PROJECT REPORT

On

"EXPLORING THE CONCENTRATION EFFECT OF ACID-AMINE ADDUCT TO THE INTERGALLERY OF Na$^+$-MONTMORILLONITE"

Submitted by

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In partial fulfilment for the award of the
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B.Sc. CHEMISTRY PROJECT REPORT

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This is to certify that the project "**EXPLORING THE CONCENTRATION EFFECT OF ACID-AMINE ADDUCT TO THE INTERGALLERY OF Na$^+$-MONTMORILLONITE**" is the work done by **ANN TREESA THOMAS, ANUSHA JOHN K, MARIYA DAS, SREELAKSHMI RAMESAN.**

Dr. Ushamani M   **Dr. Annu Raju**
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Submitted to the Examination of Bachelor's Degree in Chemistry

Date   :……………

Examiners:………………………………….

DECLARATION

We hereby declare that the project work entitled "**EXPLORING THE CONCENTRATION EFFECT OF ACID-AMINE ADDUCT TO THE INTERGALLERY OF Na$^+$-MONTMORILLONITE**" submitted to Department of Chemistry, St. Teresa's College (Autonomous) affiliated to Mahatma Gandhi University, Kottayam, is a record of an original work done by me under the guidance of Dr. Annu Raju, Assistant Professor, Department of Chemistry, St. Teresa's College (Autonomous), Ernakulam and this project work is submitted in the partial fulfilment of the requirements for the award of the degree of Bachelor of Science in Chemistry.

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Chapter 1

Introduction

Clays have been receiving a lot of attention over the years. Clay minerals belong to the main group of silicates with layered structure known as layered silicates [1]. Recently, they have received a great deal of attention for its ability to impart mechanical reinforcement [2, 3, 4], gas barrier [5,6] and even flame retardant characteristics to polymers [7]. Also because of the low price, availability, high aspect ratio as well as desirable nanostructure and interfacial interactions, clays can provide dramatic and adjustable improved properties at very lower loadings without the sacrificing of pure polymer processability. Nowadays, clays have been widely used as nanofillers for thermoplastics like polypropylene, polyethylene, polystyrene and nylon due to its natural abundance, low cost and broadest commercial viability. In order to promote clay dispersion in polymer matrices, organically modified clays or organoclays are commonly used, providing strong interaction between polymers and nanoparticles which facilitates formation of intercalated and/or exfoliated morphologies [8]. Hence, the process of Organomodification is of great importance in accordance with its wide variety of applications and uses.

Organoclays are highly effective in removing oils, greases and other high molecular weight, low solubility organic compounds from aqueous streams. The use of organo-clays in wastewater treatment has become commonplace in industry today [10].They are used in cosmetics, paint, personal care products, as adsorbents of organic pollutants [1] etc. The most interesting and promising applications of the organo-modified clays

currently are polymer clay nanocomposite (PCN), as sorbents, catalyst and biomaterials.

1.1 Layered Silicates

The layered silicates are natural or synthetic minerals consisting of the regular stacks of aluminosilicate layers with a high aspect ratio and high surface area. Layered silicates are easily available and have low cost. The current most popular layered silicates used in polymer nanocomposites preparation are clays.

Clay is referred to a part of soil fraction with the particle size of less than 2 μm. The clay layers have a thickness of about 1 nm which is in the nanoscale. There are many members of clays with some difference in their formula, structure and properties including swelling and exfoliation. Those members who are able to be exfoliated by polymer chains or monomers and distributed as individual clay layers within polymer matrix are suitable for the preparation of polymer nanocomposites. The individual clay layers can cause to the dramatic improvements in polymer properties due to their high aspect ratio and high interfacial interactions with polymer matrix.

1.2 Structure of Clay

Clays are layered silicates, comprised of stacks of hydrated aluminosilicate with thickness of minimum 1 nm and lateral dimension of 50-1000 nm. Their basic building blocks are tetrahedral sheets [fig 1.1] in which silicon is surrounded by four oxygen atoms and octahedral sheets [fig 1.2] in which a metal like aluminium is surrounded by eight oxygen atoms. The tetrahedral and octahedral sheets are fused together by sharing

the oxygen atoms. Unshared oxygen atoms are present in hydroxyl form. Tetrahedral and octahedral sheets stack naturally in specific ratio and mode, leading to the formation of 1:1(e.g. in kaolinite), 2:1 layered silicates or phyllosilicates etc.

In 1:1 layered structures known as kaolin group having general composition $Al_2Si_2O_5(OH)_5$ and with a layer thickness of ~ 0.7 nm, a tetrahedral sheet is fused with an octahedral sheet, whereby the oxygen atoms are shared [11]. On the other hand, the crystal lattice of 2:1 layerd silicates (or 2:1 phyllosilicates), consists of two- dimensional layers where a central octahedral sheet of alumina is fused to two external silica tetrahedra by the tip, so that the oxygen ions of the octahedral sheet also belong to the tetrahedral sheets, as shown in [fig1.3]. The layer thickness is around 1nm and the lateral dimensions may vary from 300Å to several microns, and even larger, depending on the particulate silicate, the source of the clay and the method of preparation (e.g. clays prepared by milling typically have lateral platelet dimensions of approximately 0.1-1.0 μm). Therefore, the aspect ratio of these layers (ratio length/thickness) is particularly high, with values greater than 1000 [11-13]

