

# PROJECT REPORT

On

## **“Study on the Concentration of Adduct Modifier for the Synthesis of Polymethyl Methacrylate Clay Nanocomposite”**

Submitted by  
**ANNIE S.**  
**(AM22CHE001)**

*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**

**2023-2024**



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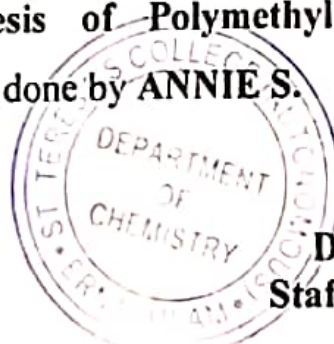


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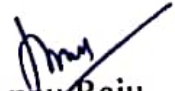
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This is to certify that the project work entitled **"Study on the Concentration of Adduct Modifier for the Synthesis of Polymethyl Methacrylate Clay Nanocomposite"** is the work done by **ANNIE S.** under my guidance in the partial fulfilment of the award of the Degree of Master of Science in Chemistry at St. Teresa's College (Autonomous), Ernakulam affiliated to Mahatma Gandhi University, Kottayam.

  
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## **DECLARATION**

I hereby declare that the project work entitled "**Study on the Concentration of Adduct Modifier for the Synthesis of Polymethyl Methacrylate Clay Nanocomposite**" submitted to Department of Chemistry and Centre for Research, St. Teresa's College (Autonomous) affiliated to Mahatma Gandhi University, Kottayam, Kerala is a record of an original work done by me under the guidance of Dr. Annu Raju, Assistant Professor, Department of Chemistry and Centre for Research, St. Teresa's College (Autonomous), Ernakulam (Internal Guide) .This project work is submitted in the partial fulfillment of the requirements for the award of the Degree of Master of Science in Chemistry.

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## Abbreviations

<b>AMC</b>	<b>Adduct modified clay</b>
<b>CA-AMC</b>	<b>Cinnamic acid-Adduct Modified clay</b>
<b>CTAB</b>	<b>Cetyl trimethyl ammonium bromide</b>
<b>CTAB-CA AMC</b>	<b>Cinnamic acid- cetyl trimethyl ammonium bromide adduct modified clay</b>
<b>CMS</b>	<b>Clay Minerals Society</b>
<b>JNCs</b>	<b>Joint nomenclature committees</b>
<b>CEC</b>	<b>Cation Exchange Capacity</b>
<b>HDT</b>	<b>Heat Distortion Temperature</b>
<b>Na-MMT</b>	<b>Sodium Montmorillonite</b>
<b>PMMA/PMA</b>	<b>Polymethyl methacrylate</b>
<b>PCN</b>	<b>Polymer Clay Nanocomposite</b>
<b>PMMA-CC</b>	<b>Polymethyl methacrylate-Cinnamic clay nanocomposite</b>

<b>BPO</b>	<b>Benzoyl Peroxide</b>
<b>XRD</b>	<b>X-ray diffraction</b>
<b>FTIR</b>	<b>Fourier transformation infrared spectroscopy</b>
<b>S. aureus</b>	<b>Staphylococcus aureus</b>
<b>E. coli</b>	<b>Escherichia coli</b>
<b>Gen10</b>	<b>Gentamicin</b>

## *Contents*

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# Chapter 1

## Introduction

### 1. General Introduction

Clays and the minerals of clay are important in the field of agriculture, industry as well as in the field of geology. It is important in construction field also. Clay has become unavoidable in modern man's life. It is used for the manufacture of many kinds of ceramics, porcelain, bricks, tiles and sanitary wares as well as an essential constituent of paints, rubber, cosmetics.etc. The various minerals of clay in its pure or modified form is a promising material of the 21<sup>st</sup> century because of its abundant, inexpensive and environment friendly characteristics.

Clays are composed of microcrystalline particles of a small group of minerals, referred to as the clay minerals[1]. Clay science or 'argillology' is an autonomous, multi-faceted emerging discipline to study the features of clays and clay minerals[2]. Despite being traditionally labeled as "silicates," clay minerals can be considered hydroxide due to their higher oxygen content compared to Si, Al, or Mg. These minerals may be considered as hydroxides of silicon, aluminium, or magnesium.

Some clays have the potential to be dispersed as nanocomposites during the polymer phase, which can create novel materials with excellent thermomechanical properties. Due to its numerous features, forms and applications , clay is a promising research field [3].

Some polymer nanocomposites have been used as automobile components, packaging materials, construction materials, flame retardants, protective films and so on. It is seen that the properties of polymers can be largely improved and novel unexpected features may appear after the addition of clay[4]. This is because the properties of polymers can be tuned precisely by incorporation of nanofillers into it. In multiphase systems, nanoparticles are distributed throughout a polymer matrix with at least one nanoscale dimension in the case of polymeric nanocomposites.

The term “nanocomposites” was introduced by Toyota Central Research Laboratory at the end of 1985, while they fabricated nylon montmorillonite (MMT) clay-based nanocomposites to produce car cover belts[5], [6]. Following this, substantial research in the field of polymer nanocomposites was conducted all over the world.

## **1.1 Clay**

A portion of the soil fraction with particles smaller than 2  $\mu\text{m}$  is referred to as clay. The clay layers are of nanoscale dimensions, with a thickness of roughly 1 nm. Clay is categorized as a layered silicate, which is a class of natural or artificial minerals made up of regular stacks of high aspect ratio, high surface area, aluminosilicate layers. Layered silicates are inexpensive and widely accessible. Clays are currently the most widely employed layered silicates in the manufacture of polymer nanocomposites. Numerous types of clay exist, each with unique qualities such as swelling and exfoliation, as well as differences in formula and structure. Polymer nanocomposites (PCNs) can be prepared using members that can be exfoliated by polymer chains or monomers and distributed as individual clay layers inside the polymer matrix. Because of their high aspect ratio and strong interfacial interactions with the polymer matrix, individual clay

layers have the potential to significantly improve the characteristics of polymers[7].

### **1.1.1 Clays and clay minerals**

Clay is a naturally occurring substance made mostly of fine-grained minerals that becomes elastic in the presence of water and rigid when dried or burned, according to the Clay Minerals Society (CMS) and Joint Nomenclature Committees (JNCs) of AIPEA, expanded as the Association Internationale pour l'Etude des Argiles. But it was noted that the term "clay" is used to refer to minerals (as well as rocks and related materials)[3], [8].

But we should concur with the JNCs that 'clay' and 'clay mineral' should be distinguished clearly and clay should not be only referred to as a mineral. Regarding the use of clay as a rock word, the JNCs' stance is still unclear. Thus, we come to the conclusion that the term "clay" can refer to a rock, a sedimentary deposit, and the byproducts of primary silicate mineral weathering. This is based on historical usage.

The titles "ball clay," "fire clay," "bentonite," "bleaching earth," and "fuller's earth" have all been used in literature in one form or another. It is important to always remember the differences between the terms clay and clay mineral. Despite this, because the term "clay" is shorter and less complicated than "clay mineral," it is frequently used in the literature. This report focuses on clay minerals instead of clays.

### **1.1.2 Structure of Clay**

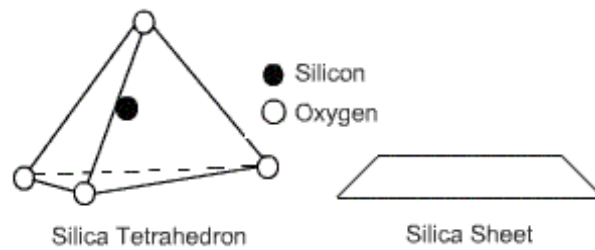
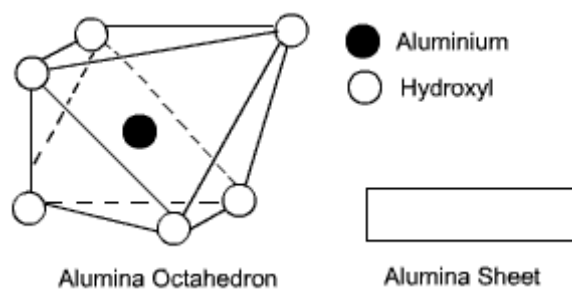
Clays are layered silicates made up of stacks of hydrated aluminosilicates that have lateral dimensions ranging from 50 to 1000 nm with a minimum thickness of 1 nm. Tetrahedral sheets containing four oxygen atoms

surrounding silicon and octahedral sheets containing eight oxygen atoms surrounding a metal such as aluminum are their fundamental building components. By exchanging oxygen atoms, the tetrahedral and octahedral sheets are linked. There are unshared oxygen atoms in the hydroxyl form. Typically, tetrahedral and octahedral sheets stack in a particular ratio and mode to make 1:1 layered silicates, also known as phyllosilicates.

An example for phyllosilicates are clay layers, composed of octahedral sheets with eight oxygen atoms encircling a metal like magnesium or aluminum and tetrahedral sheets with four oxygen atoms surrounding a silicon atom. The sheets that are octahedral (O) and tetrahedral (T) are joined by oxygen atoms. The oxygen atoms in the hydroxyl form are not shared. There are primarily two T and O layer combinations seen in most clays.

One such combination is the kaolin group. Here, one octahedral and one tetrahedral fused together make the kaolin group (1:1). The kaolin group is a 1:1 layered structure where an octahedral sheet and a tetrahedral sheet fuse together. The layers have a thickness of 0.7 nm and a typical composition of  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_5$ , with shared oxygen atoms.

Conversely, the 2:1 layered silicate crystal lattice, also known as 2:1 Phyllosilicate, is made up of two-dimensional layers in which a central alumina octahedral sheet is fused by the top to two external silica tetrahedra, meaning that the octahedral sheet's oxygen ions are also part of the tetrahedral sheets. The figures showing the structure of silica sheet and Alumina sheets are given below (Fig.1.1 and Fig.1.2) [7].

**Fig .1.1: Silica sheet****Fig.1.2: Alumina sheet**

The layer thickness is around 1 nm, with lateral dimensions ranging from 300 Å to several micrometers or even larger, depending on the particulate silicate, clay provided, and manufacturing method. Therefore, the aspect ratio (length/thickness ratio) of these layers is particularly high, with values exceeding 1000. With a total thickness of 0.94 nm, phyllosilicates are made up of one octahedral sheet joined between two tetrahedral sheets (2:1)[9].

A smectite clay group is formed by a central layer that has an octagonal symmetry of  $\text{MO}_4(\text{OH})_2$  and two tetrahedral layers ( $\text{MO}_4$ ), which forms alternating T: O: T. The octahedral layer contains aluminum cations that are partially substituted by divalent magnesium or iron cations.

Pyrophyllites are structures with a basic 2:1 configuration that are electrostatically neutral and lack interlayer ions. The layers do not expand

in water as there are no ions between them. Therefore, pyrophyllite has only an external surface and virtually no internal surface.

If we replace the silicon in the tetrahedral layer with aluminum, the resulting structure is called mica. Due to this substitution, the mineral is characterized by a negative surface charge, balanced by potassium cations in the interlayer. However, since the size of the potassium ions corresponds to the hexagonal holes created by the tetrahedral Si/Al layers, the potassium ions fit very tightly between the layers. As a result, the 2: 1 layer is held together by electrostatic attraction between the negatively charged tetrahedral layer and the potassium cations, and the layers do not swell or exfoliate into layers. Therefore, mica does not swell in water and, like pyrophyllite, does not have an internal surface. The electrostatic and van der Waals forces holding the layers together are relatively weak, and the distance between the layers depends on the charge density of the layers, the cation radius between the layers, and the degree of hydration.

Due to the distance between the layers (interlayer spacing) and the weak forces between the layers, the cations present between the layers can become hydrated in the aqueous solution, which is known as clay swelling. Swelling further increases the interlayer space. The charge density of clay layers differs for different clay groups with different clay structures[10].

Due to the interlayer spacing and the weak forces between the layers, other molecules can also become embedded between the layers, especially in the hydrated state, leading to the expansion of the layer lattice and ultimately to the separation of the individual layers.

### **1.1.3 Clay Properties**

Clay minerals are characterized by certain properties, they include;

- Layered structure with dimensions in nanometer range
- The anisotropy of the layers
- The 1: 1 (T:O) layer thickness is approximately 0.7 nm, 2: 1 (T:O:T) layer thickness is approximately 1 nm
- The presence of several types of surfaces: external basal (planar) and peripheral surfaces as well as internal (interlayer) surfaces[3]
- The ease with which external, and often internal, surfaces can be modified (by adsorption, ion exchange, or grafting)
- Plasticity
- Solidification upon drying or firing; this is true for most (but not all) clay minerals

Mostly used clay minerals are smectites. Smectites have the following properties:

Colloidal-sized particles, highly disordered layer stacking, high specific surface area, moderate layer charge, high cation exchange capacity, and low environmental pH. Also, a small anion exchange capacity that is dependent on pH, interlayer separation that varies depending on ambient humidity, a propensity for intercalation of foreign substances including organic compounds and macromolecules, and the ability of some members (e.g.,  $\text{Li}^+$  and  $\text{Na}^+$  exchange types) to exhibit strong swelling of the interlayer in water. Under optimal conditions, the layers can be completely dissolved (exfoliated).

