PROJECT REPORT

On

“Synthesis and characterizations of polymethyl methacrylate nanocomposite using adduct modified clays”

Submitted by

LIYA ANTONY
(AM21CHE011)

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)
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M.Sc. CHEMISTRY PROJECT REPORT

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CERTIFICATE

This is to certify that the project work entitled **“SYNTHESIS AND CHARACTERIZATIONS OF POLYMETHYL METHACRYLATE NANO COMPOSITE USING ADDUCT MODIFIED CLAYS”** is the work done by **LIYA ANTONY** under the guidance of **Dr.Annu Raju, Assistant professor,** Department of Chemistry and Centre for Research, St. Teresa’s College, Ernakulam in partial fulfilment of the award of the Degree of Master of Science in Chemistry at St. Teresa’s College, Ernakulam affiliated to Mahatma Gandhi University, Kottayam.

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CERTIFICATE

This is to certify that the project work entitled is **“SYNTHESIS AND CHARACTERIZATIONS OF POLYMETHYL METHACRYLATE NANO COMPOSITE USING ADDUCT MODIFIED CLAYS”** the work done by **LIYA ANTONY** 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.

DR. ANNU RAJU
Project Guide

DECLARATION

I hereby declare that the project work entitled **“SYNTHESIS AND CHARACTERIZATIONS OF POLYMETHYL METHACRYLATE NANO COMPOSITE USING ADDUCT MODIFIED CLAYS ”** 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.

LIYA ANTONY

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ABBREVIATIONS

JNCs	Joint nomenclature committees
CMS	Clay Minerals Society
Na-MMT	Sodium montmorillonite
AMC	Adduct modified clay
SA-AMC	Stearic acid-adduct modified clay
CA-AMC	Cinnamic acid-adduct modified clay
CTAB	Cetyl trimethyl ammonium bromide
SA-CTAB AMC	Stearic acid-cetyl trimethyl ammonium bromide adduct modified clay
CA-CTAB AMC	Cinnamic acid- cetyl trimethyl ammonium bromide adduct modified clay
PCN	Polymer clay nanocomposite
PMMA/PMA	Polymethyl methacrylate
PMMA-SC	polymethyl methacrylate-stearic clay nanocomposite
PMMA-CC	polymethyl methacrylate-stearic clay nanocomposite
XRD	x-ray diffraction
FTIR	Fourier transformation infrared spectroscopy

Chapter 1

Introduction

For different groups of people, the term clay might have distinct connotations. Clays are the mechanical and chemical environment in which most plants thrive, according to the farmer. For over 4000 years, it has been the raw material of the ceramist's creations. According to the editor, it softens the surface of the paper in high-quality printing. In the medical field, it could be used to treat diarrhoea, among other things. In fact, there is no standardized terminology for clay and clay products [1, 2].

Georgius Agricola (1494-1555), the inventor of geology, appears to be the first to define clay in 1546. It has been updated multiple times, as a result of which the clay definition raises questions about the elements of clay, which was highly important [3]. The Joint Nomenclature Committees (JNCs) of the Association Internationale pour l'Etude des Argiles (AIPEA) and the Clay Minerals Society (CMS) made the most recent effort to resolve all of these difficulties. Clay, a naturally occurring material comprised primarily of fine-grained minerals, becomes elastic in the presence of water and rigid when dried or burnt, according to these societies [4, 5].

Polymer clay nanocomposites (PCN) are a new family of materials with a polymer matrix reinforced by uniformly dispersed inorganic particles of at least one nanometer dimension. They frequently display physical and chemical properties that differ significantly from pure polymers, and typical microcomposites have a broad range of applications as sophisticated functional materials. Clays have been widely employed as fillers for commodity thermoplastics such as polypropylene, polyethylene, polystyrene, and nylon due to their natural abundance, low cost, and wider economic viability.

The field of polymer-clay nano-composites has recently gained popularity due to improvements in the thermal and mechanical properties of the matrix polymer and the ability to melt the polymer with clays without the need of organic solvents. The improved characteristics were attributable to the dispersion of nanometer-thick clay layers in the polymer matrix.

PCNs have found widespread application in industry as a high-performance structural material. With pre-existing industrial equipment, they may be moulded into intricate shapes. Because the nano-dispersed clay layers lower the permeability of the polymer matrix, PCNs can also be employed for packing or storage tank applications. Polymer clay nanocomposites have grabbed the interest of researchers over the last two decades because they frequently exhibit extraordinary thermal, mechanical, and barrier capabilities due to the dispersion of nanometer-sized silicate layers in a polymer matrix. It has been claimed that by tuning the polymer-clay interactions, nanocomposites with diverse structures/morphology, characteristics, and applications can be generated.

1.1 : CLAY, CLAY MINERALS

Clay is a soft, flexibly bonded, fine-grained natural rock or earthy substance with a diameter of less than 0.005 mm that is primarily formed of clay particles. Clays, according to the traditional definition of mineral, are primarily inorganic materials, with the exception of peat, muck, and some soils, which contain a significant quantity of organic/natural components. Over long periods of time, clay particles are generated by the weathering and erosion of rocks containing soil, ceramic clays, clay sandstone, glacial clays (including a large volume of detrital and transportable clays), and the mineral group feldspar (known as the ”mother of clay'). During weathering, the feldspar concentration is distorted by the hydrolysis process, resulting in the formation of clay minerals such as kaolinites (the primary minerals in kaolin clays) and smectite (the primary minerals in smectite clays). Even in the presence of trace amounts of quartz ($SiO2$), metal oxides ($Al2O3$, MgO, etc.), and organic matter, clay can integrate with one or more clay minerals [6, 7].

Clays' plasticity is caused by particle size, geometry, and water content, and they become hard, stiff, cohesive, and non-plastic after drying or burning. The chemical composition of the material found in clay has a significant impact on plasticity and hardness. When clays hold water, they can be fashioned into any shape. Some chlorite and mica species, for example, have been discovered to be non-plastic when grinding macroscopic flakes, even when more than 70% of the material is 2 m esd (equivalent spherical diameter).Clay minerals are a type of hydrous aluminum silicate with a layer (sheet-like) structure and relatively small particle size. Clay materials have unique qualities due to their small particle size and unusual crystal formations. The features of clays include cation exchange capabilities, plastic behaviour when wet, catalytic abilities, swelling behaviour, and limited permeability. They increase the use of clay and clay-based minerals in a variety of businesses and activities. Organically modified clay or organoclays are used to enhance clay dispersion in polymer matrices; this offers a strong interaction between polymers and nanoparticles, allowing the generation of intercalated and/or exfoliated morphologies. Hence the process of organo-modification is of great importance in terms of its wide variety of applications because organically modified clays swell in the presence of organic fluids like gasoline or fuel oil, they can be used as sorbents in spill control or as liners for fuel oil tank containment areas. They are good at removing grease, oils, and organic substances with limited solubility from aqueous streams. They are also employed as organic pollutant adsorbents in paint, cosmetics, and personal care goods.

Clays have been receiving a lot of attention in recent years. Clay minerals are classified as layered silicates, which are silicates with a layered structure [8]. They have recently attracted a lot of attention for their ability to provide mechanical reinforcement [9], gas barrier [10, 11], and even flame-retardant properties to polymers [12]. Clays are also capable of providing dramatic and variable enhanced characteristics at extremely low loadings without sacrificing pure polymer processability due to their inexpensive price, availability, high aspect ratio, and favourable nanostructure and interfacial interactions [13]. Because of their natural availability, low cost, and widespread commercial viability, clays are now commonly used as nanofillers for thermoplastics such as polypropylene, polyethylene, polystyrene, and nylon. Organically modified clays or organoclays are often used to increase clay dispersion in polymer matrices, offering strong interaction between polymers and nanoparticles, facilitating the production of intercalated and/or exfoliated morphologies. As a result of its vast range of applications and uses, the process of organo-modification is critical.

Organo-clays are exceptionally effective at removing oils, greases, and other organic substances with high molecular weights and limited solubility from aqueous streams. The use of organoclays in waste water treatment is becoming commonplace in industry. They have applications in cosmetics, paint, personal care products, and as organic pollutant adsorbents, among other things. Polymer clay nanocomposite (PCN) as sorbents, catalysts, and biomaterials are now the most appealing and promising applications of organomodified clays.

1.2 : STRUCTURE OF CLAY

Clays are layered silicates composed up of stacks of hydrated aluminosilicates with a minimum thickness of 1 nm and lateral dimensions ranging from 50 to 1000 nm. Their basic building blocks are tetrahedral sheets [fig 1.0] with four oxygen atoms surrounding silicon and octahedral sheets [fig 1.1] with eight oxygen atoms surrounding a metal like aluminum. The tetrahedral and octahedral sheets are joined by exchanging oxygen atoms. The hydroxyl form has unshared oxygen atoms. Tetrahedral and octahedral sheets typically stack in a specific ratio and mode, resulting in the formation of 1:1 layered silicates or Phyllosilicates, for example.

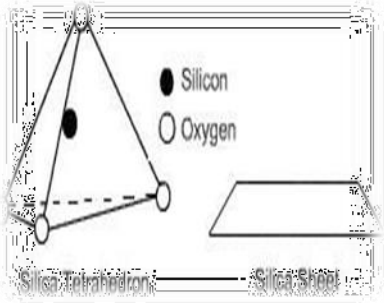


Fig 1.0: Silica sheet

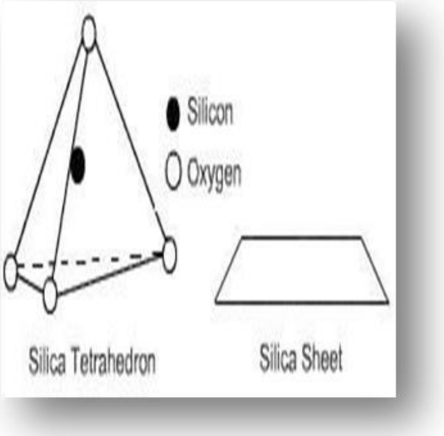


Fig 1.1: Alumina sheet

Clay layers are made up of tetrahedral sheets with four oxygen atoms surrounding a silicon atom and octahedral sheets with eight oxygen atoms surrounding a metal such as aluminium or magnesium [14, 15]. The oxygen atoms connect the tetrahedral (T) and octahedral (O) sheets. The hydroxyl form has unshared oxygen atoms. In most clays, there are two main configurations of T and O layers. The kaolin group is composed of one tetrahedral fused to one octahedral (1:1). A tetrahedral sheet is fused with an octahedral sheet in a 1:1 layered structure known as the kaolin group, with a layer thickness of 0.7 nm and a typical composition of $Al_2Si_2O_5(OH)_5$. , the oxygen atoms are shared.

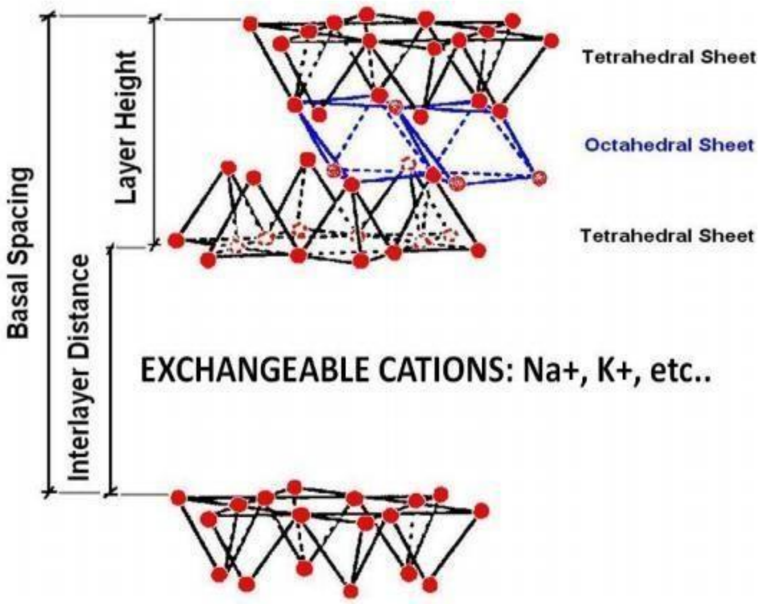
On the other hand, the crystal lattice of 2:1 layered silicate (or 2:1 Phyllosilicate), consists of two- dimensional layers where a central octahedral sheet of alumina is fused to two external silica tetrahedra by the tip, so that the oxygen ions of the octahedral sheet also belong to the tetrahedral sheets, as shown in [fig1.2]. 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.