The basic 2:1 structure without interlayer ion (or any substitution of atoms) which is electrostatically neutral is called pyrophyllite. Due to the

absence of interlayer ions, the layers do not expand in water. Therefore,

pyrophyllite has only an external surface and essentially no internal one.
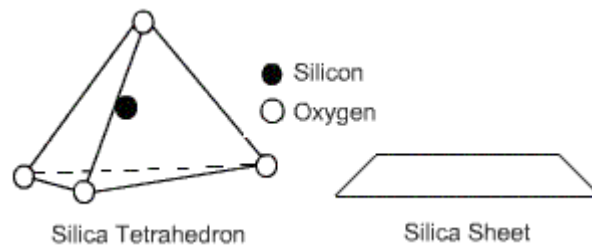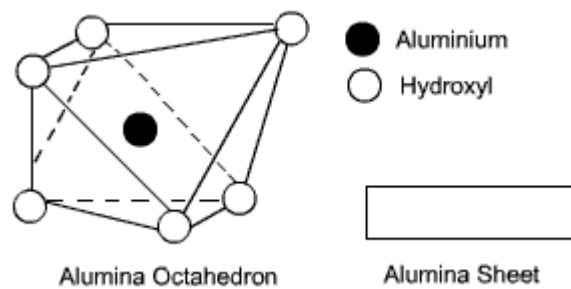

Fig 1.1: *Silica sheet*

Fig1. 2: *Alumina sheet*

When silicon in tetrahedral sheet is substituted by aluminium, the resulting

structure is called mica. Due to this substitution, the mineral is

characterised by a negative surface charge, which is balanced by interlayer

potassium cations. However, because the size of the potassium ions

matches the hexagonal hole created by the Si/Al tetrahedral layer, it is

able to fit very tightly between the layers. Consequently the 2:1 layers are

held together by the electrostatic attraction between the negatively charged

tetrahedral layer and the potassium cations and the swelling or exfoliation of layers is not possible. Therefore, micas do not swell in water and, like pyrophyllite, have no internal surface [14].
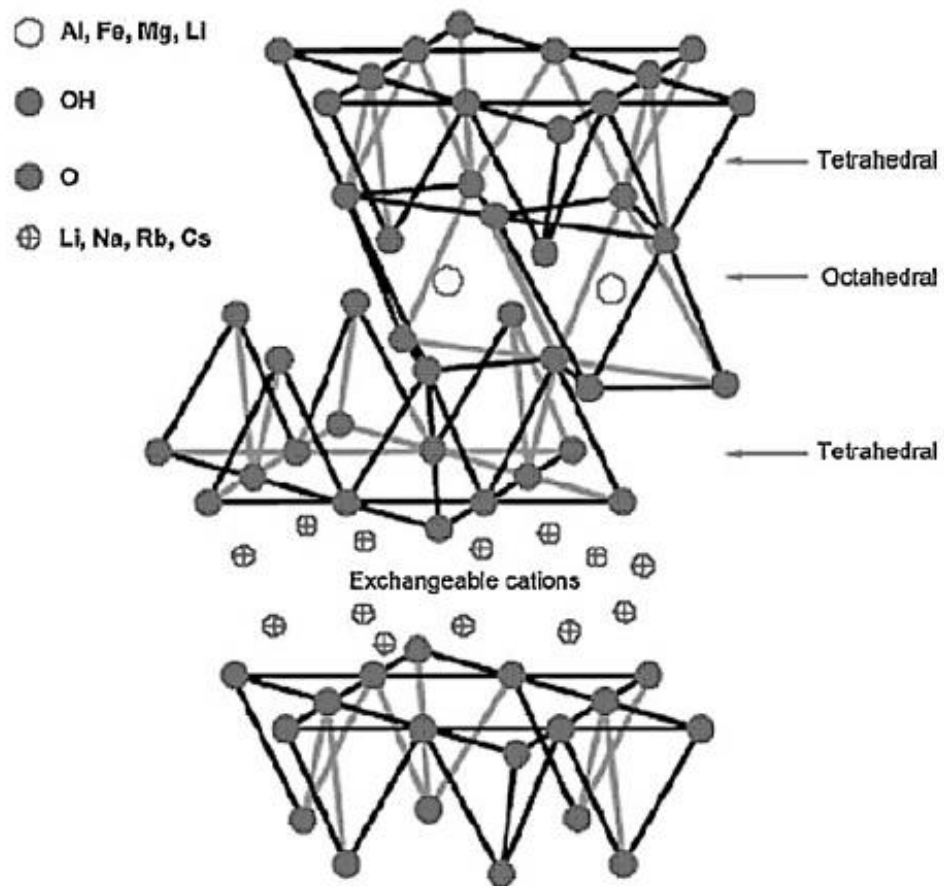

Fig 1.3: *The structure of 2:1 layered silicate [11].*

On the other hand, if in the original pyrophyllite structure the trivalent Al-cation in the octahedral layer is partially substituted by the divalent Mg^{2+} or Fe^{2+} cations, the structure of smectite clays is formed. In this case, the overall negative charge is balanced by sodium and calcium ions, which exist, hydrated in the interlayer [15]. A particular feature of the resulting

structure is that, since these ions do not fit in the tetrahedral layer, as in mica, and the layers are held together by relatively weak forces, water and other polar molecules can enter between the unit layers, causing the lattice to expand [16]. Hence, the presence of interlayer cations causes to an interlayer spacing. The layers are held together with a regular gap between them. The gap is called interlayer or intergallery. The thickness of the repeated units in a regular multilayer structure containing one layer and one inter layer space is called d-spacing (d_{001}) or basal spacing. The basal spacing of clays can be measured from X-ray diffraction patterns. The charges created on the layers vary from layer to layer and so, an average charge value is considerd for the layers which can be determined by a measurement called cation exchange capacity (CEC). The cation exchange capacity (CEC) is expressed as M equiv/ 100g clay [Table 1.1]. Smectite group can be further divided in to montmorilllonite (MMT), nontronite, and saponite and hectorite species.