#### **1.1.4 Smectites**

Smectites are one of the biggest and most vital classes of layered silicate clay minerals. It is common in temperate soils. The excellent cation exchange capacity (CEC) and very high specific surface area tend to dominate the cation adsorption chemistry of these soils. Additionally, due to their small particle size (typically  $< 1 \mu\text{m}$ ) and high aspect ratio, they can significantly influence the physical properties of soils and sediments. These chemical and physical properties explain the suitability of clay as a catalyst and as a pond lining for separating hazardous wastes

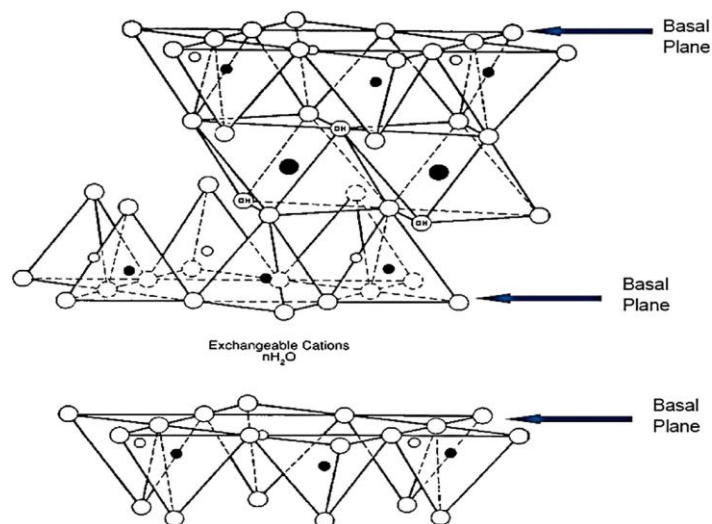
Smectites form a group of mineral class known as phyllosilicates or sheet silicates. Other groups in this class include mica, kaolin, vermiculite, chlorite, talc, and pyrophyllite. The structure of layered silicates consists of layers in which the planes of oxygen atoms coordinate with cations such as Si, Al, Mg, and Fe to form two-dimensional sheets.

The coordination of cations in adjacent layers typically alternates between tetrahedrons and octahedrons. Tetrahedral layers usually contain Si and Al and consist of hexagonal or tetragonal rings of oxygen tetrahedra connected by common basic oxygen atoms. The apical oxygen atoms of these tetrahedra contribute to the formation of the base of the octahedral layer.

A regularly repeating arrangement of sheets (eg, tetrahedron-octahedron or tetrahedron-octahedron-tetrahedron) is called a layer. Smectite, mica, vermiculite, talc, and pyrophyllite are characterized by a monolayer structure in which two tetrahedral layers are on either side of an octahedral layer formed by shared apical oxygen atoms[11] .

Since the oxygen atoms at the pinnacle of the tetrahedral layer frame ditrigonal or hexagonal rings, one oxygen atom of the octahedral layer is found at the center of each ring and is protonated to give the structural hydroxyl group. In 2:1 layered silicates, isomorphic substitution of cations with different valences can lead to charge imbalance within the layers. These can be partially balanced by charge imbalances of opposite nature in adjacent sheets (e.g., a positively charged octahedral layer has a negative charge associated with a tetrahedral layer).

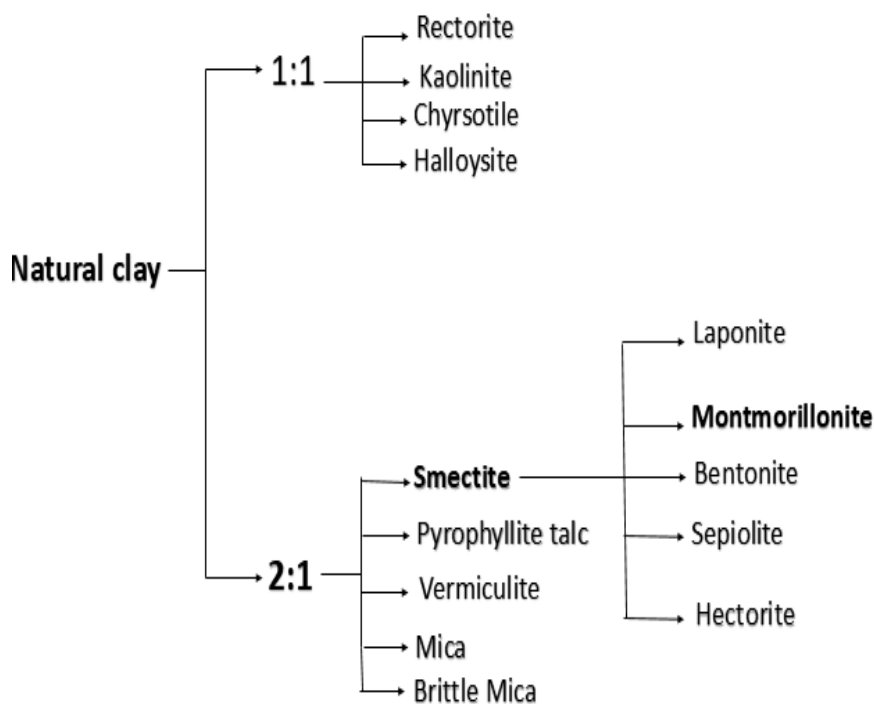
The net charge imbalance of one 2:1 layer is negative (if it occurs). This charge is called the mineral's layer charge and is balanced by the larger cations (e.g.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) that coordinate to the bottom surfaces of the tetrahedral layer of the adjacent layers. These charge-balancing cations are called "interlayer cations" because they are located between adjacent 2:1 layers. The 2:1 phyllosilicates are recognized mainly on the premise of their layer charge. The structure of a 2:1 phyllosilicate is given below (Fig.1.3)[9].



**Fig .1.3: The structure of 2:1 Smectite clays**

### 1.1.5 Classification of clay and its characteristics

Clays can be classified based on their arrangement as 1:1 and 2:1 type of clays. Smectites come under the class of 2:1 clays. Montmorillonite is an important example of Smectite clay. The classification of the types of clay are given in the flow chart below (Fig.1.4)[12].



**Fig.1.4: Classification of clay materials.**

### 1.2 Montmorillonite (MMT)

Montmorillonite (MMT) is a natural clay mineral belonging to the smectite group of clays and a popular nanoclay raw material. It is a family of 2:1 layer silicate clays with a permanent layer charge. MMT is a dioctahedral 2:1 phyllosilicate, consisting of two tetrahedral layers and one octahedral layer (T:O:T). When montmorillonite comes into contact with

water, it expands to many times its original volume. They have a very high specific surface area (i.e. inner surface area  $\gg$  outer surface area) and high cation exchange capacity (CEC).

Not at all like other clay nanoparticles, Montmorillonite has interlayer gaps between each triple-sheet layer. Chemically, MMT consists of  $\text{Si}^{4+}$  being replaced by  $\text{Al}^{3+}$  in the tetrahedral layer and  $\text{Al}^{3+}$  being replaced by  $\text{Mg}^{2+}$  in the octahedral layer. This arrangement gives Montmorillonite, a negative residual charge, balanced by cations in the interlayer spaces

### **1.2.1 Cation-exchange capacity**

The ability of clay minerals to adsorb and adhere specific cations and anions around the exterior of structural units is determined by the absence of positive or negative charges in their mineral structure. Absorbed ions are substituted by other ions. Quantitative relationships between interacting ions distinguish exchange reactions from simple sorption. The number of cations retained on the surface of soil particles is measured by the cation exchange capacity (CEC). It is defined as the number of cations that can be exchanged for other cations at a given pH and is often expressed in milliequivalents per 100 grams of dry clay.

Negatively charged ions on the surface of soil particles can combine with positively charged ions and exchange with other positively charged particles in the surrounding soil water, resulting in chemical changes in the soil. CEC affects several areas of soil chemistry. CEC measures soil fertility as it indicates the soil's ability to store nutrients such as  $\text{K}^+$ ,  $\text{NH}_4^+$ , and  $\text{Ca}^{2+}$ . It also refers to the ability to retain environmentally harmful cations such as  $\text{Pb}^{2+}$ .

Because CEC is influenced by particle size, crystallinity, and adsorbed ions, the value of CEC for a particular mineral lies within a range rather than a single specific value. The exchange capacity is also pH dependent due to the presence of hydroxyl groups on the surface of certain clay minerals such as allophane and kaolinite. The adsorbed cations displace or replace the initial negatively charged layer. This capacity of colloidal particles, such as clay minerals, to hold and trade positively charged ions is vital since it affects the mobility of positively charged species in soils and the overall geochemical cation cycle. CEC is a reversible process commonly associated with clay minerals due to the presence of exchangeable cations between the layers.

### **1.2.2 Swelling capacity**

When dry clay minerals adsorb water in a controlled environment, water is introduced into the interlayer space in more or less separate layers, resulting in expansion of the interlayer space. The increase in interlayer spacing in clay minerals is caused by hydration energy forces associated with particle contact. Expanded clays tend to change volume significantly with changes in moisture content. The swelling ability of clay minerals is determined by the following factors: Charge density of clay mineral layers, type of interlayer ions (monovalent or divalent), ion concentration in the surrounding solution containing clay mineral, clay mineral composition.

### **1.3 Need for modification of clay**

Dispersion of clay in polymer matrices is a problem caused by the presence of covalent bonds between interlayers of clay layers. To overcome this difficulty, clay particles undergo modification before being dispersed into the polymer matrix. Basically, during the modification

process, the distance between the interlayers of clay particles is increased by incorporation of surfactants or grafting of hydrophobic functional units. Such modifications make it possible to incorporate hydrophobicity into the clay particles, allowing them to be finely dispersed in the polymer matrix

### **1.3.1 Modification of Clay Particles**

There are two main ways to modify clay particles.

(1) Physical modification method and (2) chemical modification method.

In the physical modification method, only the adsorption of the modifier onto the clay surface occurs. This method does not change the clay structure and slightly improves the properties of the resulting polymer composites. The slight improvement in properties can be attributed to the fact that there is only a weak physical attraction between the clay and the modifier.

During chemical modification, polymers or organosilane compounds with functional groups are usually attached to the clay surface. Additionally, modification is accomplished through ion exchange processes using cationic or anionic functional groups. Therefore, chemical modification helps to achieve a stronger interaction between clay particles and modifiers. This improves the dispersion of clay particles in the polymer matrix. The nanoscale thickness of the individual layers of clay particles, the high aspect ratio, and the large surface area that the clay material has when dispersed in the polymer matrix improve the thermal, barrier, optical, and mechanical properties. This intercalation is the most important because it changes two special properties of the layered silicates. First, we change the surface chemistry of clay minerals through ion exchange with organic cations. Second, the basal distance between clay layers increases.

The smectite group of clay minerals, which includes Montmorillonite, is widely recognized for its exceptional properties, including high cation exchange capacity, swelling behavior, adsorption properties and large surface area.

the These surface-modified montmorillonites have other interesting potential applications. Besides applications in polymers, nanofillers can be used as adsorbents for organic pollutants, rheology control agents, wastewater treatment, thickening and gelling agents in paints, lubricants, ointments, etc.

### **1.3.2 Different Intercalating Agents Used for Intercalation of Montmorillonites**

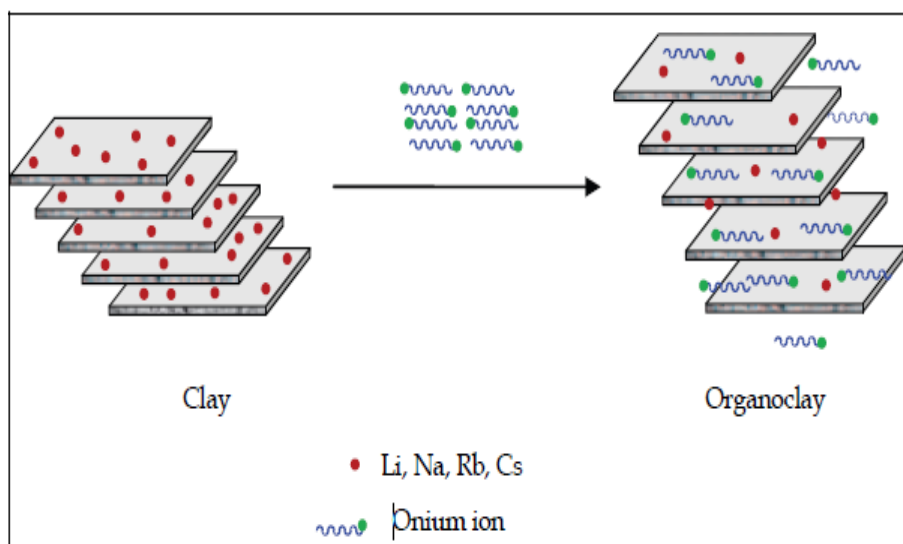
To date, alkylammonium salts have been widely used to insert Montmorillonites, and these inserted montmorillonites are used in different fields. Various alkyl ammonium salts such as octadecyl ammonium chloride, methyl, propyl, butyl chloride, and dodecyl ammonium chloride, as well as tetraalkylammonium salts (dodecyltrimethylammonium bromide, octadecyltrimethylammonium bromide) were used for the incorporation of Montmorillonite.

### **1.4 .Organo clay**

To make the clay layer more compatible with the polymer chains, modification of the clay layer with hydrophobic agents is required. This is a surface modification in which the surface energy of the clay layer is reduced and its surface polarity is adjusted to that of the polymer's polarity. Organoclays with low surface energy are highly compatible with polymers, allowing polymer molecules to insert (intercalate) into interlayer spaces or galleries under well-defined experimental conditions.

Surface modification of clay layers can be achieved through cation exchange processes by replacing the sodium and calcium cations present in the interlayer spaces or clay galleries with alkyl ammonium or alkyl phosphonium (onium) cations. In addition to surface modification and increasing the hydrophobicity of the clay layer, the incorporation of alkyl ammonium or alkyl phosphonium cations into the galleries results in a certain increase in the interlayer distance, which promotes the incorporation of alkyl ammonium or alkyl phosphonium cations into the galleries during nanocomposite fabrication[13].

Thus, the incorporation of polymer chains into the clay layers are promoted. Alkyl ammonium or alkyl phosphonium cations can also enhance interfacial interactions by providing functional groups that interact with polymer chains or initiate polymerization. Schematic illustration of organic modification of clay layer with alkyl ammonium cations by ion exchange process is given below (Fig.1.5)[8].