Phyllosilicates are formed by one octahedral sheet bonded between two tetrahedral sheets (2:1) with a total thickness of 0.94 nm. When the aluminum cations in the octahedral layers are partially substituted by divalent magnesium or iron cations, the smectite clay group is formed, whose structure consists of a central sheet containing groups $MO_4(OH)_2$ of octahedral symmetry associated with two tetrahedral sheets (MO_4) producing layers designated as T:O:T (see Figure 1.2)

Fig 1.2: **The structure of 2:1 layered silicate**

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

When silicon in tetrahedral sheet is substituted by aluminum, the resulting structure is called mica. Due to this substitution, the mineral is characterized 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.



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 [16]. Due to the inter layer spacing and weak forces between layers, especially in the hydrated form, other molecules also intercalate between layers, leads to the expansion of layered lattice and may finally cause the separation of individual layers.

1.3: Characteristics of clay minerals

Clay minerals are regarded as a gift for humans, since they are regularly explored through study due to their low cost, environmental friendliness, ease of availability, and non-toxicity. Clay minerals are so common that there is barely any country on the globe that does not have deposits of one or more types of clay minerals. Clay minerals are found in nature and have unique physical and chemical properties that make them useful in a variety of sectors, ranging from research to industry [17]. Clay minerals are a type of rock-forming mineral that has a porous-like sheet structure with varying distances between the sheets. The electrical conductivity (mS/m) of the porous material is the sum of the electrical conductivity of the matrix material and the pore fluid. The cation exchange capacity of clay materials, defined as the number of potentially charged ions exchanged by the negatively charged surface, is determined by the number of sheets and the cations distributed in these structures [18]. As a result, the physical and chemical properties of clay minerals are heavily influenced by their sheet structure, cation- and anion-exchange capacity, and adsorption ability, which define their value in various applications [19].

MONTMORILLONITE

Montmorillonite (MMT) is a natural clay mineral that belongs to the smectite group. It is a dioctahedral 2:1 phyllosilicate composed of two tetrahedral and one octahedral sheet (T:O:T) [20].

It is the most commonly used nano clay raw material. It is the Mg form of smectite. It is the family of 2:1 phyllosilicate clay having permanent layer charge. Montmorillonite can expand by several times its original 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).

In contrast to other clay nanoparticles, montmorillonite has an interlayer gap between each triple-sheet layer. Chemically, the MMT consists of isomorphic substitutions of Si4+ by Al3+ in the tetrahedral sheet and Al3+ by Mg2+ in the octahedral sheet. Because of this arrangement, montmorillonite has a negative residual charge that is compensated for by cations in the interlayer space[21].

1.4: cation-exchange capacity

The ability of clay minerals to adsorb specific cations and anions and retain them around the exterior of structural units is determined by a lack of positive or negative charge in their mineral structure. The ions that are absorbed trade places with other ions. The quantitative connection between the interacting ions distinguishes the exchange reaction from simple sorption. The number of cations retained on the surface of soil particles is measured by cation-exchange capacity (CEC) [22]. It is defined as the number of cations accessible for exchange with other cations at a certain pH and is often represented in milliequivalent per 100 grams of dry clay.

Negatively charged ions on the surface of soil particles link with positively charged ions but are allowed to exchange in the surrounding soil water with other positively charged particles, resulting in a modification in soil chemistry [23]. CEC has an impact on several areas of soil chemistry. CEC measures soil fertility since it indicates the soil's ability to retain nutrients such as K+, NH4+, and Ca2+. It also denotes the ability to retain polluting cations such as Pb2+. Because CEC is affected by particle size, crystallinity perfection, and adsorbed ion, values for a given mineral exist in a range rather than a single specific capacity. Because of the presence of hydroxyl groups on the surface of certain clay minerals, such as allophane and kaolinite, exchange capabilities are also pH-dependent.

The adsorbed cations either replace or exchange the initial negative charge layer. This ability of colloidal particles, such as clay minerals, to retain and exchange positively charged ions is significant because it influences the mobility of positively charged chemical species in soils as well as the overall geochemical cycling of cations [24]. Because of the existence of interlayer exchangeable cations such as smectites, CEC is a reversible process that is generally associated with clay minerals.

1.5: Swelling capacity

When dry clay minerals are allowed to adsorb water in a controlled setting, water is introduced into their interlayer space in more or less separate layers, causing swelling or expansion of the interlayer space. The enlargement of clay mineral interlayer space is caused by hydration energy forces associated with particle contact [25]. Swelling clays are prone to substantial volume changes caused by changes in water content. Clay minerals' swelling capacity is determined by the following factors:

- **Clay mineral layer charge density**
- **The type of interlayer ions, whether monovalent or divalent.**
- **The ion concentration in the surrounding solution containing clay minerals.**
- **The amount of water present in the interlayer of clay minerals.**
- **The quantity and types of minerals present, i.e. clay mineral composition**.

1.6: Organo clay

Organoclay is an organically modified clay layer with hydrophobic agents that is required to make the clay layers compatible with polymer chains. This is a surface modification that reduces the surface energy of clay layers and matches their surface polarity with the polarity of the polymer. Under well-defined experimental conditions, organoclays with lower surface energy are more compatible with polymers, and polymer molecules can intercalate within their interlayer space or galleries.

Organoclay is a naturally occurring clay mineral that has been organically transformed into a phyllosilicate. The original interlayer cations are replaced with organo-cations (usually quaternary alkyl ammonium ions), resulting in an organophilic surface composed of covalently bonded organic moieties. The lamellar structure is still similar to the parent phyllosilicate. Sodium montmorillonite (Na-MMT) is a layered silicate that belongs to the 2:1 phyllosilicate structural family of smectite clay. It is commonly used as nanofiller in the synthesis of polymer clay nanocomposites (PCNs) because it has improved mechanical properties, heat resistance, and barrier properties [26].

Clay layer surface modification can be accomplished using a cation exchange method in which sodium and calcium cations present in the interlayer space or clay galleries are replaced with alkyl ammonium or alkyl phosphonium (onium) cations [27].

The fundamental difficulty in the design of PCNs is how to monitor the dispersion of clay platelets in a polymer matrix at the nanoscale. As a result, it is critical to comprehend the interaction between the clay surfaces and the intercalants. In other words, knowing the structure of organoclays and surfactant interactions in clays is critical in the design, production, and characterization of PCNs. The type of polymer used is crucial to the proper selection of organoclays. When hydrated cations are ion-exchanged with organic cations such as bulky alkyl ammonium or alkylphosphonium cations, the inter layer space often increases. Furthermore, alkyl ammonium or alkyl phosphonium cations can give functional groups that can react with the polymer matrix or, in some situations, trigger monomer polymerization to improve the strength of the interface between the inorganic and the polymer matrix. The chains were assumed to lay either parallel to the silicate layers, producing mono or bilayers, or radiate away from the silicate layers, forming mono or bimolecular rearrangements, depending on the packing density, temperature, and alkyl chain length.

In addition to surface modification and increased hydrophobicity of clay layers, the insertion of alkyl ammonium or alkyl phosphonium cations into the galleries increases interlayer spacing, which promotes the subsequent intercalation of polymer chains into the galleries during nanocomposite preparation [28]. Furthermore, alkyl ammonium and alkyl phosphonium cations can offer functional groups that interact with polymer chains or induce polymerization, increasing interfacial contacts. [Fig. 1.3] depicts the organic alteration of clay layers via the ion exchange process utilizing alkylammonium cations.

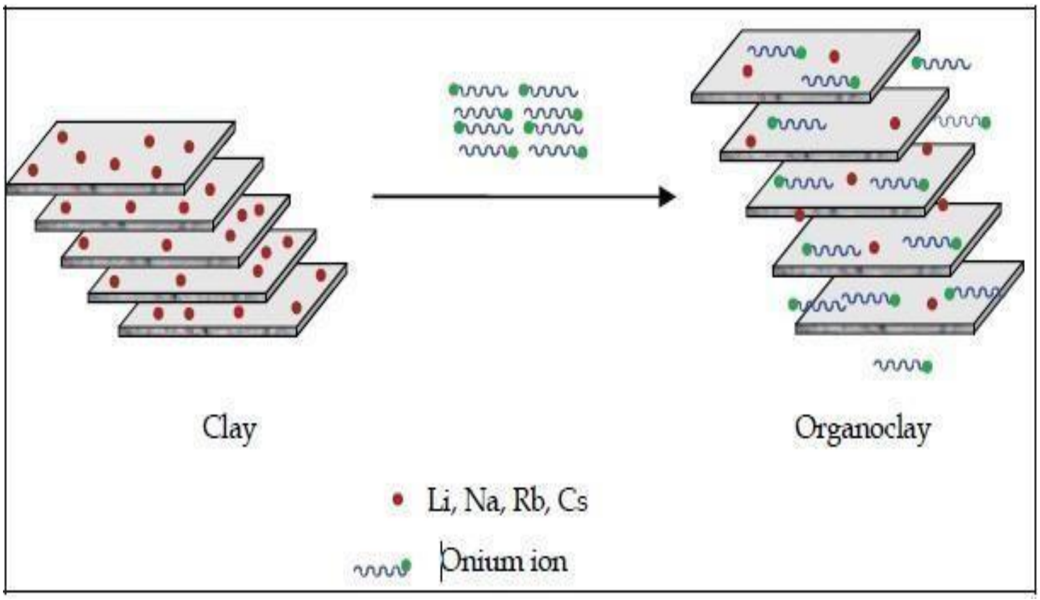


Fig 1.3: scheme of the modification of clay layers by organic onium ions

1.7: Polymer-clay materials

A polymer-clay substance is generated by combining a polymer with synthetic or natural clay. The incorporation of clay can increase the polymer's mechanical, thermal, barrier, and fire retardancy properties. A polymer-clay structure is called a nanocomposite if it contains at least one phase with nanometer-scale organization. It is noteworthy to point out that the primary properties of polymer-clay composites are highly related to the physical and chemical properties of each component, as well as the nanosize aspect and interfacial adhesion between the nanocomposite portions [29, 30].

Polymer nanocomposites have at least one component on the nanometer scale (100 nm). Despite the fact that the term "nanocomposite" is relatively new, it has been possible to identify a diverse range of materials in nature, such as bones, shells, and wood that can be considered nanocomposites because they are formed by carbohydrates, lipids, and proteins organized in the nanometer regime [31]. Characterization and control of structures at the nanoscale level have been examined, investigated, and exploited in recent years. As a result, nanocomposite technology has evolved into a potent and efficient technique for improving the structural and functional properties of synthetic polymers. Due to the demonstration of better qualities such as strength, toughness, and fire barrier much above those of typical microcomposites and comparable with those of metals, polymer nanocomposites have garnered considerable attention. In addition to improving the polymer bulk phase's mechanical, thermal, barrier, durability, chemical stability, flame retardancy, scratch and wear resistance, biodegradability, and optical, magnetic, and electrical properties, the presence of one nanoscale phase causes significant interfacial contacts between the polymer and clay [32–35]. Clay content and aspect ratio are associated with the improved mechanical performance of nanocomposites [36].

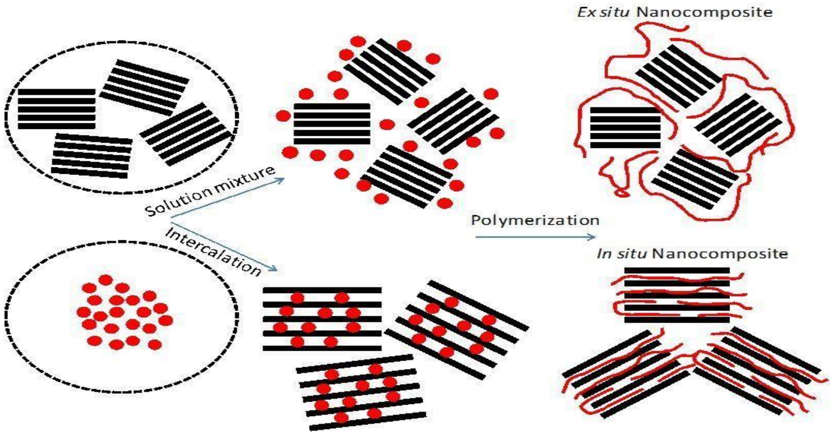


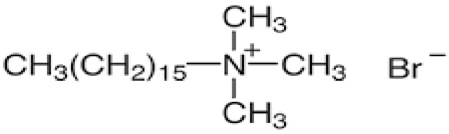
Fig 1.4: Schematic representation of two types of preparations of polymer-clay nano composite

Clays have been used frequently to create polymer nanocomposites. Due to their significantly better properties than traditional polymer composites in a relatively small percentage, polymer-clay nanocomposites have recently attracted increasing interest [37, 38]. As shown in Figure 1.4, polymer-clay nanocomposites can be made by mixing two aqueous solutions containing the monomer and the clay suspension directly. The polymer can then be created by adding a polymerization agent or by inducing it with heat or light. The final product is known as an ex situ nanocomposite since the majority of the polymer may be located outside the clay's interspaces. It is significant to note that the initial clay concentration can be adjusted and that the clay layers can occasionally be completely separated. As a result, the final product is referred to as an exfoliated polymer-clay nanocomposite. The monomer is intercalated in the interlayer space of the clays in a second approach (see Figure 1.4) by charge exchange or by diffusion inside the clay galleries that have been previously altered with an organic salt. Because the majority of the polymeric content is located inside the clay interspaces, the intercalated polymer can then be polymerized to create what is known as an in situ nanocomposite.

