PROJECT REPORT

On

“SYNTHESIS AND CHARACTERIZATION OF POLYMETHYL METHACRYLATE NANOCOMPOSITE USING CTAB -MALEIC ACID ADDUCT MODIFIED CLAY”

Submitted by

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AB21CHE004, AB21CHE008, AB21CHE014, AB21CHE015

In partial fulfillment for the award of the

Bachelor’s Degree in Chemistry

DEPARTMENT OF CHEMISTRY AND CENTRE FOR RESEARCH

ST. TERESA’S COLLEGE (AUTONOMOUS)
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2023-2024

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This is to certify that the project "**SYNTHESIS AND CHARACTERIZATION OF POLYMETHYL METHACRYLATE NANOCOMPOSITE USING CTAB-MALEIC ACID ADDUCT MODIFIED CLAY**" is the work done by **ANCIYA FRANCIS.**

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CERTIFICATE

This is to certify that the project work entitled “**SYNTHESIS AND CHARACTERIZATION OF POLYMETHYYL METHACRYLATE NANOCOMPOSITE USING CTAB-MALEIC ACID ADDUCT MODIFIED CLAY**” is the work done by **GOPIKA P.S., RIYA MARY, ANCIYA FRANCIS, DARSANA DINESH** under my guidance in the partial fulfilment of the award of the Degree of Bachelor 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 CHARACTERIZATION OF POLYMETHYL METHACRYLATE NANOCOMPOSITE USING CTAB-MALEIC ACID ADDUCT MODIFIED CLAY**" submitted to Department of Chemistry and Centre for Research, St. Teresa's College (Autonomous) affiliated to Mahatma Gandhi University, Kottayam, is a record of an original work done by me under the guidance of **Dr. Annu Raju, Assistant Professor,** Department of Chemistry and Centre for Research, St. Teresa's College (Autonomous), Ernakulam and this project work is submitted in the partial fulfilment of the requirements for the award of the Degree of Bachelor of Science in Chemistry.

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Chapter 1

Introduction

1.1 Polymer clay nanocoposite

Polymer clay nanocomposites (PCN) constitute a new class of materials in which the polymer matrix reinforced by uniformly dispersed inorganic particles having at least one dimension in the nanometer. They often exhibit physical and chemical properties that are entirely different from pure polymers, and conventional micro composites having wide potential for applications as advanced functional materials. Among the inorganic nano-fillers, clays have been widely used as fillers for commodity thermoplastics like polypropylene, polyethylene, polystyrene and nylon due to its natural abundance, low cost and broader commercial viability[1].

Nowadays the field of polymer-clay nano-composites gained momentum due to the enhancement in thermal and mechanical properties of the matrix polymer and possibility of melting the polymer with the clays without the use of organic solvents. The improvement in properties was attributed to the dispersion of clay layers having nanometer thickness in the polymer matrix[2].

PCNs found wide applications in industry as high performing structural materials [3-7]. They can be molded in to complex shapes with pre-existing industrial equipments. PCNs can also be used for packing or storage tank applications because the nano-dispersed clay layers reduce the permeability of the polymer matrix. Polymer clay nanocomposites 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[8,9]. It was reported that nanocomposites with various structures/morphology, properties and applications can be produced by tuning the polymer- clay interactions.

Polymer-clay nanocomposites are formed through the union of two very different materials with organic and mineral pedigrees. The hybrid compositions, however, exhibit large increases in tensile strength, modulus, and heat distortion temperature as compared with the pristine polymer. The composites also have lower water sensitivity, reduced permeability to gases, and a smaller thermal coefficient of expansion. Additionally, nanocomposites impart a level of flame retardance and UV resistance all without any loss of clarity.

Recent advancement in these polymer clay composites in self-assembly and formation of different morphologies resulted in its applications as advanced functional materials in controlled delivery systems also [10].

1.2 Structure of Clays

Clays or layers silicates ate comprised of stacks of hydrated aluminosilicate with thickness of 1nm and lateral dimension of 50-100 nm^2. Frame work layers of clays are generated by tetrahedral sheets and octahedral sheets. Silica is the major component of tetrahedral sheet whereas octahedral sheet comprises diverse elements such as Aluminum, Magnesium and Iron. Tetrahedral and octahedral sheets stack naturally in specific ratio and mode, leading to the formation of 1:1, 2:1 layered silicates or phyllosilicates. Among these 2:1 phyllosilicates have been used for PCNs due to the ease of separation of individual silicate layers owing to its structural features [11]. The crystal lattice of 2:1 phyllosilicate consists of 1 nm thick aluminosilicate layers with an octahedral alumina sheet sandwiched between two tetrahedral silica sheets [12] (fig.1.1).

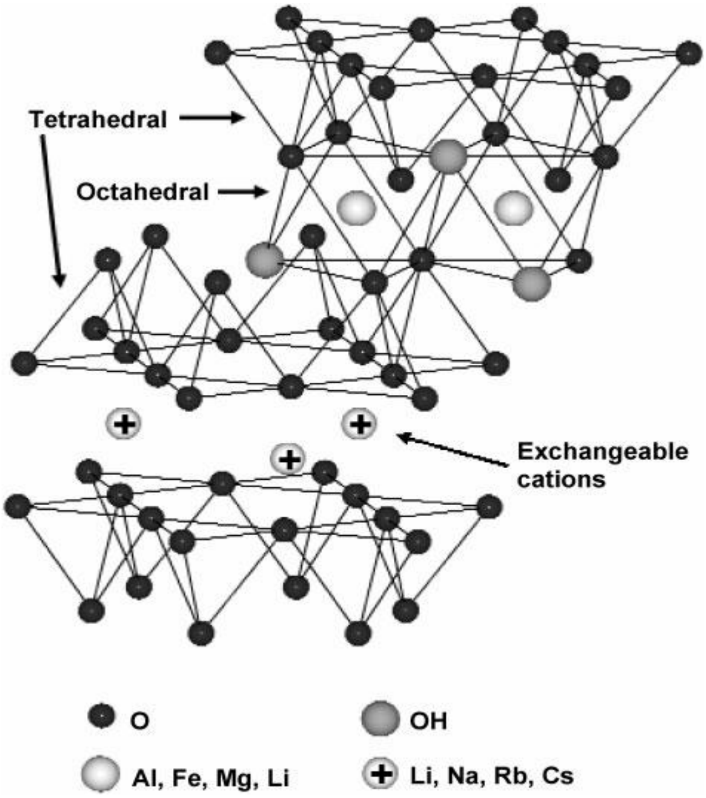

Fig.1.1 Structure of 2:1 Aluminosilicate

The stacking of the platelets leads to Vander Waals gap or gallery between the platelets. Isomorphic substitution of Al^{3+} in the alumina sheet with cations such as Mg^{2+} or Fe^{2+} produces negative charges to the layers. This negative charge is balanced by alkali cations positioned in the gallery between the aluminosilicate layers which are exchangeable with other inorganic and organic cations. The cation exchange capacity (CEC) is expressed as M equiv/ 100g clay (Table 1.1). Clays having high CES are generally used for PCNs. 2:1 phyllosilicate include mica, smectite, vermiculite and chlorite. Smectite group can be further divided in to montmorilllonite (MMT), nontronite, and saponite and hectorite species.