**Fig.1.5: Diagram depicting the modification of clay layer by organic onium ions.**

To achieve exchange of onium ions and cations within the gallery, the silicate must be swollen with water. For this reason, alkaline cations are preferred in galleries. Cations with a valence of two or more cannot be easily hydrated, so they prevent swelling due to water thus, monovalent alkali cations are preferred. Monovalent intergallery cations' formation of hydrate is responsible for the swelling observed.

Natural clays may contain divalent cations such as calcium, which require an exchange step with sodium before further treatment with onium salts. Alkali cations are not structural and can be easily replaced by other positively charged atoms or molecules, hence they are called exchangeable cations. Organic cations lower the surface energy of silicate surfaces. Furthermore, the long organic cations with positively charged ends of such surfactants bind to the surface of the negatively charged silicate layer, resulting in an increase in the intergallery height. This increase in intergallery height enables organic species (i.e. polymers) to diffuse between the layers and eventually cause the layers to separate.

In some cases, alkyl ammonium cations can even provide functional groups that can react with polymers or initiate polymerization of monomers. In summary, surface alteration increments the basal distance of the clay while acting as a compatibilizer between the hydrophilic clay and the hydrophobic polymer.

The excess negative charge of layered silicates and their ion exchange capacity are quantified by a specific property known as cation exchange capacity (CEC), expressed in mequiv/g. This property largely depends on the nature of the isomorphous replacement of the tetrahedral and octahedral layers, and thus on the nature of the soil in which the clay was formed. Instead of being locally constant, the charge in a layer fluctuates

varies from layer to layer, and should be viewed as the average value for the whole crystal. In common, as the length of the surfactant chain increases and the higher the charge density of the clay, the clay layer will be pushed separated further. This is expected since both parameters contribute to the increase in interlayer space.

#### **1.4.1 Limitations of Conventional Organoclays**

Melt intercalation is used as a method for the large-scale synthesis of many polymer nanocomposites. The disadvantages of melt intercalation are related to the low thermal stability of organic modifiers. Typically, alkylammonium or alkylphosphonium cations are used as organic modifiers. These modifiers make the layered silicates organophilic, but they are not thermally stable.

#### **1.5 Polymer-clay nanocomposite**

Polymer clay materials are created by combining polymers with synthetic or natural clays. Incorporation of clay improves the mechanical, thermal, barrier, and fire protection properties of polymers. Polymer-clay structures are called Polymer-clay nanocomposites (PCNs) when they contain at least one phase with a nanometer-scale texture.

Nanocomposites have great potential for application as highly functional materials, as they often exhibit physical and chemical properties that are quite different from pure polymers and conventional microcomposites. It is worth noting that the main properties of polymer-clay composites strongly depend on the physical and chemical properties of the individual components, nanosize and the interfacial adhesion forces between the nanocomposite parts. Among inorganic nanofillers, clay is widely used as a filler in standard thermoplastics such as polypropylene, polyethylene,

polystyrene, and nylon due to its naturally occurring, low cost, and wide commercial potential[14].

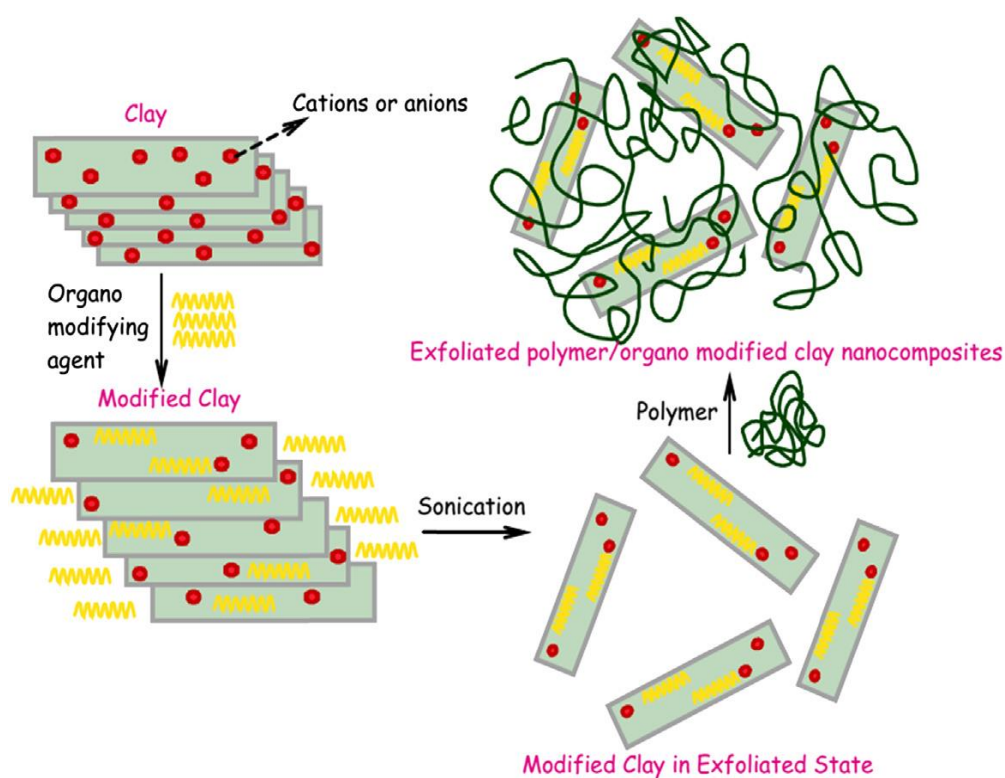
Currently, the field of polymer-clay nanocomposites is gaining momentum due to improvements in the thermal and mechanical properties of matrix polymers and the possibility of melting polymers and clays without the use of organic solvents. This improved quality is due to the dispersion of nanometer-thick clay layers within the polymer matrix[15] .

Polymer nanocomposites have attracted much attention because they exhibit superior properties such as strength, toughness, and fire resistance that far exceed common microcomposites and are comparable to metals. PCNs are also widely applied in industry as high-performance structural materials[16], [17], [18], [19] .

PCNs can be formed into complex shapes using existing industrial equipment. PCNs can also be used in packaging and storage tank applications, as the nanodispersed clay layer reduces the permeability of the polymer matrix. Polymer-clay nanocomposites have attracted significant interest over the past two decades because they often exhibit significant thermal, mechanical, and barrier properties due to nanometer-scale silicate layers dispersed within the polymer matrix.

It has been reported that by tuning the polymer–clay interaction, nanocomposites with different structures/morphologies, properties, and applications can be produced. Recent advances in these polymer-clay composites regarding self-assembly and formation of different morphologies have also enabled their application as highly functional materials in controlled delivery systems [20] .

In addition to the improvement in the mechanical, thermal insulation, durability, chemical stability, flame retardancy, scratch and abrasion resistance, biodegradability, optical, magnetic, and electrical properties of polymer bulk phases, the presence of nanoscale phases has important consequences. One such consequence is the interfacial contact between the polymer and the clay. Clay content and aspect ratio are related to the improvement of mechanical performance of nanocomposites.. The formation of polymer clay nanocomposites can be illustrated in the figure below (Fig.1.6)[12].



**Fig.1.6: Schematic illustration of the preparation of exfoliated polymers and organomodified clay nanocomposites.**

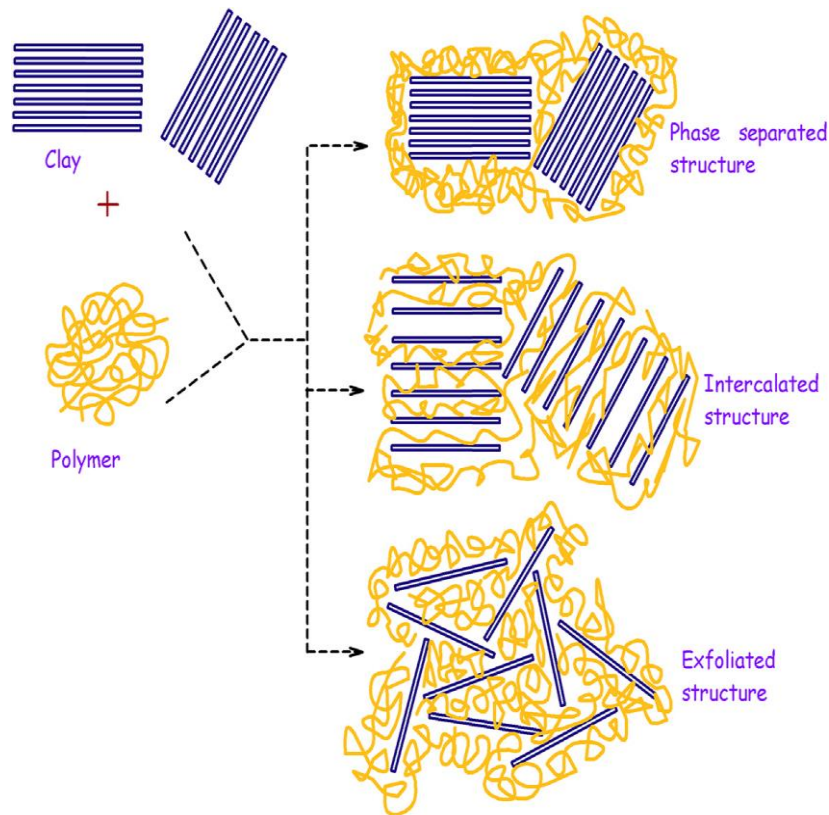
Polymer-clay nanocomposites have recently become increasingly popular as they possess properties significantly superior to traditional polymer composites in a relatively small proportion. Polymer-clay nanocomposites can be prepared by directly mixing a clay suspension with two aqueous solutions containing monomers. Polymers can then be created by adding polymerizing agents or by induction with heat or light. The final product is called an ex-situ nanocomposite because the majority of the polymer can be found outside the clay interspaces.

It is important to note that the initial clay concentration is adjustable and in some cases the clay layers can be completely separated. Therefore, here the final product is called exfoliated polymer-clay nanocomposite. In the second approach, monomers are incorporated into the clay interlayer space by charge exchange or by diffusion within clay galleries which has been previously modified with organic salts. Since most of the polymer content is located in the interstices of the clay, the embedded polymer can be polymerized to create so called in-situ nanocomposites.

### **1.6 Polymer clay nanocomposite structure**

Generally, the degree of insertion and exfoliation of polymer chains into clay galleries is used to classify the structure of polymer-clay nanocomposites. The degree of insertion and exfoliation is influenced by many factors such as clay type, organic modifier, polymer matrix, and manufacturing process. Therefore, a variety of composite microstructures can be fabricated depending on the type and quality of the clay and polymer and the method used to synthesise the nanocomposite[21].

The figure showing , possible types of polymer clay nanocomposite structures is shown below (Fig.1.7)[12].



**Fig .1.7: Possible types of polymer clay nanocomposite structures.**

### **1.6.1 Phase separated structure**

When an organic polymer intercalates into an inorganic clay (unmodified clay), the polymer cannot intercalate into the clay layer and the clay is disseminated as layered aggregates or particles in the polymer network. The resulting composite structure is considered to be "phase separated". The properties of phase-separated polymer-clay composites are within the range of conventional microcomposites.

### **1.6.2 Intercalated structure**

An intercalated nanocomposite is generated when one or more polymer chains are inserted into the interlayer space, leading to an increase in the

interlayer distance, but the periodic arrangement of clay layers is still present. The presence of polymer chains within the galleries reduces, but does not completely resolve, the electrostatic forces between the layers. This configuration results in an ordered multilayered hybrid morphology with strong interfering interactions between the polymer chains and clay layer.

### **1.6.3 Exfoliated structure**

Layers are separated from one another by the insertion of polymer chains into clay galleries. An exfoliated or delaminated structure is produced when the individual layers are dispersed throughout the polymer matrix. When the polymer chains increase the interlayer distance by more than 80-100 Å, exfoliated structure is obtained. Due to the good distribution of the individual clay layers, a high aspect ratio is achieved and the required clay content in the exfoliated nanocomposite is low. The large surface interactions between the polymer and clay also significantly improve the properties of the polymer.

### **1.7 Characterisation methods**

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

measured diffraction angle is denoted by  $\theta$ , whereas  $d$  represents the spacing between layers in the clay lattice.

Any altering within the inter-layer or  $d$ -spacing of a clay lattice by organic modification causes the shift in the position, broadness and intensity of the characteristic peak in XRD spectra. According to Bragg's law, as the  $d$ -spacing increases, the associated XRD peaks broaden and shift toward lower diffraction angles ( $2\theta$ ). By monitoring the position ( $2\theta$ ), shape and intensity of the characteristic peaks of organoclay, it is possible to judge the degree of insertion/exfoliation.

Thus, the XRD technique provides a standard method to calculate the  $d$ -spacing in pure clay as well as in the organo-modified clay, using the position, broadness and intensity of characteristic peak in XRD diffractogram.

The FT-IR spectroscopy studies indicate whether the desired chemical groups were successfully inserted into the spaces of the modified clay. The modified clay shows additional characteristic peaks other than the bands due to Si-O-Si asymmetric stretching of silicate layer at  $1008\text{cm}^{-1}$  and structural hydroxyls at  $3600\text{cm}^{-1}$ . Thus, FT-IR gives a confirmation that the pristine clay has been effectively converted into the corresponding modified clay.

### **1.8 Properties of PCNs**

Nanocomposites consisting of polymers and layered silicates have essentially progressed mechanical and material properties compared to pure polymers. Improvements include enhanced modulus, strength and heat resistance, as well as reduced gas permeability and flammability. These composites also exhibit better biodegradable properties. PCNs also

show improvements in the most common polymer properties. In addition to reduced liquid and gas permeability, the nanocomposites also exhibit significant improvements in solvent absorption. Another property is scratch resistance, which is significantly improved by the use of layered silicates. The main reason for these improvements is the stronger interfacial interaction between the matrix and the silicate compared to traditional filler-reinforced systems.