1.8: Formation of organoclay

1.8.1 STEARIC ACID-CTAB adduct as a clay modifier and formation of organoclay

A saturated fatty acid with an 18-carbon chain is stearic acid. Octadecanoic acid is known by its IUPAC name. It has the chemical formula $CH_3(CH_2)_{16}CO_2H$ and is a waxy solid. In nature, stearic acid is a colorless substance that has no odour [39]. Its melting point is 69.3 °C. Through the long chain, it can improve clay polymer intercalation. The quaternary ammonium surfactant CTAB (cetyl trimethyl ammonium bromide) has the chemical formula $[(C_{16}H_{33})N(CH_3)_3]Br$. Stearic acid reacts with CTAB to form CTAB-SA adduct.



$$CH_3(CH_2)_{15}-\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}-CH_3 \quad Br^-$$

Fig 1.5: structure of CTAB

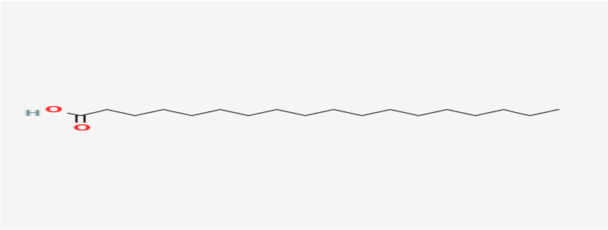
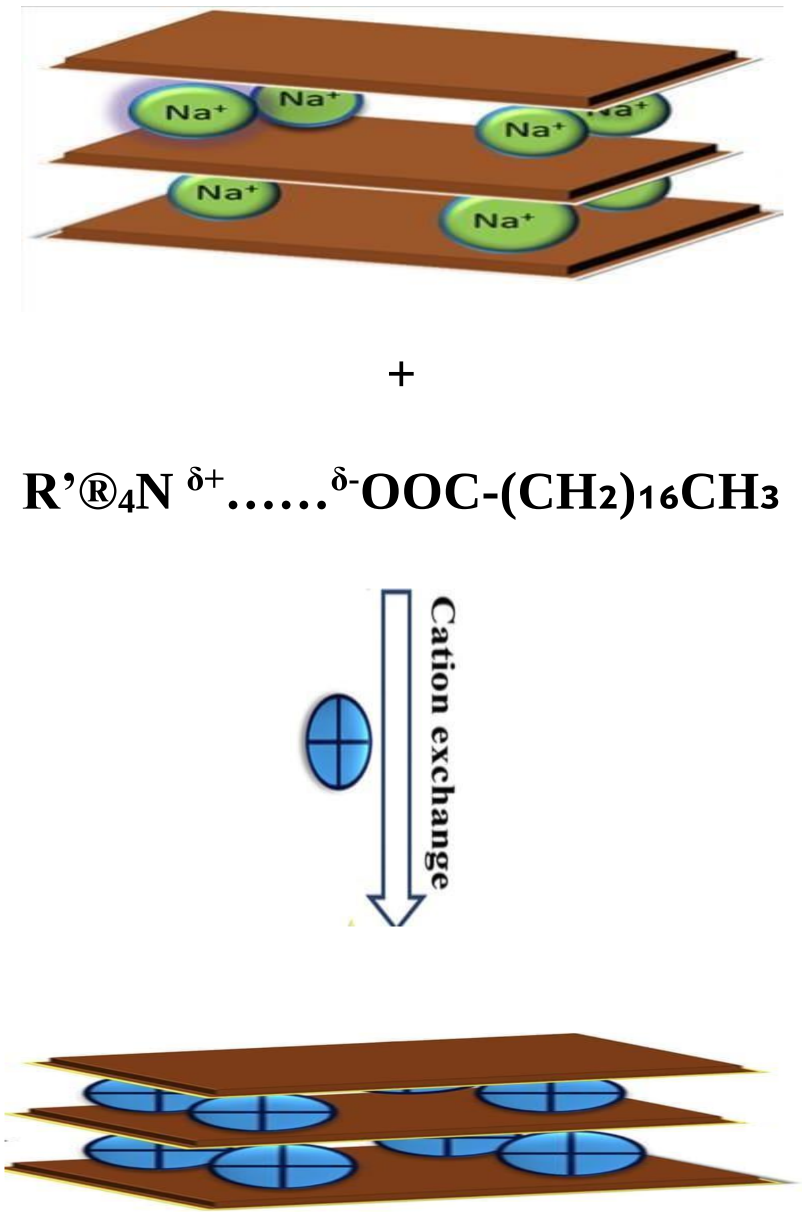


Fig 1.6: structure of stearic acid

$$R'(R)_4N^{\delta+}\ldots\ldots{}^{\delta-}OOC\text{-}(CH_2)_{16}CH_3$$

$$R': CH_3\ (CH2)_{15},\ R: CH_3$$

Fig 1.7: CTAB–SA adduct



$$R'®_4N^{\delta+}\ldots\ldots{}^{\delta-}OOC\text{-}(CH_2)_{16}CH_3$$

Fig 1.8: formation of organoclay

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. See fig 1.8.

1.8.2 CINNAMIC ACID-CTAB adduct as a clay modifier and formation of organoclay

The chemical formula for cinnamic acid is C_6H_5-CH=CH-COOH. This carboxylic acid is naturally occurring and fragrant. It is a white, crystalline substance that is easily soluble in various organic solvents and only marginally soluble in water [40]. Numerous plants naturally contain it [41]. Here cinnamic acid reacts with CTAB to form CTAB-CA adduct.

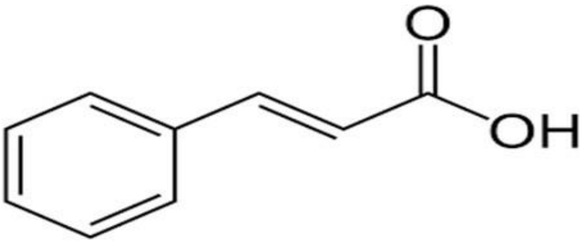
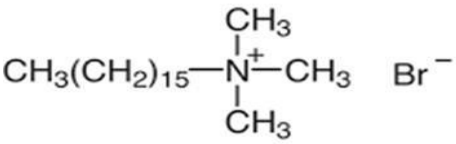


Fig 1.9: Structure of cinnamic acid



$$CH_3(CH_2)_{15}-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_3 \quad Br^-$$

Fig 2.0: structure of CTAB

$$\mathbf{R'(R)_4N^{\delta+}\ldots\ldots{}^{\delta-}OOC\text{-}CH{=}CHC_6H_5}$$

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

Fig 2.1: CTAB–CA adduct

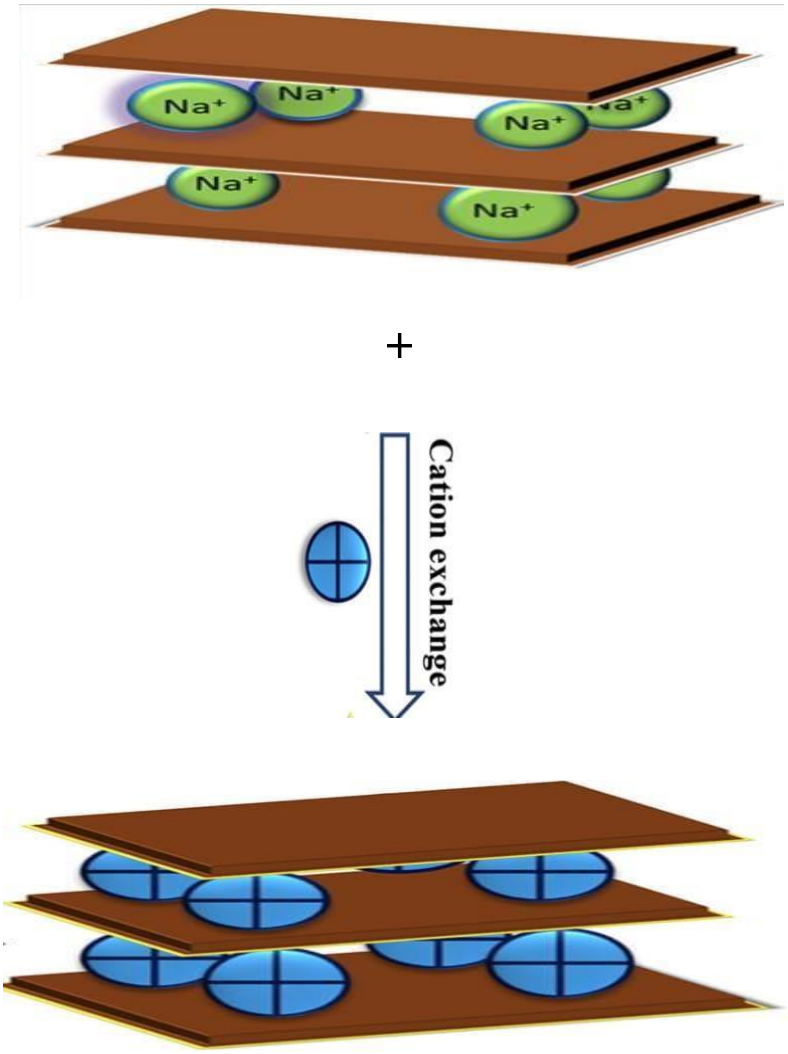


Fig 2.2: formation of organoclay

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. See fig 2.2.

1.9: Polymer clay nanocomposite structure

Nanocomposite structure

In general, the degree of intercalation and exfoliation of polymer chains into the clay galleries is used to categorize the architectures of polymer and clay nanocomposites. The intercalation and exfoliation levels are influenced by a number of factors, including the kind of clay, organic modifier, polymer matrix, and production process. Therefore, a variety of composite microstructures can be produced based on the nature and qualities of the clay and polymer as well as the method used to prepare the nanocomposite [42].

Phase separated structure

When the organic polymer is interacted with inorganic clay(unmodified clay), the polymer is unable to intercalate within the clay layers and the clay is dispersed as aggregates or particles with layers stacked together within the polymer matrix. The obtained composite structure is considered as “phase separated”. The properties of phase separated polymer/ clay composites are in the range of traditional micro composites.

Intercalated structure

When one or more polymer chains are inserted into the interlayer space and cause to the increasing of the inter layer spacing, but the periodic array of the clay layer is still exist, the intercalated nanocomposite is formed. The presence of polymer chains in the galleries causes to the decreasing of electrostatic forces between the layers but it is not totally dissolved. A well-ordered multilayer hybrid morphology with a high interference interactions consisted of polymer chains and clay layer is obtained in this configuration.

Exfoliated structure

Exfoliated or delaminated structure is obtained when the insertion of polymer chains into the clay galleries causes to the separation of the layers one another and individual layers are dispersed within the polymer matrix. At all, when the polymer chains cause to the increasing of interlayer spacing more than 80-100 A°, the exfoliated structure is obtained. Due to the well dispersion of individual clay layers, high aspect ratio is obtained and lower clay content is needed for exfoliated nanocomposites. Also most significant improvement in polymer properties is obtained due to the large surface interactions between polymer and clay. Various polymer/ clay structural configurations have been shown in figure: 2.3.

