Organic Modification of Clay

A

Thesis Submitted

in partial fulfillments of requirements for the

Degree of

Master of Science in Chemistry

Submitted By

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I thank all my friends who constantly motivated me and supported me throughout the project.

Pankil Singla

Pankil Singla

Candidate's Declaration

I hereby declare that the work being presented in the dissertation entitled **"Organic Modification of Clay",** in partial fulfillment of the requirements for the award of the degree of Masters in Chemistry, School of Chemistry and Biochemistry (SCB), Thapar University, Patiala, is my own work during the period of Jan 2009 to May 2009, under the supervision of Dr. Rajeev Mehta, Associate professor of Department of Chemical Engineering, Thapar University, Patiala. I have not submitted the matter embodied in this dissertation for the award of any other degree.

Patiala

Date: 3rd June, 2009

Pankil Singla

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This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

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Certificate

This is to certify that the project entitled **"Organic Modification of Clay",** being submitted by Ms. Pankil Singla in partial fulfillment of the requirement for the award of degree of Master of Science in the School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonifide work carried out under the supervision of Dr. Rajeev Mehta and that no part of this project has been submitted for the award of any other degree.

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Introduction

Clays find wide range of applications, in various areas of science, due to their natural abundance and the propensity with which they can be chemically and physically modified to suit practical technological needs. In recent years polymer/layered silicates nanocomposites have attracted great interest, both in industries and academia. This report highlights the modification of Montmorillonite Clay. Montmorillonite (MMT) is commonly used as a nanofiller in the preparation of polymer nanocomposites. MMT structure, uses and the need for modification of Clay are discussed in this section.

1.1 What is Clay?

Clay is a naturally occurring material composed primarily of fine-grained minerals, which show plasticity through a variable range of water content, and which can be hardened when dried or fired. Clay deposits are mostly composed of clay minerals (phyllosilicate minerals) and variable amounts of water trapped in the mineral structure by polar attraction. Organic materials which do not impart plasticity may also be a part of clay deposits. Figure 1.1 shows the naturally occurring Clay.

Fig.1.1 Natural Clay

Clays are distinguished from other fine-grained soils by various differences in composition. Silts, which are fine-grained soils which do not include clay minerals tend to have larger particle sizes than clays but there is some overlap in both particle size and other physical properties, and there are many naturally occurring deposits which include both silts and clays. The distinction between silt and clay varies by discipline. Geologists

and soil scientists usually consider the separation to occur at a particle size of 2 μm (clays being finer than silts), sedimentologists often use 4-5 μm, and colloid chemists use 1 μm. Geotechnical engineers distinguish between silts and clays based on the plasticity properties of the soil, ISO 14688 grades: clay particles as being smaller than 0.063 mm and silts one larger.

Depending upon academic source, there are three or four main groups of clays: kaolinite, montmorillonite-smectite, illite and chlorite. Chlorites are not always considered a clay, sometimes being classified as a separate group within the phyllosilicates. There are approximately thirty different types of "pure" clays in these categories but most "natural" clays are mixtures of these different types along with other weathered minerals.

1.2 Clay Minerals

Clay minerals are hydrous aluminium phyllosilicates, sometimes with variable amounts of iron, magnesium, alkali metals, alkaline earths and other cations. Clays have structures similar to the micas and therefore form flat hexagonal sheets. Clay minerals are common weathering products (including weathering of feldspar) and low temperature hydrothermal alteration products. Clay minerals are very common in fine grained sedimentary rocks such as shale, mudstone and siltstone and in fine grained metamorphic slate and phyllite.

Clay minerals include the following groups:

- Kaolin group which includes the minerals kaolinite, dickite, halloysite and nacrite. Some sources include the serpentine group due to structural similarities (Bailey 1980).
- Smectite group which includes dioctahedral smectites such as montmorillonite and nontronite and trioctahedral smectites for example saponite.
- Illite group which includes the clay-micas. Illite is the only common mineral.
- Chlorite group includes a wide variety of similar minerals with considerable chemical variation.

