

Clay Modification by the Use of Organic Cations

Pankil Singla¹, Rajeev Mehta^{2*}, Siddh Nath Upadhyay³

¹School of Chemistry and Biochemistry, Thapar University, Patiala, India

²Department of Chemical Engineering, Thapar University, Patiala, India

³Department of Chemical Engineering, IT-BHU, Varanasi, India

Email: *rajeevmehta33@yahoo.com

Received November 16, 2011; revised December 25, 2011; accepted January 5, 2012

ABSTRACT

To render layered silicates miscible with polymer matrices, one must convert the normally hydrophilic silicate surface to an organophilic one, making the intercalation of polymeric chain between silicate layers possible. This can be done by ion-exchange reactions with cationic surfactants. Sodium montmorillonite (Na-MMT) was modified with several organic cationic surfactants. Organoclays with water soluble surfactants were prepared by the traditional cation exchange reaction. An alternative procedure was used to prepare organoclays with water insoluble salts. The basal spacing and thermal behavior of organoclays were characterized by X-ray diffraction, XRD and Thermogravimetric analysis, TGA respectively.

Keywords: Montmorillonite; Organo-Montmorillonite; Surfactant; Basal Spacing

1. Introduction

In recent years polymer/layered silicates nanocomposites have attracted great interest, both in industries and academia. Montmorillonite (Na-MMT) is commonly used as a nanofiller in the preparation of polymer nanocomposite. The possible application of generated organoclay is the better intercalation of polymer chains between stacks of MMT clay. The modified Na-MMT is used for making eco-friendly polymer clay nanocomposite with improved physical and mechanical properties.

Montmorillonite, and other layered silicate clays are naturally hydrophilic. This makes them poorly suited to mixing and interacting with most polymer matrices which are mostly hydrophobic [1-3]. Moreover, the stacks of clay platelets are held tightly together by electrostatic forces. For these reasons, the clay must be treated before it can be used to make a nanocomposite. Making a composite out of untreated clay would not be a very effective because most of the clay would be unable to interact with the matrix. An easy method of modifying the clay surface is traditional ion exchange method. The cations are not strongly bound to the clay surface, so small molecule cations can replace the cations present in the clay. By exchanging ions present in between layers 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.

By exchanging of sodium cations for organic cations that are also called surfactants, the surface energy of MMT decreases and the interlayer spacing expands. The resulting material is called organoclay. The basal spacing of the resulting organoclays depends on the chemical structure of the surfactant, the degree of cation exchange, and silicate layer thickness [4]. Organically modified montmorillonites have been widely studied fundamentally and in practical applications in the area of organic-inorganic hybrids, composites and nano-scale composites [5]. Ammonium surfactants used in commercially available organoclays usually incorporate short aliphatic chains and benzyl groups [7-9]. Phosphonium surfactants have been used in the preparation of organoclays [10-14]. Phosphonium surfactants are thermally stable than ammonium surfactants.

In this paper, we present preparation and characterization of new organo-montmorillonite clays by using ammonium surfactant and phosphonium surfactant which contain one or more hydrophobic groups such as long alkyl chains, phenyl and stearate. We report the basal spacing by XRD measurements and thermal behavior by TGA.

2. Experimental Section

2.1. Materials

Unmodified montmorillonite clay with Cation Exchange Capacity, CEC 86 meq/100 g was supplied by GM Chemicals, Ahmadabad. The surfactants were purchased from

*Corresponding author.

SD fine chemicals and used as received. The basal spacing of MMT is 0.75nm. This MMT was used as such without any further purification. The specification of clay is given in **Table 1**. The solvent diethyl ether and petroleum ether were used without further purification. However realizing that these solvents are not ecofriendly, hence almost all the solvent recovered by using rota-evaporator.

2.2. Choice of Organic Cations

The chemical composition of the surfactants is given in **Table 2**. The surfactants were used on the basis of the long hydrophobic carbon chains attached to the central atom. It results in increasing surface area that will lead to better intercalation of organic cation between the layers of unmodified MMT clay. Phosphonium ion has four phenyl rings attached to it. The rigidity of the phenyl groups facilitates packing and elevates the melting point relative to quaternary ammonium salts. Zinc Stearate is a fatty acid which has hydrophobic effect. Its main application areas are the plastics and rubber industry where it is used as a releasing agent and lubricant which can be easily incorporated. The potential application of surfactants used is their role in biological system. They play a vital role in drug delivery. Specifically quaternary ions are used on skin for cleansing wounds or burns. They are mostly used for their disinfectant and preservative prop-

erties as they have good bactericidal properties. Hence the used surfactants have wide potential applications.

2.3. Organoclay Preparation

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 [15].

The following procedure was used for the salts which were soluble in aqueous phase. 5 g 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°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 desiccator.

The procedure to produce organoclays with water insoluble salts was as follows. 5 g 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 stoichiometric 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. The 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.

2.4. Characterization

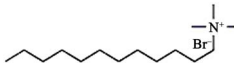
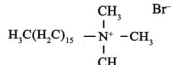
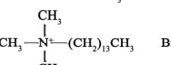
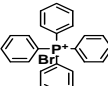
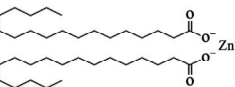
2.4.1. X-Ray Diffraction

X-ray diffraction (XRD) was performed on dried powder samples. The organoclays were grounded into a fine pow-

Table 1. Specification of MMT clay.