The electrostatic and Van der Waals forces holding the layers together are relatively weak and inter layer distance varies depending on the charge density on the layers, inter layer cation radius and its degree of hydration. Because of the inter layer spacing and weak interlayer forces, the cations present between the layer can be hydrated in aqueous solutions, well known as clay swelling. The swelling causes further increasing of inter layer space. The charge density on the clay layers is different in various clay groups with different clay structures [17]. Due to the inter layer spacing and weak forces between layers, especially in the hydrated form, other molecules also can be intercalate between layers, leads to the expanding of layered lattice and finally may be caused to the separation of individual layers.

Montmorillonite (or Mg-smectite clays)- It is the most commonly used nanoclay raw material.It is the Mg form of smectite .It is the family of 2:1 phyllosilicate clays having permanent layer charge. Montmorillonite can expand by several times its orginal volume when it comes in contact with water.They have very high specific surface (i.e., internal surface>> external surface area) and high cation exchange capacity (CEC) .

Table 1.1: *Chemical formula and cation exchange capacity (CEC) of commonly used 2:1 phyllosilicates*

Silicate	Formula	CEC (m equiv/100 g)
Montmorillonite	Mx(Al4-xMgx)Si8O20(OH)4	92.6–120
Hectorite	Mx(Mg6-x Lix)Si8O20(OH)4	120
Saponite	MxMg6(Si8-xAlx)Si8O20(OH)4	86.6
Vermiculite	(Mg, Fe, Al)3[(Al, Si)4O10](OH)2Mx-nH2O	150

M represents exchangeable cation and x is the layer charge

In the manufacture of nanocomposite materials, montmorillonite, hectorite and saponite are the layered silicates that are most commonly used. The reason why these materials have received a great deal of attention recently, as reinforcing materials for polymers, is their potentially high aspect ratio and the unique intercalation/exfoliation characteristics.

In its pristine state clay is hydrophilic and miscible only with hydrophilic polymers. Therefore the clay surface often requires organo modification to make the platelets compatible with organophilic polymer matrix

1.3 Organoclay

Modification of clay layers with hydrophobic agents is necessary in order to render the clay layers more compatible with polymer chains. This is a surface modification which causes to the reduction of surface energy of clay layers and match their surface polarity with polymer polarity. The organoclays with lowered surface energy are more compatible with polymers and polymer molecules are able to intercalate within their interlayer space or galleries under well- defined experimental condition.

The surface modification of clay layers can be achieved through a cation exchange process by the replacement of sodium and calcium cations present in the interlayer space or clay galleries by alkylammonium or alkylphosphonium (onium) cations [18]. In addition to the surface modification and increasing the hydrophobisity of clay layers, the insertion of alkylammonium or alkylphosphonium cations into the galleries causes to some degree of increasing in the interlayer spacing which promotes the following intercalation of polymer chains into the galleries during nanocomposite preparation [19]. Also the alkylammonium

or alkylphosphonium cations can provide functional groups which interact with polymer chains or initiate the polymerization and therefore increase the interfacial interactions. [Fig1.4] schematically shows the organically modification of clay layers using alkylammonium cations via the ion exchange process.
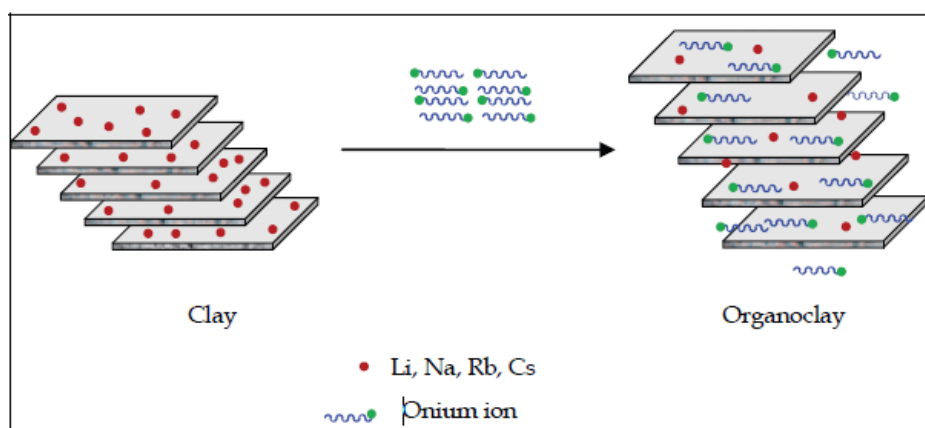

Fig 1.4*: Scheme of the modification of clay layers by organic onium ions.*

In order to obtain the exchange of the onium ions with the cation in the galleries, water swelling of the silicates is needed. For this alkali cations are preferred in the galleries because divalent and higher valent cations prevent swelling by water as they cannot be easily hydrated. Indeed, the hydrate formation of monovalent intergallery cations is the driving force for water swelling. Natural clays may contain divalent cations such as calcium and require exchange procedures with sodium prior to further treatment with onium salts [20].The alkali cations, as they are not structural, can be easily replaced by other positively charged atoms or molecules, and thus are called exchangeable cations [21].

The organic cations lower the surface energy of the silicate surface. Moreover, the long organic cations of such surfactants, with positively charged ends, are tethered to the surface of the negatively charged silicate

layers, resulting in an increase of the intergallery height [22]. It then becomes possible for organic species (i.e. polymers) to diffuse between the layers and eventually separate them [23]. Sometimes, the alkylammonium cations may even provide functional groups that can react with the polymer or initiate polymerization of monomers [16]. Conclusively, the surface modification both increases the basal spacing of clays and serves as a compatibilizer between the hydrophilic clay and the hydrophobic polymer [23].