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

Silicate	Formula	CEC (m equiv/100 g)
Montmorillonite	$Mx(Al_4\text{-}xMgx)Si_8O_{20}(OH)_4$	92.6–120
Hectorite	$Mx(Mg_6\text{-}x\ Lix)Si_8O_{20}(OH)_4$	120
Saponite	$MxMg6(Si_{8\text{-}x}Alx)Si_8O_{20}(OH)_4$	86.6
Vermiculite	$(Mg, Fe, Al)_3\,[(Al,Si)_4O_{10}](OH)_2$ $M_{x\text{-}n}H_2O$	150

M represents exchangeable cation and x is the layer charge

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

1.3 Organoclays

Clays can be organo-modified via cation exchange of Na^+ with alkyl ammonium ions including primary, secondary, tertiary and quaternary alkyl ammonium cations under proper conditions [13]. The space between the silicate layers in the organo clay depends greatly on the length of the alkyl chain of organo modifier and the ratio of cross-sectional area to available area per cation as shown in fig.1.2 [14]. Organomodification of clays improves the interfacial adhesion properties between the inorganic phase and hydrophobic polymer matrix.

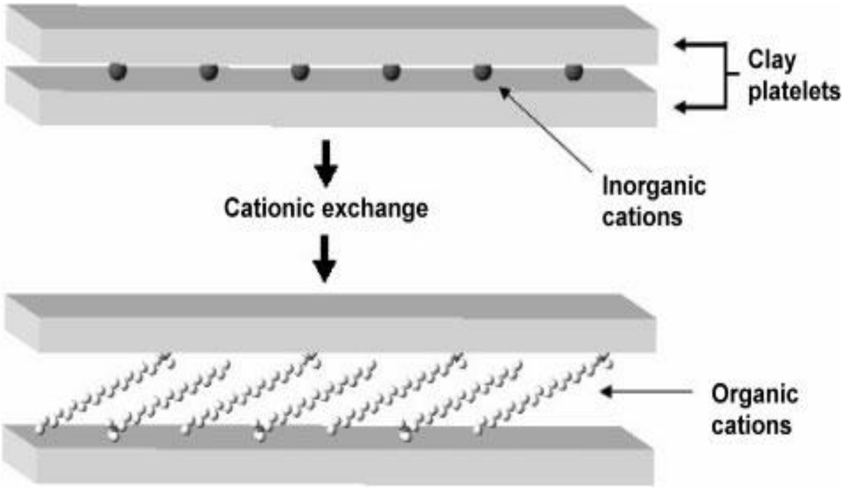

Fig.1.2 Scheme of effect of cationic exchange on interlayer spacing

The key issue in the design of PCNs is how to monitor the dispersion of clay platelets at nanometer scale in a polymer matrix. Accordingly, it is necessary to understand the interaction between the clay surfaces and the intercalants. In other words, understanding the structure of organoclays and the interaction of surfactant in clays is of crucial importance in design, fabrication and characterization of PCNs. Proper selection of organoclays depends mainly on the type of polymer used. When the hydrated cations are ion-exchanged with organic cations such as bulky alkyl ammonium or phosphonium cations, it generally results in larger inter layer spacing. Additionally, the alkyl ammonium or alkyl phosphonium cations can provide functional groups that can react with the polymer matrix, or in some cases initiate the polymerization of monomers to improve the strength in the interface between the inorganic and the polymer matrix. Depending on the packing density, temperature and alkyl chain length, the chains were thought to lay either parallel to the silicate layers forming mono or bimolecular arrangements as shown in fig.1.3 [15].

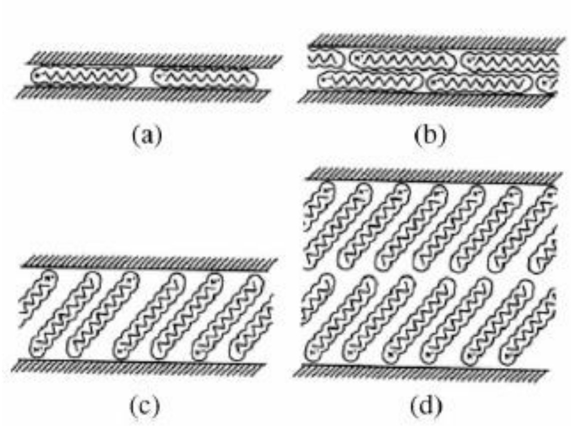

Fig.1.3 arrangements of alkyl ammonium ions in mica type layered silicates with different layer charges.

However these idealized structures have been shown to be unrealistic by Vaia et al [3], using experiments. They showed that alkyl chains could vary from liquid- like to solid-like, structure dominating as the interlayer density or chain length decreases, or as the temperature increases. This occurs because of the relatively small energy difference between the trans and gauche conformers; the idealized models described earlier assume all trans conformations. In addition, for longer chain length surfactants in the layered silicate can show thermal transition akin to melting or liquid-crystalline to liquid-like transitions upon heating.

1.4. Classification of PCNs

Depending on the strength of interfacial interactions between the polymer matrix and layered silicate, three different types of PCNs are thermodynamically achievable (Fig 1.4)

1.4.1 Intercalated Nanocomposites

In intercalate nanocomposites; the insertion of polymer matrix to the layered silicate structure occurs in a crystallographically regular fashion, regardless of the clay to polymer ratio[16]. Properties of the composites typically resemble those of ceramic materials.

1.4.2 Flocculated Nanocomposites

Conceptually this is same as intercalated nanocomposites. However, silicate layers are sometimes flocculated due to hydroxylated edge-edge interaction of the silicate layers

1.4.3 Exfoliated Nanocomposites

In an exfoliated nanocomposite, the individual clays are separated in a continuous polymer matrix by an average distance that depends on clay loading[17]. Usually the clay content of an exfoliated nanocomposite is much lower than that of an intercalated nanocomposite.

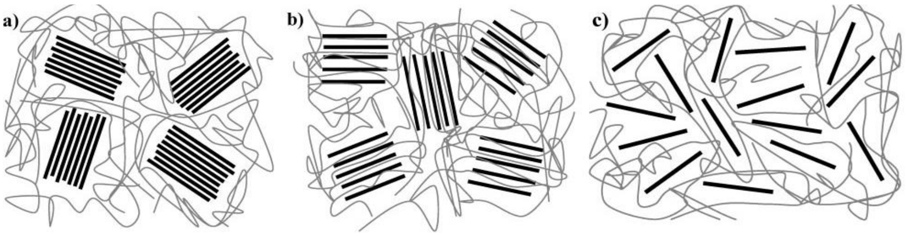

Fig.1.4 Schematic illustration of a) immiscible microcomposite; b) intercalated nanocomposite; c) exfoliated nanocomposite

The typical TEM Images showing the clay platelets in the polymer matrix of the Intercalated and exfoliated nanocomposites are shown in Fig 1.5[18].

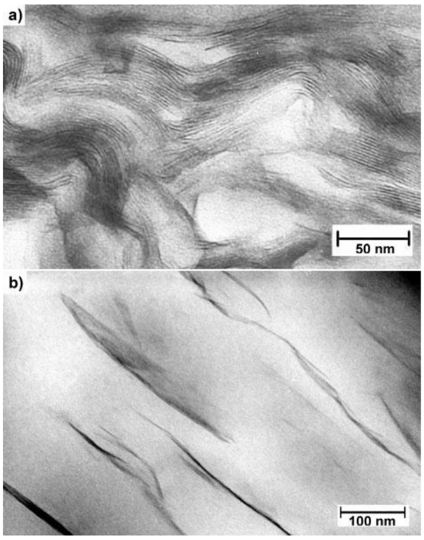

Fig.1.5 Typical TEM Images of PCN (a) intercalated (b) exfoliated

1.5 Preparative Methods of PCNs

The preparative methods are divided in to three main groups depending on starting materials and processing techniques.