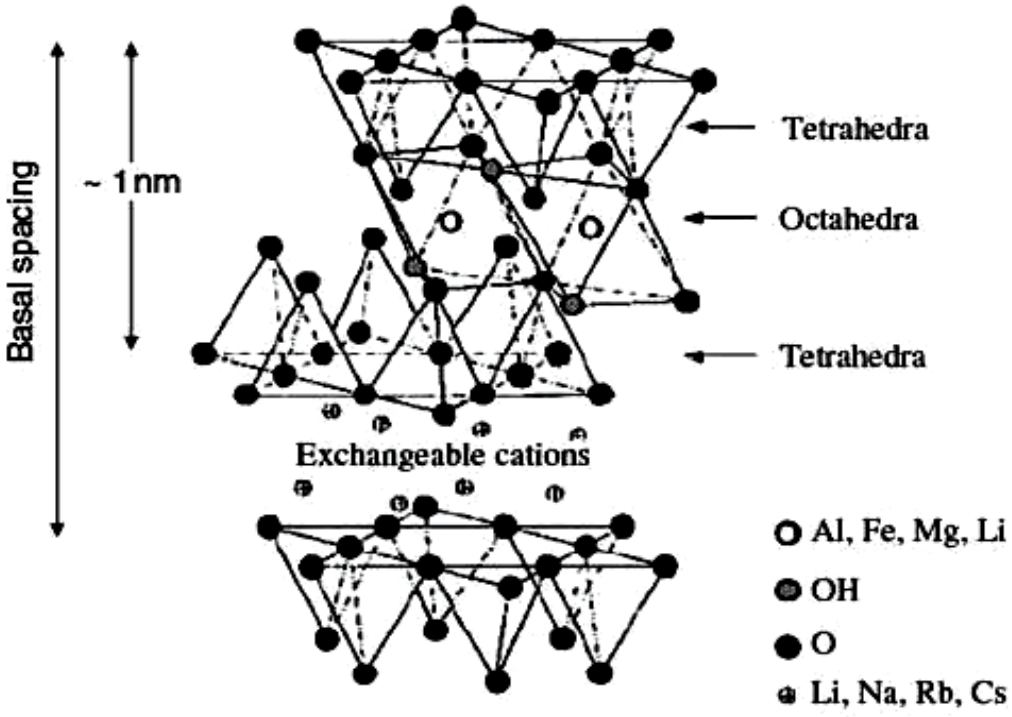


Fig.1.2 Structure of clay

Clay minerals are characterised by

1. Two-dimensional sheets of corner sharing SiO_4 and AlO_4 tetrahedra. These tetrahedral sheets have the chemical composition $(AlSi)_3O_4$, and each tetrahedron shares 3 of its vertex oxygen atoms with other tetrahedra forming a hexagonal array in two-dimensions as shown in above Figure 1.2. The fourth vertex is not shared with another tetrahedron and all of the tetrahedra "point" in the same direction.
2. In clays the tetrahedral sheets are always bonded to octahedral sheets formed from small cations, such as aluminium or magnesium, coordinated by six oxygen atoms shown in Fgure.1.2.
3. The unshared vertex from the tetrahedral sheet also form part of one side of the octahedral sheet but an additional oxygen atom is located above the gap in the tetrahedral sheet at the center of the six tetrahedra. This oxygen atom is bonded to a hydrogen atom forming an OH group in the clay structure.

4. Clays can be categorized depending on the way that tetrahedral and octahedral sheets are packaged into layers. If there is only one tetrahedral and one octahedral group in each layer the clay is known as a 1:1 clay. The alternative, known as a 2:1 clay, has two tetrahedral sheets with the unshared vertex of each sheet pointing towards each other and forming each side of the octahedral sheet.
5. Depending on the composition of the tetrahedral and octahedral sheets, the layer will have no charge, or will have a net negative charge. If the layers are charged this charge is balanced by interlayer cations such as Na^+ or K^+. In each case the interlayer can also contain water. The crystal structure is formed from a stack of layers interspaced with the interlayer.

