PREPARATION OF ORGANOCLAY FROM MONTMORILLONITE AND CHITOSAN

Mr.KAMOL KATIKUMJORN
MissTANTIKA AKSONNUM
Mr.UDOMSAP VISESBURANA

A SPECIAL PROJECT SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIRMENT FOR THE DEGREE OF
BACHELOR OF SCIENCE PROGRAM IN
SCIENCE AND TECHNOLOGY OF POLYMER
FACULTY OF SCIENCE
KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG
2005

Special Project Title	Preparation of Organoclay from Montmorillonite and Chitosan
Student Names	Mr. Kamol Katikumjorn Miss Tantika Aksonnum Mr. Udomsap Visesburana
Department	Chemistry, Faculty of Science
Program	Science and Technology of Polymer
Academic Year	2005
Special Project Advisor	Asst.Prof.Dr. Punnama Siriphannon Asst.Prof.Dr. Pathavuth Monvisade

---

International Programs of Faculty of Science, King Mongkut's Institute of Technology Ladkrabang had approved this special submitted in partial fulfillment of the requirement for Degree of Bachelor of Science.

____________________ Dean, Faculty of Science
(Assoc.Prof.Dr. Teerawat Mongkolassavarat)

Project Committee:

____________________ Project Advisor
(Asst.Prof.Dr. Punnama Siriphannon)

____________________ Project Advisor
(Asst.Prof.Dr. Pathavuth Monvisade)

____________________ Committee
(Assoc.Prof.Dr. Ittipol Jangchud)

____________________ Committee
(Dr.Chonlada Ritvirulh)

Special Project Title	**Preparation of Organoclay from Montmorillonite and Chitosan**
Name	**Mr.Kamol Katikumjorn 45050894**
	MissTantika Aksornnum 45050900
	Mr.Udomsap Visesburana 45050920
Department	**Chemistry**
Program	**Polymer Science and Technology**
Academic	**2005**
Special Project Advisor	**Asst.Prof.Dr.Punnama Siriphannon**
	Asst.Prof.Dr.Pathavuth Monvisade

Abstract

The chitosan-MMT organoclays was prepared by the mixing of MMT with chitosan solution (acetic acid as solvent), continuously stirred for 24 hours. The studied parameters were the weight ratio of starting MMT to chitosan (2.5:4, and 1:4), concentration of chitosan in acetic acid (0.5% 1.0%, and 2.0%), and reaction temperature (room temperature, and 60 °C). The expected organoclay were characterized by XRD, XRF, FTIR, TGA, and methylene blue (MB) absorption, compared with MMT, chitosan, and MMT grinded with chitosan. It was found that the Na^+ ions of MMT was exchanged with NH_3^+ ions of chitosan. Therefore, the d_{001} plane of the organoclay was wider than that of the starting MMT. The MB absorption showed the increased of specific surface area of clay sheets due to the delamination of modified MMT. Decomposition of the modified MMT was observed in the temperature range of 180-800 °C. This result indicated that decomposition temperature of the organoclays was higher than that of the starting MMT and chitosan.

ACKNOWLEDGMENTS

The author would like to take this opportunity to express sincere thanks to their advisors and people who gave useful advice and full support in this research.

The author wishes to express them deep gratitude to Asst. Prof. Dr. Pumnama Siriphanon, and Asst. Prof. Dr. Pathavuth Monvisade, for them valuable guidance, attention, and encouragement throughout this research. It goes without saying to the special project committee, Assoc. Prof. Dr. Ittipol Jangchud and Asst. Prof. Dr. Chonlada Ritvirulh, for reading and criticizing the manuscript.

They greatly appreciate all the professor who have invaluable knowledge while studying in the department of chemistry, faculty of science, King Mongkut's Institute of Technology Ladkrabang.

Special thanks to Scientific Instruments Service Center at the department of chemistry, faculty of science, King Mongkut's Institute of Technology Ladkrabang for them help in XRD, XRF, TGA, and FTIR analysis. In the addition, thanks also to faculty of science, King Mongkut's Institute of Technology Ladkrabang for instrumental process and instrument analysis.

They also would like to give the special thanks to all of their friends at department of science who have been helping and encouraging them while studying at King Mongkut's Institute of Technology Ladkrabang.

Last but not least, the author would like to express them the deepest appreciation their dearest father, mother, brother and sister for love, care, and encouragement that they have, which is the most important in their life forever.

Mr.KAMOL KATIKUMJORN

MissTANTIKA AKSORNNUM

Mr.UDOMSAP VISESBURANA

TABLE OF CONTENTS

		Page
Abstract		i
Acknowledgement		ii
Table of Contents		iii
List of Tables		v
List of Figures		vi
Chapter 1	Introduction	1
	1.1 Introduction	1
	1.2 Objectives	2
	1.3 Scope of Study	2
	1.4 Expected Results	3
Chapter 2	Theory and Literature Reviews	4
	2.1 Clays and Clay Modifications	4
	2.1.1 The physical characteristics of clays	4
	2.1.2 Clay Classification	5
	2.2 Chitin and Chitosan	9
	2.2.1 Preparation of Chitin and Chitosan	12
	2.2.2 Spectra of Chitin and Chitosan	14
	2.2.3 Characterization	15
	2.2.4 Applications	15
	2.3 Nanocomposite	15
	2.4 Methylene Blue Test	17
	2.5 Literature Reviews	19

TABLE OF CONTENTS (CONTINUED)

		Page
Chapter 3	Experimental Details	22
	3.1 Materials	22
	3.2 Apparatus	22
	3.3 Preparation of the Organoclay	23
	3.3.1 Preparation of Chitosan Solution	23
	3.3.2 Preparation of Modified MMT (Organoclays)	24
	3.4 Characterization of Modified MMT	26
	3.4.1 X-ray Diffractometer (XRD)	26
	3.4.2 X-ray Fluorescence (XRF)	26
	3.4.3 Fourior Transform Infrared Spectroscopy (FT-IR)	26
	3.4.4 Methylene Blue Absorption	27
	3.4.5 Thermogravimetric Analysis (TGA)	28
Chapter 4	Results and Discussion	33
	4.1 X-ray Diffractometer (XRD)	33
	4.2 X-ray Fluorescence (XRF)	36
	4.3 Fourior Transform Infrared Spectroscopy (FT-IR)	38
	4.4 Methylene Blue Absorption	41
	4.5 Thermogravimetric Analysis (TGA)	44
Chapter 5	Conclusion and Recommendations	49
	5.1 Conclusion	49
	5.2 Recommendations	50
References		51
Appendix-A		52
Appendix-B		54

LIST OF TABLES

Table		Page
3.1	The viscosity of Chitosan solution	23
3.2	The variation of chitosan, MMT and amount of acetic acid in the experiment	25
4.1	Ratio of Al: Si and Na: Al from XRF	37
4.2	Absorption Band assignments of MMT, Chitosan, and Modified MMT	40
4.3	UV Absorbance of MMT, Chitosan, MMT grinded with Chitosan, and Modified MMT in MB solution	42

LIST OF FIGURES

Figure Page

2.1 Bright pink of montmorillonite.. 6

2.2 Montmorillonite overgrown on pore spaces and authigenicly-overgrown quartz grains in a sandstone. SEM image of a core sample...................... 6

2.3 Illite.. 7

2.4 Structure of chitin... 9

2.5 Structure of chitin and chitosan.. 11

2.6 Preparation of chitin and chitosan.. 13

2.7 IR Spactra of Chitin(A) ,and Chitosan(B).. 14

2.8 ^{13}C NMR Spactra of Chitin(A) ,and Chitosan(B) by CP-MAS................ 14

2.9 Three types of polymer-clay composites, (A) conventional composite, (B) intercalated nanocomposite, and (C) exfoliated nanocomposite........... 16

2.10 Structure of methylene blue... 17

2.11 Spectrum of methylene blue with HP Spectrophotometer using 1 cm quartz 17

2.12 Methylene blue absorption... 19

3.1 Apparatus to Preparation Organoclay... 25

3.2 The Methylene Blue Absorption of the modified MMT (A) initial state (B) final state (one night)... 28

3.3 Preparation of Clays... 29

3.4 Preparation of Chitosan solution.. 30

3.5 Preparation of Chitosan-Montmorllonite Organoclays............................. 31

4.1 The XRD patterns of MMT, chitosan and modified MMT........................ 34

4.2 Schematic of Chitosan interacted MMT...35

4.3 Sedimentation Test...36

4.4 The FTIR spectrum of the starting MMT, Chitosan, and modified MMT.... 39

4.5 MB Absorption of MMT, Chitosan, MMT grinded with Chitosan, and Modified MMT.. 43

4.6 Thermogram of MMT.. 45

4.7 Thermogram of Chitosan.. 46

LIST OF FIGURES (CONTINUE)

Figure Page

4.8 Thermogram of MMT grinded with Chitosan... 47

4.9 Thermogram of Modified MMT.. 48

Chapter 1

Introduction

1.1. Introduction

Due to the plastics industry is continually looking for ways to increase the benefit from the additive filler. In the last few years one of the most significant technological breakthroughs in the plastics industry is the development of polymer nanocomposites, i.e. plastics resins reinforced with nanosize additives. The most common nanoadditive in nanocomposites research is organoclay, a nano-size silicate material.

Common organoclay have been used as inorganic fillers for the conventional polymer composites to reduce the cost or to give them special properties such as modulus, hardness, thermal stability, opacity and brightness, etc. One types of clay is aluminosilicates, which have a sheet-like (layered) structure, and consist of silica SiO_4 tetrahedra bonded to alumina AlO_6 octahedra in a variety of ways. A 2:1 ratio of the tetrahedra to the octahedra results in smectite clays, the most common of which is montmorillonite. Depending on the precise chemical composition of the clay, the sheets bear a charge on the surface and edges, this charge being balanced by counter-ions, which reside in part in the inter-layer spacing of the clay. The thickness of the layers (platelets) is of order of 1 nm. The clay platelets are truly nanoparticulate.

In the past, the chemical was used for improve the specific properties is a long chain amine or aliphatic amine polymer. In the other hand the problem from the intercalation is high cost of chemical raw material. One way to solve this problem is using natural polymers that consist of the amine functional group. Crab and shrimp shells are one of the good examples of natural polymer system formed in layer structure that consists of chitin-chitosan, protine, and inorganic minerals. Due to its properties, such as high mechanical strength, hydrophilic character, good adhesion and non-toxicity, we may claim that crustacean shell is a perfect bionanomaterial where multicomponent of chitin-chitosan, protein, and mineral co-exists with miscibility resulting in a material which possesses water-insolubility, high strength, and good mechanical properties with complete biodegradability.

In this study, the organoclay made of montmorillonite and chitosan has been developed. The montmorillonite and chitosan was mix using mechanical stirrer. Concerning synthetic polymers, improving the properties of biodegradable polymer matrix. By varying the weight ratio of montmorillonite to chitosan, the concentration of acetic acid, and varying the temperature during the preparation. The chemical and physical characteristics of organoclay are investigated in order to the characterization by using XRD, TGA, FTIR, XRF and methylene blue absorption.

1.2. Objective

1.2.1 To study a suitable method for modification of montmorillonite with chitosan.

1.2.2 To investigate the suitable condition for modification of montmorillonite with chitosan.

1.3. Scope of study

1.3.1 Preparation of organoclay filler from montmorillonite and chitosan.

- Varying the weight ratio of montmorillonite to chitosan, i.e., 2.5:4, 1.0:4, and 0.5:4

- Varying the concentration of chitosan, i.e., 0.5%, 1.0%,and 2.0% weight by volume of acetic acid.

- Varying the temperature during the preparation, i.e., room temperature and 60°C.

1.3.2 Characterization of nanoclay by using XRD, TGA, FTIR, XRF and methylene blue absorption.

1.4. Expected results

1.4.1 Organoclay from intercalation of chitosan into montmorillonite can be successfully the preparation.

1.4.2 The knowledge from this project can be used to improve the properties of organoclay filler made from montmorillonite with chitosan in the future.

Chapter 2

Theory and Literature Reviews

2.1 Clays and Clay Modifications [1,2]

Clay is a generic term for an aggregate of hydrous silicate particles less than 4 μm in diameter. Clay consists of a phyllosilicate minerals in silicon and aluminium oxides and hydroxides which include amounts of structural water. Clays are formed by the chemical weathering of silicate-bearing rocks by carbonic acid, but some are formed by hydrothermal activity, and they are distinguished from other small particles in soils such as silt by their small size, flake or layered shape, affinity for water and high plasticity index. Most clays are chemically and structurally analogous to other phyllosilicates but contain water and allow more substitution of their cations. There are many important uses and considerations of clay minerals, such as manufacturing, drilling, construction and paper production.

2.1.1 The physical characteristics of clays [2]

- Clay minerals tend to form microscopic to sub microscopic crystals.
- They can absorb water or lose water from simple humidity changes.
- When mixed with limited amounts of water, clays become plastic and are able to be molded and formed as children's clay.
- When water is absorbed, clays will often expand as the water fills the spaces between the stacked silicate layers.
- Due to the absorption of water, the specific gravity of clays is high variable and is lowered with increased water content.
- The hardness of clays is difficult to determine due to the microscopic nature of the crystals, but the hardness is usually between 2 - 3 and many clays give a hardness of 1 in field tests.

- Clays tend to form from weathering and secondary sedimentary processes with only a few examples of clays forming in primary igneous or metamorphic environments.
- Clays are rarely found separately and are usually mixed not only with other clays but with microscopic crystals of carbonates, feldspars, micas and quartz.

2.1.2 Clay Classification [2,3,4]

Clay minerals are divided into four major groups. These are the important clay mineral groups:

1.) The Kaolinite Group, this group has three members (kaolinite, dickite and nacrite) and a formula of $Al_2Si_2O_5(OH)_4$. The different minerals are polymorphs, meaning that they have the same chemistry but different structures (polymorph = many forms). The general structure of the kaolinite group is composed of silicate sheets (Si_2O_5) bonded to aluminum oxide/hydroxide layers ($Al_2(OH)_4$) called gibbsite layers. The silicate and gibbsite layers are tightly bonded together with only weak bonding.

Uses: In ceramics, as a filler for paint, rubber and plastics and the largest use is in the paper industry that uses kaolinite to produce a glossy paper such as in most magazines.

2.)The Montmorillonite/Smectite Group ,this group is composed of pyrophyllite, talc, vermiculite, sauconite, saponite, nontronite and montmorillonite. The general formula is (Ca, Na, H)(Al, Mg, Fe, Zn)$_2$(Si, Al)$_4$O$_{10}$(OH)$_2$ - xH$_2$O, where x represents the variable amount of water that members of this group. Talc's formula, for example, is $Mg_3Si_4O_{10}(OH)_2$. The gibbsite layers of the kaolinite group can be replaced in this group by a similar layer that is analogous to the oxide brucite, ($Mg_2(OH)_4$). The structure of this group is composed of silicate layers sandwiching a gibbsite (or brucite). Moreover, water content in montmorillonite is absorbed by the crystal and tend to swell to several times their original volume. This makes montmorillonite a useful minerals purposes.

Uses: a facial powder (talc), filler for paints and rubbers, an electrical, heat and acid resistant porcelain, in drilling muds and as a plasticizer in molding sands and other materials, prevent leakage of fluids, a component of foundry sand, a desiccant to remove moisture from air and gases.

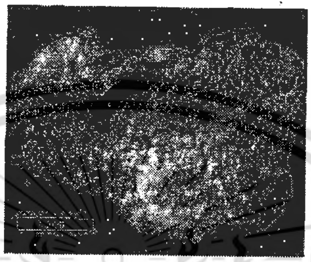


Fig.2.1 Bright pink of montmorillonite.

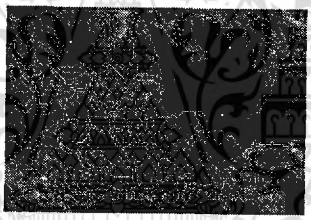


Fig.2.2 Montmorillonite overgrown on pore spaces. SEM image of a core sample.

3.)The Illite (Clay-mica) Group, the mineral illite is the only common mineral represented, however it is a significant rock forming mineral that is a main component of shales and other argillaceous rocks. The general formula is (K, H)$Al_2(Si, Al)_4O_{10}(OH)_2$ - xH_2O, where x represents the variable amount of water. The structure of this group is similar to the montmorillonite group with silicate layers sandwiching a gibbsite-like layer. The variable amounts of water molecules would lie as well as the potassium ions.

Uses: A common constituent in shales and is used as a filler and in some drilling muds.

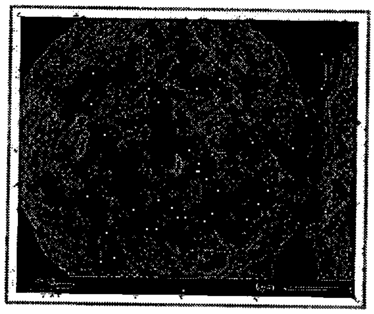


Fig.2.3 Illite

4.)The Chlorite Group ,this group is not always considered a part of the clays and is sometimes left alone as a separate group within the phyllosilicates. It is a relatively large and common group and its members are not well known. These are some of the members:

- **Amesite** $(Mg, Fe)_4Al_4Si_2O_{10}(OH)_8$
- **Baileychlore** $(Zn, Fe^{+2}, Al, Mg)_6(Al, Si)_4O_{10}(O, OH)_8$
- **Chamosite** $(Fe, Mg)_3Fe_3AlSi_3O_{10}(OH)_8$
- **Clinochlore (kaemmererite)** $(Fe, Mg)_3Fe_3AlSi_3O_{10}(OH)_8$
- **Cookeite** $LiAl_5Si_3O_{10}(OH)_8$
- **Corundophilite** $(Mg, Fe, Al)_6(Al, Si)_4O_{10}(OH)_8$
- **Daphnite** $(Fe, Mg)_3(Fe, Al)_3(Al, Si)_4O_{10}(OH)_8$
- **Delessite** $(Mg, Fe^{+2}, Fe^{+3}, Al)_6(Al, Si)_4O_{10}(O, OH)_8$
- **Gonyerite** $(Mn, Mg)_5(Fe^{+3})_2Si_3O_{10}(OH)_8$
- **Nimite** $(Ni, Mg, Fe, Al)_6AlSi_3O_{10}(OH)_8$
- **Odinite** $(Al, Fe^{+2}, Fe^{+3}, Mg)_5(Al, Si)_4O_{10}(O, OH)_8$
- **Orthochamosite** $(Fe^{+2}, Mg, Fe^{+3})_5Al^2Si_3O_{10}(O, OH)_8$
- **Penninite** $(Mg, Fe, Al)_6(Al, Si)_4O_{10}(OH)_8$
- **Pannantite** $(Mn, Al)_6(Al, Si)_4O_{10}(OH)_8$
- **Rhipidolite (prochlore)** $(Mg, Fe, Al)_6(Al, Si)_4O_{10}(OH)_8$
- **Sudoite** $(Mg, Fe, Al)_{4-5}(Al, Si)_4O_{10}(OH)_8$
- **Thuringite** $(Fe^{+2}, Fe^{+3}, Mg)_6(Al, Si)_4O_{10}(O, OH)_8$

The term chlorite is used to denote any member of this group when differentiation between the different members is not possible. The general formula is $X_{4-6}Y_4O_{10}(OH, O)_8$. The X represents either aluminum, iron, lithium, magnesium, manganese, nickel, zinc or rarely chromium. The Y represents aluminum, silicon, boron or iron but mostly aluminum and silicon. The gibbsite layers of the other clay groups are replaced in the chlorites by a similar layer that is analogous to the oxide brucite. The structure of this group is composed of silicate layers sandwich with a brucite or brucite-like layer, however, in the chlorites, there is an extra weakly bonded in brucite layer.

