2. LITERATURE REVIEW

2.1. Clay Minerals

Clay minerals are the basic component of the clay raw materials. Clay minerals are mostly phyllosilicates i.e. hydrous silicates of Al, Mg, Fe and other elements. These are plastic in nature when accumulate water and harden when dried or fired. Clay minerals have very high aspect ratio, large specific surface areas, consequently high adsorptivity and surface reactivity. Clay minerals have basal surface, edge surface and interlayer surface. Their crystal structure generally consists of sheets and so they are termed as phyllosilicates. The crystalline lattice of phyllosilicates consists of two structural units. One structural unit is tetrahedron with oxygen at the corner and a silicon atom in the centre of the tetrahedron. Another structural unit consists of octahedron of oxygen atom and hydroxyl groups at the corner and aluminium at the centre. In the tetrahedral sheet each tetrahedron are linked to the adjacent tetrahedron by sharing three corners whereas in the octahedral sheet each octahedron are connected by sharing edges. There are two different topologies of octahedrons e.g. cis and trans related to (OH) position.

The crystalline clay minerals are classified into seven groups depending on the criteria like the number and the ratio of sheets in a fundamental structural layer, the existing cation substitutions in the octahedrons and tetrahedrons and the resulting charge of the layers. The groups are (1) The kaolinite and serpentine group (2) The group of micas (3) The vermiculite group (4) The group of smectites (5) The pyrophyllite and talc group (6) The chlorites group (7) The palygorskite and sepiolite group.

The kaolin group of minerals belongs to dioctahedral 1:1 type with a general composition of $Al_2Si_2O_5(OH)_4$. The two sheet phyllosilicates contain no layer charge. Kaolinite, nacrite and dickite are three members of this group. Halloysite is a hydrated polymorph of kaolinite. The composition of the kaolin group of

minerals is characterized by a predominance of Al^{3+} in octahedral sites, although some isomorphous substitution of Mg^{2+}, Fe^{3+}, Ti^{4+} and V^{3+} for Al^{3+} can occur.
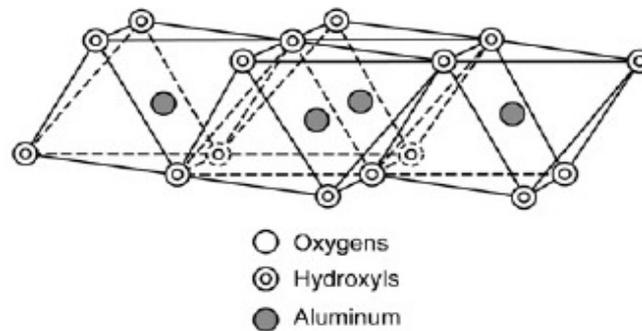
Figure.2.1. Sketch of octahedral sheet

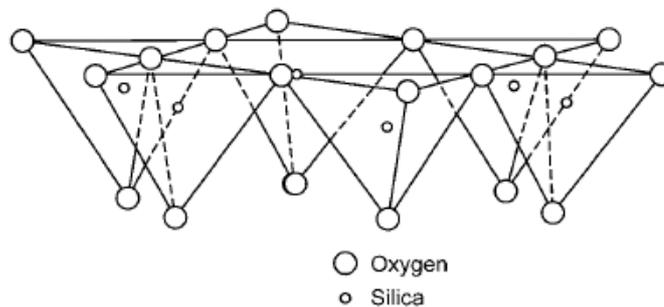(Reproduced from *H.H. Murray*, *Applied Clay Mineralogy, Elsevier, 2007*)

Figure.2.2. Sketch of tetrahedral sheet

(Reproduced from *H.H. Murray*, *Applied Clay Mineralogy, Elsevier, 2007*)

The serpentine group of minerals belongs to trioctahedral 1:1 phyllosilicates. The layer of 2:1 phyllosilicates is formed by three sheets where an octahedral sheet is sandwiched between two tetrahedral sheets. Among its members the pyrophyllite (dioctahedral) and talc (trioctahedral) are negatively charged. Other 2:1 phyllosilicates like smectites and vermiculites posses fractional value for layer charge. While smectites posses a layer charge of between 0.2-0.6 and vermiculites possess a layer charge between 0.6-0.9 per half unit cell. Another common

characteristic of smectites and vermiculites is presence of hydrated interlayer cations. In chlorite the negative layer charge is neutralized by positively charged octahedral sheet in the interlayer space. Chlorites are usually trioctahedral in nature.

A palygorskite and and sepiolite group of minerals posses layer fibrous structure and belongs to 2:1 layer silicates.

The crystalline clay minerals also occur as mixed layer clay or interstratified clay such as rectorite, corrensite etc.

2.1.1. Smectite Group of Minerals

Smectites are 2:1 layer clay minerals with a layer charge of between 0.2-0.6 and it consists of hydrated exchangeable interlayer cations. These are the most widely used clays for non-ceramic applications. Like other 2:1 phyllosilicates smectites are formed by an octahedral sheet sandwiched between two opposing tetrahedral sheets. The octahedral sheet may be dominantly occupied by trivalent cations forming dioctahedral smectites or divalent cations forming trioctahedral smectites. General formula for dioctahedral smectites is $(M^+_{x+y}*nH_2O)$ $(R^3_{2-y}R^{2+}_y)(Si^{4+}_{4-x} Al^{3+}_x) O_{10}(OH)_2$. (X = Layer charge resulting from substitution in tetrahedral sites. Y= Layer charge resulting from substitution in octahedral sites, R^{2+} =divalent octahedral cation, R^{3+} = trivalent octahedral cation, M^+ = Monovalent interlayer cation. In dioctahedral smectites substitutions of the divalent cations for trivalent cations create an excess of negative layer charge. The excess charge is compensated by the interlayer cations like Na^+, Ca^{2+}, and K^+ etc. There are several species of smectite clay. Among those the most important species in terms of commercial importance is montmorillonite. The most common occurrences of this smectite clay mineral is in bentonite which is a clay altered from a glassy igneous materials like volcanic ash. The other important species of dioctahedral smectite are beidellite, nontronite and volkonskoite. General formula for trioctahedral smectites is $(M^+_x*nH_2O)(R^3_{3-y}R^{3+}_y)(Si^{4+}_{4-x-y} Al^{3+}_{x+y})O_{10}(OH)_2$. In trioctahedral smectites substitutions of the trivalent cations for divalent cations create an excess

of positive layer charge. The members of trioctahedral smectites are hectorite, saponite and sauconite. Smectites have expandable clay layer structures. Its characteristics are its fractional layer charge value and the property of swelling due to presence of hydrated exchangeable cations in the interlayer. Smectites are widespread in nature. As the main component of bentonites, they have a large number of technical and geotechnical applications.

Bentonite

Bentonite is the ore predominantly containing smectite and other non clay mineral. The bentonite was named after Ford Benton, Wyoming. It contains 80% montmorillonite. The color of the bentonite varies from white to yellow to olive green to brown to blue. In the field of civil engineering, bentonites are commonly used in the construction of landfills, for the encapsulation of contaminated soils, as drilling fluids and slurry shields for tunneling processes. Commercial applications cover a wide range of applications from cat litter, odor adsorbents, paint, paper industry and foundry industry, waste-water treatment to bleaching agents in the food industry, as an additive in detergents and in many more applications.

Bentonite is formed by alteration of volcanic ash deposited in different fresh water and marine basins. The deposits are as old as Jurassic era to as recent as the Pleistocene epoch. Most of these are from the cretaceous period (85-125 million years ago). Bentonite has a number of deposits in all over the world. Deposits of bentonite in USA are found in Wyoming, Montana and South Dakota. It can also be found in Texas, Nevada, Arizona, Mississippi and Alabama. A white variety of bentonite is found in Cheto, Arizona is mainly a calcium montmorillonite. The deposits of bentonite are found in Argentina, Morocco and Algeria of Africa. The bentonite deposits in Europe are found also in England, Germany, Greece and Italy. In Asia the major deposits are in China, India and Japan.[1]

Table 2.1. Deposits of Bentonite in Different Countries (Utracki, 2004[2]).

Country	Bentonite Deposits
Canada	British Columbia, Alberta, Saskatchewan, Manitoba
USA	Wyoming, Georgia, Florida, Mississippi, South Dakota, Montana, Utah, Nevada, California.
Algeria	
Tasmania	
Australia	Mildura, Scone
Argentina	San Juan
Brazil	Campina Grande
China	Guangxi, Hangzhou Linan
Egypt	Hamza
Ethiopia	Gewane, Mille, Ounda Hadar
Germany	Landshut
Greece	Milos
India	Gujrat, Rajasthan, Jharkhand, Tamil Nadu, Jammu and Kashmir[3]
Indonesia	Java
Japan	Annaka, Kuroishi
Turkey	Eskisehir, Biga Peninsula
Vietnam	Tam Bo
Poland	Holicross Mountains, Upper Silesia Coal Besin, Studetes
Pakistan	Perswar

Total resources of bentonite in India are about 531 million tonnes. 25 millions tonnes of these are found as reserves. 80% of total resources are found in Rajasthan and 18% of these are found in Gujarat. Remaining is found in Tamil

Nadu, Jharkhand and in Jammu and Kashmir. Bhabnagar and Kachch districts of Gujarat and Barmer district of Rajasthan are the major producers of bentonite.[3]

Montmorillonite is the most widely known and applied mineral from the smectite group. The name 'montmorillonite' is given to the clay found in Montmorillon near France. Montmorillonite was identified by Knight in the year 1896. It is the major component in bentonites and used for various advanced applications due to some typical properties like its fine particle size, large specific surface area, high cation exchange capacity, excellent swelling capacity and consequential adsorption and absorption capacities. The composition of montmorillonite widely varies depending not only on geographical location but also with the deposit strata. With composition montmorillonite colour also varies mainly due to the presence of Fe^{3+}. The specific surface area of montmorillonite is about 750-800 m^2/gm. It has a monoclinic crystal system and density 2.3-3 g/ml. It has Moh's hardness at 20ºC about 1.5-2.0. It gives a soapy feel when touched. Montmorillonite is commercially available in the form of powder where each particle of around 8 μm diameter contains about 3000 platelets. Montmorillonite swells in water and expands its volune upto 30 fold.[2]

Structure of Montmorillonite (Mt)

Mt is the end member of dioctahedral smectites. The unit layer includes an octahedral sheet of alumina or magnesia sandwiched between two tetrahedral silica sheets where the adjacent sheets are bonded together through the sharing of oxygen atoms between silica and aluminum atoms. The Mt clay particles carry a negative charge arising from isomorphous replacement of Al^{3+} by Mg^{2+} in the octahedral sheet or of Si^{4+} by Al^{3+} in the tetrahedral sheet. At the edges where the clay layers are disrupted, polar sites exist due to broken bonds. These sites carry a pH-dependent variable charge caused by the protonation and deprotonation of surface hydroxyl groups. The negative layer charge is neutralized, attracting alkali or alkaline earth cations (Na^+, Li^+, Ca^{2+}) to the mineral surface. The number of the exchangeable cations that a mineral can adsorb is determined by its cation exchange capacity (CEC). Mt is one of the most extensively studied layered

silicates due to their vast natural abundance and structural variety. Also they are the most commonly employed clay mineral in polymer composits. For good compatibility between polymer and hydrophilic Mt clay surface modification of the pristine clay is necessary.
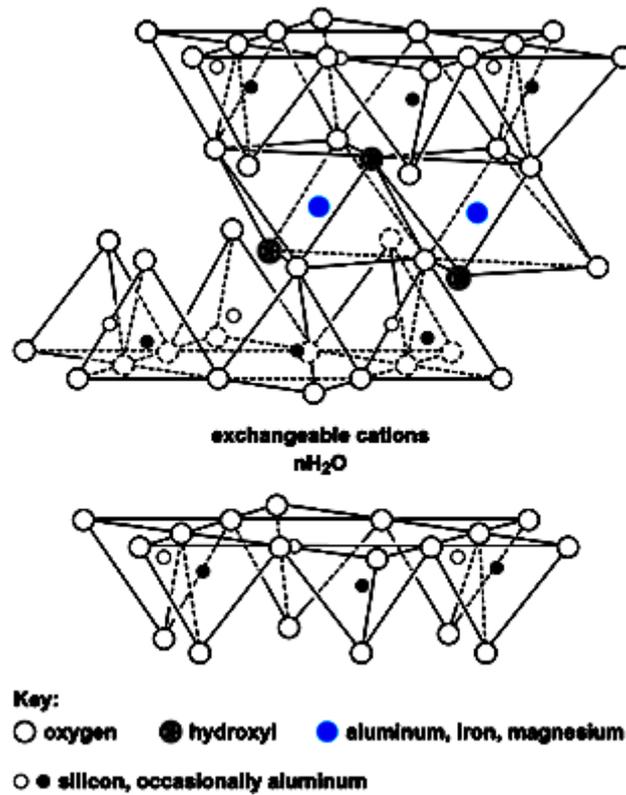

exchangeable cations
nH_2O

Key:
○ oxygen ● hydroxyl ● aluminum, iron, magnesium

○ ● silicon, occasionally aluminum

Figure.2.3. Structure of Montmorillonite
(Reproduced from *R. E. Grim*, *Clay Mineralogy*, *McGraw-Hill*, *1953*)

2.2. Intercalation

Intercalation literally means incorporation of a foreign atom in the interstitial space of some crystal lattice. Intercalation reactions occur by the topotactic insertion of the mobile guest species like neutral molecules, anhydrous or solvated ions into the accessible crystallographically defined vacant sites located between the interlayer spacing in the layered silicate structures. Also weak interactions occur between the host clay layers with the guest species and the co intercalated solvents.[4] Alternatively intercalation can be described as the penetration of the organic molecules in the interlayer space of clay minerals. Expanding layered silicates predominantly smectites can take up a wide range and variety of organic compounds between their layers to form interlayer-clay organic complexes and form intercalated clays, commonly known as organoclays. Thus intercalated clays may result from exchanging the interlayer inorganic cations with organic cations or by replacing the interlayer water by neutral polar organic molecules.[5] Intercalation chemistry of layered clay minerals such as smectites has extensively been studied due to their swelling behavior, ion exchange property, adsorptive property and large surface area.[6]

2.2.1. Objective of Intercalation

The objective of intercalation is to organophilize the hydrophobic clay surface to make it compatible with organic phases for advanced applications. For that purpose the first aim of intercalation is to expand the interlayer spacing and hence to reduce the solid-solid interaction between the clay platelets. The final aim is to improve the interaction between the clay and matrix. Clay minerals have layered structure and due to their unique layer structures, ion exchange capacity and variability in chemical composition and in electrical charge of particles, etc. they present special interactions with organicmolecules.

Various interactions are involved in the clay organic reactions. They are presented the table 2.2.[7]

Table 2.2. Different Clay-Organic Interactions

Nature of Interactions	Characteristics
Electrostatic	Ion exchange of interlayer metal cations with organic cations
Van der Waals Forces Hydrogen bonding and water bridges Ion dipole and coordination Proton Transfer Electron Transfer	Adsorption of neutral molecules by interactions with external or internal (intracrystalline region of silicates) surfaces
Covalent bonding	Grafting reactions of organic groups

2.2.2. Common Techniques for Organic Modification of Layered Silicates via Intercalation

2.2.2.1. Solid-State Reactions

Without the use of solvents organic molecules can be intercalated in dried clay minerals by solid-state reactions. The absence of solvents in the technique reduces the related health hazards and thus makes the intercalation process eco friendly. Solid–solid reactions are one of the most suitable techniques for intercalation processing because of the facile operation and the possibility to prepare compounds, which are not accessible from solutions, as reported in the earlier works.[8-11] Ogawa et al.[12] reported the intercalation of Mt with organic molecules by solid-state reactions. Since then several studies were done on intercalation of cationic and nonionic species into layered silicates.[13-23]

Use of dry method was reported by Breakwell et al.[24] involving clay and the quaternary ammonium salts. They found that the dry process gave partially exchanged organoclay.

