

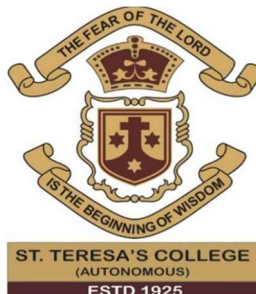
PROJECT REPORT

On

**“EFFECT OF MODIFIER CONCENTRATION FOR
PREPARATION OF ORGANOCLAY”**

Submitted by
MISHMA SIMON
(AM20CHE011)

*In partial fulfillment for the award of the
Post graduate Degree in Chemistry*



**DEPARTMENT OF CHEMISTRY
AND
CENTRE FOR RESEARCH**

**ST TERESA'S COLLEGE (AUTONOMOUS)
ERNAKULAM
2021-2022**

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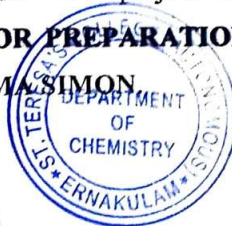



M.Sc. CHEMISTRY PROJECT REPORT

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Year of Work : 2020-2021

This is to certify that the project "**EFFECT OF MODIFIER CONCENTRATION FOR PREPARATION OF ORGANOCCLAY**" is the work done by MISHMA SIMON.


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Submitted to the Examination of **Master's** Degree in Chemistry

Date: 9/6/2022

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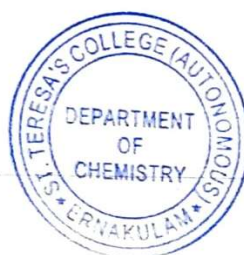


CERTIFICATE

This is to certify that the project work entitled **“EFFECT OF MODIFIER CONCENTRATION FOR PREPARATION OF ORGANOCCLAY”** is the work done by MISHMA SIMON under the guidance of Dr. ANNU RAJU, Assistant Professor, Department of Chemistry and Centre for Research, St. Teresa's College, Ernakulam in partial fulfillment of the award of the Degree of Master of Science in Chemistry at St. Teresa's College, Ernakulam affiliated to Mahatma Gandhi University, Kottayam.

Dr. Annu Raju
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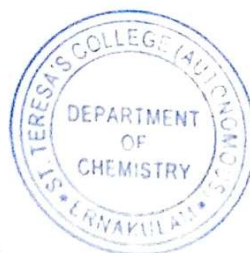
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Dr. Annu Raju
Project Guide



DECLARATION

I hereby declare that the project work entitled “**EFFECT OF MODIFIER CONCENTRATION FOR PREPARATION OF ORGANOCLAY**” submitted to Department of Chemistry and Centre for Research, St Teresa’s College affiliated to Mahatma Gandhi University, Kottayam, Kerala is a record of an original work done by us under the guidance of **Dr. ANNU RAJU**, Assistant Professor, Department of Chemistry and Centre for Research, St. Teresa’s College (Autonomous), Ernakulam. This project work is submitted in the partial fulfillments for the requirements for the award of the Degree of Master of Science in Chemistry.

MISHMA SIMON

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LIST OF ABBREVIATIONS	
Cetyl Trimethyl Ammonium Bromide	CTAB
2-Acrylamido-2-methyl propane sulfonic acid	AMPS
Cetyl Pyridinium Chloride	CPC
Montmorillonite Clay	MMT
Adduct Modified Clay	AMC
X ray diffraction	XRD
Infrared	IR

Chapter 1

Introduction

Clays are naturally occurring layered mineral materials that are low cost and environment friendly. Nano clays are clay minerals with at least one dimension in the order of 1-100nm [1]. With an increasing understanding of clay structure, montmorillonite is realized viable for an enhanced performance in a variety of materials and products in the areas of catalysis, food additive, antibacterial function, polymer, sorbent, etc. Significant development in the use and application of montmorillonite is seen in recent time [2]. Clays have stimulated much research interest as filler materials in composites due to their unusual mechanical, electrical, optical, and magnetic properties [3,4,5]. Additionally, with their large surface area [6], high cation exchange capacity [6], possibility of easy modification [8,9], unique structural properties and nanometre sized platelets with very small cross-sectional area makes them attractive candidates as filler additives [10]. Nanoclays, based on montmorillonite, are currently used to modify the polymer performance [2]. Clay minerals are abundant in soils, they have appreciable internal and external surfaces accessible to organic or inorganic molecules [11].

Organoclay materials are defined as hybrid materials resulting from the association of clay minerals with surfactants and/or other various organic compounds. With the incorporation of the surfactants in their internal structure through different chemical and physical processes, the obtained materials combine a large specific surface and a hydrophobic behaviour,

enhancing the applications of clay minerals in various fields. A large volume of the research work focused on and pointed out the use of organoclays as reinforcers in polymer nanocomposites, starting materials for photophysical films, rheological agents, and as adsorbents for organic pollutants in soil and aquatic environments. The final characteristics of organoclays mainly depend on the type of inorganic layered materials used and the chemical nature of the surfactant for the surface modification. Among the expandable clay minerals, Mt was the most popular material for preparation of organoclays because of its singular properties: charge density, cation exchange capacity (CEC) and swelling ability, its abundance in the ground, and thus its low cost [12,13,14,15]. Organoclays show several promising applications in contamination prevention and environmental remediation, including the treatment of waste effluents, as extenders for activated carbon and as components of clay barriers, for example in clay slurry walls, hazardous waste landfills etc[11].

1.1 Structure of Clay

A common characteristic of clay mineral is a fine-grained natural structure in a sheet-like geometry. The sheet-structured hydrous silicates are generally called phyllosilicates [4]. The natural clay particle is smaller than 0.004 mm in diameter that may range from 0.002 to 0.001 mm for quartz, mica, feldspar, iron, and aluminium oxides [11]. Colloidal clay particles are finer and found in layered silicates (<0.001 mm in diameter). The variety of clay minerals is based on the arrangement of tetrahedral and octahedral sheets. The atomic structure of a clay mineral consists of two basic units, an octahedral sheet and a tetrahedral sheet. The octahedral sheet is comprised of closely packed

oxygen and hydroxyls in which aluminium, iron and magnesium atoms are arranged in octahedral coordination (fig 1.2). When aluminium with a positive valence of three is the cation present in the octahedral sheet, only two thirds of the possible positions are filled in order to balance the charges. When only two thirds of the positions are filled, the mineral is termed dioctahedral. When magnesium with a positive charge of two is present, all three positions are filled to balance the structure and the mineral is termed trioctahedral.

The second structural unit is the silica tetrahedral layer in which the silicon atom is equidistant from four oxygens or possibly hydroxyls arranged in the form of a tetrahedron with the silicon atom in the centre. These tetrahedrons are arranged to form a hexagonal network repeated infinitely in two horizontal directions to form what is called the silica tetrahedral sheet (fig 1.1). The silica tetrahedral sheet and the octahedral sheet are joined by sharing the apical oxygens or hydroxyls to form what is termed 1:1 clay mineral layer (eg kaolinite) or the 2:1 clay mineral layer (eg illite). 1:1 clay mineral would have one tetrahedral and one octahedral sheet per clay layer; 2:1 clay mineral would contain two tetrahedral sheets and one octahedral sheet sandwiched between the two tetrahedral sheets (montmorillonite is an example of clay mineral having 2:1 sheet structure); and 2:1:1 clay mineral is composed of an octahedral sheet adjacent to a 2:1 layer.[16]