### **1.8.1 Mechanical Properties**

The tensile and flexural properties of the polymeric materials showed significant improvement when the nanocomposites were formed with layered silicates

### **1.8.2 Thermal Stability**

Incorporation of clay into the polymer matrix has been shown to improve thermal stability by acting as a good insulator and mass transport barrier for volatile products formed during decomposition. In some cases, clays were found to shift the initial stages of pyrolysis to higher temperatures. A reversal of thermal stability was also observed due to the heat barrier effect of the laminated silicate layer, which stores the accumulated heat. This, in conjunction with the heat flux provided by the external heat source, could potentially be used as a heat source to accelerate the decomposition process.

### **1.8.3 Heat Distortion Temperature (HDT)**

The HDT of a polymeric material is a measure of its resistance to heat towards applied loads. The increase in HDT due to clay dispersion may be an exceptionally critical property enhancement for any polymeric material.

It is very difficult to achieve similar HDT improvements using conventional fillers.

#### **1.8.4 Fire Retardant Properties**

The improved flame retardant properties observed in nanocomposites can be attributed to the formation of high performance material of silicate containing carbon char that accumulates on the surface during firing. This separates the underlying material and slows the mass loss of decomposition products.

#### **1.8.5 Optical Properties**

The lateral size of layered silicates is in the micrometer range, but the thickness is only less than 1 nm. Therefore, when the individual layers are dispersed in a polymer matrix, the resulting nanocomposite is optically transparent or more transparent in visible light.

#### **1.8.6 Biodegradability**

Another interesting and exciting aspect of PCNs is the significant improvement in biodegradability after formation of nanocomposites, probably due to the catalytic role of organoclays in the biodegradation mechanism[22].

#### **1.8.7 Packing material**

PCN can be used as a new and innovative packaging material. Mixing the most commonly used packaging materials, such as polymethyl methacrylate and polystyrene, with organoclays results in nanocomposite films with improved thermal, optical, and barrier properties. The obtained nanocomposite films can be used as packaging materials in the food industry [19].

### **1.8.8 Antibacterial Property**

The addition of certain modifiers with antibacterial activity confers antibacterial activity on PCNs. The potential benefit of this include the ability to create new antimicrobial materials for packaging material.

### **1.9 Objectives of the current study**

- To synthesize organomodified clay nanocomposites using different modifier concentrations
- To determine the modifier concentration which brings most effective d spacing of modified clay.
- To synthesise organoclay modified Poly Methylmethacrylate polymer nanocomposite.
- To study the the potential application of organoclay modified PMMA as an effective packing material with antibacterial properties.

# Chapter 2

## 2.1. Literature review

Advances in the field of polymer nanocomposites are very promising, as the properties of polymers can be precisely tuned through the incorporation of nanofillers. According to Saheli Ganguly and others , “polymer nanocomposites” are multiphase systems in which nanoparticles with at least one dimension in nanoscale are dispersed in a polymer matrix[23]. By reinforcing nanofillers, it is possible to significantly improve the properties of polymer matrices even at low loadings.

It has been widely reported in the literature that the incorporation of nanofillers into pure polymer matrices improves several pertinent material properties, including: Mechanical properties and thermal stability. It has gas barrier properties without significantly sacrificing toughness or transparency, making it suitable for packaging applications. Layered materials as drug delivery vehicles have attracted more attention in recent years. Layered silicate accepts polar organic compounds between its layers and forms various interlayer compounds. Since the release of drugs in layered materials could be controlled by drug intercalation, these new materials have great potential as delivery hosts in the pharmaceutical field[23].

According to Riya Mascarenhas and others., the use of nanocomposites in the preparation of materials results in multi- or single-phase glass, ceramic, or porous materials with better properties. Compared to polymer nanocomposites and pure polymers, nanocomposites have improved

properties such as bond strength, reduced gas permeability, and improved thermal and mechanical properties[24].

Polymer-inorganic composites offer dramatic changes in mechanical properties, thermal stability, flame retardancy, better gas barrier properties, and corrosion resistance. Additionally, small amounts of clay doping cause either intercalation or exfoliation, and these changes in the composite can be detected using X-ray diffraction (XRD) techniques. The exfoliated composites have significantly improved physical and chemical properties due to the clay surface as well as the large aspect ratio[25].

Natural smectite clays are hydrophilic and are traditionally treated with quaternary ammonium salts to make them organophilic. In this way, they are compatible with most hydrophobic polymers to form intercalated and exfoliated nanocomposites. The search for thermally stable surfactants that withstand melt processing at the temperatures used to process thermoplastics is ongoing[4].

Polymer clay nanocomposites are mainly prepared by in situ polymerization, melt processing, and solution methods. Due to their excellent mechanical and transport properties, they not only have the potential to improve the performance of pure polymeric materials, but can also replace some of the existing metals or other composite materials. Addition of small amounts (typically less than 5% by volume) of properly pretreated clays significantly improves the mechanical and barrier properties of polymers without loss of optical clarity. The ionic and electrical conductivity of conductive polymers, as well as the biodegradability of polymers, can also be improved by adding clay. Furthermore, the presence of a small amount of clay produces a

nanocomposite that can be processed in the same way as unfilled polymer [4].

In addition to several nanofillers that have been tested for their reinforcing abilities, clay materials have been extensively studied as fillers in polymer matrices to achieve significant enhancements in their properties. Polymer clay composites have fascinated researchers over the past decade due to dramatic changes in mechanical properties, improved thermal stability, flame retardance, gas barrier properties, and corrosion resistance compared to traditional alternatives[26].

The substance called "clay" is actually composed of layered silicates and clay minerals (aluminum layered silicates), and contains especially trace amounts of metal oxides such as alkaline earth metals, alkali metals, and magnesium, as well as organic substances [12].

Dispersion of clay in polymer matrices is a challenge due to the presence of covalent bonds between interlayers of clay layers. To overcome this difficulty Syed Abusale Mhamad Nabirqudri and others noted that, clay particles undergo modification before being dispersed into the polymer matrix. The clay-polymer interaction mechanism is as follows. The metal cation on the clay exchanges with the carbocation of the surfactant to form a long alkyl chain. This process improves the interface and improves the physical and chemical properties of polymer-clay composites[25]. Such modifications allow the incorporation of hydrophobicity into the clay particles, allowing them to be finely dispersed within the polymer matrix [12].

The most commonly used clay mineral for the preparation of nanocomposites is montmorillonite (MMT) due to its high cation exchange capacity (CEC) . Modification of montmorillonite (MMT) is

carried out in two or more steps by first replacing  $\text{Na}^+$  in the spaces between the layered structures of montmorillonite with either surfactants, monomers, or initiators. This expands the basal space and facilitates monomer penetration. This occurs before the polymerization process begins, as reported by . Ahmed M. Youssef and others[27].

Montmorillinate clay significantly improves the electrical and mechanical properties of composite materials. Therefore, these composites are potentially useful in many technological applications such as transistors, microelectronics, sensors, and solar encapsulation materials, as reported by Syed Abusale Mhamad Nabirqudri and others[25].

MMT allows the extraction of nanostructures that can be used as new and innovative packaging materials. The most commonly used polymers for packaging films (PP, PE, PET, PS, etc.) are blended with MMT to create nanoclays with improved mechanical, thermal, optical, and/or barrier properties. Composite film can be obtained by this method as reported by F. Vilarinho and others[28].

Synthesis of polymer/clay nanocomposites can be performed using various methods such as in situ polymerization, intercalation of polymers from solution, melt intercalation of polymers, and sol-gel techniques .The idea of which nanocomposites were created is mainly based on performing a polymerization process on the elementary space of the clay on the nanometer scale. Accumulation of polymer chains growing within this confined space leads to expansion of at least the base space of the clay (intercalation), maximal exfoliation of the ordered layered structure and complete distribution within the polymer matrix. It becomes many separate layers (exfoliation). Poly(methyl methacrylate) (PMMA) is a transparent, rigid material with excellent UV stability, low water

absorption, and excellent outdoor weatherability. PMMA/montmorillonite clay composites are engineered to have enhanced electrical, thermal, and mechanical properties. These polymer composites have very low dielectric constants and tangent losses. Therefore, the electrical conductivity of these polymer composites is very low [27].

It also has low heat resistance. To solve this problem, PMMA/clay nanocomposites were developed using polymer melt intercalation and in situ intercalation polymerization with organically modified clay. Partially exfoliated or intercalated structures of nanocomposites showed improved thermal and mechanical properties and similar optical transparency compared to pure PMMA. PMMA/Mt-CTA nanocomposites were successfully prepared by in situ emulsion polymerization of hydrophobic montmorillonite applied at 11.48 Å to 19.49 Å. Additionally, Mt-CTA foam was used as a host for the preparation of poly(methyl methacrylate) nanocomposites[27].

Microwave-assisted in situ polymerization was used to successfully synthesise PMMA/clay nanocomposites. The organophilic clay content of PMMA/clay nanocomposites had a significant impact on their intercalated or exfoliated nanostructures [29]. It was reported by Paulo Meneghetti and Syed Qutubuddin that the synthesis of PMMA/clay nanocomposites by emulsification and in situ polymerization resulted in partially exfoliated and intercalated nanocomposites, respectively. The thermomechanical properties of the nanocomposites were significantly enhanced by their diverse morphologies, in contrast to the pure polymer

Ayşe Cagil Kandemir and others, reported the synthesis of biocompatible nanocomposites using polyvinylpyrrolidone (PVP) and bentonite nanoclay

(BNT) coatings with improved mechanical properties and significantly increased elastic modulus[30].

A new polymer gel electrolyte with improved ionic conductivity and stable lithium interfacial resistance was synthesized using PMMA/clay nanocomposite and could be used for battery applications. Other potential applications for these nanocomposites include film packaging and gas storage[31].

# Chapter 3

## Materials and Methods

### 3.1 Work plan

The primary goals of our project were to prepare modified clays using Cinnamic acid-CTAB and investigate the concentration effects of the Cinnamic acid-CTAB adduct on clay modification and characterize the modified clay using FTIR and XRD. Using the organo-modified clay our project also aims to prepare Polymethyl methacrylate clay nanocomposite and study one of its application that is its antibacterial activity.

### 3.2 Work carried out

- Synthesis of organomodified clay nanocomposites using different modifier concentrations.
- Study the intercalation chemistry of different modifier concentrations using FT-IR and XRD.
- Synthesis of organoclay modified Polymethyl methacrylate polymer nanocomposite.
- Study the potential application of organoclay modified PMMA that is its antibacterial activity.

### 3.3 Experimental Procedure

#### 3.3.1 Materials required

Sodium Montmorillonite clay with cation exchange capacity (CEC) 92.6mEq/100 g purchased from Southern Clay Products, USA. Cinnamic acid, Cetyltrimethylammonium bromide (CTAB) was purchased from Merk Specialties Pvt Ltd, India. Methyl methacrylate monomer was purchased from Merk Specialties Pvt Ltd. The initiator benzoyl peroxide (BPO) was provided by S.D. Fine Chemicals Ltd, India. Ethanol, Toluene, and distilled water.

#### 3.3.2 Synthesis of modified clay using 0.5x:0.5x Cinnamic acid-CTAB adduct.

Weight of the clay = 4 g

Weight of the Cinnamic acid. = 0.592 g

Weight of the CTAB. = 1.456 g

Total volume of distilled water = 800 ml

4g of clay was dispersed in 100mL of distilled water in a 1000mL beaker and similarly 0.5x:0.5x equimolar concentration of the Cinnamic acid-CTAB mixture was prepared in about 100mL of water in a 250mL beaker. The above dissolved suspensions were stirred separately in a magnetic stirrer for about 30 minutes. The Cinnamic acid-CTAB mixture was slowly added to the clay suspension and diluted up to 800mL into the 1000ml beaker with distilled water. Then it was kept for continuous stirring uninterrupted for 48 hours using magnetic stirrer. The adduct modified clay suspension resulted was separated by centrifuge at 1500 rpm for 30 minutes. Finally, the adduct modified clay [CA-CTAB adduct modified clay or CA-

AMC] was dried overnight in a hot air oven at 105°C and powdered using a mortar and pestle to obtain Cinnamic acid-CTAB adduct modified clay.

### **3.3.3 Synthesis of modified clay using 1x:1x Cinnamic acid-CTAB adduct**

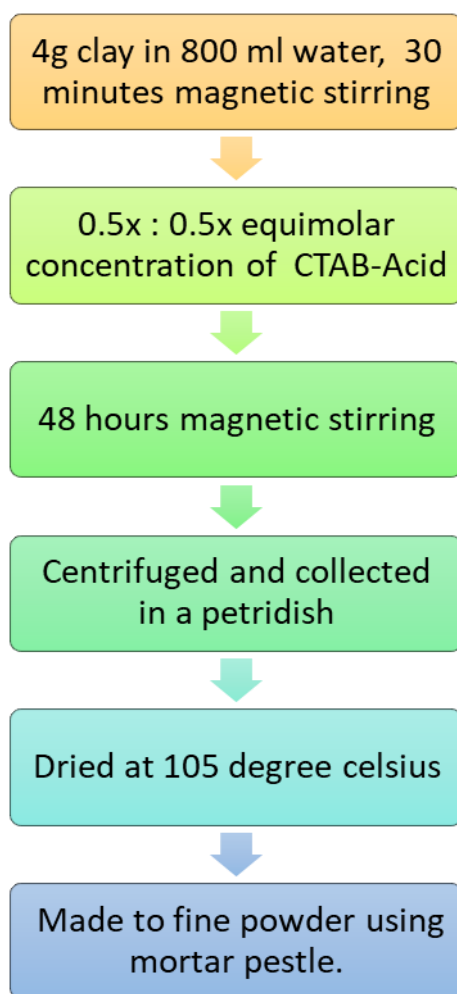
Weight of the clay = 4 g  
Weight of the Cinnamic acid = 1.184 g  
Weight of the CTAB. = 2.912 g  
Total volume of the distilled water = 800 ml

Here, the same steps of 0.5x:0.5x was used for the organoclay modification by varying the modifier concentration to 1x:1x keeping the concentration of clay as constant.