Yoshimoto et al.[23] reported the intercalation of aniline salts with different counter ions in Mt. Several scientists reported the solid state reactions based on the ion-dipole interaction [23, 25, 26] Merinska et al.[25] intercalated Mt by octadecylamine through ion-dipole interaction. Beall and Goss[26] intercalated Mt by three different families of organic compound. Those are alcohols, aldehydes and *n*-alkyl pyrrolidones. They concluded that the ion dipole interaction between the small polar molecules and the exchangeable cations to be controlled by the polar head group as well as the chain length of the alkyl group. The studies are being continued. Khaorapapong et al. made several studies on the intercalation of organic material in different metal exchanged Mt.[27-32]

Khaorapapong et al.[27] investigated intercalation of 4,4'-bipyridine into the interlayer spaces of cobalt(II), nickel(II) and copper(II)-Mt by solid-solid reactions. The successful intercalation of 4,4'-bipyridine and the complex formation in the interlayer spaces of Mt was confirmed by powder XRD , IR and the thermal analysis of the products. In another paper[28] they reported intercalation of 4,4'-bipyridine (4BPY) and 1,2-di(4-pyridine)ethylene (DPE) into the interlayer spaces of cobalt(II)-, nickel(II)- and copper(II)-Mt by solid-solid reactions. The successful intercalation of these compounds with the interlayer exchangeable cations was confirmed by powder X-ray diffraction, infrared spectroscopy, elemental (CHN) analysis and thermal analysis of the products. They concluded that solid-state intercalation of bidentate bridging ligands and in situ complex formation in the interlayer spaces of Mt is a more feasible way than conventional ion exchange reactions. In the paper[29] they investigated the formation of three fluorescent complexes, Li(I)-, Zn(II)- and Mn(II)-8-hydroxyquinoline complexes in the interlayer spaces of Mt by solid-solid reactions between homoionic Li(I), Zn(II) and Mn(II)) Mt and neat 8-hydroxyquinoline at room temperature. The intercalation of 8-hydroxyquinoline molecules into the interlayer spaces of Li(I)-, Zn(II)- and Mn(II)-montinorillonites was confirmed by powder XRD, FTIR, TG-DTA and chemical analysis. The in-situ complex formation was confirmed by FTIR, UV-Vis and photoluminescence spectroscopies. They found that different microstructures including molecular packing of the complexes in the interlayer

spaces of Mt resulted due to host-guest interactions. Khaorapapong et al.[31] studied intercalation of thiourea into the interlayer space of Cu(II)-Mt by solid-solid reaction at room temperature. The successful intercalation was proved by powder X-ray diffraction data and spectroscopic results. The basal spacing of the intercalation compound was larger than that of the starting host material. Elemental (CHN), thermogravimetry analysis, Raman and Infrared spectroscopy of the intercalation compound supported the insertion of the copper (I) thiourea complex in the interlayer space of Mt.

2.2.2.2. Cation Exchange

The intercalation of organic surfactants/intercalants is mostly achieved by cation exchange reaction. The intercalation depends on the nature of the intercalant, the nature of the clay mineral and also on the amount of intercalant added. Cation exchange which is one of the most important methods for the preparation of intercalated clays consists of exchange interlayer cations of the layered silicate clays by alkyl onium ions in aqueous solution. Giesking[33] and Hendricks[34] showed that the exchangeable inorganic cations in the clay interlayer can be replaced by organic cations by ion exchange in aqueous solution. This method was followed by a group of researchers since then. A large variety of intercalants as well as different experimental conditions in this technique have been used so far. Variation of host materials including Mt has been reported. Besides this with advancement of characterization technique useful information is gained which led to extensive research on intercalated clay for advanced practical applications. The bonding mechanism between the organic cation and the charged clay layers is electrostatic. Other noncoulombic forces may also contribute to the adsorption. Thus van der Waals attractions between the organic species and the silicate surface, as well as between adjacent organic species also contribute to the adsorption forces.

2.2.3. Intercalated Clay Minerals/ Organoclays

2.2.3.1. Earlier Studies

Van Olphan in the year 1966 in Science referred that the ancient Maya blue was an organic–inorganic clay-dye hybrid. It is said that it is an indigo-polygorskite complex. In the 1920s the research of intercalation of organic molecules into the interlayer space of clay minerals started after the advent of X-ray Diffraction.[35] Montland in the year 1911 studied the catalytic transformation of organic compounds activated by clays where he studied pynene to camphor over palygorskite.[7] One of the earliest paper in this area was study on interactions of nicotine with clay minerals in the year 1934 investigated by smith.[36] Giesking studied the cation exchange of methylene blue in Mt, beidelite and nontronite of clay minerals in the year of 1939.[33] The expansion of basal spacing was observed when the organic ions were adsorbed by the clay minerals. Hendricks in 1941[34] studied base exchange of Mt with alkaloids, purines and pyrimidines. In the year 1944 MacEwan[37] reported intercalation of glycerol, a neutral molecule into the Mt clay interlayer for identification of Mt. Intercalation of Mt with glycerol gave an expanded basal spacing at 1.77 nm. In the year 1945 Bradley[38] studied molecular associations of organic liquids like aliphatic di- and poly amines, glycols, polyglycols and polyglycol ethers in Mt. He concluded that amines were base exchanged but glycerol and glycol entered into the clay gallery without displacement of cations. In the year 1949 Jordan[39] first applied thermal analysis for characterization of clay organic complexes. He performed DTA of Mt and alkylammonium complexes. After then Jordan[40-42] published several important papers on the properties of organophilic clays from bentonites. Jordan[40] investigated the factors involved with the swelling of the organoclays and the extent of organophilization of hydrophobic clay. He prepared organophilic bentonites from various aliphatic ammonium salts. He studied swelling of the organoclays in several organic liquids and mixture of liquids. He mentioned three key factors controlling the degree of solvation. According to him these are (1) the extent of the surface coating of the clay particles by organic matter, (2) the degree of saturation of the clay mineral by organic cations and (3) the nature of the

organic liquids. In the paper[41] Jordan investigated the formation of gels of organoclays in several organic liquids and mixture of liquids and got an optimum gelation. In the year 1950 Hauser in his patent (US 2,531,427) described procedures for preparation of organoclays that swell and form gels in organic liquids.

2.2.3.2. Structure of Intercalated Clay

Some pioneering work in the intercalation of mica type clay minerals gave the idea on the structure of intercalated clays.[43] Weiss in the year 1961[44] reported the orientation of alkyl chains in the interlayer of mica type clay minerals depending on the basal plane spacing measurement. He prepared different derivatives of mica type layer silicates such as muscovite, biotite, illite, vermiculite, beidellite, Mt by alkylammonium ions and prepared different organic molecules as swelling liquids. The prepared organic complexes were characterized by X-ray Diffraction. He concluded that alkyl chains might lie flat or take a tilted up right position to the alumino silicate surface depending on the charge density of the surface and the length of the chains. Lagaly et al.[45-50] suggested that the alkyl chains of the organic cations lie flat on the alumino silicate surface forming monolayer, bilayer or pseudotri molecular arrangement via kink formation or radiate away from the surface forming paraffin type arrangement. These arrangement depends both on the charge density of the layered silicate clay and the chain length of the alkylammonium cations. The arrangement also influenced by the degree of exchange and the geometry of the clay surface. Lagaly et al.[46] studied the formation of monolayer, bilayers and pseudotri molecular layers in the gallery of Mt where the basal spacing of the alkylammonium intercalated Mt with above arrangements changed in a characteristic way. A flat monolayer structure results with a basal spacing value ~1.4 nm and a flat bilayer structure results with a basal spacing value ~1.8 nm.[51] The monolayer rearranges into the bilayer when the area of the flat-lying alkylammonium ions becomes larger than the equivalent area. From the monolayer to bilayer transition the layer charge distribution of the clay and mean layer charge is determined.[52] In some cases alkylammonium cations form paraffinic layer rather than pseudotri molecular layer for better fit of

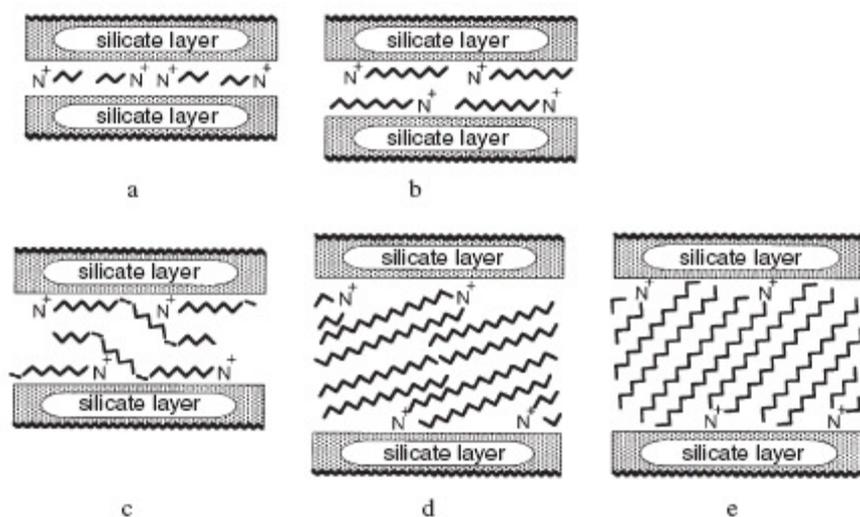alkylammonium cations to the surface oxygen atoms than the closely packed pseudotri molecular arrangement.[48]

Figure.2.4. a) Monolayer b) Bilayer c) Pseudotri molecular layer d) & e) Paraffinic arrangements of alkylammonium cations in smectite interlayer

(Reproduced from *F. Bergaya et al., Hand Book of Clay Science, Elsevier, 2006*)

Vaia et al.[53] investigated the structure of dioctadecyl dimethylammonium films on Mt with different mean charge densities by XRD, IR and differential scanning calorimetry (DSC) and depicted a picture of intercalated clay interlayer structure. By monitoring the shift in the position of methylene stretching and scissoring band of the intercalant alkyl chain they concluded that the intercalant in the clay interlayer remained in ordered or disordered state i.e. molecular arrangement varied from solid like to liquid like. According to them this ordered or disordered state depends on the surfactant packing density, alkyl chain length and on the temperature.

Hackett et al.[54] studied the orientation of alkylammonium cations in the clay interlayer by molecular dynamic simulation. They used two types of clay- Mt and flurohectorite. The computer modeling provided the structure and dynamics of the

intercalated surfactants. They also determined the trans-gauche conformer ratio which supported the findings of FTIR investigation. According to Hackett a disordered liquid like structure results by the intercalated surfactants interwining the chains in the opposite layer instead of forming a single layer. The further conclusion is that when almost half of the CH_2 are in the opposite of the ammonium, bilayer is formed. When trilayer is formed few is noticed at the opposite of the chain end.
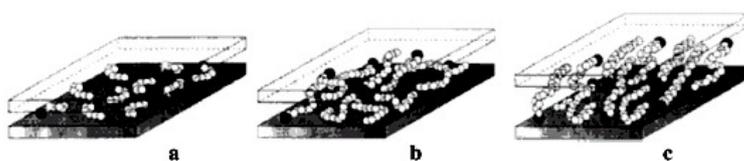

Figure 2.5. Alkyl chain aggregation model as shown by Vaia representing a) short alkyl chain b) medium alkyl chain c) long alkyl chain
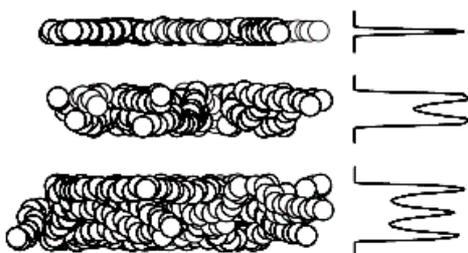
(Reproduced from Ref .32)

Figure 2.6. Intercalant configurations and corresponding density profiles of organoclays – monolayer, bilayer and trilayer.

(Reproduced from Ref. 52)

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2.2.4. Different Conditions of Intercalation

Xi et al.[55] presented a complete study of the intercalation of Mt with octadecyltrimethylammoniumbromide changing the ratio of amine and clay between 0.2 and 4 times the CEC of the clay. They found a progress in amount of intercalated surfactant in their study as well as increased basal spacings value corresponding to three interlayer arrangements with varying amine and clay ratio.

Perez–Santano et al.[56] reported the intercalation of Mt with octylamine under several conditions. They used water and water / ethanol mixture as reaction medium. They varied the ratio of amine and clay. They also varied the ratio of HCl and amine. They found that intercalation was successful when amine and clay ratio was in the range of 1-3 mmol/ g and the optimal result was obtained when amine and clay ratio was 2 mmol/ g. They further found that for a given amine and clay ratio the HCl and amine ratio influenced the intercalation.

Vazquiz et al.[57] synthesized four organoclays using Cloisite Na$^+$ with aliphatic and aromatic ammonium bromide or chloride salts. They studied the thermal stability of the prepared organoclays. They found that the suitable eluent or washing liquid influenced the first degradation peak of the prepared organoclays. They further observed that among all the surfactants hexadecyl trimethylammonium was more sensitive to water and ethanol/water as eluents. They found that sonication and use of polar activator led more exchanged surfactant cation in the clay. They determined CEC of the prepared organoclay by ammonium acetate method and concluded that determination of loaded surfactant by this method excluded the unfixed surfactant.

2.2.5. Different Intercalants

2.2.5.1. Ammonium

Favre and Lagaly[58] reported the modification of bentonites by quaternary alkylammonium cations. They used three bentonites from Bavaria, Wyoming and Brazil which were separated at various fractions. They determined the layer charge of the bentonites by alkylammonium ion exchange method which varied with particle size of the clay fractions. They found that the excess adsorbed intercalant over CEC was bound at the edges. Both the total and the interlayer amount were found to decrease with increase in particle size of the clay fractions. Small alkylammonium cation affected the adsorption of long chain alkylammonium cations. They found that the smaller particles with lower charge density preferentially were attached to the longer chain intercalant whereas larger particles with higher charge density were bound to the small intercalants.

Yang et al.[59] prepared organo-soluble polyimide and Mt hybrids with various chemical surface modification methods. They prepared the hybrids using a monomer solution intercalation polymerization method. They modified Mt using three types of intercalation agents. These are amino acids, primary aliphatic amines and quaternary ammonium salt. They found that the dispersion of Mt in organic solvents depends on the type of the functional group and the bulky group of the intercalation agent. The properties of the hybrids were found to depend on the dispersion behavior of Mt particles. According to them a well dispersed hybrid can exhibit improved mechanical properties and thermal stability, decreased thermal expansion coefficient, retaining of the solubility of the polyimide matrix and high optical transparency.

Moraru[60] investigated the mechanism for the gel formation of the alkylammonium derivatives of Mt in organic liquids of different polarity. He evaluated the influence of modification, type of the organic cations, length of the alkyl chain, type of organic liquid and polar additive as well as traces of water on

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the swelling volume, enthalpy of immersion, zeta potential and the Bingham yield stress of the organo-gels. He concluded about the correlation between the swelling volume, the ability for gel formation and the basal spacing of the intercalated clay.