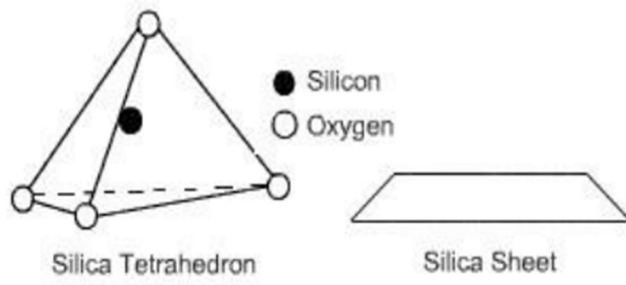


Figure 1.1: Silica Sheet

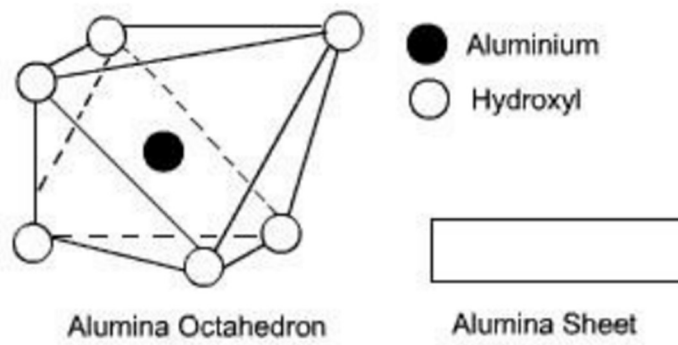


Figure 1.2: Alumina Sheet

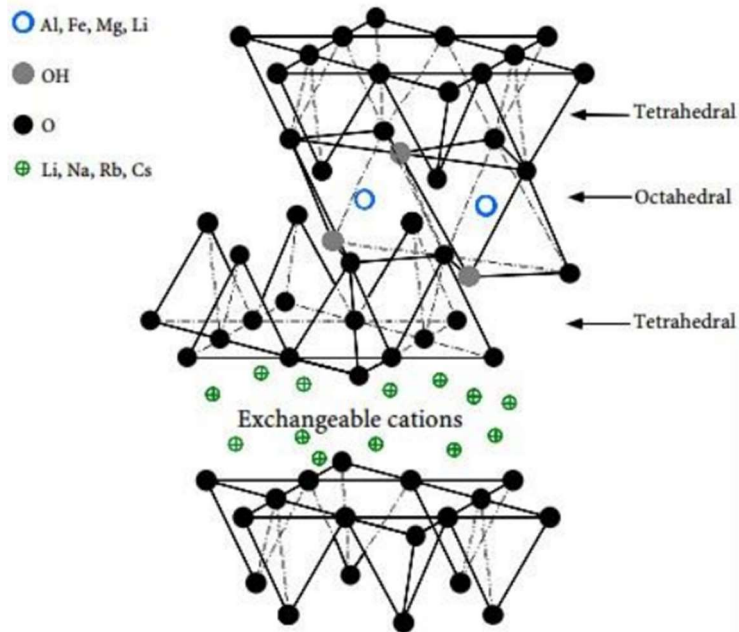


Figure 1.3: The structure of 2:1 layered silicate

1.2 Montmorillonite Clay

With an increasing understanding of clay structure, montmorillonite is realized viable for an enhanced performance in a variety of materials and products in the areas of catalysis, food additive, antibacterial function, polymer, sorbent, etc. Significant development in the use and application of montmorillonite is seen in recent time.

Theoretical formula for montmorillonite clay is $M^+_y(Al_{2-y}Mg_y)Si_4O_{10}(OH)_2.nH_2O$. Montmorillonite is the basic raw material used in producing nanoclay. Chemically, it can be described as hydrated sodium calcium aluminium magnesium silicate hydroxide. The interaction between

nanoclay particles and polymer matrix significantly depends upon the hydroxyl groups and charges present in the nanoclays particle.

The physical structure of montmorillonite particle is generally perceivable in sheets and layers. Each layer is composed of two types of structural sheets: octahedral and tetrahedral. The tetrahedral sheet is composed of silicon-oxygen tetrahedra linked to neighbouring tetrahedra by sharing three corners resulting in a hexagonal network. The remaining fourth corner of each tetrahedron forms a part to adjacent octahedral sheet. The octahedral sheet is usually composed of aluminium or magnesium in sixfold coordination with oxygen from the tetrahedral sheet and with hydroxyl. The two sheets together form a layer. Several layers may be joined in a clay crystallite by interlayer cations, by Van der Waals force, by electrostatic force, or by hydrogen bonding.

The important natural physical properties of montmorillonite are given in Table 1.1.

S.no.	Property Name	Description
1	Density	2-3g/cm ³
2	Crystal system	Monoclinic
3	Hardness	Soft, possess fine grained occurrence
4	Fracture	Irregular, uneven
5	Cleavage	Perfect
6	Lustre	Earthy, dull
7	Transparency	Translucent

Table 1: Important natural and physical properties of montmorillonite

1.3 Organoclay

In clay-polymer system, the clay nanoparticle can be intercalated or exfoliated. Where clay crystal is used as nanoparticle, it can be referred as intercalated clay and when the single particle of clay is the constituent unit, it is referred as exfoliated. The important required characteristics include are particle size, surface area, and aspect ratio. The length and breadth of the particles can range from 1.5 μm down to few tenths of a micron. The third dimension of particle, in the study, is described as thickness, width, or diameter; however, diameter may be used. The diameter of the particle is exceptionally smaller relative to its length, measuring to only one-billionth part of a meter (=1 nm). Therefore, an extremely high average length-to-diameter ratio (called aspect ratio) of 200–500 is achievable. An increased aspect ratio produces a higher surface area. A smaller mass of nano clay shows a high surface area. [2]

1.4 Structures of Clay Modifiers

1.4.1 CTAB

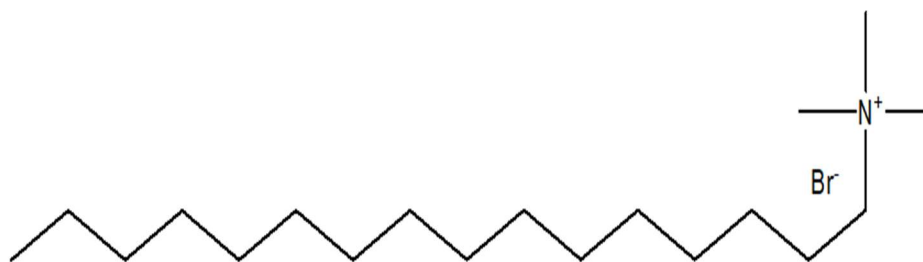


Figure 1.4: Structure of CTAB

1.4.2 AMPS

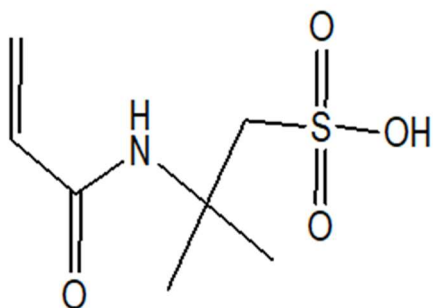


Figure 1.5 Structure of AMPS

1.4.3 CPC

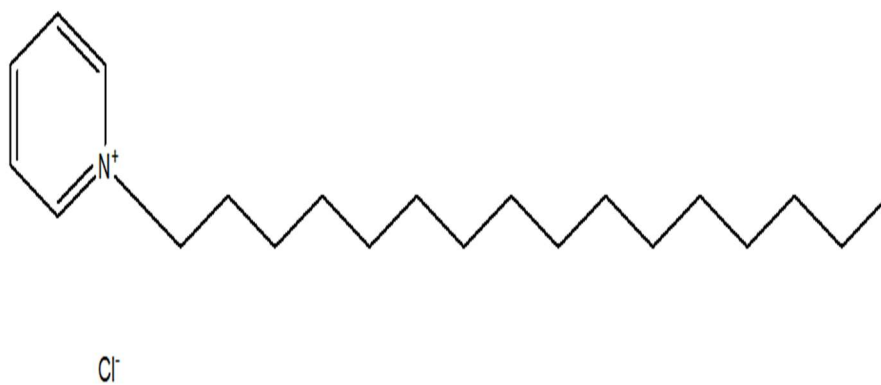


Figure 1.6: Structure of CPC

1.4.4 CPC-AMPS ADDUCT

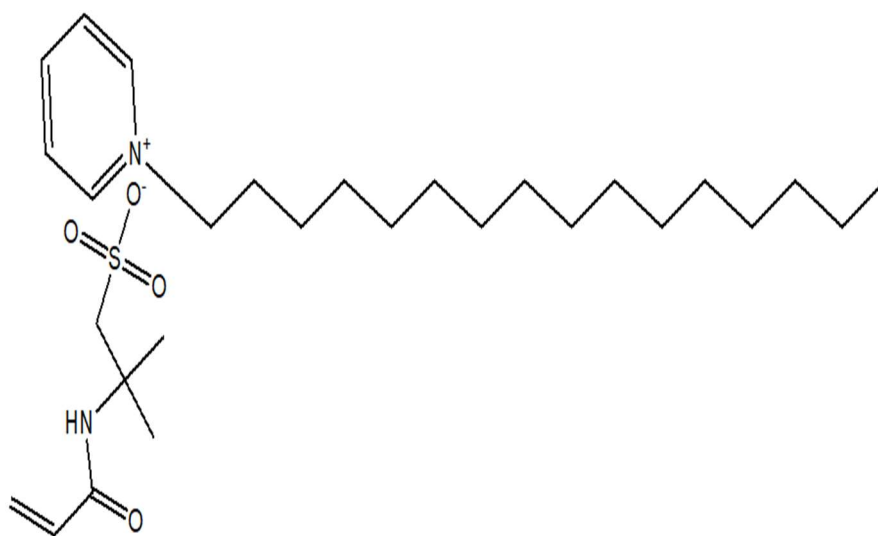


Figure 1.7: Structure of CPC- AMPS adduct

1.5 Modification of Clay Using CPC-AMPS adduct

CPC will react with the AMPS to form a CPC-AMPS adduct. The cationic exchange between the Na^+ MMT clay and the adduct leads to the insertion of adduct into the clay interlayer spacing to produce modified organoclay.