### **3.3.4 Synthesis of modified clay using 2x:2x Cinnamic acid-CTAB adduct**

Weight of the clay = 4 g  
Weight of the Cinnamic acid. = 2.368g  
Weight of the CTAB. = 5.824 g  
Total volume of the distilled water = 800 ml

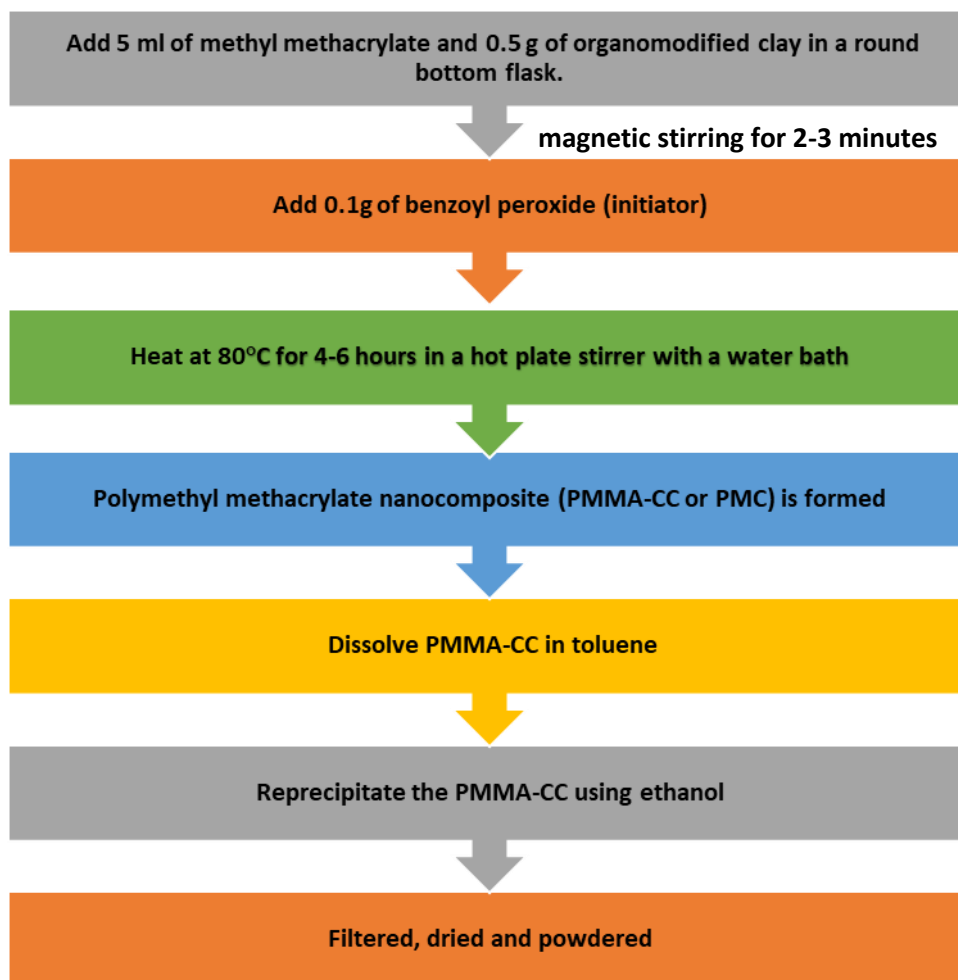
In order to prepare 2x:2x adduct modified clay the same steps of 1x:1x was used for the clay modification by varying the CTAB-Cinnamic acid modifier concentration keeping the concentration of clay as constant.



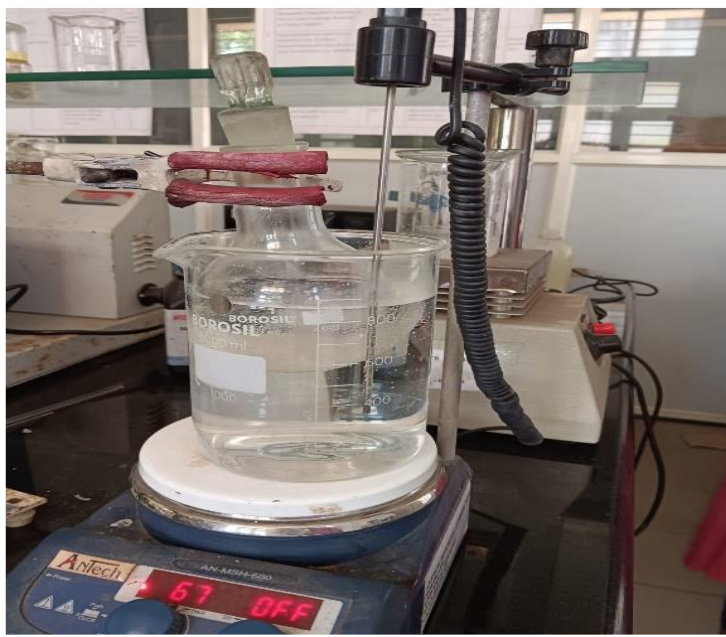
**Fig.3.1: Flow chart for clay modification**

### **3.3.5 Synthesis of Polymethylmethacrylate Clay nanocomposite (PMMA-CC)**

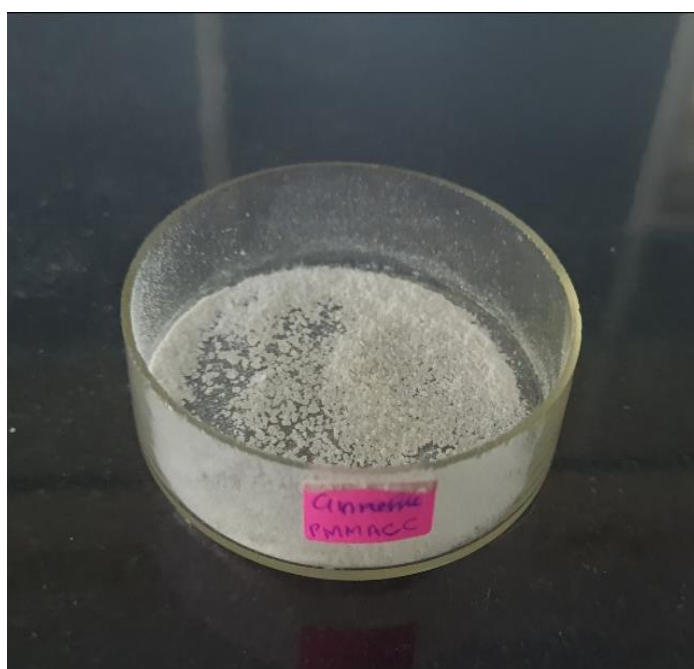
Add 5 ml of methyl methacrylate and 0.5 g of organomodified (2x:2x) clay in a round bottom (RB) flask. After 2-3 minutes of mixing by using a magnetic stirrer add 0.1g of benzoyl peroxide to the RB flask. Place the RB flask (mouth closed using a lid & sealed with paraffin film) in the hot plate stirrer along with a water bath and heat it to 80°C for four to six hours. The product Polymethyl methacrylate nanocomposite (PMMA-CC) was formed. For about five minutes let it sit at room temperature. Dissolve the PMMA-CC in toluene after it reaches room temperature (if it doesn't dissolve again heat it using a water bath). Once it was dissolved it was transferred to a 250ml beaker and use a small quantity of toluene to wash the RB flask. It is then reprecipitated using ethanol and filtered using Whatman filter paper and dried at 60°C in oven to obtain pure PMMA-CC as product. The white colored PMMA-CC obtained was ground into fine powder using a motor pestle.



**Fig.3.2:** Flowchart for the preparation of PMMA-CC from adduct modified clay.



**Fig.3.3: Experimental setup for polymerization using organoclay**

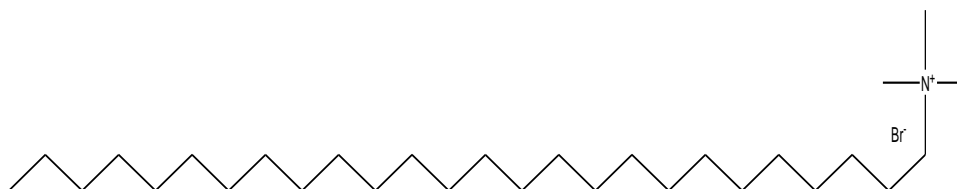


**Fig.3.4: Powdered PMMA-CC**

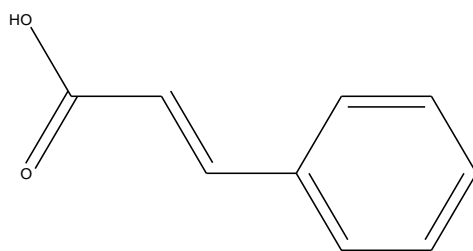
### 3.4 Formation of adduct modified organoclay

#### 3.4.1 Cinnamic acid-CTAB adduct as a clay modifier and formation of organoclay

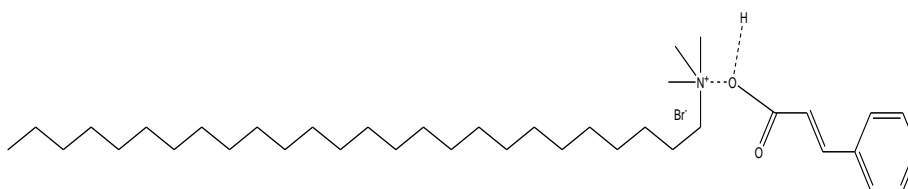
The chemical formula for Cinnamic acid is  $\text{C}_6\text{H}_5\text{-CH=CH-COOH}$ . This carboxylic acid is naturally occurring and has a scent. It is a white crystalline substance that is easily soluble in various organic solvents and slightly soluble in water. It occurs naturally in many plants. Here, Cinnamic acid reacts with the quaternary ammonium surfactant CTAB (Cetyl trimethyl ammonium bromide) has the chemical formula  $[(\text{C}_{16}\text{H}_{33})\text{N}(\text{CH}_3)_3]\text{Br}^-$  to form a CTAB-CA adduct. Cation exchange between the  $\text{Na}^+$ -MMT clay and the adduct results in insertion of the adduct into the clay space, forming a modified organoclay. The structures of CTAB, Cinnamic acid as well as CTAB-Cinnamic acid adduct are shown. (Fig.3.4.1, Fig.3.4.2, Fig.3.4.3).



**Fig.3.4.1: Structure of CTAB**



**Fig.3.4.2: Structure of Cinnamic acid**



**Fig.3.4.3: Structure of CTAB-Cinnamic acid adduct.**

### 3.5 Characterization

The functional group characterization of the adduct modified clay and d-spacing studied using FT-IR and XRD studies.

#### 3.5.1 Characterization using FT-IR

The purpose of using FT-IR analysis on the modified clay is to determine its absorption capacity at each wavelength. The molecular vibrations are examined by infrared spectroscopy. The only bonds that can absorb infrared light are the those with a dipole moment that varies during the vibration. The sample of adduct modified clay and polymer clay nanocomposite prepared using Cinnamic acid-CTAB adduct modified clay was characterized using FT-IR. The spectrum recorded in the range  $4000\text{cm}^{-1}$  to  $400\text{cm}^{-1}$  using KBr pellets. A plot of percentage transmittance verses wavenumber is obtained. Regardless of the composition some groups in the

molecule give rise to distinctive absorption bands whose wavenumber falls within the specific range. The presence of functional groups can be determined from the values of wave number at which absorption is observed. In the present study IR data was used for confirming the intercalation of the modifiers in the clay.

### 3.5.2 Characterization using XRD

In order to learn more about the structure of crystalline materials, X-ray diffraction uses the dual wave/particle duality of X-rays. This technique's primary use is the identification and characterization of substances according to the pattern of their diffraction. Monochromatic X- rays that are falling from an incident beam of radiation interact with atoms within a target material, scattering the falling radiation. The reflected X-ray intensity is plotted against  $2\theta$  values in the XRD graph.

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

where  $n$  is the order of reflection and  $\theta$  is the angle at which the x-ray falls on the sample.  $d$  is the distance between two comparable planes, and  $\lambda$  is the wavelength of monochromatic X-rays. Bragg's equation can be used to compute the d-spacing. In the current work, the angle of diffraction and d-spacing values were analyzed using XRD in order to evaluate the intercalation of clay.

### **3.6 Application - Determination of Antibacterial Activity**

#### **3.6.1 Preparation of nutrient media**

100ml of distilled water was used to dissolve 1.3g of nutritional broth. 5ml of it were poured into the test tubes which were then autoclave to sterilize. In 100ml of distilled water 1.3g of nutrient broth and 2g of agar-agar were combined to create the nutrient media. After the media had been autoclaved 20ml of each was put in sterilized petri dish.

#### **3.6.2 Preparation of microbial cultures**

The test organisms used were *Escherichia coli* (E. coli) and *Staphylococcus aureus* (S. aureus) which were inoculated into 5 ml of sterilized nutrient broth and kept for it for overnight incubation at a temperature of 37°C.

#### **3.6.3 Well diffusion method**

Cotton swabs that had been sanitized were used to create a lawn culture of each one of the bacteria. After being dipped into the bacterial suspension, a sterile swab was pushed from top to bottom leaving no area unoccupied. To cover the entire plate with germs the plate was rotated 90 degrees and the same process was carried out again. After the lawn was ready a sterile well cutters were used to cut 6 mm diameter wells into agar plates. After labeling the wells 20μL of samples AMC, PMMA, PMMA-CC, Ethyl acetate(control) were added to the appropriate wells. The samples AMC, PMMA, PMMA-CC, Ethyl acetate of antibacterial activity was contrasted with that of the common antibiotics on hand (Gen<sup>10</sup>). For about 24 hours this plate was incubated at 37°C. Using a normal ruler the diameter of each zone was calculated in centimeters. No colonies will form if the substance is efficient against bacteria at a particular concentration. This zone of

inhibition serves as a gauge for the compound's efficacy. The greater the clear space surrounding the well the more potent the compound.