1.5.1 Intercalation of Polymer or Pre-polymer from solution

This method is based on a solvent system in which the polymer or pre-polymer is soluble and the silicate layers are swelllable[19]. The layered silicate is first swollen in solvents such as water, chloroform or toluene. When the polymer and the layered silicate solutions are mixed, the polymer chain intercalate and displace the solvent within the interlayer of the silicate. Upon solvent removal, the intercalated structure remains and forms the nanocomposite. Water soluble polymers such as poly(ethylene oxide), poly(vinyl alcohol) and poly(vinyl pyrolidone) have been intercalated in to the clay galleries using this method. This method is useful only for certain polymer/ solvent pairs.

1.5.2 In situ Intercalative Polymerization

In this method, the layered silicate is swollen within the liquid monomer or a monomer solution[20]. So the polymer formation can occur within the inter-lamellar region. Polymerization can be initiated either by heat or radiation, by diffusion of suitable initiator or by an organic initiator or catalyst fixed through cation exchange before the swelling step. Poly(caprolatam), polyurethane, polystyrene, polypropylene, polyethylene, poly(ethylene terephthalate) and epoxy resin are examples of polymers used for in situ intercalation.

1.5.3 Melt Intercalation

This method involves annealing, statically or under shear, a mixture of the polymer and organoclay above the softening point of the polymer. This is the easiest and widely utilized method for the preparation of PCNs.

The entropy change associated with the surfactant increases until the inter layer separation is equal to the fully extended length of the surfactant chains. On the other hand, as the inter layer separation increases, more polymers confined ad total penalty of polymer confinement per unit are continuously increases up to a critical gallery height. The extend of inter molecular interactions would determine the amount of intercalated polymer beyond the critical gallery height. When the total entropy change is small, small changes in the free energy of the system determine whether intercalation is thermodynamically stable or not.

The entropy of mixing could be rendered favorable by maximizing the polymer-clay interactions. At later stage, the clay factoids are exfoliated under shear and stacks of clay platelets tends to slide apart from each other. High shear intensity would assist the formation of PCNs by breaking up the clay platelets and increasing sample uniformity. The process is thus facilitated by both residence time and screw configuration in the extruder.

1.6 Techniques used for the characterization of PCNs

In addition to the techniques used for the characterization of the respective polymers, the structure of the nanocomposites has typically established using Wide Angle X-ray Diffraction (WAXD) analysis and Transmission electron micrographic (TEM) observations [21]. Due to its easiness and availability, WAXD is most commonly used to probe nanocomposites structure and occasionally to study the kinetics of the polymer melt intercalation.

1.7 Properties of PCNs

Nanocomposites consisting of a polymer and layered silicate exhibit remarkably improved mechanical and material properties when compared to those of pristine polymers. Improvements include higher modulus, increased strength and heat resistance in addition to decreased gas permeability and flammability. These composites show better biodegradability properties also. PCNs also show improvement in most general polymeric properties [22]. In addition to the decreased permeability of liquids and gases, nanocomposites show significant improvement in solvent uptake also. Scratch résistance is another property that is strongly enhanced by the incorporation of layered silicate. The main reason for these improvements is the stronger interfacial interactions between the matrix and the silicate, compared to conventional filler-reinforced systems.

1.7.1 Mechanical Properties

Tensile and flexual properties of polymeric materials showed remarkable improvement when nanocomposites are formed with layered silicates.

1.7.2 Thermal Stability

The incorporation of clay in the polymer matrix was found to enhance he thermal stability by acting as a superior insulator and mass transport barrier to the volatile products produced during decomposition [23]. In some cases the clay was found to shift the early stages of thermal decomposition to higher temperature. A reversal in thermal-stability due to the heat barrier effect of the stacked silicate layers holding accumulated heat that could be used as heat source to accelerate the decomposition process in conjunction with the heat flow supplied by the outside heat source was also observed.

1.7.3 Heat Distortion Temperature (HDT)

HDT of a polymeric material is an index of heat resistance towards applied load. The increase of HDT due to clay dispersion is a very important property improvement for any polymeric material. It is very difficult to achieve similar HDT enhancement by conventional filler.

1.7.4 Fire Retardant Properties

The improved flame retardant properties observed in the case of nanocomposites may be attributed to the formation of a high-performance carbonaceous-silicate char which builds up on the surface during burning. This insulates the underlying material and slows the mass loss rate of decomposition products.

1.7.5 Gas Barrier Properties

Clays are believed to increase the barrier properties by creating a maze or tortuous path that retard the progress of gas molecule through the matrix-resin. The reduction in permeability arises from the longer diffusive path that the penetrant must travel in the presence of filler.

1.7.6 Optical Properties

Although layered silicates are microns in lateral size, they are only just 1nm thick. Thus when single layers are dispersed in polymer matrix, the resulting nanocomposite is optically clear or more transparent in visible light.

1.7.7 Biodegradability

Another interesting and exciting aspect or PCNs is the significant improvement in biodegradability after nanocomposites may due to catalytic role of organoclay in the bio-degradation mechanism [24].

1.8 Limitations of Conventional Organoclays

Melt intercalation is the broadly applicable method for the synthesis of many commodity and engineering polymer nanocomposites. These polymers are produced on large scale and it is desirable to use these materials as they currently produced.The disadvantage of melt intercalation is related to low thermal stability of the organomodifiers. The conventional organomodifiers used are alkyl ammonium or alkyl phosphonium cations. These modifiers render the layered silicates more organophilic, but they are thermally not stable.

Chapter 2

Materials and Methods

This chapter gives a brief description of the materials and experimental procedures adopted for the present investigation.

2.1 WORK PLAN

The main aim of the project is to synthesize polymer clay nanocomposites by using organomodified modified montmorillonite (MMT) clay. The synthesis of organically modified clay was carried out using,Unsaturated acid - Amine adduct of different concentrations. Adduct was prepared using Cetyltrimethylammonium bromide (CTAB) and Maleic acid. Using the organomodified clay we have to synthesis polymer clay nanocomposite using methyl methacrylate monomer and characterize the modified clay and polymer composite using FTIR and X-ray Diffraction studies.

2.2 WORK CARRIED OUT

Synthesis of modified MMT clay with varying modifier concentrations utilizing CTAB and the Maleic Acid(MA) adduct. In this project, we have carried out the synthesis of modified MMT clay using 0.5x 1x and 2x concentrations of CTAB-MA adduct.

(i) Synthesis of modified MMT clay using Cetyl Trimethyl Ammonium Bromide – Maleic Acid (CTAB-MA) Adduct

(ii) Synthesis of Polymethylmethacrylate (PMMA)-Clay Nanocomposite using organomodified clay

(iii) Study the intercalation chemistry of orgnomodification and d-spacing using FTIR and XRD.