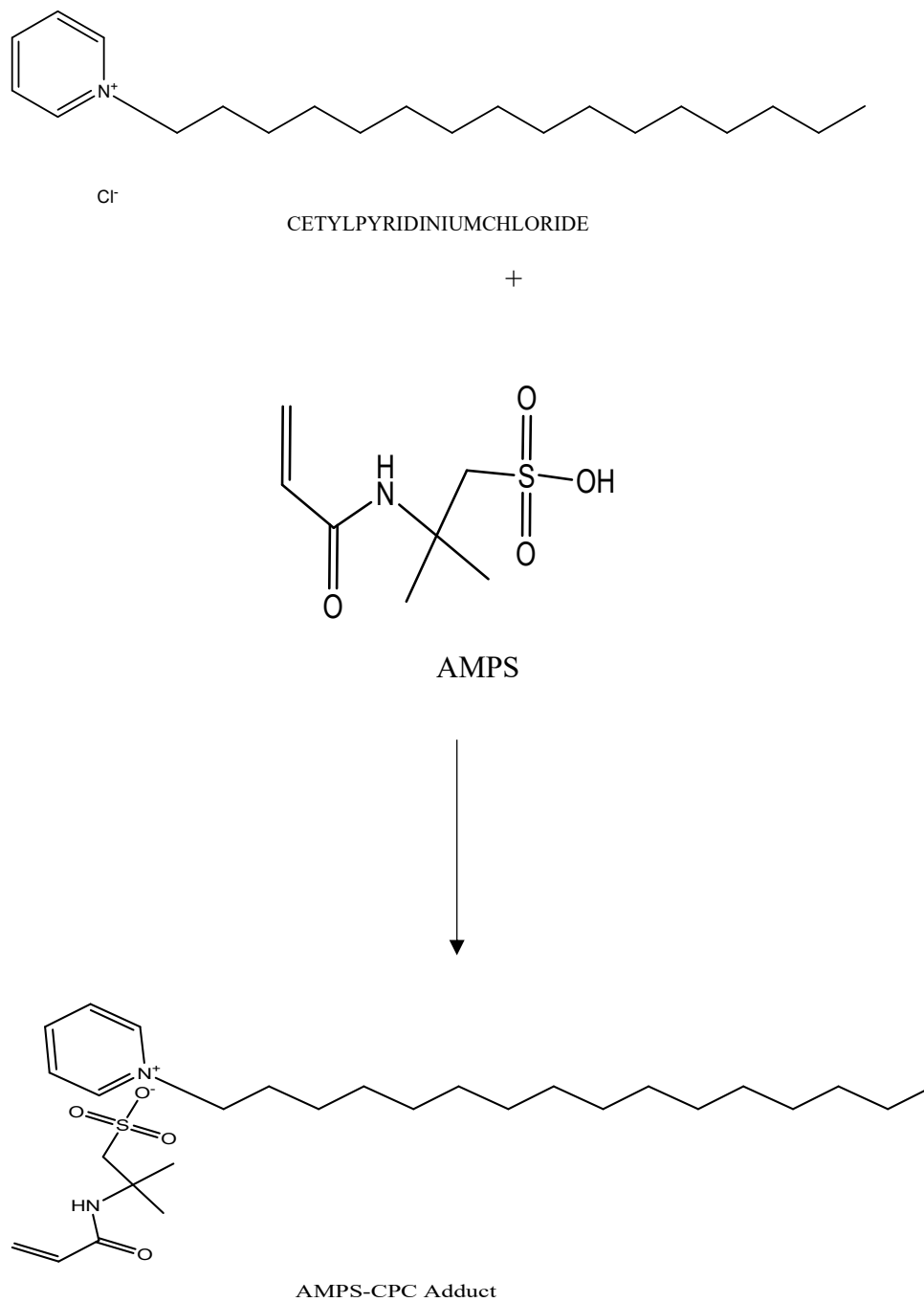


Figure 1.8: General mechanism for adduct formation

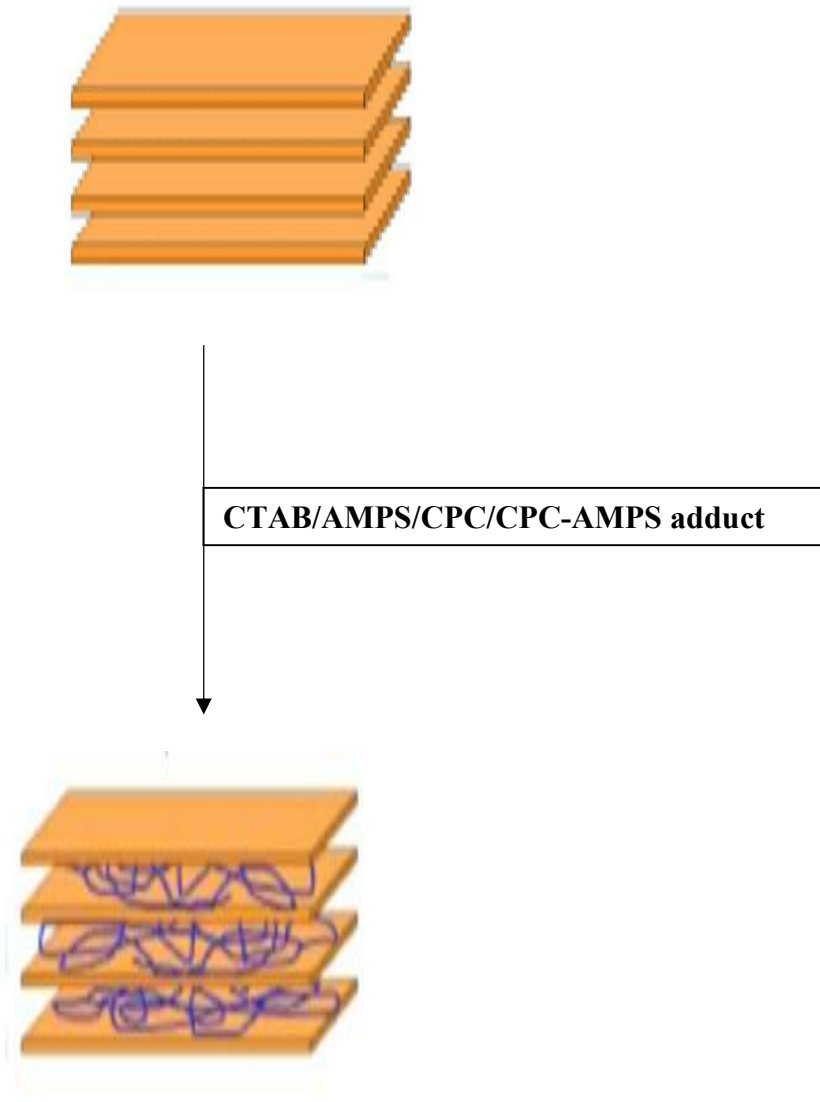


Figure 1.9: Modification of clay

1.6 Structural characterization of modified clay

In order to analyse the structure of organo-modified clays, two common techniques including X-ray diffraction (XRD) analysis and Fourier Transform Infrared (FT-IR) spectroscopy are widely used.

1.6.1 IR

Infrared spectroscopy (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemicals. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The higher energy near-IR, approximately $14000\text{-}4000\text{ cm}^{-1}$ ($0.8\text{-}2.5\text{ }\mu\text{m}$ wavelength) can excite overtone or harmonic vibrations. The mid-infrared, approximately $4000\text{-}400\text{ cm}^{-1}$ ($2.5\text{-}25\text{ }\mu\text{m}$) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately $400\text{-}10\text{ cm}^{-1}$ ($25\text{-}1000\text{ }\mu\text{m}$), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. In an IR spectrum absorption intensity is plotted against wavenumber. Absorption occurs when frequencies of infrared radiation match the natural vibrational frequencies of the molecule. It can be

used to characterize new material or identify, verify known and unknown samples.

1.6.2 XRD

Clays and organoclays show a characteristics peak in XRD analysis due to their regular layered structures. The peak is indicative of platelets separation or d spacing in clay structures. Using the peak width at half maximum height and peak position (2θ) in the XRD spectra the inter layer space can be calculated utilizing Braggs law,

$$\text{Sin}\theta = \frac{n\lambda}{2d}$$

where λ is wavelength of Xray radiation used in the diffraction experiments, d is the space between layers in the clay lattice and θ is measured diffraction angle. Any change in the interlayer or d spacing of a clay lattice by organic modification causes to change in position, broadness and intensity of characteristics peak in XRD spectra.

