CERTIFICATION OF APPROVAL

Synthesis and Characterization of Imidazolium Based Ionic Liquid-Intercalated Bentonite

by:

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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ABSTRACT

Intercalation of ionic liquid in clay, mostly imidazolium based ionic liquid has been recently evaluated. However, from the results obtained they have shown low expansion of the interlayer spacing after the process. The low expansion of the interlayer spacing is most probably due to ineffective intercalation process as the process is affected by many factors such as Cations Exchange Capacity (CEC) values of the clay, concentration of ions, temperature and reaction time. Besides that, the commercially available organic modifier has lower thermal stability and caused a limited usage of commercial organo-clay as adsorbents. Thus, ionic liquids which have high thermal stability can be a good alternative to replace the lower thermal stability of conventional organic modifier. Therefore, this project which based on modification of clay with ionic liquids is proposed to analyze other factors that can affect the intercalation process. The parameters that were taken into account; different types of exchangeable cations (e.g. Na^+ and Ca^{2+}) and types of halides in the imidazolium based ionic liquid. The other parameters such as types of clay, concentration of ions, temperature and time of reaction were kept constant. Then, the efficiency of intercalation was measured as expansion of the basal spacing by X-Ray Diffraction (XRD) analysis, while the thermal stability was evaluated via thermo gravimetric analysis (TGA). Additional qualitative characterization such as Fourier Transform Infrared (FTIR) analysis and observation of morphology structure using Scanning Electron Microscope (SEM) were also conducted. From the results obtained at the end of this project, the bentonite with Na^+ exchangeable cations had shown an expansion in its interlayer spacing (from 13.70 Å to 13.90 Å) when reacted with 1-Butyl-3-methylimidazolium chloride. Moreover, all the samples had shown a high thermal stability characteristic through TGA Analysis. Thus, they have the potential to encounter the limited usage of commercial organoclay as adsorbents which has low thermal stability.

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CHAPTER 1
INTRODUCTION

1.1 Background of Study

There are many techniques used for the separation of carbon dioxide from fuel gas streams. Absorption is the large-scale separation of carbon dioxide and commercially used throughout the world. Other techniques exist are cryogenic separation, membrane separation, and adsorption processes. Starts from 1991, Yang & Baksh have proposed modified clays as new class of adsorbent for gas separation.

The previous research includes modification of clay with inorganic hydroxyl cations which are polymeric hydroxyl metal cations formed by hydrolysis of metal salts. Recently, clay modified with organic cations from imidazolium based ionic liquid has been evaluated. Important advantage of using organic cations from ionic liquid is the improvement of the thermal stability compared to the commercial organic modifier.

However, from the available research, there still inadequate information about retention of gases by this organo-clay. This is most probably due to the lower expansion of the interlayer spacing after the intercalation process, compared to the modification of clay with inorganic cations. Lower expansion might related to ineffective intercalation process as the process is affected by many factors such as Cation Exchange Capacity (CEC) values of the clay, concentration of ions, temperature and time of reaction.

Therefore, this project which based on modification of clay with ionic liquids is proposed to analyze other factors that can affect the intercalation process. For this project, the imidazolium based ionic liquid is intercalated with bentonite /montmorillonite clay. The parameters that were taken into account; the different types of exchangeable cations (e.g. Na^+ and Ca^{2+}) and types of halides in the imidazolium based ionic liquid. The other parameters such as types of clay, concentration of ions, temperature and time of reaction were kept constant.

Then, the efficiency of intercalation was measured as expansion of the basal spacing by X-Ray Diffraction (XRD) analysis, while the thermal stability was evaluated via thermo gravimetric analysis (TGA). Additional qualitative characterization such as Fourier Transform Infrared (FTIR) analysis and observation of morphology structure using Scanning Electron Microscope (SEM) were also conducted.

It is experimentally proven that the interlayer spacing of the organo-montmorillonites, structure of the intercalated organic molecule and type of montmorillonite influenced the adsorption values. Therefore, a critical analysis of the comparisons for different types of clay, ionic liquid and intercalation methods were conducted in the research period before proceeding to synthesize and characterize the sample.

1.1.1 Ionic Liquid

Ionic liquids consist of a salt where one or both the ions are large, and the cation has a low degree of symmetry. These factors tend to reduce the lattice energy of the crystalline form of the salt and hence lower the melting point (Earle and Seddon, 2000). Thus, ionic liquids are often fluid at room temperature.

Ionic liquids come into two main categories, namely simple salts (made of a single anion and cation) and binary ionic liquids. They have been described as designer solvents (Freemantle, 1998) as the properties can be adjusted to suit the requirements of the particular process. Properties such as melting point, viscosity, density, and hydrophobicity can be varied by simple changes to the structure of the ions.

No measurable vapor pressure is one of the important properties, hence can emit no volatile organic compounds (VOCs). Ionic liquids have generated significant interest in wide range of industrial application such as catalysis, gas separation and substituting various organic solvent.

For this project, commercial available ionic liquid is selected from imidazolium based ionic liquid. Two types of imidazolium based ionic liquid from the same carbon chain but different halides had been used in the intercalation process. Details regarding these types of ionic liquids are explained in Chapter 2.

1.1.2 Clay

The clay minerals such as kaolinite, smectite and sepiolite are among the most important and useful industrial minerals. Montmorillonite is one of clay minerals within the Smectite Group. It forms by weathering or hydrothermal alteration of other aluminum-rich minerals, and is particularly common in altered volcanic ashes called bentonite. Bentonite is a native, colloidal, hydrated, non-metallic mineral of the Smectite Group that is primarily composed of the mineral montmorillonite.

The important physical properties which related to the application are the particle size, shape, distribution of the clay minerals, surface characteristics (chemistry, area and surface charge), color and brightness (Zhao et al., 2003).The montmorillonite clays are recognized as good adsorbents due to their ability to exchange interlayer cations for charged organic or metal cations in solution (Volzone and Ortiga, 2002). A thorough explanation about different types of clay will be provided in Chapter 2.

1.1.3 Preparation of Imidazolium based Ionic Liquid-Intercalated Bentonite by Intercalation

There is a number of different approaches can be adopted to prepare hybrids using sol-gel, intercalation or other chemical reaction. Due to the ability of bentonite which tends to exchange interlayer cations in solution, intercalation is justified to be the suitable method. The aims of intercalation are to:

- Expand the interlayer spacing
- Reduce solid-solid interaction between the clay platelets
- Improve interactions between the clay and the matrix.

This project is conducted to analyze the expansion of interlayer spacing after intercalation process. The details regarding intercalation process will be explained in Chapter 2.

1.2 Problem Statement

Intercalation of ionic liquid in clay, mostly imidazolium based ionic liquid has been recently evaluated. However, from the result it has shown low expansion of the interlayer spacing after intercalation process. Interlayer spacing is an important parameter due to the previous research which indicates that it affects the retention of gases.

Low expansion of the interlayer spacing after the intercalation process is most probably due to ineffective intercalation process as the process is affected by many factors such as Cation Exchange Capacity (CEC) values of the clay, concentration of ions, temperature and time of reaction.

Besides that, the commercially available organic modifier has lower thermal stability and caused a limited usage of commercial organo-clay as adsorbents. Thus, ionic liquids which have high thermal stability can be a good alternative to replace the lower thermal stability of conventional organic modifier.

Therefore, this project which based on modification of clay with ionic liquids is proposed to analyze other factors that can affect the intercalation process. As stated earlier, the parameters that were taken into account; the different types of exchangeable cations (e.g. Na^+ and Ca^{2+}) and types of halides in the imidazolium based ionic liquid. The other parameters such as types of clay, concentration of ions, temperature and time of reaction were kept constant.

1.3 Objectives

i) To synthesize the imidazolium based ionic liquid-intercalated bentonite
ii) To analyze the efficiency of intercalation between imidazolium based ionic liquid and bentonite by evaluating expansion of the basal spacing and the thermal stability.

Below is the scope of studies for this project which cover a pre-requisite analyses and two different parameters; the exchangeable cations in bentonite and halides in imidazolium-based ionic liquid.

1.4 Scope of studies

i) To determine the Cation Exchange Capacity (CEC) of Bentonite as a pre-requisite before proceeding with intercalation process.
ii) To study the effects of different exchangeable cations (e.g.; Ca^{2+} and Na^{+}) in the intercalation process.
iii) To study the effects of different halides of ionic liquids (e.g.; Br^{-} and Cl^{-}) in intercalation process.

1.5 The Relevancy of the Project

The availability of inexpensive clays of controlled quality is ensured by the synthetic clay which can outweigh the expensive ionic liquids. Thus, further investigation as possible adsorbent for gas separation and purification is warranted due to this commercial synthetic clay. This project is hopefully will be beneficial to R&D Industry and produce an alternative way of CO_2 adsorptions.

1.6 Feasibility of the Project within the Scope and Time frame

The author was given 2 semesters to accomplish the project under course of Final Year Project 1 for the past semester and Final Year Project 2 for this semester. Basically, the first semester was utilized to document a thorough analysis of available literature and purchase the consumables (e.g: ionic liquid and clay).

CHAPTER 2
LITERATURE REVIEW

2.1 Critical analysis of literature

2.1.1 Selection of Bentonite/Montmorillonite Clay

Clays are classified on the basis of their crystal structure besides the amount and locations of charge (deficit or excess) per basic cell. Clay particles are usually plate-shaped, less often tubular or scroll-like (Utracki, 2004, p.73).Smectites or phyllosilicates are the most frequently used clays for a variety of non-ceramic application. These 2:1 phyllosilicates (Figure 2.1) have a triple layer sandwich structure that consists of a central octahedral sheet dominated by alumina, bonded to two silica tetrahedral sheets by oxygen ions that belong to both sheet (Utracki, 2004, p.76).

These layers are linked together by Vander Waals forces (Neung et. al, 2006). MMT is highly reactive to interact through electrostatic interaction (e.g. ion-exchange), secondary bonding (e.g. adsorption of neutral species) or covalent bonding (e.g. grafting). Deficit of a surface charges due to isomorphic substitution in octahedral and in tetrahedral sheets is balanced by exchangeable cations situated in the interlayer position, e.g. Na^+, K^+ and Ca^{2+}, etc. (Volzone et al., 2004). Size of exchangeable cations influences the microporosity and surface area of the montmorillonites (Rutherford et al., 1997).