Tamura and Nakazawa[61] synthesized organoclays from synthetic Li-fluorotaeniolite (Li-FTN) and Li-fluorohectorite (Li-FHT) by using trimethylammonium ions (TMA(+)) with formula $CH_3(CH_2)N^+(CH_3)_3$, with n = 4, 8, 12, 16, 18 and 22. They obtained different basal spacings of the organoclays depending upon the the exchange ratio of TMA(+)/Li+ and the carbon number of TMA(+). They concluded about the structure of the organoclays and the mechanism of intercalation. They found that at the final stage of the intercalation the long chain of the intercalants became inclined to the silicate sheets at an angle of approximately 30º. But during the intermediate stage of the reaction, units of this structure and those of hydrated mica formed randomly and regularly interstratified structures.

Kwolek et al.[62] investigated the adsorption of homologous alkyldimethylbenzylammonium bromides, $[C_6H_5CH_2N(CH_3)_2R]Br$ on sodium Mt from aqueous NaCl solutions at room temperature. R stands for the methyl-, butyl-, hexyl-, octyl-, decyl-, and dodecyl-group. Their study showed for short chain homologue the adsorption onto Na^+–Mt decreased linearly from methyl to hexyl. This is due to growing steric hindrance at the surface of the clay. For higher homologue the adsorption increased linearly from short to longer chain length. The adsorption for the higher homologue exceeded the CEC value which indicates the commencement of formation of a bilayer or admicelle. According to them for short chain homologues the ammonium cations lie flatly and interact strongly with alumino silicate surface. They concluded further that the long chain homologue formed an interdigitated system of coiled hydrocarbon chains.

Lee and Lee[63] modified a Mt rich fraction of a bentonite clay by alkylammonium cations. The modified clay as well as the composite with epoxy was investigated by them. To calculate the exchanged content of intercalant they

performed thermogravimetric analysis and expansion of basal spacing in organoclay was monitored by XRD. They observed that organoclay was delaminated in epoxy matrix forming nanocomposites. Loading of organoclay increased tensile strength and Young's modulus.

Lerari et al.[64] prepared nanocomposites of poly(methyl methacrylate) (PMMA) filled with 3 wt% of modified natural Algerian Mt type clay. They used either in situ polymerization of methyl methacrylate initiated by 2,2'-azobisisobutyronitrile or a melt-mixing process with preformed PMMA via twin-screw extrusion. The organo-modification of the Mt was achieved by ion exchange of Na^+ with octadecyl dimethyl hydroxyethylammonium bromide. XRD of the organoclay showed remarkable shift of the interlayer spacing after modification. They evaluated the degree of dispersion of the clay in the polymer matrix and the resulting morphology of nanocomposites using XRD and transmission electron microscopy (TEM). The PMMA nanocomposites were investigated using thermogravimetric analysis and differential scanning calorimetry. According to them the glass transition temperature of the nanocomposites is not influenced by the modified clay while the thermal stability improves compared to unfilled PMMA.

Akcay[65] modified Mt through ion-exchange reaction by tetrabutylammonium bromide (TBAB). The modified clay was studied by XRD technique, FTIR and thermogravimetric analysis (TGA) methods. The basal spacing increased after intercalation. The IR spectra of modified Mt showed C-H vibrations. The also studied the adsorption of p-chlorophenol on intercalated Mt as a function of the solution concentration and temperature. They observed that that the adsorption rate followed the pseudo-second order kinetics. They determined the adsorption energy and the adsorption capacity for the phenolic compounds using Dubinin-Radushkevich equation. The adsoption isotherms of p-chlorophenol on intercalated Mt were modeled according to Freundlich and Dubinin-Radushkevich adsorption isotherms.

Bergaya in a review[66] concluded that several aspects of clay minerals should be considered in the preparation and optimization of clay containing polymer nanocomposites. She concluded that structural detail of clay minerals should be specified because small changes in clay minerals could influence the nanocomposites preparation. According to her for the formation of polymer nanocomposites the most important step is the hydrophilic-lipophilic balance (HLB) to the polymer matrix. Also the HLB depends on the chemical nature of the surfactants and on the surfactant/CEC ratio.

Cui et al.[67] investigated the thermal stability and degradation of various intercalants and their corresponding intercalated clays. Their study tried to explore the key factors which control the thermal stability of the organoclays. They used nuclear magnetic resonance (NMR) spectroscopy to analyze the decomposition products. They used thermogravimetric analysis as the primary characterization technique to determine the thermal stability of the organoclays. Accorrding to them washing the organoclay with methanol is an effective way to remove the excess surfactant from the clay galleries. They further concluded that the organoclays decomposed via either S_N2 nucleophilic substitution or Hoffmann elimination pathways.

Galimberti et al.[68] investigated the thermal stability of alkyl and arylalkyl quaternary ammonium cation using TGA and mass spectrometry pyrolysis/GC-MS in starting chloride salt, in organoclay obtained after exchange with Mt and after mixing of the organoclay with isoprene rubber. They identified the degradation temperature for organoclays and the main volatile compounds which were tertiary amines, chloroalkanes and alkenes. They also proposed the mechanism for their formation.

Klapyta et al.[69] studied the adsorption of *n*-alkyltrimethylammonium ions with alkyl chain lengths of C12 and C18 on a natural smectite and on synthetic fluorotetrasilicic mica (TSM) and fluorotaeniolite (TN). They found for smectite when a concentration of surfactant used less or equal to the CEC of the clay, the

maximum amount adsorbed was close to its CEC. But in case of TSM and TN fluoromicas only part of inorganic ions in the interlayer spaces were replaced by the organic ions even with excess surfactant addition. According to them the alkylammonium-exchanged micas represent polyphase systems consisting of regularly and randomly interstratified layers differing in the amount of alkylammonium cations adsorbed.

Yilmaz and Yapar[70] investigated adsorption properties of organo-bentonites by adsorption of phenol. They prepared intercalated clays using tetradecyl trimethylammonium bromide and hexadecyl trimethylammonium bromide and exchanged the clays with the intercalants at different concentration with respect to the CEC of the clay. XRD study revealed bilayer structure with 100% exchanged bentonite and random interstratification of monolayer and bilayer for the organoclay exchanged with lower loading of intercalants. They achieved significant adsorption efficiency with 100 % loading of intercalant.

Klapyta et al.[71] prepared a series of organoclay from synthetic Na-fluorotetrasilicic mica by ion exchange with dodecyl-, tetradecyl-, hexadecyl- and octadecyltrimethylammonium (C12, C14, C16 and C18) bromides. After concentration variation of alkylammonium ions from 0.43 to 3.4 mmol/g, the maximum amount adsorbed on the mica was found by them as 0.92 mmol/g. XRD revealed that alkylammonium ions were distributed inhomogeneously within the mica interlayers. According to them organo-micas contain several phases consisting of randomly and regularly interstratified layers differing in terms of the amount of alkylammonium ions adsorbed. They found that these different layers swelled in ethylene glycol in the same manner and formed new interlayers with identical spacings. From XRD they concluded about the orientation of alkylammonium ions after glycolation.

Kozak and Domka[72] modified sodium Mt by a number of alkyloxymethyl dodecyldimethylammonium chlorides with the general formula $[C_{12}H_{25}N^+(CH_3)_2CH_2OR]Cl^-$. FTIR characterization of the modified clays revealed

structural differences between the modified and unmodified Mt samples. SEM revealed a tendency of agglomeration of the organophilized particles of Mt.

Lakshmi et al.[73] prepared epoxy–clay nanocomposites using hexadecylammonium clay and hexadecylphosphonium clay. The XRD characterization of the nanocomposites confirmed nanodispersion of organoclay in epoxy matrix. The ammonium salt intercalated clays showed appreciable mechanical and glass-transition temperature properties and the phosphonium salt intercalated clays showed high thermal resistance properties.

Lee et al.[74] investigated surfactant adsorption by two different Mt by examining the time dependence of surfactant behavior on clay surfaces. Surfactants with different micelle concentration were chosen for intercalation. They found that more active intrusion of surfactant molecules into the interlayers were found for Na-Mt over Ca-Mt. Initially the basal spacing of Na-Mt increased much rapidly but later stage the abrupt basal spacing increase occurred for Ca-Mt. According to them the difference in adsorption behaviour is due to the difference in the nature of exchangeable cations. Also the micelle concentration of the surfactants affected the development of organo-Mt, the intercalant formation and stabilization under nonequilibrium.

Li and Ishida[75] studied the intercalation of hexadecylamine into bentonite and the structure of hexadecylamine in nanoscale confined space by differential scanning calorimetry and X-ray diffraction. Intercalated amine showed multiple melting temperatures higher than the bulk amine. This gave strong evidence of ordered structures of amine molecules within silicate layers. Packing density of amine influenced the interlayer structures of amine and the stacking regularity of the silicate layers.

In another paper[76] Li and Ishida investigated conformation and melting of both hexadecylammonium ion and neutral hexadecylamine within the clay silicate gallery by FTIR. According to them the conformational ordering of the alkyl tail in

the confined system is strongly dependent on amine concentration and orientation. They concluded that amine chains with orientation parallel to the silicate surface were in various disordered state but those with orientation radiating from the clay surface took mostly ordered conformation. Ammonium ion showed similar trend of ordering dependence on the concentration as neutral amine.

Majdan et al.[77] investigated the sorption of U(VI) on octadecyltrimethyl-bentonite. They varied the pH values of the aqueous phase and also the concentration of U(VI). They also varied the concentrations of alkylammonium cation in bentonite from 21% to 150% of CEC. They observed that the sorption of U(VI) on modified bentonite decreased with the percent of mineral modification upto a certain surfactant concentration and then increased again. The effective sorption of U(VI) in the pH range 6-10 for the modified bentonite was explained by them as the consequence of U(VI) anionic hydroxy complexes sorption. FTIR and XRD study of intercalated clays showed the existence of monolayer and bilayer arrangement of the surfactant cations in the clay interlayer. The luminescence spectra of bentonite suspensions revealed the existence of hydroxide-like planar polymeric U(VI) species in the bentonite phase at a particular pH.

Massinga et al.[78] prepared organo-bentonites containing quaternary ammonium surfactants with purified bentonite from the Boane deposit in Mozambique. Thermogravimetric analysis revealed organic contents over CEC by up to 21 mass %. From XRD the arrangement of intercalants was found as paraffin-type extended chain with tilt angles of 27º to 33º. XRD further showed interdigitated monolayer intercalation of C14 single alkyl chain surfactant, bilayer intercalation of the C16 double alkyl chains and its 1:1 mixture with single chain intercalant. FTIR analysis revealed disordered alkyl chain conformations. White oil dispersion of organobentonite showed shear thinning behavior indicating exfoliating ability of Mt particles.

Merinska et al.[79] modified Na-Mt samples by co-intercalation of octadecylamine (ODA) and stearic acid (STA). Co intercalation was carried out by

ion-dipole reaction mechanism. They prepared intercalated clay-PP nanocomposites by one screw kneader using maleic-anhydride-modified PP (PPMa) as a compatibilizer. The extent of Mt exfoliation in nanaocomposite was measured by SEM. An improvement in mechanical properties of the nanocomposites resulted only for lower value of ODA/STA concentrations.

Zeng et al.[80] prepared oganoclay by modifying bentonite with cetyltrimethylammonium bromide. Then they investigated the sorption of two nonionic pesticides, methyl-parathion and carbaryl by this organoclay. The distribution coefficient of partitioned pesticides in the surfactant increased with low surfactant loading and decreased with high surfactant loading. They found an optimum surfactant uptake by the clay when surfactant concentration in water was greater than the critical micelle concentration.

Mittal[81] modified two Mt of different CEC with various alkylammonium cations. Then he compounded these with polypropylene and investigated the effect of filler matrix behaviour on the mechanical properties of the composites. He observed that with increasing chain packing density the d spacing increased. Also the d spacing was higher for the higher CEC clay. Use of large intercalant molecules led to effective preparation of polymer composite without any compatibilizer. He observed an improvement only in tensile modulus.

Patel et al.[82] chemically treated Indian bentonite to remove iron and to improve whiteness of the clay. They observed that dithionate method to remove iron was beneficial without destructing clay layer structure. They prepared intercalated clay from this chemically treated bentonite under varying reaction parameters and optimized these reaction parameters to prepare intercalated clays with controlled particle size and whiteness.

Richards and Bouazza[83] assessed the adsoption of phenol by organoclays from the bentonite. They modified bentonite by hexadecyltrimethylammonium (HDTMA) and phenyltrimethylammonium (TMPA) cations. They observed

significant increase in organic compound adsorption capacity for smectite clay minerals by this organic modification.

Slade and Gates[84] investigated the effect of layer charge on the hexadecyltrimethylammonium (HDTMA) bromide modified organoclays from different layer silicates with different layer charge. Both aquous and ethanolic solution of HDTMA bromide were used for clay modification. Layer sapcing varied with the layer charge of the clay. Toluene sorption isotherms showed that toluene uptake from water by an intercalant increased in case of a highly charged smectite. They found salt molecules coadsorbed with HDTMA cations when intercalation reaction took place in aqueous solution. Coadsorption of salt molecules did not occur in ethanol medium. Layer spacings of organoclays increased in the presence of neat toluene indicating that the sorption from solution was accompanied by interlayer expansion.

Tabak et al.[85] synthesized organo-bentonites by treating two Na^+-bentonites with cetylpyridinium chloride. They obtained higher basal spacing and higher organic loading from higher CEC bentonite. With organophilization the intensity of the HOH stretching and bending peaks of bentonites became sharper. They concluded that higher amount of m-cresol was retained by the low CEC bentonite as a result of influence of intercalant on the adsorption process.

Yuan et al.[86] studied the effects of thermal stability of surfactants with amino and imido groups on thermal properties of poly(ethylene terephthalate) (PET)/clay composites. They synthesized imidosilane surfactant from the imide reaction between amino silane and phthalic anhydride. They concluded that the decomposition of amino functional groups in amino surfactants decreased the thermal stability of organoclay and thus accelerated the degradation behavior of PET composites. They found enhanced thermal stability in case of PET/imido-palygorskite composites due to more thermally stable imidosilane surfactants.

Tiwari et al.[87] modified Na$^+$-Mt using three different organic cations and characterized. They found a good agreement in basal spacing increment with simple theoretical calculations based on van der Waals volume of the cationic ammonium ions. TG study also revealed a good agreement between the amount of organic modifier with that of the theoretically calculated stoichiometric content of modified clays at complete exchange.

Yui et al.[88] studied the intercalation of polyfluorinated surfactants and few other cationic surfactants on to saponite. They found that all surfactants were intercalated over the CEC of the clay. On surfactant intercalation the interlayer space of saponite increased and reached a constant value at intercalation over CEC. They observed that in all the polyfluorinated surfactants intercalated saponite bilayer was formed and the surfactants formed a tilt angle of 35º with respect to the clay surface.

Zhou et al.[89] prepared hexadecyltrimethylammonium bromide modified Mt by pillaring different amounts of the surfactant into sodium Mt in an aqueous solution. They reported in their study the optimum conditions and batch kinetics of sorption of p-nitrophenol from aqueous solutions. According to them the solution pH has a very important effect on the sorption of p-nitrophenol. XRD investigation revealed that p-nitrophenol affected the arrangement of surfactant pillared into the clay. This arrangement was also affected by change in the surfactant concentration. They found that with the increase in the surfactant concentration the sorption of p-nitrophenol increased.