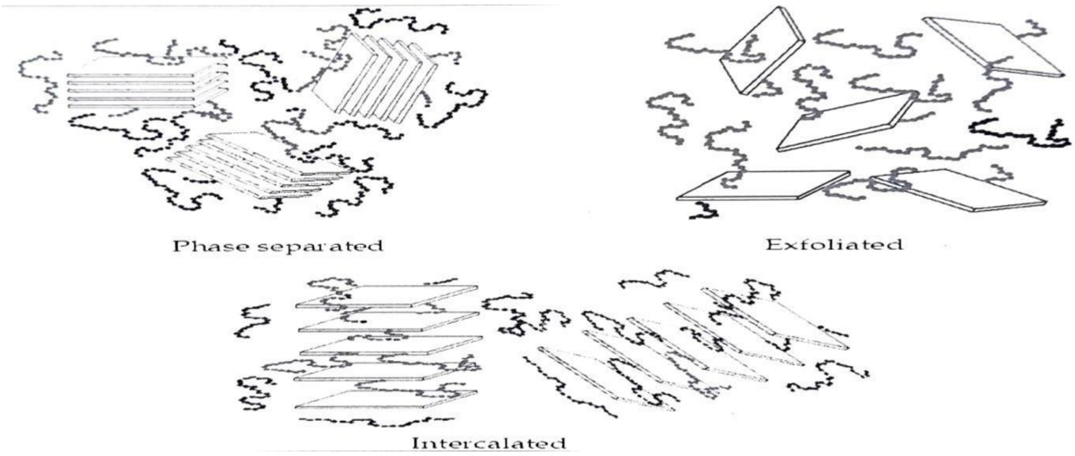


Fig.2.3: Various micro-structures of polymer/ clay nanocomposites

1.9.1: Formation of polymer clay nanocomposite

Exfoliated and intercalated polymer and clay nanocomposites with better characteristics have undergone extensive processing. The intercalation of polymer chains within the clay galleries is influenced by a number of polymer properties, including polarity, molecular weight, hydrophobicity, and reactive groups, as well as clay properties such as charge density and its changed structure. As a result, various synthetic techniques have been employed to create polymer and clay nanocomposites. In general, there are four preparation techniques: melt intercalation, in-situ intercalative polymerization, solution intercalation, and in-situ template synthesis

Bulk polymerization is accomplished by combining a vinyl monomer, such as methyl methacrylate, with a stearic acid-CTAB adduct-modified clay and utilizing BPO (benzoyl peroxide) as an initiator. As a result, polymethyl methacrylate-stearic acid clay nanocomposite [PMMA-SC] is formed. Bulk polymerization is also carried out by treating methyl methacrylate with cinnamic acid-CTAB adduct-modified clay and using BPO (benzoyl peroxide) as an initiator. As a result, a polymethyl methacrylate-cinnamic acid clay nanocomposite [PMMA-CC] is formed.

1.9.2 : Structural Characterization

X-ray diffraction (XRD) analysis is employed to examine the structure of organo-modified clays and polymer clay nanocomposites [43]. Because of their regular layered structures, clays and organoclays exhibit a distinct peak in XRD examination. The peak indicates platelet separation, or d-spacing, in the clay structure. Using the peak width at half maximum height and peak position, (2θ) the interlayer space in the XRD spectra may be determined using Bragg's law.

$$\mathrm{Sin}\, \theta = n\, \lambda / 2\, d$$

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. The measurements were performed over a 2θ range of 0° to 50°.

The structural characterization of organo-modified clays and polymer clay nanocomposites were also done using Fourier Transform Infrared Spectroscopy (FTIR). This method is used for structural determination of monomers, polymers and for the analysis of functional groups. The spectrum is plotted with wavenumber (cm–1) on the X-axis and

%transmittance on the Y-axis. The absorption was measured in a wavenumber range between 4000 and 400cm^{-1}.

OBJECTIVES

1. Synthesis of **adduct** with reactive functional groups.
2. Synthesis of adduct-modified Organoclay (structure, characterization).
3. Preparation of **polymer clay nano composite** (structure, characterization)

Chapter 2

2.1: LITERATURE REVIEW

The paper “Polymer-layered silicate nanocomposites: an overview” written by Peter C LeBaron and co-workers provides an overview of polymer-clay hybrid nanocomposites, with an emphasis on the utilisation of alkylammonium exchanged smectite clays as the reinforcing phase in selected polymer matrices. A few weight percent of organoclay added to nylon 6 raises its heat distortion temperature by 80°C, allowing structural applications in conditions where the pristine polymer would usually fail. A comparable loading of clay nanolayers in elastomeric epoxy and polyurethane matrices considerably increases the toughness and tensile properties of these thermoset systems. Under compressive stress-strain conditions, the yield strength and modulus of glassy epoxy nanocomposites considerably increase. The most recent advancement in polypropylene hybrids has produced nanocomposites with higher storage moduli. With 2% clay loading, polyimide hybrids in thin-film form showed a 10-fold decrease in permeability towards water vapour. Processes like as in situ and melt intercalation can be used to create reinforced polystyrene hybrids. Nitrile rubber hybrids have higher storage moduli and lower permeabilities, even towards small gases like hydrogen. Water adsorption is significantly reduced in poly(-caprolactone)-clay nanocomposites produced by in situ polymerization of -caprolactone in organoclay galleries. Improved tensile properties, thermal stability, and resistance to swelling solvents are shown in polysiloxane nanocomposites made from poly (dimethylsiloxane) and organoclay combinations. Solvent casting technique was used to create an organoclay-poly (l-lactide) composite film. Clay nanolayers dispersed in liquid crystals serve as structure directors, resulting in hybrid composites that may be converted from very opaque to highly transparent by applying an electric field of short duration [44].

Paolo Cosoli and co-workers (2008) published a paper titled "Many-scale molecular simulation for ABS-MMT nanocomposites: Upgrading of industrial scraps" in which they developed and applied an innovative many-scale molecular procedure to study possible ways to improve and recycle automotive reinforced acrylonitrile-butadiene-styrene (ABS) scraps by converting them into organoclay nanocomposites. In this work they simulated modified organoclay exfoliation and intercalation at an atomistic level, thus providing information about the rational choice of compatibilizers and polymer insertion behaviour. The phase morphology and segregation domains were then determined resorting to mesoscale simulation techniques. Finally, finite element calculations at micrometric level were done, taking into account the entire structure of the nanocomposite (i.e., mineral filler and polymer blend), to calculate the corresponding improvement in mechanical properties. Output data, such as phase morphologies and mechanical characteristics, were evaluated against experimental data from the literature and found to be in good agreement. The proposed procedure relies solely on input data obtained by molecular simulations, exception made for the experimental value of the Young modulus of the filler. Accordingly, computational recipe constitutes a sort of innovative, atomistic-based, step-by-step procedure, in which each level calculations produce information necessary to perform simulation at the next, higher level length/time scale [45].

The study "An overview on the degradability of polymer nanocomposites," authored by Jitendra K. Pandey and co-workers (2005), discusses the durability of several polymer nanocomposites, primarily under thermal and photoaging conditions. Biodegradable nanocomposites of various polymers are also discussed briefly. Polymer material properties can be greatly improved by introducing layered silicates at low concentrations. The durability of any material depends on a variety of factors such as light, heat, microwaves, mechanical abrasion, and so on. The study and the effect of these factors on the performance are necessary to extend the application limits. Under various environmental conditions, the durability of polymer nanocomposites has been evaluated [35].

The paper "Characteristics of clay minerals relevant to bioremediation of environmental contaminated systems," written by Uzochukwu C. Ugochukwu, describes how clay minerals are used in bioremediation, adsorption, and redox processes to remove contaminants from the environment, with surface area, CEC, surface acidity, and interlayer cations playing a crucial role. Clay minerals are nontoxic and are very cheap due to their ubiquity as they are found almost everywhere in the world. The use of clay minerals in remediation of contaminated environmental systems is one of the most recent applications of this material in environmental control. Clay minerals mediate remediation via bioremediation, adsorption, and redox processes that eliminate contaminants from the environment. Surface area, cation exchange capacity (CEC), surface acidity, and interlayer cations are all important factors to consider when selecting clay minerals for any of the above remediation methods. Clay minerals having a large surface area, a high CEC, and either calcium ion or ferric ion as sole interlayer cations are quite successful in bioremediation. Organoclays are effective in adsorbing hydrophobic contaminants, whereas acid-activated clay minerals are effective at adsorbing heavy metals, dyes, and phenolic compounds from wastewater. Clay minerals with structural ferric ion like nontronite are used in redox processes to eliminate chlorinated organic compounds. Pillared clays are used in the catalysis of aqueous oxidative processes to remove refractory nonbiodegradable pollutants found in wastewater. Most of the studies carried out to date in the application of clay minerals for bioremediation purposes are largely laboratory or pilot scale [18].

The paper “Nanocomposites in context” written by Erik T. Thostenson and co-workers provides an overview of recent advances in nanocomposites research. In the context of traditional fibre composites, the important research opportunities and problems in the development of structural and functional nanocomposites are addressed.The state of knowledge in nanocomposites processing, characterisation, and analysis/modelling is provided, with a focus on establishing fundamental structure/property relationships. Critical concerns in nanocomposites research as well as promising techniques for processing precursors for macroscopic nanocomposites are also discussed [46].

The paper “The surface properties of clay minerals” written by Robert A Schoonheyd, Cliff T. Johnston (2011) describes that clay minerals have both interlayer and edge surfaces, with the former being the most important especially in the case of swelling clays or smectites. Water is by far the most important molecule adsorbed in the interlayer space, where it interacts with the exchangeable cations and with the siloxane surface. In the interlayer space of smectites, transition metal ion complexes are preferentially ion-exchanged. Poly-amine complexes easily lose their axial ligands, resulting in a square planar structure. The more stable and bulky tris(bipyridyl) and tris(phenanthroline) complexes in the interlayer space result in chiral clay mineral composites that can be employed in chiral chromatography columns, asymmetric catalysis, and non-linear optics. Clay mineral-dye complexes are formed in two steps: instantaneous adsorption of the dye molecules, primarily as aggregates, followed by a slower redistribution process over the clay mineral surface. With careful choice of dye molecules, non-linear optical materials can be made which exhibit properties such as second harmonic generation and two-photon absorption. Ion exchange of cationic proteins occurs in three stages: (1) instantaneous adsorption at the edges, (2) adsorption in the interlayer space, and (3) weak adsorption in excess of the cation exchange capacity. The extent to which these three processes occur is affected by (1) the type of exchangeable cation in the interlayer and (2) the protein molecules' molecular weight, shape, and charge.[22]

Chapter 3

Materials and Methods

3.1 : work plan

The main aim of the project is to synthesize polymethylmethacrylate nano composite using stearic acid-CTAB and cinnamic acid-CTAB adduct modified clays and characterize the modified clays and the corresponding polymethylmethacrylate nano composite.

Our project deals with the synthesis of a facile, cost effective method for clay modification using different aromatic aliphatic Acid-Amine adduct having reaction sites and prepare polymethylmethacrylate nanocomposite using adduct organo-modified clays.

3.2 : Work carried out

Synthesis of modified MMT clay using different adducts:

1. Stearic acid- cetyl trimethyl ammonium bromide adduct (SA-CTAB Adduct)

2. Cinnamic acid – cetyl trimethyl ammonium bromide adduct (CA-CTAB Adduct)

Synthesis of polymethyl methacrylate using different adduct modified clays:

1. Polymethyl methacrylate stearic acid nanocomposite (PMMA-SC) can be synthesised using SA-CTAB Adduct modified clay.

2. Polymethyl methacrylate cinnamic acid nanocomposite (PMMA-CC) can be synthesised using CA-CTAB Adduct modified clay.

3.3: Experimental procedure

3.3.1 Materials required

1. Montmorillonite clay
2. Stearic acid
3. Cinnamic acid
4. Cetyl trimethyl ammonium bromide
5. Methyl methacrylate

3.3.2: modification of clay using equimolar concentration of different modifiers

Modification of clay using 1x: 1x equimolar concentration of clay-stearic acid ctab modifier

Weight of clay = 1g
Weight of stearic acid = 0.5689g
Weight of CTAB = 0.7289g
Total volume of distilled water = 200ml

Modification of clay using 1x:1x equimolar concentration of clay-cinnamic acid ctab modifier

Weight of clay = 1g
Weight of cinnamic acid = 0.2963g
Weight of CTAB = 0.7289g
Total volume of distilled water = 200ml

Modification of clay using 2x: 2x equimolar concentration of clay-stearic acid ctab modifier

Weight of clay = 2g
Weight of stearic acid = 1.1379g
Weight of CTAB = 1.4578g
Total volume of distilled water = 400ml

Modification of clay using 2x:2x equimolar concentration of clay-cinnamic acid ctab modifier

Weight of clay = 2g
Weight of cinnamic acid =0.5926g
Weight of CTAB = 1.4578g
Total volume of distilled water = 200ml

3.3.3: Synthesis of modified clay using stearic acid-CTAB 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, Stearic acid.