Uses : No industrial uses.

Some minerals listed above (especially chlorite, pyrophyllite and talc) as belonging to one of the clay groups are often excluded by some minerologists. Usually, their crystal size and character due not consistently conform to those parameters that define a clay. Such minerals are listed here more for their structural similarities, however, all three minerals are quite often found associated with and behave like clays occassionally.

2.2 Chitin and Chitosan [6,7,8,9,10]

Chitin is not exactly a household word, but most are familiar with its source. It is found naturally in the shells of crustaceans, such as crab, shrimp and lobster, as well as in the exoskeleton of marine zoo-plankton, including coral and jellyfish. Insects, such as butterflies and ladybugs, have chitin in their wings. And the cell walls of yeast, mushrooms and other fungi also contain this natural substance.

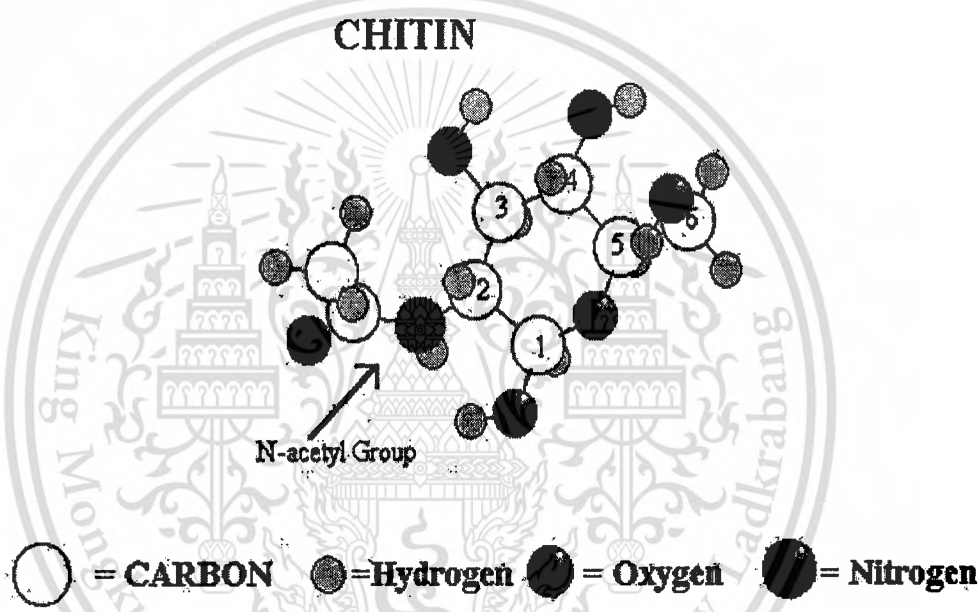


Fig.2.4 Structure of chitin

Chitin was first found in mushrooms in 1811 by Professor Henri Braconnot while he was Professor of Natural History and Director of the Botanical Gardens at the Academy of Sciences in Nancy, France. In the 1830's, it was isolated in insects and named chitin. Professor C. Rouget discovered chitosan in 1859, and over the next century, much fundamental research took place on these compounds. An intense interest in new applications grew in the 1930s and early 1940s, as evidenced by almost 50 patents; however, the lack of adequate manufacturing facilities and competition from synthetic polymers hampered commercial development. Renewed interest in the 1970s was encouraged by the need to better utilize shellfish shells. Scientists worldwide began to chronicle the more distinct properties of chitin and its derivatives and understand the potential of these natural polymers. Since then, numerous research studies have been undertaken to find ways to use materials. Over the last 200 years, the exploration of chitosan has taken on many difference forms. Several other researchers continuto build on the original finding of Bracannot, discovering new use for chitin as they find different forms of it in nature.

Chitin and its derivatives have many properties that make them attractive for a wide variety of applications. Their antibacterial, anti-fungal and anti-viral properties make them particularly useful for biomedical applications, such as wound dressings, surgical sutures and as aids in cataract surgery and periodontal disease treatment. Chitin and chitosan are non-toxic and non-allergenic, so the body is not likely to reject these compounds as foreign invaders. Chitin's biodegradable and anti-fungal properties are a plus for environmental and agricultural uses.

Chitin is one of the three most abundant polysaccharides in nature, in addition to cellulose and starch. It ranks second to cellulose as the most plentiful organic compound on earth. Cellulose and starch are key carbohydrates which plants use as a food source and to build cell walls. In addition, they have widespread use in the industry. Researchers and entrepreneurs see similar potential for chitin.

Chemically, cellulose, starch and chitin are polysaccharides consisting of smaller sugar molecules strung together, like pearls on a strand. Chitin can be processed into many derivatives, the most readily available being chitosan, which is formed when chitin is heated with a chemical solution.

Chitosan is a linear polysaccharide composed of randomly distributed ß-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). Chitosan is produced commercially by deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans (crabs, shrimps etc.). The degree of deacetylation (%DA) can be determined by NMR spectroscopy, and the %DA in commercial chitosans is in the range 60-100 %. The amino group in chitosan has a pKa value of ~6.5, thus, chitosan is positively charged and soluble in acidic to neutral solution with a charge density dependent on pH and the %DA-value. In other words, chitosan is bioadhesive and readily binds to negatively charged surfaces such as mucosal membranes. Chitosan enhance the transport of polar drugs across epithelial surfaces, and is biocompatible and biodegradable. Purified qualities of chitosans are available for biomedical applications.

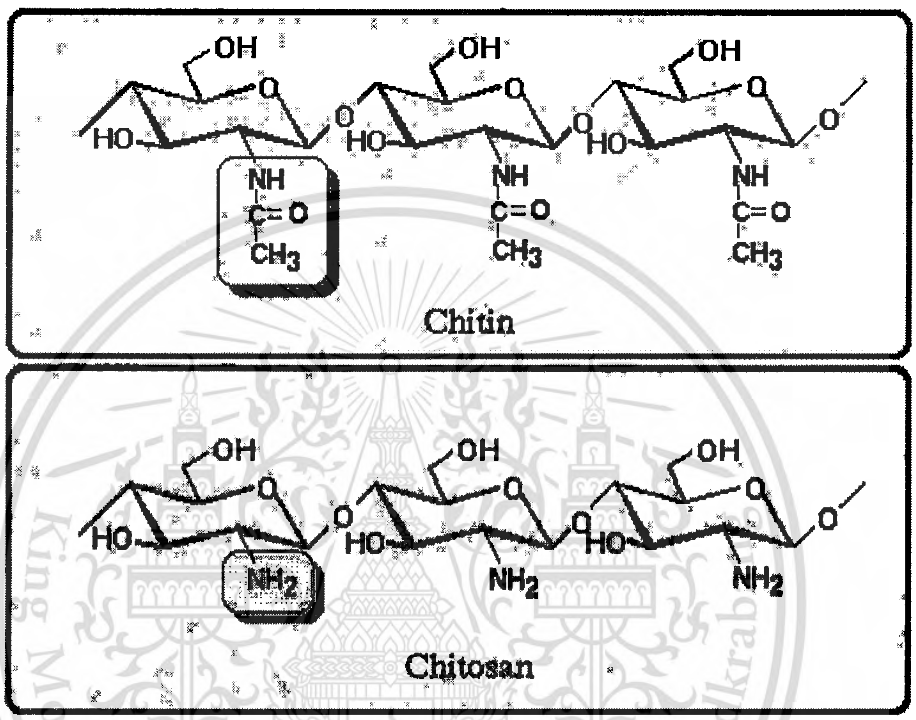


Fig.2.5 Structure of chitin and chitosan

Chitosan is used in processes like detoxifying water. When is spread over the surface of water, it literally absorbs greases, oils, heavy metals and other potentially toxic substances. Like a "fat magnet," it attracts these bio-hazardous substances from drinking water to such an extent that a scum forms in the water, which can be easily removed. Water purification plants throughout the nation use chitosan for this purpose. What this indicate to scientists was that chitosan can selectively absorb fats even in a water medium.

Nowadays, many countries already use chitin and chitosan in a variety of products, yet a whole array of possible materials could be made from these compounds. In Japan, chitosan was first used for waste water treatment because of its metal-binding properties, but today chitin and chitosan are found in everything from antibiotics and surgical sutures to dietary supplements, foods and cosmetics. It also can be found in pet foods and is used to make cloth for undergarments and socks. In the U.S., chitin and chitosan are being used in seed treatment, animal feed supplementation and water purification, as well as in hair care products and dietary supplements.

2.2.1 Preparation of Chitin and Chitosan [11]

A variety of processes have been developed for the preparation of chitin and chitosan because their physicochemical characteristics differ with crustacean species and preparation methods. The utilization of existing methods needs their modification to be applied with new raw material regarding each case. Depending on the process to obtain chitosan, this can be produced with different degrees of deacetylation. These chitosans have different quantities of free amine groups and therefore different capacities to trap metal ions.

At present time, the easiest and famous method was suggested by Muzzarelli, which the decalcification was carried out by soaking the crushed crab shells in HCl at room temperature. After that, NaOH solutions is used to remove the proteins (deproteination), and washed to neutral. The deacetylation of chitin is achieved by soaking the chitin samples in NaOH solutions of various concentrations. The decolorization in $KMnO_4$ and oxalic acid with autoclave or sunshine..

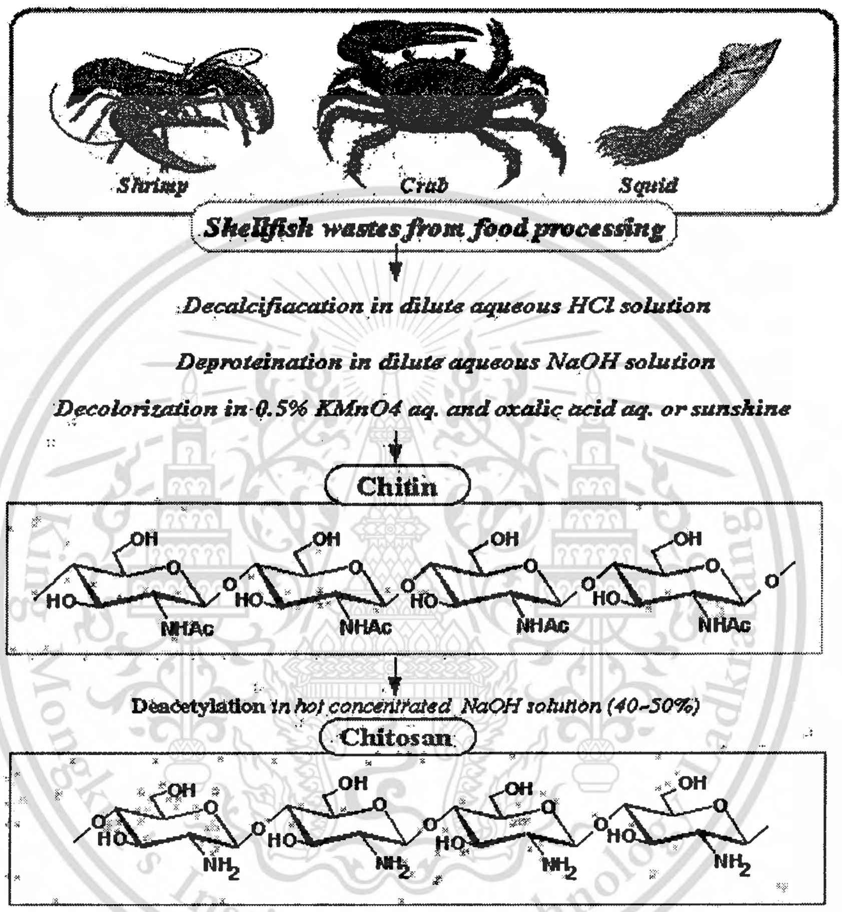


Fig.2.6 Preparation of chitin and chitosan

2.2.2 Spectra of Chitin and Chitosan [12]

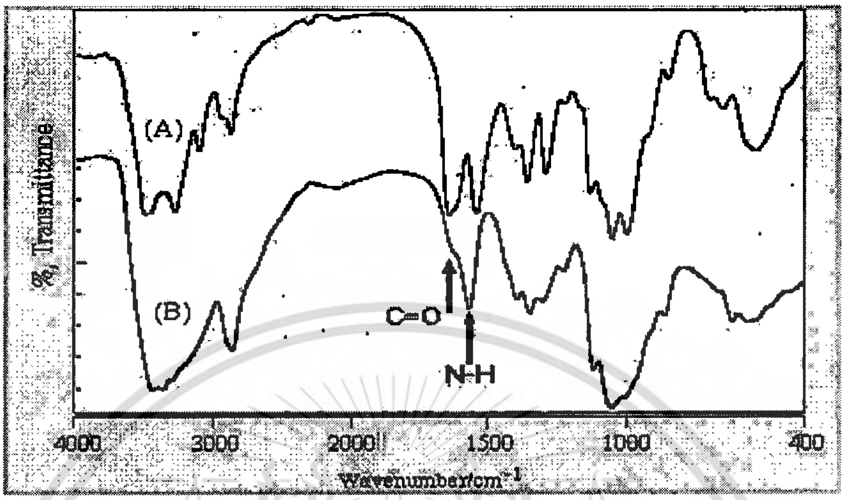


Fig.2.7 IR Spactra of (A) chitin, and (B) chitosan

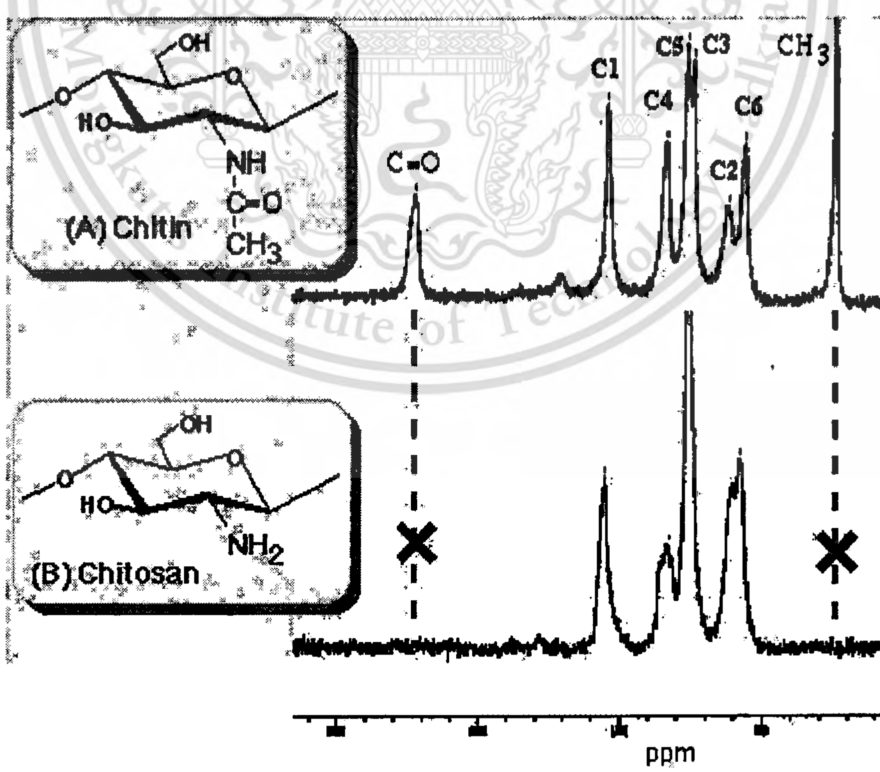


Fig.2.8 ^{13}C NMR spactra of (A) chitin, and (B) chitosan

2.2.3 Characterization [13]

Both chitin and chitosan are naturally biodegrable and nontoxic.Chitosan can be described in general by the following parameters: degree of deacetylation (%) , dry matter (%), ash (%) , protein (%) ,viscosity in centipoise, intrinsic viscosity (η_{sp}/C) , molecular weight (g/mol) , and turbidity (NTU units). All these parameters can be adjusted to the application chitosan is being used for. The main parameters that influence on the product properties is as mentioned above, the degree of deacetylation and viscosity. The deacetylation is very important to get a soluble product. But it is not only the degree of deacetylation that influence on the solubility. The distribution of the acetyl groups are also important. Moreover, viscosity can be adjusted to each application, by controlling process parameters.

2.2.4 Applications [13,14]

Chitosan is unique, with a polyamine character which makes it soluble (at acid pH), positively charged, different viscosity and easily modified chemically. These properties confer upon chitosan potential applications in nutritional uses, food, biomedicine, skin and hair care, environment and agriculture, and others.

2.3 Nanocomposite [15,16]

Nanocomposite is a type of composites containing filler that has at least one dimension in the range of nanometer. Most of the nanocomposites can be produced by using metal particles, colloids, and smectic-clay minerals. Nanotechnology has gained interest in the development such as polymer nanocomposite, typically, smectic-clay are used as fillers. Montmorillonite and hectorite layered structure are dispersed in polymer matrix.

Dispersion of clay minerals in a polymer matrix is categorized into three types, i.e., conventional composite, intercalated nanocomposite and exfoliated nanocomposite. **Conventional composite** contains the existing clay tactoids in original aggregated state with an unintercalated polymer chain along the silicate layers. The clay tactoids are simply dispersed as a segregate phase. **Intercalated nanocomposite** is formed by the insertion of one or more polymer chains into the clay galleries resulting in a well ordered multilayer with alternating polymer chains and nanoscale inorganic layers, owing to the spatial confinement of the polymer between the densed clay layers. Intercalated polymer-clay nanocomposites can exhibit impression conductivity. **Exfoliated nanocomposite** can be obtained by separating a single silicate layer in the polymer matrix with the average distance of each layer depending on the clay content. The clay contents in exfoliated nanocomposite are usually much lower than in intercalated one. In addition, the undispersed hybrid corresponds to a conventional composite whereas the fine dispersed hybrid corresponds to either an intercalated or and exfoliated nanocomposite.