Zhu et al.[90] proposed a model about the orientation of surfactant in the interlayer of organic pillared Mt prepared at different concentrations of hexadecyltrimethylammonium cation. A series of arrangement models they proposed. The arrangements and the packing density of surfactants in the interlayer changed with the concentration of hexadecyltrimethylammonium cation.

Zhu et al. in another paper [91] investigated the influence of the charge characteristics and loading amount of the surfactant on the microstructure of organo-Mt modified with cetyltrimethylammonium cations. The hybrids were characterized by XRD and FTIR. They found that basal spacing of the organoclay, packing density and ordering of the surfactant in the clay interlayer increased with surfactant loading and clay layer charge density. They proposed the structural model of the organoclay considering the heterogeneous distribution of the intercalated surfactant in the adjacent layers and in the same clay layer. According to them the structures of organoclay can be controlled by simultaneous control in organic loading and clay layer charge density.

Zidelkheir and Abdelgoad[92] modified sodium Mt with octadecylammonium cations in various concentrations and characterized by thermogravimetric analysis and XRD. They described different mass loss steps of the organoclays and investigated the conformation of the surfactants by XRD.

2.2.5.2. Pyridinium & Quinolinium

Akyuz et al.[93] studied adsorption of 2-aminopyridine on natural and ion-exchanged bentonites (Mn-, Fe-, Co- or Ni-bentonite) by IR and Raman Spectroscopy. Increase in interlayer spacing confirmed the intercalation of 2-aminopyridine within natural and ion-exchanged bentonites. Characterization through the vibrational spectroscopy revealed that intercalated 2-aminopyridine molecules were coordinated to Lewis acid sites or exchangeable cations through water bridges. According to them ring nitrogen is involved in coordination and amino group hydrogens are involved in hydrogen bonding interaction with water molecules.

Akyuz et al.[94] studied the adsorption of 3-aminopyridine on sepiolite and Mt using FTIR spectrometry. The adsorption was investigated in the temperature range from 20 to 125 ºC by infrared spectrometry using a variable temperature unit. The spectroscopic results indicated that the adsorbed 3-aminopyridine molecules on sepiolite were coordinated to Lewis acidic sites and/or surface hydroxyls by H-

bonding interaction through pyridine ring nitrogen lone pairs. The intercalation of 3-aminopyridine within Mt increased the interlayer spacing. According to them sorbed 3-aminopyridine molecules by Mt are mostly coordinated to exchangeable cations directly or indirectly through water bridges.

Akyuz and Akyuz[95] studied the adsorption of 2-amino pyrimidine on sepiolite and Mt using FTIR spectrometry. X-ray diffraction showed the expanded interlayer spacings in the modified Mt. They concluded that 2-amino pyrimidine interacted with Mt by direct or indirect coordination to the exchangeable cations. Adsorption on sepiolite was due to hydrogen bonding with surface Si-OH groups. According to them endocyclic nitrogen is mainly involved in coordination and amino group hydrogens may be involved in hydrogen bonding interaction with water molecules.

Pozsgay et al.[96] organophilized Wyoming Mt with N-cetylpyridinium chloride and investigated its gallery structure by Wide Angle X-ray Scattering (WAXS). Then they prepared polypropylene nanocomposites using this modified Mt and investigated their structure and tensile properties. Multiple peaks were observed in organoclay due to presence of several populations of layer distances. Water residing in organoclay separated the clay layers and generated new scattering peaks. According to them exfoliation occurs above a critical gallery distance.

Chigwada et al.[97] in their paper modified Mt with pyridine and quinoline-containing salts. TGA analysis showed that the quinolinium modified clay had higher thermal stability than the pyridinium modified clay. They prepared polystyrene nanocomposites by in situ bulk polymerisation and direct melt blending using both clays. They used XRD and TEM for confirmation of intercalation. Cone calorimetric results confirmed the lowering of flammability of the polymer.

Andrades et al.[98] modified Mt, illite, kaolinite, muscovite, sepiolite and atapulgite with hexadecylpyridinium cation and studied the prepared organoclays as sorbents of two fungicides of different hydrophobicity, penconazole and metalaxyl, using adsorption-desorption isotherms. The results revealed the potential value of clay minerals modified with HDPY for immobilising pesticides with different degrees of hydrophobicity. According to them organoclay prepared from Mt is useful in clay barriers for protection of soil and water pollution by hydrophobic pesticides.

2.2.5.3. Phosphonium

Avalos et al.[99] modified Na-Mt by tri-phenyl vinylbenzyl phosphonium chloride and tetraoctyl phosphonium bromide salts as intercalanting agents. They used FTIR and Thermogravimetric Analysis coupled with Mass-spectrometry (TG/DTG-MS) to characterize the modified Mt and the thermal decomposition products. XRD and TEM techniques were used to evaluate the increase of the basal spacing. They observed easier and effective intercalation with tetraoctyl phosphonium salt. According to them the phosphonium salt modified Mt is thermally more stable and easier to exfoliate during the compounding process.

Cai et al.[100] modified three Na^+-Mt by exchanging with decyl tributylphosphonium bromide, dodecyl tributylphosphonium bromide and hexadecyl tributylphosphonium bromide. They investigated the effect of phosphonium salts species and the relative molecular mass on the characteristics, morphology, thermal stability and long acting anti bacterial properties of resulting organoclays. According to them organoclay prepared with dodecyl tributylphosphonium salts has excellent thermal stability and long acting antibacterial activity.

Leite et al.[101] modified sodium bentonites with quaternary ammonium and phosphonium surfactants by ion exchange reaction in order to investigate the effect of the chemical identity of the surfactant. They also investigated the effect of clay purification procedure in the intercalation process, final structure and thermal

stability of organobentonites. They found that the bentonite purification treatment and chemical structure of the surfactant affected the thermal behavior of the organobentonites. Phosphonium modified Mt was thermally more stable than those modified with ammonium, particularly the purified bentonite, they concluded.

Tan et al.[102] prepared four kinds of modified Na^+-Mt using different content of hexadecyltriphenyl phosphonium cations and characterized. They also studied the zeta potentials and antibacterial activity of the organoclays. They obtained good thermal stability of the organoclays. They found that the basal spacing, zeta potential and antibacterial activity increased with the content of quaternary phosphonium cations.

2.2.5.4. Imidazolium

Awad et al.[103] prepared a series of alkyl-imidazolium molten salts and characterized by elemental analysis, thermogravimetry (TGA) and thermal desorption mass spectroscopy (TDMS). They investigated the effect of counter ion, alkyl chain length and structural isomerism on modified clay property. They characterized the organoclays by XRD, TDMS and thermogravimetry coupled with Fourier transform infrared spectroscopy (TGA-FTIR) and compared to the conventional quaternary alkylammonium Mt. According to them the counter ion has an effect on the thermal stability of the imidazolium salts. They further observed a correlation between the chain length of the alkyl group and the thermo-oxidative stability.

Cipriano et al.[104] studied the adsorption of 1,2-dimethyl-3-N-hexadecyl imidazolium tetrafluoroborate onto the mica surface. The surface tension of 1,2-dimethyl-3-N-hexadecyl imidazolium tetrafluoroborate (Im BF_4) as a function of concentration was measured. Their result showed that the surfactant was adsorbed on the mica surface and thus a hydrophobic surface was produced.

Cui et al.[105] prepared polyamide- and polycarbonate-based nanocomposites from thermally stable imidazolium organoclay.

Langat et al.[106] synthesized imidazolium salts from 2-methyl imidazole and ion exchanged it with clay minerals to prepare thermally stable nanocomposites. Their study focused on the role of the chemistry of imidazolium salts used in functionalizing clay and and also on the processing conditions in the formulation of epoxy nanocomposites. They evaluated the nano dispersion of clay in epoxy matrix by XRD, TEM and Laser Scanning Confocal Microscopy (LCSM). The morphological characterization showed that the hand mixed nanocomposite had tactoid morphology. They found that ultrasonicated organoclay (without hydroxyl group) epoxy nanocomposite exhibited a mixed morphology and an ultrasonicated organoclay (with hydroxyl group) epoxy nanocomposite exhibited well dispersed clay in the epoxy matrix.

Mittal[107] synthesized dialkyl imidazolium salt and ion exchanged on the Mt surface. After that polypropylene nanocomposites with different volume fractions of organoclay were prepared and the mechanical, gas barrier properties of the nanocomposites were studied. Greater thermal stability and decreased gas permeability of the nanocomposites were obtained with filler volume fraction. Crystallization behaviour of the PP remained unaffected in the nanocomposites. Linear increase in the tensile modulus of the nanocomposites was observed with filler volume fraction due to partial exfoliation of the clay.

Mittal[108] prepared polymer composites from thermally stable imidazolium modified Mt clays. He used different volume fractions of organo-Mt to generate polymer nanocomposites and studied the effect of the modified clay on mechanical properties of polymer nanocomposites. Mechanical properties of the nanocomposites were compared with Helpin-Tsai models to give better insight into the system. The compatibilizers used for the preparation of polymer nanocomposites were selected on the basis of their chemical nature, molecular weight, amount of grafting and location of the polar groups. He found an increase in tensile modulus on addition of compatibilizer. The addition of compatibilizer did not influence the crystalline behavior of polymer matrix and the thermal stability of the nanocomposites.

Monemian et al.[109] prepared polymer nanocomposites using Poly(ethylene terephthalate)/(PET) and imidazolium modified organoclay by in situ polymerization. The microstructure of the polymer nanocomposites were investigated using XRD, TEM, and AFM. They found a correlation between the thermal stability and the dispersion characteristics of the polymer nanocomposites. Nonisothermal crystallization behavior of the nanocomposites was investigated by means of modified Avrami's equation, which revealed a crystallite tridimensional growth in nanocomposite samples.

Stoeffler et al.[110] studied the effect of intercalating agent on the clay dispersion and thermal properties of polyethylene/ organoclay nanocomposites. So they used alkyl pyridinium, 1-vinyl alkyl imidazolium, 1,3-dialkyl imidazolium, and tetraalkyl phosphonium bromides as intercalants for themally stable organo-Mt. For nanocomposite preparation they used linear low density polyethylene (LLDPE) and linear low density polyethylene grafted with maleic anhydride (LLDPE/LLDPE-g-MAH) as matrices. They found that TGA from in oxidative atmosphere was very sensitive to the dispersion state of the organoclay. They also found that the inherent thermal stability of the organoclay did not influence significantly the overall thermal stability of the composite in the range of temperature of investigation.

Trulove et al.[111] in a book chapter discussed the application of trialkyl-imidazolium ionic liquids and salts for the preparation of polymer nanocomposites. They concluded that the imidazolium treated Mt by ion exchange produced the most thermally stable organoclays than any other treatments. And they evaluated the thermal stability and structural properties of these imidazolium treated Mt clays. They concluded that polystyrene (PS) and poly(ethylene terephthalate) (PET) nanocomposites from these imidazolium treated Mt by melt blending process showed good compatibility between the matrix and the organo-Mt.

2.2.5.5. Ionic Liquids

Ding et al.[112] investigated the physicochemical adsorption of 1-octadecyl-3-methylimidazolium cation $[C_{18}mim]^+$ which was formed from an ionic liquid $[C_{18}mim]Br$, in the interlayer of Mt. They concluded that the ionic liquid can go into the interlayer of Mt by cation exchange reaction. They characterized the intercalated Mt by TGA, XRD and FTIR to study the aggregative structure of the organic cations in the interlayer of Mt. They concluded that with increase in adsorbed surfactant in the interlayer the aggregative structure of the surfactant became more and more ordered.

Ding et al.[113] investigated the aggregative structure of 1-octadecyl-3-methylimidazolium cation ($[C18mim](+)$) in the interlayer of Mt. They synthesized a series of organo-Mt with 1-octadecyl-3-methylimidazolium chloride, a kind of ionic liquid as a modifier by ion exchange in toluene. The intercalated Mt structure was investigated by TGA, XRD and FTIR. They further studied the effects of the aggregative structure of $[C18mim](+)$ in the interlayer of Mt on polypropylene melt intercalation. On the basis of TGA result they concluded about the three different arrangements of surfactant cations in the clay interlayer.

Fox et al.[114] investigated the thermal properties of trialkylimidazolium room temperature ionic liquids (RTILs) using a flashpoint apparatus. They found that all the salts had flashpoint above 200 ºC. The used TGA for the study of the decomposition of imidazolium based RTILs. The effects like hydrogen substitution, structural isomerism, alkyl chain length, anion type, purge gas type etc were discussed. They further investigated the decomposition kinetics 1,2-dimethyl-3-butylimidazolium hexafluorophosphate by TGA. They determined the TGA Arrhenius parameters by employing both constant heating rate and isothermal programs.

Fox et al.[115] used polyhedral oligomeric silsesquioxanes (POSS)- cation as the organic modifier for Mt. they prepared several Mt by exchanging the Na^+ with POSS imidazolium cations equivalent to 100%, 95%, 40%, 20% and 5% of the

cation exchange capacity of the clay. They characterized the organoclays by thermal analysis techniques like DSC, SDT and TGA. They also used Si-29 NMR to determine the POSS content in the clay interlayer both before and after thermal oxidation degradation. They concluded that the solvent choice could change the efficiency of the ion-exchange reaction of the clay. They further concluded that the prepared POSS-imidazolium exchanged clays had higher thermal stabilities than any previously prepared imidazolium or ammonium exchanged Mt.

Kim et al.[116] modified sodium Mt with three low molecular weight pyridinium and imidazolium based ionic liquids. The unmodified clay was treated under different conditions with aqueous solutions of three ionic liquids: N-ethyl pyridinium tetrafluoroborate, 1-ethyl 3-methyl imidazolium bromide and 1-hexyl 3-methyl imidazolium chloride. They found improved thermal stability of these ionic liquids modified organoclays than the commercial nanoclays modified with long chain quaternary ammonium salts.

Tokuda et al.[117] studied the physicochemical properties and structures of room temperature ionic liquids. They varied the alkyl chain length of 1-alkyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide. They measured the thermal behaviour, density, viscosity, self-diffusion coefficients of the cation and anion and ionic conductivity of the prepared room temperature ionic liquids over a wide temperature range. They discussed about the balance between the electrostatic and induction forces in terms of the main contribution factor in determining the physicochemical properties.

2.2.5.6. Stibonium
Wang and Wilkie[118] prepared triphenylhexadecylstibonium trifluoromethylsulfonate and ion-exchanged with sodium Mt to obtain a new organoclay. The clay was found to have higher thermal stability than ammonium clay. They prepared polystyrene nanocomposites from it and found that the clay was uniformly distributed throughout the matrix. The study concluded that

stibonium modified clay would be useful for the polymer composite with high thermal stability.

2.2.5.7. Crown Ethers/ Cryptands

Yao et al.[119] prepared crown ether modified Mt clays. They prepared it from Na^+ and K^+ form of Mt with crown ethers and cryptands. Then polystyrene nanocomposites were formed from these clays by bulk polymerization. The prepared nanocomposites were characterized by XRD, TEM, TG analysis and cone calorimetry. They found that nanocomposites were only formed by organoclays from K^+-Mt.

2.2.5.8. Dye Molecules

Yermiyahu et al.[120] studied the adsorption of the anionic dye congo-red (CR) by Na-, Cs-, Mg-, Al- and Fe-Mt by simultaneous DTA-TG. Thermal analysis curves of adsorbed CR were compared with the neat CR. Thermal analysis curve for the adsorbed CR showed three regions representing dehydration of the clay, oxidation of the dye, dehydroxylation of the clay combined with the oxidation of residual organic matter. The oxidation of dye produced water and two types of charcoal. Low temperature stable charcoals exhibited an exothermic peak in the second region and high temperature stable charcoals exhibited an exothermic peak in the third region of thermal analysis curve. They concluded that the ratio between these two types of charcoal was dependent on the acidity of the exchangeable metallic cation present in the Mt. They observed different thermal behaviour of the dye complex of Cu-Mt due to the catalytic effect of Cu.

