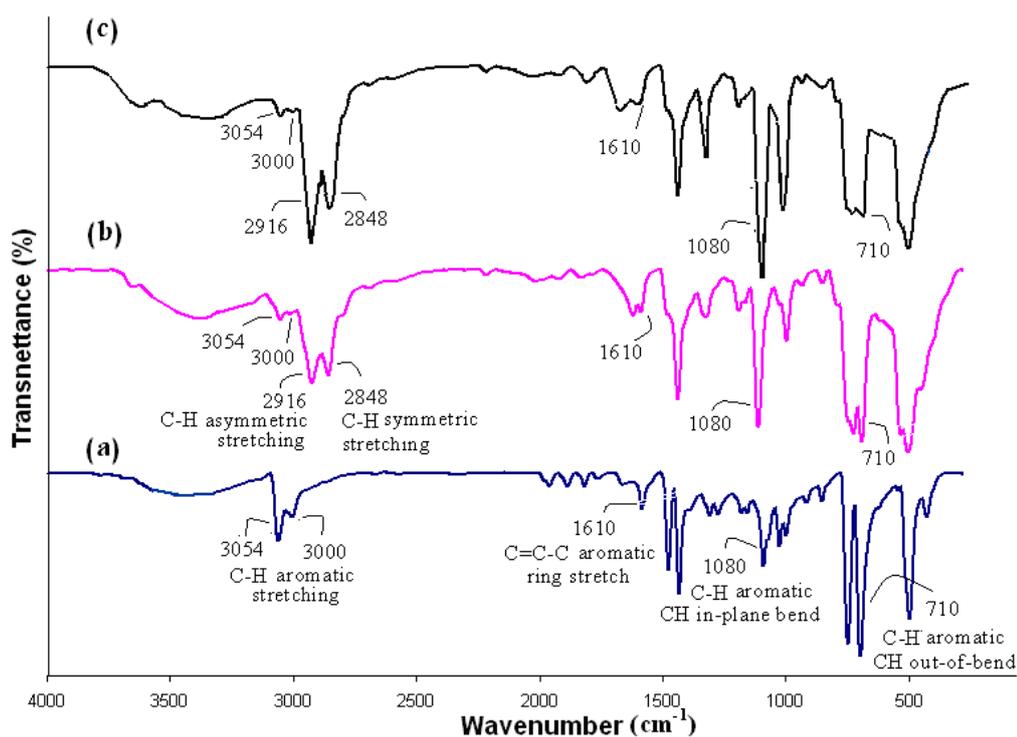


FIG. 4: Ftir spectra of (a) Tpp-Cl, (b) C8pph-Br and (c) C16pph-Br

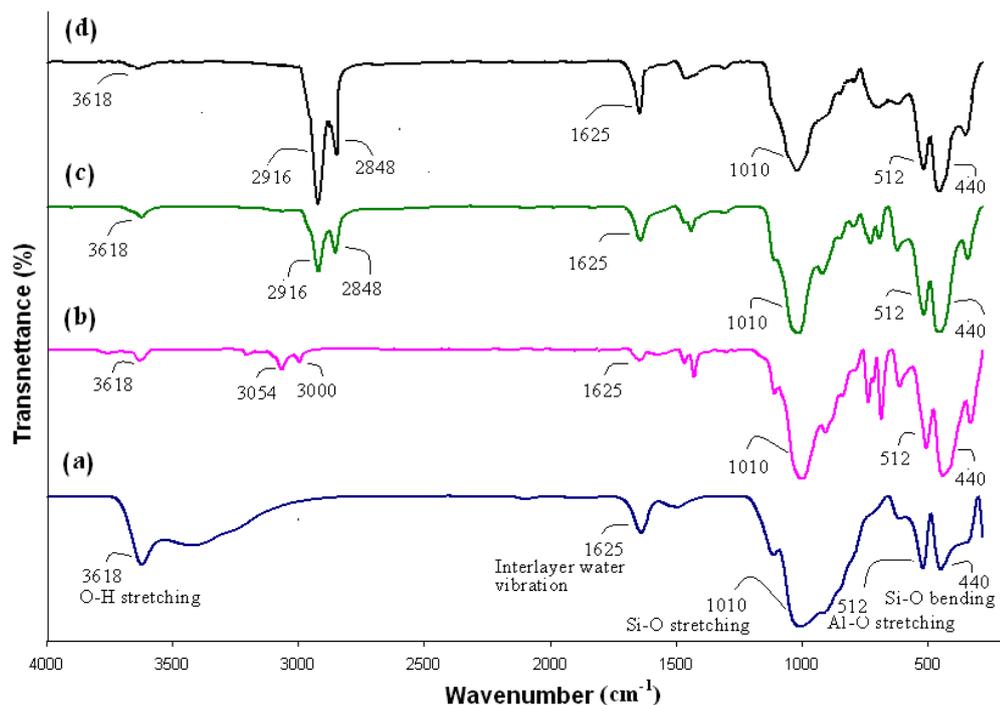


FIG. 5:: Ftir spectra of (a) Na-MMT, (b) Tpp-MMT, (c) C8pph-MMT and (d) C16pph-MMT

Elemental Analysis: Elemental analysis was used to estimate the amount of Tpp, C8pph and C16pph as cations being intercalated into the clay galleries. Table 2 shows the results of C percentage and amount of phosphonium salts in 1 gm clay of the Tpp, C8pph and C16Ppph modified clays. The calculation is based on atom carbon because of the increase of its content is due to the presence of the organic molecule. All samples of the different modified clays contained high percentage of carbon (between 31.45 and 31.97) indicating that phosphonium cations were successfully exchanged with Na present in the clay layers.

Table 2: The experimental and computed results of C percentage and phosphonium cations of Tpp+, C8pph+ and C16pph+ presence in the clay layers

Phosphonium cations %C mmol of phosphonium
modified clay cations/ 1gm clay based on C calculation

Tpp	31.45	1.45
C8pph	31.75	1.02
C16pph	31.97	0.78

IV. CONCLUSIONS

MMT has been modified using triphenylphosphonium chloride, octyl triphenylphosphonium bromide and hexadecyl triphenylphosphonium bromide. The organo-montmorillonites have been characterized and compared to unmodified MMT using X-Ray Diffraction, FTIR spectroscopy, elemental and TG analysis.

Based on the laboratory experimental results, the following conclusions can be drawn:

1. The optimum values of basal spacing (d 001) of the natural clay (Na-MMT) modified by phosphonium salts was at 2 CEC.