2.3 EXPERIMENTAL PROCEDURE

2.3.1 Materials Required

Montimorillonite clay (Cloisite-Na^+, Southern Clay Products, USA) of CEC 92.6 mequiv/100g, Maleic acid and CTAB (Merck Specialties Pvt Ltd, India) were used as received. Methyl methacrylate monomer was purchased from Merck Specialties Pvt Ltd and Benzoyl peroxide(BPO) from S.d fine chemical Ltd, India. Ethanol of AR grade and Toluene, Tetrahydrofuran (THF) of HPLC grade was obtained from Merck Specialties Pvt Ltd, India.

2.3.2 Synthesis of 1x:1x Adduct Modified Clay

Weight of the clay=4 g
Weight of the maleic acid=0.4642 g
Weight of CTAB=2.9232 g
Total volume of distilled water=800ml

Here, the adduct was prepared by mixing an organic acid called maleic acid with cetyltrimethylammonium bromide (CTAB) using the 1x;1x concentration as mentioned above. In a 1000 ml beaker, 4g of MMT clay and 100 ml of distilled water were combined. In a 200 ml beaker, the required concentrations of CTAB and maleic acid were combined with 100 ml of distilled water. Using a magnetic stirrer, the two suspensions mentioned above were mixed independently for 30 minutes. This clay suspension was supplemented with the synthesized adduct and combined with 600 ml of distilled water. For 48 hours, it was covered and continuously stirred using magnetic stirrer. The modified clays were separated by centrifugation, washed with ethanol by redispersing. Lastly, an 80^{o}C hot air oven was used to dry the adduct modified clay. To get finely powdered organomodified clay, these were grounded using a mortar and pestle.

2.3.3 Synthesis of 2x:2x Adduct Modified Clay

Weight of clay=4 g

Weight of maleic acid=0.9284 g

Weight of CTAB=5.8469 g

Total volume of distilled water=800 ml

Here, the same procedure for 1x : 1x was followed for the organoclay modification by changing the modifier concentration to 2x:2x.

2.3.4 Synthesis of 0.5x:0.5x Adduct Modified Clay

Weight of clay = 4 g

Weight of maleic acid=0.2321 g

Weight of CTAB=1.4616 g

Total volume of distilled water= 800 ml

For the synthesis of 0.5x:0.5x adduct modified clay the same procedure for 1x : 1x was followed for the clay modification by changing the CTAB-Acid modifier concentration. The dried and powdered modified organoclay were shown in the below Figure 2.1 and Figure 2.2, respectively.

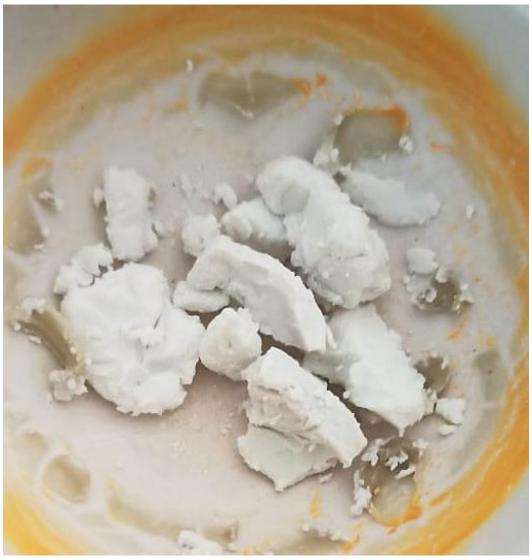

Fig.2.1 Dried adduct modified organoclay in a china dish

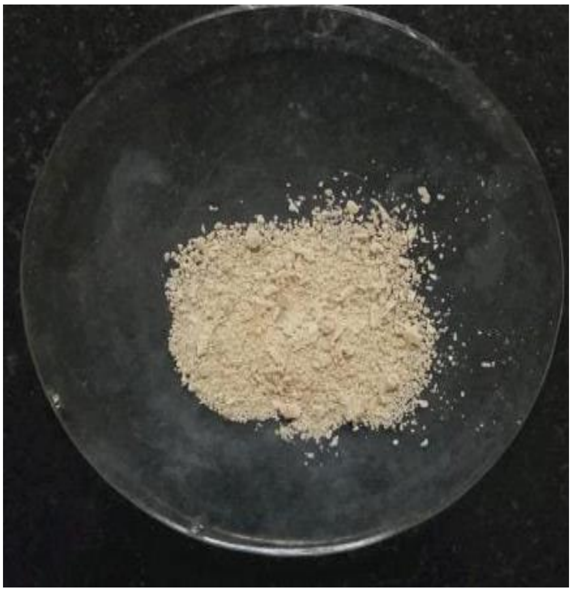

Fig.2.2 Powdered adduct modified organoclay

2.3.5 Synthesis of Polymethyl methacrylate -Clay Nanocomposite

5ml of methyl methacrylate (monomer) and 0.5 g organoclay is placed in 50 ml round bottom (RB) flask. To the round bottom flask, then 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 Celsius for 4 - 6 hours. Polymethyl methacrylate nanocomposite (PMMAC) was obtained. Dissolve the PMMAC in toluene at room temperature (if it is not dissolved, provide heating on a water bath). After it is dissolved, transfer it to a beaker and wash the RB with little amount of toluene. Reprecipitate the polymer nanocomposite using sufficient amount of alcohol.

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

Fig.2.3 Experimental setup for polymerization

2.4 Characterization

2.4.1 Characterization of modified clays using IR analysis

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

2.4.2 Characterization of modified clays using XRD analysis

The samples of modified clays using different modifiers were characterized by X-ray diffraction studies. X-ray diffraction relies in the dual wave or particle nature of X-rays to obtain information about the structure of crystalline materials. Primary use of the technique is the identification and characterization of compounds based on their diffraction pattern. When an incident beam of monochromatic X-rays interacts with a target material the falling rays gets scattered from those atoms within the target material. In an XRD graph, the intensity of reflected X-ray is plotted against 2θ values.

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

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

Chapter 3

Results and discussion

3.1 FTIR SPECTROSCOPY

The FTIR spectrum of pure MMT clay and organomodified clays with different adduct concentrations are shown in fig 3.1, fig.3.2 and fig.3.3.

3.1.1 FTIR Spectral Studies of Pristine Clay

FT-IR spectroscopic studies support the successful intercalation of adduct onto the interlayer space of MMT. The unmodified clay showed bands due to Si–O–Si asymmetric stretching of silicate layer at 1046 cm^{-1} and structural hydroxyls at 3448cm^{-1}. The bands at 3633cm^{-1} and 1641cm^{-1} are due to -OH stretching and -OH bending vibrations due to hydration, respectively.