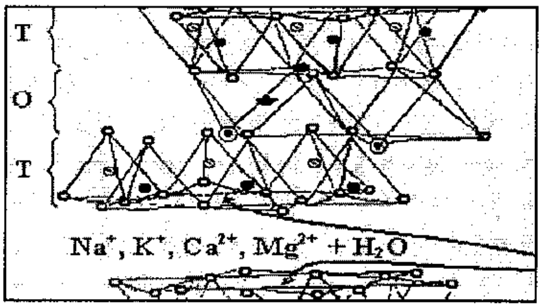

Figure 2.1: Montmorillonite structure. T, tetrahedral sheet; O, octahedral sheet

There are several species of smectite clay, but the two of greatest commercial importance and value are montmorillonite (MMT) and hectorite (HT). Commercial availability of HT is limited whereas MMT deposits are large and widely spread around the globe such as Canada, USA, South Africa, Europe, Africa, Australia and Asia (Utracki, 2004, p.79).

As mentioned earlier, synthetic clays are already produced commercially. The availability of this synthetic clay which is inexpensive with controlled quality will warrant further investigations of modified clay as possible sorbents for gas separation and purification (Yang, 2003).

MMT is the most common phyllosilicates used for the production of commercial Clay-Containing Polymeric Nanocomposite (CPNC). MMT color varies from brick red (due to Fe^{3+}) to pale yellow or blue-grey. Commercially, MMT is supplied in the form of powder (Utracki, 2004, p.80-83).

For successful intercalation, the selected clay should have a cation-exchange capacity, (CEC) = 0.5-2.0 meq/g.

- For CEC < 0.5, the ion exchange is insufficient
- For CEC > 2.0, the interlayer bonding is too strong for easy intercalation

Thus, smectites and vermiculites have the optimum CEC, theoretically 1.39 and experimentally 0.8 to 1.2 meq/g. By contrast, kaolin has a CEC < 0.1 meq/g while mica, illites, attapulgite and sepiolite are about 0.2 meq/g.

As a consequence, MMT, saponite and hectorite are the preferred clays for CPNCs, but since MMT is more abundant and it has a fairly large aspect ratio, p= 300 (natural hectorite has the smallest), it became the main nanofiller for Polymeric Nanocomposite (PNC) technology (Utracki, 2004, p.97-98).

2.1.2 Selection of Imidazolium based Ionic Liquid

A number of investigations have shown that CO_2 is remarkably soluble in imidazolium-based ionic liquid (Husson Borg et al., 2003). More detailed investigations have shown that the anion and substituent on the cation did affect the CO_2 solubility. All of the imidazolium-based ILs for which CO_2 solubility has been measured previously possessed hydrogen attached to the C2 carbon. Acidic hydrogen on the imidazolium ring is particularly intriguing as a potential additional mechanism for CO_2 solvation (Cesar et al., 2003).

Based on the available literature, many ionic liquids (ILs) show good selectivity for CO_2 and SO_2 over gases such as N_2, O_2 and H_2 (Anthony et al., 2002; 2005; Anderson et al., 2006). The most common organic cations containing nitrogen are imidazolium and pyridinium derivatives which potentially increase the effectiveness of CO_2 adsorption. In fact, ionic liquids containing long chain cations (mostly imidazolium based) have been recently evaluated as montmorillonite (MMT) modifiers (Neung et al. 2006).

Therefore, the author has decided to choose ionic liquid from imidazolium based. The ionic liquids which will be used in the intercalation process are 1-butyl-3-methylimidazolium bromide and 1-butyl-3-methylimidazolium chloride as shown in Figure 2.2 and Figure 2.3.

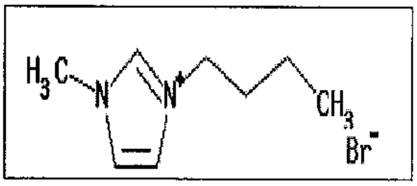

Figure 2.2:
1-Butyl-3-methylimidazolium bromide

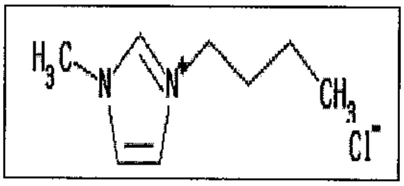

Figure 2.3:
1-Butyl-3-methylimidazolium chloride

2.1.3 Cation Exchange Capacity (CEC)

CEC is a numerical value to describe the ion exchange capability of clay minerals, in particular smectites. This property influences their unique physical properties, such as the cation retention and diffusion processes of charged and uncharged molecules. CEC values are dependent on the method used. The exchange with ammonium acetate is the standard method for CEC determination (Mackenzie, 1951).

Other methods for determining CEC involve the complete exchange of the naturally-occurring cations by a cationic species, such as ammonium, K, Na, methylene blue, and Co (II) hexamine complex. Methylene blue can be used in a rapid qualitative procedure, but the results are not reliable in comparison to other methods (Kahr and Madsen, 1995; Yariv et al., 1990).

Therefore, the author has decided to use ammonium acetate method as it is well-known as standard method for CEC determination. CEC determines the amount of negative charge of 100g of soil. Analysis of the CEC value for clay is very important as this value is varies even though the clays come from the same group (e.g. smectite).

Basically, in determination of cation exchange capacity of soils and clays, it is expected to saturate the exchange sites with an index cation, which is then replaced and determined. CEC value can be obtained from various methods as stated earlier. This value is used as reference for the ionic liquid's concentration which intercalated in clay.

2.1.4 Intercalation Method

Clay minerals are the common group of self-assembling ceramic host materials for intercalation. For this project, intercalation process involves a mixing of clay and ionic liquid at specific concentration, temperature and time. Then, the mixture is washed with distilled water to get rid excess ionic liquid. The amount of ionic liquid added to clay is determined by considering the clay's Cation Exchange Capacity (CEC). The details of calculation are explained in the Appendix.

Montmorillonite (MMT) which consists of anionic charge of the aluminosilicate layer will be neutralized by the intercalation of exchangeable cations (e.g. Na^+ and Ca^{2+}) (Neung et al., 2006). It is an important step in order to achieve electroneutrality as the substitution of the trivalent aluminium by divalent Mg or Fe imparts a net charge to the clay layer (Yang, 2003). The interlayer accessible exchangeable cations can be exchanged with a wide variety of hydrated inorganic cations or organic cations in the modification of montmorillonites by ion exchange.

Based on the preparation of pillared clay (Yang, 2003), the charge compensating cations between the clay layer are exchanged with larger inorganic hydroxyl cations, which are polymeric hydroxyl metal cations formed by hydrolysis of metal salts. Upon heating, the metal hydroxyl cations undergo dehydration and dehydroxylation, forming stable metal oxide clusters. They act as pillars to keep the clay layers separated and thus creating interlayer spacing as shown in Figure 2.4.

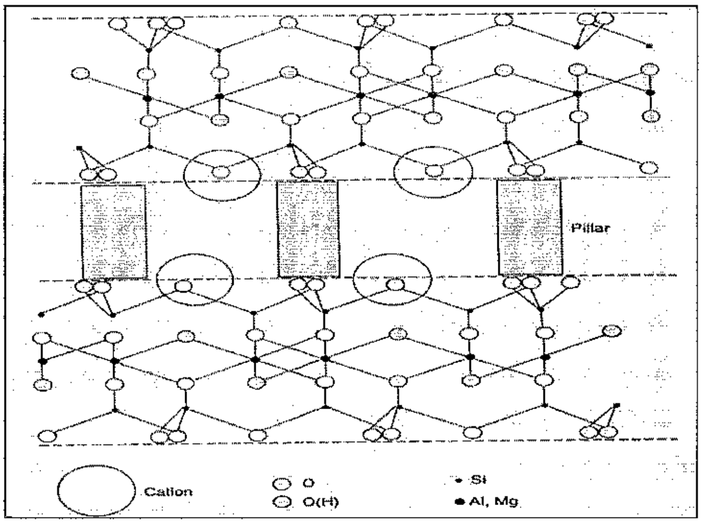

Figure 2.4: Schematic of Structures of clay and pillared clay, with cation sites (Yang, 2003)

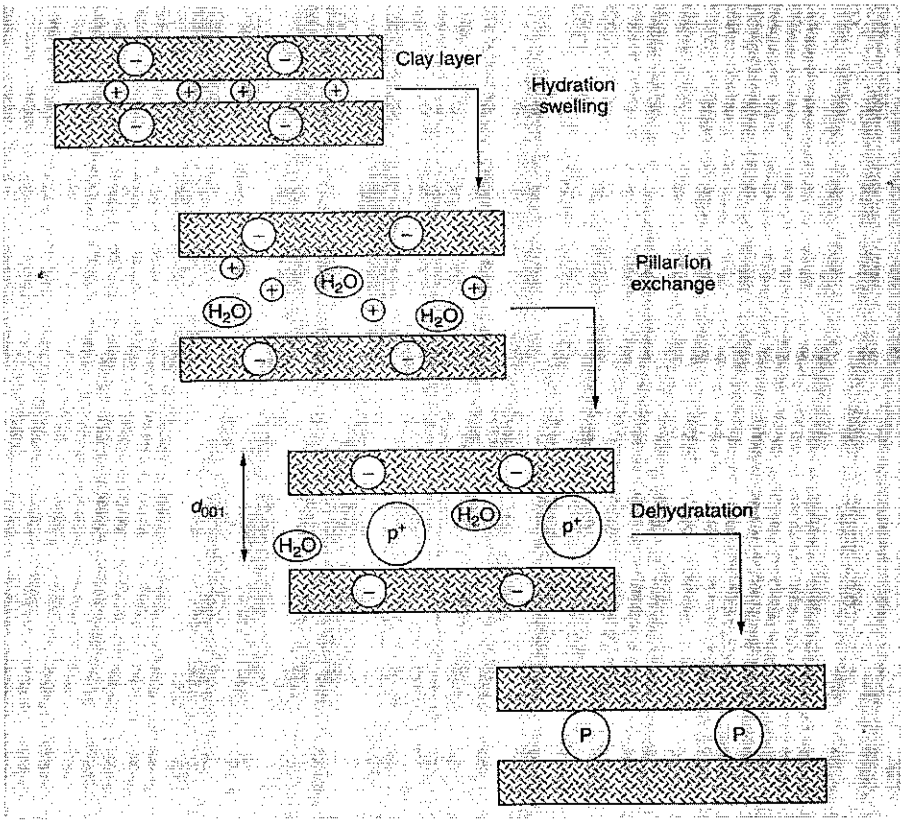

Figure 2.5: General scheme for synthesis of pillared clays (Yang, 2003)

The intercalation of organic cations from imidazolium based ionic liquid will basically follow the same concept as explained previously for the inorganic hydroxyl cations intercalated in the clay. The details of intercalation process will be explained in the methodology part under Chapter 3.