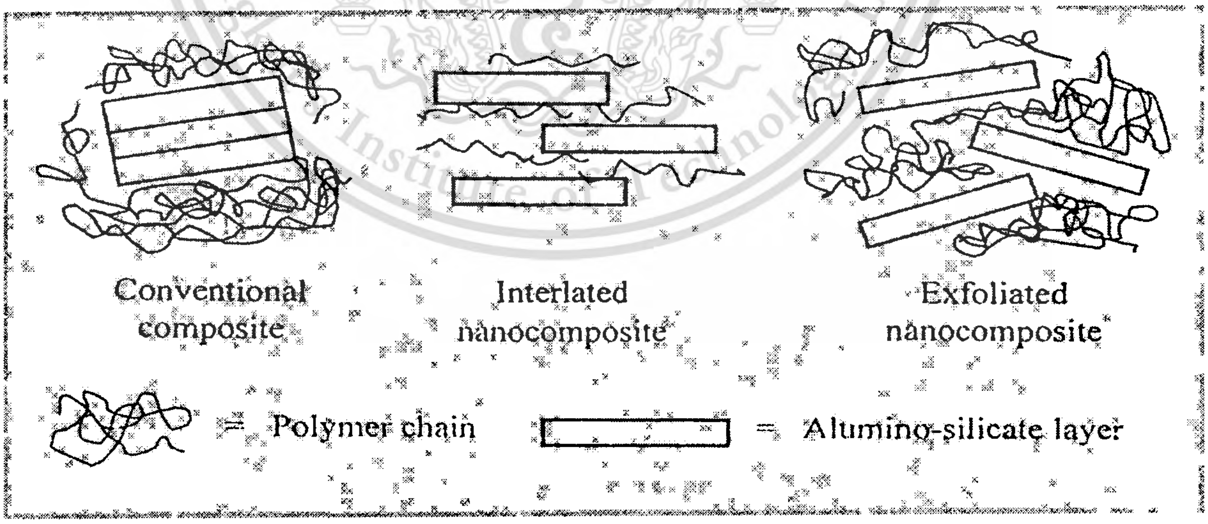


Fig. 2.9 Three types of polymer-clay composites, (A) conventional composite, (B) intercalated nanocomposite, and (C) exfoliated nanocomposite

2.4 *Methylene Blue Test [17]*

Methylene blue (MB) dye has been used to determine the surface area of clay minerals for several decades. The chemical formula is $C_{16}H_{18}ClN_3S$, with a corresponding molecular weight of 319.87 g/mol.

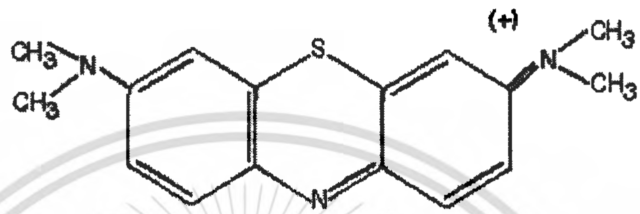


Fig2.9 Structure of methylene blue

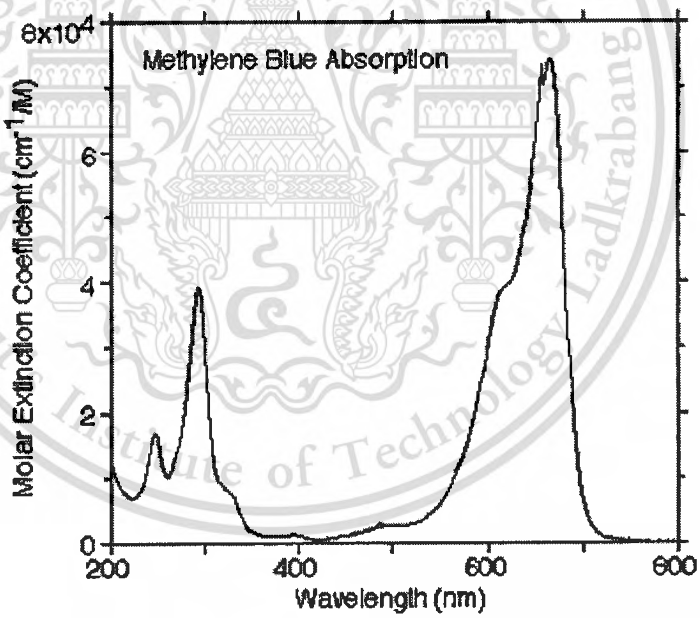


Fig. 2.10 Spectrum of methylene blue with HP Spectrophotometer using 1 cm quartz

Methylene blue in aqueous solution is a cationic dye, $C_{16}H_{18}N_3S^+$, which absorbs to negatively charged clay surfaces. Hence, the specific surface of particles can be determined by the amount of absorbed methylene blue. This molecule may attach to the mineral surface in various orientations, so the area covered by one methylene blue molecule may vary: (*i*) if the molecule lies on its largest face on the surface under study, the covered area is about 130 Å^2 per molecule. It is important to highlight that the technique is done in water suspensions, thus expansive minerals can expose all available surface area.; (*ii*) if the molecule is tilted (65–70°) with respect to the surface under study, the covered area is about 66 $Å^2$ per molecule; and (*iii*) if the longest axis is oriented perpendicular to the surface, the covered area is about 24.7 $Å^2$ per molecule.

The uncertainty in the assumption of the covered area can affect the estimation of specific surface by more than 100%. The most common assumption is that the molecule lies flat on the mineral surface on its largest face; in this case, the area covered by one methylene blue molecule is about 130 $Å^2$. Results in this study using kaolin confirm this value. The amount of absorption increases with surface area and surface charge density, which is affected by pH and ionic concentration. Furthermore, absorption involves ion replacement, which depends greatly on the valence, size, and

relative concentration of ions. The MB cations replace Na^+ more easily than Fe^{3+} and Al^{3+}, therefore MB yields higher specific surface values for Na-montmorillonite compared with Fe-montmorillonite and Al-montmorillonite. Similarly, excess salts in the solution not only alter the effective surface charge density, but also compete with methylene blue to be absorbed onto the surface. The dissolution of $CaCO_3$ and clay particles may influence the accuracy of measurements. Furthermore, the accuracy of this method is limited by the size of adsorbates.

The methylene blue technique involves high bonding energy (ionic Coulombian attraction -chemisorption) and it is generally limited to a monolayer. The MB absorption method renders higher values of specific surface in swelling clays, as interlayer surfaces can be reached by exchangeable ions after hydration. However, for nonswelling clay minerals such as kaolinite, there is no significant difference in specific surface determined with either dry or wet measurement procedures.

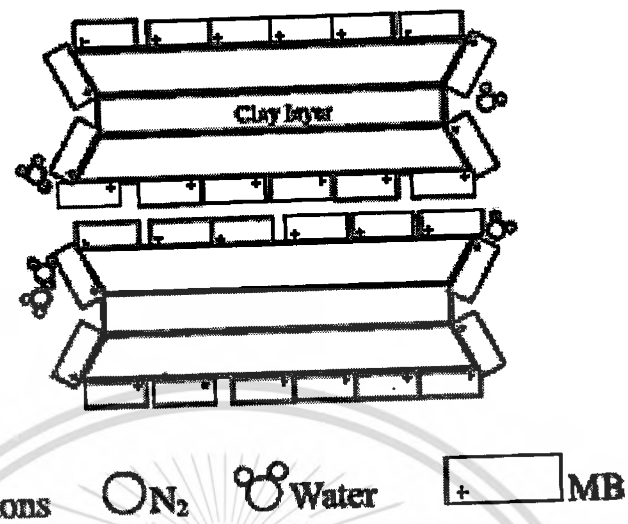


Fig2.11 Methylene blue absorption

2.5 Literature Reviews

Hajjaji M, Kacim S, Alami A, Bouadili A, Mountassir M [18], 2001 , concerned in a chemico-mineralogical characterization of a Lutetian sedimentary clay from the phosphateous basinof Ouled Abdoun (Moroccan Meseta). The clay fine fraction (<2 μm in size) has been saturated by Na^+ ions and used for the retention of methylene blue (MB). The UV-VIS was used to follow the kinetics of the process ,measure the adsorption isotherms and identify the nature of the MB species fixed to the fine fraction. The nature of MB^+ deriving species fixed to Na^+-saturated fine fraction was found to be dependent on the MB loading. For the smallest loadings, MB^+ ions are preferentially fixed to external acid sites, thus leading to the formation of MBH^{2+}. As the loading in creased, $(MB^+)_3$ developed while the protonated specoes disappeared. It was also found that some amount of the monomer MB^+ occurred exclusively on the external surface.

Darder M, Colilla M, and Ruiz-Hitzky E [19], 2003, studied on the intercalation of the cationic biopolymer chitosan in Na^+ - montmorillonite, providing compact and robust three-dimensional nanocomposites with functional properties.

CHN chemical analysis, X-ray diffraction, Fourier transform infrared spectroscopy, scanning transmission electron microscopy, energy-dispersion X-ray analysis, and thermal analysis have been employed in the characterization of the nanocomposites, confirming the adsorption in mono- or bilayers of chitosan chains depending on the relative amount of chitosan with respect to the cationic exchange capacity of the clay. The first chitosan layer is adsorbed through a cationic exchange procedure, while the second layer is adsorbed in the acetate salt form. Because the deintercalation of the biopolymer is very difficult, the $-NH_3^+ Ac^-$ species belonging to the chitosan second layer act as anionic exchange sites and, in this way, such nanocomposites become suitable systems for the detection of anions.

Adriana Czímerová, L'uboš Jankoviˇc, and Juraj Bujdák [20], 2004,concerned in the adsorption of a cationic dye, methylene blue (MB), on the surface of montmorillonite. The montmorillonite samples, saturated with various inorganic cations (mono-, bi-, and trivalent, including those of transition metals), were used. Influence of the exchangeable cations on the MB aggregation was tested. It was found that the available surface area and some phenomena related to the parameter, such as swelling, tactoid formation, did not significantly affect dye cation aggregation under the conditions used. However, layer charge distribution, as an intrinsic property of clay surface, may not be the only parameter that significantly affects the dye aggregation. The presence of large alkali metal cations (K^+, Rb^+, and Cs^+) or NH_4^+, which are less mobile and partially fixed on the clay surface, may significantly influenced an ion exchange reaction. The lower mobility of these cations may lead to incomplete ion exchange.

Darder M, López-Blanco M, Aranda P, Leroux F, and Ruiz-Hitzky E [21], 2005, concerned in synthesization of $[Zn_2Al]$ LDH (layered double hydroxide). The "coprecipitation" or "co-organized assembly" method has been successfully employed for the intercalation of such polysaccharides within the $[Zn_2Al]$ LDH. The "reconstruction" procedure from the calcined LDH in the presence of the anionic polysaccharides only resulted in a partial intercalation of the organic guest. Particular effort was devoted to the study of È-carrageenan-$[Zn_2Al]$ systems. XRD clearly shows the intercalation of alginate, pectin, and È-carrageenan between the layers of Zn_2Al LDH. The alginate and pectin are intercalated as a monolayer of the biopolymer, whereas ι-carrageenan showing a higher ΔdL is intercalated as a bilayer or most likely as a double helix. It is difficult at this stage of the investigation to confirm this last conformation. IR, EDX, and ^{13}C NMR techniques corroborate that the intercalation is always driven by electrostatic interactions between the negatively charged groups of the biopolymer and the positively charged LDH layers.

Darder M, Colilla M, and Ruiz-Hitzky E [22], 2005, the objective was the application of biopolymer-clay nanocomposites in the development of electrochemical sensors for the potentiometric determination of anionic species. Since chitosan-montmorillonite nanocomposites exhibited good functional and mechanical properties, they are employed in the construction of bulk-modified sensors for the detection of anions. These nanocomposites were combined with graphite particles to provide the system with electronic conductivity. Besides, the developed electrodes ware provided of low environment impact, and this devices are successfully applied in the potentiomeric determination of several anions, showing a higher selectivity towards monovalent rather than to di- or trivalent anions and the best potentiometric response towards nitrate ions. Moreover, chitosan-montmorillonite nanocomposites appeared as excellent materials for the development of bulk-modified potentiometric sensors for the anionic detection in aqueous samples.

Chapter 3

Experimental

3.1. Materials

3.1.1 Chitosan of %DD = 82.5, which is obtained from deacetylation of chitin, ELAND Corporation LTD.

3.1.2 Glacial acetic acid (HAc) (AR grade) used as solvent of chitosan, CARLO ERBA.

3.1.3 Mac-gel Montmorillonite (MMT), Thai Nippon.

3.1.4 Sodium hydroxide (NaOH) (Com. grade), CARLO ERBA.

3.1.5 Methylene blue ($C_{16}H_{18}ClN_3S$) (Spectroscopy grade), CARLO ERBA.

3.2. Apparatus

3.2.1 Beaker

3.2.2 Graduate cylinder

3.2.3 Magnetic stirrer

3.2.4 Mechanical stirrer

3.2.5 Hot plate with Thermocouple

3.2.6 Universal indicator

3.2.7 Vacuum filter

3.2.8 Uniaxial pressing

3.2.8 Peristaltic pump, V 77120-52, Cole Parmer

3.2.9 Brook field viscometer, RVT, Brook field Engineering Laboratories, INC.

3.2.10 Benchmill, A 1, Rocklabs Ltd.

3.2.10 Centrifuge machine, Centaur 2, Sanyo

3.2.11 X-ray diffractometer (XRD), D8 Advance, Bruker AG

3.2.12 Fourior transform infrared spectrometer (FT-IR), Spectrum GX, PerkinElmer

3.2.13 Thermogravimetric analyser (TGA), Pyris 1 TGA, PerkinElmer

3.2.14 X-ray fluorescence spectroscometer (XRF), SRS 3400, Bruker AG

3.3. Preparation of the Organoclays

3.3.1 Preparation of clays

1. Add 5 g of MMT into 3000 ml distilled water.
2. Sonicate the mixture in ultrasonic bath for 2 hours in order to separate the clay tactoids.
3. Dry the MMT in the hot air oven at 60°C for 48 hours.
4. Grind the MMT with mortar.

3.3.2 Preparation of Chitosan solution

1. Disslove 4 g of chitosan into 196, 396, and 796 ml of 2 % v/v acetic acid in order to obtain various concentration of the chitosan solutions, i.e., 2, 1, and 0.5 % respectively.
2. Adjust the pH of the solution to about 5 with 1M NaOH in order to avoid any structural change of the MMT.
3. Determine the viscosity of chitosan solution by Brook field viscometer and the value is shown in table.

% of chitosan in acetic acid (%)	Viscosity (mPa . S)
2	65
1	20
0.5	12.5

Table 3.1 The viscosity of Chitosan solution

3.3.3 Preparation of Modified MMT (Organoclays)

A. At Room Temperature

1. Swell 1 and 2.5 g of the MMT in 100 ml of distilled water using ultrasonic bath for 1 hour.
2. Slowly add the chitosan solution into the swelled clay suspension using peristaltic pump at the rate about 0.83 ml/min with vigorous stir. The mixture was kept at room temperature for 24 hours.
3. Rinse the chitosan-clay compound by distilled water until the pH of the washed water about 6-7.
4. Separate the modified MMT from the solution using centrifuge machine.
5. Dry the modified MMT clay in the oven at 60°C for 48 hours.
6. Grind the modified MMT with mortar.
7. Characterize the modified MMT using various techniques.

B. At 60°C

1. Swell 1 and 2.5 g of the MMT in 100 ml of distilled water using ultrasonic bath for 1 hour.
2. Slowly add the chitosan solution into the swelled clay suspension using peristaltic pump at the rate about 0.83 ml/min with vigorous stir. The mixture was kept at 60 °C for 24 hours.
3. Rinse the chitosan-clay compound by distilled water until the pH of the washed water about 6-7.
4. Separate the modified MMT from the solution using centrifuge machine.
5. Dry the modified MMT in the oven at 60°C for 48 hours.
6. Grind the modified MMT with mortar.
7. Characterize the modified MMT using various techniques.

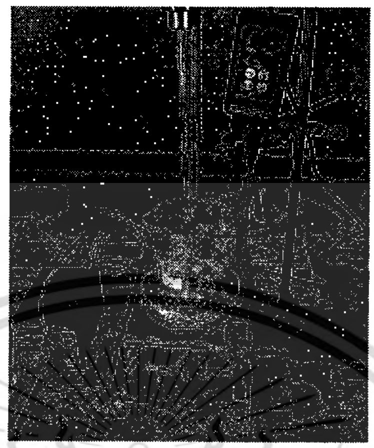


Fig. 3.1 Apparatus for preparation of organoclays

Table 3.2 The variation of chitosan, MMT and amount of acetic acid in the experiment

Sample No.	MMT (g)	Chitosan (g)	% wt/v of Acetic acid (%)	Temperature (C°)
1	2.5	4	2	RT
2	2.5	4	2	60
3	2.5	4	1	RT
4	2.5	4	1	60
5	2.5	4	0.5	RT
6	2.5	4	0.5	60
7	1	4	2	RT
8	1	4	2	60
9	1	4	1	RT
10	1	4	1	60
11	1	4	0.5	RT
12	1	4	0.5	60

3.4. *Characterization of Modified MMT*

3.4.1. *X-ray Diffractometer (XRD)*

X-ray diffraction (XRD, D8 advance, Bruker AG) pattern is recorded using Cu Kα radiation ($\alpha = 154$ nm) at a voltage of 30 kV and a current of 30 mA.

3.4.2. *X-ray Fluorescence (XRF)*

The samples (0.5 g) were mixed with boric acid(4.5 g), ground by benchmill (A 1, Rocklabs) for 1 min, and then compress to pellet by uniaxial pressing. The chemical composition of the samples was determined by XRF. The XRF method is widely used to measure the elemental composition of materials. Since this method is fast and non-destructive to the sample. XRF is an elemental analysis technique with unique capabilities including highly accurate determinations for major elements and a broad elemental survey of the sample composition without standards.

3.4.3. *Fourior Transform Infrared Spectroscopy (FT-IR)*

The Fourior transformed infrared spectra (FT-IR) of chitosan, MMT, and modified MMT were recorded using FT-IR spectrometer, Spectrum GX, PerkinElmer. The characteristics of the organophilic-MMT were obtained using a transmission mode of FTIR. The samples were ground with KBr powder and compressed the pellet form by using uniaxial pressing. The samples were scanned from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

3.4.4. *Methylene Blue Absorption*

Methylene blue in aqueous solution is a cationic dye, which absorbs to negatively charged MMT surfaces. Methylene blue (MB) was used to determine the surface area of MMT minerals. The specific surface of particles can be determined by the amount of absorbed methylene blue. This technique consist of 2 parts :

1. Standard Calibration Curve

1.1 Prepare MB standard solution by mixing 100 ml of distilled water with 0.5 g of methylene blue (0.5 %wt/v).

1.2 Dilute the standard solution into 0.005, 0.01, 0.05, and 0.1 %wt/v.

1.3 Using UV absorption spectrometer to detect absorbance of the standard solution of 665 nm.

1.4 Determine the absorbance at the standard solution at wavelength of 665 nm.

2. Absorption of MB in MMT, Chitosan, and Modified MMT

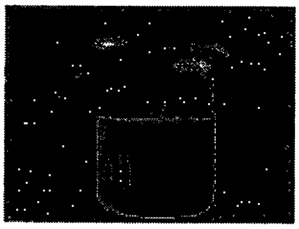
2.1 Mix 1 g of MMT, chitosan, or modified MMT with 0.5 ml MB standard solution(0.5 %wt/v) and 100 ml of distilled water.

2.2 Continuously stir the mixture for 2 hours(wrap the beaker with aluminium foil to protect the samples beaker from light).

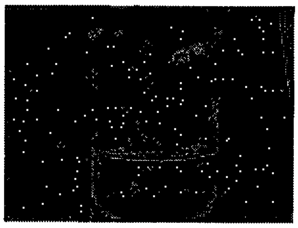
2.3 Age the mixture for 1 night.