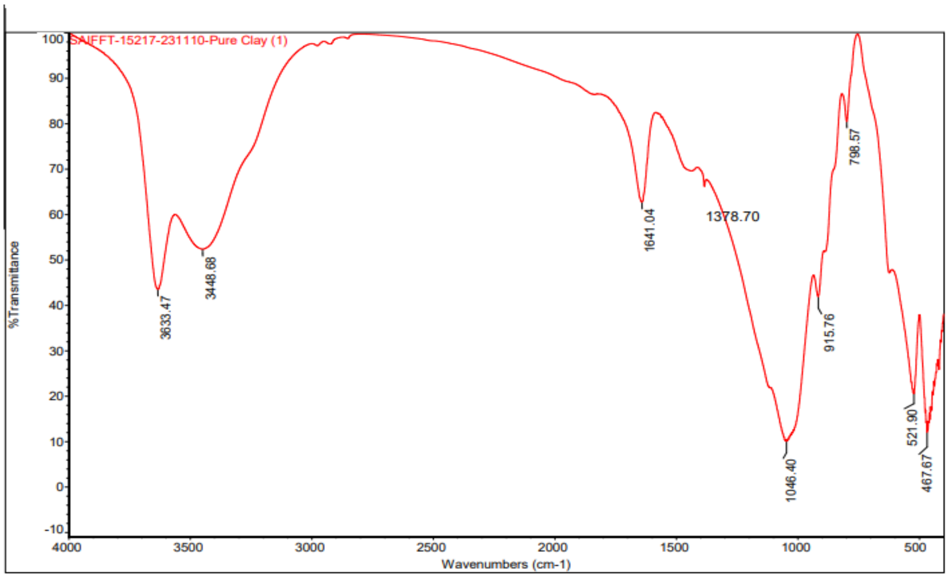

Fig.3.1 FTIR spectrum of pure MMT clay

3.1.2 FTIR Spectral Studies of 1x:1x Equimolar Concentration of Adduct Modified Clay

The FTIR spectrum of modified clay with adduct of 1x:1x equimolar concentration is shown in fig.3.2. For the modified clay, additional bands appeared due to the intercalation of organic moiety. The absorption peak at 3413cm^{-1} attributed to the –OH stretching vibration of the acid group. The intense characteristic peaks at 2849cm^{-1} and 2918cm^{-1} were observed due to the stretching vibration for $–CH_2$ and $–CH_3$, respectively. These absorption bands confirm the intercalation of the alkyl group of CTAB in the interlayer of modified clay. In the low frequency region, the bands appears at 1624cm^{-1} is attributable to C=O stretching vibration related to carboxylic group. The absorption peak at 1487cm^{-1} indicates double bond of alkene.

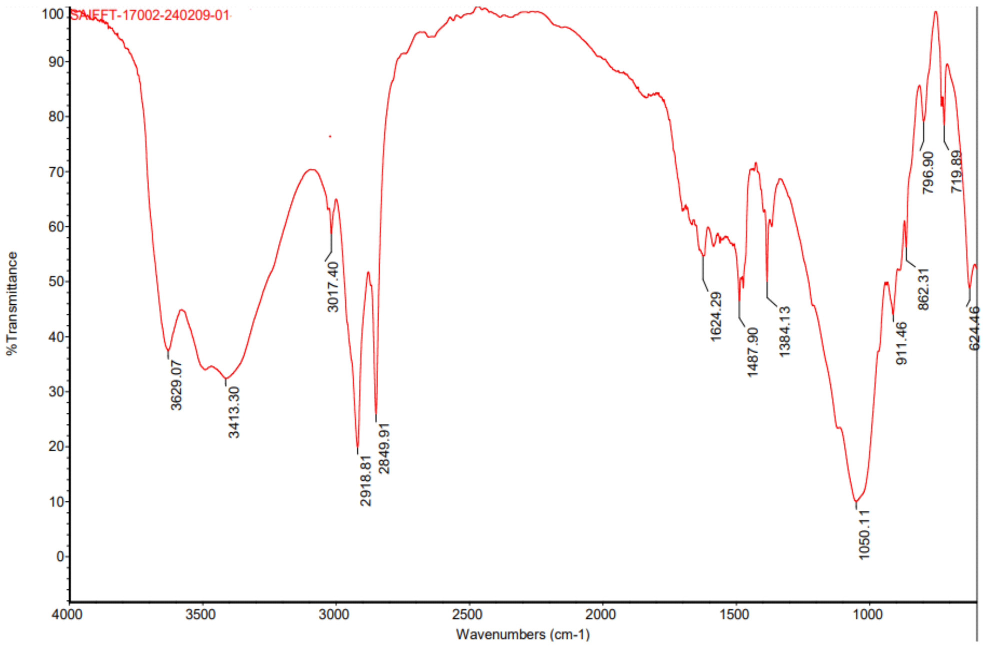

Fig.3.2 FTIR spectrum of 1x:1x concentration of adduct modified clay

3.1.2. FTIR Spectral Studies of 0.5x:0.5x Equimolar Concentration of Adduct Modified Clay

The FTIR spectrum of modified clay using Maleic acid-CTAB adduct of 0.5x: 0.5x concentration is shown in fig.3.3.

For the modified clay additional characteristic peaks were observed at 3421cm^{-1}, which attributed to the -OH stretching vibration of acid group. The absorption peaks at 2852cm^{-1} and 2924cm^{-1} are observed due to the stretching vibration for -CH_2 and -CH_3, respectively of CTAB. These absorption bands confirm the intercalation of the alkyl group of CTAB in the interlayer of modified clay. The characteristic peak at 1637cm^{-1} was assigned to C=O stretching of unsaturated maleic acid and characteristic peak found at 1488.72cm^{-1} corresponds to the C=C symmetric stretching of alkene.

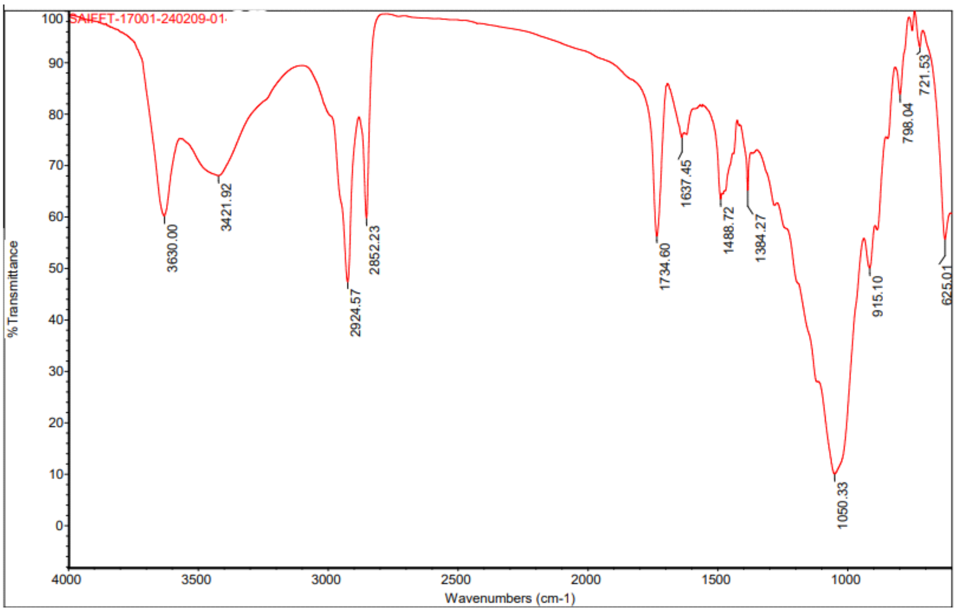

Fig.3.3 FTIR spectrum of 0.5x:0.5x concentration of adduct modified clay

3.1.3 FTIR Spectral Studies of 2x:2x Equimolar Concentration of Adduct Modified Clay

The FTIR spectrum of modified clay using Maleic acid-CTAB adduct of 2x:2x concentration is shown in fig.3.4.