Basically, intercalation will result in overall changes (e.g.; increase or decrease) in the interlamellar spacing due to sodium cations exchange with the cations of the ionic liquid. For the author's case study, the cations of the ionic liquid will be the imidazolium cations, which will undergo ion exchange with sodium cations in montmorillonite. As mentioned earlier, this process will be based on the scope of studies which are to study the effects of different exchangeable cations (e.g.: Ca^{2+} and Na^+), different halides of ionic liquid (e.g.: Br^- and Cl^-) and different concentration of ionic liquid in the intercalation process.

2.1.5 Characterization of Imidazolium based Ionic Liquid-Intercalated Bentonite: X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) will be used to measure quantitatively the expansion of the basal spacing or interlayer spacing of the clay after intercalation process. It is an important analysis as a guide for determining the pore size (Yang, 2003). Due to the statement that cation situated in interlayer position can have an effect on clay characterization (MacEwan and Wilson, 1980), therefore the author decided that this test is fairly important to determine the effectiveness of the intercalation process.

Theoretically, larger cations will produce greater expansion of interlayer spacing. Larger cations can be explained by larger ionic radius for example Na^+ compared with Ca^{2+}. Clay modified with Ca^{2+} will produce larger expansion compared to clay modified with Na^+ due to larger ionic radius of Ca^{2+} (Volzone, 2004).However, as stated earlier the intercalation process depends on various factors which the author has to be thoroughly taken into consideration.

Basically, XRD is a non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials.XRD applies the *Bragg's Law*; when a monochromatic x-ray beam with wavelength λ is incident on the lattice planes in a crystal planes, in a crystal at an angle θ, diffraction occurs only when the distance traveled by the rays reflected from successive planes differs by a complete number n of wavelengths.

A crystal consists of a periodic arrangement of the unit cell into a lattice. The unit cell can contain a single atom or atoms in a fixed arrangement. Crystals consist of planes of atoms that are spaced a distance d apart, but can be resolved into many atomic planes, each with a different *d* spacing. By varying the angle θ, the Bragg's Law conditions are satisfied by different d-spacing in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffraction peaks produces a pattern which characterized the sample.

2.1.6 Characterization of Imidazolium based Ionic Liquid-Intercalated Bentonite: Thermal Gravimetric Analyzer (TGA)

Basically, TGA measures weight changes in a material as a function of temperature (or time) under a controlled atmosphere. Measurements are used mainly to determine the composition of materials and to predict their thermal stability at temperatures up to 800°C.

Thermal Gravimetric Analyzer is used to measure the thermal stability of the intercalated clay. The main problem faced by the previous research (Barrer, 1978) is low thermal and hydrothermal stabilities of the modifier, thus their product has limited usage as adsorbents and catalyst (Yang, 2003). Therefore, after the weakness of the research was pointed out, the following researches have been directed towards the synthesis of pillared clays with high thermal and hydrothermal stabilities.

Therefore, the author has decided to include this analysis as thermal stability is rather an important specification of a good adsorbent. Besides that, the commercial modifiers are not thermally stable even though they can produce a great expansion of the clay's interlayer spacing (Neung et al., 2006). In fact, ionic liquids have been recently evaluated as montmorillonite (MMT) modifiers due to important incentive of thermally stable.

Imidazolium-based ionic liquid is proved to be a thermally stable as shown in Figure 2.6 of characteristic decomposition curve, determined by TGA. From this graph, the decomposition of the sample begins at fairly high temperature which is 220°C, represent by T_{start} as stated on the graph.

Bentonite/montmorillonite also considered as thermally stable as shown in Figure 2.7. From the graph, it shows two mass loss steps at 25-500 °C and 500-1000 °C. They correspond to the dehydration at 20-300 °C and dehydroxylation at 500-900 °C. The physically bounded molecular water was eliminated at 100-120 °C and the water in interlayer space at 120 °C and above. The OH groups began to release at 500 °C (Lalikova et al., 2010).

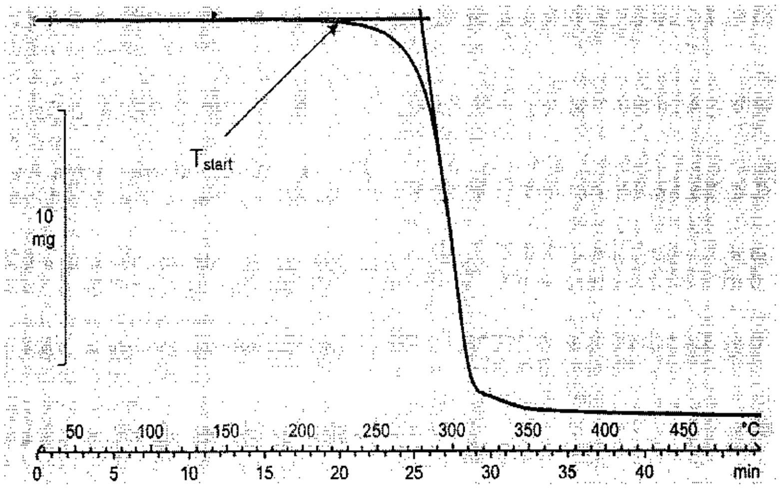

Figure 2.6: Characteristic decomposition curve, determined by TGA for imidazolium ILs, indicating the start temperature (Christopher et al, 2004)

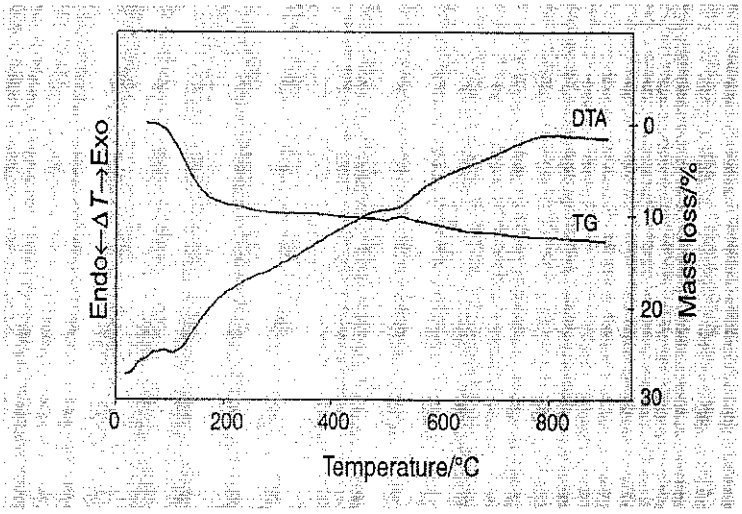

Figure 2.7: DTA and TG of natural bentonite (Lalikova et al., 2010)

2.1.7 Characterization Imidazolium based Ionic Liquid-Intercalated Bentonite: Fourier Transform Infrared (FTIR) Spectrometer

FTIR is useful for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint". The data collected and converted from an interference pattern to a spectrum. The analysis involves can be divided into two kind of analysis which are qualitative and quantitative analysis.

For qualitative analysis, FTIR is capable to identify types of chemical bonds (functional groups) by interpreting the infrared absorption spectrum. The wavelength of light absorbed is the characteristic of the chemical bond as can be seen in the annotated spectrum. Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. There are several specific frequencies at which it can vibrate for any given bond. These frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies), according to quantum mechanics.

The spectrum of an unknown can be identified by comparison to a library of known compounds. IR will need to be combined with nuclear magnetic resonance, mass spectrometry, emission spectroscopy, X-ray diffraction or other technique, in order to identify less common materials. On the other hand, quantitative analysis can be conducted using FTIR due to the proportionality of the strength of the absorption to the concentration.

2.1.8 Characterization of Imidazolium based Ionic Liquid-Intercalated Bentonite: Scanning Electron Microscope (SEM)

SEM will be used to study the morphology and surface atomic analysis of ionic liquid-clay hybrid. The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image. There are many advantages to use the SEM, instead of a light microscope.

During SEM inspection, a beam of electrons is focused on a spot volume of the specimen, resulting in the transfer of energy to the spot. These bombarding electrons, also referred to as primary electrons, dislodge electrons from the specimen itself. The dislodged electrons, also known as secondary electrons, are attracted and collected by a positively biased grid or detector, and then translated into a signal.

To produce the SEM image, the electron beam is swept across the area being inspected, producing many such signals. These signals are then amplified, analyzed, and translated into images of the topography being inspected. Finally, the image is shown on a CRT.

CHAPTER 3
METHODOLOGY

3.1 Research Methodology

The research process starts with stating the hypothesis after choosing the problem. Then, the author has to formulate the research design which is mainly related to laboratory experiment in the synthesis period. After the synthesis period, the products were characterized under specific parameters. After that, available data and information were collected from reliable sources, followed by analysis and interpretation of result obtained from the characterization.

3.2 Project Activities

3.2.1 Literature Review

Project activities for the first semester of the course are mainly on documentation of literature review which is related to the project. Literature review is a formal survey of professional literature and review theories and research already done on the topic. A thorough literature search which covers the background studies of ionic liquids, clay and intercalation process is conducted in order to obtain a clear picture of what the project is all about as documented in the previous chapter.