Stearic acid modified organic clays were prepared by reacting aqueous clay suspension with calculated amount of the Stearic acid.

2g of clay having cationic exchange capacity (CEC) of 92.6mEq/100g was dispersed in 50mL of distilled water taken in a 1000mL beaker and similarly equimolar concentration of the Stearic acid-CTAB mixture was prepared in about 50mL of water in a 200mL beaker. The above dissolved suspensions were stirred separately for about 30 minutes. The Stearic acid-CTAB mixture was slowly added to the clay suspension and mixed with 400mL of distilled water. Then it is kept for continuous stirring uninterrupted for 48 hours. The adduct modified clay suspension resulted was recovered by ultracentrifuge at 5000 rpm for 30 minutes. Finally, the adduct modified clay [SA-CTAB adduct modified clay or SA-AMC] was dried overnight in a hot air oven at 80 degree Celsius to obtain Stearic acid-CTAB adduct modified clay. Figure 2.4 represents stearic acid-CTAB adduct modified clay

Fig 2.4 SA-CTAB AMC

3.3.4: Synthesis of modified clay using cinnamic acid-CTAB 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, cinnamic acid.

Cinnamic acid modified organic clays were prepared by reacting aqueous clay suspension with calculated amount of the cinnamic acid.

2g of clay having cationic exchange capacity (CEC) of 92.6mEq/100g was dispersed in 50mL of distilled water taken in a 1000mL beaker and similarly equimolar concentration of the cinnamic acid-CTAB mixture was prepared in about 50mL of water in a 200mL beaker. The above dissolved suspensions were stirred separately for about 30 minutes. The cinnamic acid-CTAB mixture was slowly added to the clay suspension and mixed with 400mL of distilled water. Then it is kept for continuous stirring uninterrupted for 48 hours. The adduct modified clay suspension resulted was recovered by ultracentrifuge at 5000 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 80 degree Celsius to obtain Cinnamic acid-CTAB adduct modified clay.

Figure 2.5 represents cinnamic acid-CTAB adduct modified clay

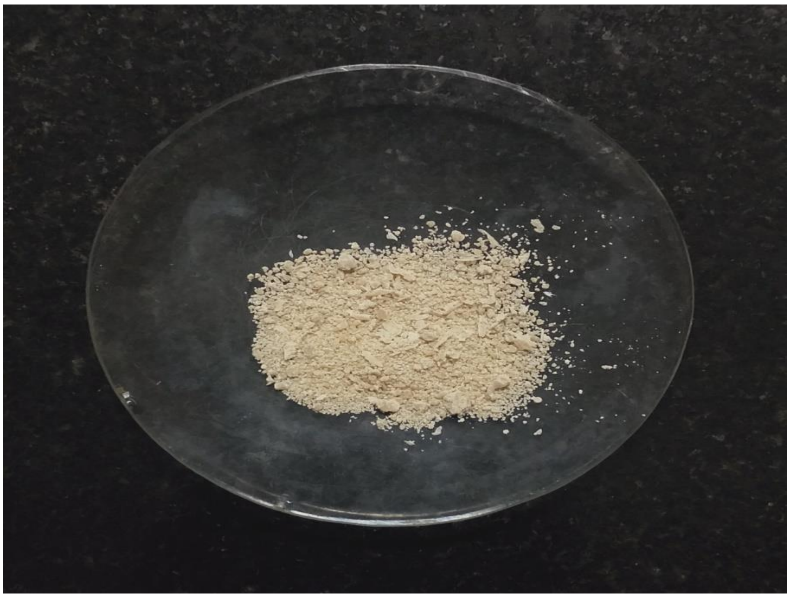


Fig 2.5 CA-CTAB AMC

3.3.5 : polymerization of methyl methacrylate

1. **5ml of methyl methacrylate (monomer) and 0.5g organoclay is placed in 50 ml round bottom flask and stir using magnetic stirrer for about 2-3 minutes.**
2. **To the round bottom flask, add 0.1 ml benzoyl peroxide as an initiator. Place the RB flask in water bath (mouth closed using a lid) and heated at 80 degree c for 4-6 hours. Polymethyl methacrylate nano composite is obtained (PMMAC OR PMC)**
3. **Put it on a rack for about 5 min at room temperature.**

4. **Dissolve the PMMAC in toluene at room temperature (if it is not dissolved, provide heating on a water bath).**
5. **After it is dissolved, transfer it to a beaker and wash the RB with little amount of toluene**
6. **Reprecipitate the polymer using sufficient amount of alcohol**

PMMAC obtained is filtered using a standard filter paper, collected and further dried at 60 degree Celsius in a hot air oven under reduced pressure. The product is powdered and PMMA thus obtained was of fine white powder in appearance.

Fig 2.6: Experimental setup

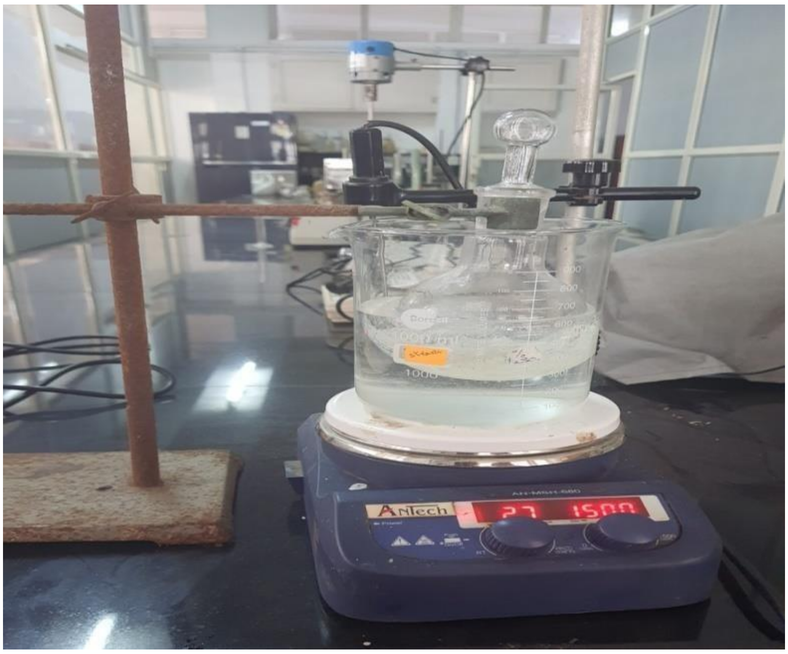


Fig 2.7 represents the polymethyl methacrylate nanocomposite obtained from SA-AMC

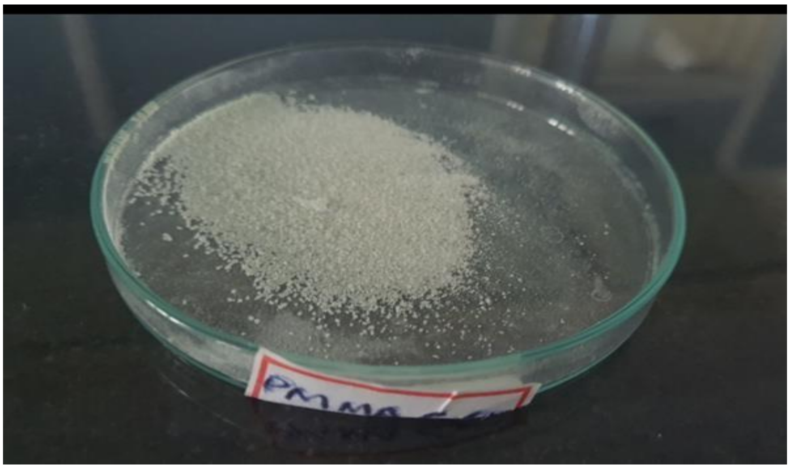


Fig 2.7 PMMA-SC

Fig 2.8: represents the polymethyl methacrylate nanocomposite obtained from CA AMC

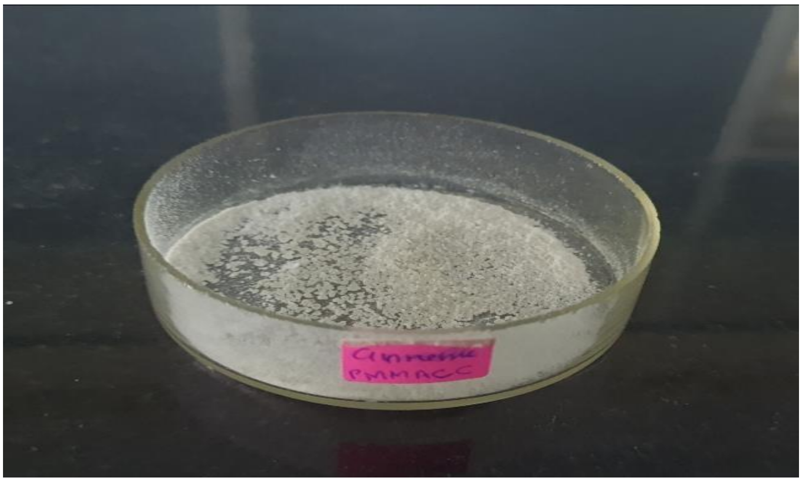


Fig 2.8 PMMA-CC

3.4: Characterizations

Characterizations using XRD

The samples of modified clay prepared using different modifiers were characterized using XRD. Similarly the samples of polymer clay nanocomposites prepared using different acid-CTAB addut modified clays were also characterised using XRD.

X-ray diffraction is widely used experimental method for the determination of the crystal structure. The technique's main application is the characterization and identification of compounds based on their diffraction pattern. X-rays are electromagnetic radiations with a wavelength of the order of 1A°.Because of its inherent electric field, it interacts with charged particles such as electrons in solid. These interactions cause the electrons to emit wavelets. When the wavelets interfere with each other constructively diffraction takes place. In an XRD graph, the intensity of reflected X-ray is plotted against 2Θ values where Θ is the angle at which X-ray falls on the sample and n the order of reflection. The d-spacing is calculated using the Bragg’s equation,

$$\mathbf{n\lambda = 2d\ sin\Theta}$$

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. In the present study, XRD was used for assessing intercalation of clay by measuring the angle of diffraction.

Characterization using FTIR

The samples of modified clay prepared using different modifiers were characterized using FTIR.

Similarly the samples of polymer clay nanocomposites prepared using different acid-CTAB adduct modified clays were also characterized using FTIR. It is a method used for the investigation of the structure of monomers, polymers and for the analysis of functional groups. This involves interaction of materials with electromagnetic radiation. The interaction results in the absorption on certain wavelength of radiation, the energy of which corresponds to the energy of transition between various vibrational and rotational states.

Specific groups of atoms in the molecule give rise to characteristic absorption; bands whose wave number falls within a definite range regardless of the composition. The presence of functional groups can be determined from the exact values of wave number at which absorption is observed. In the present study IR data was used for confirming the intercalation of clay.

Chapter 4

Results and discussion

4.1.0 : IR Spectrum analysis of pristine clay, modified clays

The FTIR spectrum of the pristine clay and organo modified clay are shown in fig 2.9, fig 3.0 and fig 3.1. It was observed that in all cases FTIR showed typical absorption confirming the successful intercalation.

4.1.1 : FTIR SPECTRAL STUDIES OF PRISTINE CLAY

The IR spectrum of pristine clay and the band assignments is shown in fig 2.9

The FTIR spectrum for montmorillonite clay is recorded as KBr pellet. The broad band centered near 3400cm^{-1} is due to –OH stretching band for interlayer water molecule. The bands at 3636.34cm^{-1} and 1640cm^{-1} are due to –OH stretching band for –Al-OH and OH bending vibration indicating hydration.

The strongest and complex band at near 1048.85 cm^{-1} is related to the Si - O in-plane stretching, while the broad ones at 526-529 cm^{-1} and 466cm^{-1} are due to the Al-O-Si and Si-O-Si bending vibrations, respectively. The absorption peak at 917cm^{-1} is attributed to the AlAlOH bending vibration. The shoulder between 1300cm^{-1} and 1150 cm^{-1} is originated from the Si-O out-of-plane stretching vibrations and the broad peak at 799cm^{-1} and 693 cm^{-1} indicates the presence of quartz.