Yermiyahu et al.[121] investigated the adsorption of protonated Congo red (CR) by Mt by thermo-XRD-analysis. They loaded Mt with increasing amount of CR. Samples treated at 420 ºC was investigated by XRD and the broad diffractogram was curve fitted to get the different basal spacings composing the XRD peaks. They analyzed the components present in the sample. Different diffractograms were obtained with variation in amount of adsorbed CR.

Yermiyahu et al.[122] investigated napthylammonium and naphthylazonapthyl ammonium Mt by XRD and DTA. They synthesized blue organoclay pigment naphthylazonaphthylammonium Mt from the white naphthylammonium Mt with $NaNO_2$. They investigated the effect of the amount of naphthylammonium loading in the clay and the amount of $NaNO_2$ used for the staining on the basal spacing of naphthylazonaphthylammonium and naphthylammonium clay. They further investigated the effect of aging of the preparation suspension on the basal spacing. Thermal treatment investigation through DTA proved the reaction of naphthylammonium with $NaNO_2$ to form organoclay color pigment.

2.2.5.9. Biomolecules

Gopinath and Sugunan[123] investigated the enzyme immobilized Mt. Three enzymes were immobilised on acid activated Mt clays using adsorption and covalent bonding.

In another paper Gopinath and Sugunan[124] investigated enzyme immobilized Mt K-10 to study the effect of adsorption and grafting on the surface properties and enzyme activity.

2.2.5.10. Polymer Molecules

Burmistr et al.[125] prepared an organo-bentonite by surface treatment of Na^+-bentonite with polymeric quaternary ammonium salts. Then they prepared polymer nanocomposites by melt blending this organoclay with linear polymers. XRD showed that organo-bentonite layers were exfoliated and dispersed into polyamide and polystyrene. They observed improvement in tensile strength and Sharpy impact of polymer nanocomposites from these two polymers. But in case of polypropylene nanocomposites no such improvement was found due to the absence of reinforcement. TGA showed that the polyamide and polystyrene nanocomposites had higher thermal stability in comparison with the original polymers.

Byrne and Mcnally[126] modified a natural and a synthetic layered silicate with trihexyltetradecylphosphonium tetrafluoroborate, an ionic liquid by a cation

exchange reaction. They investigated the exchange reaction and loading of modifier using a combination of WAXD, inductively coupled plasma-optical emission spectroscopy (ICP-OES) and TGA. They concluded that the thermal stability of the modified clay was enhanced by 150 ºC compared to conventional quaternary ammonium cations.

Huskic et al.[127] modified Mt using quaternary polyesters. They synthesized the polyester from N-methyldiethanolamine and succinic acid anhydride and converted it to the quaternary polyester using benzyl bromide. The prepared organo-Mt was characterized by nuclear magnetic resonance (NMR), size exclusion chromatography (SEC), DSC and TGA. They concluded that the thermal stability of polyester bound to Mt was greatly increased.

Yue et al.[128] studied the adsorption of a cationic polymer epicholorohydrin-dimethylamine polyamine (EPI-DMA) on bentonite under various conditions of bulk polymer concentration, inorganic salts, pH and temperature. They observed high adsorption rate and alkaline solution as a result of strong electrostatic interaction between the clay particles and EPI-DMA molecules. XRD study revealed the intercalation of EPI-DMA molecules in the bentonite and excess adsorption of polymer molecules on polymer loops. TGA and DSC study ensured the intercalation of the EPI-DMA polymer into the clay layers.

Zhang and Wilkie[129] prepared an organoclay by modifying sodium Mt with a new polymeric surfactant. They found that due to high molecular weight of the surfactant incomplete cation exchange occurred but nanocomposites formation with polyethylene and polypropylene occurred. XRD and TEM study revealed a mixed morphology. They evaluated thermal stability and the flammability of the nanocomposites by TGA and cone calorimetry. They did not find any enhancement in mechanical properties like Young's modulus and elongation.

Li et al.[130] prepared polystyrene sulfonic acid doped water-soluble polyaniline / Mt clay composite by intercalation polymerization in aqueous

medium. The prepared composites were characterized by XRD, TEM, FTIR, TGA, DSC, XPS and conductivity measurement. The composite exihibited mixed morphology. The clay nanolayers were found to be dispersed in the polymer matrix. The composites were more thermally stable than the polymer and showed good stable temperature dependent conductivity.

2.2.5.11. Oligomers

Zhang et al.[131] modified Mt with an surfactant having an oligomeric group and prepared polyethylene and polypropylene nanocomposites via melt blending in absence of any compatibilizer. They investigated the morphology of the nanocomposites by XRD and TEM. They described the prepared composites as mixed immiscible/ intercalated/ delaminated systems. The flame properties and thermal stability of the composites were investigated by cone calorimetry and TGA.

Zhang et al.[132] in another paper reported the modification of Mt with a surfactant having an oligomeric group where they varied the oligomer content from their earlier work and finally prepared polyethylene and polypropylene nanocompiosites from this oligomerically modified clay. They prepared the nanocomposites by melt blending with various clay loadings. Besides investigation of morphology, thermal stability and flame properties they investigated the mechanical properties of the nanocomposites also. They found the increase in Young's modulus and decrease in elongation for polyethylene nanocomposites. But little change was observed in case of polypropylene nanocomposites.

Zhang et al.[133] in another work prepared polyethylene and polypropylene nanocomposites from an oligomerically modified clay. The clay denoted as tri clay, was prepared from an oligomeric surfactant which was an ammonium salt of the terpolymer from vinylbenzyl chloride (VBC), styrene (St) and lauryl acrylate. The mechanical properties of the polyethylene nanocomposites exhibited enhanced Young's modulus and decreased elongation. However, polypropylene nanocomposites did not show any remarkable difference.

In another paper Zhang et al.[134] reported the fire properties of styrenic polymer clay nanocomposites using oligomerically modified clay. In their paper they melt blended four different styrenic polymers at different clay loadings. They characterized the morphology and also investigated the fire properties and thermal stability of the nanocomposite. They concluded that the reduction in peak heat release was comparable to their previously reported oligomerically modified Mt.

Zhao et al.[135] modified sodium Mt oligometrically using various amounts of aminopropylisooctyl polyhedral oligomeric silsequioxane (POSS) and another alkylammonium based surfactant via ion-exchange reactions. These organoclays were characterized by WAXD, TGA and contact angle measurement. They found that the interlayer space of POSS-modified clay was strongly dependent on the arrangement of POSS surfactant but less on the POSS concentration. They found that the dual modified clays exhibited increased exchange ratios by controlling the amount of the second surfactant and also maintained a good balance between hydrophobicity and polarity of the organoclays. Dual surfactant modified clays were well dispersed in the matrix when melt compounded with polypropylene.

2.2.6. Characterizations

Progress in instrumental and analytical techniques gave a thrust to the organoclay research. These techniques are constantly being improved and revisited. Along with the major characterization techniques like X-ray diffraction, Differential Thermal Analysis, Thermo gravimetric Analysis, FTIR, Electron Microscopy etc. new techniques like NMR, Raman, Neutron and Mossbauer spectroscopy, AFM, controlled rate thermal analysis (CRTA), plasma and laser techniques etc. are being used.

2.2.6.1. Thermal Study: Thermogravimetric Study/Differential Thermal Analysis

Xie et al.[136] studied the thermal degradation chemistry of the alkyl quaternary ammonium Mt. They investigated the nonoxidative thermal degradation of Mt and alkyl quaternary ammonium-modified Mt using conventional and high-resolution TGA combined with FTIR spectroscopy and mass spectrometry (TG-FTIR-MS) and pyrolysis/GC-MS. They observed that initial degradation of the modified clays followed a Hoffmann elimination reaction. They concluded that the surfactant architecture, chain length, exchanged ratio or washing etc did not alter the initial onset temperatures. They observed that catalytic sites on the aluminosilicate layer reduced the thermal stability of the surfactants to some extent relative to the surfactant itself. They found that the release of the decomposition product from organoclay was stepwise and was dependent on clay morphology.

Xie et al.[137] investigated the non oxidative thermal degradation chemistry of alkyl and aryl quaternary phosphonium-modified Mt clays using TGA combined with pyrolysis/GC-MS. They observed that the onset degradation temperature of phosphonium modified Mt was in the temperature range from 190 to 230 ºC. They concluded that the degradation pathways of alkyl phosphonium intercalated clays followed two reaction pathways. They are (1) Beta elimination and (2) nucleophilic displacement at phosphorus. On the other hand in case of the aryl phosphonium intercalated clays they found that the degradation followed either a reductive elimination through a five-coordinate intermediate or radical generation through homologous cleavage of the phosphorus-phenyl bond. Thus they concluded about the more thermal stability of the phosphonium surfactant modified Mt than the ammonium-modified Mt.

Xi et al.[55] investigated the structure of the organoclays by XRD study and TGA. With the help of XRD they monitored the changes in the surface properties after intercalation. They found that variation in the d-spacing of organoclays was a step function of the surfactant concentration. High-resolution thermogravimetric analysis (HRTG) study showed that thermal decomposition of the

octadecyltrimethylammonium bromide modified Mt took place in four steps. The initial two mass loss steps at the lower temperature range were associated with the dehydration of adsorption water. The third mass loss was due to loss of surfactant. The fourth and final mass loss step occurred due to dehydroxylation of the Mt. They proposed a model regarding the interlayer expansion with the modifier concentration. They concluded that surfactant monolayer between the Mt clay layers was formed up to 0.4 CEC, a lateral-bilayer was formed up to 0.8 CEC and a pseudotri-molecular layer with excess surfactant adsorbed on the clay surface was formed above 1.5 CEC.

Xi et al.[138] investigated thermal decomposition of the Mt modified with octadecyltrimethylammonium bromide by HRTG. They concluded that the thermal decomposition occurred in four steps. The first step in mass loss occurred at ambient to 100 ºC temperature range and was associated with dehydration of adsorbed water. The found the second mass loss occurred for dehydration of water hydrating metal cations. The next mass loss occurred due to loss of surfactant. The fourth step of mass loss was due to dehydroxylation of the Mt. Their study gave an idea of the stability of organoclays.

He et al.[139] in their study mentioned the thermal stability as the key factor in the synthesis and processing of organoclay based nanocomposites. In this study they used different thermal analysis technique like DTA, TGA and DSC to monitor thermal stability of hexadecyltrimethylammonium bromide-modified Mt clays prepared at different surfactant concentrations. Analysis by DSC showed that the molecular environment of the surfactant within the Mt galleries was different from that in the bulk state. The study showed the amount of water residing in the interlayer of organoclay decreased with increase in surfactant packing density and at the same time thermal stability of the organoclays also decreased. The study further showed that the cationic surfactant inserted into the Mt interlayer not only by cation exchange but also by physical adsorption.

Kajino et al.[140] investigated the effect of confined interlayer space in Mt on the conformational changes of the chain segment of the cationic surfactants. For that purpose they modified Mt with dioctadecyl dimethylammonium (DC(18)DM) ions. They characterized the resulting organoclay using temperature modulated differential scanning calorimeter (TMDSC), WAXD and FTIR techniques. They observed that for the organoclay the chain conformational disorder order phase transition took place during the cooling process. The study showed that in organoclay the gauche conformers increased and the chains were less densely packed than in crystalline surfactant itself.

Carventes-UC et al.[141] studied the thermal decomposition products evolved during the degradation of several commercially available organoclays (Cloisites (TM) Na^+, 10A, 15A, 20A, 25A, 93A and 30B) using TGA/FTIR. They found that the decomposition pattern and the onset of the decomposition product of the organoclays were different for each sample. FTIR analysis of the evolved products showed the release of water, aldehydes, carboxylic acids, aliphatic compounds aromatic compounds and CO. They concluded that the tallow residue and the unexchanged surfactant were among the evolved degradation products.

Thermo-XRD-analysis study by Ovadyahu et al.[142] dealt with Mt and laponite loaded with different amounts of tributylammonium cations with different organic loading. Their thermal study showed four stages of mass loss. They concluded that first mass loss accompanied by an endothermic DTA peak was for dehydration. The next three mass losses accompanied by exothermic DTA peaks were due to three oxidation steps of the organic matter. They concluded that the dehydroxylation step occurred together with second and third oxidation steps.

Yariv[143] discussed DTA and EGA (Evolved Gas Analysis) curves of three metachromic dye treated Mt and laponite clays. He also discussed DTA and EGA curves of butylamine and pyridine treated sepiolite and polygorskite. His study focused on the role of EGA for the interpretation of DTA peaks.

Yariv[144] in his paper discussed the use of thermo-IR spectroscopy study in organoclay complexes prepared from Mt, laponite etc. For this purpose self supported film prepared from Mt and laponite were heated and studied by IR spectroscopy at different temperatures. For other clays alkyl halide disk prepared from these were heated and studied by IR. He concluded that this study was useful for the determination of fine structure of organoclays.

Yariv [145] discussed the role of charcoal on DTA curves of organoclay complexes. The study focused on the role of the combustion of charcoal for investigating fine structure of the organoclay complexes and the type of associations between the organic compound and the clay.

In their paper Yariv et al.[146] discussed the role of thermo-XRD analysis for the study of organo-smectite complexes. They concluded that Thermo-XRD analysis was useful for identification of penetration of adsorbed organic species into the interlayer space of the smectites mineral.

2.2.6.2. Spectroscopic Study

Xi et al.[147] studied the spectra of octadecyltrimethylammonium (ODTMA) bromide modified Mt by Infrared (IR) spectroscopy using attenuated total reflection (ATR) cell to give an insight into the intercalation process. They observed decrease in the wavenumbers of bands attributed to CH-stretching and CH-bending vibrations with concentration of surfactant up to 1.0 CEC. They also observed significant changes in the HCH deformation modes of the methyl groups of the surfactant which was attributed to the methyl groups locking into the siloxane (SiO) surface of the Mt. This was further supported by changes in the SiO-stretching bands of the Mt siloxane surface.

Madejova et al.[148] used transmission and reflection FTIR techniques to distinguish between different types of clay minerals and to provide information concerning their structure, composition and structural changes upon chemical modification. They identified the most useful sampling technique depending on the

physical state of the sample. They concluded that diffuse reflectance (DRIFT) technique in the middle IR region was suitable for the study of organoclays prepared by adsorption of alkyammonium cations on smectites.

He et al.[149] performed Raman spectroscopic study on the organo-Mt prepared at different concentrations for the investigation of the ordering conformation of hexadecyl trimethyl ammonium cations confined within the Mt interlayer. They showed that the ordering conformation has a strong dependence on the concentration of the confined amine. They concluded that both the wavenumber and bandwidth of antisymmetric and symmetric stretching modes were sensitive to the ordering conformation of the inserted organic cation. They also observed that the wavenumber of the antisymmetric stretching mode was more sensitive than that of the symmetric stretching mode to the mobility of the tail of the amine chain. They concluded that at room temperature the conformational ordering was more easily affected by the packing density in the lateral model than in the paraffin-type model. They found that at liquid nitrogen temperature the bandwidth of the symmetric stretching were sensitive to the ordering conformation. And the positions of symmetric and anti symmetric stretching mode were found independent of amine concentration. They observed both the positions of symmetric and anti symmetric stretching bands shifted to higher wavenumbers on heating of organoclay indicating a decrease in conformational ordering.