3.2.2 Materials for Synthesis

The consumables which were used in the synthesis are listed in Table 3.1. The Material Safety Data Sheet (MSDS) were obtained and understood before conducting any experiment in the lab to avoid any accident in handling the chemicals. Besides that, the author had conducted a thorough Job Safety Analysis (JSA) and Hazard Identification before starting the laboratory's work.

i) **Ionic Liquid**

No	*Ionic Liquid*	*Physical & Chemical Properties*
1	1-Butyl-3-methylimidazolium bromide Formula: $C_8H_{15}BrN_2$	i) Melting Point: 76°C ii) Molecular Weight: 219.13 g/mol iii) Form : Solid
2	1- Butyl-3-methylimidazolium chloride Formula: $C_8H_{15}ClN_2$	i) Melting Point: 60 °C ii) Molecular Weight: 174.68 g/mol iii) Form: Solid

Table 3.1: List of Ionic Liquid

ii) **Bentonite (Homoionic Bentonite)**

1) Bentonite-Ca^{2+}
2) Bentonite-Na^{+}

Note: Homoionic Bentonite are synthesized from the pure Bentonite.

iii) **Others**

1) Silver Nitrate (0.1 M)

3.3 Determination of Cation Exchange Capacity (CEC)

The method was carried out as described by Dohrmann (1997). The sample must be prepared distilled and titrated. The sample is first ammonium exchanged. Then the ammonium ions in the supernatant are deprotonated into ammonia with sodium hydroxide solution. Then the ammonium content is obtained by back-titrating the ammonium nitrate result from reaction between ammonia and nitric acid. Details of calculation are shown in the Appendix.

3.4 Synthesis

3.4.1 Synthesis of homoionic clay

The CEC often occupied with variety of cations; H^+, Ca^{2+}, K^+, Mg^{2+}, but can occupy with only one type of cation or is named as homoionic clay. Ca^{2+} and Na^+ are used respectively to produce two types of homoionic clay, Bentonite-Ca^{2+} and Bentonite-Na^+. It is an important step as it will neutralize the anionic charge of the aluminosilicate layer in clay before proceeding to synthesis of ionic liquid-clay hybrid by intercalation process. Then, the homoionic clay is preceded with the XRD analysis to observe the effects of different exchangeable cations in clay.
Characterization of these two types of homoionic clay proved that Bentonite-Ca^{2+} has larger basal spacing compared to Bentonite-Na^+ which is due to larger ionic radius of Ca^{2+} compared to Na^+. The author will continue to evaluate the effects of these homoionic clays in intercalation process with the ionic liquids.

3.4.2 Synthesis of Imidazolium based Ionic Liquid-Intercalated Bentonite

Cationic exchange of Bentonite-Na^+ and Bentonite-Ca^{2+} is carried out with ionic liquids by stirring at 80 °C for 6 hours at 2X concentrations of the clay based on CEC (Appendix). Centrifugation is used to separate the supernatant and solid phase. Then, all modified clays will be repeatedly (more than 5 times) washed with distilled water. Washing is continued until no residual halogen anion is detected by adding 0.1 M silver nitrate solution in the filtrate. After 24 h at room temperature, drying continued at 80 ° C under vacuum in order to avoid oxidation. Water has to be totally extracted out during drying process as it can affect the adsorption of CO_2. The synthesis will produce 12 different products based on 2 types of ionic liquid available in UTP, namely as IL-1 and IL-2, as listed in Table 3.2:

Table 3.2: List of Imidazolium based Ionic Liquid-Intercalated Bentonite

No	**Imidazolium based Ionic Liquid-Intercalated Bentonite**
1.	IL1+ Bentonite-Na$^+$ (2XCEC)
2.	IL2 + Bentonite-Na$^+$ (2XCEC)
3.	IL1+ Bentonite-Ca^{2+} (2XCEC)
4.	IL2 + Bentonite-Ca^{2+} (2XCEC)

Note:

i) IL1and IL2 refer to 1- Butyl-3-methylimidazolium chloride, 1- Butyl-3-methylimidazolium bromide.

ii) Different types of clay (e.g. Bentonite-Na$^+$, Bentonite-Ca^{2+}) refer to different type of cations (e.g. Na$^+$, Ca^{2+}).

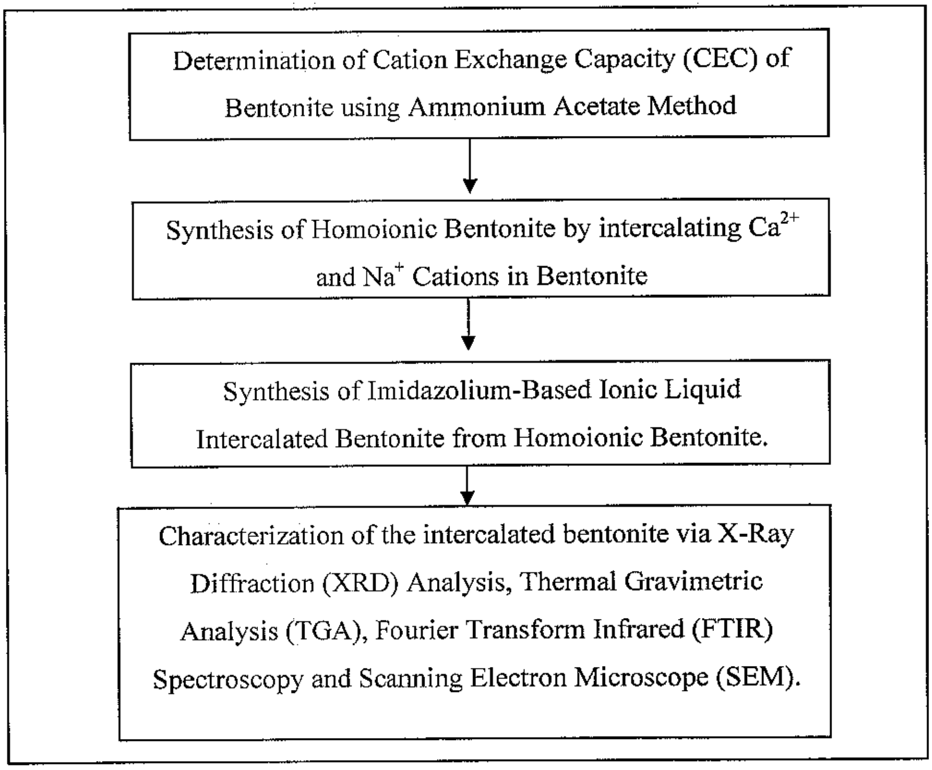

Figure 3.1: Flow Diagram of Synthesis & Characterization

3.5 Characterization

As stated earlier, this step will consist of 4 characterizations:

i) Basal spacing using XRD
ii) Thermal stability using TGA
iii) Analysis on functional groups using FTIR
iv) Analysis on morphology structure using SEM

X-ray diffraction has been used to study the changes in the surface properties of montmorillonitic clay through the changes in the basal spacing of montmorillonite (Yunfei Xi, 2004). Variation in the *d*-spacing was found to be a step function of the surfactant concentration.

Organo-montmorillonites are synthesized by grafting cationic surfactants such as quaternary ammonium compounds into the interlayer space (Chaiko et al., 2002). When long chain alkylammonium cations are used, a hydrophobic partition medium can form within the clay interlayer. The clay which has not been organically modified has a relatively small intergallery distance of the *d* (001) plane and the intergallery environment is hydrophilic. Intercalation of organic surfactant between layers of clays not only changes the surface properties from hydrophilic to hydrophobic, but also greatly increases the basal spacing of the layers.

Next, the ionic-clay hybrid will be characterized under thermal stability analysis using TGA. It is important in order to obtain their thermal stability as the products are heated up to 800 °C. Then the weight changes in a material as a function of temperature (or time) under a controlled atmosphere. The highest thermal stability can be explained by the product which obtains the highest temperature before its weight % decreases significantly.

On the other hand, the peaks obtained from the FTIR can illustrate functional groups in the products. Therefore, a comparison of FTIR spectra of unmodified clay, pure ionic liquid and clay modified by the ionic liquids can be obtained.

3.6 Tools required

Table 3.3: Synthesis of Imidazolium-based Ionic Liquid Intercalated Bentonite

No.	Process	Figure
1.	The mixture is stirred at 80 °C for 6 hours using hot plate with stirrer.	3.2
2.	Supernatant and solid phase is separated using centrifuge.	3.3
3.	Modified clays are repeatedly (more than 5 times) washed with distilled water and continued until no residual halogen anion is detected by adding 0.1 M silver nitrate solution in the filtrate.	3.4
4.	After 24 h at room temperature, drying continued at 80 ° C in vacuum oven in order to avoid oxidation of organic compound.	3.5
5.	The modified clay is grinded using ceramic mortar	3.6

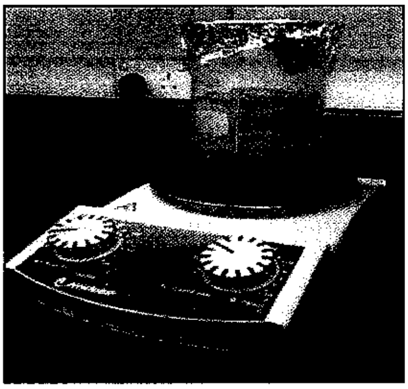

Figure 3.2: Stirred by Hot Plate with Stirrer

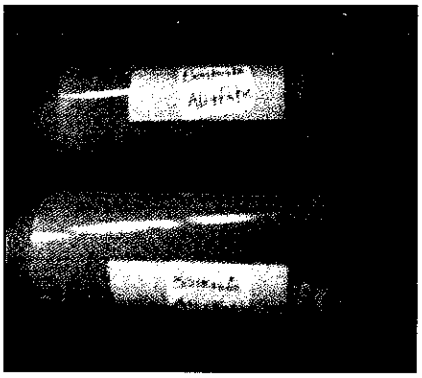

Figure 3.3: Centrifuge Tubes

Figure 3.4: White precipitates which represented residual halogen ion detected by Silver Nitrate