The frequencies of all the peaks are summarized in table 1.

Frequency (cm-1)	**Vibration**
3636.34	OH stretching for Al-OH
3449.59	OH (stretching hydration)
1640.09	OH (Bending hydration)
1048.85	Si-O (Str)
917.02	AlAlOH (bend)
799.53	Tridymite
522.59	Al-O-Si (Bend)
466.86	Si-O-Si(Bend)

Table 1: vibrational frequencies of pristine clay

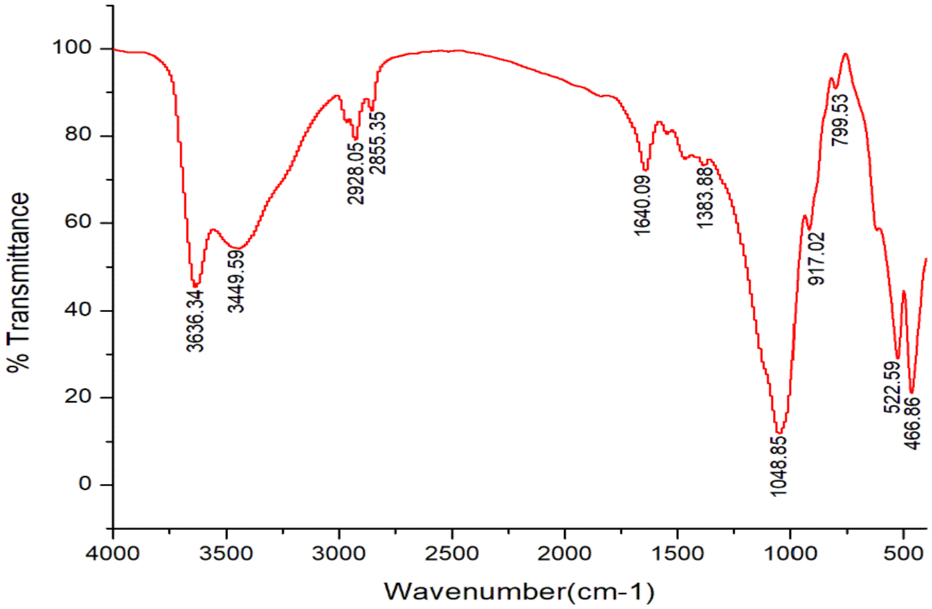


Fig 2.9: FTIR spectrum of pristine clay

4.1.2 : FTIR SPECTRAL STUDIES OF SA-AMC

The FTIR spectrum of stearic acid-adduct modified clay is shown in fig 3.0.

The absorption peaks at 2918.03 cm^{-1} indicates the –CH_3 asymmetric stretching. Similarly the absorption peak at 2849.94cm^{-1} is attributed to –CH_2- symmetric stretching. The peak at 3425.11cm^{-1} is attributed to the OH stretching of -COOH group. In the low frequency region, the bands at 1724.94cm^{-1} is attributable to C=O stretching vibration related to carboxylic group.

The strongest and complex band near 1046.91 cm^{-1} is related to the Si - O in-plane stretching, while the peaks at 522.07cm^{-1} and 463.50cm-1 are due to the Al-O-Si and Si-O-Si bending vibrations, respectively.

The broad band centered near 3631.86cm^{-1} is due OH stretching for Al-OH

The absorption peak at 913.33cm^{-1} is attributed to the AlAlOH bending vibration.

The frequencies of all the peaks are summarized in table 2.

FREQUENCY (cm^{-1})	**Vibration**
3631.86	OH stretching of Al-OH
3425.11	OH stretching of acid
2849.94	-CH_2 Asymmetric stretching
2918.03	-CH_3 symmetric stretching

1724.94	C=O stretching from –COOH
1046.91	Si-O stretching
913.33	AlAlOH (Bend)
522.07	Al-O-Si (Bend)
463.50	Si-O-Si (Bend)

Table 2: vibrational frequencies of SA-AMC

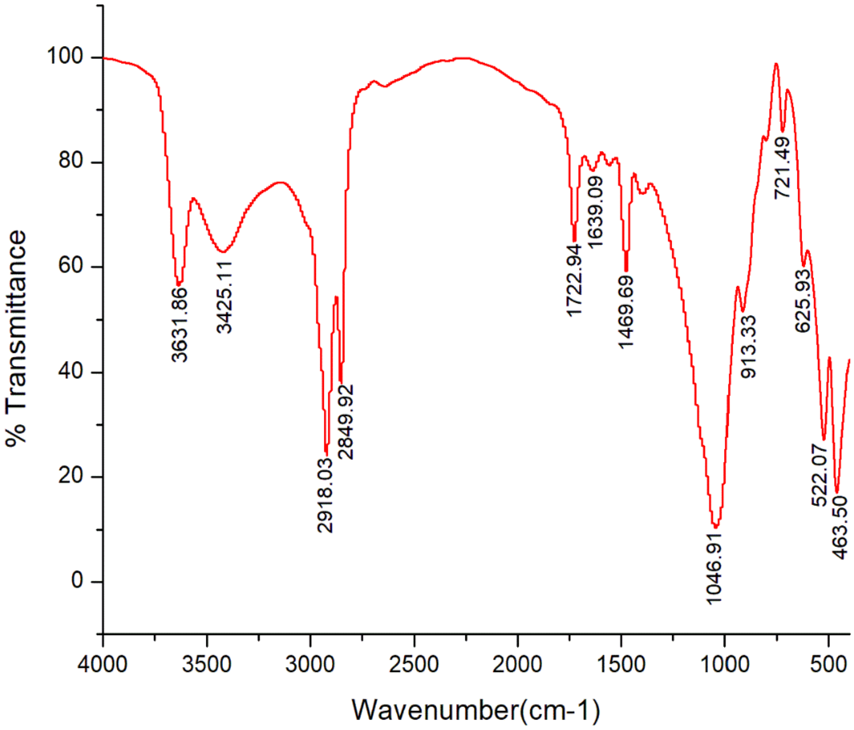


Fig3.0: FTIR spectrum of SA-AMC

4.1.3 : FTIR SPECTRAL STUDIES OF CA-AMC

The FTIR spectrum of cinnamic acid-adduct modified clay is shown in fig 3.1

The absorption peak at 3427.92 cm^{-1} is attributed to the –OH stretching vibration of the acid group.

The absorption peak lies between 2851 cm^{-1}-2923 cm^{-1} are attributable to the CH vibrations of arenes and alkenes.

In the low frequency region, the bands appears at 1707cm^{-1} is attributable to C=O stretching vibration related to carboxylic group.

The absorption peak at 1638.55 cm^{-1} indicates C=C of alkenes. Similarly the peak appears at 1485.93 cm^{-1} indicates C=C of arenes.

The strongest and complex band near 1048.56 cm^{-1} is related to the Si - O in-plane stretching, while the peaks at 522.20cm^{-1} and 463.27cm-1 are due to the Al-O-Si and Si-O-Si bending vibrations, respectively. The broad band centered near 3629.97 cm^{-1} is due OH stretching for AlOH.

The absorption peak at 911.75cm^{-1} is attributed to the AlAlOH bending vibration.

The frequencies of all the peaks are summarized in table 3.

Frequency (cm-1)	**Vibration**
3629.97	OH stretching for Al-OH
3427.92	OH stretching of acid
2851-2923	CH vibrations of arenes and alkenes

1707.61	C=0 stretching
1638.55	C=C of alkene
1485.93	C=C Arene
1048.56	Si-O stretching
911.75	AlAlOH (Bend)
522.20	Al-O-Si (Bend)
463.27	Si-O-Si (Bend)

Table 3: vibrational spectrum of CA-AMC

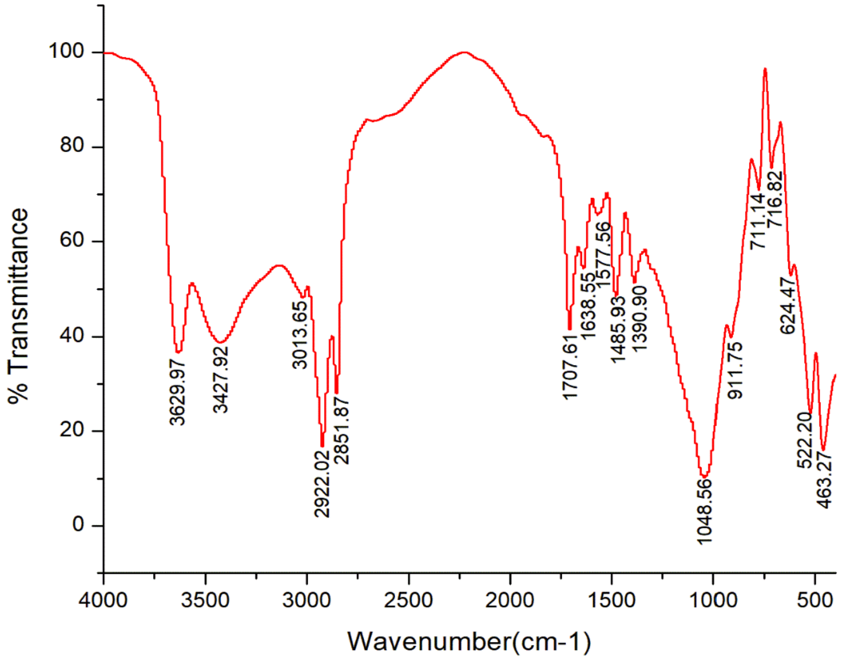


Fig 3.1: FTIR spectrum of CA-AMC

4.2.0 : XRAY DIFFRACTION STUDIES OF PRISTINE CLAY, MODIFIED CLAY

The XRD patterns for the pristine clay and modified clays are shown in fig 3.2, 3.3 and 3.4. In order to analyze the structure of the organo-modified clays, a commonly used technique is X-ray diffraction (XRD) analysis and spectroscopy is widely used. Clays and organoclays show a characteristic peak in XRD analysis due to their regular layered structures. The peak is indicates d-spacing in clay structure. The inter layer space can be calculated utilizing Bragg's law,

$$\mathrm{Sin}\ \theta = n\lambda / 2d$$

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.