The excess negative charge of layered silicates and their capability to exchange ions is quantified by a specific property known as the cation-exchange capacity (CEC) and expressed in mequiv/g. This property is highly dependent on the nature of the isomorphous substitutions in the tetrahedral and octahedral layers and therefore on the nature of the soil where the clay was formed. The charge of the layer is not locally constant, as it varies from layer to layer and must rather be considered as an average value over the whole crystal.

In general, the longer the surfactant chain length, and the higher the charge density of the clay, the further apart the clay layers will be forced. This is expected since both of these parameters contribute to increase the interlayer space. For example, Wang et al. prepared organoclays with different alkylammonium chain lengths and found that the interlayer spacing increases with the increase in size of alkylamine chain length.

1.4 Limitations of Conventional Organoclays

The conventional organomodifiers used are alkylammonium or alkylphosphonium cations. These modifiers render the layered silicates organophilic, but they are thermally not stable.

1.5 Structural Characterisation of Modified clay

In order to analyze the structure of the organo-modified clays, two common techniques including X-ray diffraction (XRD) analysis and Fourier Transform Infrared (FT-IR) spectroscopy are widely used. Clays and organoclays show a characteristic peak in XRD analysis due to their regular layered structures. The peak is indicative of the platelet separation or d-spacing in clay structure. Using the peak width at half maximum height and peak position (2θ) in the XRD spectra the inter layer space can be calculated utilizing Bragg's law, $\sin \theta = n \lambda / 2 d$

Where λ is wave length of X-ray 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 inter-layer or d-spacing of a clay lattice by organic modification causes to the change in the position, broadness and intensity of the characteristic peak in XRD spectra. According to the Bragg's law, increase in d-spacing results to the broadening and shifting of related XRD peak toward lower diffraction angles (2θ). By monitoring the position (2θ), shape and intensity of the characteristic peak for organoclay, it is possible to determine the degree of intercalation/exfoliation. Wide angle X-ray diffraction is used to identify the modified clay structures in the range $1^{o} < 2\Theta < 10^{o}$ 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 the pure clay as well as in the organo-modified clay, within 1-4 nm, using the position, broadness and intensity of characteristic peak in WAXD diffractogram.

The FT-IR spectroscopic studies reveal whether the desired chemical groups have been successfully inserted onto the intergallery of the

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modified clay. The modified clay shows additional characteristic peaks other than the bands due to Si-O-Si asymmetric stretching of silicate layer at 1008 cm^{-1} and structural hydroxyls at 3600 cm^{-1}. Thus, FT-IR gives a confirmation that the pristine clay has been effectively converted into the corresponding modified clay.
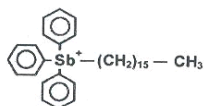
1.6 Common Organic modifiers used in clays

For the process of organomodification of clay, the inorganic cations can be substituted by organic cations, usually by quaternary ammonium salts, which increase the original clay interlayer spacing and behave as organophilic surfactants. The common quaternary ammonium salts used as modifiers are shown in [fig1.5].
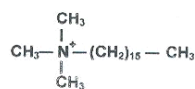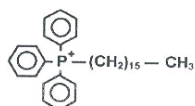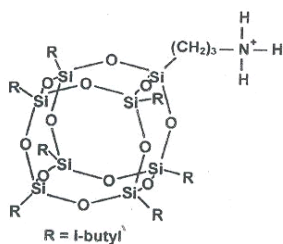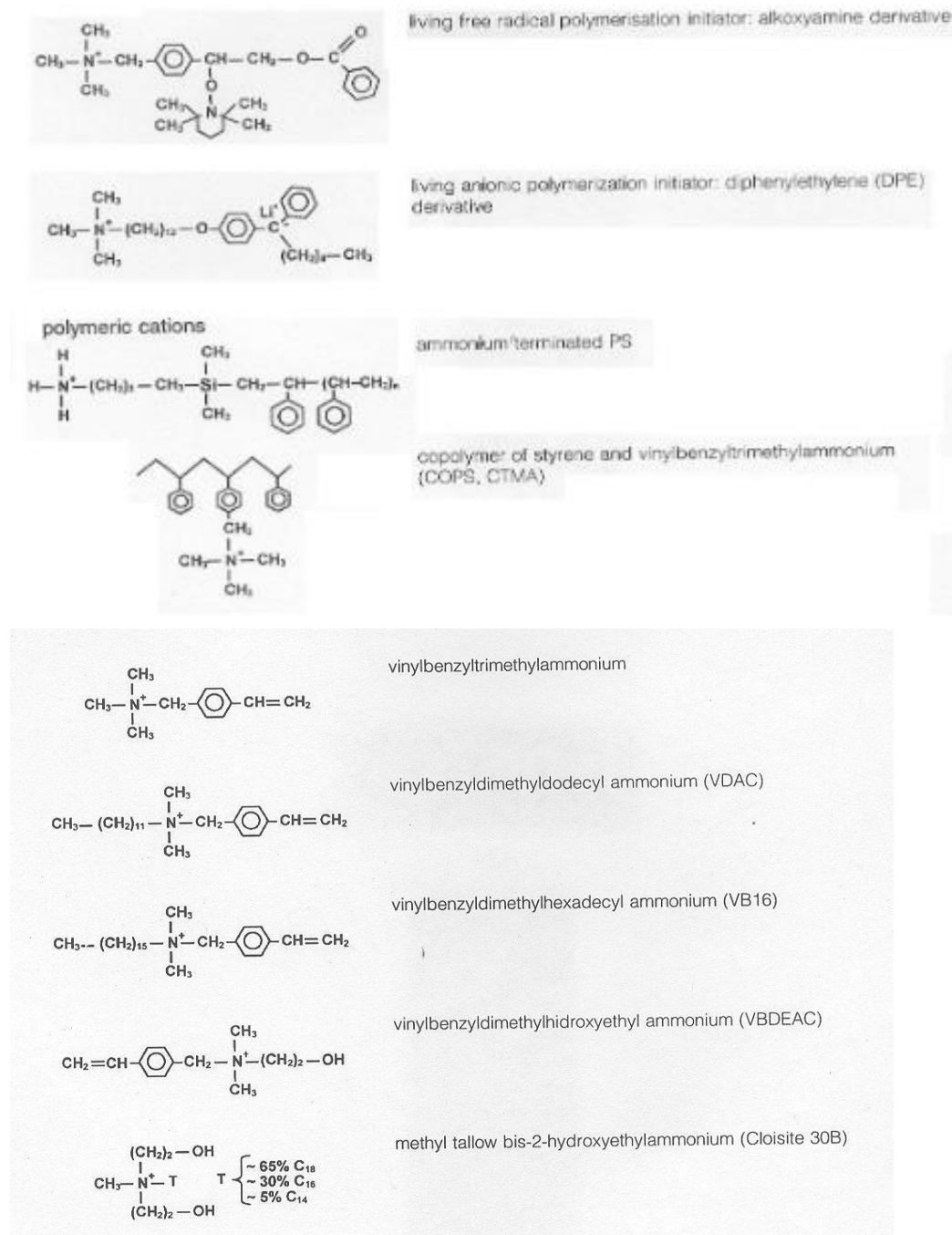
Fig1.5: the common modifiers used for organomodification of clay