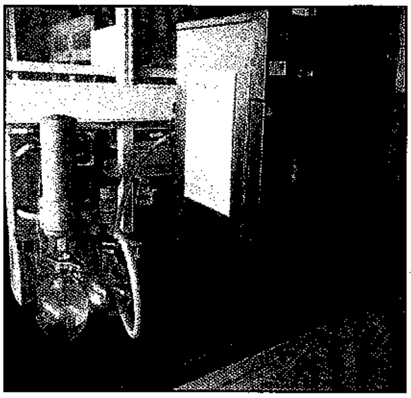

Figure 3.5: Vacuum Oven

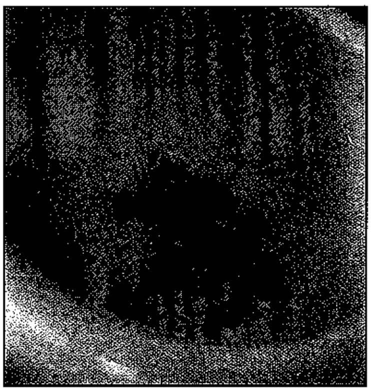

Figure 3.6: Grinded using Ceramic Mortar

3.7 Key Milestone

Detail/ Week	1	2	3	4	5	6		7	8	9	10	11	12	13	14	15	16	17	18	19	20
Project Work Continue	▨	▨	▨	▨			MID-SEM BREAK								STUDY WEEK		EXAM WEEK				
Submission of Progress Report 1					★																
Project Work Continue						▨		▨	▨	▨	▨										
Submission of Progress Report 2												★									
Pre-EDX (Poster Exhibition)												★									
EDX (Selected and Open Category)													★								
Submission of Dissertation														★							
Oral Presentation																			★	★	
Submission of Project Dissertation																					★

☆ Milestone

▨ Process

3.8 Gantt Chart

Detail/ Week	1	2	3	4	5	6		7	8	9	10	11	12	13	14	15	16	17	18	19	20
-Synthesis of Ionic Liquid-Clay Hybrid	√	√			√	√	MID-SEM BREAK			√	√						EXAM WEEK				
-Characterization of Hybrid (XRD, TGA, FTIR, SEM)			√	√				√	√			√	√								
-Submission of Progress Report 1					√																
-Interpretation of Result					√	√				√	√			√	√						
-Submission of Progress Report 2																					
-Pre-EDX (Poster Exhibition)												√									
EDX (Selected and Open Category)													√								
Submission of Dissertation														√							
Oral Presentation																			√	√	
Submission of Project Dissertation																					√

CHAPTER 4

RESULT AND DISCUSSION

4.1 The Synthesized Imidazolium based Ionic Liquid-intercalated Bentonite

Four samples are synthesized as listed in Table 4.1, and sent for characterization (e.g. FTIR, XRD, TGA and SEM). Interpretation of results was conducted in order to analyze the efficiency of intercalation of ionic liquid in bentonite and discover the potential of the sample to be used as a good adsorbent.

Table 4.1: List of Synthesized Ionic Liquid-Clay Hybrid

No. of Sample	Sample
1.	IL1+ Bentonite-Na^+ (2XCEC)
2.	IL2 + Bentonite-Na^+ (2XCEC)
3.	IL1+ Bentonite-Ca^{2+} (2XCEC)
4.	IL2 + Bentonite-Ca^{2+} (2XCEC)

** IL1 is referring to 1-Butyl-3-methylimidazolium chloride
and IL2 is referring to 1-Butyl-3-methylimidazolium bromide

4.2 Result and Discussion for FTIR

The purpose of having this characterization is to prove that the intercalation occured by analyzing the peaks that appear by comparing the sample before and after intercalation. As mentioned earlier, the sample consists of different homoionic clay, interact with two types of ionic liquid. The author has arranged the result of FTIR into 4 set of comparisons in order to analyze the pattern of peaks before and after intercalation under different ionic liquid (e.g. bmimCl and bmimBr) and different types of homoionic clay (e.g. Na^+ and Ca^{2+}).

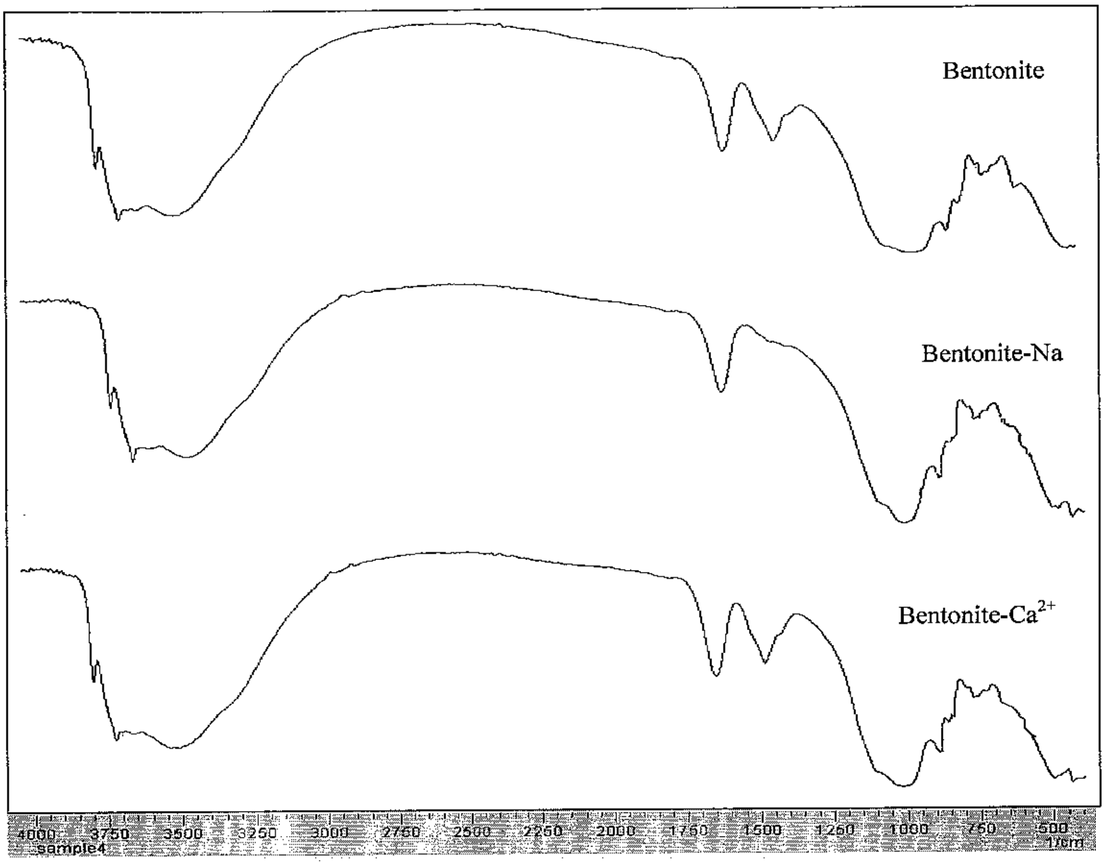

Figure 4.1: FTIR's result for Homoionic Clay

The silicon-oxygen stretching vibrational modes give rise to strongly absorbing bands in the 1100-1000 cm^{-1} region. Some of these involve the basal oxygens of the silicon oxygen tetrahedra, i.e., they correspond to Si-O-Si linkages at the surface of the clay layers and have their transition moment (the direction of dipole oscillation during the vibration) lying in the plane of the layer; they are thus designated "in-plane" (Cole, 2008).

A sharp peak at 3618 cm^{-1} was due to Al-OH stretching vibration. The peaks at 3420 and 1629 cm^{-1} were the H-O-H stretching and bending vibrations of the adsorbed water respectively. The peak at 1,018 cm-^{1} was attributed to Si-O stretching frequency. Tetrahedral bending modes were observed for Si-O-Al at 516 cm^{-1}. OH bending vibrations in octahedral 2:1 layer silicates were assigned for Al-Al-OH at 908 cm^{-1} and for Mg-Fe-OH at 783 cm^{-1}. A peak at 682 cm^{-1} was due to the bending vibration of Si-O-Si (Farmer and Russell, 1964).

Table 4.2: The Group Wavenumbers

Vibration	Wavenumber Range (cm^{-1})
Silanol SiO-H Stretch	3700-3200
Si-O-Si Asymmetric stretch	1200-1000
Silanol Si-O Stretch	~940
Si-O-Si Symmetric stretch	~805
Si-O-Si Bend	~450

Significant differences in the silicate stretching region, v_{Si-O} = 1150 to 950 cm^{-1} are related to water (H_2O) and hydrated cation of Na^+ and Ca^{2+} content, which in turn is related to the spacing between the clay platelets (Shrewing et al., 1995). In the spectrum of Bentonite-Na^+, the silicon-oxygen and aluminum-oxygen bonds are respectively observed at 1044cm^{-1} and 620cm^{-1}, and the magnesium-oxygen is assigned to a band between 530-470 cm^{-1}. The strong peak at 1650 cm^{-1} and the broad band at 3440 cm^{-1} have been assigned to the bending and stretching modes of absorbed water (Gustavo et al., 2004).

Based on Figure 4.2, the spectrum of bmimCl shows peaks for the imidazolium group in the range between 1650 and 1000 cm^{-1}; for example the peaks in the range between 1600 to 1320 cm^{1} are due to carbon-carbon and carbon-nitrogen vibrations. The conjugated strong peaks around 1630 and 1570 cm^{-1} are due to carbon-nitrogen-carbon or carbon-carbon bonds. The spectrum of Bentonite-Na^+-bmimCl shows a resemblance with peaks due to homoionic bentonite and ionic liquid (*refer to arrows*).