#### **3.6.4 Killing and disposing**

After the experiment the bacteria used which were destroyed by autoclaving the petri dish for about 20 minutes and then all the glassware which used for the experiment were also autoclaved to remove any bacteria if present.

# Chapter 4

## Results and discussion

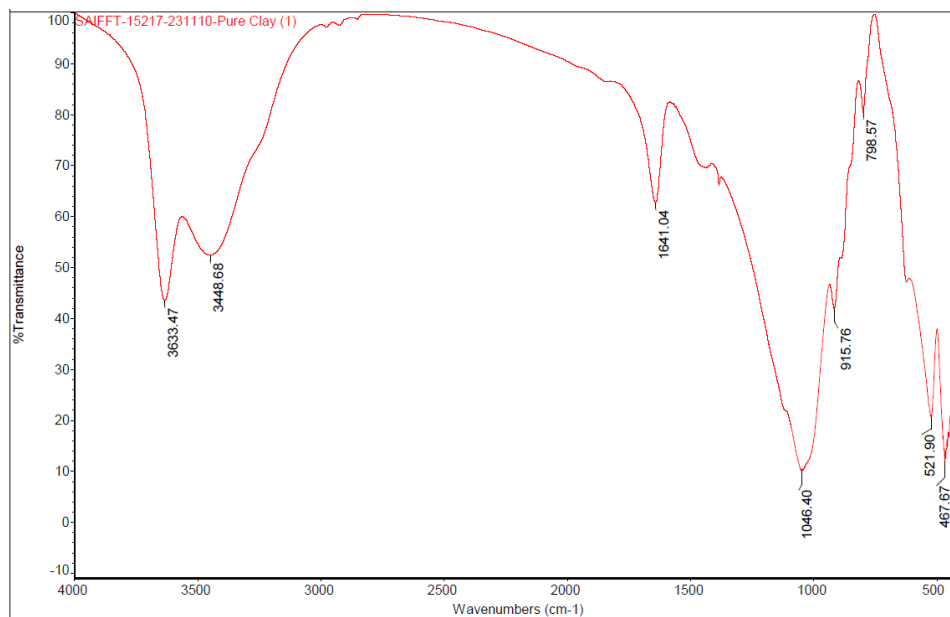
### 4.1 FT-IR Spectroscopy Analysis

The FT-IR spectrum of the Pure Na<sup>+</sup>-MMT clay and organomodified clay with different concentrations were shown in fig.4.1, fig.4.2, fig.4.3, fig.4.4. The FT-IR absorption bands were confirmed in every instance by analysing the characteristics bands[8],[34].

#### 4.1.1 FT-IR Spectrum analysis of Pure Na<sup>+</sup>-MMT Clay

The FTIR spectrum of the Pure Na<sup>+</sup>-MMT clay is shown in fig.4.1.

For pure Na<sup>+</sup>-MMT clay, a broad band at 3448.68cm<sup>-1</sup> indicates the -OH stretching of water molecule in the interlayer of the clay. The band at 3633.47cm<sup>-1</sup> which represents to the -OH stretching of Al-OH bond. The band observed at 1641.04cm<sup>-1</sup> which corresponds to -OH bending vibration of water molecule in the interlayer of the clay. The band identified at 1046.40cm<sup>-1</sup> which represents to the Si-O-Si stretching vibration and the bands at 521.90cm<sup>-1</sup> & 467.67cm<sup>-1</sup> identified as the Al-O-Si and Si-O-Si bending vibrations respectively. The band observed at 915.76cm<sup>-1</sup> which belongs to the bending vibration of Al-OH.



**Fig.4.1: FT-IR of Pure Na<sup>+</sup>-MMT Clay**

The vibrational frequencies of the peaks are listed in the below table 1.

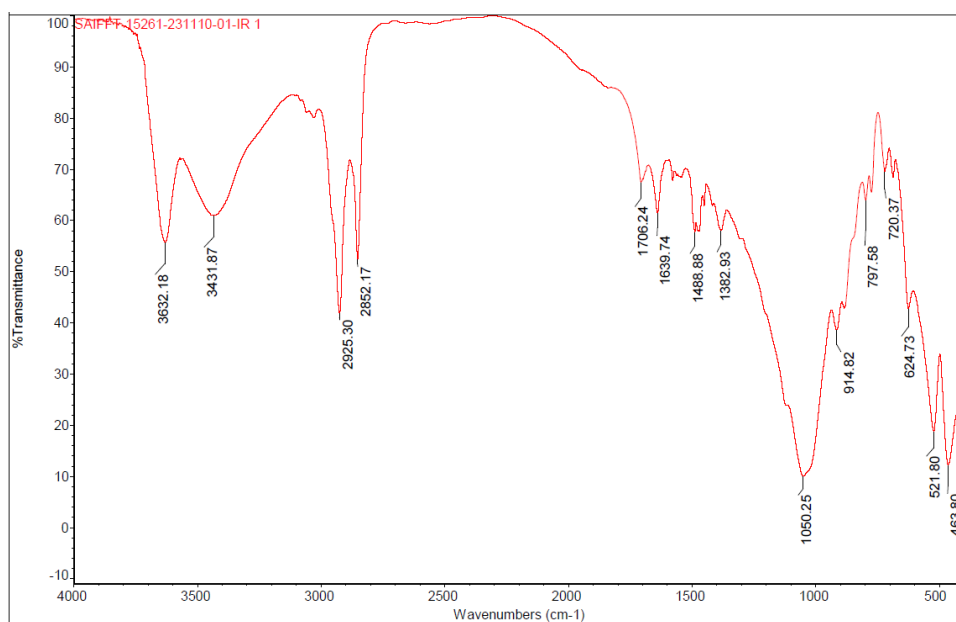
Wavenumber ( $cm^{-1}$ )	Vibration
3633.47	-OH stretching for Al-OH
3448.68	-OH stretching of water
1641.04	-OH bending of water
1046.40	Si-O-Si stretching
915.76	Al-OH bending
521.90	Al-O-Si bending
467.67	Si-O-Si bending

**Table 1: Vibrational frequencies of Pure Na<sup>+</sup>-MMT clay**

#### 4.1.2 FT-IR Spectrum analysis of 0.5x:0.5x concentration of CA-AMC

The FT-IR spectrum of modified clay using Cinnamic acid-CTAB adduct of 0.5x: 0.5x concentration was shown in fig.4.2.

The bands in the pure Na<sup>+</sup>-MMT clay were observed in the 0.5x:0.5x modified clay. In addition to that many absorption bands were observed in the 0.5x:0.5x modified clay. The absorption at 3431.87cm<sup>-1</sup> which corresponds to the -OH stretching vibration of acid group. The additional bands at 2852.17cm<sup>-1</sup> and 2925.30cm<sup>-1</sup> were found which represents the stretching for -CH<sub>2</sub> and -CH<sub>3</sub> respectively of CTAB. These bands support the intercalation of the alkyl group of CTAB into the interlayer of the clay. The band at 1706.24cm<sup>-1</sup> is due to the C=O stretching of cinnamic acid and the absorption band found at 1639.74cm<sup>-1</sup> and 1488.88cm<sup>-1</sup> corresponds to the C=C stretching vibration of alkene and arene respectively.



**Fig. 4.2: FT-IR of 0.5x:0.5x CA-AMC**

The vibrational frequencies of the peaks are listed in table 2.

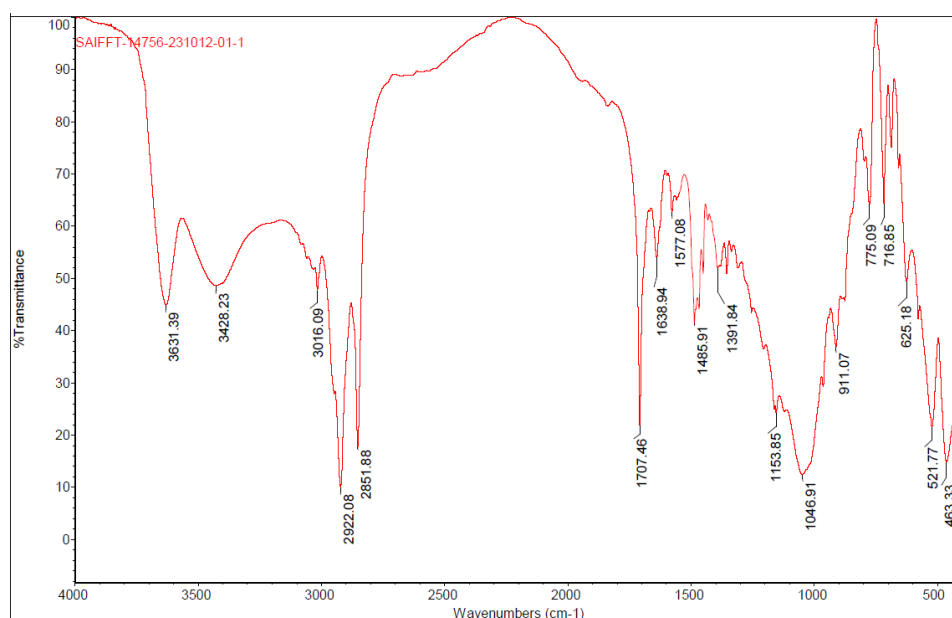
Wavenumber ( $cm^{-1}$ )	Vibration
3632.18	-OH stretching of Al-OH
3431.87	-OH stretching of acid
2852.17	-CH <sub>2</sub> stretching
2925.30	-CH <sub>3</sub> stretching
1706.24	C=O stretching
1639.74	C=C stretching of alkene
1488.88	C=C stretching of arene
1050.25	Si-O-Si stretching
914.82	Al-OH bending
521.80	Al-O-Si bending
463.80	Si-O-Si bending

**Table 2: Vibrational frequencies of 0.5x:0.5x CA-AMC**

#### 4.1.3 FT-IR Spectrum analysis of 1x:1x concentration of CA-AMC

The FTIR spectrum of modified clay with adduct of 1x:1x equimolar concentration was shown in fig.4.3.

The bands in the pure  $\text{Na}^+$ -MMT clay were observed in the 1x:1x modified clay. In addition to that many absorption bands were observed in the 1x:1x modified clay. The absorption band at  $3631.39\text{cm}^{-1}$  corresponds to the -OH stretching vibration of the acid group. The bands at  $2851.88\text{cm}^{-1}$  and  $2922.08\text{cm}^{-1}$  were observed due to the vibration for  $-\text{CH}_2$  and  $-\text{CH}_3$  of CTAB respectively. These bands support the intercalation of the alkyl group of CTAB in the interlayer of the clay. The bands appeared at  $1707.46\text{cm}^{-1}$  corresponds to the  $\text{C}=\text{O}$  stretching vibration related to carboxylic group of the acid. The bands at  $1638.94\text{cm}^{-1}$  and  $1485.91\text{cm}^{-1}$  indicates double bond of alkene and arene respectively.



**Fig.4.3: FT-IR of 1x:1x CA-AMC**

The vibrational frequencies of the peaks are listed in table 3

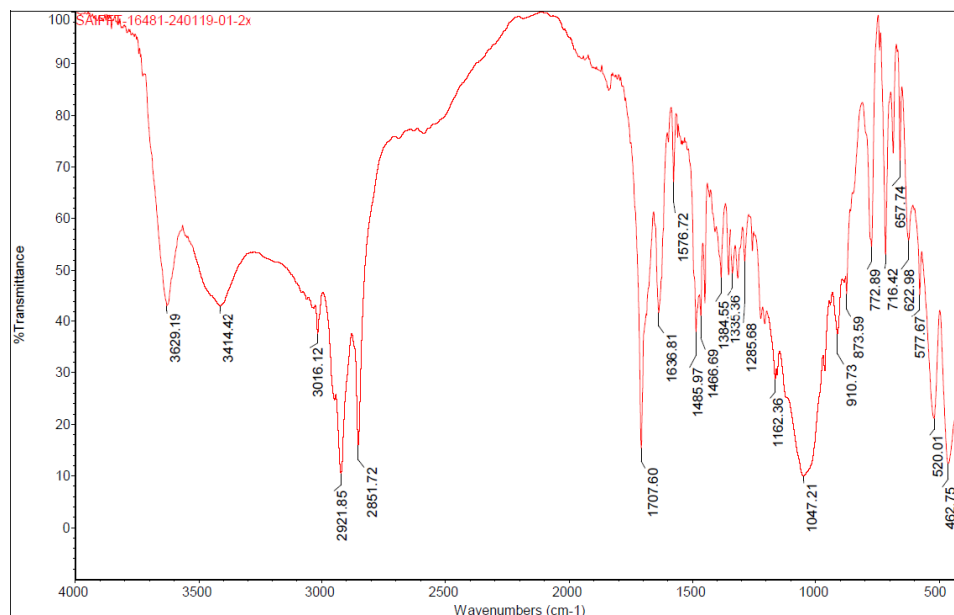
Wavenumber ( $cm^{-1}$ )	Vibration
3631.39	-OH stretching of Al-OH
3428.23	-OH stretching of acid
2851.88	-CH <sub>2</sub> stretching
2922.08	-CH <sub>3</sub> stretching
1707.46	C=O stretching
1638.94	C=C stretching of alkene
1485.91	C=C stretching of arene
1046.91	Si-O-Si stretching
911.07	Al-OH bending
521.77	Al-O-Si bending
463.33	Si-O-Si bending

**Table 3: Vibrational frequencies of 1x:1x CA-AMC**

#### 4.1.4 FT-IR Spectrum analysis of 2x:2x concentration CA-AMC

The FTIR spectrum of modified clay with adduct of 2x:2x equimolar concentration is shown in fig.4.4.