1.7 Natural long chain unsaturated aliphatic acid-CTAB adduct as clay modifier

Adducts of quaternary ammonium Salt of natural unsaturated fatty acids having aliphatic long side chains are expected to be better candidate for the preparation of PCNs. In this context Sorbic acid (SA), a natural molecule with unsaturated aliphatic side chain is quite important which can impart better clay-polymer interaction through the unsaturation. Sorbic acid is a fatty acid that occurs naturally and was first isolated from the unripe berries of the Sorbus aucuparia (Rowan tree). It has a faint odour and astrtingent taste. It is crystalline in nature and has a melting point of 134.5°C. It has the chemical formula $CH_3(CH)_4CO_2H$. Its IUPAC name is 2,4-hexadienoic acid [fig1.6]. It reacts with CTAB (cetyl trimethyl ammonium bromide) to form a CTAB-SC adduct [fig1.7].
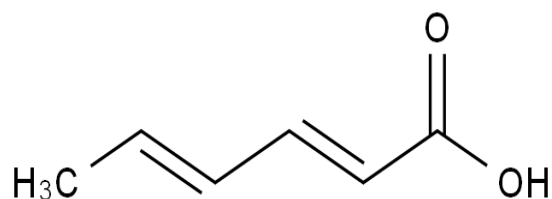

Fig1.6:Structure of Sorbic Acid

$$R'(R)_4N^{\delta+\cdots\cdots}O^{\delta-}\text{-OC-CH=CH-CH=CH-CH3}$$

R': $CH_3(CH_2)_{15}$, R: CH_3

Fig1.7: CTAB-SC Adduct

The cationic exchange between the Na+-MMT clay and the adduct leads
to the insertion of the adduct into the clay intergallery producing modified
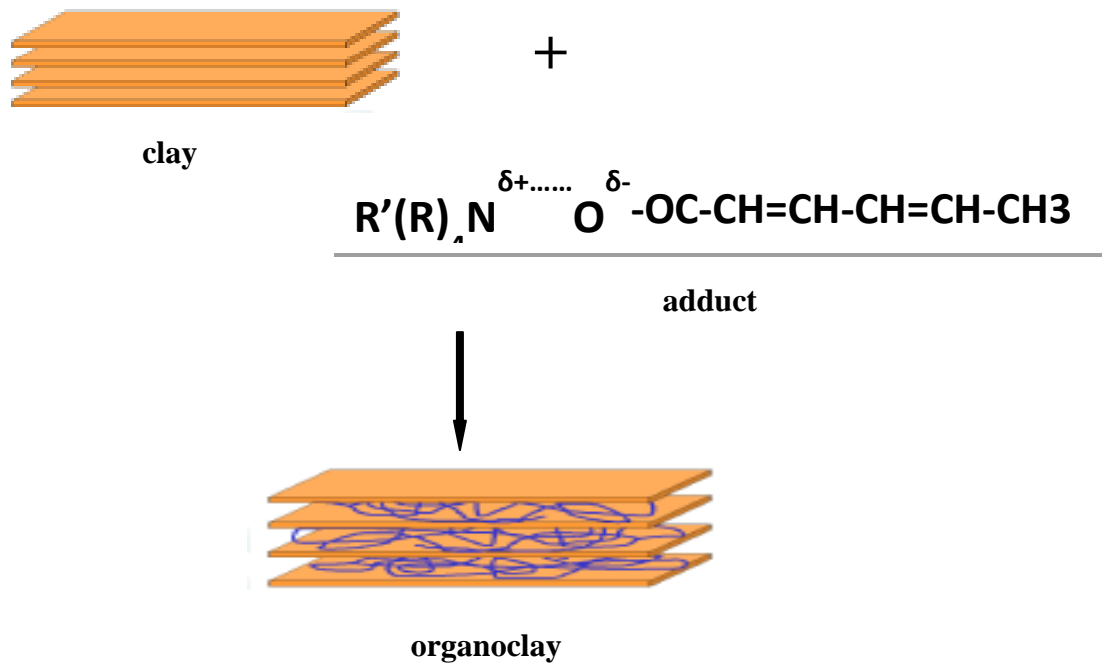organoclay as shown in [fig1.8].

clay $+$

$$R'(R)_3N \overset{\delta+......}{} \overset{\delta-}{O} \text{-OC-CH=CH-CH=CH-CH3}$$

adduct

organoclay

Fig1.8: formation of organoclay

Chapter 2

Materials and Methods

2.1 Work plan

The main aim of the project is to study the concentration effects of Sorbic acid-CTAB adduct on the clay modification and to characterize the corresponding modified clay.