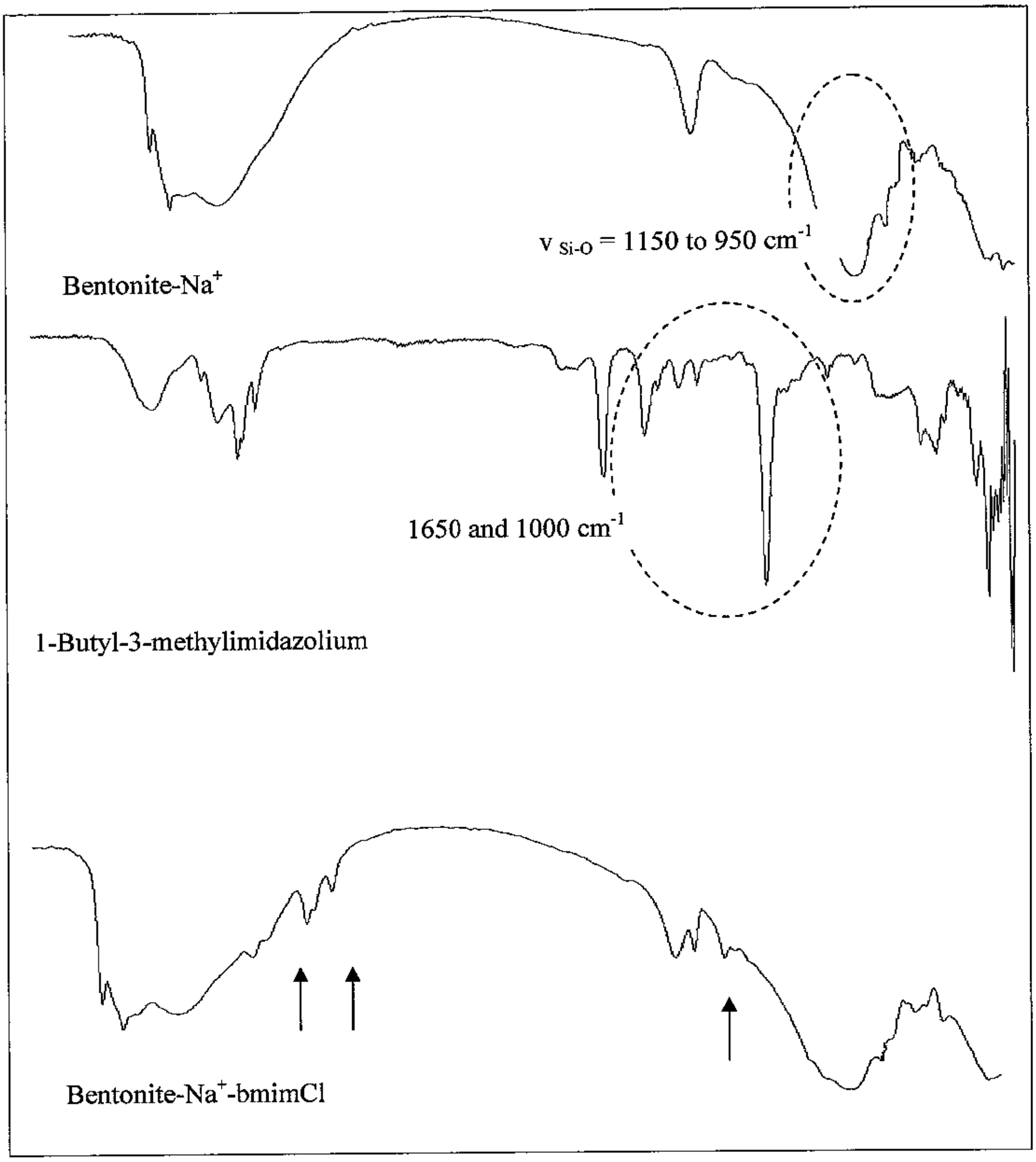

Figure 4.2: FTIR's Result for Bentonite-Na$^+$, 1-Butyl-3-methylimidazolium chloride and Bentonite-Na$^+$-bmimCl

Based on Figure 4.3 and 4.4, the similar pattern is observed for both types of homoionic, Bentonite-Ca^{2+} or Bentonite-Na$^+$ which interacts with different ionic liquids, 1-Butyl-3-methylimidazolium chloride and 1-Butyl-3-methylimidazolium bromide. It is qualitatively proven that different halides in the ionic liquid does not give significantly difference in the spectra. This is due to the ion exchange of Na$^+$ or Ca^{2+} with imidazolium cations which then producing the same product regardless types of halides in ionic liquid, Br$^-$ or Cl$^-$

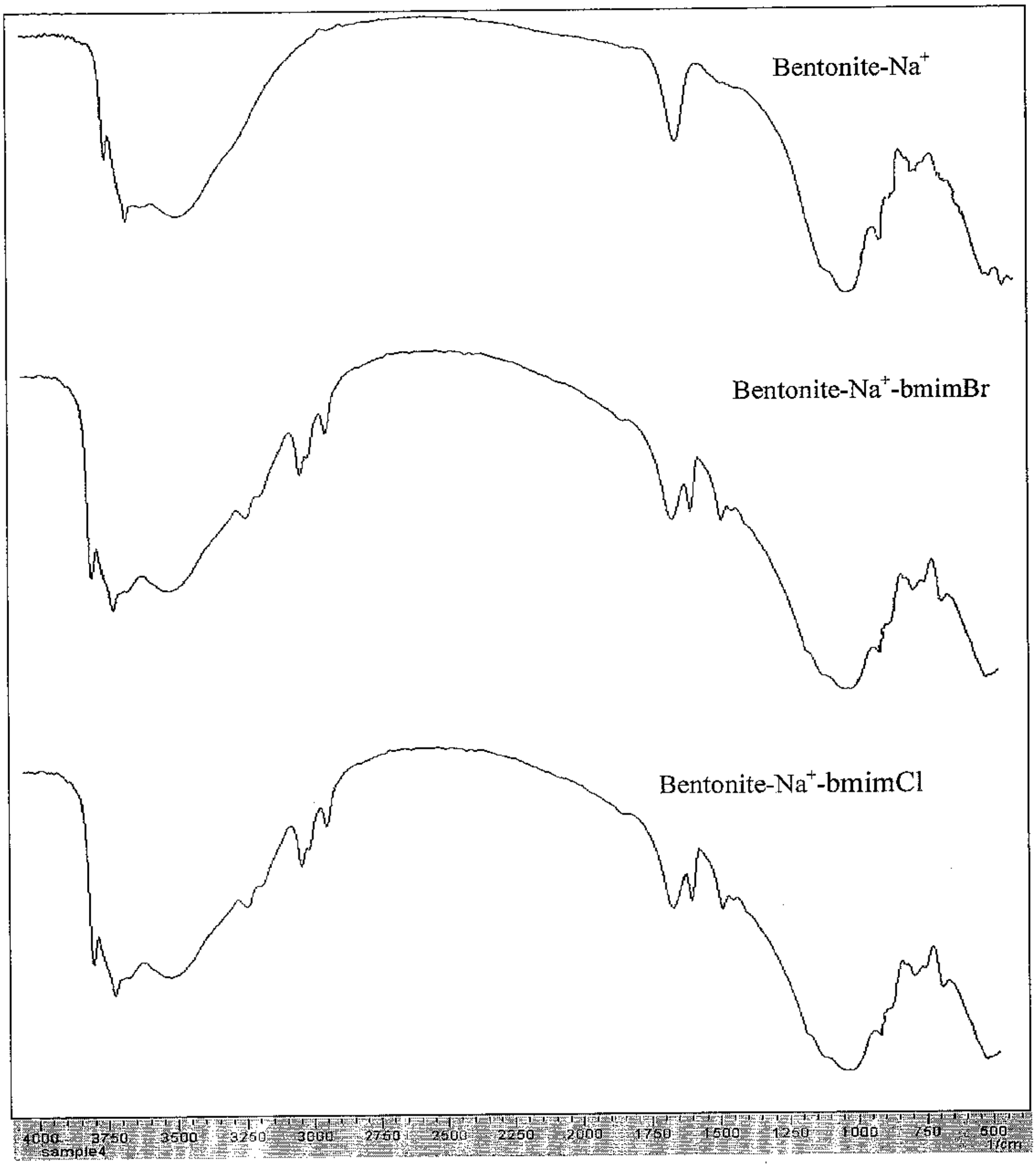

Figure 4.3: FTIR's Result for Bentonite-Na$^+$, Bentonite-Na$^+$-bmimBr and Bentonite-Na$^+$-bmimCl

Nevertheless, this is a qualitative characterization as we cannot conclude that all the exchangeable cations in the homoionic clay exchanged with the imidazolium cations. Further quantitatively analysis should be conducted to analyze about this matter.

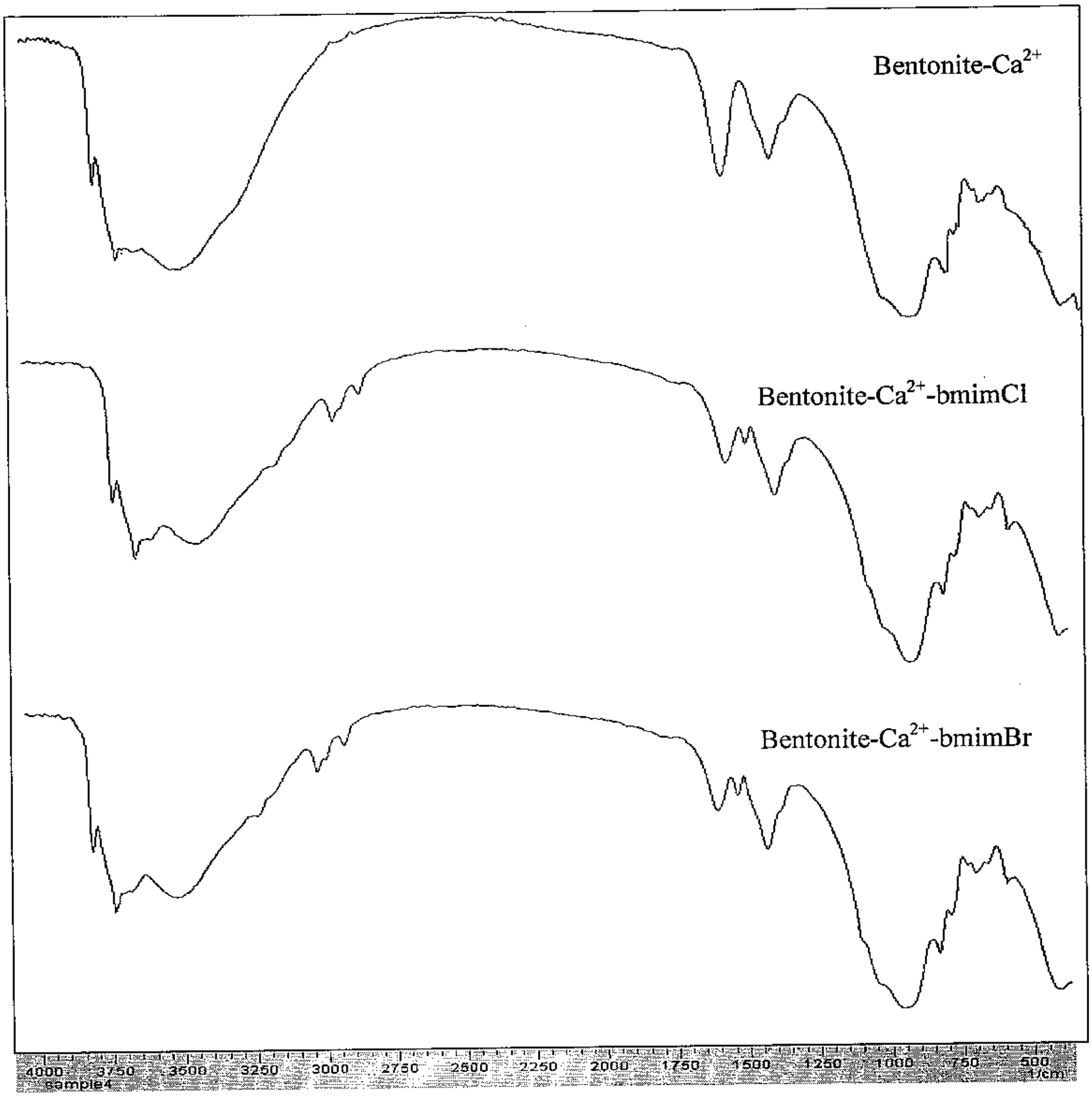

Figure 4.4: FTIR's Result for Bentonite-Ca^{2+}, Bentonite- Ca^{2+}-bmimBr and Bentonite- Ca^{2+}-bmimCl