Ma et al.[150] prepared a series of organoclays from Mt clays with different CEC and surfactants with different alkyl chain numbers and chain length. FTIR spectroscopy using ATR, DRIFT and KBr pressed disk techniques were used to characterize the organoclays under wet and dry states. They concluded that the alkyl chain length and chain number had significant influences on the local environment of the intercalated surfactants. The study also indicated that the surface property of the resulting organoclays was affected by the loading and configuration of the intercalated surfactants. The study showed that in wet state with low surfactant loading more gauche conformer were present in the alkyl chains. High surfactant loading organoclays showed splitting of Si-O stretching

vibration which indicates rearrangement of SiO_4 tetrahedral sheets. They further concluded that the KBr pressed disk technique was suitable to probe the conformational ordering of the confined amine chains whereas the reflectance spectroscopy with ATR and/or DRIFT technique was more suitable to probe the water in organoclays.

He et al.[151] in their paper investigated sorbed water and hexadecyl trimethyl ammonium cations (HDTMA) in organoclay by FTIR spectroscopy. From the shift of the position of v (2) band to higher frequency and stretching vibration towards lower frequency they concluded that amount of sorbed water decreased on intercalation. From the shift in position of both the symmetric and antisymmetric stretching to low frequencies they confirmed the increase in conformation ordering with increase in concentration of amine within the gallery of Mt. They concluded that antisymmetric CH_2 stretching mode was more sensitive to the conformational ordering than the symmetric stretching mode. They concluded that FTIR spectroscopy using KBr pressed disk technique was more suitable to probe the conformational ordering of surfactant in organoclays than ATR technique.

He et al.[152] investigated the surfactant distribution within the organoclays using X-ray Photoelectron Spectroscopy (XPS) in combination with XRD and HRTG. They concluded that when surfactant loading was low, surfactants resided at clay interlayer but with high surfactant loading these occupied both the clay interlayer and the interparticle pores. It was confirmed by pore volume decrease. From XPS survey scans observation they concluded that at low surfactant concentration the ion exchange between $HDTMA^+$ and Na^+ cations were dominant. Their study showed that the modification of clay with surfactants had prominent effect on the binding energies of the atoms in both clays and surfactants. The study further showed that nitrogen was the most sensitive to the surfactant distribution within the organoclays.

He et al.[153] investigated the ordering conformation of surfactant molecules by C-13 MAS NMR in intercalated clays prepared from Mt at various surfactant

concentrations. The study showed that the ordering conformation of surfactant molecules within the gallery of Mt depended very much on their orientation and packing density. They concluded that when amine chains were oriented parallel to the silicate layers, the amount of all-trans conformer decreased with the increase of amine concentration. However, when amine chains radiated away from the silicate layers, the amount of all-trans conformer increased with the increase of amine concentration. Their study further showed that the intercalated surfactant molecules in the clay minerals never attained the complete liquid like or solid like behavior.

Dickey et al.[154] investigated the sorption of benzene, ethylbenzene, tert-butylbenzene, and quadricyclane onto cetyltrimethylammonium bromide (CTAB) modified Mt by NMR spectroscopic study. From this study they concluded about the usefulness of Raman spectroscopy for the study of sorption onto the organoclay.

Zhu et al.[155] investigated the molecular conformation and mobility of the surfactant cetyltrimethylammonium cation in the interlayer of Mt using FTIR and high-resolution single-pulse C-13 magic angle spinning nuclear magnetic resonance (C-13 SP MAS NMR) spectroscopy. They found that the conformation and mobility of the surfactant's alkyl chains were a function of the surfactant concentration. They further found that the conformational freedom decreased with increase of surfactant concentration.

Sagitova et al.[156] applied Raman spectroscopy for interlayer structure of organoclay prepared from Mt with ditetradecyl dimethylammonium bromide. The study concluded about different conformational states and the ratio of trans to gauche conformers.

Salahuddin et al.[157] prepared polyurethane (PU)/organo-Mt nanocomposites using varying concentration of organoclay. To change the degree of surface modification, sodium Mt was reacted with polyoxyalkylene amine hydrochloride in equivalent ratios (1:1 and 1:2). They used dimethyl formamide (DMF) as a

swelling agent for the organoclays. They found that the organo-Mt with polyoxyalkylene of higher molecular mass produced the exfoliated PU nanocomposites. But the organo-Mt with polyoxyalkylene of lower molecular mass produced only the intercalated PU nanocomposites.

Zhou et al.[158] used Near Infra Red Spectroscopy (NIR) to measure the adsorption of p-nitrophenol on untreated Mt and surfactant exchanged Mt. The shift of the characteristic NIR band for p-nitrophenol revealed that it was adsorbed on organoclay but not on untreated Mt. Their study revealed that the organoclay was more useful for removal of organic pollutants than the untreated Mt clays.

2.2.6.3. Morphology

He et al.[159] used TEM, SEM along with XRD for the detail understanding of the interlayer structure and morphology of organoclays. The study showed that the thermal treatment had an important effect on stability of organoclays as reflected by significant changes in the basal spacing. The TEM and SEM studies showed that lower surfactant packing density led to irregular layer stacking while higher surfactant packing density led to regularly intercalated and flat layers. They concluded that morphology of organoclay in the clay interlayer was strongly dependent on the surfactant packing density.

Zhu et al.[160] investigated the surface microtopography of the organoclay. For that purpose they used low-pressure gas adsorption experiments and AFM. These two methods were useful for measurement of the specific surface area, mapping the images of surfactant modified Mt clays on the nano-scale, measurement of surface roughness and irregularities. Their study showed that the surface roughness was influenced by the surfactant loading. AFM observation supported the finding that higher loading resulted smoother surface.

2.2.6.4. Computer Modeling

He et al.[161] investigated the basal spacing of organoclay using simulation technique on the basis of the energy minimum by the canonical NVT ensemble.

The interlayer structure and mobility of alkyl chains were explored based on the interlayer atomic density profiles. They observed lateral-bilayer accompanied by partial a pseudotri-layer and a transition structure between the two basic lateral models besides the basic lateral-monolayer arrangement. According to them this observation excellently explained 16 A° basal spacing observed in the literatures. Their study indicated that the molecular mobility of the confined alkyl chains decreased from lateral-monolayer to lateral-bilayer with the increase of the intercalated surfactant. Their study further indicated the mobility of the alkyl chains strongly depended on the surfactant arrangement rather than the surfactant packing density.

2.2.7. Applications

2.2.7.1. Polymer Nanocomposites

Utracki and Kamal[162] reviewed on clay-reinforced polymeric nanocomposites (PNC). They concluded that preparation of polymer nanocomposite with exfoliated morphology was obtained via multiple steps. The first step was the swelling of Mt in water to increase its interlayer spacing at ~0.96 nm in dry state to ~ 1.3 nm. The next step was the modification of pristine Mt with organic modifier for further expanded interlayer spacing. And the final step was reactive compatibilization of the organoclay/matrix polymer system for an exfoliated polymer nanocomposite structure.

Vaia et al.[163] reported the direct intercalation poly(ethylene oxide) into Na^+ and Li^+-exchanged layered silicates and the properties of the resulting nanocomposites. They concluded that the polymer nanocomposites could improve the performance of the electrolytes.

Vaia et al.[164] evaluated the microstructure of polymer nanocomposites. They evaluated melt intercalated polymer nanocomposites by XRD and TEM. They found that the ordered intercalates exhibited similar microstructures to the

unintercalated organoclays. The disordered hybrid exhibited heterogeneous microstructures having increased layer disorder and spacing.

Vaia and Giannelis[165] developed a lattice model of polymer melt intercalation of organically modified layered silicates. They found that for alkylammonium modified layered silicates a favourable energy change was attained by maximizing the magnitude and number of favorable polymer-surface interactions. At the same time the magnitude and number of unfavorable apolar interactions between the polymer and the functionalizing alkyl surfactants was minimized.

In another paper Vaia and Giannelis[166] studied the polymer melt intercalation in layered silicate through model prediction and experiment. They examined the effect of silicate functionalization, anneal temperature, polymer molecular weight and constituent interactions on polymer melt intercalation. They studied the polymer melt intercalation of styrene derivative polymers in alkylammonium modified silicates. They observed that hybrid formation required an optimal interlayer structure for organoclays depending on the number per host area, size of the alkylammonium chains and polar interactions between organoclay and polymer. They concluded that the most effective polymer for intercalation should have either polar character or contain Lewis-acid/base groups.

Shi et al.[167] investigated the interfacial effects on the reinforcement properties of polymer / clay nanocomposites. They modified smectite clay with *n* alkylammonium cations having three carbon atoms and prepared epoxy/ organoclay nanocomposites from it. They achieved an exfoliated structure in epoxy nanocomposites using a short chain alkylammonium cation. They compared the properties of organoclay and the prepared nanocomposites varying the number of exchange cycle. And found exfoliated nanocomposites structure resulting from organoclays with higher exchange cycles. They depicted three interactions between the polymer matrix with the alkylammonium cations and the clay surface. They

found that among the three interactions the most important one was the binding interaction of the polymer to the siloxane basal surfaces.

Jiang et al.[168] prepared organo-Mt with hydroxyl, epoxy and no polar groups. The prepared organoclays were then used for the preparation of PP/ clay nanocomposite with maleic anhydride-PP as a compatilizer. The structure and the mechanical properties were measured via XRD, TEM, DSC and TGA. They studied the effect of organo-Mt structure on the structure and properties of PP/clay nanocomposites. They concluded that organo-Mt with polar group has a strong affinity to maleic anhydride-PP. So better intercalation and exfoliation of clay took place for those.

Jiang et al.[169] prepared phenolic resin (PF)/ Mt nanaocomposites using intercalative polymerization. The Mt clay was modified by octadecylamine (C18), benzyldimethylhexadecylammonium chloride (B2MH), benzyltriethylammonium chloride (B3E), and benzyldimethylphenylammonium chloride (B2MP). XRD and TEM study showed that the clay platelets were partially exfoliated or intercalated in nanocomposite. They concluded that the thermal stability of the nanocomposites was dependent on the chemical structure of the intercalants. Highest thermal stability was obtained for those nanocomposites prepared from organoclay containing both benzyl and phenyl groups.

Chen and Curliss[170] used epoxy matrix for the preparation of polymer nanocomposites. The characterization by WAXD, SAXS and TEM demonstrated that exfoliated nanocomposites were formed. Dynamic mechanical analysis (DMA) showed that the storage modulus of the nanocomposite was higher than that of the pristine polymer due to the high aspect ratio and high strength of the nanoclay. The solvent uptake for the nanocomposite became significantly reduced compared with the pristine polymer as a result of the barrier effect of the nanoclay.

Chigwada et al.[171] modified Mt using an ammonium salt containing 4-acetylbiphenyl. They used this clay for preparation of polystyrene (PS),

acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS) nanocomposites. XRD and TEM study confirmed nanocomposites formation. They investigated thermal stability by thermogravimetric analysis and flammability properties by cone calorimetry.

Galeski and Piorkowska[172] discussed the factors which influenced the efficiency of the clay exfoliation in a polymer during melt processing. The factors like the type of machine used, mixing conditions, molecular characteristics of polymers and polymeric compatibilizers were discussed. They also described the new methods leading to clay exfoliation in a polymer matrix. They concluded weak shearing could induce alignment of clay platelets resulting polymer chain orientation and enhance the nucleation of crystallization.

Gao et al.[173] prepared organoclay and fluroelastomer nanocomposites by melt intercalation. They investigated the microstructure of the nanocomposites by TEM and XRD. The mechanical properties, thermal stability and solvent resistance were also evaluated. They concluded that when Mt content was lower than 12 wt % the prepared nanocomposites showed excellent tensile properties due to the nanometer scale dispersion. They further observed that introduction of small amount of organoclay improved the thermal stability and the solvent resistance of nanocomposites.

Hrachova et al.[174] prepared natural rubber nanocomposites with organo-bentonite. They modified the bentonites with the organic salts tetra methylammonium (TMA) chloride, octyltrimethylammonium (OTMA) bromide and octadecyltrimethylammonium (ODTMA) bromide. They concluded that the ODTMA bromide modified bentonite was the most effective organoclays for the mechanical property improvement of the nanocomposites.

LeBaron et al.[175] published a review of polymer nanocomposites with use of alkylammonium exchanged smectite clays as the reinforcement phase in selected polymer matrices. A few weight percent of organoclay in nylon 6 improved heat

distortion temperature over pristine polymer. Similar loading of organoclay in elastomeric epoxy and polyurethane matrices also improved both the toughness and the tensile properties. Organic loading in glassy epoxy nanocomposites exhibited substantial improvement in yield strength and modulus under compressive stress-strain conditions. Organoclay polypropylene hybrids gave improved storage moduli. Only 2 wt % organoclay loading in polyimide showed a 10-fold decrease in permeability toward water vapor. It was revealed from the literatures they studied, that in situ and melt intercalation processing methods were effective in producing reinforced polystyrene hybrids. Nitrile rubber hybrids showed improved storage moduli and reduced permeabilities toward gases. Poly(epsilon-caprolactone)-clay nanocomposites prepared by in situ polymerization of epsilon-caprolactone in organoclay galleries showed a substantial reduction in water adsorption while polysiloxane nanocomposites produced from poly(dimethylsiloxane) and organoclay mixtures showed improved tensile properties, thermal stability and resistance to swelling solvents.

Liu et al.[176] studied the effect of Mt (Cloisite 6A) on the bulk polymerization of styrene initiated by benzoyl peroxide by the dilatometric determination of the polymerization rates. They found that the bulk polymerization rates increased as the Mt input quantity increased. They observed increase in effect when benzoyl peroxide (BPO) decreased. XRD and TGA showed that that the structure and properties of the polystyrene-Mt-nanocomposites were greatly affected by the BPO concentration. They found that with lower BPO concentrations a larger basal spacing, higher extent of delamination and higher heat-decomposition-resistance temperatures resulted.

Tang et al.[177] used two different methods to prepare polypropylene/clay nanocomposites. In one method they used pristine Mt clays and a reactive compatibilizer hexadecyltrimethylammonium bromide and in another method they used different organophilic Mt clays. Their study showed that different methods and organophilic Mt influenced the morphology and thermal stability of polypropylene/clay nanocomposites.

Liu et al.[178] synthesized polyurethane/Mt nanocomposites and used those materials for fiber spinning. They investigated the viscosity of the spinning solutions, the mechanical properties of polyurethane/Mt fibers along with the dispersion of Mt in cast films and drawn fibers. They found that the viscosities of spinning solutions containing Mt were lower than that of the pure polyurethane solution. The viscosity of spinning solutions increased after standing 24 hours at room temperature. TEM images confirmed the nanometric dispersion of Mt particles in fiber matrix. However, the mechanical properties except the elongation at break did not increase much in the polymer nanocomposites.

Liu and Wu[179] prepared polypropylene clay nanocomposites by grafting-melt compounding. They used a co-intercalation organophilic clay which had a larger interlayer spacing than the ordinarily organophilic clay only modified by alkylammonium. TEM and XRD confirmed the dispersion effect of silicate layers in the PP matrix. They observed the increase in the mechanical properties of polypropylene clay nanocomposites by the addition of organoclay.

Manias et al.[180] published a review on the synthetic routes and materials properties of polypropylene/Mt nanocomposites. They concluded that the nanocomposites formation was achieved by using functionalized polypropylenes and common organo-Mt, or by using neat/unmodified polypropylene and a semi-fluorinated organic modification for the silicates. They found that the solvent less melt-intercalation or extrusion could form the hybrids form both by coexisted intercalated and exfoliated Mt layers. Very small amount of these organoclay fillers could improve tensile properties, heat deflection temperature, optical clarity, high barrier properties, scratch resistance and flame retardancy of the polymer nanocomposites.