The bands in the pure Na<sup>+</sup>-MMT clay were observed in the 2x:2x modified clay. In addition to that, the absorption band at 3629.19cm<sup>-1</sup> corresponds to the -OH stretching vibration of the acid group. The characteristic peaks at 2851.72cm<sup>-1</sup> and 2921.85cm<sup>-1</sup> were observed due to the stretching vibration for -CH<sub>2</sub> and -CH<sub>3</sub> of CTAB respectively. These bands support the intercalation of the alkyl group of CTAB in the interlayer of the clay. The band appear at 1707.60cm<sup>-1</sup> corresponds to C=O stretching vibration related to carboxylic group. The absorption peaks at 1636.81cm<sup>-1</sup> and 1485.97cm<sup>-1</sup> indicate the double bond of alkene and arene respectively.



**Fig.4.4: FT-IR of 2x:2x CA-AMC**

The vibrational frequencies of the peaks are listed in table 4.

Wavenumber ( $cm^{-1}$ )	Vibration
3629.19	-OH stretching of Al-OH
3414.42	-OH stretching of acid
2851.72	-CH <sub>2</sub> stretching
2921.85	-CH <sub>3</sub> stretching
1707.60	C=O stretching
1636.81	C=C stretching of alkene
1485.97	C=C stretching of arene
1047.21	Si-O-Si stretching
910.73	Al-OH bending
520.01	Al-O-Si bending
462.75	Si-O-Si bending

**Table 4: Vibrational frequencies of 2x:2x CA-AMC**

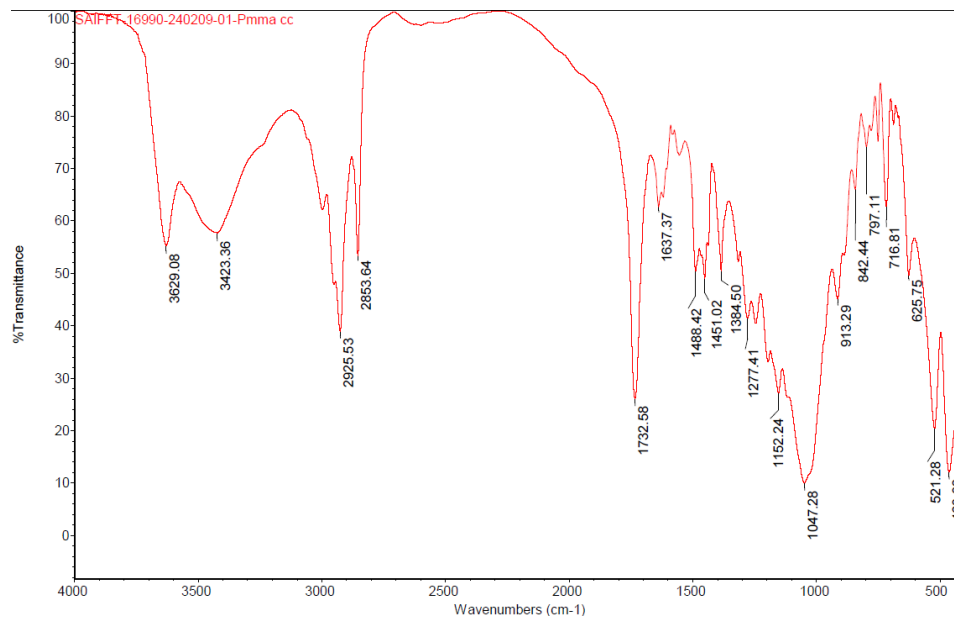
The bands in the pure Na<sup>+</sup>-MMT clay can be observed in these three types of the modified clays with some shifts due to the modifications. All three of the modified clays characteristic peak shifts show that the unmodified clay was completely transformed into the suitable adduct modified clays. And it is also observed that, out of all the three modified clays CA-AMC 2x:2x has the highest intense characteristics bands.

#### **4.1.5 FT-IR spectrum analysis of PMMA clay nanocomposite (PMMA-CC)**

The FTIR spectrum of polymer nanocomposite using Cinnamic acid-CTAB adduct of 2x:2x concentration is shown in fig.4.5.

The PMMA clay nanocomposite (PMMA-CC) was prepared using 2x:2x adduct modified clay (2x:2x CA-AMC). The bands observed in the FT-IR spectrum of 2x:2x CA-AMC were also present in the polymer clay nanocomposite spectrum. The absorption band at  $3629.08\text{cm}^{-1}$  indicates the  $\text{-OH}$  stretching of  $\text{Al-OH}$  present in 2x:2x CA-AMC. The absorption band at  $3423.36\text{cm}^{-1}$  indicates the  $\text{-OH}$  group of the acid present in CA-AMC. The absorption band at  $2925.53\text{cm}^{-1}$  indicates the  $\text{-CH}_3$  symmetric stretching. Similarly, the absorption band at  $2853.64\text{cm}^{-1}$  represents to the  $\text{-CH}_2$  stretching.

In addition to the bands observed in the modified clay, the bands of esters ( $\text{C=O}$ ,  $\text{C-C-O}$ ,  $\text{C-O-C}$  linkages) were identified in the FT-IR spectrum of polymer clay nanocomposite, PMMA-CC. That is the bands identified at  $1732.58\text{cm}^{-1}$ ,  $1277.41\text{cm}^{-1}$ ,  $1152.24\text{cm}^{-1}$  which corresponds to the stretching of the  $\text{C=O}$ ,  $\text{C-C-O}$  and  $\text{C-O-C}$  respectively. Also the absorption band observed at  $1732.58\text{cm}^{-1}$  represents the  $\text{C=O}$  stretching of ester group. So the FT-IR of PMMA-CC validates the intercalation of methyl methacrylate group in between the clay layers.



**Fig.4.5: FT-IR of PMMA-CC synthesized using 2x:2x CA-AMC**

The vibrational frequencies of the peaks are listed in table 5

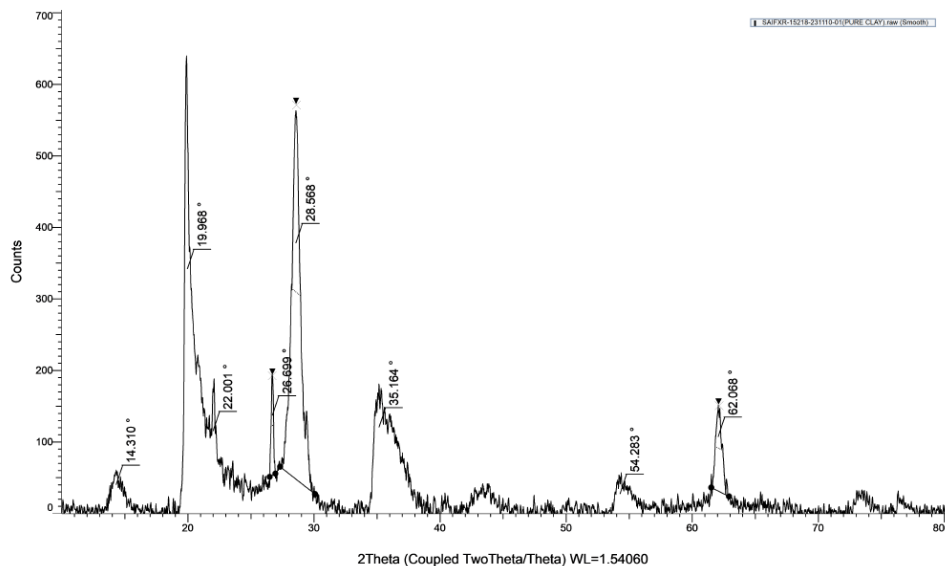
Wavenumber ( $cm^{-1}$ )	Vibration
3629.08	-OH stretching of Al-OH
1277.41	C-C-O stretching
1732.58	C=O of ester
1637.37	C=C of alkene
1488.42	C=C of arene
1047.28	Si-O-Si Stretching
913.29	Al-OH bending
521.28	Al-O-Si bending
463.02	Si-O-Si bending
1152.24	C-O-C stretching
2853.64	-CH <sub>2</sub> stretching
2925.53	-CH <sub>3</sub> stretching

**Table 5: Vibrational frequencies of PMMA-CC synthesized using 2x:2x CA-AMC**

## 4.2 XRD Analysis

The degree of intercalation/exfoliation can be determined by observing the position, shape and intensity of the XRD peak for organomodified clay. We observed the change in (001) reflection peak in each graph. The d-spacing were calculated by considering the (001) reflection [34].

### 4.2.1 XRD analysis of Pure Na<sup>+</sup>-MMT clay

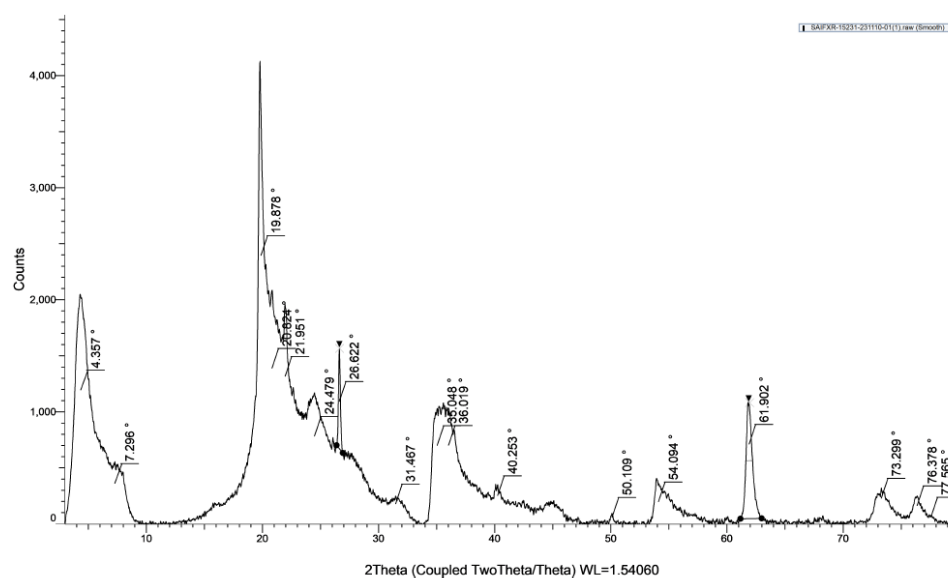


**Fig.4.6: XRD of Pure Na<sup>+</sup>-MMT clay**

Sample	Angle 2θ (degree)	d – spacing (Å°)
Pure Na <sup>+</sup> -MMT clay	14.310	6.18

**Table 6: d-spacing of Pure Na<sup>+</sup>-MMT clay**

### 4.2.2 XRD of 0.5x:0.5x CA-AMC



**Fig.4.7: XRD of 0.5x:0.5x CA-AMC**

Sample	Angle 2 $\theta$ (degree)	d-spacing ( $\text{\AA}^\circ$ )
0.5x:0.5x CA-AMC	4.357	20.26

**Table 7: d-spacing of 0.5x:0.5x CA-AMC**

## 4.2.3 XRD of 1x:1x CA-AMC

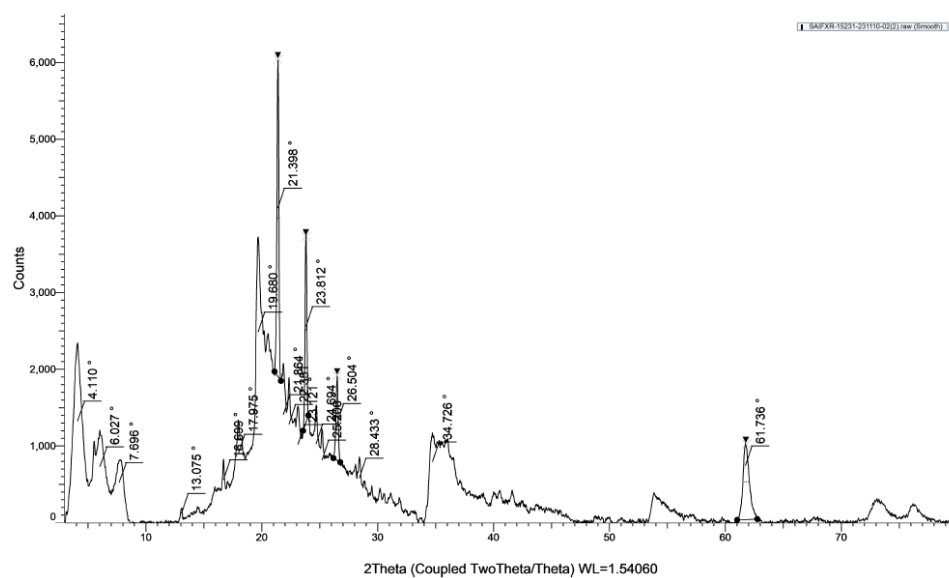
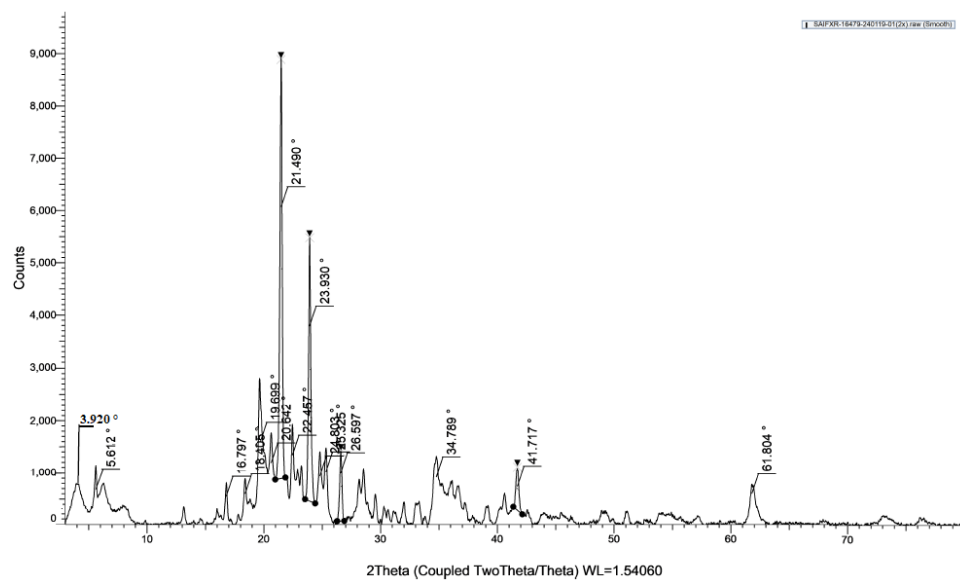