The absorption peaks at 2850cm^{-1} and 2918cm^{-1} are observed due to the stretching vibration for -CH_2 and -CH_3, respectively of CTAB. The peak at 3442cm^{-1} attributed to the -OH stretching of COOH group. The characteristic peak at 1631cm^{-1} was assigned to C=O stretching of acid group and characteristic peak found at 1488 cm^{-1} corresponds to the C=C symmetric stretching of unsaturated maleic acid

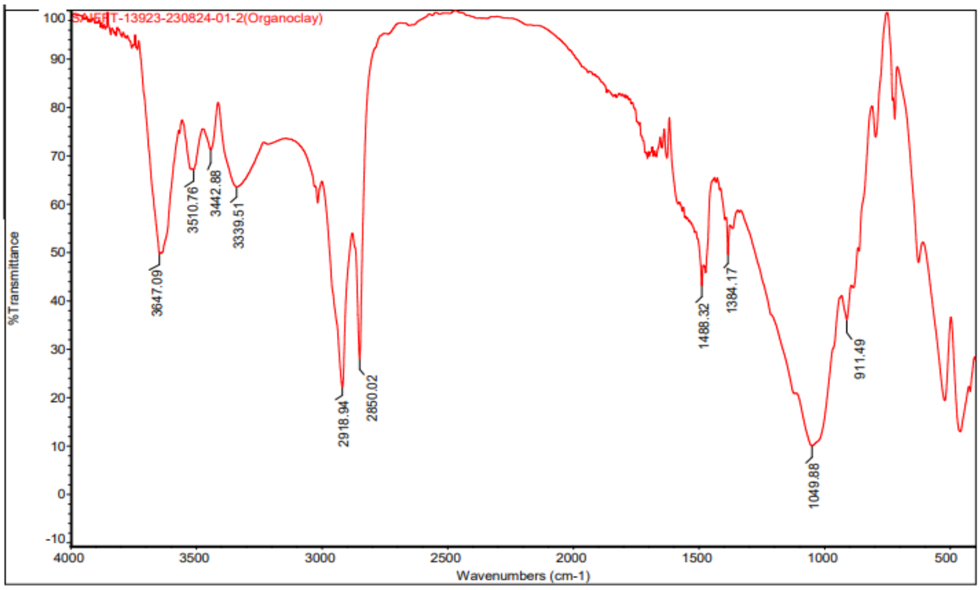

Fig.3.4 FTIR spectrum of 2x:2x concentration of adduct modified clay

3.1.4 FTIR Spectral Studies of PMMA Nanocomposite (PMMAC)

The FTIR spectrum of polymer nanocomposite using Maleic acid-CTAB adduct of 2x:2x concentration is shown in fig.3.5.

The PMMA Nanocomposite was prepared using 2x:2x adduct modified clay. All the peaks observed in the IR spectrum of adduct modified clay were also present in the polymer nanocomposite spectrum. The absorption peak at 3431cm^{-1} indicates the -OH group of the acid present in adduct modified clay (AMC). The absorption peaks at 2924cm^{-1} indicates the -CH_3 asymmetric stretching. Similarly the absorption peak at 2851.09 cm^{-1} is attributed to -CH_2 symmetric stretching. In addition to these peaks, the characteristic peaks of esters (C=O, C-C-O, O-C-C linkages) were observed in the given spectrum of nanocomposite. This means IR spectrum have three intense peaks at approximately 1621-1488cm^{-1}, 1250-1160cm^{-1}, 1030-1050cm^{-1}.These corresponds to the stretching of the C=O , C-C-O and O-C-C, respectively. That is, in the low frequency region, the bands at 1734cm^{-1} is attributable to C=O stretching vibration related to ester group. The band appears at 1384 cm^{-1} and 1050 cm^{-1} attributable to C-C-O stretching. The FTIR confirms the interaction of methyl methacrylate group onto the inter-gallery of clay layers.

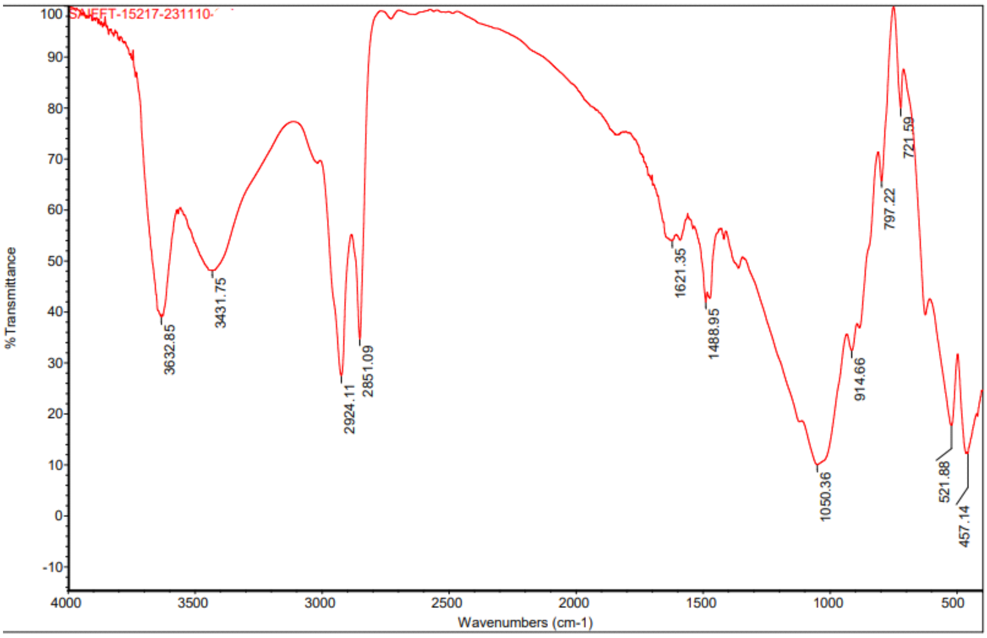

Fig.3.5 FTIR spectrum of PMMAC synthesized using 2x:2x modified clay

3.2 XRD ANALYSIS

The samples of modified clay prepared using different concentrations were characterized using XRD. In an XRD graph, the intensity of reflected X-ray is plotted against 2 is the angle at which X-ray falls on the samples and n- the order of reflection. The d-spacing is calculated using the Bragg’s equation,

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

where is the angle at which X-rays falls on the sample, n is the order of reflection, λ is the wavelength of the 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.