4.2.1 : XRAY DIFFRACTION STUDIES OF PRISTINE CLAY

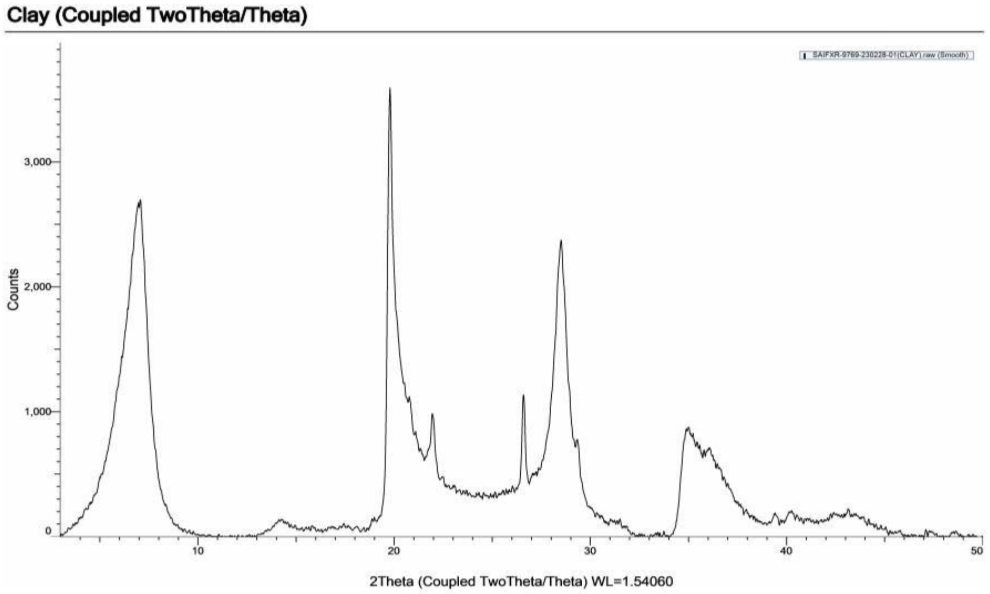


Fig3.2: x-ray diffraction pattern of pristine clay

Sample	2θ (degree)	d (Armstrong)
Pristine clay	7	12

Table 4: d spacing of pristine clay

4.2.2 : XRAY DIFFRACTION STUDIES OF SA-AMC

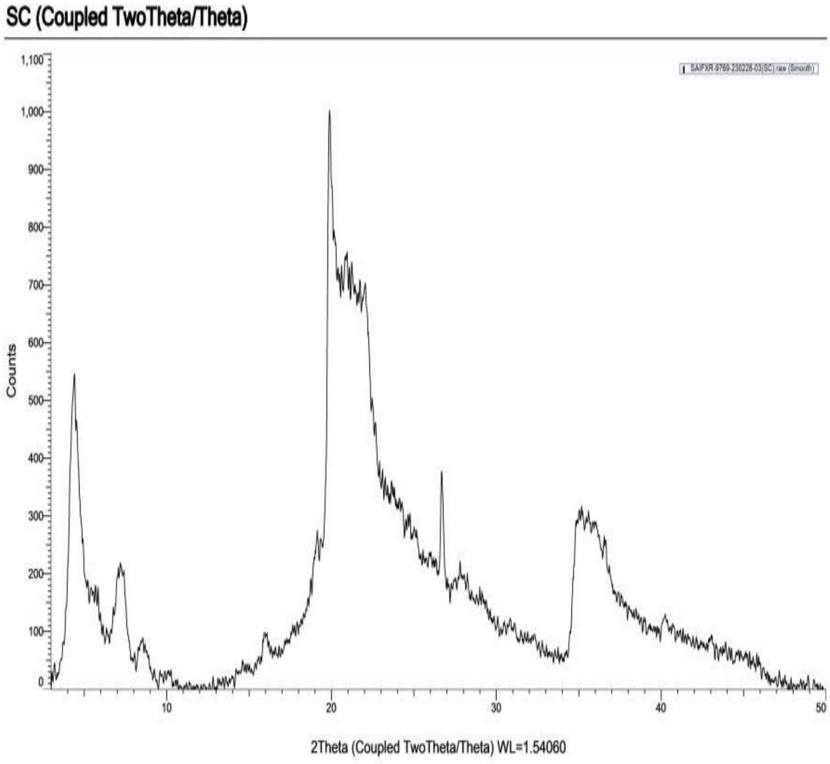


Fig3.3: x-ray diffraction pattern of SA-AMC

Sample	2θ (degree)	d (Armstrong)
SA-AMC	**4.402**	**20.11**

TABLE 5: d spacing of SA-AMC

4.2.3 : XRAY DIFFRACTION STUDIES OF CA-AMC

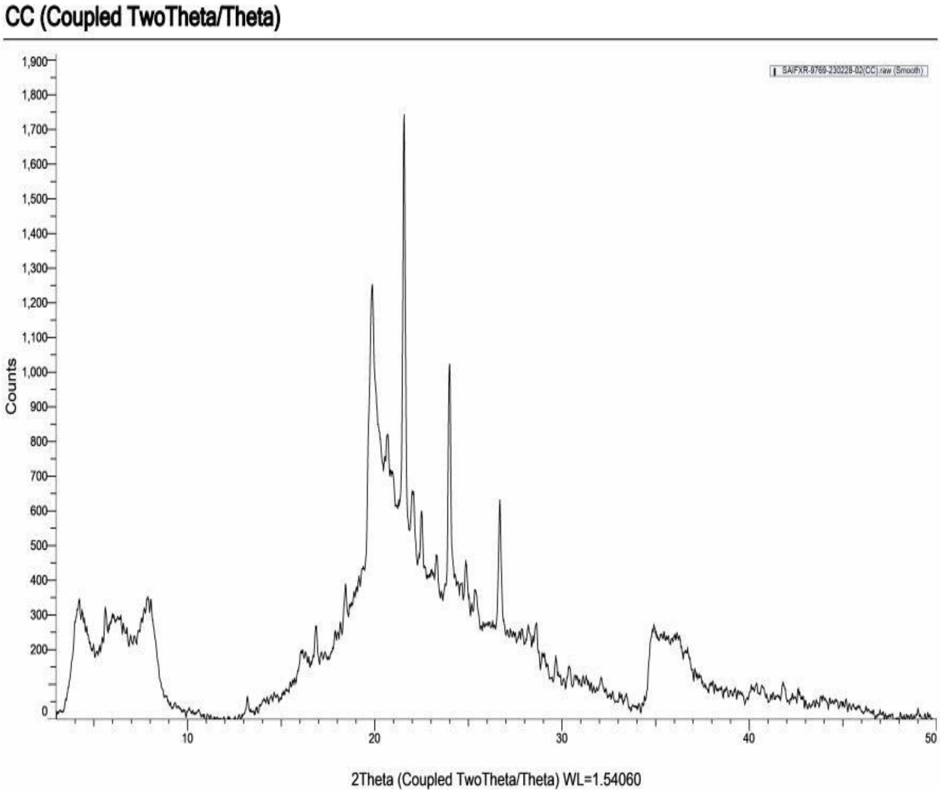


Fig 3.4: x-ray diffraction studies of CA-AMC

Sample	2θ(Degree)	d(Armstrong)
CA-AMC	4.218	21.57

TABLE 6: d spacing of CA-AMC

In XRD, it was observed that the (001) reflection of both the adduct modified clays (AMC) appeared at smaller angles (2θ) when compared to the pristine clay. It indicates the successful ion exchange. The d-spacing increased from 12 Armstrong (2θ =7°) for pristine clay to 20.11 Armstrong (2θ=4.402°) for SA-AMC 2x and 21.57 Armstrong (2θ=4.218°) for CA-AMC 2x. These results showed that there was an increase in the basal spacing which was due to the inclusion of adduct within the interlayer of the unmodified clay.

Sample	**2 theta (degree)**	**d (Armstrong)**
Pristine clay	7	12
SA-AMC	4.402	20.11
CA-AMC	4.218	21.57

Table 7: comparison of pristine clay with modified clays

4.3.0 : IR Spectrum analysis of polymer clay nanocomposite

The FTIR spectrum of polymer clay nanocomposite prepared from different adduct modified clays are shown in fig 3.5 and fig 3.6. It was observed that in all cases FTIR showed typical absorption confirming the successful intercalation/exfoliation.

4.3.1 : FTIR SPECTRAL STUDIES OF PMMA-SC

The FTIR spectrum of PMMA-CC is shown in fig 3.5.

The absorption peak at 3725.84 cm^{-1} gives indication of the OH stretching of Al-OH present in adduct modified clay. The absorption peak at 3439.46 cm^{-1} indicates the –OH group of the acid present in AMC.
The absorption peaks at 2921.76cm^{-1} indicates the –CH_3 asymmetric stretching. Similarly the absorption peak at 2851.53cm^{-1} is attributed to –CH_2- symmetric stretching.

Esters are characterized by C=O, C-C-O, O-C-C linkages and the assignment of the wavenumber depends upon the carbon attached to the carbonyl carbon. This means the IR spectrum of PMSC have three big peaks at approximately 1730-1750 cm^{-1}, 1250-1160 cm^{-1}, 1030-1050 cm^{-1}

These corresponds to the stretching of the C=O, C-C-O, O-C-C respectively.
That is, in the low frequency region, the bands at 1724.94cm^{-1} is attributable to C=O stretching vibration related to ester group. The band

appears at 1243 cm^{-1} and 1148 cm^{-1} attributable to C-C-O stretching. The absorption band appears at 1051.63 cm^{-1} indicates the O-C-C stretching.

The peaks at 522.20cm^{-1} and 463.27cm-1 are due to the Al-O-Si and Si-O-Si bending vibrations, respectively.

The frequencies of all the peaks are summarized in table 8.

FREQUENCY cm^{-1}	**Vibration**
3725.84	OH stretching of Al-OH in AMC
3439.46	OH of the acid present in AMC
2921.76	-CH_3 symmetric stretching in AMC
2851.53	-CH_2 asymmetric stretching in AMC
1734.91	C=O stretch of ester
1450-1390	CH modes of methylene group
1243 – 1148	C-C-O stretch
1051.63	O-C-C stretch
526.81	Al-O-Si (Bend) present in AMC
459.19	Si-O-Si (Bend) present in AMC

Table 8: vibrational spectrum of PMMA-SC

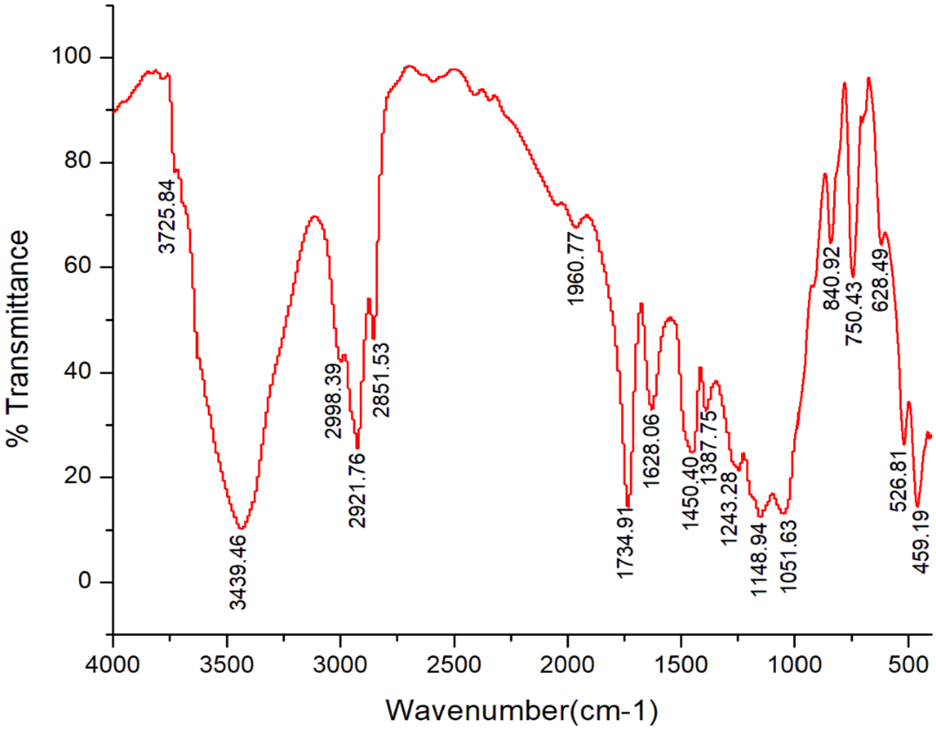


Fig 3.5: FTIR spectrum of PMMA-SC

4.3.2 : FTIR SPECTRAL STUDIES OF PMMA-CC

The FTIR spectrum of PMMA-CC is shown in fig 3.6.

The absorption peak at 3625.23cm^{-1} gives indication of the OH stretching of Al-OH present in adduct modified clay. The absorption peak at 3439.46 cm^{-1} indicates the –OH group of the acid present in AMC.

The absorption peaks at 2921.76cm^{-1} indicates the –CH_3 symmetric stretching. Similarly the absorption peak at 2851.53cm^{-1} is attributed to –

CH_2- asymmetric stretching.

Esters are characterized by C=O, C-C-O, O-C-C linkages and the assignment of the wavenumber depends upon the carbon attached to the carbonyl carbon. This means the IR spectrum of PMSC have three big peaks at approximately 1730-1750 cm^{-1}, 1250-1160 cm^{-1}, 1030-1050 cm^{-1}

These corresponds to the stretching of the C=O, C-C-O, O-C-C respectively.

That is, in the low frequency region, the bands at 1732.83 $cm^{-1}$is attributable to C=O stretching vibration related to ester group. The band appears at 1244.09 cm^{-1} and 1149.24 cm^{-1} attributable to C-C-O stretching. The absorption band appears at 1050.17cm^{-1} indicates the O-C-C stretching.

The peaks at 522.20cm^{-1} and 463.27cm-1 are due to the Al-O-Si and Si-O-Si bending vibrations, respectively.

The frequencies of all the peaks are summarized in table 9.