1.3 Montmorillonite Clay (MMT)

Montmorillonite is a very soft phyllosilicate mineral that typically forms in microscopic crystals, forming a clay. It is named after Montmorillon in France. Montmorillonite, a member of the smectite family, is a 2:1 clay, meaning that it has 2 tetrahedral sheets sandwiching a central octahedral sheet as shown in Figure 1.3. The particles are plate-shaped with an average diameter of approximately 1 micrometer. It is the main constituent of the volcanic ash weathering product, bentonite.

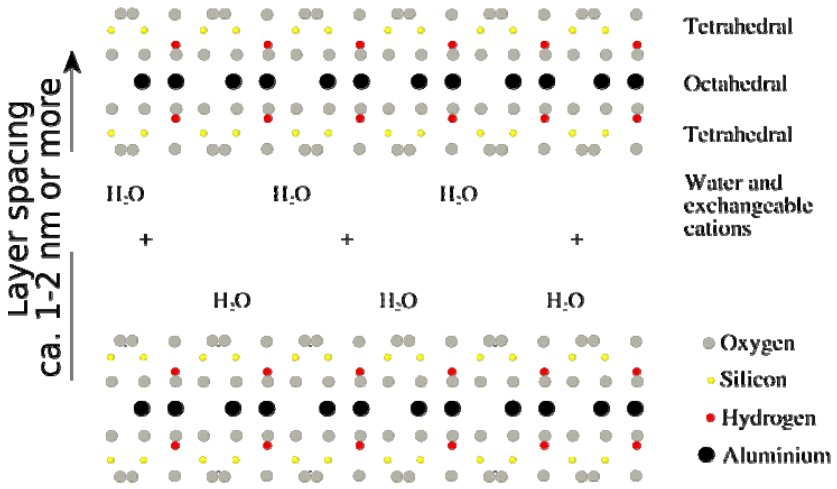


Fig.1.3 Structure of MMT clay

Montmorillonite's water content is variable and it increases greatly in volume when it absorbs water. Chemically it is hydrated sodium calcium aluminium magnesium silicate hydroxide $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2.nH_2O$.

Potassium, iron, and other cations are common substitutes, the exact ratio of cations varies with source. It often occurs intermixed with chlorite, muscovite, illite, cookeite and kaolinite.

1.3.1 Uses

Montmorillonite swells with the addition of water. However, some montmorillonites expand considerably more than other clays due to water penetrating the interlayer molecular spaces and concomitant adsorption. The amount of expansion is due largely to the type of exchangeable cation contained in the sample. The presence of sodium as the predominant exchangeable cation can result in the clay swelling to several times its original volume. Hence, sodium montmorillonite has come to be used as the major constituent in non-explosive agents for splitting rock in natural stone quarries in order to limit the amount of waste, or for the demolition of concrete structures where the use of explosive charges is unacceptable.

This swelling property makes montmorillonite-containing bentonite useful also as an annular seal or plug for water wells and as a protective liner for landfills.

1.3.2 Objective of Modification of Clay

Montmorillonite, and other layered silicate clays, are naturally hydrophillic. This makes them poorly suited to mixing and interacting with most polymer matrices which are mostly hydrophobic.

Moreover, the stacks of clay platelets are held tightly together by electrostatic forces. As shown in figure 1.4, counterions are attracted to the net negative charge within the clay platelets. The counterions can be shared by two neighboring platelets, resulting in stacks of platelets that are tightly held together.

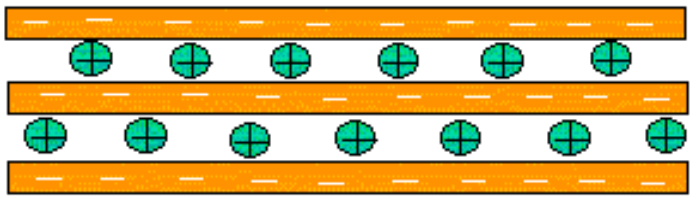


Fig. 1.4 layered structuere of silicate clay

For these reasons, the clay must be treated before it can be used to make a nanocomposite.These stacks of clay platelets are much larger than one nanometer in every dimension. Making a composite out of untreated clay would not be a very effective use of material, because most of the clay would be stuck inside, unable to interact with the matrix.

