PREPARATION OF MONTMORILLONITE/ ACRYLATE BASED NANOCOMPOSITE USING ACRYLATE SYSTEMS

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Abstract

This research involves preparation of montmorillonite/acrylate based nanocomposites using acrylate systems. It was prepared by *in-situ* polymerization in compression molding at initiator at 85 °C for 12 min. The preparation condition were studied, that is the clay loading (0, 0.5, 1 and 2 wt %) and copolymer systems. The composite systems were exfoliated structures investigate by XRD. The mechanical properties of composites depend on clay loading and monomer systems. The higher the clay loading the higher tensile strength and modulus were obtained all systems and the highest tensile strength and Young's modulus of composites were obtained in P(MMA-co-AA/HEMA) with MMT containing 2%. The % transmittance of UV and visible light would decrease when the amount of MMT in acrylate polymer increased.

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Especially, I would like to give my special thanks to my parent whose patient love enabled me to complete this work.

Ms. Titirat Teerapakul

Ms. Rattanapatum Piladaeng

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Chapter 1

Introduction

1.1 Introduction

Nowadays, there has been growing interest in nanotechnology, which applied to use in the convergence of information and communication technology, life sciences, and biotechnology. Due to nanotechnology will usher in the Industrial Revolution of the 21st century as a platform technology with potential to revolutionize a broad range of industries. Nanomaterials are materials that have one or more dimensions less than 100 nm. Some of the major industries using or planning to use nanotechnology manufactures.

The nanocomposite-clay which has been widely used in the development of new reinforced nanocomposite polymers to improve their mechanical properties. The nanocomposites exhibit substantial increase in many physical properties, including mechanical properties (tensile modulus and strength flexural modulus and strength) thermal stability, flame retardance and barrier resistance.

The popular clay to used such as montmorillonite*(*MMT*)* are of particular interest because the offer a high aspect ratio (10-1000) and a high surface area.

In this study, the preparation and characterization of acrylic polymers that high gloss, glassy polymer transparent and very brittle. Therefore, we prepare montmorillonite/acrylate based nanocomposite using acrylate systems, for improve the mechanical properties, thermal resistance while the material still transparence. Then the nanocoposite can be applied for the product in the industry.

1.2 Objectives

1.2.1 To study and investigate the suitable method for preparation of montmorillonite/ acrylate based nanocomposite using various acrylate systems.

1.2.2 To study the physical properties and mechanical properties of the nanocomposites.

1.3 Scope of study

1.3.1 Preparation of montmorillonite/acrylate based nanocomposite using various parameters, as follow:

- Varying monomer systems used for swelling MMT , i.e. AA, AA/HEMA, and AA/MAA.
- Varying concentrations of MMT in the nanocomposite, i.e. 0, 0.5, 1 and 2 %wt.

1.3.2 Characterization of sample by using X-ray diffractometer (XRD), UV-visible spectrometer.

1.3.3 Mechanical testing of the namocomposite film by using universal testing machine.

1.4 Expected result

- Montmorillonite/acrylate based nanocomposite using acrylate systems film with more flexible, better physical and mechanical properties and higher thermal stability will be prepared.

Chapter 2

Theory and Literature Reviews

2.1 Clays

Clays are naturally occurring phyllosilicate minerals and are thus subject to natural variability in their constitution. Clay particles are less than 0.00015 inch (0.004 mm) in diameter; The crystalline structure of a typical clay mineral is a multi-layered structure comprised of combinations of layers of silicon oxide units and aluminum oxide units. Other metals such as magnesium may replace the aluminum in the crystal structure. Depending on the precise chemical composition of the clay, clay minerals vary based upon the combination of their constituent layers and cations.

2.1.1 Properties of Clays [1-5]

An important property of clay minerals, this is the ability to exchange ions, relates to the charged surface of clay minerals. The property of clay minerals that causes ions in solution to be fixed on clay surfaces or within internal sites applies to all types of ions. Some physical characteristic of clay are listed as follows:

- Clay mixed with water, clay becomes plastic-that is, it can be readily molded.
- Clay minerals tend to form microscopic to sub microscopic crystals.
- Clay can absorb water or lose water from normal humidity changes.
- Normally clays will expand as the water fills the spaces between the stacked silicate layers.