According to Braggs law increase in d spacing results to the broadening and shifting of related XRD peaks towards lower diffraction angles (2θ). By monitoring the position (2θ) shape and intensity of characteristics peak for organoclay, it is possible to determine the degree of intercalation/exfoliation. Wide angle Xray diffraction is used to identify the modified clay structure in the range $1^\circ < 2\theta < 10^\circ$ and that corresponding to a d spacing of at least 6nm. Hence the XRD technique offers a conventional method to determine the d spacing in pure clay as well as in organomodified clay, within 1-4nm, using the position, broadness and intensity of characteristic peak in WAXD diffractogram.

Chapter 2

Material and Methods

2.1 Work Plan

The main aim of the project is to study the effects of CPC– AMPS adducts in different concentration on the clay modification and to characterize the modified clays using X-ray Diffraction and IR studies.

2.2 Work carried out

Synthesis of modified MMT clay using CTAB, AMPS, CPC and different concentrations of CPC and AMPS adduct. In this project, we carried out the synthesis of modified MMT clay using 1x, 2x, 3x, concentrations of CPC-AMPS adduct.

2.3 Experimental Procedure

Synthesis and characterisation of modified Na⁺-MMT clay using CTAB, AMPS, CPC and 1x, 2x and 3x concentration of CPC-AMPS adduct.

2.4 Materials Required

1. Na montmorillonite clay
2. Cetyltrimethyl ammonium bromide (CTAB)

2. Cetylpyridinium chloride (CPC)
3. 2-acrylamido-2-methylpropane-sulfonic acid (AMPS)

2.5 Synthesis of modified clay using CTAB, AMPS CPC and different concentrations of CPC-AMPS adduct

The clay is modified using the CPC and AMPS. It was synthesized through the exchange of CPC-AMPS adduct. An adduct is the product of direct addition of two or more distinct molecules, resulting in a single reaction product containing all atoms of the reacting compounds. Here the adducts were prepared by treating 1x, 2x and 3x concentrations of AMPS with CPC.

2.5.1 Synthesis of modified clay using CTAB

CTAB modified clay was prepared by reacting aqueous clay suspension with calculated amount of CTAB. 2g of clay having cationic exchange capacity (CEC) of 92.6 meq/100g was dispersed in 100 ml of distilled water taken in a 1000 ml beaker and 1.457g CTAB was dispersed in 50ml distilled water and stirred both for about 30 minutes in a magnetic stirrer. CTAB suspension was added slowly into the clay suspension along with 250ml distilled water. Then it is kept for continuous stirring for 48 hours. The CTAB modified clay suspension resulted was recovered by ultracentrifuge at 1500 rpm for 30 minutes. Finally, the CTAB modified clay was dried overnight in a hot air oven at 60⁰C to obtain CTAB modified clay.

2.5.2 Synthesis of modified clay using AMPS

AMPS modified clay was prepared by reacting aqueous clay suspension with calculated amount of AMPS. 2g of clay having cationic exchange capacity (CEC) of 92.6 meq/100g was dispersed in 100 ml of distilled water taken in a 1000 ml beaker and 0.829g AMPS was dispersed in 50ml distilled water and stirred both for about 30 minutes in a magnetic stirrer. AMPS suspension was added slowly into the clay suspension along with 250ml distilled water. Then it is kept for continuous stirring for 48 hours. The AMPS modified clay suspension resulted was recovered by ultracentrifuge at 1500 rpm for 30 minutes. Finally, the AMPS modified clay was dried overnight in a hot air oven at 60⁰C to obtain AMPS modified clay.

2.5.3 Synthesis of modified clay using CPC

CPC modified clay was prepared by reacting aqueous clay suspension with calculated amount of CPC. 2g of clay having cationic exchange capacity (CEC) of 92.6 meq/100g was dispersed in 100 ml of distilled water taken in a 1000 ml beaker and 1.432g CPC was dispersed in 50ml distilled water and stirred both for about 30 minutes in a magnetic stirrer. CPC suspension was added slowly into the clay suspension along with 250ml distilled water. Then it is kept for continuous stirring for 48 hours. The CPC modified clay suspension resulted was recovered by ultracentrifuge at 1500 rpm for 30 minutes. Finally, the CPC modified clay was dried overnight in a hot air oven at 60⁰C to obtain CPC modified clay.

2.5.4 Synthesis of modified clay using 1x concentration of CPC and AMPS adduct

CPC-AMPS modified clays with 1x concentration were prepared by reacting aqueous clay suspension with calculated amount of CPC and AMPS. 2g of clay having cationic exchange capacity (CEC) of 92.6 meq/100g was dispersed in 100 ml of distilled water taken in a 1000 ml beaker. Similarly, 1x concentration of CPC-AMPS mixture was prepared by taking 0.7160g CPC and 0.4145g AMPS in about 50 ml of water in a 250 ml beaker. The above dissolved suspensions were stirred separately for about 30 minutes in magnetic stirrer. The CPC-AMPS mixture was slowly added to the clay suspension and mixed with 250 ml of distilled water. Then it is kept for continuous stirring for 48 hours. The adduct modified clay suspension resulted was recovered by ultracentrifuge at 1500 rpm for 30 minutes. Finally, the adduct modified clay was dried overnight in a hot air oven at 60⁰C to obtain CPC-AMPS adduct modified clay.

2.5.5 Synthesis of modified clay using 2x concentration of CPC and AMPS adduct

CPC-AMPS modified clays with 2x concentration were prepared by reacting aqueous clay suspension with calculated amount of CPC and AMPS. 2g of clay having cationic exchange capacity (CEC) of 92.6 meq/100g was dispersed in 100 ml of distilled water taken in a 1000 ml beaker. Similarly, 2x concentration of CPC-AMPS mixture was prepared by taking 1.432g CPC and 0.829g AMPS in about 50 ml of water in a 250 ml beaker. The above dissolved suspensions were stirred separately for about 30 minutes in

magnetic stirrer. The CPC-AMPS mixture was slowly added to the clay suspension and mixed with 250 ml of distilled water. Then it is kept for continuous stirring for 48 hours. The adduct modified clay suspension resulted was recovered by ultracentrifuge at 1500 rpm for 30 minutes. Finally, the adduct modified clay was dried overnight in a hot air oven at 60°C to obtain CPC-AMPS adduct modified clay.

2.5.6 Synthesis of modified clay using 3x concentration of CPC and AMPS adduct

CPC-AMPS modified clays with 3x concentration were prepared by reacting aqueous clay suspension with calculated amount of CPC and AMPS. 2g of clay having cationic exchange capacity (CEC) of 92.6 meq/100g was dispersed in 100 ml of distilled water taken in a 1000 ml beaker. Similarly, 3x concentration of CPC-AMPS mixture was prepared by taking 2.1480g CPC and 1.2435g AMPS in about 50 ml of water in a 250 ml beaker. The above dissolved suspensions were stirred separately for about 30 minutes in magnetic stirrer. The CPC-AMPS mixture was slowly added to the clay suspension and mixed with 250 ml of distilled water. Then it is kept for continuous stirring for 48 hours. The adduct modified clay suspension resulted was recovered by ultracentrifuge at 1500 rpm for 30 minutes. Finally, the adduct modified clay was dried overnight in a hot air oven at 60°C to obtain CPC-AMPS adduct modified clay.

2.6 Modification of clay using different concentrations of CPC-AMPS adduct modifiers

2.6.1 Modification of Clay using CTAB

Weight of clay = 2g

Weight of CTAB = 1.457g

Total volume of distilled water = 400ml

2.6.2 Modification of Clay using AMPS

Weight of clay = 2g

Weight of AMPS = 0.829g

Total volume of distilled water = 400ml

2.6.3 Modification of Clay using CPC

Weight of clay = 2g

Weight of CPC = 1.432g

Total volume of distilled water = 400ml

2.6.4 Modification of clay using CPC and AMPS adduct-1x concentration

Weight of clay = 2g

Weight of CPC = 0.7160

Weight of AMPS = 0.4145

Total volume of distilled water = 400ml

2.6.5 Modification of clay using CPC and AMPS adduct-2x concentration

Weight of clay = 2g

Weight of CPC = 1.432g

Weight of AMPS = 0.829g

Total volume of distilled water = 400ml

2.6.6 Modification of clay using CPC and AMPS adduct-3x concentration

Weight of clay = 2g

Weight of CPC = 2.1480g

Weight of AMPS = 1.2435g

Total volume of distilled water = 400ml

2.7 Characterization

2.7.1 Characterization of modified clays using IR analysis

The samples of modified clays using different modifiers were characterized by IR studies. In IR spectroscopy molecules are excited to higher energy state when they absorb infrared radiation. The absorption of infrared radiation is a quantized process. A molecule absorbs only selected frequencies (energies) of infrared radiation. In the absorption process, those frequencies of infrared radiation that match the natural vibrational frequencies of the molecule, and the energy absorbed serves to increase the amplitude of the vibrational motions of the bonds in the molecule. Only those bonds that have a dipole moment that changes as a function of time are capable of absorbing infrared radiation. An infrared spectrometer determines the positions and relative sizes of all the absorptions, or peaks, in the infrared region and plots them on a piece of paper. This plot of absorption intensity versus wavenumber (or sometimes wavelength) is referred to as the infrared spectrum of the compound. [17]

2.7.2 Characterization of modified clays using XRD analysis

The samples of modified clays using different modifiers were characterized by X-ray diffraction studies.