***Recommendation*:**

i) Pellet spectra recorded immediately after the preparation of the disk generally shows water bands. This water is adsorbed from the atmosphere during the preparation of the disk. Therefore, pellet spectra in the O-H stretching region (3750-3200 cm^{-1}) should be analyzed carefully. A reliable interpretation of the spectrum in this region can be made only by thermo-IR spectroscopy analysis.

ii) In preparing the disk, it is advisable not to grind the clay vigorously without the alkali halide. The mechanochemical reactions occurring during the grinding of clay minerals can be classified into four groups; delamination, thermal diffusion, layer breakdown and sorption of water. Grinding the neat clay gives particle of lower crystallinity, with a lower proportion of structural hydroxyls and a lower temperature of dehydroxylation than unground clay. The hydration energy increases with grinding time.

4.3 Result and Discussion for XRD

XRD is used to obtain the interlayer spacing of the clay, before and after modification. Basically, the interlayer spacing, basal spacing or d(001) spacing of the MMT is measured from the top of the Si tetrahedral silica sheet (T) to the top of the Si tetrahedral sheet of the following layer. The clay which has not been organically modified has a relatively small intergallery distance of the *d* (001) plane and the intergallery environment is hydrophilic. Intercalation of organic surfactant between layers of clays not only changes the surface properties from hydrophilic to hydrophobic, but also greatly increases the basal spacing of the layers.

From the result of XRD analysis obtained for Homoionic Bentonite (e.g.; Bentonite-Na^+ and Bentonite-Ca^{2+}) in Table 4.3 and 4.4, it is proved that the Bentonite-Ca^{2+} has larger basal spacing compared to Bentonite-Na^+ which is due to larger ionic radius of Ca^{2+} compared to Na^+. Then, after the homoionic clay proceeded with the modification using ionic liquid, the samples of modified clay are sent again for XRD's characterization.

Based on the result obtained, only one sample (Bentonite-Na^+-bmimCl) as tabulated in Table 4.5, has shown an increment of basal spacing compared to the homoionic clay. It is most probably due to insufficient amount of ionic liquid being added during the intercalation process as the different basal spacing of the montmorillonite is a function of the saturated interlayer cation characteristics (MacEwan and Wilson, 1980).Besides that, the duration of reaction might be one of the factors as the ions are not totally exchanged during the 6 hours period.

Table 4.3: Result of XRD for Bentonite-Na^+

Caption	**Angle**	**d value**
	2-Theta °	Angstrom
2th=26.720 °, int=91.4 Cps, d=3.33360	26.72	3.3336
2th=19.621 °, int=40.5 Cps, d=4.52070	19.621	4.5207
2th=6.461 °, int=32.8 Cps, d=13.66977	6.461	13.66977

Table 4.4: Result of XRD for Bentonite-Ca^{2+}

Caption	**Angle**	**d value**
	2-Theta °	Angstrom
2th=26.626 °, int=55.9 Cps, d=3.34515	26.626	3.34515
2th=5.740 °, int=50.3 Cps, d=15.38497	5.74	15.38497
2th=19.711 °, int=25.1 Cps, d=4.50040	19.711	4.5004

Table 4.5: Result of XRD for Bentonite-Na^+ modified with Ionic Liquid

No. of Sample	**Samples**	**d(001) spacing Å**
1	Bentonite-Na^+	13.70988
2	Bentonite-Na^+-bmimCl	13.90302
3	Bentonite-Na^+-bmimBr	13.27835

Table 4.6: Result of XRD for Bentonite-Ca^{2+} modified with Ionic Liquid

No. of Sample	**Samples**	**d(001) spacing Å**
1	Bentonite-Ca^{2+}	15.50013
2	Bentonite- Ca^{2+}-bmimCl	14.15735
3	Bentonite- Ca^{2+}-bmimBr	14.10206

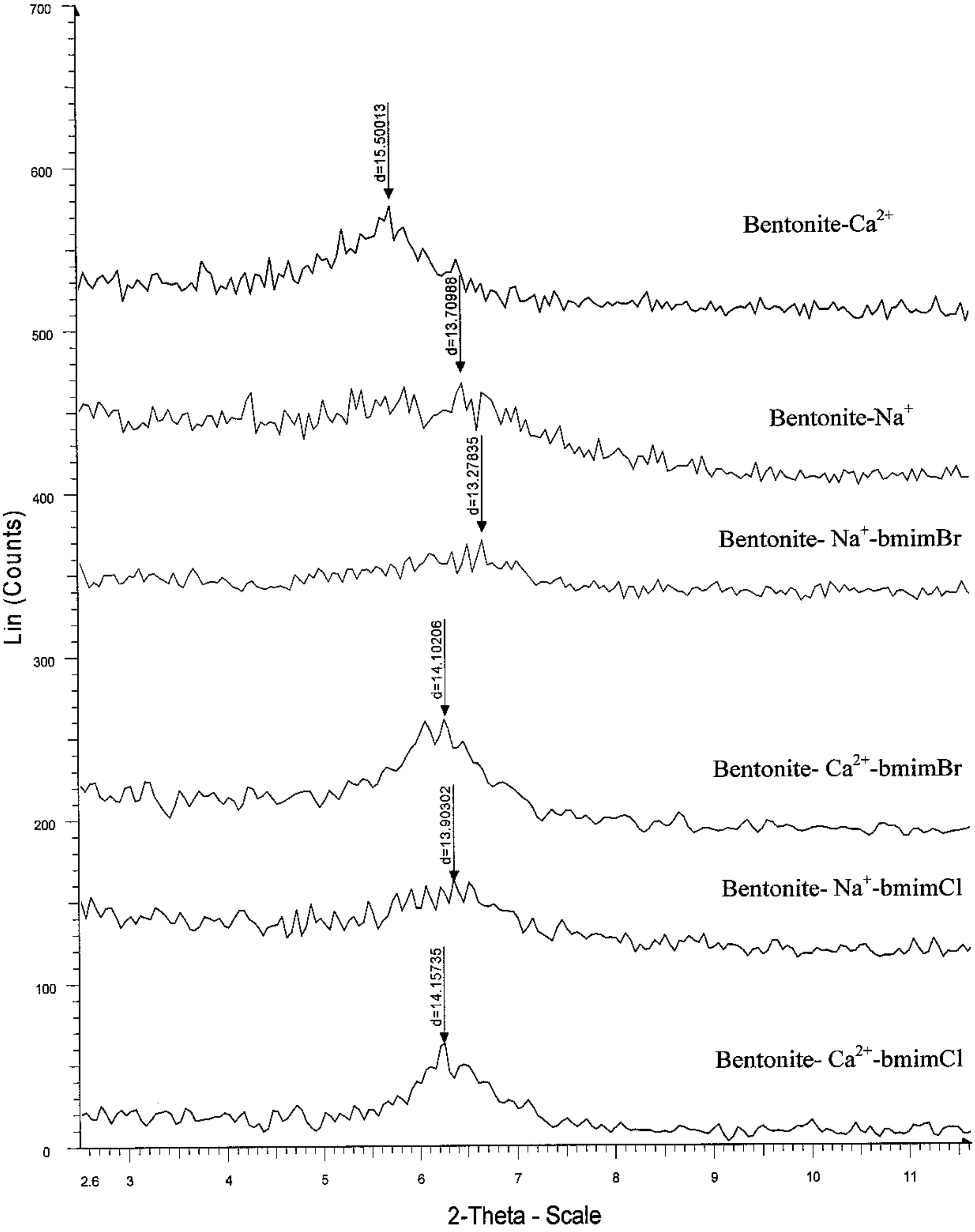

Figure 4.5: Compilation of XRD's Result

4.4 Result and Discussion for TGA

As mentioned earlier, TGA is used to measure any weight changes in a material as a function of temperature (or time) under a controlled atmosphere. Measurements are used mainly to predict the thermal stability of the sample up to 800 °C. Based on the result obtained as plotted in a graph (Figure 4.6), overall weight losses of the modified clay are considered low as the samples are heated up to 500°C.

As the temperature increased from room temperature up to 100°C, all sample shown some weight loss (10%) which is referring to evaporation of water. The moisture content might probably due to unavoidable exposure to the open air during handling the sample for characterization. Previously, the samples went to a long drying period as they were dried 24 hours at room temperature after centrifugation. Then, the samples were dried in the oven at 80°C for 6 hours in the vacuum environment in order to avoid oxidation.

Thermal stability of the samples is higher compared to the commercial organoclays. Based on the graph, the commercial organoclays shows tremendously weight loss (30%) after 250°C. As compared with the modified clay, the samples only shows 10% weight losses as they are heated from 100°C up to 500°C. One of the factors which contributed to the results might due to the large amount of thermally unstable based quaternary ammonium salts in the commercial organoclays compared to the high thermal stability of ionic liquid used to modify the clay.