Fig.4.8: XRD of 1x:1x CA-AMC

Sample	Angle 2 $\theta$ (degree)	d-spacing ( $\text{\AA}^\circ$ )
1x:1x CA-AMC	4.110	21.48

Table 8: d-spacing of 1x:1x CA-AMC

#### 4.2.4 XRD of 2x:2x CA-AMC



**Fig.4.9: XRD of 2x:2x CA-AMC**

Sample	Angle 2 $\theta$ (degree)	d-spacing ( $\text{\AA}^\circ$ )
2x:2x CA-AMC	3.920	22.52

**Table 9: d-spacing of 2x:2x CA-AMC**

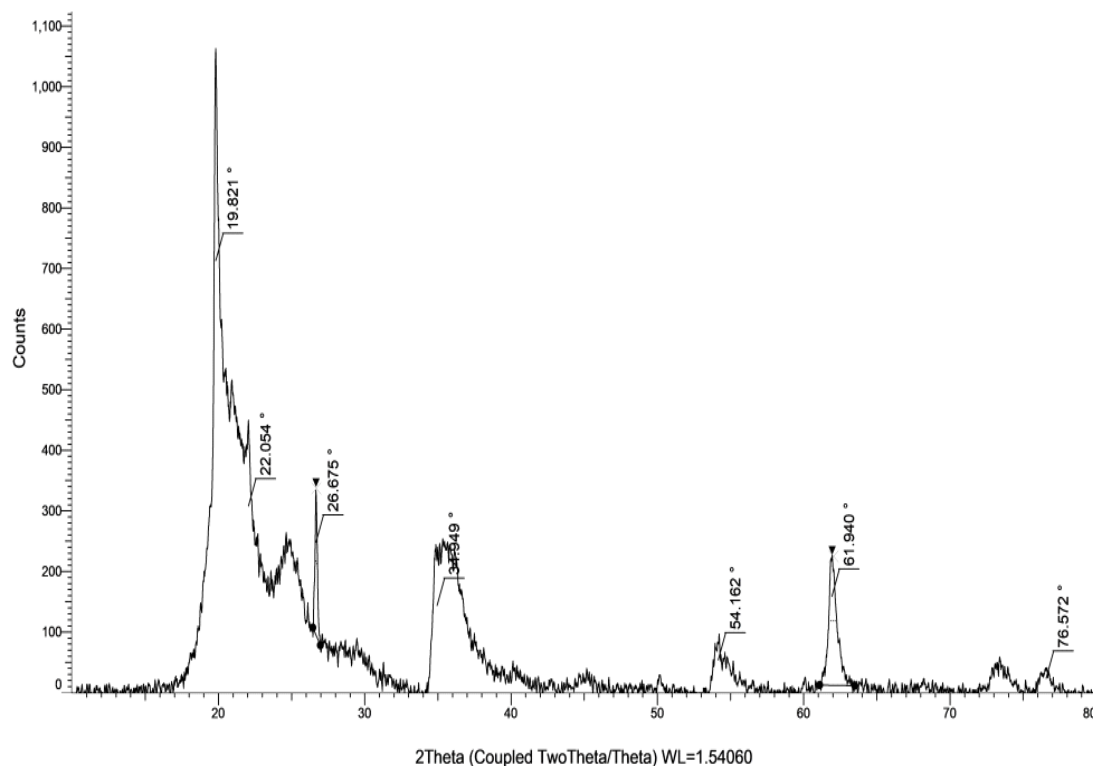
On comparing all the (001) reflection peak of the modified clays (CA-AMC) is listed in the table 10.

Sample	Angle 2 $\theta$ (degree)	d-spacing ( $\text{\AA}^\circ$ )
Pure Na <sup>+</sup> -MMT clay	14.310	6.18
0.5x:0.5x CA-AMC	4.357	20.26
1x:1x CA-AMC	4.110	21.48
2x:2x CA- AMC	3.920	22.52

**Table 10: Comparison of d-spacing of CA-AMC's**

In comparison to the pure Na<sup>+</sup>-MMT clay, it was noted that all of the adduct modified clays (CA-AMC's) (001) reflection peak appeared at smaller angles (2 $\theta$ ), indicating a successful ion exchange. The d-spacing increased from 6.18 $\text{\AA}^\circ$  for pure Na<sup>+</sup>-MMT clay to 20.26 $\text{\AA}^\circ$  for 0.5x:0.5x CA-AMC and 21.48 $\text{\AA}^\circ$  for 1x:1x CA-AMC to 22.5 $\text{\AA}^\circ$  for 2x:2x CA-AMC. These data conclusively show that the addition of an adduct to the unmodified clay's interlayer was responsible for of the increase in d-spacing.

#### 4.2.5 XRD analysis of Polymethyl methacrylate clay nanocomposite (PMMA-CC)



**Fig.4.10: XRD of PMMA-CC**

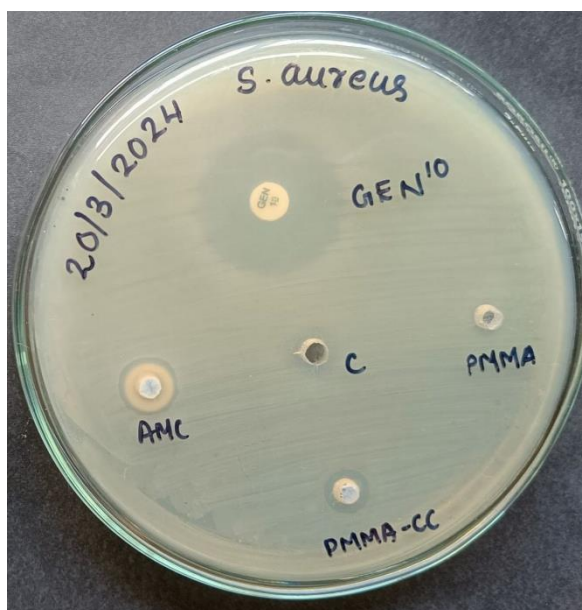
The production of exfoliated nanocomposites was indicated by the disappearing of PMMA-CC (001) reflection peak. The absence of the (001) reflection indicates that either the clay layers are randomly distributed throughout the polymethyl methacrylate matrix or the  $d_{(001)}$  value between the layered silicates is intercalated to a spacing larger than the measurable range. The integration of well exfoliated clay layers into the polymer matrix considerably enhances the nanocomposite characteristics.

#### 4.5 Study of antibacterial activity

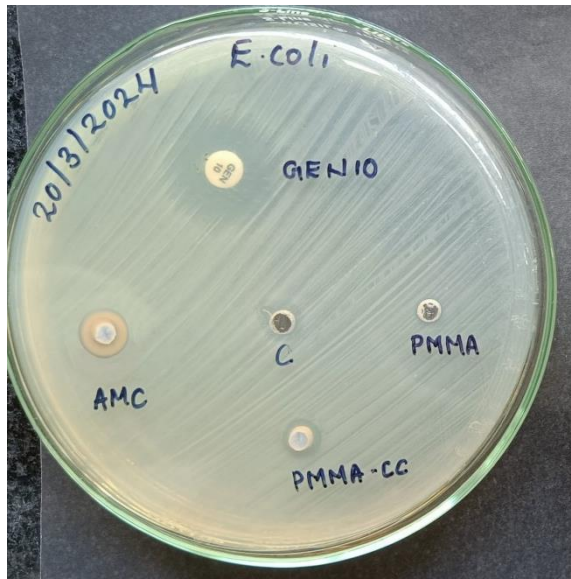
The samples 2x:2x CA-AMC, PMMA, PMMA-CC each was prepared by dissolving 0.064g in 2mL of ethyl acetate. These solutions were kept in the ultrasonicator for 10 minutes. Then the studies were conducted using *S. aureus* and *E. coli* by well diffusion method.

Name of the organism		Zone of inhibition in centimeters			
		Sample No.1 PMMA	Sample No.2 PMMA-CC	Sample No.3 CA-AMC (2x:2x)	Antibiotic disc Gen <sup>10</sup>
<i>S. aureus</i>	Gram positive	No activity	0.9	1.1	2.3
<i>E. coli</i>	Gram negative	No activity	0.7	0.9	2

**Table 11: Antibacterial studies on different bacteria**



**Fig.4.11: Antibacterial study done on *S. aureus***



**Fig.4.12: Antibacterial study done on *E. coli***

From the results we found that PMMA-CC shows good antibacterial activity for both *S. aureus* and *E. coli* on performing well diffusion method. The antibiotic Gentamicin (Gen<sup>10</sup>) which has been taken as a standard has a zone diameter of 2.3cm on the *S. aureus* and 2cm on the *E. coli*. For PMMA alone there is no inhibition zone for *S. aureus* and *E. coli* which indicates no activity. There's a clear inhibition zones for *S. aureus* and *E. coli* in PMMA-CC and AMC(2x:2x CA-AMC). The zone diameter for PMMA-CC is 0.9cm and AMC is 1.1cm for *S. aureus*. The zone diameter of PMMA-CC is 0.7cm and AMC is 0.9cm for *E. coli*. It indicates the good antibacterial property against *S. aureus* and *E. coli*. The tabular column shows how the incorporation of modified clay into the PMMA makes the polymer clay nanocomposite (PMMA-CC) antibacterial compared to that of polymer PMMA alone.

# Chapter 5

## Conclusions

The process of creating modified clay involved exchanging  $\text{Na}^+$  with an acid amine adduct. A direct addition of two or more different molecules produces an adduct which is a single reaction product that has every atom from the interacting compounds in it. Here, equimolar concentrations of Cinnamic acid, an organic acid and Cetyltrimethylammonium bromide were used to prepare the adduct modifier.

The alteration of  $\text{Na}^+$ -MMT by Acid-Amine adducts is done in a simple way. Adduct modifiers were created by reacting aromatic organic acid and CTAB with varying concentrations (0.5x:0.5x, 1x:1x and 2x:2x) by keeping the weight of clay as constant. The effective intercalation of adducts into the interlayer space of  $\text{Na}^+$ -MMT is supported by the FT-IR spectra. The successful ion exchange was further validated by XRD analysis, where all of the adduct modified clays (001) reflections occurred at smaller angles ( $2\theta$ ) than the pure clay. According to the results of FT-IR and XRD, the concentration of acid-amine adduct modifiers on the  $\text{Na}^+$  MMT has exhibited an intense peak in CA-AMC 2x:2x. This also suggests that the same CA-AMC 2x:2x has a greater d-spacing ( $22.52 \text{ \AA}$ ) than the other two low concentrations. This means that the intercalation chemistry of the clay increases with the modifier concentration.

Polymer clay nanocomposite can be created by the use of organically modified clays as efficient reinforcing agents. By introducing a modifier

into the clay's hydrophilic galleries, the interlayer distance grows and the surface chemistry of the clay is altered. In a perfect system, these freshly created organophilic pathways permit polymer or monomer intercalation, which ultimately leads to the synthesis of exfoliated nanocomposite. From the FT-IR and XRD analysis, it is observed that the 2x:2x has the best intercalated structure. Our work aims to create a simple technique for modifying clay by varying the proportion of reactive acid-amine adduct modifiers concentrations.

Polymer clay nanocomposites were synthesized by bulk polymerization of Methyl methacrylate monomer by treating 2x:2x organo-modified clay using Benzoyl Peroxide(BPO) as an initiator. The Polymethylmethacrylate clay Nanocomposite (PMMA-CC) obtained is also characterized using XRD and FTIR spectroscopy. In the case of PMMA-CC, FT-IR showed absorptions of C-O stretching, C=O stretch of ester, C=C of alkene, C-C stretching and C-H stretching of alkane in addition to the characteristic vibrations present in the adduct modified clay. The disappearance of (001) peaks of the PMMA-CC indicates the formation of exfoliated nanocomposites. This supports the successful formation of highly exfoliated polymer clay nanocomposite.

PMMA-CC is obtained which has significant properties. The incorporation of well-exfoliated clay layers into the polymer matrix considerably enhances the nanocomposite characteristics. It generally displays antibacterial properties, enhanced mechanical strength, fire retardancy, thermal stability, and barrier qualities.

Polymethyl methacrylate clay nanocomposite was prepared by bulk polymerization, has the most exfoliated structures and consequently, the

best properties. This is mainly due to the possibility of growing polymer molecules from the clay surface using cationic initiators

One of the applications we carried out is the Antibacterial study of organoclay modified PMMA. And it is found that the PMMA-CC shows good antibacterial activity towards *E. coli* and *S. aureus* whereas unmodified, regular PMMA does not show any antibacterial activity. So the incorporation of the adduct modified clay (AMC) into the polymer produces modified PMMA (PMMA-CC) which shows antibacterial properties. This is because the AMC used in the study contains Cinnamic acid and CTAB, both known for their antibacterial activity.

Hence AMC used in this study can be used as a filler in the PMMA polymer to make the polymer antibacterial. Hence the synthesised polymer, PMMA-CC can be used as a potential packing material with antibacterial activity and it can also be used for waste-water treatment by destroying the disease-causing deadly bacteria, especially *E. coli* and *S. aureus*.



## References

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