2.4 Use centrifuge machine to settle the solid content.

2.5 Sampling the clear solution to determine the UV absorbance at the wavelength of 665 nm.



(A)



(B)

Fig. 3.2 The methylene blue absorption of the modified MMT (A) initial state (B) final state (one night)

3.4.5. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of chitosan, MMT, and modified MMT was performed by using thermogravimetric analyzer (TGA, Pyris 1 TGA, PerkinElmer). This technique is use to determine the chitosan content in the modified MMT and chitosan by putting dry powder in a small furnace inside the heater chamber. TGA was performed under air flow using temperature range of 50 – 800 °C at a heating rate of 10 °C/min.

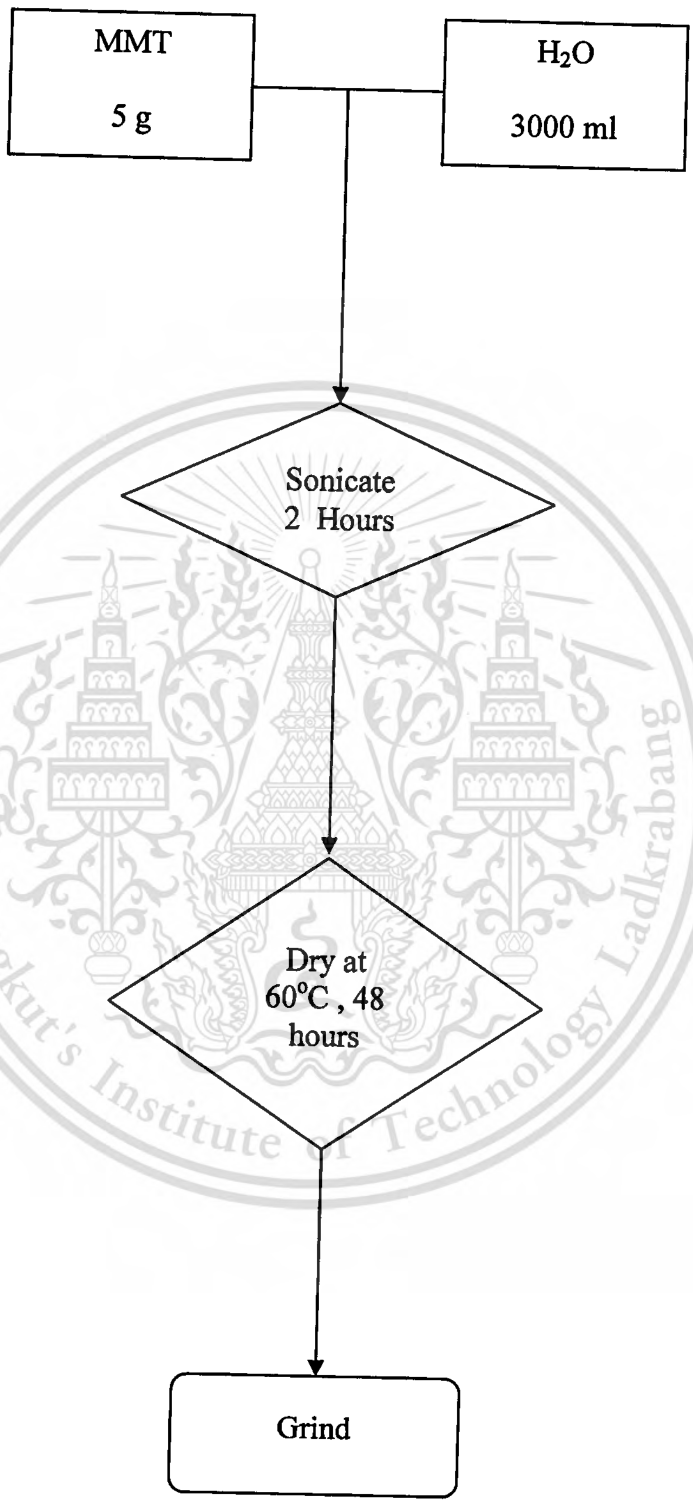


Fig. 3.3 Preparation of organoclays

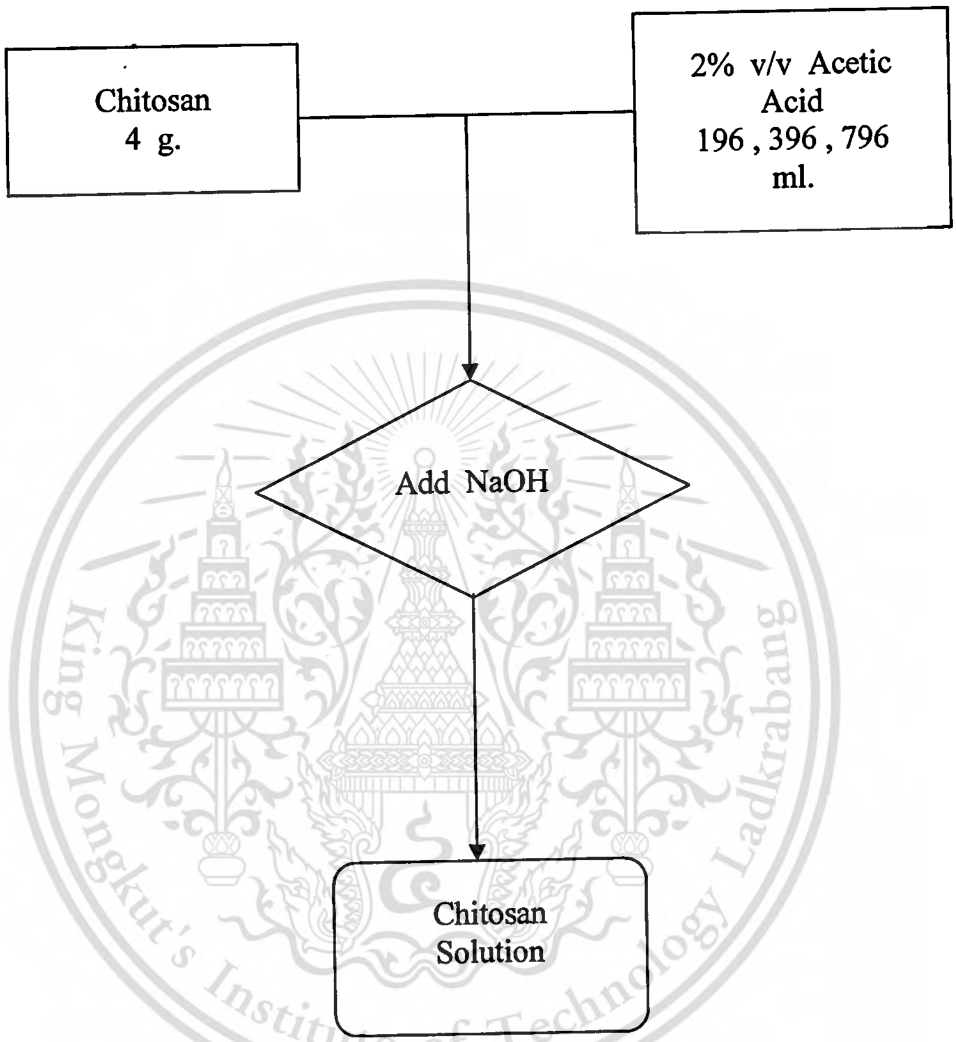
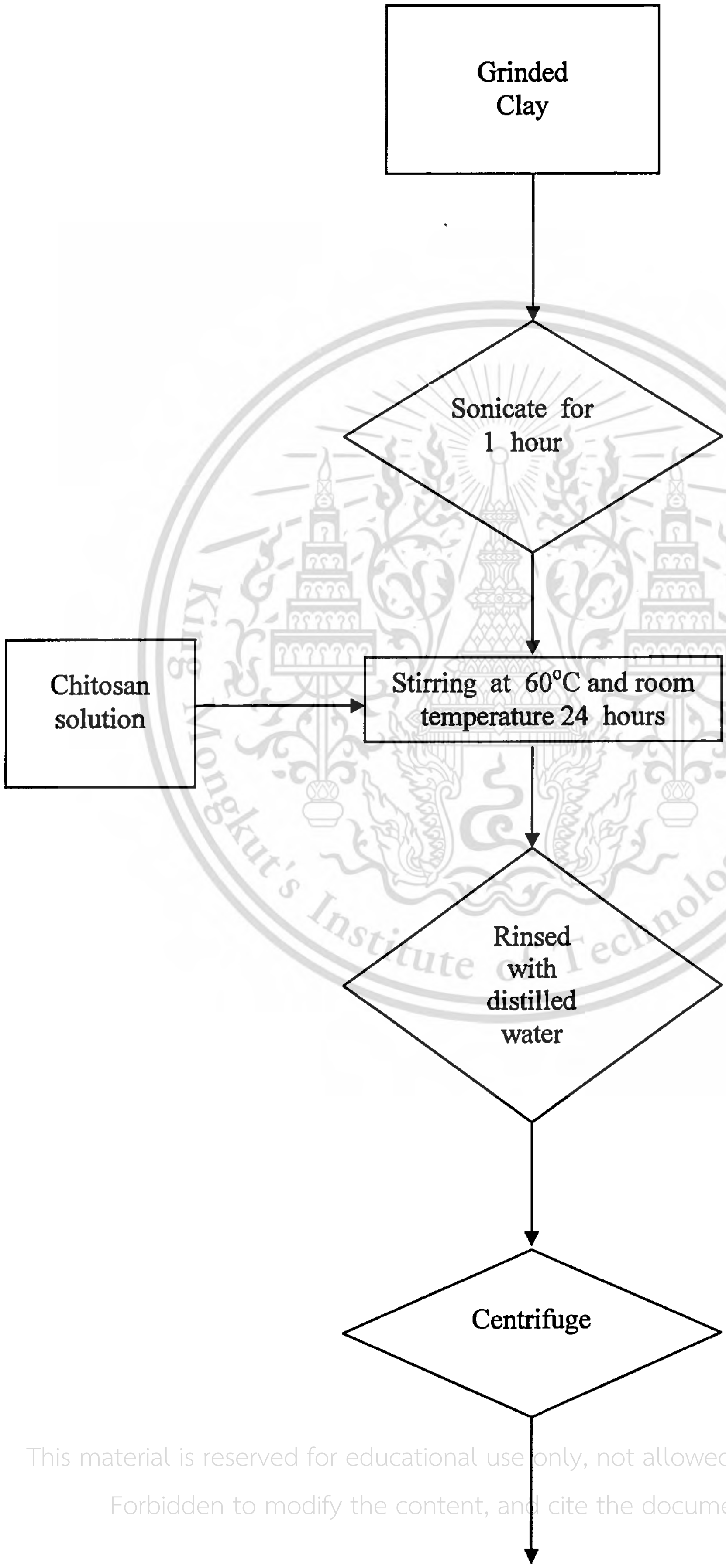


Fig. 3.4 Preparation of chitosan solution


Grinded
Clay
Sonicate for
1 hour
Chitosan
solution
Stirring at 60°C and room
temperature 24 hours
Rinsed
with
distilled
water
Centrifuge

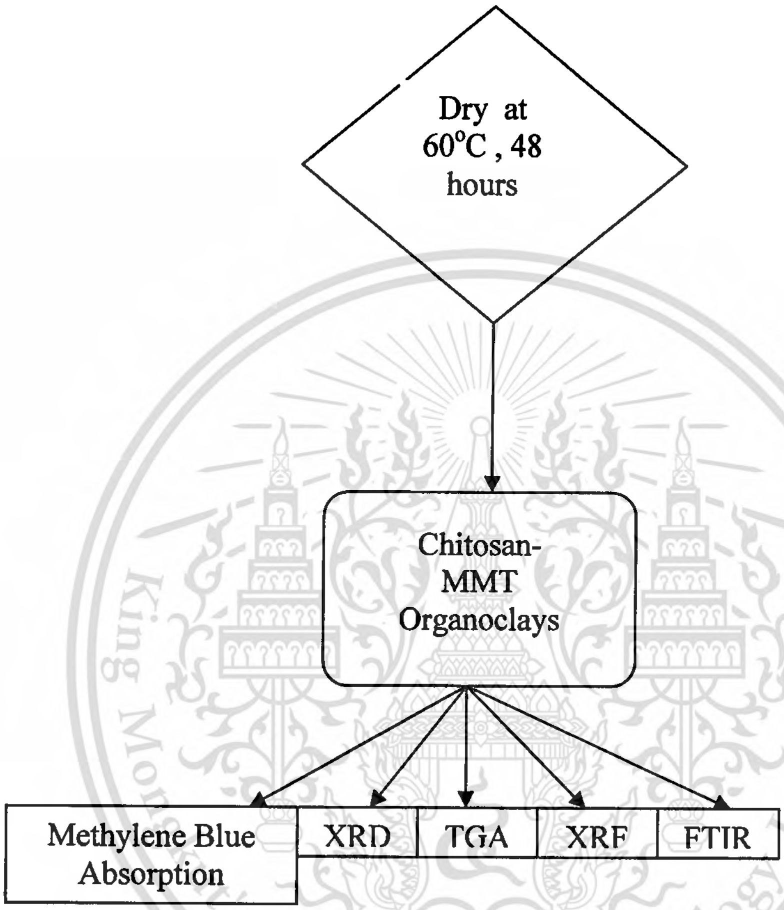


Fig. 3.5 Preparation of chitosan-MMT

Chapter 4

Results and Discussion

The preparation of organoclays from starting MMT and chitosan was synthesized by mixing the starting MMT in chitosan solution, varying the weight ratio of MMT:chitosan, concentration of chitosan in acetic acid, and temperature. The modified MMT could be characterized by XRD, XRF, FTIR, MB absorption, and TGA.

4.1 X-ray Diffractometer (XRD)

Fig 4.1 shows the XRD patterns of starting MMT, chitosan, and modified MMT. The XRD pattern of the starting MMT showed the crystalline peaks at around $2\Theta = 5°-6°$, corresponding to the d_{001} of 14.71 Å. The chitosan is an amorphous phase, thus, the XRD pattern was observed as a halo peak.

From the XRD pattern of the modified MMT, the peak shifted from $2\Theta = 6°$ to $2\Theta \sim 3°-6°$, indicating that chitosan could be interacted into the layer of MMT. Accoarding to Darder et. al.[19], the d_{001} peak shifted to $2\Theta = 4.6^{o}$ ($d_{001} \sim 3.8$ Å), and at $2\Theta = 3.6^{o}$ ($d_{001} \sim 9.6$ Å). The broadening d_{001} peak was observed in all modified MMT, indicating the disordered structure, which chitosan might be coated or penetrated into the layers of MMT and delaminate the order structure of MMT, as shown in Fig. 4.2 (A) become to (B). And Fig. 4.2 (C) was occur when MMT was dry. However, the interlayer of modified MMT was not stack, but formed disordered structure. From this phenomena, the starting MMT and modified MMT were tested by sedimentation test as shown in Fig. 4.3 to confirm interaction between MMT and chitosan in 2 %v/v acetic acid. The result shown that the sedimentation of starting MMT was faster than the modified MMT, corresponding to the hydrophilic behavior of the modified MMT, which lead to suspend in acetic acid. From the broadening XRD pattern, indicating at least one interaction was occurred.

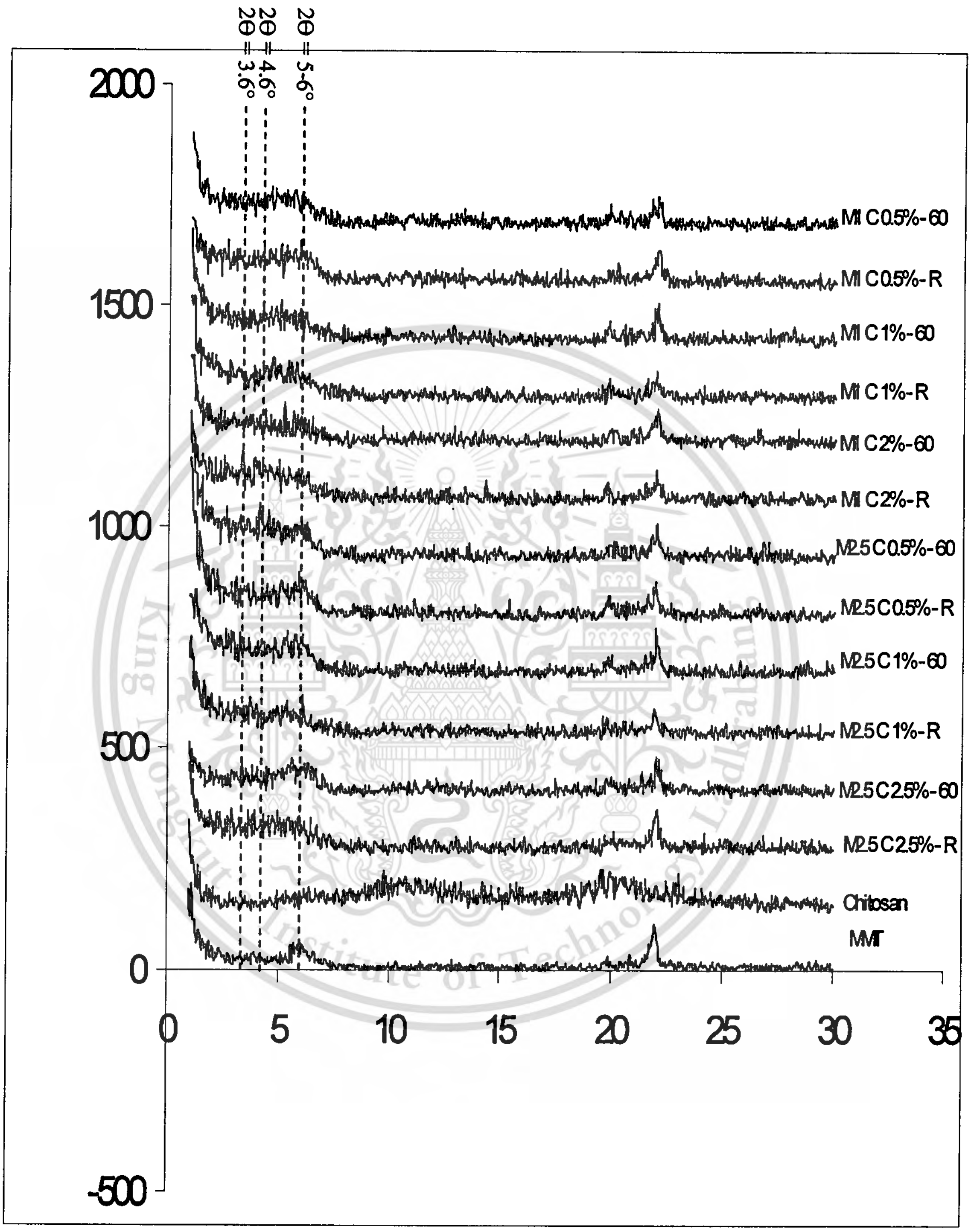


Fig.4.1 The XRD patterns of MMT, chitosan and modified MMT.