SiO ₂	45.3%
Al ₂ O ₃	18.3%
Na ₂ O	1.5%
Ca ₂ O	1.2%
Fe ₂ O ₃	14.3%
Moisture	11.0
pH	8.5

Table 2. 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		-----

der prior to XRD measurements using 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 diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). The experiments were run at room temperature with an angle range (2θ) from 4° to 15° for Zinc Stearate and 2° to 70° for rest of the four ions at $4^\circ/\text{min}$ and step size of 0.02° . The machine was operated at 40 kV and 40 mA.

2.4.2. Thermogravimetry

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 $10^\circ\text{C}/\text{min}$. 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.

3. Results and Discussion

3.1. X-Ray Diffraction of the Organo-Montmorillonite Clay

XRD of different samples of modified MMT clay give the values of basal spacing. The basal spacing of the different samples is given in **Table 3**. The diffraction patterns of the different samples are given in **Figure 1**. 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 the 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 Tetraphenyl Phosphonium ion then the basal spacing increases to 2.26 nm which is sufficiently large value for its potential as reinforcement in a polymer nanocomposites. The increase in basal spacing by Tetraphenyl phosphonium ion is due to the four phenyl groups attached to phosphorous cation which helps in pulling apart the two stacks of MMT clay. The XRD of pure organic cation such as Zinc Stearate and Triphenyl Phosphonium bromide do not show any peak at the angle where XRD of modified MMT clay has shown after treating with the respective ions. Hence the shift in angle to the lower angle shows the increase in basal spacing. Increase in basal spacing is successfully achieved by using Zinc Stearate which is a known fatty acid. This opens up a great interest in the potential of fatty acids for clay modification that are cheap and easily available. One can easily increase the organic content in fatty acids and it is quite possible that one

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)

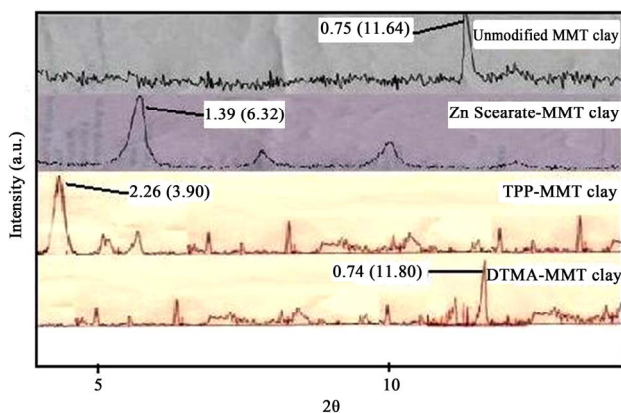


Figure 1. XRD pattern of modified MMT clay with different organic cations.

should be able to tweak the interlayer spacing of MMT clays. In case of ammonium ions treated MMT clay, no effect on basal spacing was seen and it has not changed significantly.

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 increase in basal spacing results in formation of better intercalated or exfoliated polymer clay nanocomposite with improved physical and chemical properties.

The initial basal spacing in the organoclay is an important parameter for the determination of the potential for polymer intercalation and clay mineral delamination [16]. Organoclays with smaller interlayer distances have reduced probabilities for polymer intercalation.

3.2. Thermal Stability and Degradation Behavior of Organo-Montmorillonite Clay

The low thermal stability of ammonium surfactants presents a problem for melt compounding and processing of polymer nanocomposites. 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. TGA gives us information about the thermal stability of the organoclay. The TGA curves for unmodified Na-MMT clay and organically modified clays are shown in **Figure 2**. It is noted

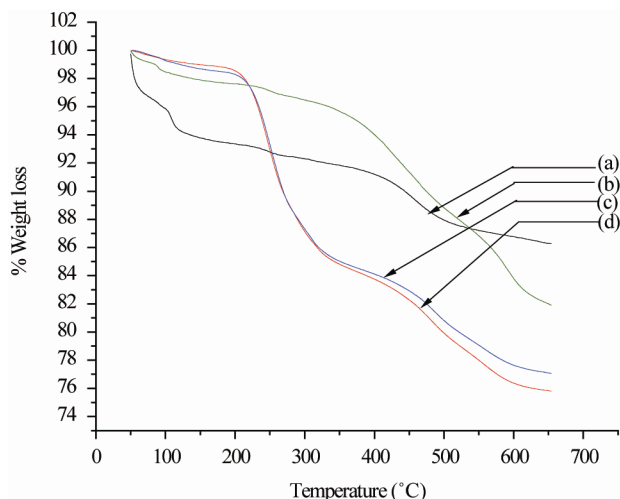


Figure 2. TGA curves for unmodified NaMMT clay and organically modified montmorillonites. (a) Unmodified NaMMT clay; (b) Triphenyl phosphonium-MMT clay; (c) Dodecyltrimethyl ammonium-MMT clay; (d) Tetradecyltrimethyl ammonium-MMT clay.

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.

The presence of organic cation increase the number of decomposition steps. Four steps of the mass loss steps are observed for the organoclays [17,18]. In case of TPP-MMT, the first step is from the ambient to 66.9°C temperature range 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 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.

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.

4. Conclusions

Montmorillonite has been successfully modified using organic cationic surfactants. The XRD results show intercalation of the organic cations between the clay mineral layers. Zinc Stearate is a fatty acid and is successfully used for increasing basal spacing. Hence basal spacing is also increased by using fatty acid with long hydrophobic chains. They are cheap and easily available. The phosphonium-MMT clay shows increase in basal spacing but 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 that 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 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.

5. Acknowledgements

We thank the School of Chemistry and Biochemistry, Thapar University, GM Chemicals, Ahmedabad and appreciate the generous gift of the clay.

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