A popular and relatively easy method of modifying the clay surface, making it more compatible with an organic matrix, is ion exchanging. The cations are not strongly bound to the clay surface, so small molecule cations can replace the cations present in the clay. For example, in the picture below, the gray cations are sodium ions. Some of them have been replaced by another cations.

If the black cations are quaternary ammonium ions with long alkyl chains, this clay would be much more compatible with an organic matrix. By exchanging it with various organic cations, montmorillonite clay can be compatibilized with a wide variety of matrix polymers. At the same time, this process helps to separate the clay platelets so that they can be more easily intercalated and exfoliated.

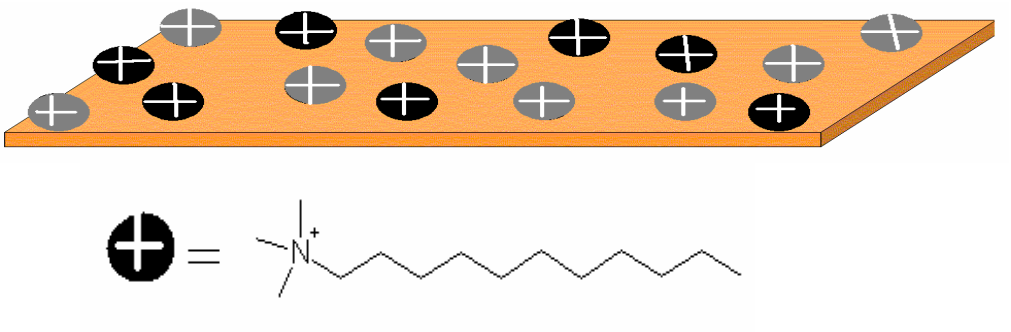


Fig.1.5 Clay surface containing organic and metal ions

2.0 Literature Review

The first generation of MMT-based organoclays employed ammonium surfactants. Ammonium surfactants used in commercially available organoclays usually incorporate short aliphatic chains and benzyl and sometimes hydroxyl groups. They also contain at least one long aliphatic chain (C 12-C 18) to cause expansion of the distance between the layers (Liu et al, 2005, Zha et al., 2005, Tanoue et al., 2004, Carastan and Demarquette, 2006, Kim et al., 2003, Lee and Kim, 2004, Zhang et al., 2004). Other MMT modifiers include alkyl amines (Li and Ishida, 2003), alkyl carbazol (Chigwada et al., 2005), poly(dimethylsiloxane) (Li and Ishida, 2005) and quinolinium or pyridinium (Chigwada et al., 2006).

Other ammonium surfactants are more complex molecules (Yao et al., 2002, Yein et al., 2005, Chigwada et al., 2006 b), oligomers (Chen and Vyazovkin, 2006, Lagaly and Ziesmer, 2005, Sepehr et al, 2005, Zheng and Wilkie, 2003, Gilman et al., 2000) and reactive groups (Ding et al., 2005, Zhang and Wilkie, 2004, Bourbigot et al., 2003).The low thermal stability of ammonium surfactants presents a problem for melt compounding and processing of polymer nanocomposites, where high processing temperatures exceeding 200 °C are commonly encountered. Thermal degradation during processing could initiate/catalyze polymer degradation, in addition to causing a variety of undesirable effects during processing and in the final product.

Efforts have been made to synthesize thermally stable organoclays based on stibonium (Wang and Wilkie, 2003) or imidazolium surfactants (Bourbigot et al., 2003). Phosphonium surfactants have been used in the preparation of organoclays (Maiti et al., 2002, Zhu et al., 2001, Hartwig et al., 2003, Hrobarikova et al., 2004, Kim et al., 2004, Xie et al., 2002). These phosphonium surfactants incorporate mainly short alkyl chains, benzene and usually a long alkyl chain. Arroyo et al (2006) reported the synthesis of a promising organoclay based on triphenyl vinylbenzyl phosphonium chloride. The organoclay exhibited substantially higher thermal stability than ammonium surfactant modified organoclays. The basal spacing of the resulting organoclays depends on the chemical structure of the surfactant, the degree of cation exchange, and silicate layer