2.2 Work carried out

Synthesis of modified MMT clay using different concentrations of Cetyl Trimethyl Ammonium Bromide (CTAB) –Sorbic acid (SC) adduct.

2.3 Experimental procedure

Synthesis and characterization of modified Na^+-MMT clay using different concentrations of CTAB –Sorbic acid adduct

2.3.1 Materials

Montimorillonite clay (Cloisite-Na^+, Southern Clay Products, USA) of CEC 92.6 meq/100g, Sorbic acid (Loba Chemie Pvt.Ltd, India) and CTAB (Sisco Research Laboratories Pvt.Ltd, India) were used as received.

2.3.2 Synthesis of modified clay using Cetyl Trimethyl Ammonium Bromide –Sorbic acid Adduct

The clay was synthesized via exchange of Na^+ with an acid amine adduct. An adduct is a 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 equimolar concentration of cetyl trimethyl ammonium bromide[CTAB] with an organic acid, sorbic acid.

Sorbic acid modified organoclays were prepared by reacting aqueous clay suspension with calculated amount of the sorbic acid. 1g of clay having cationic exchange capacity (CEC) of 92.6meq/100g was dispersed in 60 ml of distilled water taken in a 500ml beaker and similarly equimolar concentration of the sorbic acid – CTAB mixture was prepared in about 20 ml of water in a 50 ml beaker. The above dissolved suspensions were stirred separately for about 15 minutes. The sorbic acid CTAB mixture was slowly added to the clay suspension and mixed with 120 ml of distilled water. Then it is kept for continous stirring uninterrupted for 48hrs.The adduct modified clay suspension resulted was recovered by ultra-centrifuge at 5000 rpm for 30 minutes. Finally the adduct modified clay was dried overnight in a hot air oven at 80°C to obtain sorbic acid-CTAB adduct modified clay.

This procedure was carried out at different concentrations of modifiers.

2.3.3 Modification of clay at different concentrations of modifiers.

Case 1

Modification of clay using 0.5:0.5 equimolar concentration of modifiers.

Weight of clay =1g

Weight of sorbic acid =0.5605g

Weight of CTAB =. 182225

Total volume of distilled water =200ml

Case 2

Modification of clay using 1:1 equimolar concentration of modifiers.

Weight of clay=1g

Weight of sorbic acid =0.11213g

Weight of CTAB =. 36445g

Total volume of distilled water =200ml

Case 3

Modification of clay using 1.5:1.5 equimolar concentration of modifiers.

Weight of clay =1g

Weight of sorbic acid =1.68195

Weight of CTAB =. 546675g

Total volume of distilled water=200ml

2.4 Characterisation

The samples of modified clay prepared at different concentration were characterised using FT-IR and XRD.

2.4.1 Spectroscopic studies

FT-IR

The goal of analysing the modified clay through FT-IR is to measure how will the modified clay absorb light at each wavelength. Infrared spectroscopy investigates the molecular vibrations. Functional groups can be associated with characteristic infrared absorption bands, which correspond to the fundamental vibrations of the functional groups [24].

XRD

X-ray diffraction relies on the dual wave/particle nature of X-rays to obtain information about the structure of crystalline materials. Primary use of the technique is the identification and characterisation of compounds based on their diffraction pattern. When an incident beam of monochromatic X-rays interact with a target material the falling monochromatic X-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.