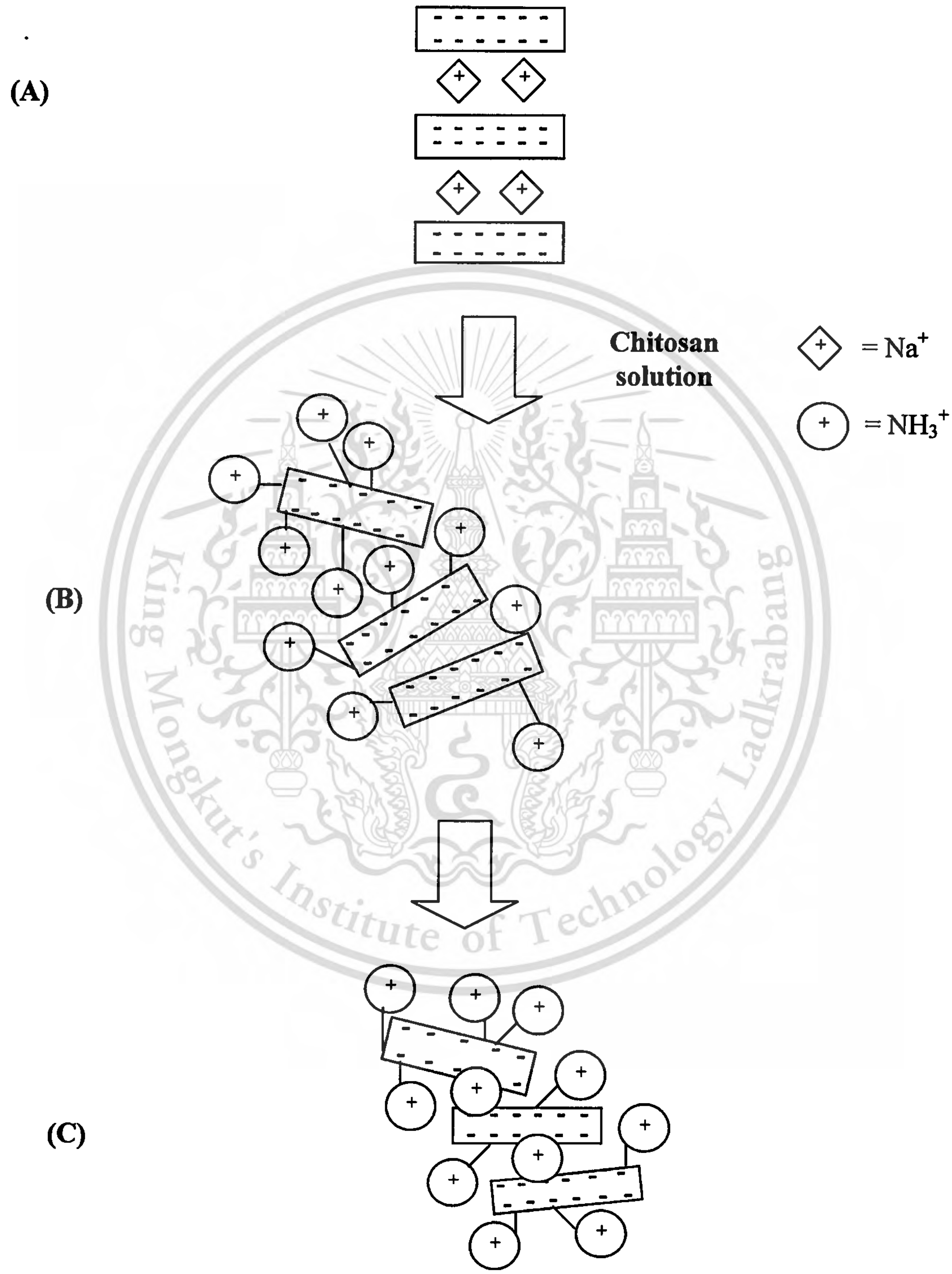
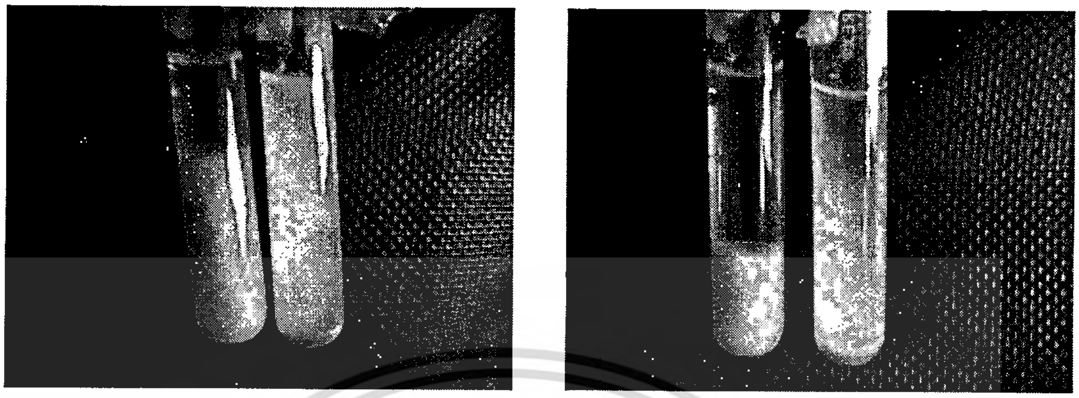


Fig. 4.2 Schematic of chitosan interacted with MMT



(A) (B)

Fig. 4.3 Sedimentation Test (A) 30 minutes (B) 1 day

4.2 X-ray Fluorescence (XRF)

The chemical composition of the starting MMT and modified MMT determined by XRF were shown in Appendix-A. The results were compared between MMT and modified MMT, and also shown the different of the composition in each sample. The molar ratios of Al:Si and Na:Al were calculated and concluded in Table 4.2. The Na content could be determined in the starting MMT, corresponding to the Na^+ counter ion between clay layers. The Na^+ ions were exchanged with NH_3^+ ions of chitosan in the modified MMT. Thus, the Na content in modified MMT could not be detected. This result has corroborated to the interaction of chitosan into the layer MMT.

From the molar ratio of Al:Si in modified MMT, the chitosan interaction resulted in d_{001} plane become wider but crystalline structure was not change. Thus, the result of XRF could comfirm and support the result of the XRD, which chitosan could interact with the MMT.

Table 4.1 Ratio of Al: Si and Na: Al from XRF

Entry	Sample No.	Al : Si	Na : Al
1	MMT	0.2941	0.2342
2	M2.5C2%-R	0.2590	-
3	M2.5C2%-60	0.2817	-
4	M2.5C1%-R	0.3247	-
5	M2.5C1%-60	0.2849	-
6	M2.5C0.5%-R	0.2825	-
7	M2.5C0.5%-60	0.2857	-
8	M1C2%-R	0.2569	-
9	M1C2%-60	0.2604	-
10	M1C1%-R	0.2941	-
11	M1C1%-60	0.2976	-
12	M1C0.5%-R	0.2647	-
13	M1C0.5%-60	0.2851	-
14	MMT + Chitosan	0.2857	0.2481

4.3 Fourior Transform Infrared Spectroscopy (FT-IR)

Typical chemical characteristics of both organic and inorganic materials could be studied by FTIR spectra analysis, and also be an appropriate technique to study the MMT interaction, since a shift in the υ_{NH3} vibration. A similar behaviors might also be expected when $-NH_3^+$ groups interact electrostatically with the negative charged sites of the MMT.

From Fig. 4.4 shows the spectrum of the starting MMT, chitosan, and modified MMT. The result indicated the peak of starting MMT, which gave vibrational band of the silicate as follows; υ_{OH} for –OH stretching with the range at 3630-3620 cm^{-1}, υ_{HOH} for H-O-H ~ 1650-1620 cm^{-1}, and υ_{SiO} of Si-O-Si ~ 1050-1040 cm^{-1}. For the chitosan , major peaks at υ_{NH3} for N-H ~ 1600-1560 cm^{-1}, and υ_{CO} of C=O ~ 1650-1620 cm^{-1}. After modification of MMT with chitosan, the FTIR spectrum showed the peak of υ_{HOH} for H-O-H that was the overlapped peak between water in starting MMT and COO^- counter ions of chitosan in acetic acid. The modified MMT was also found the peak of υ_{NH3} for N-H ~1560-1520 cm^{-1}, indicated that modified MMT had the chitosan component, moreover, this peak also shifted with significantly as showed the result from N-H ~ 1600-1560 cm^{-1} to ~1520-1560 cm^{-1}, while the other peaks did not shift. Thus, this shifted peak revealed the interaction of NH_3^+ of chitosan with the starting MMT, due to the counter ions was changed. Then, the peak of the modified MMT was shifted at vibration that difference from starting MMT. Moreover, another peak appeared at 2915-2926 cm^{-1} in modified MMT could be confirmed the interaction between chitosan and MMT, which compared to the starting MMT. Therefore, the entire condition was found the shifted peak as show at Appendix-B.

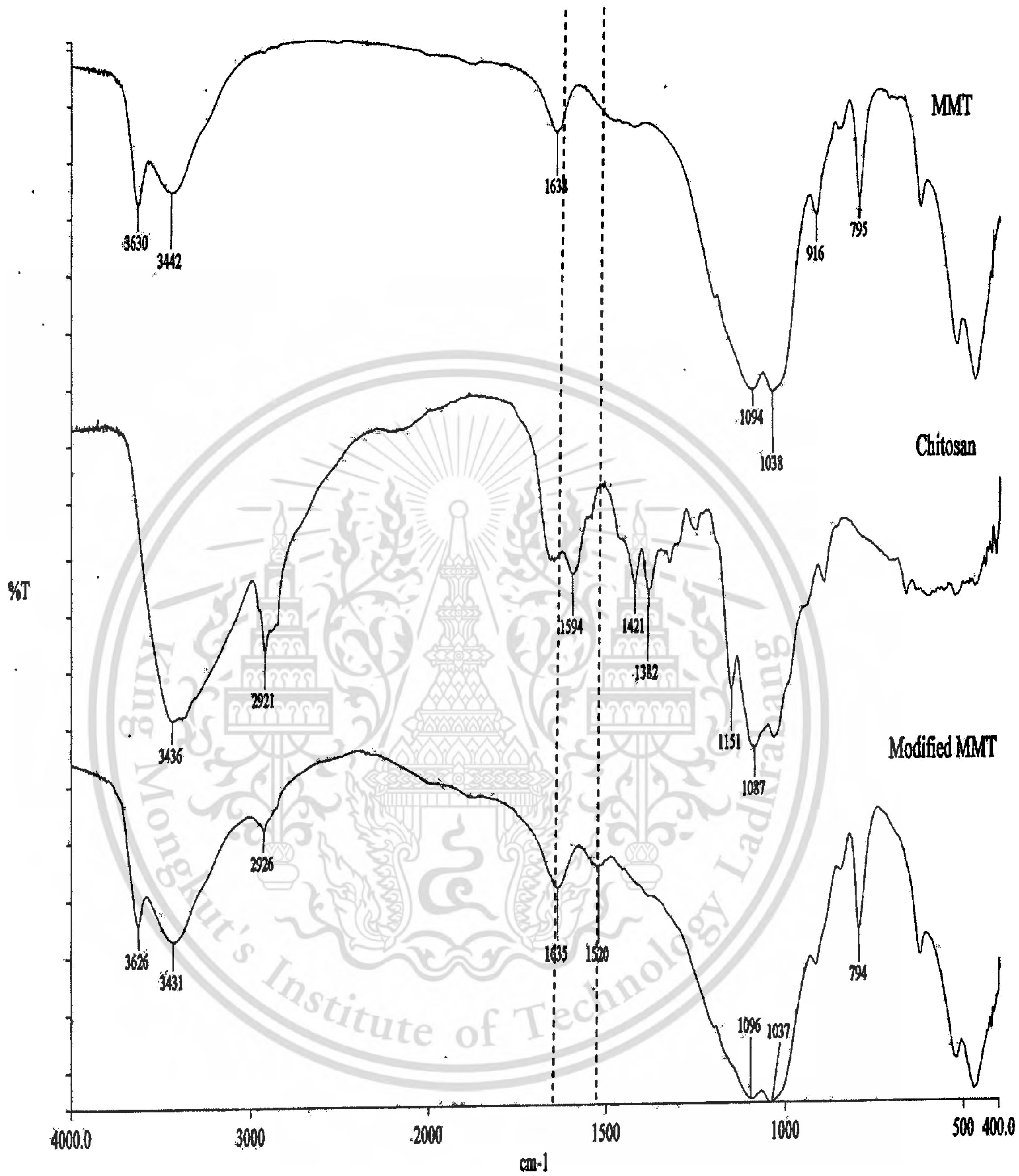


Fig.4.4 The FTIR spectrum of the starting MMT, chitosan, and modified MMT

Table 4.2 Absorption Band assignment of MMT, Chitosan, and Modified MMT

Sample	Frequencies (cm^{-1})	Assignment
MMT	~3630 - 3620	-OH stretching
	~1650 - 1620	H-O-H bending
	~1050 - 1040	-Si-O stretching
Chitosan	~2926 - 2915	-CH stretching
	~1650 - 1620	-C=O stretching
	~1600 - 1560	-NH bending
Modified MMT	~3630 - 3620	-OH stretching
	~2926 - 2915	-CH stretching
	~1640 - 1635	-C=O stretching (overlapped) H-O-H bending (overlapped)
	~1560 - 1520	-NH bending
	~1050 - 1040	Si-O-Si stretching

4.4 Methylene Blue Absorption

The reaction of silicate MMT sheets dispersed in water with MB was used for the determination of the cation exchange capacity of organoclays. When a solution of MB was mixed with clay dispersion, a significant change of color was observed and absorbance could be measured by using UV spectrometer. The specific surface in swelling clay could be determined by the MB absorption technique, i.e., the amount of absorption increased with surface area and surface charge density increased. Table 4.3 shows the result of UV absorbance of the mixture between MB solution and starting MMT, chitosan, the mixture of MMT grinded with chitosan, and modified MMT. From the result, the starting MMT showed the absorbance at 1.026 % and chitosan showed the result at 0.906 %. Both of them can absorbed the MB molecules solution in different manner, and change the color of MB solution from dark blue to lighter blue. The MMT could absorbed MB by ion exchange reaction between MB and Na^+ ion of MMT on the surface, which depended on the amount of Na^+ ions; if it had a lot of Na^+ ions, it could be absorbed more MB. In pure chitosan, it was absorbed the MB molecules on its surface. The mixture of chitosan and MMT grinded without modification was shown the UV absorbance at 0.516 % with light blue color. Because, both MMT and chitosan could absorb the MB molecules more than only MMT or chitosan itself, thus, the UV absorbance were decreased. If compared with the modified MMT, all samples could effectively absorbed the MB molecules, brought about the changing of MB solution color from dark blue to be a slightly clear solution with the percentage of absorbance of 0.009-0.240 %, due to the surface area was increased by the delamination of the MMT structure, thus, the ability of MB absorption was higher.

From this result, it was clear that the UV absorbance of the MB solution with the modified MMT, was less than those of the starting MMT, chitosan, and MMT grinded with chitosan, referring to the less amount of free MB molecules in the solution.

Table 4.3 UV absorbance of MMT, chitosan, MMT Grinded with chitosan, and modified MMT in MB Solution

Entry	Sample No.	Clay (g)	Chitosan (g)	% w/v of Acetic acid (%)	Temperature (C°)	Absorbance (%)
1	MMT	1	-	-	-	1.026
2	Chitosan	-	1	-	-	0.906
3	MMT+Chitosan	0.5	0.5	-	-	0.516
4	M2.5C2%-R	2.5	4	2	RT	0.014
5	M2.5C2%-60	2.5	4	2	60	0.009
6	M2.5C1%-R	2.5	4	1	RT	0.117
7	M2.5C1%-60	2.5	4	1	60	0.055
8	M2.5C0.5%-R	2.5	4	0.5	RT	0.182
9	M2.5C0.5%-60	2.5	4	0.5	60	0.240
10	M1C2%-R	1	4	2	RT	0.029
11	M1C2%-60	1	4	2	60	0.014
12	M1C1%-R	1	4	1	RT	0.030
13	M1C1%-60	1	4	1	60	0.027
14	M1C0.5%-R	1	4	0.5	RT	0.029
15	M1C0.5%-60	1	4	0.5	60	0.012

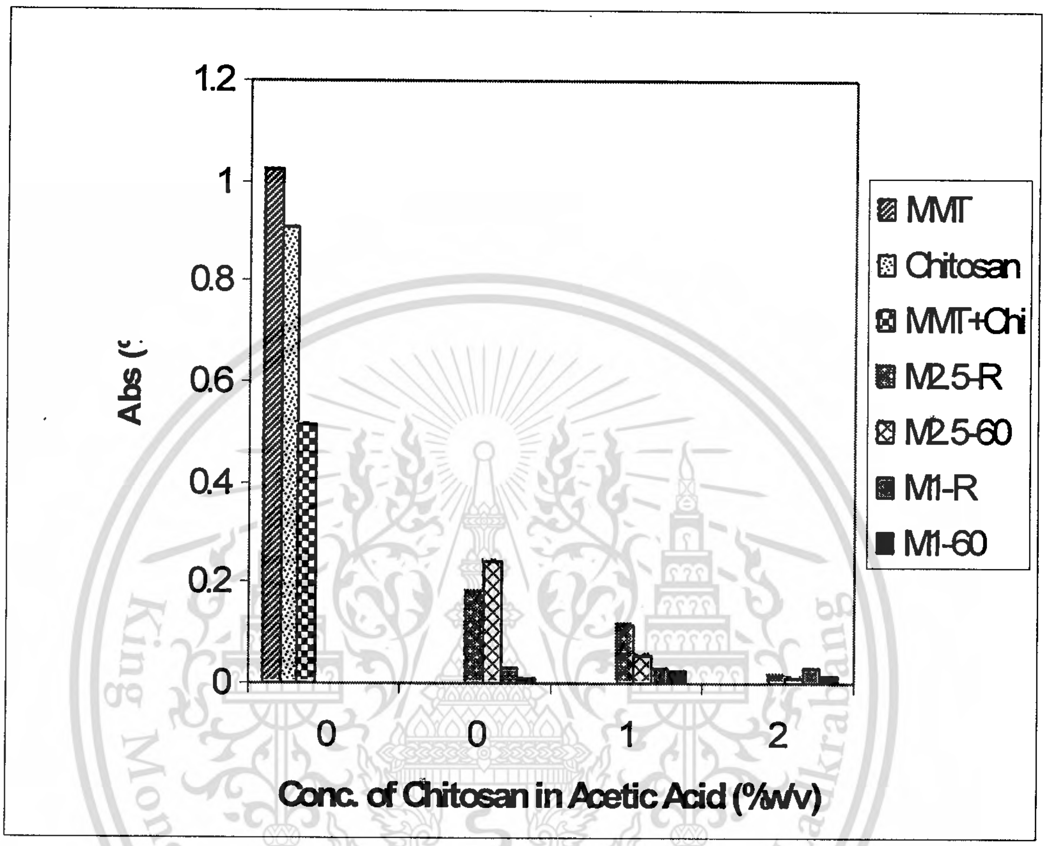


Fig. 4.5 MB Absorption of MMT, Chitosan, MMT Grinded with Chitosan, and Modified MMT

4.5 Thermogravimetric Analysis (TGA)

The decomposition temperature of the chitosan and organoclay was investigated by TGA under air atmosphere. The amount of organic matter could be determine from the weight loss of the substances in the compound.