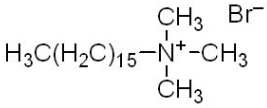
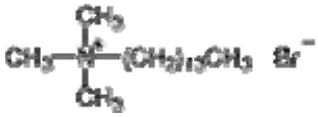
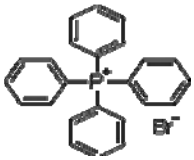
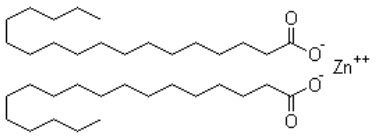
thickness (Maiti et al., 2002). Xie et al (2002) found that the thermal stability of phosphonium organoclays is superior to that of ammonium organoclays.

3. Experimental Section

3.1 Materials

Unmodified montmorillonite clay with Cation Exchange Capacity 86 meq/100gm was supplied by GM Chemicals Ahmedabad. The surfactants were purchased from SD fine chemicals. The basal spacing of MMT is 7.599 Å. This MMT was used as such without any further purification. The chemical composition of the surfactants is given in Table 1

Table 1. Main characteristics of surfactants

Surfactant, MW (g/mol)	Chemical structure	% purity
Dodecyltrimethylammonium bromide, 308.3		98%
Hexadecyltrimethylammonium bromide, 364.45		99%
Tetradecyltrimethylammonium bromide, 336.41		97.5%
Tetraphenylphosphonium bromide, 419.3		98%
Zinc stearate, 632.2		-----

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3.2 Method of Preparation of organoclay

Two procedures for modification of MMT clay were followed, depending upon the solubility of salts in aqueous phase, which are similar to the procedure reported by Calderon. J.U. (2008).

The following procedure was used for the salts which were soluble in aqueous phase. 5 gm of sodium MMT were dispersed in 500 ml of distilled water for 24 h at room temperature, using a magnetic stirrer. Using an aqueous solution of salt, the amount of surfactant added was equivalent to the CEC of clay. The cation exchange reaction occurs rapidly. The resulting organoclay suspension was mixed further for 12 h. The suspended organoclay was filtered under vacuum, using whatman filter paper. The resulting organoclay was dispersed into 50 ml of fresh distilled water and mixed further for 4 h. No chloride traces were detected by addition of silver nitrate, after two washing. The resulting organoclay was dried at 60 ^{o}C for 24 h under vacuum. Finally the resulting material was ground, using a Pestle Mortar for 30 s, in order to obtain a fine powder. The organoclay product was stored in a desiccator.

The procedure to produce organoclays with water insoluble salts was as follows. 5 gm of sodium MMT were dispersed into 500 ml of distilled water at room temperature, using a magnetic stirrer. After 24 h, mixing was stopped and 200 ml of diethyl ether solution of salt, containing the stochiometric amount of salt corresponding to the CEC of MMT, was slowly poured into the clay dispersion. The resulting system contained a clear upper organic phase and a turbid bottom mineral phase. After 12 h of moderate mixing, the mineral phase became transparent and the organic phases became turbid. Special care was taken to avoid diethyl ether evaporation. At this point, the system was warmed up to evaporate the diethyl ether (60 °C), using a Rota-evaporator. After solvent evaporation, the organic phase became a sticky solid precipitate. The precipitated organoclay was filtered and dispersed in hot water (80 °C) for 4 h. Washing was repeated three times, until no chloride traces were detected with silver nitrate after the third washing. The resulting organoclay paste was manually mixed with 40 ml of petroleum

ether using a spatula. After free petroleum ether evaporation, using Rota-evaporator, the organoclay was dried at 80 °C for 24 h under vacuum. Then it was ground, using a Pestle Mortar.