Chapter 3

Results and discussion

3.1 FT-IR spectroscopy

Spectroscopic studies back up the successful intercalation of the adduct into the intergallery of the clay. The figures below exhibits the spectra obtained for pristine clay and also for the modified clays at different concentrations. The unmodified clay showed bands due to Si-O-Si assymmetric stretching of silicate layer at 1008 cm^{-1} and structural hydroxyls at 3600 cm^{-1}as shown in [fig3.1]. For all the modified clays, in addition to the above two peaks an intense characteristic peaks at 2850 and 2926 cm^{-1} were observed due to the stretching vibration for –CH$_2$ and –CH$_3$, respectively [figs:3.2, 3.3, 3.4]. These confirm the intercalation of the alkyl group of CTAB in the interlayer of all the modified clays. The characteristic peak at 1645 cm^{-1} was assigned to C=C symmetric stretching and characteristic peak found at 1716 cm^{-1} corresponded to the C=O stretching of unsaturated sorbic acid. The changes in the characteristic peaks for all the three modified clays indicate that the unmodified clay was entirely converted into the corresponding adduct modified clays. And it is also observed that, out of all the three modified clays SC-AMC1.5x have the highest intense characteristics peaks.
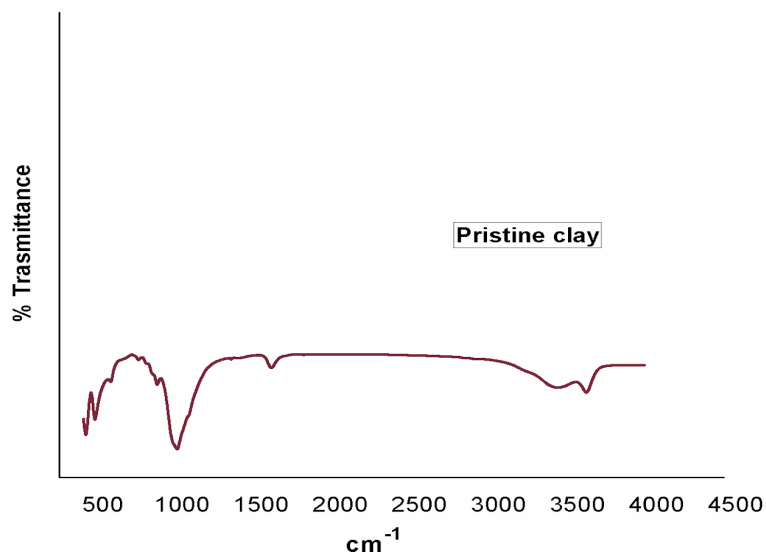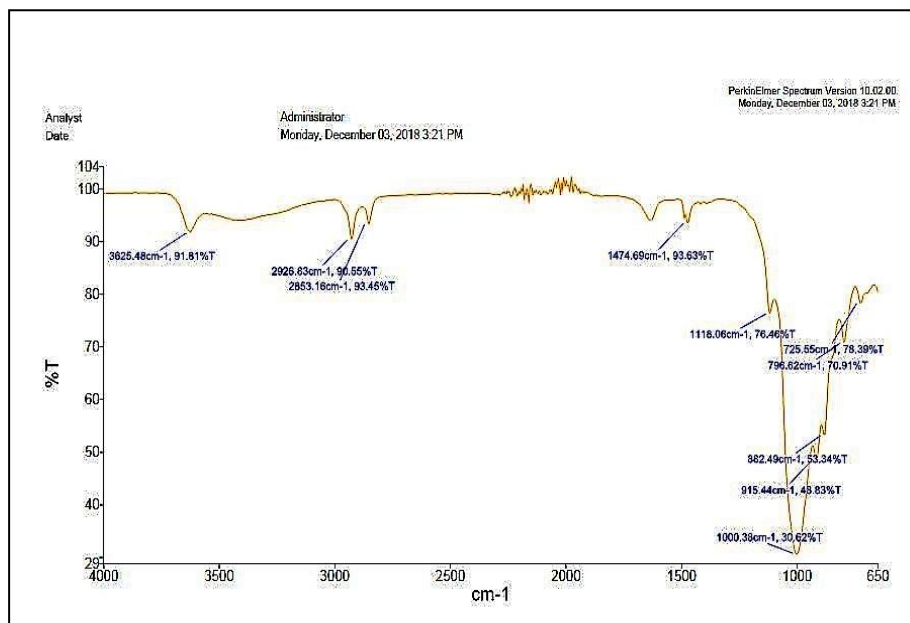
Fig3.1: FTIR- spectra of Pristine Na$^+$-MMT
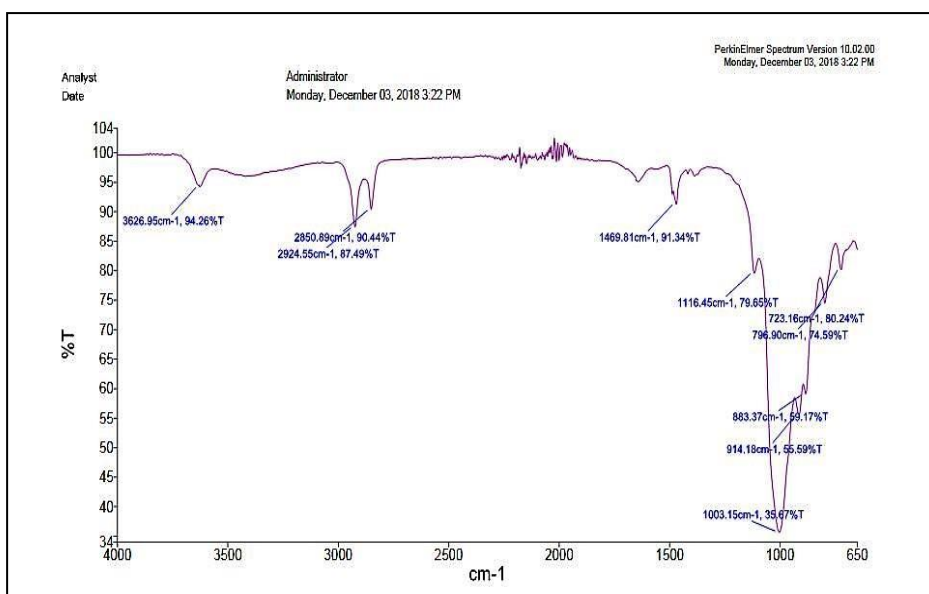

Fig3.2: FTIR- spectra of SC-AMC0.5x
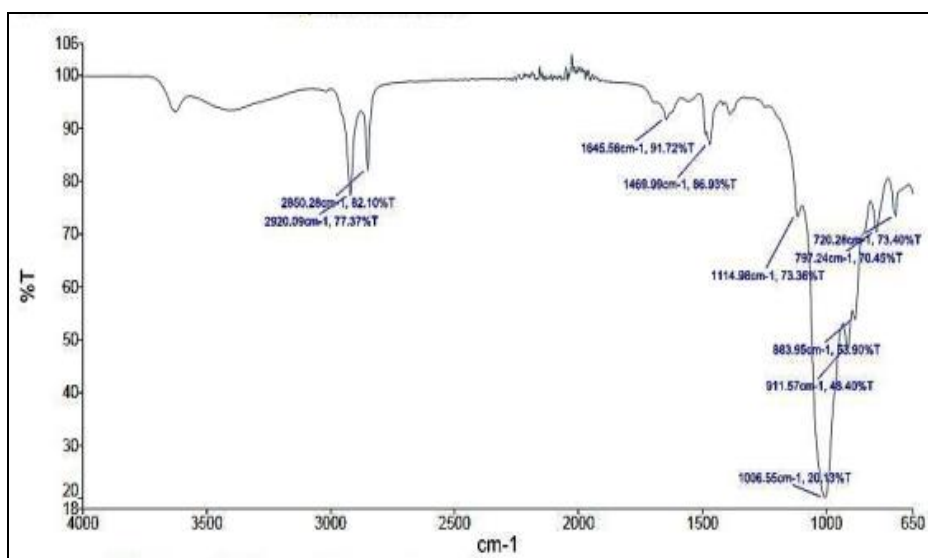
Fig3.3: FTIR- spectra of SC-AMC 1x