X-ray diffraction relies in the dual wave or particle nature of X-rays to obtain information about the structure of crystalline materials. Primary use of the technique is the identification and characterization of compounds based on

their diffraction pattern. When an incident beam of monochromatic X-rays interacts with a target material the falling rays gets scattered from those atoms within the target material. In an XRD graph, the intensity of reflected X-ray is plotted against 2θ values.

$$n\lambda = 2d\sin\theta$$

Where θ is the angle at which x-ray falls on the sample, n is the order of reflection, λ is the wavelength of monochromatic X-rays and d is the spacing between two similar planes. The d spacing can be calculated using Bragg's equation.

Results and Discussion

3.1 IR Analysis

From the IR spectra of pure and modified clay, additional intense characteristic peaks of various functional groups present in the modifier were observed. In pure clay we can observe characteristic peaks at 3632cm^{-1} , 1046cm^{-1} and 460cm^{-1} due to structural hydroxyls present in the pure clay, Si-O-Si asymmetric stretching of silicate clays and Si-O-Si bending respectively. CTAB modified clay shows additional intense characteristic peaks at 2916.70 cm^{-1} and 2848.85 cm^{-1} due to the stretching vibration of CH_3 and CH_2 . AMPS modified clay shows additional intense characteristic peaks at 3387.93 cm^{-1} due to the N-H stretching in Amide, 1628.22cm^{-1} due to C=C Symmetric stretching and at 1537.92 cm^{-1} due to NH bending. CPC modified clay shows additional intense characteristic peaks at 1635.65cm^{-1} due to C=N, 2917.80 cm^{-1} due to the stretching vibration of CH_3 , 2849.52 cm^{-1} due to the stretching vibration of CH_2 and at 997.09cm^{-1} due to C-N. CPC-AMPS adduct modified clay shows additional intense characteristic peaks at 1636.56cm^{-1} due to C=N, 2920.66 cm^{-1} due to the stretching vibration of CH_3 , 2850.26cm^{-1} due to the stretching vibration of CH_2 , 1667.80cm^{-1} due to amide and at 1489.95cm^{-1} due to aromatic C=C. These additional peaks observed in the spectrum of the modified clays indicate that, pure clay was entirely converted into the corresponding organo-modified clay. Which means FT-IR Spectroscopic studies support the successful intercalation of various organo-modifiers on to the inter layers of MMT clay.

3.1.1 IR Spectrum of Pure Clay

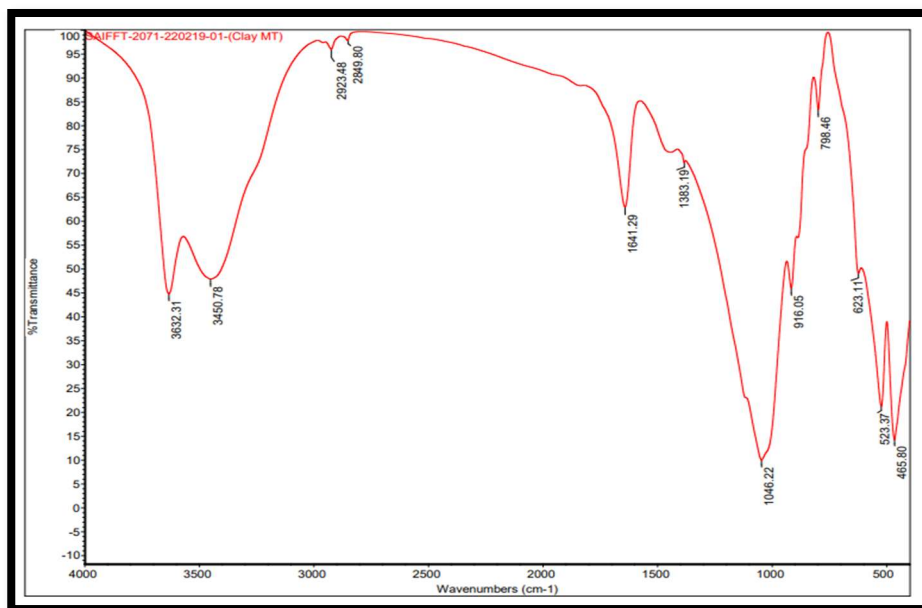


Figure3.1: IR spectrum of MMT clay

The unmodified clay show bands due to Si-O-Si asymmetric stretching of silicate clays at 1046.22cm^{-1} , Si-O-Si bending at 465.80 cm^{-1} and structural hydroxyls at 3632.31 cm^{-1} .

3.1.2 IR Spectrum of CTAB MC

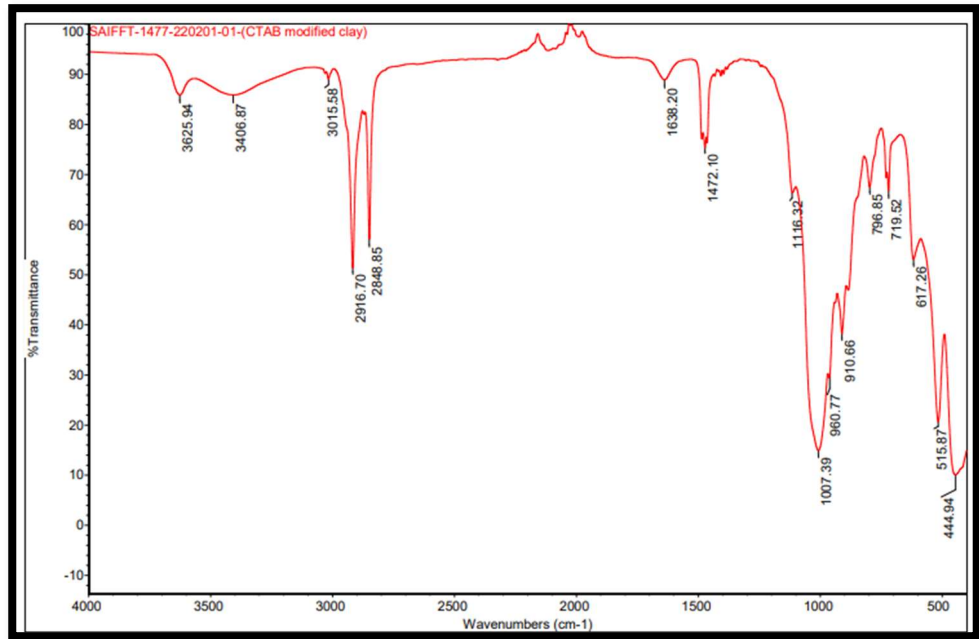


Figure 3.2: IR spectrum of CTAB MC

CTAB modified clay shows additional intense characteristic peaks at 2916.70 cm^{-1} and 2848.85 cm^{-1} due to the stretching vibration of CH_3 and CH_2 .

3.1.3 IR Spectrum of AMPS MC

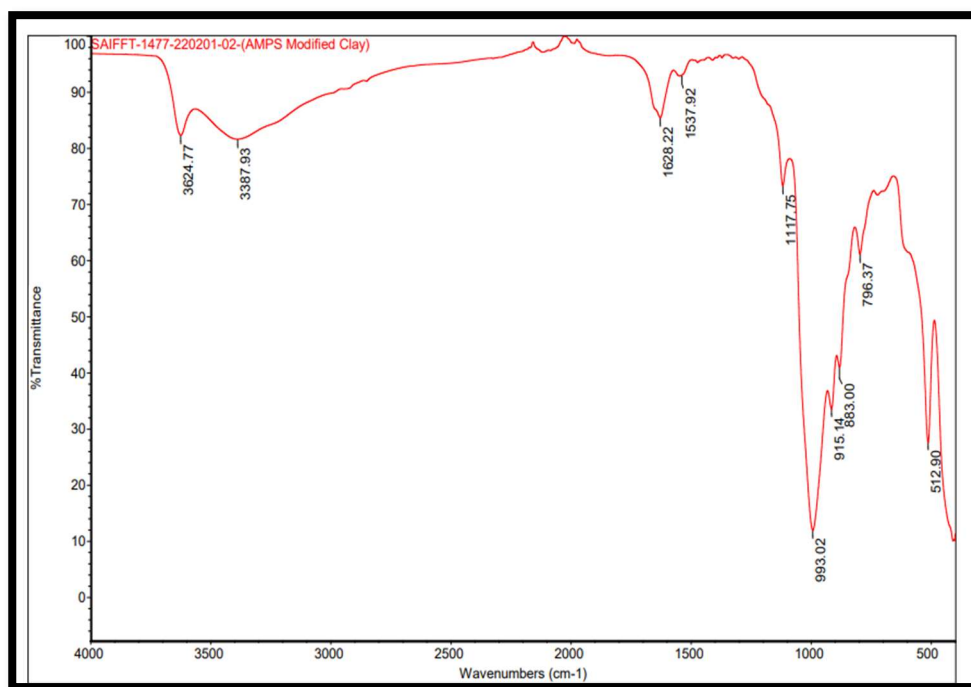


Figure3.3: IR spectrum of AMPS MC

AMPS modified clay shows additional intense characteristic peaks at 3387.93 cm^{-1} due to the N-H stretching in Amide, 1628.22 cm^{-1} due to C=C Symmetric stretching and at 1537.92 cm^{-1} due to NH bending.