4.0 Characterization techniques

X-ray Diffraction

The initial basal spacing in the organoclay is an important parameter for the determination of the potential for polymer intercalation. This is determined by X-ray diffractometer. X-ray diffraction (XRD) was performed on dried powder samples. The organoclays were grounded into a fine powder prior to XRD measurements using a Pestle Mortar with sufficient pressure so as to make a fine powder. The scans were performed for each sample and the values are reported for the basal spacing in Table 3. The x-ray diffraction patterns were obtained using a XPERT-PRO x-ray diffractomer with CuKα radiation (λ=1.54 Å). The experiments were run at room temperature with an angle range (*2*θ) from 4° to 15° for Zinc stearate and 2° to 70° for rest of the four ions at 4°/min and step size of 0.02°. The machine was operated at 40 kV and 40 mA.

Thermogravimetry

Thermogravimeteric Analysis is done to elucidate decomposition behavior thermally. The weight loss arising from the degradation was studied by TGA (Perkin Elmer Diamond TG/DTA instrument. Samples of 5–7 mg were heated from 50 °C to 650 °C at a rate of 10 °C/min. The TGA trace was used to determine the % weight loss at 650 °C which is sufficient temperature to degrade the organic content present in modified MMT clay.

5. Results and Discussion

5.1. X-ray Diffraction

XRD of different samples of modified MMT clay give the values of basal spacing. The basal spacing of the different samples are given in Table 3. The basal spacing of unmodified MMT clay is termed as initial basal spacing (0.75 nm at $2\theta = 11.64$). After modification of clay the basal spacing increased, by treating it with different organic cations. An increase of the interlayer distance, leads to a shift of the diffraction peak toward lower angles. After treating unmodified MMT clay with Zinc Stearate, the diffraction peak shifts to lower angle i.e. $2\theta = 6.32$ and basal spacing increases from 0.75 nm to 1.39 nm. Similarly, when it is treated with Triphenyl phosphonium ion then the basal spacing increases to 2.26 nm which is sufficiently large value for its potential as a reinforcement as a polymer nanocomposites.

The experimental values are found to be in good except for ammonium ion modified clay where the effect on basal spacing does not exist.

Table 3. Basal Spacing of clay Vs Surfactants

S.No	Organo-montmorillonite clay	Final basal spacing, nm, (2θ)
1.	Zn stearate-MMT	1.39, (6.32)
2.	TPP-MMT	2.26, (3.90)
3.	DTMA-MMT	0.74, (11.80)
4.	HDTMA-MMT	0.73, (12.04)
5.	TDTMA-MMT	0.73, (11.96)

The increase in value of basal spacing depends upon two factors. One is the presence of large hydrophobic groups on surfactants and second is the decrease in surface energy of MMT. As the size of hydrophobic groups increases the basal spacing increases to a large extent.

The initial basal spacing in the organoclay is an important parameter for the determination of the potential for polymer intercalation and clay mineral delamination. Organoclays with smaller interlayer distances have reduced probabilities for polymer intercalation.

5.2. Thermogravimetric Analysis

TGA gives the information about the thermal stability of the organoclay. The TGA curves for unmodified Na-MMT clay and organically modified clays are shown in Fig. 1. It is noted that the TGA of the unmodified montmorillonite has three mass loss steps: Between ambient and 100 °C, at 135 °C and at 450 °C. These mass loss steps are attributed to desorption of water from the clay, dehydration of the hydrated cation in the interlayer and the dehydroxylation of the montmorillonite respectively.

Four steps of the mass loss steps are observed for the organoclays. In case of TPP-MMT, the first step is from the ambient to 66.9 °C and is attributed to the desorption of water. The second step occurs from 135.5 °C to 310 °C and is assigned to the loss of hydration water from the Na^+ ion. The third mass loss step is attributed to the removal of the surfactant at around 440 °C. The fourth mass loss step in the TGA curves is assigned to the loss of structural hydroxyl groups from within the clay. It is around 580 °C. This is an indication of the thermal stability of modified clay.