Mittal et al.[81] prepared modified Na^+-Mt of two different CEC by various alkylammonium cations. Then he prepared polypropylene organoclay nanocomposites from these and investigated the effect of filler-matrix interactions

on the intercalation-exfoliation behavior and the mechanical properties of the composites.

Mittal et al.[108] prepared polymer nanocomposites from the thermally stable imidazolium modified clay and from conventional ammonium modified clay. Different volume fractions of organo-Mt was used to generate polymer nanocomposites and to see the effect of the modified clay on mechanical properties of nanocomposites.

Wei et al.[181] prepared nanocomposites from phenolic resin and organo-Mt. The investigated their thermal stability.

Wheeler et al.[182] modified laponite clay with combinations of organic ammonium surfactant and/or covalently bound poly(methyl methacrylate) (PMMA). They investigated two polymer attachment methods. One method involved the reaction of a methacrylate compound with the clay's silanol group followed by in situ free-radical polymerization of methyl methacrylate (MMA). The other method was reaction through attachment of an ATRP initiator followed by brush polymerization. They found that the free-radical method yielded clays with 75 wt % of polymer bound whereas the ATRP method yielded 68 wt % of polymer bound. The first mechanism yielded attachment of polymer at multiple sites of the clay whereas the second mechanism yielded attachment of polymer only at the chain end. They found that the PMMA-modified clays were very dispersible in organic solvents and were solvent-blended with commercial PMMA at 1, 3, 5, and 10 wt % concentrations. Investigation by TEM showed intercalated and exfoliated morphology of the nanocomposites. DMA analysis exhibited an increase in room temperature modulus by 50% at 5 wt % concentration for the clay with no surfactant and PMMA free-radical attachment.

Wilkie et al.[183] reviewed the fire retardancy nanocomposites. They discussed various aspects of fire retardancy. Their study focused on the areas like amount of the required clay, the role of the surfactant, synergy between conventional fire

retardants and nanocomposite formation. They also stressed on the mechanisms of formation of nanocomposites which enhanced fire retardancy.

Miyagawa et al.[184] prepared epoxy clay polymer nanocomposites from diglycidyl ether of bisphenol A and diglycidyl ether of bisphenol F. They found that basal spacing of clay nanoplatelets was expanded after mixing with either DGEBA/DGEBF or methyltetrahydrophthalic-anhydride (MTHPA) curing agent. They found that MTHPA-cured epoxy/clay nanocomposites produced more expanded d-spacing of clay nano platelets modified with methyl, tallow, bis (2-hydroxyethyl) quaternary ammonium (MT2EtOH) than triethylenetetramine-cured nanocomposites.

Modesti et al.[185] prepared Acrylonitrile--butadiene--styrene (ABS) nanocomposites containing imidazolium-modified Mt by melt-blending (MB) and solution-sonication. They investigated the structure-property relationship of the prepared composites by XRD, TEM, DMA, TGA, mechanical testing, fluorescence probe confocal microscopy and fluorescence spectroscopy (FS). Mixed morphology of intercalated and exfoliated structures of nanocomposites was characterized from TEM. They observed a homogeneous dispersion in sonicated samples by fluorescence probe confocal microscopy. They found from fluorescence spectroscopy that clay layers in ABS were preferentially located in the styrene-acrylonitrile (SAN) phase.

Mohanty and Nayak[186] prepared Poly(methyl methacrylate) (PMMA)/layered silicate nanocomposites using melt intercalation technique. They used Cloisite 30B, Cloisite 20A and Bentone 109 as the filler. PMMA matrix was grafted with maleic anhydride to modify the interfacial region and improved the interfacial adhesion between organoclays and PMMA matrix. TGA was used to study the thermal stability of the nanocomposites. The dispersion characteristic of polymer nanocomposites was investigated by TEM. Improved tensile modulus and fire retardancy were exhibited by the prepared polymer nanocomposites.

Mravcakova et al.[187] prepared Mt polypyrrole nanocomposites by the insitu polymerization in aqueous solution caontaining an oxidant and anionic surfactant using both the unmodified and organo-Mt. The difference in the behavior of organo-Mt nanocomposites and unmodified Mt nanocomposites was interpreted in terms of surface energy minimization by the alkylammonium ions present at the surface of organoclay.

Nawani et al.[188] used SAXS for the investigation of orientation distribution of organoclays in melt-pressed nanocomposite films, containing ethylene-vinyl acetate (EVA) copolymers as polymer matrices. They used different weight fractions of organoclays and obtained higher orientation for higher organoclay loading.

Ou et al.[189] poly (ethylene terephthalate)–Mt nanocomposites by solution intercalation method. The organoclay was prepared by modifying with cetylpyridinium chloride. They prepared nanocomposites using different wt % of organoclay. Their study showed increase in thermal stability of the nanocomposites by addition of 1-15 wt % organoclay. They further concluded that optimum dispersion without agglomeration was achieved at low organoclay content (5 wt %).

Pagacz and Pielichowski[190] gave an over view of the poly (vinyl chloride) (PVC)/Mt nanocomposites. They discussed different methods of this nanocomposites preparation. They observed that use of organoclay in PVC matrix increased the thermal stability of the nanocomposites and increased mechanical properties. But they concluded that the properties were strongly dependent on organic modification procedure.

Palza et al.[191] prepared a set of organoclays with different compatibilizers to alter their interactions with polypropylene matrix when melt mixed. They studied the relation between the organoclay compatibilizer system and the composite morphology.

Parvinzade et al.[192] Poly ethylene terephthalate (PET)-based nanocomposites using three differently modified clays. The influence of modified clay type on surface properties of resultant nanocomposites was investigated by them.

Paul et al.[193] prepared plasticized poly (L-lactide) (PLA) based nanocomposites by melt blending the matrix with poly (ethyleneglycol) and different amounts of organo-modified Mt or unmodified Mt. They found that organoclay prepared from bis-(2-hydroxyethyl) methyl (hydrogenated tallow alkyl) ammonium cations gave greater thermal stability of the nanocomposite.

Tjong et al.[194] published a review article discussing the structural and mechanical properties of polymer nanocomposites. In their article they discussed with the processing, structure and mechanical properties of polymer nanocomposites reinforced with layered silicates, carbon nanotubes and ceramic nanoparticles.

Paul and Robeson[195] published a review on exfoliated clay-based nanocomposites and discussed with important areas like barrier properties, flammability resistance, biomedical applications, fuel cell interests, electrical, electronic and optoelectronic applications.

Peeterbroeck et al.[196] prepared various nanocomposites containing ethylene vinyl acetate copolymer and various ammonium cation modified clays. They evaluated the morphology, tensile and thermal degradation properties of the nanocomposites after preparing them by melt blending. They investigated the influence of the clay nature, origin and also the nature of organic modifier. They concluded that nanostructure and tensile properties was dependent on the nature of the organic modifier but thermal volatilization of matrix was dependent on the clay's aspect ratio.

Qu et al.[197] prepared Poly (methyl methacrylate) (PMMA)/ Mt nanocomposites by bulk polymerization and characterized to confirm the intercalation of PMMA in the galleries of Mt. They observed enhanced mechanical properties and thermal stability of the nanocomposites.

Rama and Swaminathan [198] prepared polycarbonate (PC)/clay nanocomposites by in situ melt polycondensation. They used phosphonium and imidazolium based cations to modify the Mt. They found that exfoliated polycarbonate/clay nanocomposites resulted from organoclays with reactive bisphenol functionality in the modifier.

Ramos et al.[199] modified bentonite clay with a quaternary organic salt. Then prepared polypropylene/ clay nanocomposites using this modified clay with polypropylene by melt intercalation. They found that the modified clay had more thermal stability than the natural clay.

Rohlmann et al.[200] prepared nanocomposites using maleic anhydride modified polypropylene and different organoclays by melt mixing. They used Cloisite 15A, Cloisite 93A, Nanomer 144 and a bentonite modified with octadecylammonium cation. Many conclusions were drawn from their study. The composites prepared from Cloisite 15A and Nanomer 144 showed very similar structures. They found no exfoliation from the nanocomposites prepared from Cloisite 10A and Cloisite 30B.

Sanchez et al.[201] investigated the rheological and mechanical properties of polyethylene terephthalate (PET)/Mt nanocomposites. They used a series of additives like maleic anhydride (MAH), pentaerythritol (PENTA), alkylammonium chlorides as compatibilizers. They also evaluated the influence of the additives on the mechanical and rheological behavior of the PET matrix. They correlated the molecular weight of the polymer to the resulting rheological and mechanical properties of the system.

Sarkar et al.[202] studied the potential of organoclays to adsorb inorganic ionic components. They synthesized organoclay using bentonite and a commercially available alkylammonium surfactant Arquad 2HT-75. Then they studied their ability to adsorb hexavalent chromium (Cr (VI)) in aqueous solution. They found by isothermal and kinetic studies that the organoclays effectively removed hexavalent chromium from aqueous solution by both chemical and physical adsorption processes. They further found that higher surfactant loadings generated better adsorption efficiency and organoclay was effective for remediating Cr (VI).

Silva et al.[203] investigated the effect of clay water molar ratio on the organophilization of Mt and prepared polypropyle / organoclay nanocomposites from the cetyltrimethylammonium modified Mt. They found that the clay / water ratio influenced the degree of disorder in the organoclay. They found that the more disordered organo-bentonites dispersed better in the polymer matrix and thus clay water ratio influenced the polymer nanocomposite property.

Stoeffler et al.[204] studied the thermal decomposition of several organoclays and the effect of this decomposition on polyethylene terephthalate nanocomposites. In their work they used alkyl phosphonium, alkyl pyridinium and dialkyl imidazolium surfactants for the highly thermally stable organoclay preparation. They studied the thermal decomposition of the organoclays with the help of TGA and mass spectroscopy. They found thermal decomposition influenced the color of the nanocomposites. In case of the the alkyl pyridinium modified clay, the degradation of the intercalating agent during processing was found to alter the clay dispersion. They found that kinetics of nucleation and growth was affected by the dispersion state of the clay and also by the nature of the intercalating agent.

Wang et al.[205] prepared a nanocomposite film from polyvinyl alcohol, Ni^+-Mt, defoamer, a leveling agent and a plasticizer. They studied its thermal characteristics by DSC. They measured the intermolecular interactions by FTIR and XPS. The study showed that crosslinking tookplace between PVA and Ni^{2+}-Mt. They studied mechanical properties of this nanocomposites film. They studied

the microstructures by XRD and AFM. This study showed that PVA molecules penetrated into the clay platelets and resulted exfoliation. The tensile strength of the film was much higher than neat PVA. The dissolution temperature of the film reduced when Ni^{2+}-Mt was added into PVA.

Xie et al.[206] investigated the effects of processing history and annealing treatment on the thermal property and polymorphic structure of nylon-6/clay nanocomposites. For that purpose they prepared composites by extruding nylon-6 with Na-Mt and organo-Mt. DSC analysis revealed multiple melting endotherms in the samples. WAXD analysis of samples was done to characterize the polymorphic structure of the injection-molded nylon-6 and the composites before and after annealing.

In another paper Xie et al.[207] investigated the nanostructure and the mechanical properties of the Nylon-6/Mt nanocomposites prepared by melt processing. Thy prepared the nanocomposites in different dispersion states of clay and different clay loadings. They studied the influence of the Mt dispersion state and clay content on the tensile fracture morphology of the injection-molded nanocomposites by SEM. They observed a 'cabbage-like-sheet' structure in the fracture surface in case of well exfoliated nanocomposites. But it was not observed both in case of intercalated and poorly dispersed nanocomposite and neat nylon-6.

Wang et al.[208] prepared butadiene rubber (BR) organoclay nanocomposites by melt mixing. The organoclays were prepared by modifying Mt clays with different primary and quaternary ammonium salts. BR / pristine clay composite and BR/organoclay nanocomposites were analysed by XRD, SEM, TEM and TGA. They found that the organoclay accelerated the vulcanization of BR. The mechanical properties i.e. the tensile strength, elongation at break and tear strength of BR/organoclay nanocomposites were much higher than BR/pristine clay composite.

Wang et al.[209] prepared organo-Mt polymer nanocomposite from maleic anhydride grafted polypropylene by melt blending. They investigated the microstructure and mechanical properties of the polymer nanocomposites by TEM and mechanical tests. They investigated the properties of the polymer nanocomposites by DSC and TGA. The impact property, tensile property and the bending modulus were found to increase in the polymer nanocomposites. Thermal stability, crystailing point and the total velocity of crystallization of the nanocomposites also increased.

Xu et al.[210] prepared some organoclays and prepared polyester composites from these organoclays. They analyzed the relationship between the four influential factors and the interlayer spacing and established a mathematical model. They found a linear relationship between interlayer spacing and the concentration. They found much increase in mechanical properties of the prepared composite specimens.

Zhao et al.[211] prepared polyethylene/clay composites by melt compounding polyethylene and organo-Mt. Their investigation of the composites through XRD and TEM revealed that nanocomposites were obtained only when a reactive intercalation agent was used. And conventional microcomposites were obtained from the common alkylammonium intercalated clay.

Yang et al.[212] investigated the effect of organoclay on the compatibility and properties of Nylon 66/polypropylene blends. For that purpose they prepared Nylon 66/polypropylene (PP) blends containing maleated polypropylene and organo-Mt. Here the source of the organoclay was a master-batch of nylon 6/organo-Mt nanocomposite. The morphology of the blend was investigated by FESEM. Through the aid of XRD and TEM, location and dispersion of organoclay was investigated. FTIR and TG study revealed the high density occupation of organoclay in the interface after removal of nylon phase. They found that the stiffness of the blend increased due to organoclay.

Zhu and Wilkie[213] reported thermal and fire properties study of polystyrene clay nanocomposites. They prepared the nanocomposites using several organophoilic clays by a bulk polymerization technique. The nanocomposites showed intercalated morphology and enhanced thermal stability even with 0.1 % clay loading.

Zhu et al.[214] investigated the fire properties of polystyrene – clay nanocomposites. They prepared these nanocomposites using a bulk polymerization technique. They modified the clay by two functionalized ammonium salts and with a phosphonium salt. Characterization by TGA/FTIR showed that degradation of the organoclays followed Hofmann Elimination mechanism. They further observed that the phosphonium modified clays was more thermally stable. They characterized the prepared nanocomposites to study the morphology, thermal properties, fire properties and mechanical properties. They found that the presence of clay significantly affected the onset degradation temperature, peak heat release rate and mass loss rate.

Akbari et al.[215] published a review regarding the effect of clay and clay modifier structure on morphology of polystyrene-clay nanocomposites. And they concluded that the clay charge density and length, bulk, polarity, functional groups and polymerizability of the modifier are very significant in case of efficiency and morphology of the nanocomposites.

Camargo et al.[216] published a review on the new application opportunities, synthesis, structure and properties of nanocomposites prepared from layered silicate clay. Here they discussed three types of matrices forming nanocomposites (metal, ceramic and polymer) and their processing, structure, properties, potential application etc. Besides clay other natural materials like chrysotile and lignocellulosic fibers were also discussed.

2.2.7.2. Adsorbents of Organic Pollutants

Rodriguez-Cruz et al.[217] studied sorption-desorption of two different hydrophobic fungicides by organoclay prepared from a series of layered and non layered clay like Mt, kaolinite, illite etc. The clays were modified with dihexadecyldimetylammonium (DHDDMA) cation, octadecyltrimethylammonium (ODTMA) and hexadecylpyridinium (HDPY) cations.