3.2.1 XRD of Pristine Clay

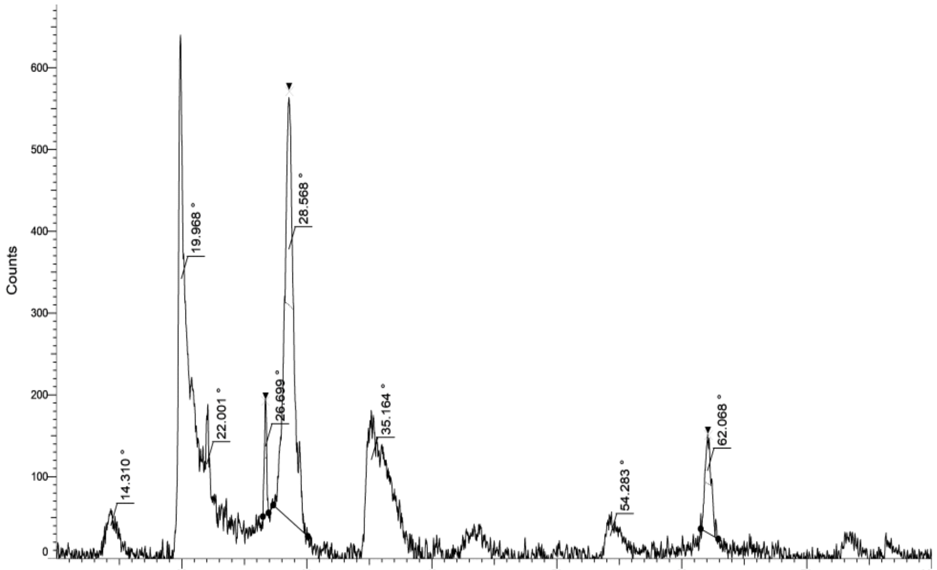

Fig. 3.4 XRD of Pristine clay

Sample	**Angle 2**	**d-spacing(Å)**
Pristine clay	14.310	6.185

3.2.2 XRD of 0.5x: 0.5x Equimolar Concentration of Modified Clay

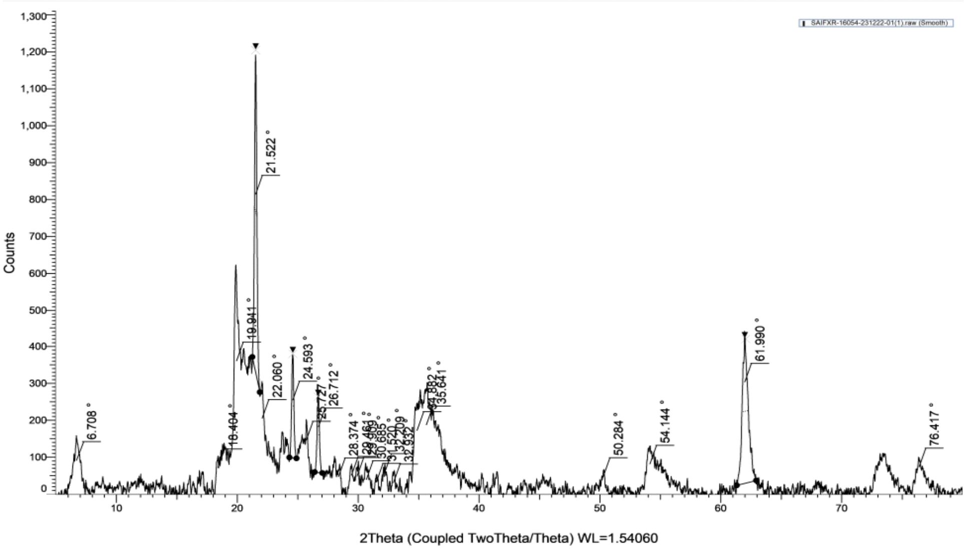

Fig.3.5 XRD of 1x:1x concentration of adduct modified clay

Sample	Angle 2	d-Spacing
0.5x concentration clay	6.708	13.167

3.2.3 XRD of 1x:1x Equimolar Concentration of Modified Clay

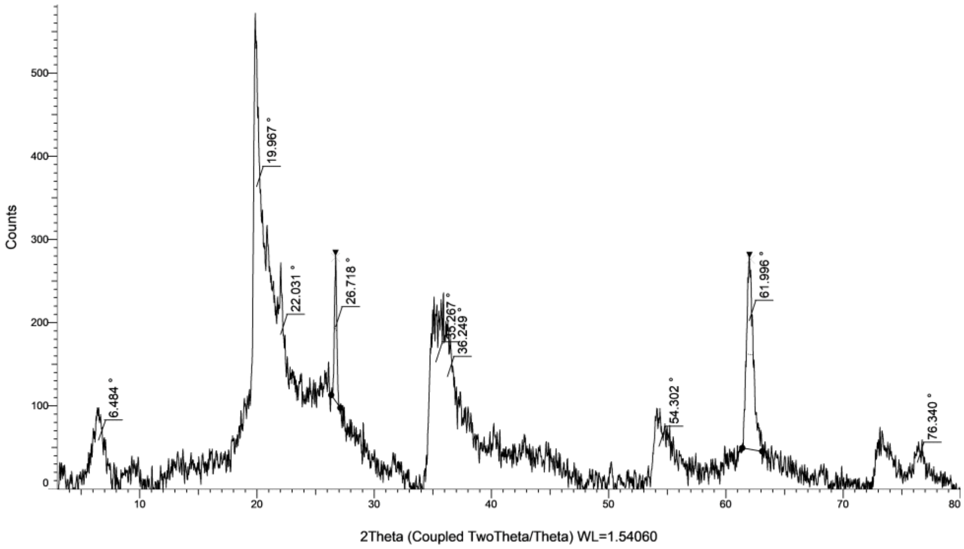

Fig.3.6 XRD of 0.5x:0.5x concentration of adduct modified clay

Sample	Angle 2	d-Spacing
1x concentration	6.484	13.619

3.2.4. XRD of 2x:2x Equimolar Concentration of Adduct Modified Clay

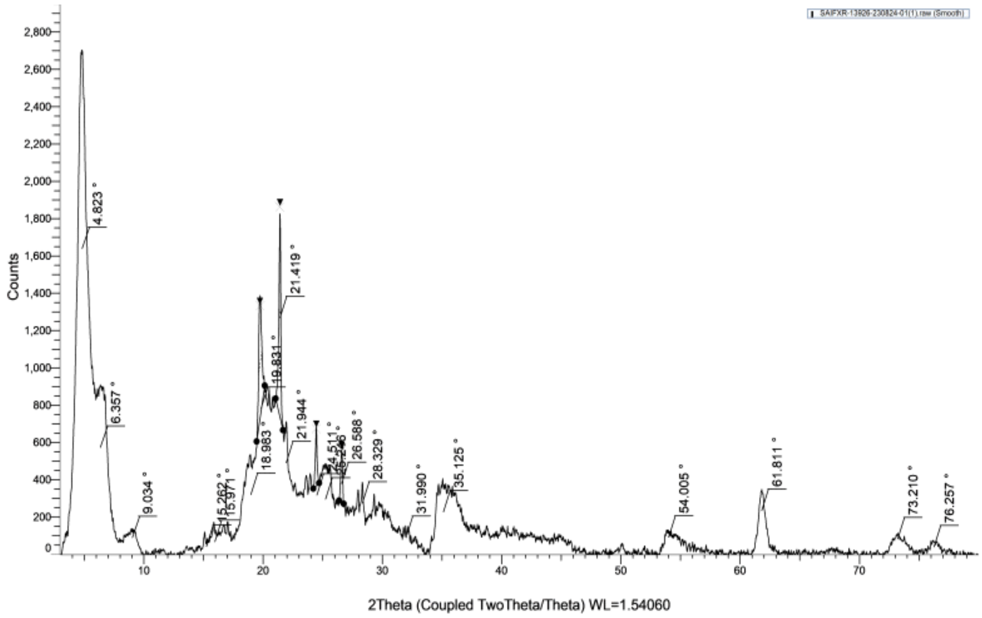

Fig.3.7 XRD of 2x:2x concentration of adduct modified clay

Sample	Angle 2	d-spacing(Å)
2x concentration clay	4.823	18.307

SAMPLE	ANGLE(2)	d-SPACING(Å)
Pristine clay	14.310	6.185
0.5x concentration	6.708	13.167
1x concentration	6.484	13.619
2x concentration	4.823	18.307

Table 3.1 The d-spacing value of pristine clay and Adduct modified clay

From the table 3.1 it’s clear that, as the modifier concentration increases the d-spacing increases. The 2x:2x adduct modified clay showed a maximum d-spacing of 18.307 A^{o}. The XRD results confirms the interaction of adduct moiety into clay layers.