Fig.4.6 - 4.9 show the TGA thermograms of the starting MMT, chitosan, MMT grinded with chitosan, and modified MMT, respectively. The thermogram of the starting MMT shows a long range of degradation period (60 °C to 600 °C) with the weight loss of about 8%, corresponding to moisture content and the organic impurities in natural clay. For the chitosan, it was shown the degradation period between 180 °C to 540 °C, due to the decomposition of chitosan. The decomposition of chitosan mixed with MMT was observed in the temperature range of 170 °C – 640 °C, corresponding to the decomposition of chitosan organic matter in clays. This decomposition period was similar to those of the starting MMT and chitosan, suggested that the chitosan did not have interaction with MMT. It was, however, the weight loss of the modified MMT was observed in the period of 70 °C – 800 °C, which was longer period than that of chitosan mixed MMT. The degradation temperature between 70 °C to 180 °C was indicated as the degradation of moisture content in its structure, and the temperature range between 180 °C to 800 °C could be determined the degradation of modified MMT. The prolonged degradation period observed in the modified MMT indicated the increasing of thermal stability of chitosan. This results were considered the MMT might protected and retarded the decomposition of the chitosan molecule in the modified MMT.

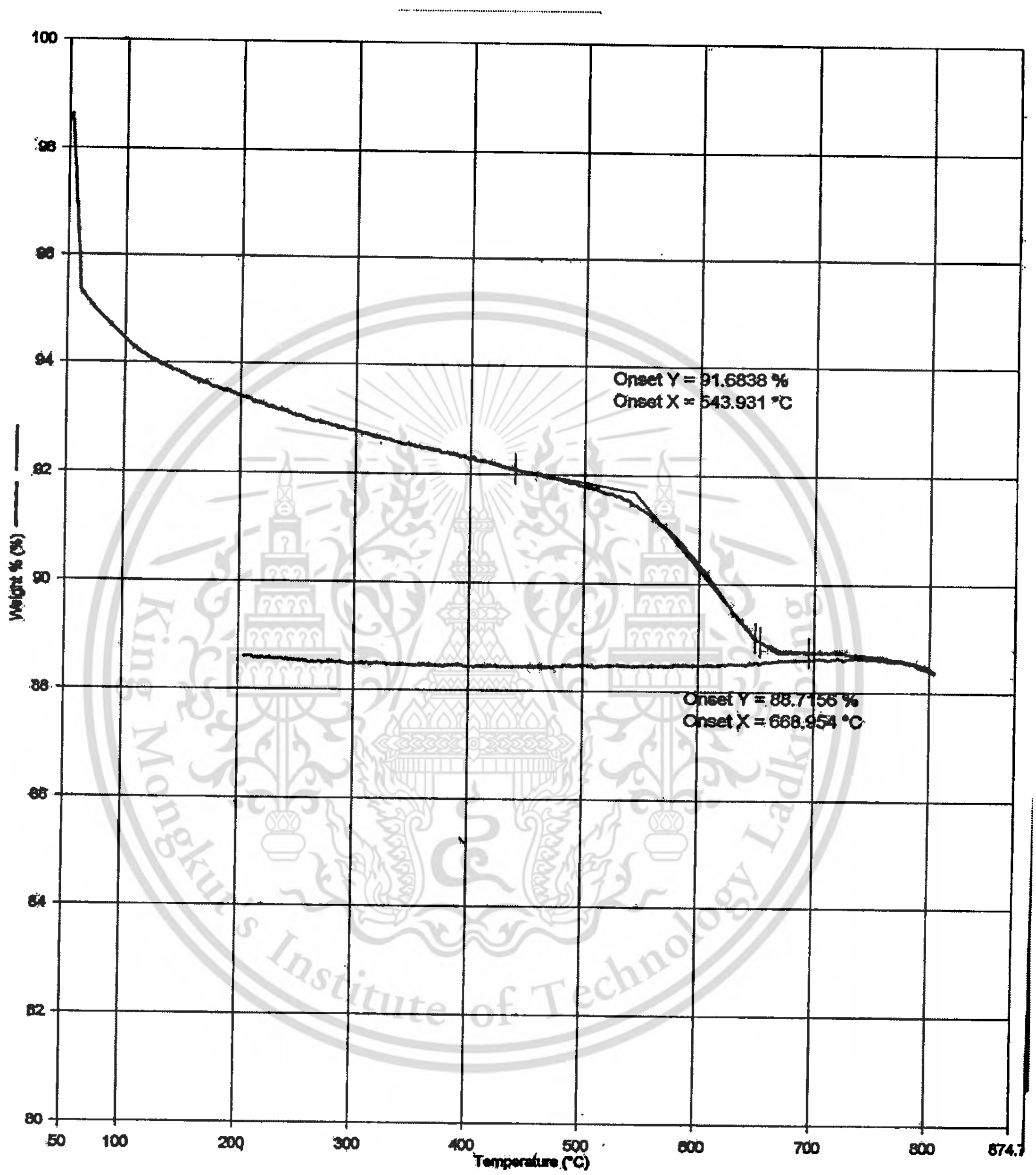


Fig. 4.6 Thermogram of MMT

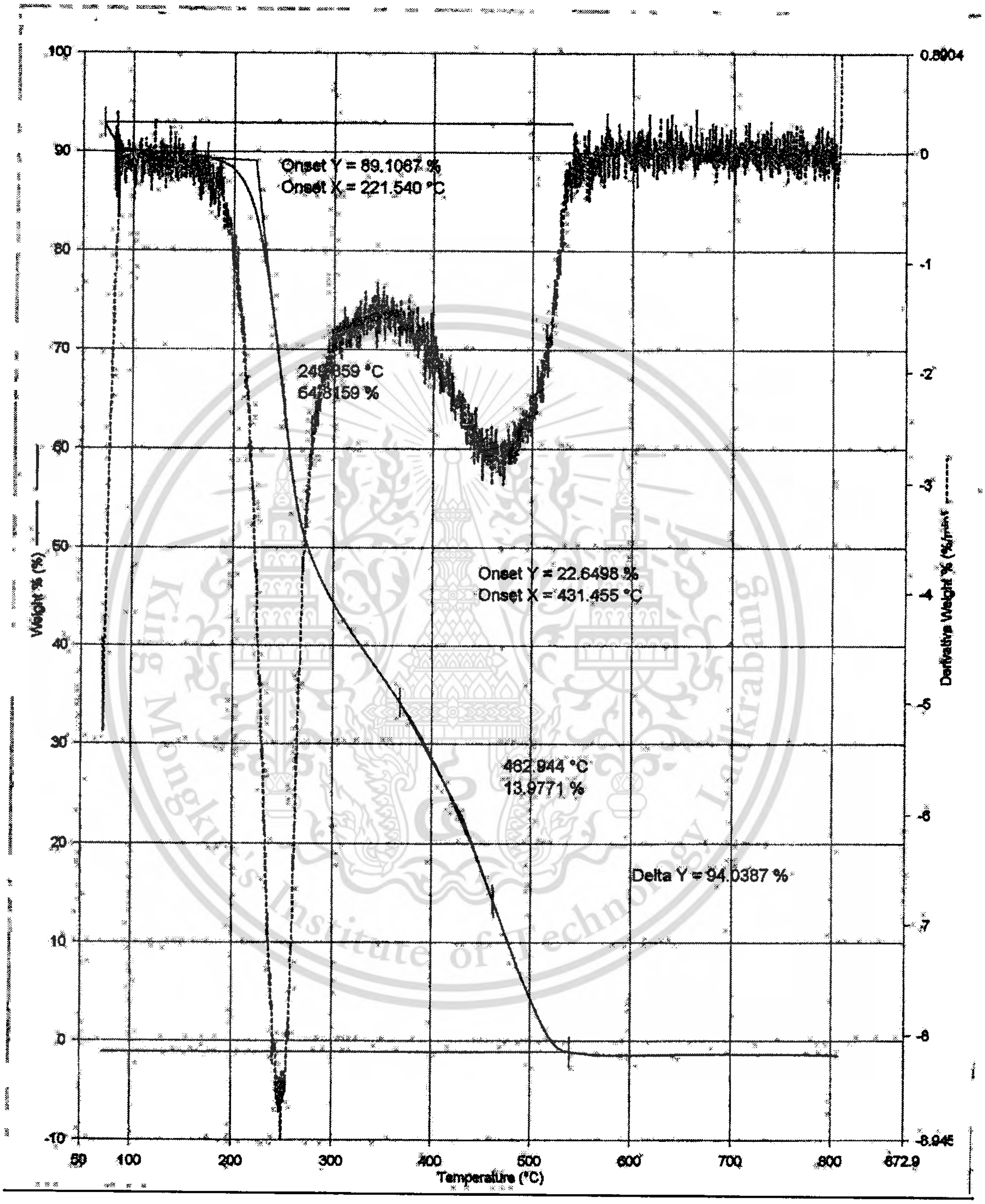


Fig. 4.7 Thermogram of Chitosan

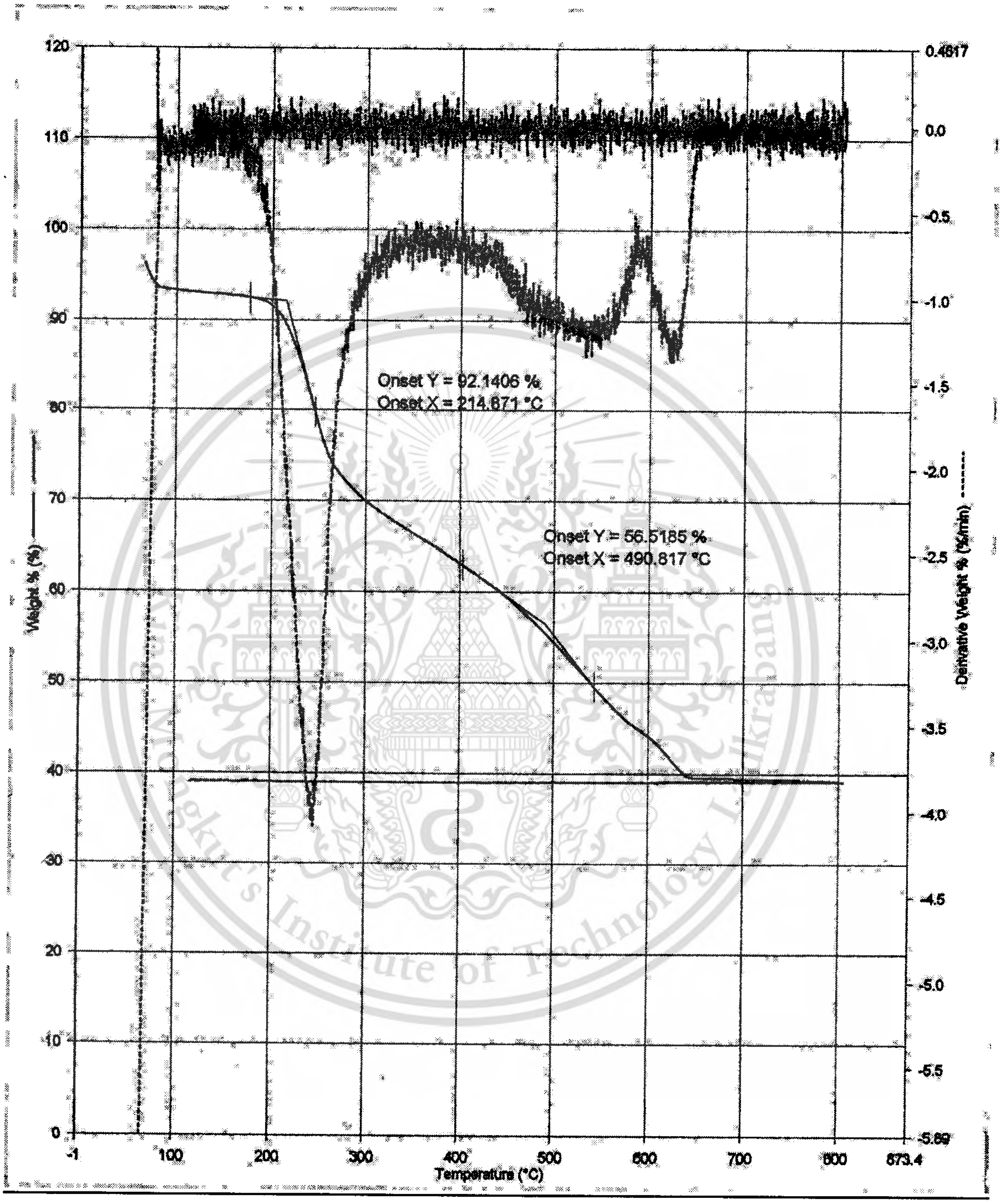


Fig. 4.8 Thermogram of MMT Grinded with Chitosan

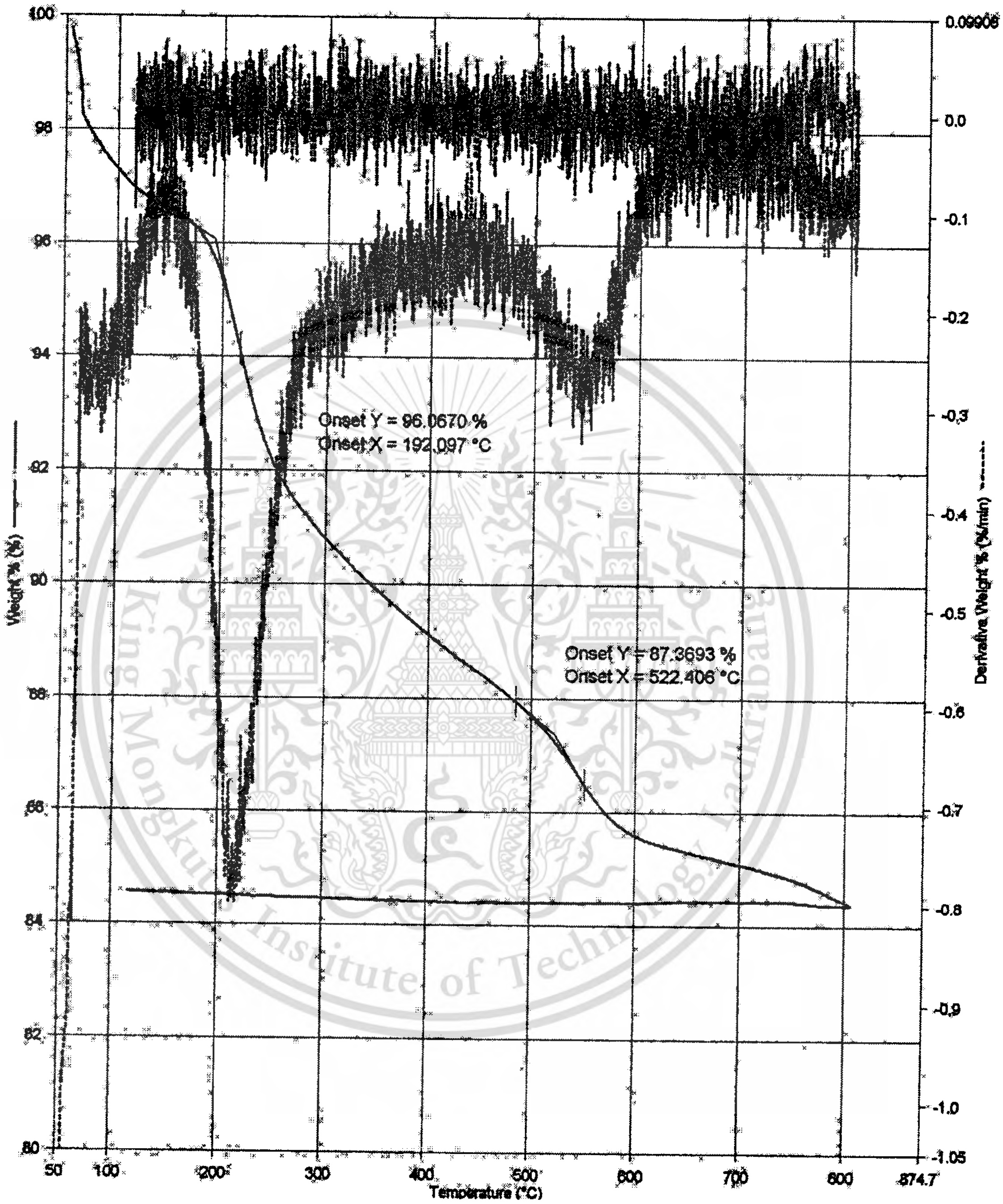


Fig.4.9 Thermogram of Modified MMT

Chapter 5

Conclusion and Recommendation

5.1 Conclusion

The organoclays were modified by the chitosan and starting MMT (Na^+ montmorillonite) through a cationic exchange reaction. The effect of the interaction between chitosan and starting MMT on varying the weight ratio of starting MMT to chitosan, the concentation of chitosan in acetic acid, and the temperature during the preparation, was studied. The techniques employed in the characterization of organoclays as follow; TGA, FTIR, XRD, XRF, and methylene blue (MB) absorption to confirm the high affinity between the starting MMT substrate and chitosan as well as the special arrangement of chitosan in the MMT structure, which confirmed by sedimentation test in acetic acid. The interaction of \chitosan occured mainly by electrostatic reaction between the $-NH_3^+$ groups in the chitosan and the negative site ($Si-O^-$) in the starting MMT, and the $-NH_3^+$ groups also form the cation exchange with Na^+ of the MMT, which comfirmed from the result in XRF that could not be detect the Na^+ in MMT. Including, the hydrogen bonds was formed between amino group of chitosan and hydroxyl group of the starting MMT substrate were established in the absorption of the second layer (bilayer).

Since the chitosan interacted with the MMT, the decomposition temperature of the chitosan in modified clay was improved, being 180 °C to 800 °C under air condition, due to the MMT act as a protector from the decomposition of the chitosan. The interaction of acetic acid was useful approach to destroy chitosan packing structure. The peak of amine functional group of the chitosan in FTIR spectrum, showed clear appearance of the band at ~1560-1520 cm^{-1} from the modified MMT, meaning that the interaction of chitosan and MMT was occurred. The effect from the delamination of the modified MMT was increased the specific surface area of the MMT as confirmed in the result in the MB absorption.

Undoubtedly, the MMT was modified by chitosan from the cation exchange with Na^+ in MMT, so, the distance between layer of MMT was increased, which so called “Organoclays”.

5.2 Recommendation

- The organoclays can be applied as a reinforcing fillers in nanocomposites with biodegradable properties, which leads to biodegradable materials.
- The organoclays can be used for waste water treatment in the recycle process such as dye industries.