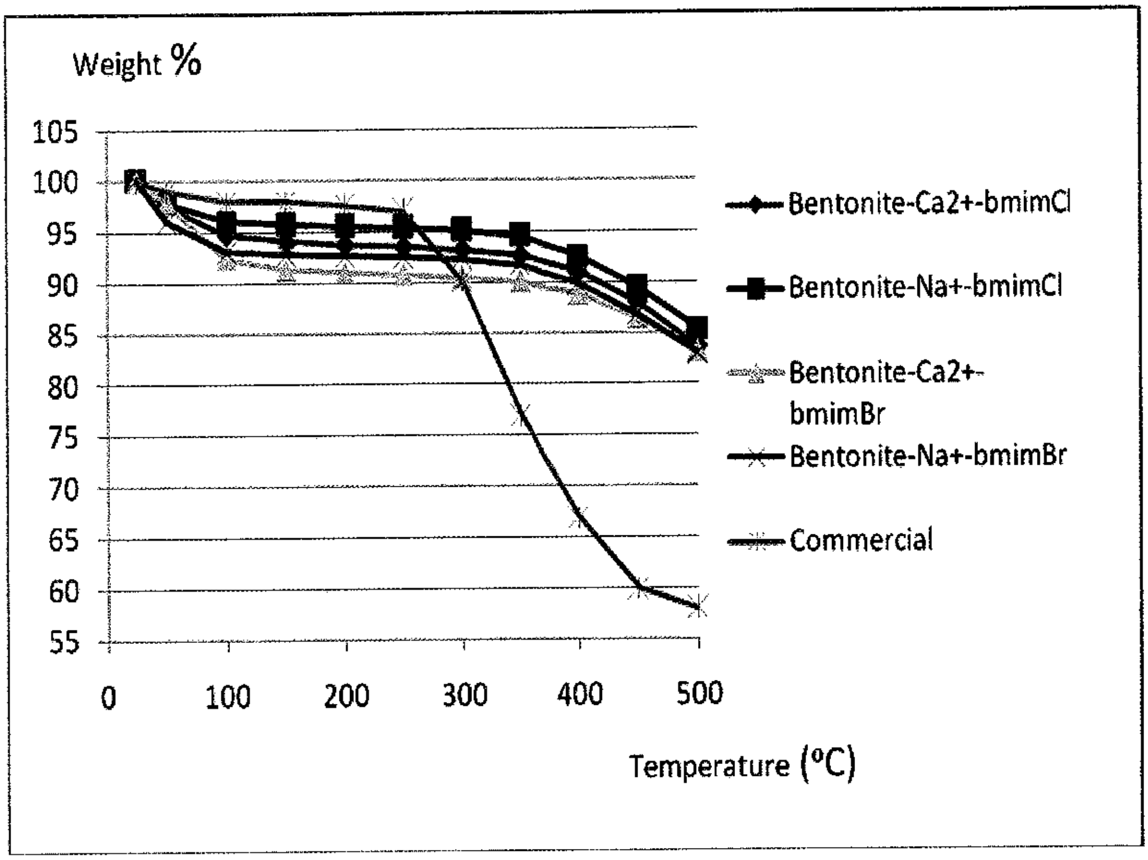

Figure 4.6: Graph of Weight % vs. Temperature for TGA

4.5 Result and Discussion for SEM

Observation of morphology structure after modification appears to be more porous.

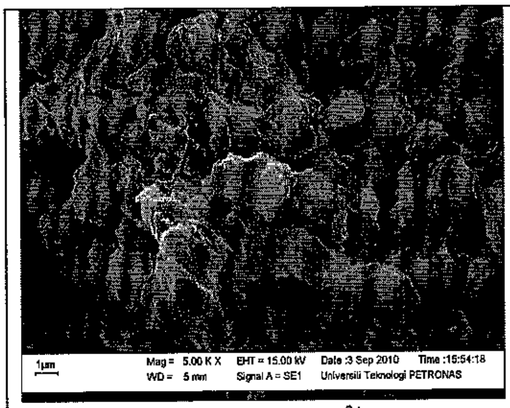

Figure 4.7: Bentonite-Ca^{2+}-bmimCl

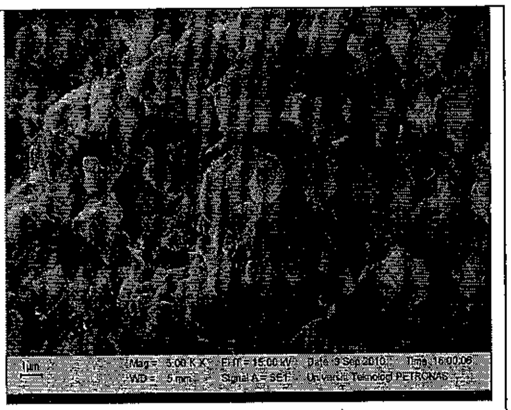

Figure 4.8: Bentonite-Na^{+}-bmimCl

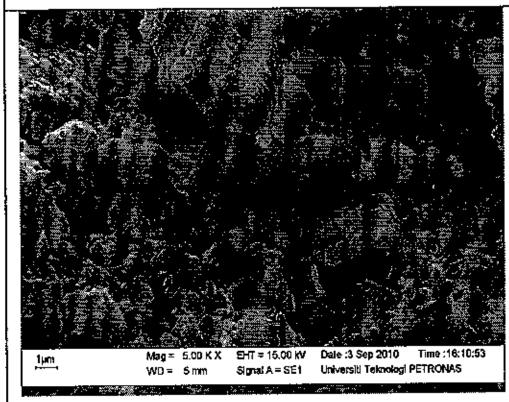

Figure 4.9: Bentonite- Ca^{2+}-bmimBr

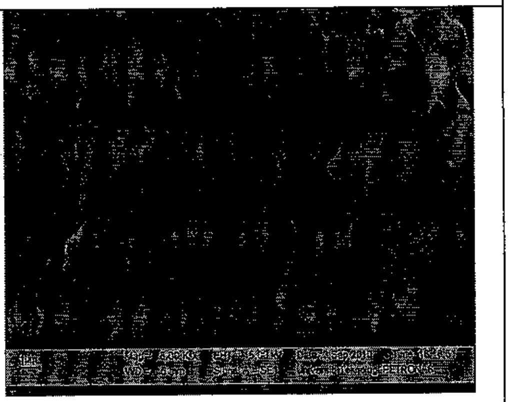

Figure 4.10: Bentonite-Na^{+}-bmimBr

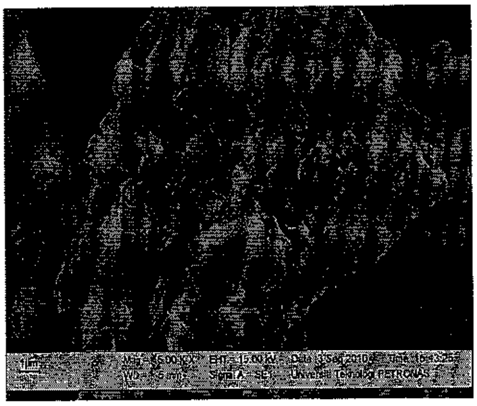

Figure 4.11: Bentonite

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusion

- Imidazolium based ionic liquid can be intercalated into bentonite. The intercalation of ionic liquid into bentonite through exchange with exchangeable Na^+ and Ca^{2+} cations is confirmed by comparing with the results of untreated bentonite and pure imidazolium based ionic liquids by the following quantitative methods (XRD and TGA) and qualitative method (FTIR and SEM).

- From XRD analysis, only one sample has shown an expansion of the basal spacing which is the bentonite with Na^+ exchangeable cations. The sample shown an expansion from 13.70 Å to 13.90 Å when reacted with 1-Butyl-3-methylimidazolium chloride. Therefore, different type of exchangeable cations (Na^+ and Ca^{2+}) and different types of halides in imidazolium based ionic liquid have not significantly affect the expansion of the basal spacing.

- From TGA analysis, the samples are identified to have a high thermal stability. Thus, they have the potential to encounter the limited usage of commercial organoclay as adsorbents which has low thermal stability.

5.2 Recommendation

Small expansion of the interlayer spacing might due to insufficient ions intercalated in the clay or insufficient time of reaction. Therefore, the author has proposed for an additional concentration of ionic liquids and proposed to increase the time of reaction for the intercalation process.

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APPENDIX

1) Determination of Cation Exchange Capacity (CEC) of Bentonite

Experiment was repeated 3 times and below is the sample calculation to determine the CEC value from the 1.101 % of Nitrogen obtained using Kjedahl Distillation:

1.10 % x 0.5 g = 5.5×10^{-3} g

= 5.5×10^{-3} g of ammonium / 0.5 g of Bentonite

= 5.5 mg of ammonium / 0.5 g of Bentonite

= 1100 mg / 100 g of Bentonite

The valence of ammonium, $[NH_4]$ = $[NH_4]^+$

Meq wt of $[NH_4]^+$ = 18.04 mg/meq

If soil can occupied 1100 mg $[NH_4]^+$ / 100 g of Bentonite ,

Therefore the CEC value of soil is;

= (1100 mg $[NH_4]^+$ / 100 g of Bentonite) x (meq /18.04 mg $[NH_4]^+$)

=0.61 meq / g of Bentonite

= 61 meq / 100 g of Bentonite

2) Determination of how much ionic liquid in clay based on CEC value.

Based on cation of butylimidazolium, [bmim]:

i) The valence of [bmim] = $[\text{bmim}]^+$ = 1 mmol/meq

ii) MW of [bmim] , $C_8H_{15}N_2$ = 8(12.01)+15(1.0)+2(14)

= 139.08 g/mol

iii) meq wt of [bmim] = MW of [bmim] / valence of [bmim]

= (139.08 mg/mmol) X (1 mmol/meq)

iv) If soil has 61 meq of CEC/100g, the amount of $[\text{bmim}]^+$, will be:

= (61 meq CEC / 100 g of bentonite) X (139.08 mg $[\text{bmim}]^+$ / meq)

= 84.84 mg

=0.8484g of $[\text{bmim}]^+$ in 100g of bentonite.

v) If the concentration of $[\text{bmim}]^+$ is 2X CEC, therefore the amount of ionic liquid$[\text{bmim}]^+$ will be :

= 2 X 0.8484 g

= 1.6968 g of $[\text{bmim}]^+$ in 100g of bentonite.