Frequency cm^{-1}	**Vibration**
3625.23	OH stretching in Al-OH
1244.09 - 1149.24	C-O stretching
1732.83	C=O of ester
1628.66	C-C of alkene
913.55	AlAlOH(bend)
526.29	Al-O-Si(bend) present in AMC

459.12	Si-O-Si(bend) present in AMC
1050.17	O-C-C stretching
2851.80	C-H of alkane
2952.34	CH3 symmetric stretching in AMC
2851.80	CH2 Asymmetric stretching in AMC

Table 9: vibrational spectrum of PMMA-CC

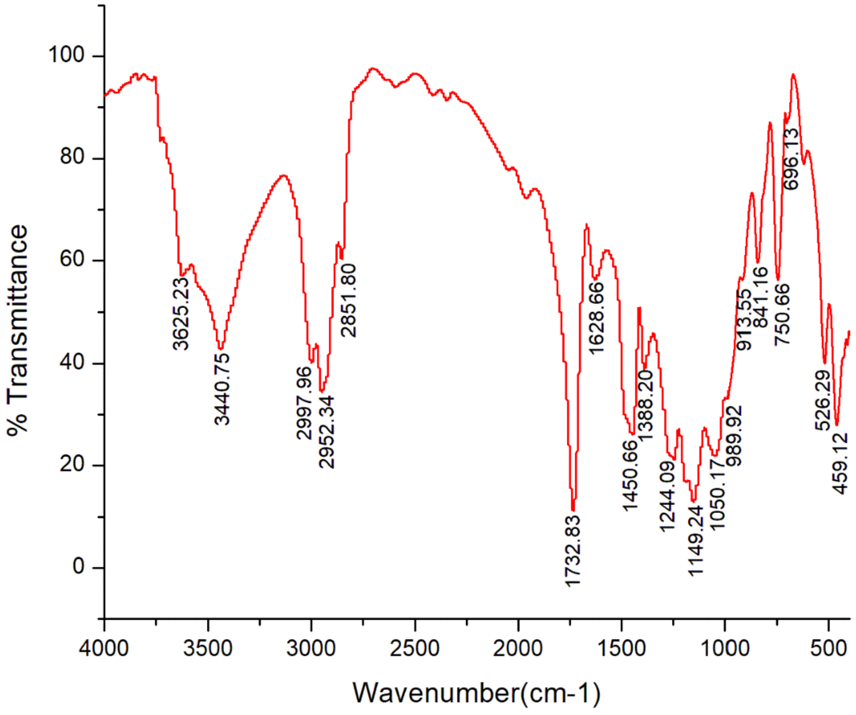


Fig 3.6: FTIR spectrum of PMMA-CC

4.4.0 : X-RAY DIFFRACTION STUDIES OF POLYMER CLAY NANOCOMPOSITE

The XRD patterns for the PMMA-SC and PMMA-CC are shown in fig 3.7 and 3.8.

4.4.1 : X-RAY DIFFRACTION STUDIES OF PMMA-SC

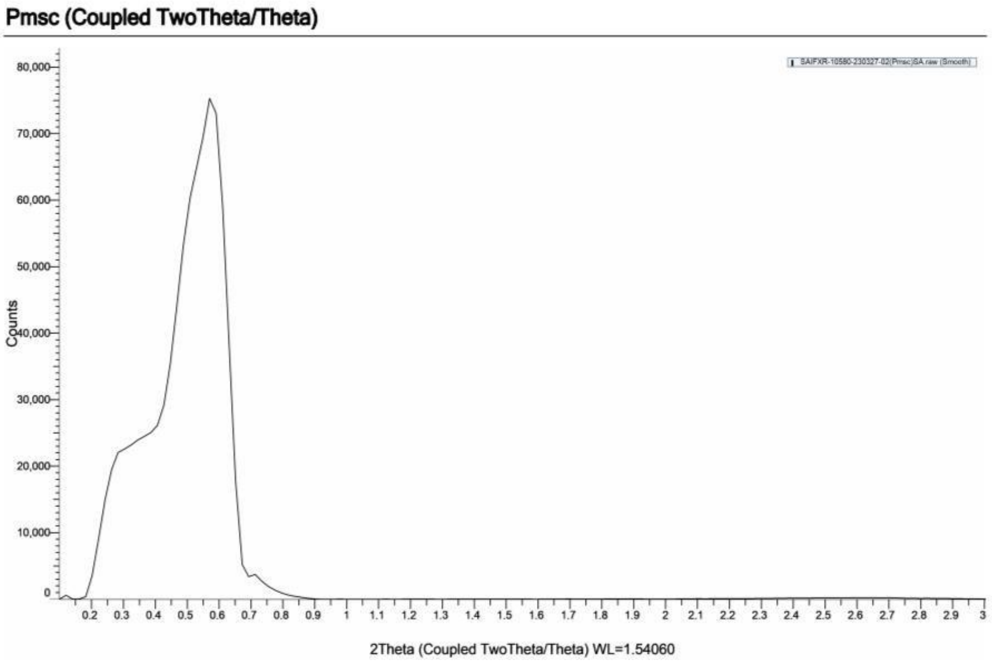


Fig 3.7: x-ray diffraction studies of PMMA-SC

Sample	2θ(Degree)
PMMA SC	**0.575**

TABLE 10: 2θ value **of** PMMA-SC

4.4.2 : X-RAY DIFFRACTION STUDIES OF PMMA-CC

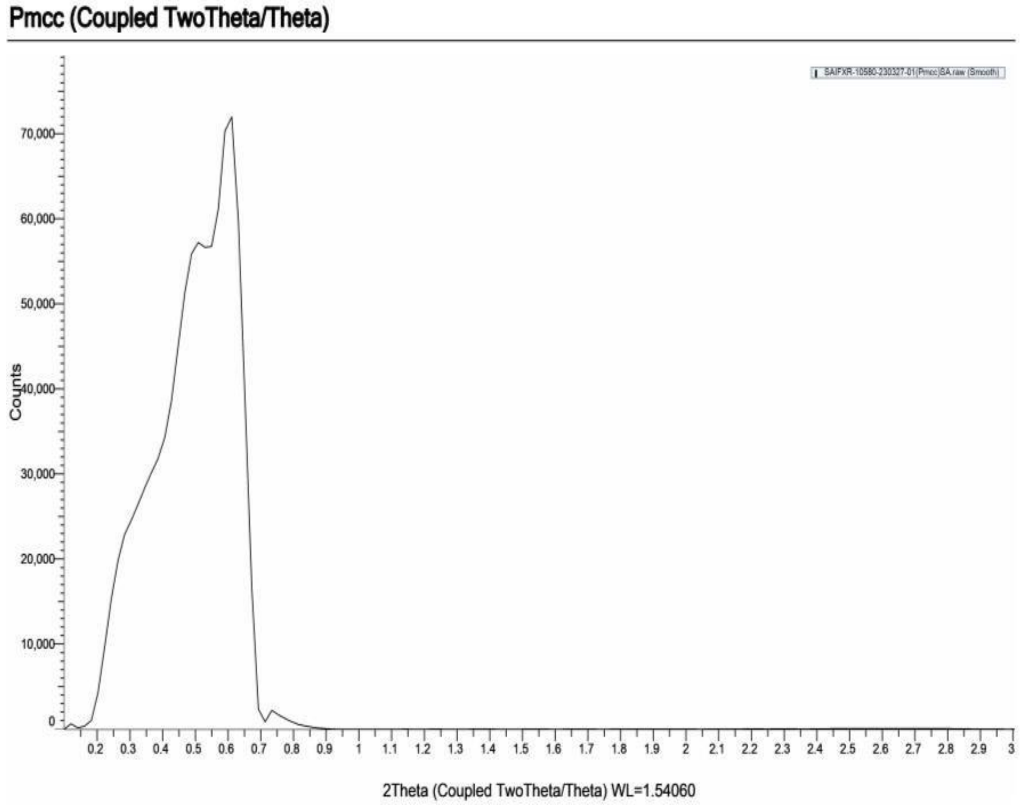


Fig 3.8: x-ray diffraction studies of PMMA-CC

Sample	**2θ(Degree)**
PMMA CC	**0.512**

TABLE 11: 2θ value of PMMA-CC

XRD results of both PMMA-SC and PMMA-CC supports the successful formation of highly polymer clay nanocomposite

Chapter 5

Conclusions

Polymer clay nanocomposites (PCN) have attracted great interest during the past two decades because they often exhibit remarkable thermal, mechanical and barrier properties due to the dispersion of silicate layers of nanometer dimensions in a polymer matrix. It was reported that nanocomposites with various structures/morphology, properties and applications can be produced by tuning the polymer-clay interactions. In this respect acid amine adduct modified organoclays incorporated polymer nanocomposites prepared is of great interest due to its high thermal stability and synthesis of nano or microsystems with controlled morphology.

Polymethyl methacrylate clay nanocomposite 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.

Organically modified clays can be effective reinforcing agents in the synthesis of polymer clay nanocomposites. The interlayer distance increases and the clay's surface chemistry is modified by inserting modifier into the hydrophilic galleries of the clay. In an ideal system these newly formed organophilic galleries allow for the intercalation of monomer or prepolymer, and eventually results in the development of exfoliated nanocomposites.

A number of factors determine whether a nanocomposite will form or not, and whether it will be intercalated or exfoliated. These include the type of polymer, layered silicate and organic modifier, the preparation technique and processing conditions. In general, nanocomposite materials, particularly those with exfoliated structures present significant improvements of modulus and strength. Other interesting characteristics of this class of materials include improved barrier properties, thermal stability and flame retardance.

Clays are layered silicates consisting of numerous stacks of hydrated aluminosilicates with lateral dimensions ranging from 50 to 1000 nm and a thickness of 1 nm. In its pristine state clay is hydrophilic and miscible only with hydrophilic polymers, whereas the majority of polymers are organophilic. Hence surface often requires organo-modification to make platelets compatible with organophilic polymer matrix. Our project deals with the synthesis of a facile, cost effective method for clay modification using different aromatic and aliphatic acid- amine adducts having reaction sites and prepare polymethyl methacrylate clay nanocomposite using adduct organo-modified clays.

In the present work the clay was modified using adducts that were prepared by treating equimolar concentration of Cetyl trimethyl ammonium bromide (CTAB) with two different acids: Cinnamic acid- an aromatic unsaturated carboxylic acid and Stearic acid – an aliphatic saturated long chain fatty acid. FTIR and XRD analysis supports the successful intercalation of Cinnamic acid–CTAB adduct and Stearic acid–CTAB adduct into the interspacing of Na+-MMT clay. In case of cinnamic acid- adduct modified clay (CA- AMC), FTIR showed absorptions of OH stretching of acid, C=O stretching, C=C of alkenes, C=C of arenes, CH vibrations of arenes and alkenes in addition to the characteristic vibrations present in the pristine clay. In the case of stearic acid- adduct modified (SA-AMC), FTIR showed absorptions of OH stretching of acid, -CH2 asymmetric stretching, CH3 symmetric stretching, C=O stretching vibrations of COOH in addition to the characteristic vibrations present in the pristine clay. In XRD, the reflection of all the adduct modified clay (AMC) appeared at smaller angles (2θ) as compared to the pristine clay, indicating the successful ion exchange. XRD analysis showed that Cinnamic acid-adduct modified clay (CA-AMC) 2x has got greater d-spacing when compared to Stearic acid- adduct modified clay (SA-AMC) 2x. From these results, we can conclude that the intercalation chemistry of clay increases in CA-AMC.

Polymer clay nanocomposites were synthesized by bulk polymerization by treating organomodified clays such as CA-AMC and SA-AMC with a vinyl monomer- methyl methacrylate using Benzoyl Peroxide(BPO) as initiator. The polymer clay nanocomposites (PCN) such as polymethyl methacrylate-cinnamic clay nanocomposite (PMMA-CC) and polymethyl methacrylate-stearic clay nanocomposite (PMMA-SC) obtained were also characterized using XRD and FTIR spectroscopy. In case of PMMA-CC, FTIR showed absorptions of C-O stretching, C=O stretch of ester, C-C of alkene, O-C-C stretching, C-H of alkane in addition to the characteristics vibrations present in the adduct modified clay. In case of PMMA-SC, FTIR showed absorptions of C=O stretch of ester, CH modes of methylene group, C-C-O stretch, O-C-C stretch in addition to the characteristics vibrations present in the adduct modified clay. This supports the successful formation of highly exfoliated polymer clay nanocomposite.

From the XRD results, it was concluded that both PMMA-SC and PMMA-CC resulted in formation of highly exfoliated structures. This well-exfoliated clay layers into the polymer matrix significantly improves the properties of both nanocomposites. Thus they exhibit typically improved barrier properties, thermal stability, mechanical strength and fire retardancy.

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