References

[1] Available online at http://www.azom.com/details.asp?ArticleID=936

[2] Available online at http://mineral.galleries.com/minerals/silicate/clays.htm

[3] Available online at http://mineral.galleries.com/minerals/silicate/montmori/montmori.htm

[4] Available online at http://encyclopedia.thefreedictionary.com/Montmorillonite

[6] Available online at http://dalwoo.com/chitosan/21c.htm

[7] Available online at http://encyclopedia.thefreedictionary.com/Chitosan

[8] Available online at http://callisto.si.usherb.ca/~rbrzezin/what_is_chitosan.htm

[9] Available online at http://www.vanderbilt.edu/AnS/psychology/health_psychology/chitosan1.htm

[10] Available online at http://dalwoo.com/chitosan/whatischitosan.html#top

[11] Available online at http://dalwoo.com/chitosan/preparation.htm

[12] Available online at http://dalwoo.com/chitosan/spectra.htm

[13] Available online at http://dalwoo.com/chitosan/chito9.htm

[14] Available online at http://dalwoo.com/chitosan/funtional.htm

[15] Available online at http://www.nanocompositech.com/review-nanocomposite.htm

[16] Mr.Noppakun Sanpo, Biometric Supra-Structured Crustacean Shell via Chitosan-Clay Bionanocomposites, thesis of Master degree at Petroleum and Petrochemical College, Chulalongkorn University, 2004

[17] http://pubs.nrc-cnrc.gc.ca/cgi-bin/rp/rp2_abst_e?cgj_t01-077_39_ns_nf_cgj

[18] Hajjaji M, Kacim S, Alami A, Bouadili A, Mountassir M . Applied Clay Science 2001;20:1-12

[19] Darder M, Colilla M, and Ruiz-Hitzky E. Chem Mater 2003;15:3774-80.

[20] Adriana Czímerová, L'uboš Jankoviˇc, and Juraj Bujdák. Colloid and Interface Science 2004;274:126-132

[21] Darder M, López-Blanco M, Aranda P, Leroux F, and Ruiz-Hitzky E. Chem Mater 2005;17:1969-1977.

[22] Darder M, Colilla M, and Ruiz-Hitzky E. Applied Clay Science 2005;28:199-208

Appendix-A

XRF Result

Table A-1 Composition of Starting MMT, Chitosan, MMT Grinded with Chitosan, and Modified MMT

Sample No.	MgO (%)	Al_2O_3 (%)	SiO_2 (%)	K_2O (%)	CaO (%)	Fe_2O_3 (%)	Others (%)
Clay swell	2.68	17.7	71.7	0.888	1.97	1.67	3.2722
Chitosan	15.6	5.71	20.6	-	35.9	8.82	13.33
Clay + Chitosan	2.72	16.8	71.2	0.916	2.73	1.65	3.9115
1	2.51	16.4	74.7	0.858	1.59	2.76	0.8583
2	2.36	18.0	75.0	0.753	0.525	2.49	0.833
3							
4	2.35	17.9	74.0	0.766	0.707	2.91	1.0601
5	2.35	18.0	75.2	0.670	0.472	2.44	0.8255
6	2.52	17.9	74.5	0.762	0.443	2.61	1.0194
7							
8	2.11	16.7	75.5	0.851	0.688	2.64	0.8254
9	2.37	17.9	75.8	0.715	0.480	2.07	0.6479
10	2.60	18.6	73.8	0.705	0.575	2.57	0.7858
11							
12							
4 + MB	2.28	18.1	73.8	0.739	0.650	2.98	1.3653

Appendix-B

FTIR Spcetrum of Starting MMT, Chitosan, MMT Grinded with Chitosan, and Modified MMT