3.1.4 IR Spectrum of CPC MC

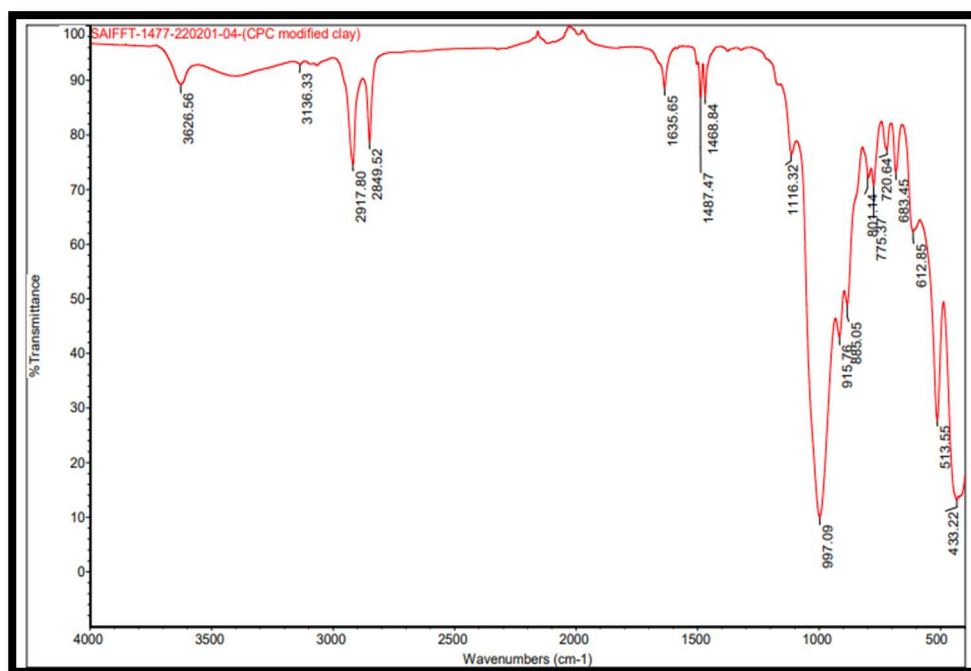


Figure 3.4: IR spectrum of CPC MC

CPC modified clay shows additional intense characteristic peaks at 1635.65cm^{-1} due to C=N, 2917.80cm^{-1} due to the stretching vibration of CH_3 , 2849.52cm^{-1} due to the stretching vibration of CH_2 and at 997.09cm^{-1} due to C-N.

3.1.5 IR Spectrum Of CPC-AMPS adduct (1x)

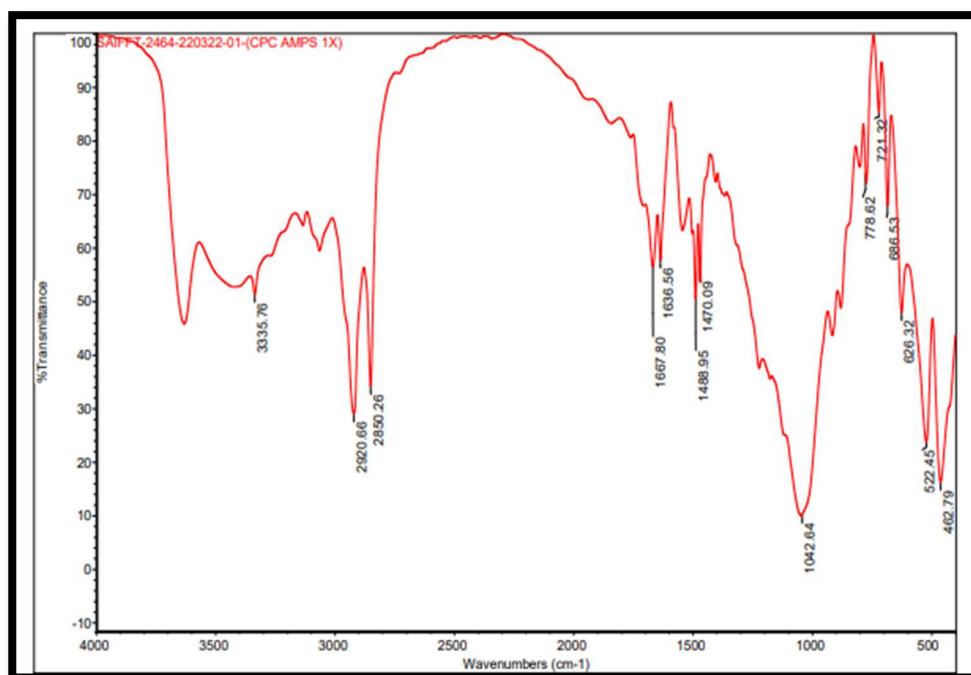


Figure 3.5: IR spectrum of CPC-AMPS adduct (1x)

CPC-AMPS adduct modified clay shows additional intense characteristic peaks at 1636.56cm^{-1} due to C=N, 2920.66 cm^{-1} due to the stretching vibration of CH₃, 2850.26cm^{-1} due to the stretching vibration of CH₂, 1667.80cm^{-1} due to amide and at 1489.95cm^{-1} due to aromatic C=C.

3.1.6 IR Spectrum Of CPC-AMPS adduct (2x)

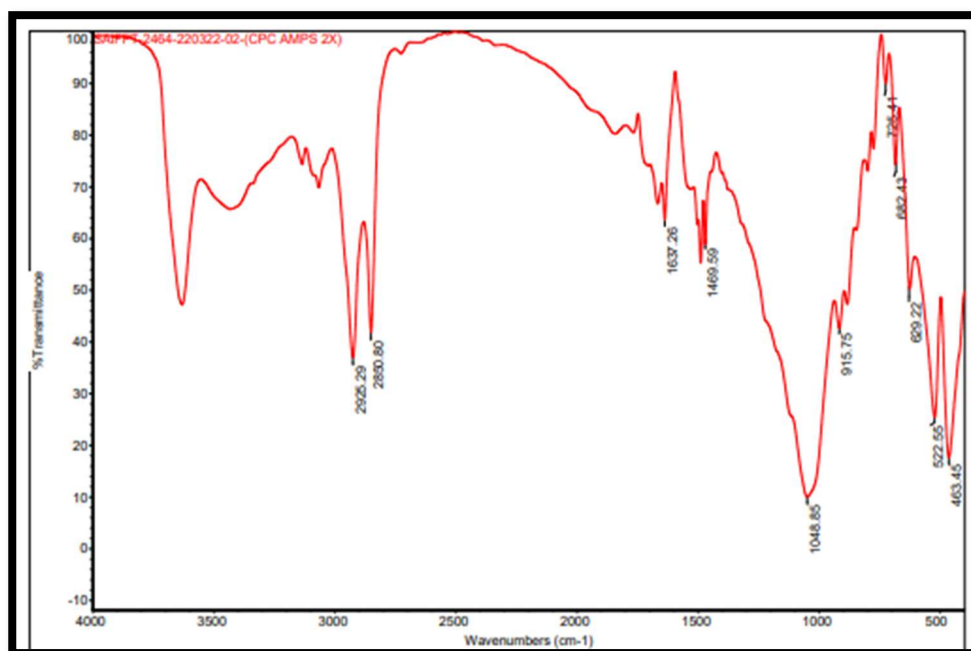


Figure 3.6: IR spectrum of CPC-AMPS adduct (2x)

CPC-AMPS adduct modified clay shows additional intense characteristic peaks at 1637.26cm^{-1} due to C=N, 2925.29 cm^{-1} due to the stretching vibration of CH₃, 2850.80 cm^{-1} due to the stretching vibration of CH₂, and at 1469.59cm^{-1} due to aromatic C=C.