3.2.5 XRD of Polymer Clay Nanocomposite

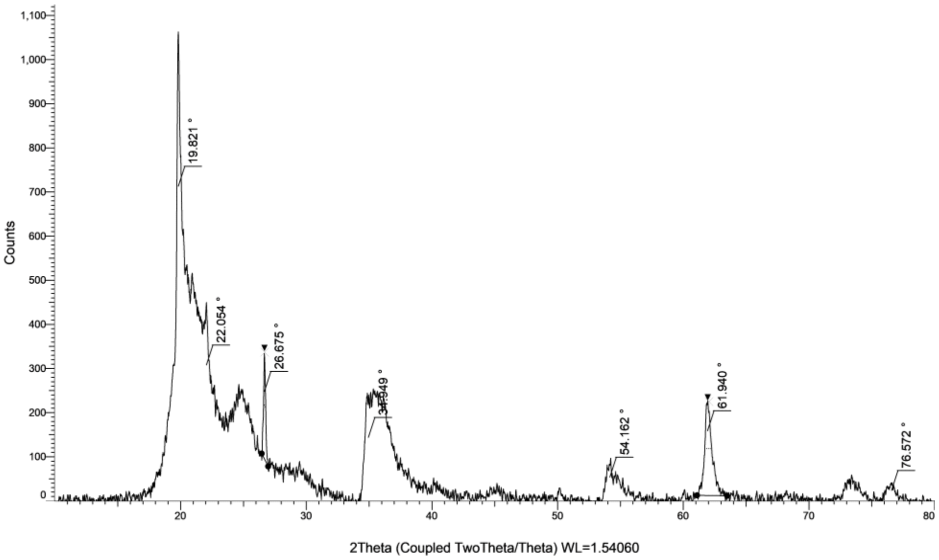

Figure 3.8 shows XRD of Polymethyl methacrylate Nanocomposite

The disappearance of $d_{(001)}$ peaks of the Polymethyl methacrylate nanocomposite PMMAC indicates the formation of exfoliated nanocomposites. The absence of the 001 reflection suggests that the $d_{(001)}$ value between the layered silicates is intercalated to spacing greater than the measurable range, or clay layers are disorderly dispersed in the PMMA matrix.

Chapter 4

Conclusions

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 and eventually results in the development of exfoliated nanocomposites.

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.

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 facile, cost effective method for clay modification using CTAB-maleic acid adduct of different concentrations 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 different concentrations of Cetyl trimethyl ammonium bromide (CTAB) with maleic acid -a dicarboxylic acid ,which is the cis-isomer of butendioic acid. FTIR and XRD analysis supports the successful intercalation of maleic acid- CTAB adduct into the interspacing of Na^+- MMT clay. In case of FTIR spectra obtained for maleic acid-CTAB adduct modified clay showed absorptions of OH stretching and C=O stretching of acid, C=C stretching frequency of alkenes, C=C of alkene, and CH_2 asymmetric stretching present in the long aliphatic chain of CTAB, in addition to the characteristic vibrations present in pristine clay.

In XRD, the (001) reflection of all the adduct modified clay appeared at small angles (2θ) as compared to the pristine clay, indicating the successful ion exchange. XRD analysis showed that adduct modified clay with double the equimolar concentration of (2x:2x)modifier, has got greater d-spacing when compared to clays modified with other adduct concentrations. From these results, we can conclude that the intercalation chemistry of clay increases with increase in adduct concentration of maleic acid-CTAB.

Polymer clay nanocomposites were synthesized by bulk polymerization of methylmathacrylate monomer by treating 2x: 2x organomodified clay using Benzoyl Peroxide (BPO) as initiator. The Polymethyl methacrylate nanocomposite (PMMAC) obtained is also characterized using XRD and FTIR spectroscopy. In case of PMMAC, FTIR showed absorptions of C-O stretching, C=O stretch of ester, C-C of alkene, C-C stretching, C-H stretching of alkane in addition to the characteristics vibrations present in the adduct modified clay. This supports the successful formation of highly exfoliated polymer clay nanaocomposites.

The disappearance of (001) peaks of the PMMAC indicates the formation of exfoliated nanocomposites. The absence of the 001 reflection suggests that the d_{001} value between the layered silicates is intercalated to spacing greater than the measurable range, or clay layers are disorderly dispersed in the polymethyl methacrylate matrix. This well- exfoliated clay layers into the polymer matrix significantly improves the properties of nanocomposites.

References

1. Bindu P Nair, Pavithran, C, Sudha, J. D, Prasad, V. S, Langmuir 2020, 26, 1431.

2. Vaia, R. A; Isti, H; Giannilis, E.P. Chem. Mater. 1993, 5, 1431.

3. Ray, S. S; Okamoto, M. Prog. Polym. Sci.2003, 28, 11, 1539.

4. Giannelis, E. P; Krishnamoorthy, R; Manias. Adv. Polym. Sci, 1999, 138

5. Vaia, R.A; Vasudevan, S; Krawiec, W. Adv. Mater. 1995, 7, 154.

6. Carastan, D. J. and N. R. Demarquette Intl Mater Rev 2017, 52, 345.

7. Hasegawa, N.; Okamoto, H.; M. Kawasumi; A. Usuki J. Appl. Polym. Sci., 1999, 4, 3359.

8. David, B. C.; Paul, D. L.; Franck, R. Chem. Rev., 2020, 110, 2081

9. Z hao, D.; Feng, J,; Huo, Q; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D Science 1998, 279, 548.

10. David R.F, Bustamante T, Francisco B.P., Polymers 2022, 14(19), 4084

11. Okomoto, M.; Morita, S.; Taguchi, H; Kim, Y. H; Kolkata, T; Tateyama, H. Polymer 2000, 41, 3887.

12. Lee, J.; Yee, A. F. Polymer 2000, 41, 8263.

13. Okomoto, M.; Morita, S.; Kolkata, T. Polymer 2001, 42, 2685.

14. Vaia, R.A.; Jandt, K. D.; Kramer, E. J.; Chem. Mater.1996, 8, 2628.

15. Jang, B. N.; Wilkie, C. C. Polymer, 2005, 46, 2933.

16. Krishanmoorti, R. Polymer Nanocomposites, ACS symposium Series: ACS, 2001.

17. Burlinos, A. B; Giannelis, E. P.; Zhang, Q.; Archer, I. A; Floudas, G.; Fytas, G. Eur. Phys. J. E. 2006, 20, 109.

18. Chang, J. H; An, Y.U.; Ryul, S.C.; Geiannelis, E.P.; Polymer Bulletin 2003, 51, 1.

19. Cowie, J. M. J., Polymer Chemistry and Physics of Modern Materials, Blackie, 1991, 23, 36.

20. Prasad, V. S., Shelma, R. Macro 2004, Intl. conf. Advanced Polymers 2021, 14-17

21. Tjong, S.C. Mater. Sci. Eng. R. 2016, 53, 73.

22. Catherine L, Patrick L.D. , Macromolecules 2009, 42, 70-84.

23. Lekshmi O, Anoop C, Reenu E. J., ACS Omega 2022, 7, 30, 25921–25947.

24. Ivaturi Siva R, Achyut K. P., Narayan Gouda, Journal of Polymer Engineering, 2023, 43,8-12.