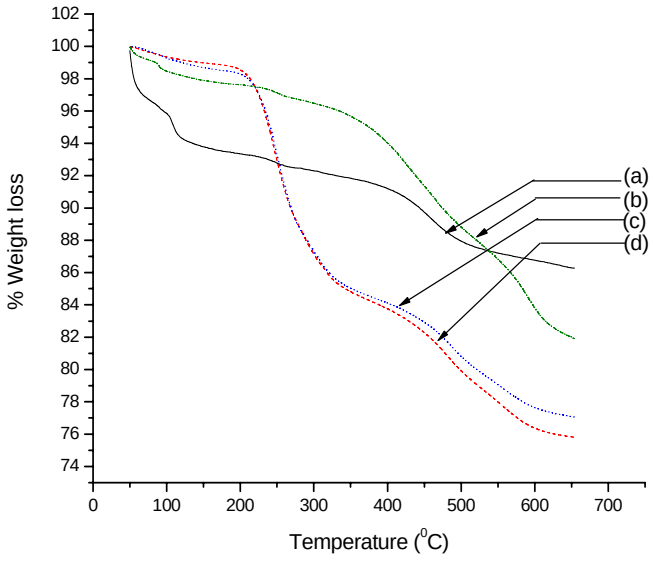

Fig. 1 TGA curves for Unmodified NaMMT clay and organically modified montmorillonites. (a) Unmodified NaMMT clay, (b) Triphenyl phosphonium-MMT clay, (c) Dodecyltrimethyl ammonium-MMT clay, (d)Tetradecyltrimethyl ammonium-MMT clay.

Further, the TGA curve of TDTMA-MMT and DTMA-MMT clay shows first degradation step from ambient to 70 °C temperature range. The second step occurs from 245 °C to 326 °C and third step occurs at 490 °C. The fourth step occurs at 560 °C. In Fig. 2, The decomposition pattern of Zinc Stearate-MMT clay shows decomposition starts at 270 °C and then it completely degrades at 500 °C.

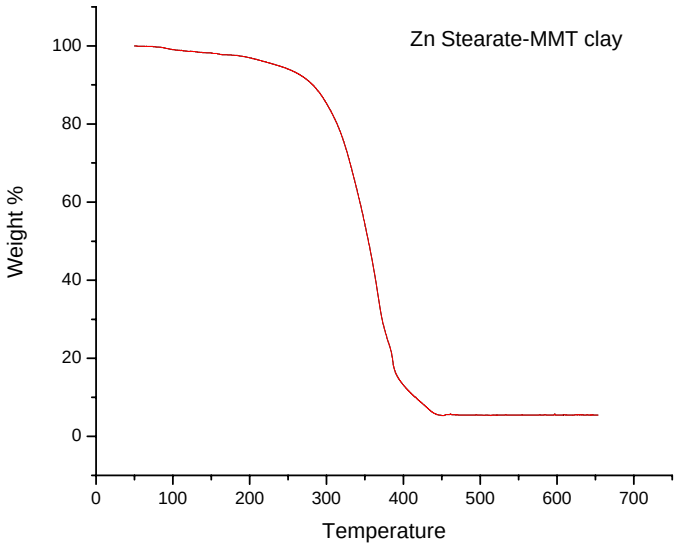

Fig. 2 The TGA curve showing thermal decomposition of Zinc stearate modified montmorillonite clay

The first and second decomposition steps are important for utility of such organically modified montmorillonites in polymer-based composite materials prepared via melt state processing, as most polymers are processed within this temperature range. Hence, these new OMMTs can be used for preparing organic–inorganic hybrids by melt processing with thermoplastic polymers such as polypropylene (PP), polystyrene (PS), Poly(methyl methacrylate) (PMMA) and others which are relatively polar, as well as for other applications and fields of technology.

6. Conclusion

Montmorillonite Clay is a phyllosilicate mineral having sheet like structure which is used as nanofiller in the preparation of polymer nanocomposites. Montmorillonite has been successfully modified using organic cationic surfactants. The XRD results show intercalation of the organic cations between the clay mineral layers. The ammonium-MMT clay does not show increase in basal spacing. One of the reasons can be the experimental procedure which is used for the ions which are soluble in aqueous phase.

The TGA curves for these organoclays show the degradation due to residual water desorption, dehydration, followed by decomposition of the organic modifier. These organically modified montmorillonites have potential utility in the preparation of polymer nanocomposites and in other possible applications. The organoclays prepared in this study can be used to prepare nanocomposites with polar polymers in order to render good level of dispersion, improved mechanical and other properties.

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