3.1.7 IR Spectrum Of CPC-AMPS adduct (2x)

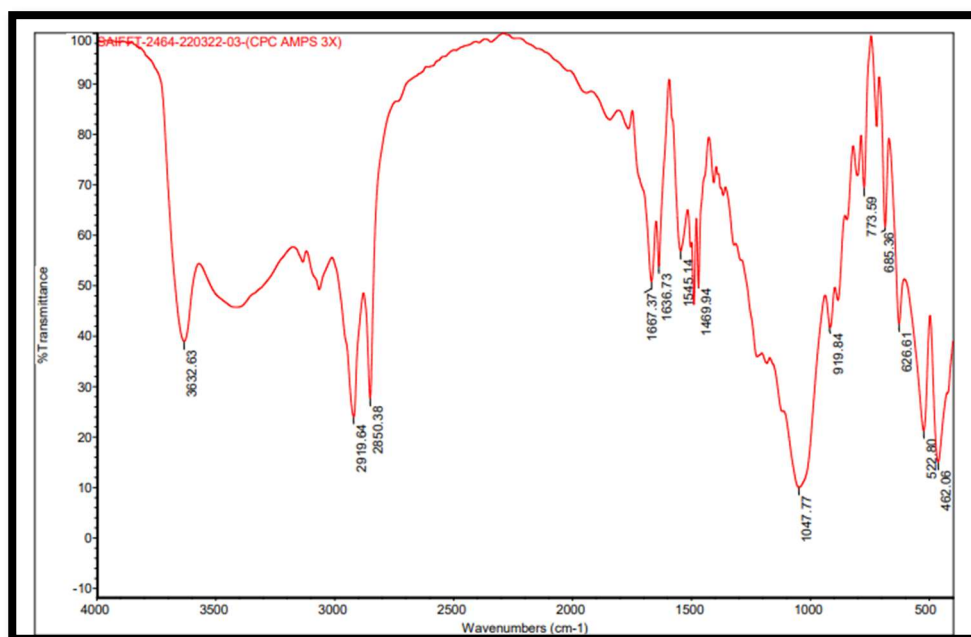


Figure 3.7: IR spectrum of CPC-AMPS adduct (3x)

CPC-AMPS adduct modified clay shows additional intense characteristic peaks at 1636.73cm^{-1} due to C=N, 2919.64 cm^{-1} due to the stretching vibration of CH₃, 2850.38 cm^{-1} due to the stretching vibration of CH₂, 1667.37cm^{-1} due to amide and at 1469.94cm^{-1} due to aromatic C=C.

3.2 XRD Analysis

Extent of the cationic exchange was further analyzed by XRD technique. It was observed from the XRD analyses that the (001) reflection of all the modified clay appeared at smaller angles (2θ) as compared to pristine clay indicating successful ion exchange. The d spacing for pristine clay is 1.24nm ($2\theta = 7.110^\circ$). The d spacing shown by CTAB MC is 1.99nm ($2\theta = 4.417^\circ$), AMPS MC is 1.50nm ($2\theta = 5.60^\circ$), CPC MC is 2.05nm ($2\theta = 4.290^\circ$). Among these CPC MC have maximum d spacing. This is due to the presence of aromatic ring. As the carbon chain length increases, intercalation chemistry of clay also increases. The d spacing shown by CPC-AMPS adduct (1x) is 2.07nm ($2\theta = 4.247^\circ$), CPC-AMPS adduct (2x) is 2.5nm ($2\theta = 3.529^\circ$) and CPC-AMPS adduct (3x) is 2.93nm ($2\theta = 3.011^\circ$). Clay modified using CPC-AMPS adduct (3x) shows maximum d spacing. As the concentration of modifier increases the d spacing also increases.