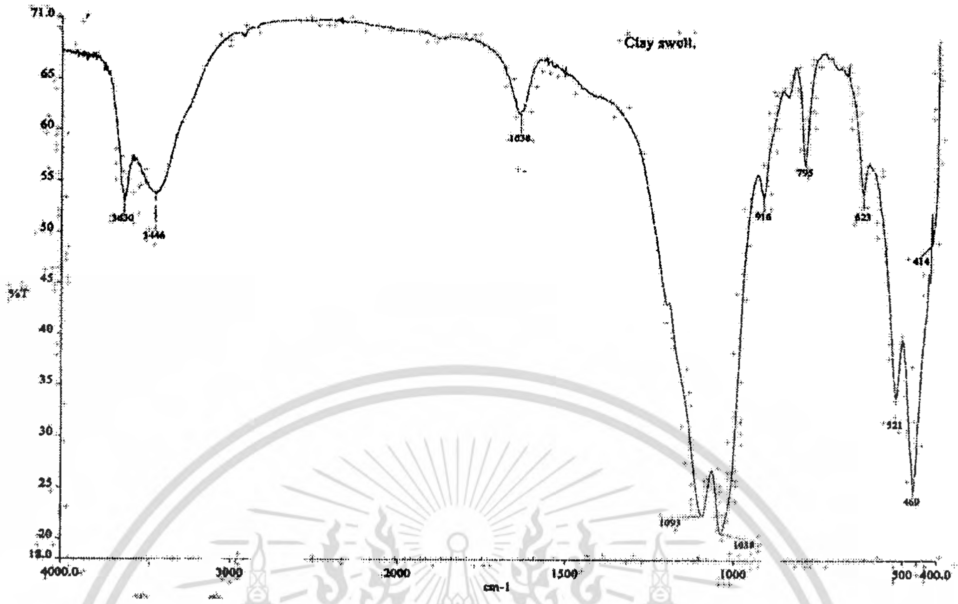


Fig. B-1 FTIR Spectrum of Starting MMT

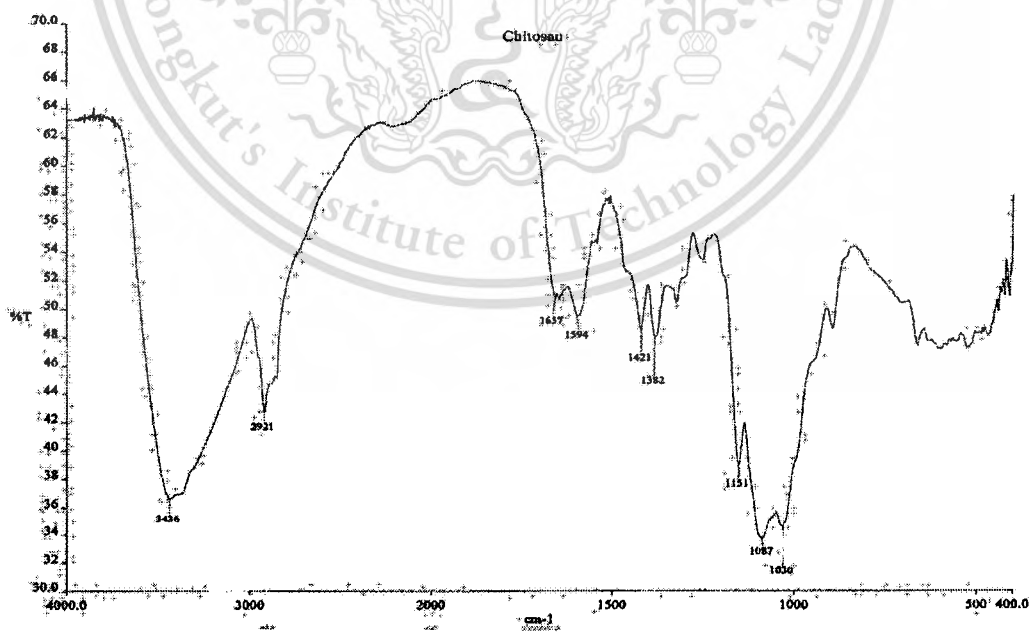


Fig. B-2 FTIR Spectrum of Chitosan

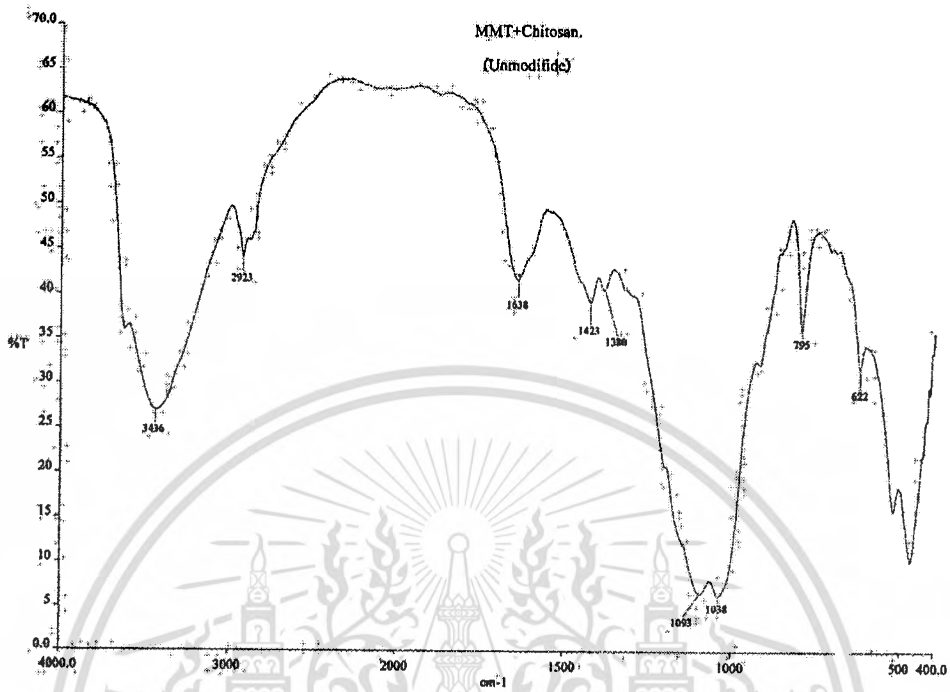


Fig. B-3 FTIR Spectrum of MMT Grinded with Chitosan

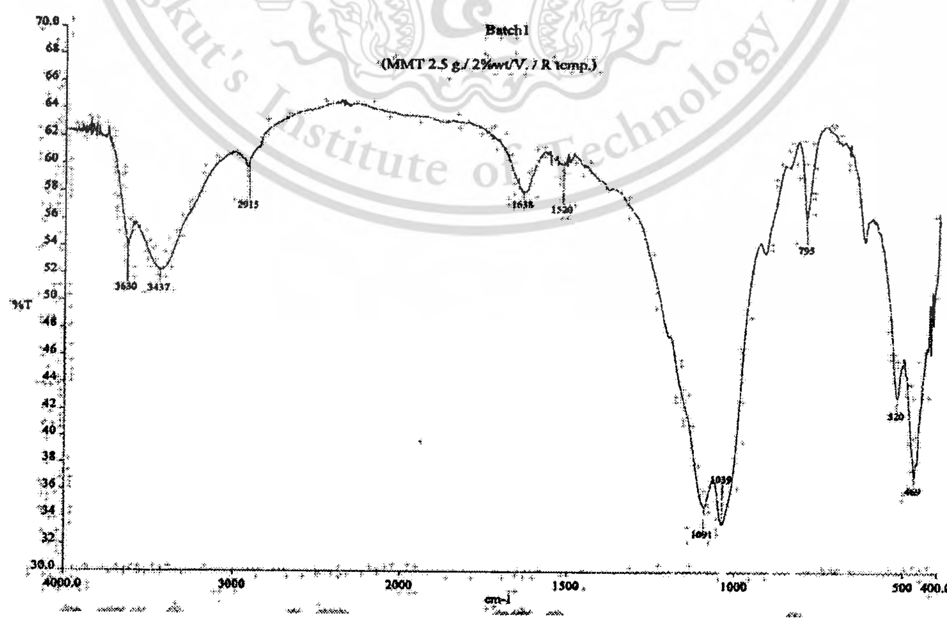


Fig. B-4 FTIR Spectrum of M2.5 C 2.0%-R

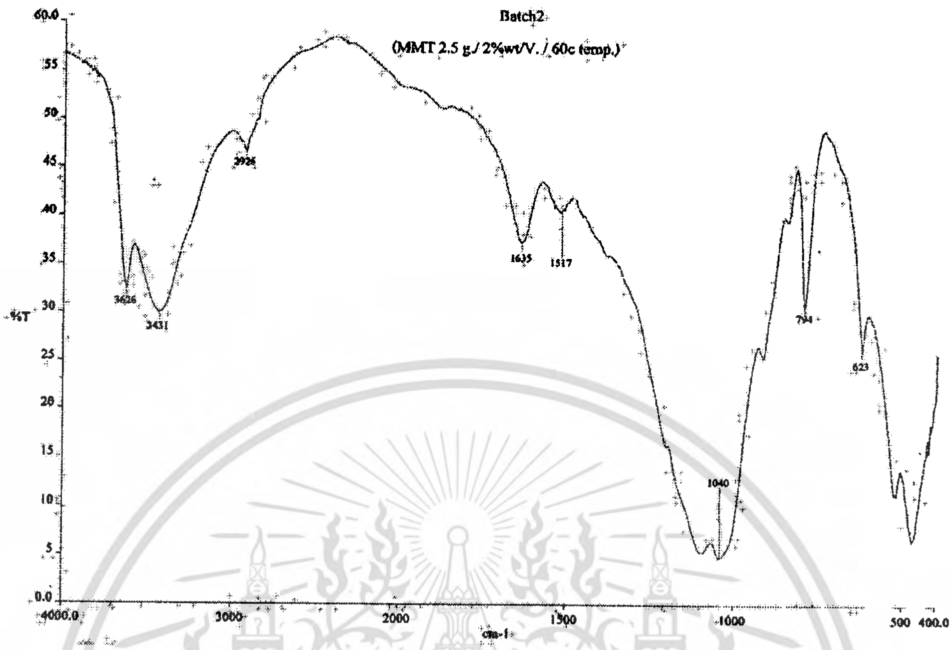


Fig. B-5 FTIR Spectrum of M2.5 C 2.0%-60

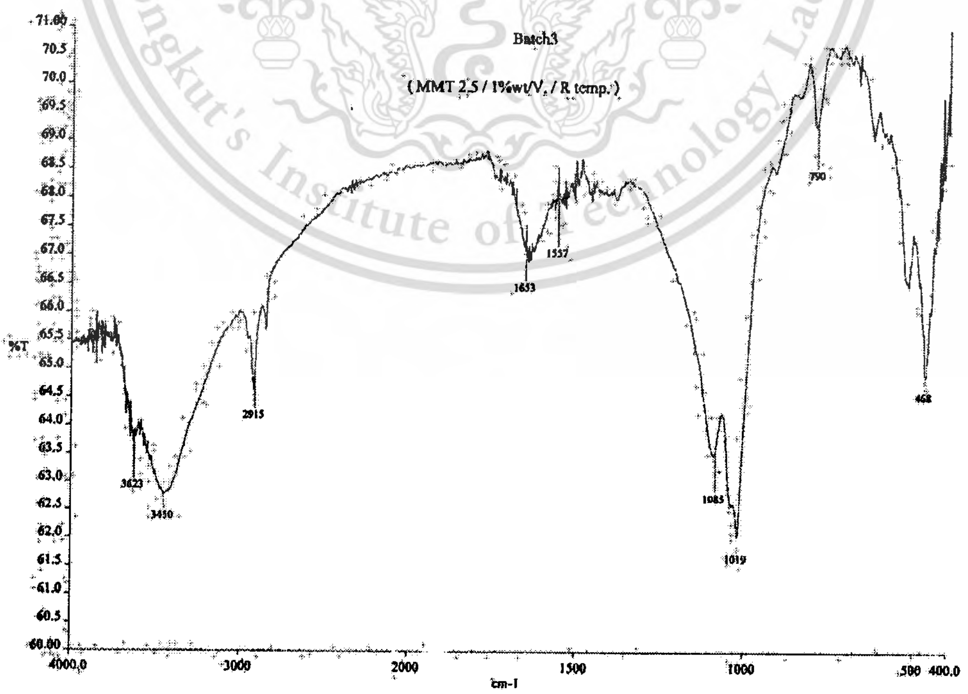


Fig. B-6 FTIR Spectrum of M2.5 C 1.0%-R

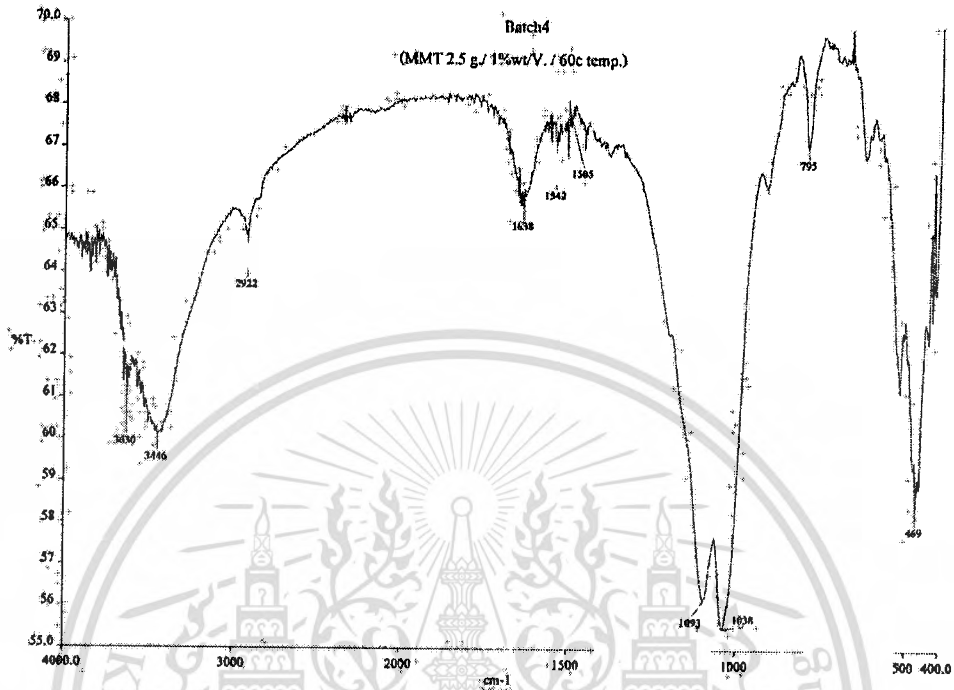


Fig. B-7 FTIR Spectrum of M2.5 C 1.0%-60

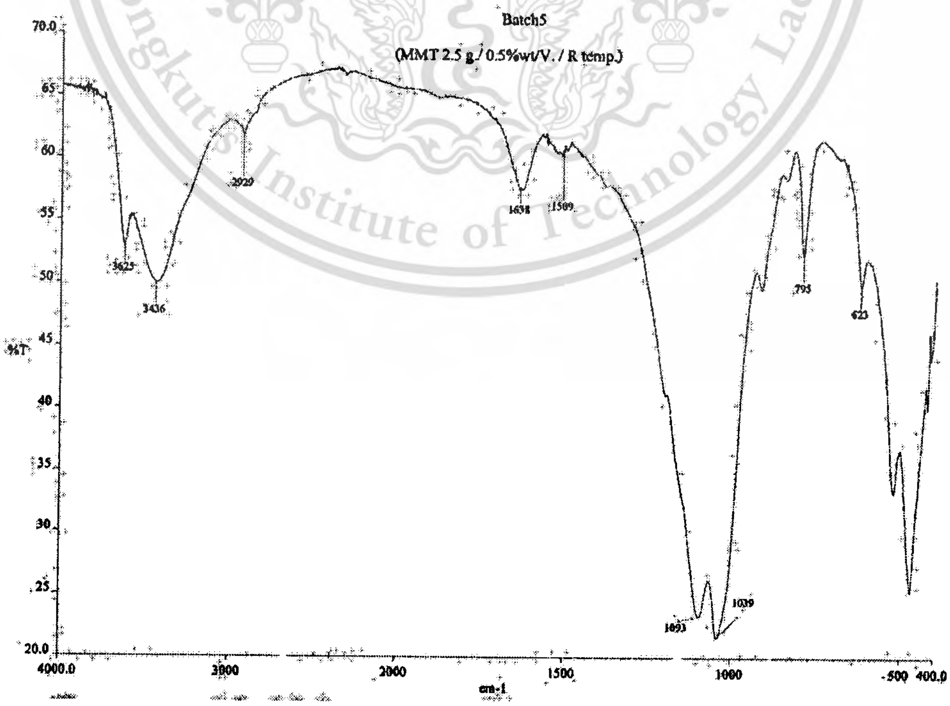


Fig. B-8 FTIR Spectrum of M2.5 C 0.5%-R

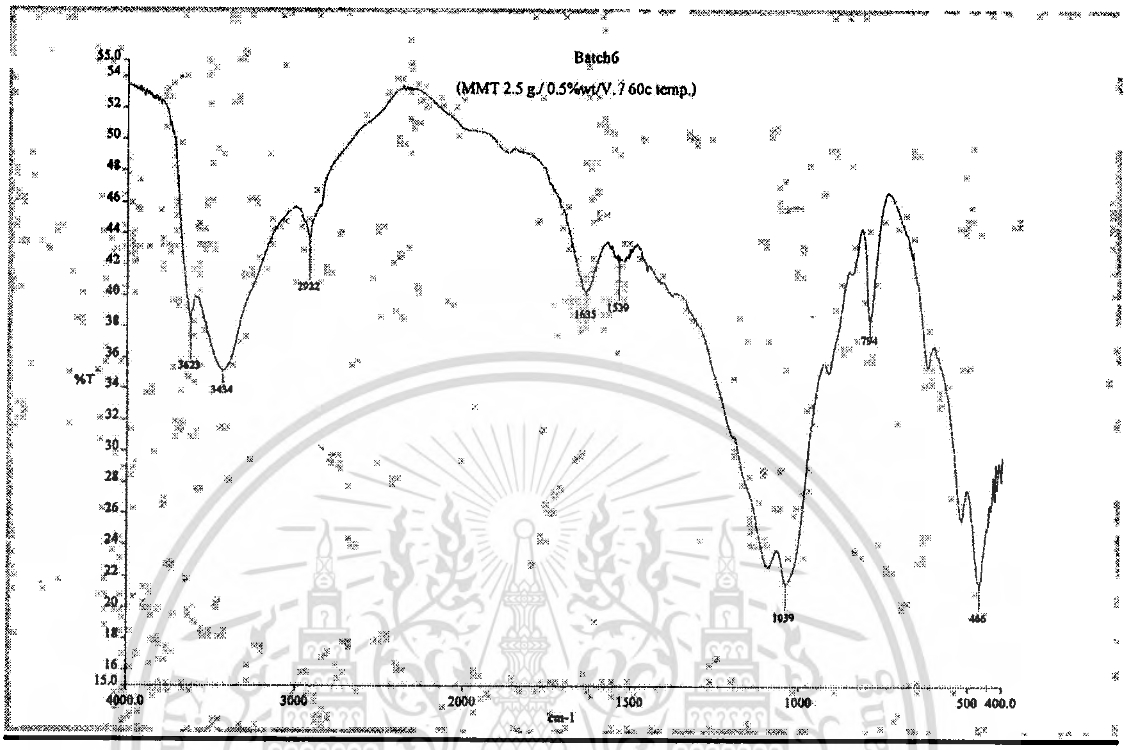


Fig. B-9 FTIR Spectrum of M2.5 C 0.5%-60

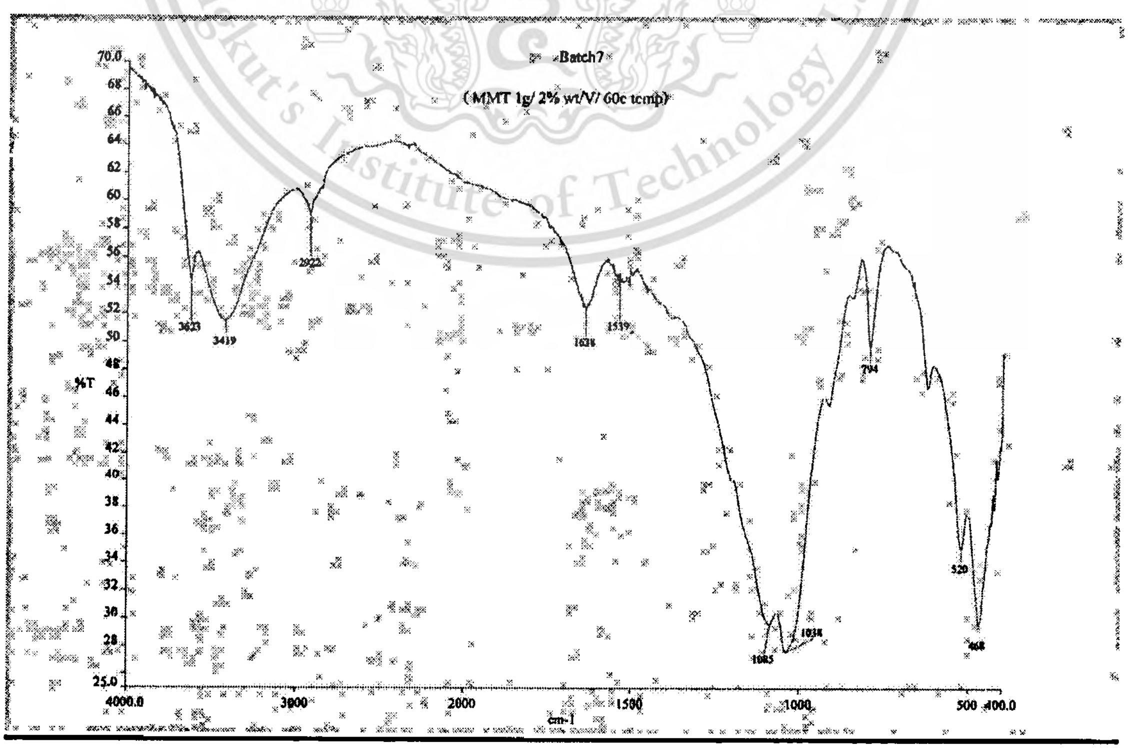


Fig. B-10 FTIR Spectrum of M1.0 C 2.0%-R

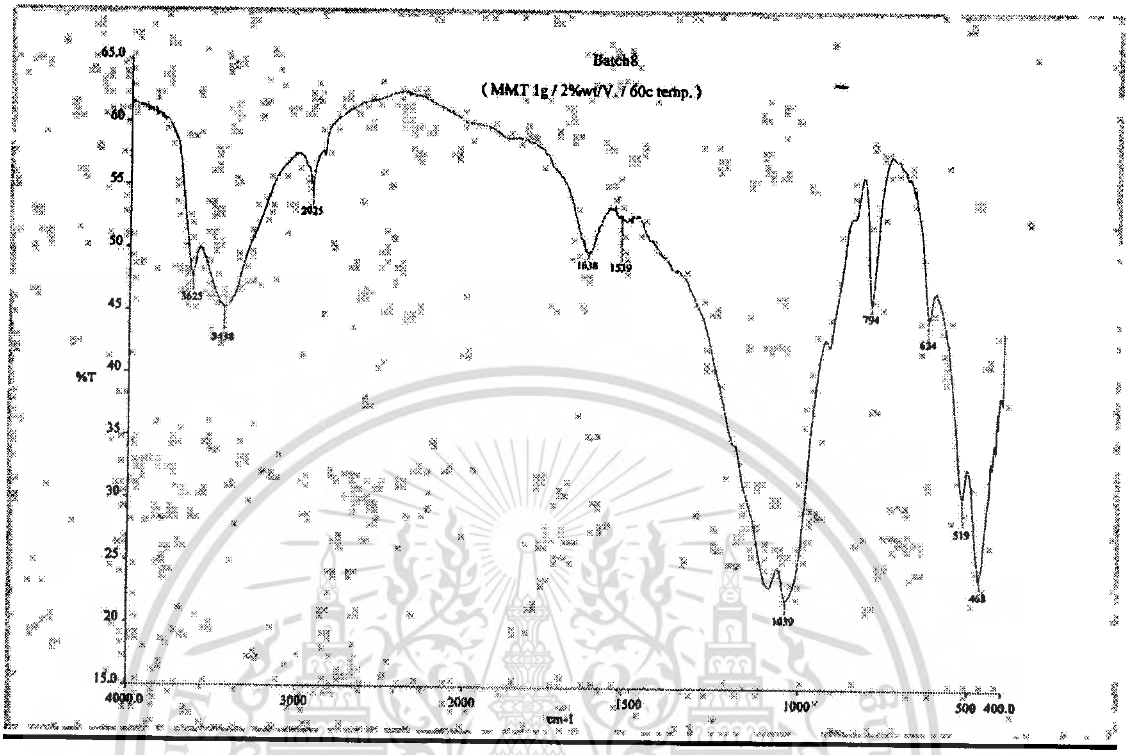


Fig. B-11 FTIR Spectrum of M1.0 C 2.0%-60

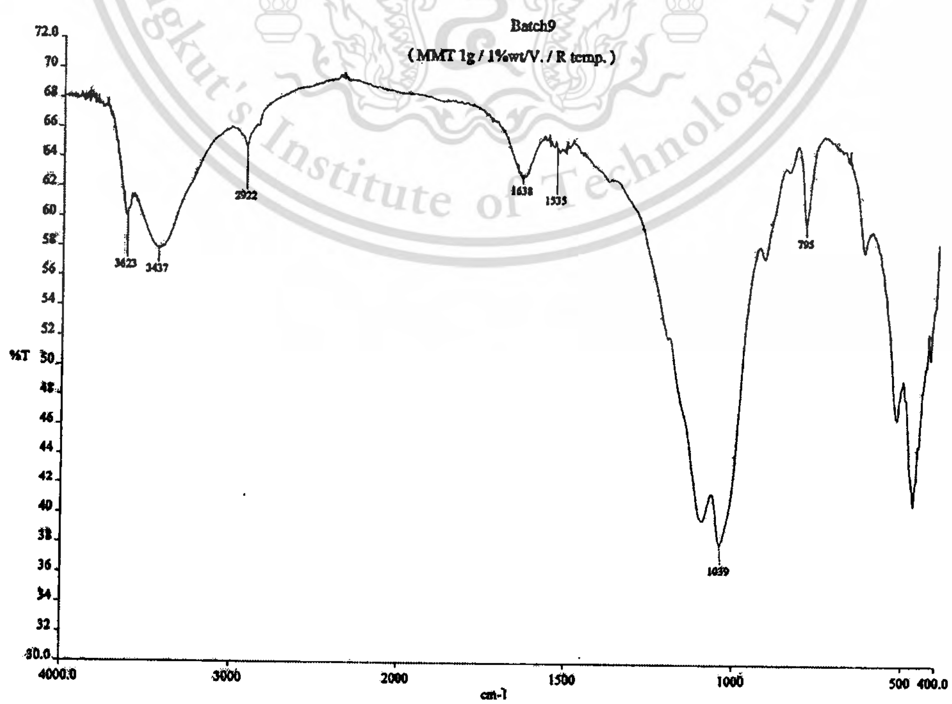


Fig. B-12 FTIR Spectrum of M1.0 C 1.0%-R

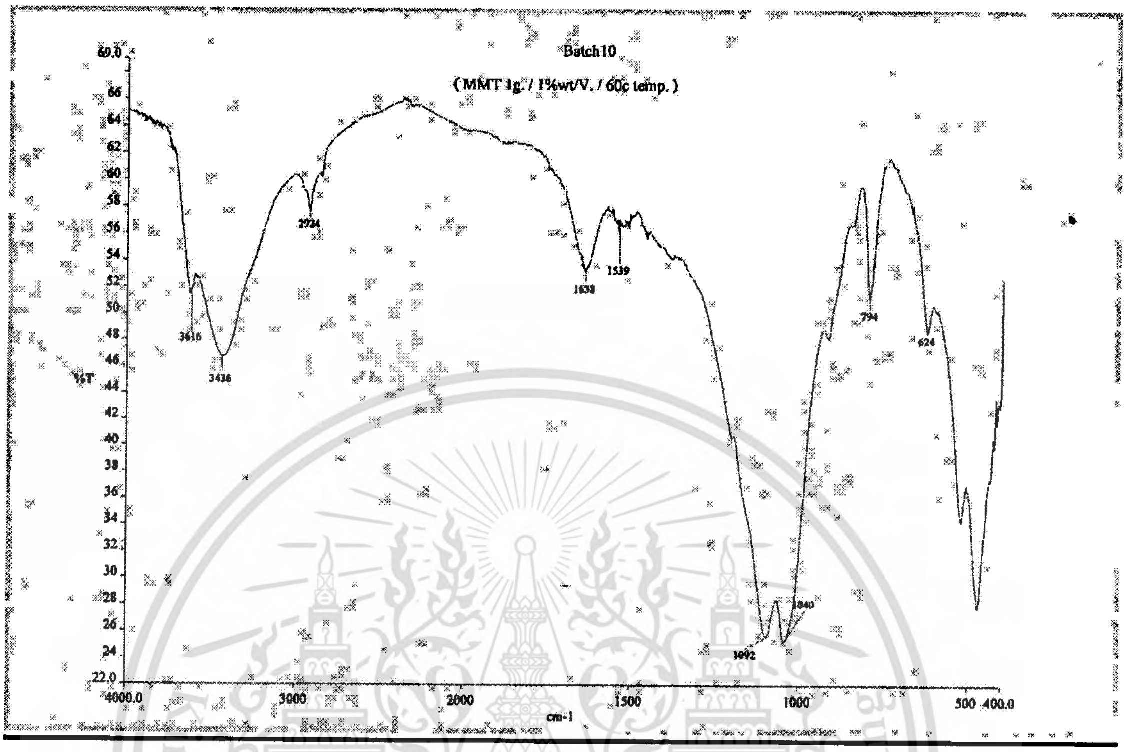


Fig. B-13 FTIR Spectrum of M1.0 C 1.0%-60

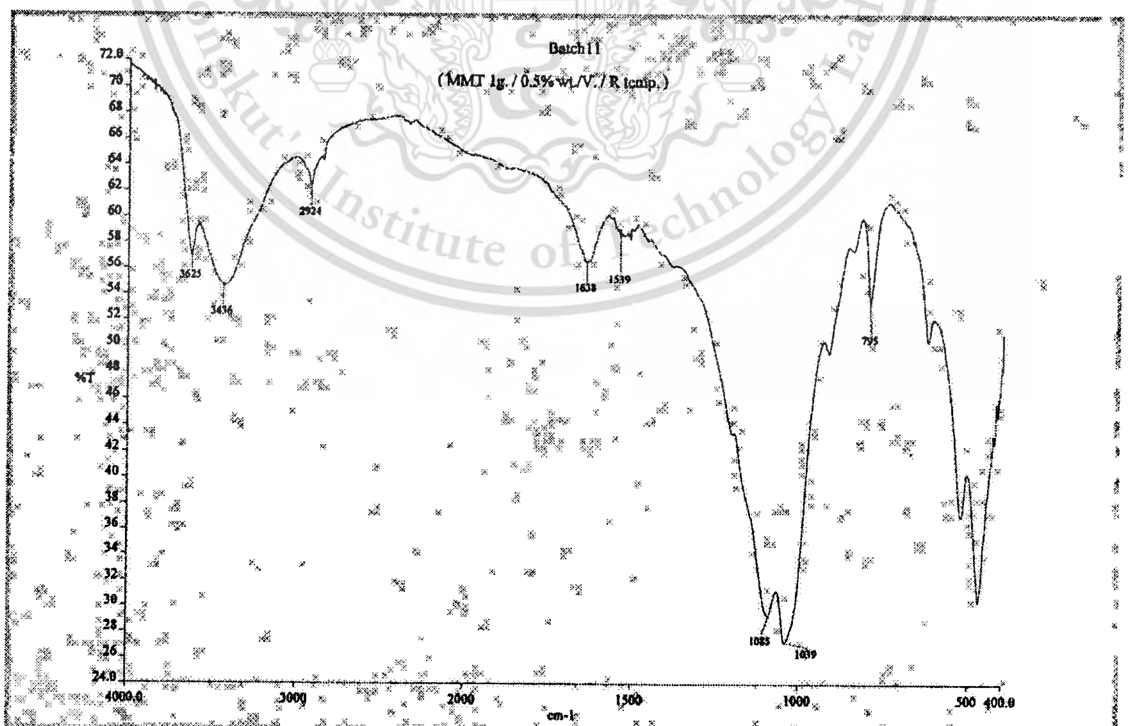


Fig. B-14 FTIR Spectrum of M1.0 C 0.5%-R

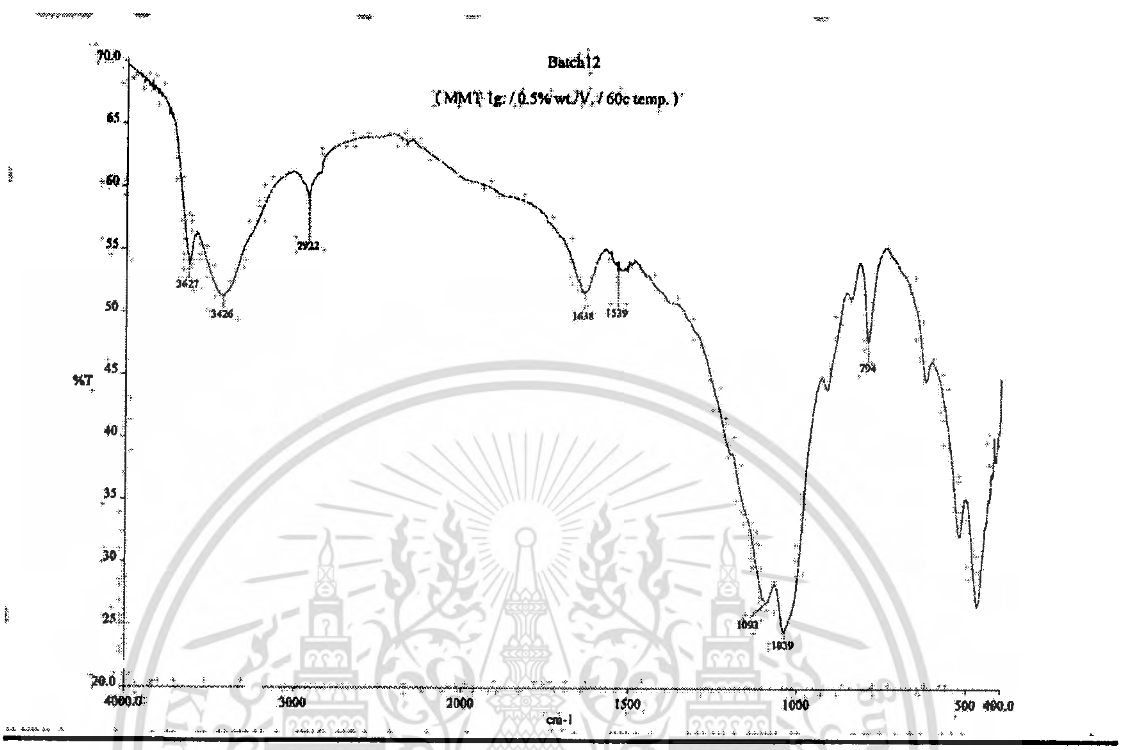


Fig. B-15 FTIR Spectrum of M1.0 C 0.5%-60