Fig3.4: FTIR- spectra of SC-AMC1.5x

3.2 XRD Analysis

Extent of the cationic exchange was further confirmed by WAXS analysis, and the results were plotted in the figures below [fig3.5, 3.6].
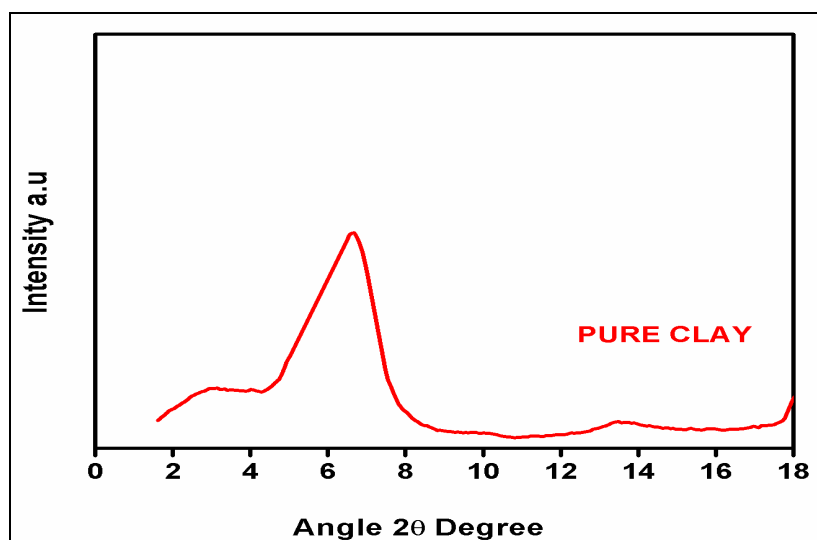

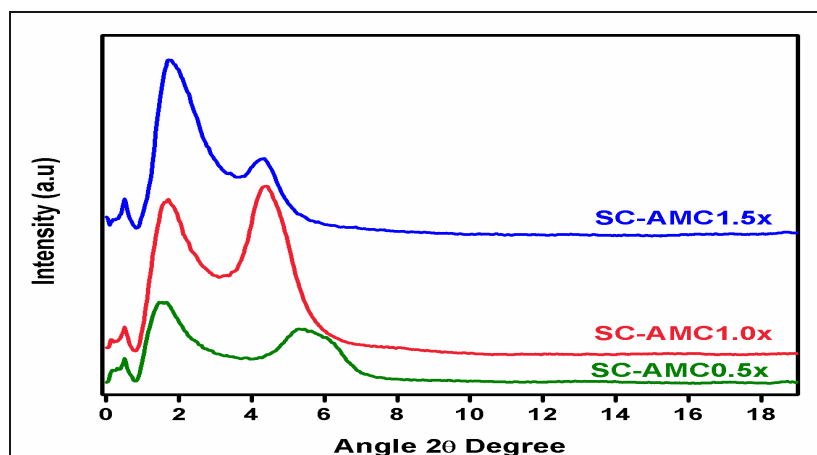**Fig3.5:WAXS diffraction patterns of Pristine Na+-MMT**

Fig3.6:Wide-angle powder X-ray diffraction patterns of SC-AMC0.5x, SC-AMC1x, and SC-AMC1.5x

It was observed that the (001) reflection of all the AMC appeared at smaller angles (2θ) as compared to the pristine clay-indicating the successful ion exchange. The basal space increased from 1.24 nm (2θ =7.12°) for pristine clay to a maximum of 2.12 nm (2θ =4.16°) for SC-AMC1.5x[fig3.6]. Similarly for SC-AMC0.5x and SC-AMC1x the basal spacing has increased to 1.75 nm (2θ =5.04°) and 1.96 nm (2θ =4.5°).These results clearly indicate that the increase in interlayer space was due to the inclusion of adduct within the interlayer of the unmodified clay.

Chapter 4

Summary and Conclusions

Clays are layered silicates, comprised of stacks of hydrated aluminosilicate with thickness of minimum 1 nm and lateral dimension of 50-1000 nm. Nowadays, clays have been widely used as nanofillers for thermoplastics like polypropylene, polyethylene, polystyrene and nylon due to its natural abundance, low cost and broadest commercial viability. In its pristine state, clay is hydrophilic and miscible only with hydrophilic polymers whereas most of the polymers are organophilic. Therefore, the clay surface often requires organomodification 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 Acid-Amine adducts having reactive sites. A facile method is adopted for the modification of Na$^+$-MMT using Acid-Amine adducts. Adducts were prepared by treating equimolar concentration of Ammonium Bromide (CTAB) with unsaturated organic acid with different modifier concentration (0.5x, 1x, 1.5x). FT-IR spectrum supports the successful intercalation of adducts into the interlayer space of Na$^+$-MMT. This was further 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. The effect of concentration of acid amine adduct on the Na$^+$ MMT leads to the conclusion that SC-AMC1.5x exhibited intense peak in FT-IR and XRD results which implies that the same SC-AMC1.5x has got higher d spacing(21.22nm) compared to other

two low concentration. From this we can conclude that, as the concentration of modifier increases the intercalation chemistry of the clay also increases.

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