Sanchez-Martin et al.[218] studied the efficiency of a series of clay minerals such as Mt, illite, muscovite, sepiolite and palygorskite in the adsorption of the pesticides after modifying them with octadecyltrimetylammonium bromide (ODTMA). The studied the effect of the structure, the surface area and charge density of the clay minerals and the hydrophobicity of the pesticides on the adsorption process. They concluded that the higher density of ODTMA in the clay can form a more effective organic phase for the partition of the pesticides.

Xu et al.[219] investigated the structures and sorption characteristics towards HOCs of organobentonites prepared from octadecyltrimethylammonium chloride and dioctadecyldimethylammonium chloride to study the variation of sorption coefficients. They found that loading of surfactant in the organoclay had a significant effect on sorption characteristics of organoclay towards HOCs.

Wu et al.[220] investigated the quaternary salt intercalated Mt for removal of Chattonella Marina. They prepared and characterized five quaternary ammonium salt intercalated Mt. They found that the Gemini tetradecyl dimethylammonium ethyl bromide intercalated Mt was very much effective for removal of Chattonella marina. They found that with the same functional group the maximum efficiency of removal was obtained with the chain length of 14. They also concluded that when the chain length was same the efficiency of Mt modified by quaternary ammonium salt with pyridine group was higher than the than that of aliphatic quaternary ammonium salt. Their findings suggested that the modified Mt was a potential algaecide for removal of Chattonella Marina.

2.2.7.3. Rheological Control Agents

Though there are intensive researches on rheology of polymer nanocomposites, limited studies reported the rheological study of organoclays. Jordon studied swelling of organo-bentonites in different organic solvents.[40] Swelling of organo-Mt also studied by Slabaugh and Hiltner in the year 1968.[221] Jones investigated the properties and the uses of organoclays which swell in the organic solvents.[222]

Lagaly and Malberg studied the desaggregation of alkylammonium Mt clays in organic solvents.[223] They found that the disarticulation of alkylammonium Mt increased in the solvents following the order: cyclohexane (no disarticulation), alcohols, cyclohexanones, formamides, and reached the maximum in nitrobenzene. At low degrees of delamination marginal changes were observed by XRD. They expressed the extent of delamination in cyclohexanone, trimethylcyclohexanone and formamides by a hypothetical stacking number n which was deduced from the heat of immersion, $\Delta_w H$ (J g^{-1}) or $\Delta_w h$ (kJ mol^{-1}). They reported the heat of immersion for alkylammonium Mt (n_c = 1, 4, 6, 8, 10, 14, 18) in cyclohexane, cyclohexanone, 3,3,5-trimethylcyclohexanone, formamide, methylformamide, dimethylformamide and nitrobenzene. They found that the most of the energy of wetting is consumed for the reorientation of the alkyl chains from a flat to an upward position.

Okamoto et al.[224] studied the dispersed structure and rheology of suspension lipophilized-smectite (SAN)/toluene (TOL) suspensions with various concentrations using a stress-controlled rheometer and Ubbelohde type viscometer. They found that the original laminate structure in the solid state of SAN was lost as revealed by XRD. They found that dense concentration region exhibited gel-like properties. The limiting value of the dynamic storage modulus G' was deduced, whereas the loss tangent delta exhibited a constant value.

Moraru[60] investigated the structure formation of organoclay in the organic media. They investigated the gel formation in alkylammonium modified Mt in different polar liquids.

Williams-Daryn and Thomas[225] investigated swelling of the organoclay compounds in several organic solvents prepared by intercalation of vermiculite by a range of cationic surfactants. They found maximum interlayer expansion of clay-surfactant hybrids in toluene for the longest chain surfactant. They found the clay-surfactant hybrids also swollen by alkanes as well as aromatic solvents due to the greater hydrophobicity of the interior of an organoclay formed from the clay of higher charge density.

Ho and Glinka[226] studied solvent's solubility parameters on organoclay dispersions. They studied the correlation between the degree of exfoliation of organoclays and the solvent with Hansen's solubility parameters. They found that the dispersion force of the solvent was the principal factor to determine for the clay platelets remain suspended in the solvent. They further found that the polar and hydrogen-bonding forces affected the tactoid formation among the suspended platelets.

Burgentzle et al.[227] investigated the dispersion of organo-Mt in different organic solvents commonly used as dispersion media for polymer coatings. They studied the suspensions in three scales: at (i) nanometer scale, when solvent surface energy is greater than organoclay surface energy resulting swelling of organoclays in the interlayer (ii) micrometer scale by studying rheology of clay suspensions and gel formation (iii) macroscopic scale by studying macroscopic swelling of organoclays in the solvents.

Patel et al.[228] reviewed the various use of organoclays as rheological modifier for paints, inks and greases, reinforcements in polymer nanocomposites, drug delivery vehicle for controlled release of therapeutic agents and in treatment of industrial waste water.

King et al.[229] characterized an organo-Mt clay dispersed in three different nonaqueous solvents using a combination of X-ray scattering, small-angle neutron scattering (SANS) and ultrasmall angle neutron scattering (USANS) together with rheological measurements. They presented a structural model for the incompletely dispersed clay as made of randomly oriented tactoids from partially overlapping clay sheets. Their model was related to a power law of about -3 over a wide range of wave numbers below the intersheet correlation peak. Their rheology data showed that both storage and loss moduli, along with yield stress scale with a power law in volume fraction of about three. They predicted the gel point equating the gel onset composition with the overlap of randomly oriented tactoids.

Wang et al.[230] synthesized organoclay from synthetic laponite by cetyltrimethylammonium bromide (CTAB) and characterized by simultaneous SAXS and WAXS, FESEM, TEM, EDS, AFM and thermal analysis. They studied the rheometry of the organoclay as well. They investigated the electrorheological effect by dispersing the organoclay in silicone oil. They observed an optimum electrorheological effect could be attained at a particular CEC substituted concentration.

Timochenco et al.[231] studied swelling of organoclays in styrene and its consequent effect on flammability of polystyrene nanocomposites.

2.2.7.4. Drug Delivery System

Davis et al.[232] studied the interactions of the amino acid lysine with sodium Mt using theoretical molecular modeling methods. They found that the interlayer spacing of Mt increased by water molecules incorporation. They performed molecular mechanics calculations. The results indicated the preponderance of configurations of surface-sodium-amino acid complexes with a variety of spatial arrangements.

Park et al.[233] synthesized donepezil molecules intercalated smectite clays (laponite XLG, saponite, and Mt) for a drug delivery system. X-ray Diffraction, TG analysis and FTIR spectra confirmed that donepezil molecules were intercalated in the interlayer space of clay forming mono or double layer stacking. They found that the adsorption amount and molecular structure of donepezil was dependent on the CEC of the clay and controlled the drug release patterns. They coated the intercalated smectite clays with Eudragit (R) E-100 using a spray dryer which enhanced the release rate.

Wang et al.[234] used the hot intercalation technique to prepare quaternized chitosan/Mt (HTCC/Mt) nanocomposites for a drug delivery system. TEM, XRD and FTIR study confirmed the intercalation of HTCC in the interlayer of Mt. Then they modified the prepared nanocomposites to prepare nanoparticles and evaluated its drug-controlled release behaviours. They found that Mt loaded with quaternized chitosan enhanced the drug encapsulation efficiency of the nanoparticles and slowed the drug release from the nanocomposites compared to pure HTCC nanoparticles.

Joshi et al.[235] studied the use of Mt as a drug delivery carrier for timolol maleate (TM), a nonselective beta-adrenergic blocking agent. They demonstrated the intercalation of TM into the interlayer of Mt at different pH and initial concentration. The characterization of prepared Mt-TM hybrid by XRD, FTIR and thermal analysis proved that TM was successfully intercalated into the interlayer of Mt. They observed controlled release of TM from Mt-TM hybrid during in vitro release experiments.

Joshi et al. in another paper[236] investigated the intercalation of vitamin B-6 (pyridoxine, VB6) into Mt as a controlled release drug carrier. They investigated the intercalation of VB6 into Mt at different times, temperatures, pH values and initial concentration. The characterization of the Mt-VB6 hybrid by XRD, FTIR and thermal studies proved successful incorporation of VB6 on Mt. They found that VB6 was steadily released from the Mt-VB6 hybrid and was pH-dependent.

Joshi et al.[237] investigated Vitamin B-1 (thiamine hydrochloride, VB1) intercalated Mt as a drug carrier. The found a gradual increase in adsorption of VB1 on Mt with increasing reaction temperature. They found that release profile of intercalated VB1 followed Higuchi kinetic model and the diffusion-controlled mechanism. It was also observed that VB1 was released from Mt-VB1 steadily as a function of pH.

2.2.7.5. Antibacterial Application

Xie et al.[238] investigated the antibacterial activity of the modified Mt. They prepared tetradecyldimethylbenzyl ammonium salt modified Mt and characterized the organoclay by FTIR, TGA, and XRD. Their investigation showed that the prepared organoclay was able to kill all the Staphylococci aureus and more than 99.99% of the Escherichia coli in a sample solution within 6 hour and thus found effective for antibacterial activity.

He et al.[239] prepared a series of organoclays with antibacterial activity from Ca-Mt and Chlorhexidini Acetas (CA) by ion-exchange. They assayed the antibacterial activities by halo method. They investigated the structure of the CA within the clay interlayer. The decrease of surface adsorbed water and interlayer water found in TG due to replacement of hydrated cations by cationic surfactant further supported by FTIR study. They concluded that antibacterial activity strongly depended on the CA content.

Hong and Rhim[240] investigated the antibacterial activities of three kinds of commercial Mt. They are naturally occurring one Cloisite Na$^+$ and two organically modified clays. Organoclays were Cloisite 20A and Cloisite 30B. These were used against four representative pathogenic bacteria. They concluded that antimicrobial activity was dependent on the type of organoclay and microorganisms. They found that Cloisite 30B had the highest antibacterial activity followed by Cloisite 20A. No antibacterial activity was shown by Cloisite Na$^+$. SEM and TEM images of cell structure confirmed that the organoclay caused inactivation of the bacteria.

Al-Sigeny et al.[241] synthesized organoclay by cation exchange between Na-Mt and vinyl benzyl triphenyl phosphonium chloride in an aqueous solution. Then they prepared a nanocomposite consisting of 4-acryloyl morpholine-chitosan and organoclay by ray irradiation polymerization. They found that the copolymer nanocomposite based on phosphonium group had broad spectrum against pathogenic bacteria such as Staphylococcus aurius, Escherichia coli and Aspergillus flavus fungi.

Meng et al.[242] prepared chlorhexidine acetate (CA)/Mt intercalation composites and evaluated its antibacterial potential with pathogenic bacteria, Staphylococcus aureus and Pseudomonas aeruginosa. They assayed the antibacterial activity by the inhibitory zone method. They found that the prepared hybrid inhibited the growth of a wide variety of microorganisms, Gram-positive bacteria and Gram-negative bacteria.

Hua et al.[243] prepared a pH-sensitive ofloxacin (OFL)/Mt/chitosan (CTS) nanocomposite microspheres to improve the burst release effect of the drug by the solution intercalation technique and emulsification crosslinking techniques. So they prepared OFL/Mt hybrids first through the solution intercalation technique and then OFL/Mt-intercalated OFL/Mt/CTS nanocomposite microspheres by emulsification crosslinking techniques. The intercalation was confirmed by characterization of nanocomposites by FTIR and XRD. They investigated the effect of Mt content on drug encapsulation efficiency and the drug release of the nanocomposite microspheres. They found that the release rate of OFL from the nanocomposite microspheres at pH 7.4 was higher than that at pH 1.2. They further found that incorporation of a certain amount of Mt enhanced the drug encapsulation efficiency and reduced the burst release.

Joshi et al. in their another paper [244] proposed a formulation of Mt and Eudragit (R) L 100 55 for controlled delivery of buspirone hydrochloride (BUH). For that purpose they studied intercalation of Mt and BUH under different reaction conditions. Their study showed controlled release of intercalated drugs from Mt-

BUH composite. They found that the presence of Eudragit (R) L 100 55 decreased the rate and amount of drug release.

Joshi et al.[245] discussed the suitability of Mt as a drug delivery carrier. For that purpose they formulated a clay drug composite of ranitidine hydrochloride (RT) intercalated in Mt. The prepared hybrid was coated with cationic polymer Eudragit (R) E-100. They found that in the case of Mt RT/Eudragit (R) E-100, both the release rate and the release percentages noticeably increased compared to the release processes of RT from Mt RT.

Kevadiya et al.[246] investigated Mt-alginate nanocomposites as a drug delivery system monitoring the intercalation and in vitro release of Vitamin B-1 and Vitamin B-6.

Viseras et al.[247] reviewed the current challenges of clay minerals in drug delivery. They found that clay minerals interact with drug molecules as well as with polymer, inactive part of medicinal component. Their review discussed recent advances in use of Mt and saponite in drug delivery. They also discussed the extensive use of synthetic clay minerals like laponite and layered double hydroxides. They also observed that preparation of composites with clay mineral particles in polymeric matrices in form of films, nanoparticles, hydrogels etc. was chosen extensively rather than use of the single component.

2.2.7.6. Catalyst Application

Leone et al.[248] synthesized organo-Mt for using as inorganic carriers for $CoCl_2(P^tBu_2Me)_2$-MAO catalyst in the polymerization of 1,3-butadiene, yielding cis-1,4-enriched polybutadiene. They prepared the organoclays by intercalation of Mt with (*ar*-vinyl-benzyl) trimethyl ammonium chloride salt through an ion exchange reaction and then grafting the edge-surface grafting by trimethylchlorosilane. They found that the grafted silane prevented the methylaluminoxane (MAO) cocatalyst from reacting with the edge-OHs. After that MAO led to methylation of the cobalt complex and carbanion abstraction to give a

cobalt-methyl cation which was stabilized by the MAO anion. They found that the nanoconfined cationic alkylated species inserted the butadiene on the Co-Me bond directing the growth of the polymer chains within the clay layers. The growth of the macromolecular chains in the interlayer silicate region produced an intercalated polybutadiene rubber nanocomposite.

Above review of literature reveals that studies on intercalation of smectites remains a dynamic research area. Useful products can be prepared by intercalating smectites for application in clay containing polymer nanocomposites, as adsorbents of organic pollutants, rheological control agents, drug delivery system, antibacterial and catalyst application. Although reserves of bentonite exist all over the world, smectite clays extracted from it varies widely in mineralogical compositions, layer charges and textures. Surprisingly, this variation in properties of montmorillonite raw material is less reported in the vast literature on intercalation of montmorillonite for different end use. Montmorillonite, like any clay has complex properties which are very sensitive to small variation in clay layer structure. To achieve commercial success of these organoclays, the properties of the montmorillonite as a raw material should not be overlooked. The high cost of purification and separation of montmorillonite phase is a deciding factor in techno-economic success of organically modified montmorillonite. Montmorillonite with low cation exchange capacity and high iron content are abundant in nature. It can be used as cheaper source of montmorillonite, but detailed scientific studies on it are rare compared to conventional montmorillonite with high purity and CEC. So, in the present investigation an attempt has been made to incorporate low-CEC and iron-rich montmorillonite of Indian origin as the smectite clay for the intercalation. The structure and properties of prepared organoclays were compared with that of a standard high CEC and low iron containing montmorillonite as a reference. This study is expected to be useful towards use of low CEC, high iron containing variety of montmorillonite as a precursor to prospective nanoclay for various applications.

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