3.2.1 XRD Spectrum of Pure Clay

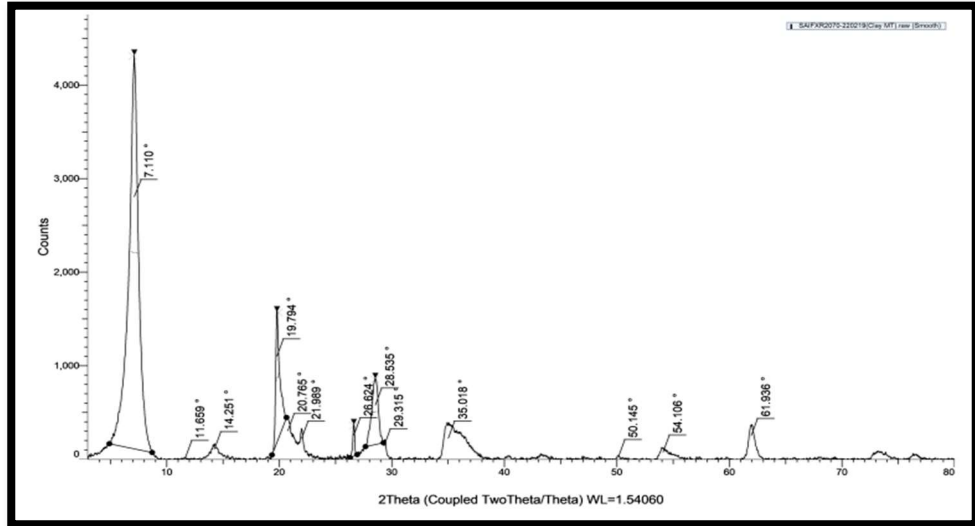


Figure 3.8: XRD spectrum of MMT clay

3.2.2 XRD Spectrum of CTAB

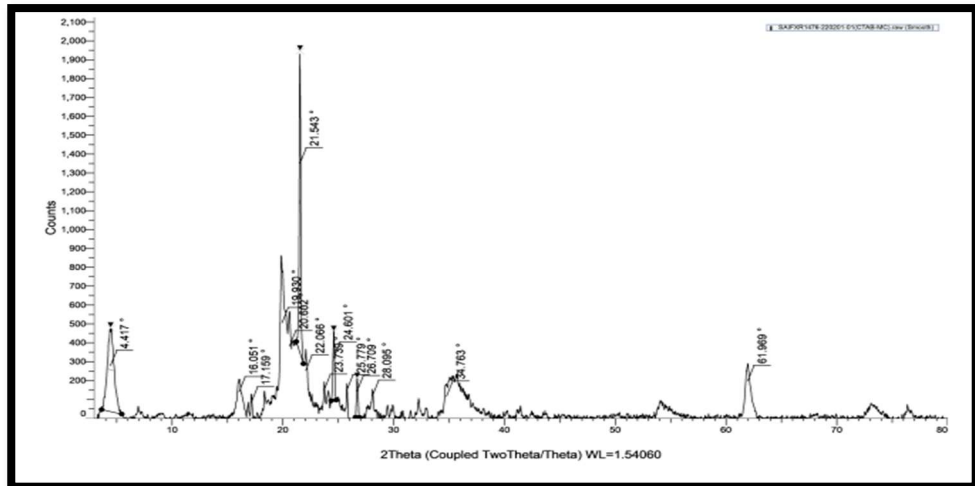


Figure 3.9: XRD spectrum of CTAB

3.2.3 XRD Spectrum of AMPS

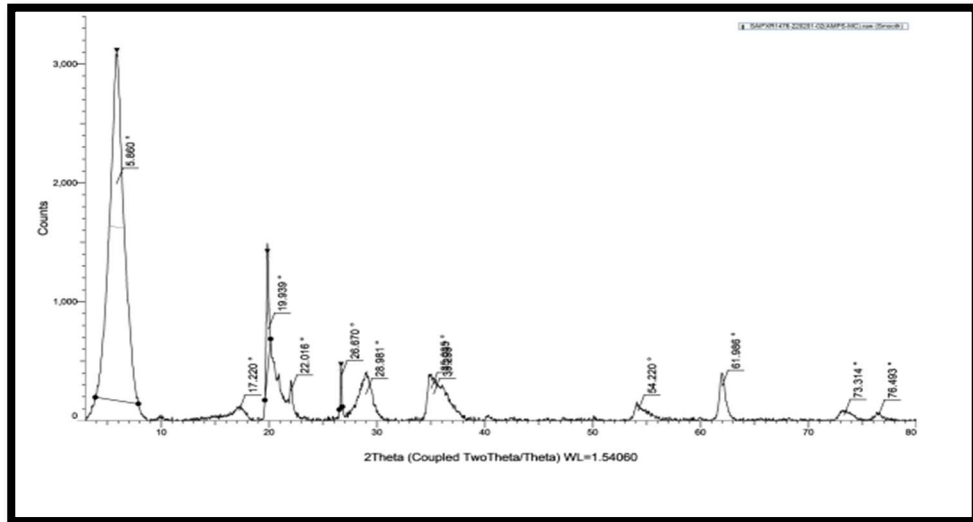


Figure 3.10: XRD spectrum of AMPS

3.3.3 XRD Spectrum of CPC

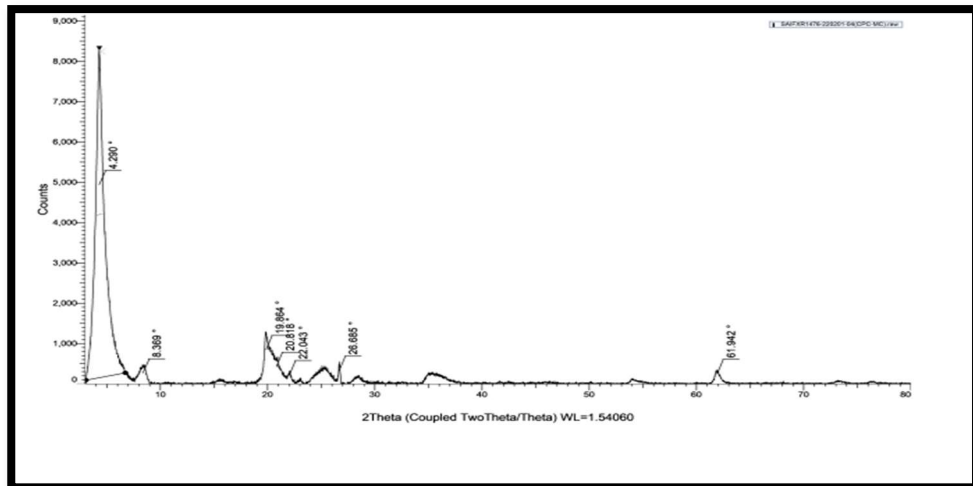


Figure 3.11: XRD spectrum of CPC

3.3.4 XRD Spectrum of CPC-AMPS adduct (1x)

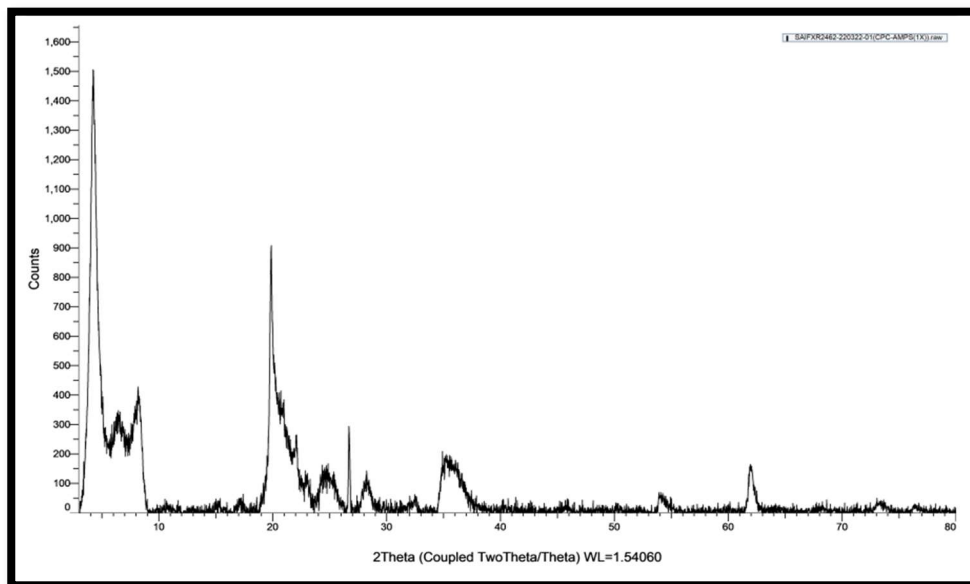


Figure 3.12: XRD spectrum of CPC-AMPS adduct (1x)

3.3.5 XRD Spectrum of CPC-AMPS adduct (2x)

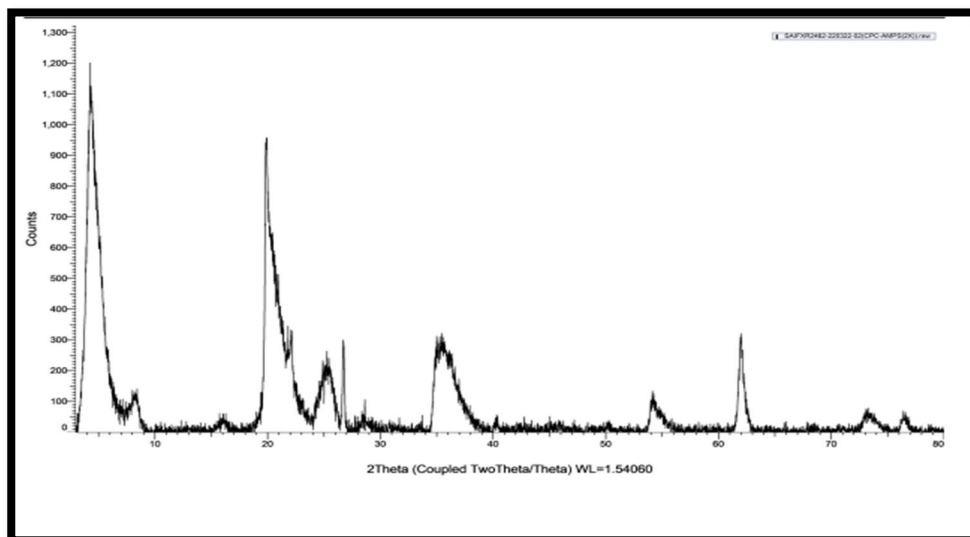


Figure 3.13: XRD spectrum of CPC-AMPS adduct (2x)

3.3.6 XRD Spectrum of CPC-AMPS adduct (3x)

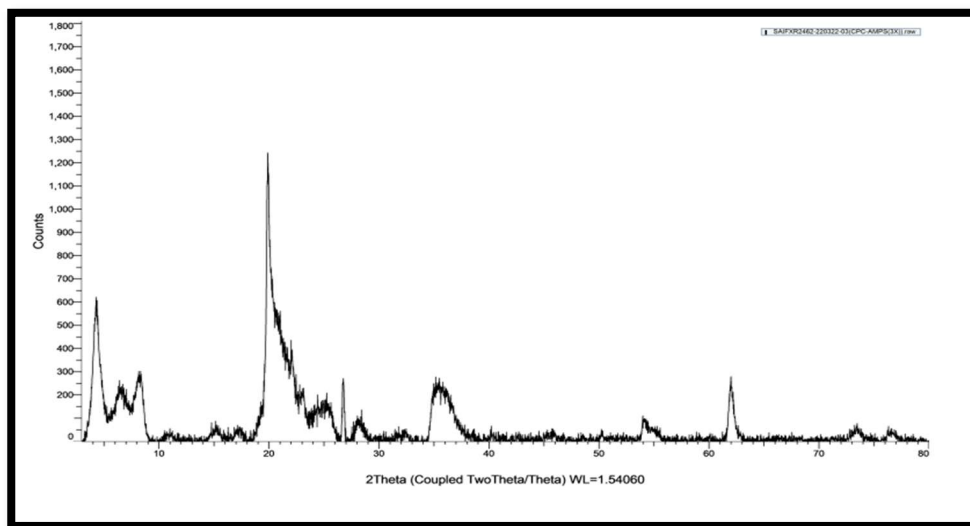


Figure 3.14: XRD spectrum of CPC-AMPS adduct (3x)

Sample	2 θ (°)	d (nm)
Clay	7.110	1.24
CTAB	4.417	1.99
AMPS	5.60	1.50
CPC	4.290	2.05
CPC-AMPS adduct (1x)	4.247	2.07
CPC-AMPS adduct (2x)	3.529	2.5
CPC-AMPS adduct (3x)	3.011	2.93

Table 2: XRD analysis data

Conclusion

Clays are layered silicates, comprising several stacks of hydrated aluminosilicates with thickness 1nm and lateral dimensions of 50- 1000nm. Nowadays clays have been widely used as nanofillers for thermoplastics like polypropylene, polystyrene and nylon due to its natural abundance, low cost and broadest commercial viability. In its pristine state, clay is hydrophilic and the miscible only with hydrophilic polymers whereas most of the polymers are organophilic. Therefore, the surface often requires organo-modification to make the platelets compatible with organophilic polymer matrix. Our project deals with the synthesis of a facile, cost-effective method for clay modification using different modifier concentration of CPC-AMPS adduct. The intercalation of clay by CTAB, AMPS, CPC and different concentrations of CPC-AMPS adduct is confirmed by XRD analysis, in which the (001) reflection of all the Adduct modified clay (AMC) appeared at smaller angles (2θ) as compared to the pristine clay indicating the successful ion exchange. From the results among CTAB, AMPS and CPC the highest d spacing is shown by CPC MC and among 1x, 2x and 3x concentrations of CPC-AMPS adduct highest d spacing is shown by CPC-AMPS (3x). On comparing these results, it can be concluded that as the length of chain increases intercalation of clay also increase. It can also be concluded that as the concentration of the modifier increase d spacing also increase.

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