2. The optimum basal spacing increased from 1.23 nm to about 1.51, 1.91 and 2.42 nm as a response to the exchange of sodium ion in the clay by phosphonium ions.
3. The FTIR spectra and elemental analysis reveal that phosphonium salts are successfully intercalated into the interlayer of MMT.
4. Thermal analysis results show the stability of the OMMTs.

These organo-montmorillonites have potential benefit in the preparation of polymer nanocomposites because it makes them have superior properties to offer high performance application.

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تحويل أطياف المونتموريلونايت باستخدام املاح فسفونينوم مختلفة ودراسة تأثير ذلك على التركيب

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الخلاصة :-

في هذه الدراسة تم تحويل مونتموريلونايت الصوديوم باستعمال ثلاثة املاح عضوية للفوسفونينوم هي ثلاثي فينيل فوسفونينوم كلوريد (Tpp-cl) واوكتيل ثلاثي فينيل فوسفونينوم بروميد (C₈tpp-Br) وهكساديكيل ثلاثي فينيل فوسفونينوم بروميد (C₁₆tpp-Br) . استعملت تقنية التشخيص بالاشعة تحت الحمراء تحويل فورير FTIR للتشخيص للمجاميع الفعالة للمونتموريلونايت العضوي وحدد الاستقرار الحراري لهذه المركبات باستعمال مطيافية حيود الاشعة السينية (XRD) والتحليل الحراري الوزني (TGA) . استعمل جهاز تحليل العناصر لتحديد التركيب للمركبات المحضرة كما درست الظروف الفضلى لسعة التبادل الايوني الموجب (CEC) لغرض تحديد الكمية المثالية المطلوبة للأملاح الفوسفونينوم لاجراء التحويل للطين . أظهرت نتائج قياسات حيود الاشعة السينية بان المسافات القاعدية للطين المعالج بواسطة Tpp-cl و C₈tpp-Br ازدادت من 1.51 الى 1.91 و 2.42 على التوالي . اظهر طيف الاشعة تحت الحمراء بان املاح الفوسفونينوم تداخلت خلال طبقات الطين واطهر تحليل العناصر بان كاتايونات الفوسفونينوم تم تبادلها بنجاح مع الصوديوم الموجود في طبقات الطين واطهرت التحاليل الحرارية مدى الاستقرار الحرارية للمركبات المحورة المحضرة .