2.1.2 Mineral Contents of Clay [6,20,21]

Clay minerals contain various proportions of alumina and silica, usually combined with water to form hydrous aluminosilicates. Some of the minerals also contain calcium, sodium, magnesium, iron, or other elements. Clay minerals are divided into four major groups. These are the important clay mineral groups:

- *Kaolinite*, which is named for its type locality, Kao-Ling, Jianxi, China; is a common phyllosilicate mineral. The Kaolinite Group, members of which also belong to the larger general group known as the Clays. Kaolinite's structure is composed of silicate sheets (Si_2O_5) bonded to aluminum oxide/hydroxide layers ($Al_2(OH)_4$) called gibbsite layers. Gibbsite is an aluminum oxide mineral that has the same structure as these aluminum layers in kaolinite. The silicate and gibbsite layers are tightly bonded together with only weak bonding existing between these silicate/gibbsite paired layers (called s-g layers). The weak bonds between these s-g layers cause the cleavage and softness of this mineral. The structure is very similar to the Serpentine Group and at times the two groups are combined into a Kaolinite-serpentine Group.

Kaolinite shares the same chemistry as the minerals halloysite, dickite and nacrite. There four minerals are polymorphs; meaning they have the same chemical composition, but different structures. All four minerals form from the alteration (mostly weathering) of aluminum rich silicate minerals such as feldspars. Kaolinite is by far the most common and most clay deposits contain at least some kaolinite. In fact, clay deposits will frequently be nearly 100% kaolinite pure.

Kaolinite is important to the production of ceramics and porcelain. It is also used as filler for paint, rubber and plastics since it is relatively inert and is long lasting. But the greatest demand for kaolinite is in the paper industry to produce a glossy paper such as is used in most magazines[7].

- *Montmorillonite*, Chemical is $(Na, Ca)(Al,Mg)_6(Si_4O_{10})_3(OH)_6{-}nH_2O$,

It typically forms microscopic or at least very small platy micaceous crystals. The water content is variable, and in fact when water is absorbed by the crystals they tend to swell to several times their original volume. This makes montmorillonite a useful mineral for several purposes. It is the main constituent in a volcanic ash called bentonite, which is used in drilling muds. The bentonite gives the water greater viscosity ("thickness" of flow), which is very important in keeping a drill head cool during drilling and facilitating removal of rock and dirt from within a drill hole [8].

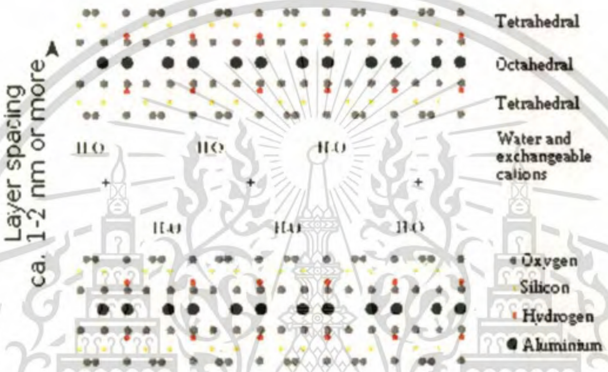


Fig.2.1 Structure of montmorillonite

Fig.2.2 Bright pink of montmorillonite

- *The Illite,* is a non-expanding, clay-sized, micaceous mineral.

Illite is a phyllosilicate or layered alumino-silicate. Its structure is constituted by the repetition of tetrahedron – octahedron – tetrahedron (TOT) layer. The interlayer space is mainly occupied by poorly hydrated potassium cations responsible for the absence of swelling. Structurally illite is quite similar to muscovite or sericite with slightly more silicon, magnesium, iron, and water and slightly less tetrahedral aluminium and interlayer potassium. The chemical formula is given as $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$, but there is considerable ion substitution. It occurs as aggregates of small monoclinic grey to white crystals. Due to the small size, positive identification usually requires x-ray diffraction analysis. Illite occurs as an alteration product of muscovite and feldspar in weathering and hydrothermal environments. It is common is sediments, soils, and argillaceous sedimentary rocks as well as in some low grade metamorphic rocks. Glauconite in sediments can be differentiated by x-ray analysis[9].

The cation exchange capacity (CEC) of illite is smaller than that of smectite but higher than that of kaolinite, typically around 20 – 30 meq/100 g [25].

2.2 Nanocomposite [10]

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 a non-intercalated 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 dense 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 non-dispersed hybrid corresponds to a conventional composite whereas the fine dispersed hybrid corresponds to either an intercalated or and exfoliated nanocomposite[11].

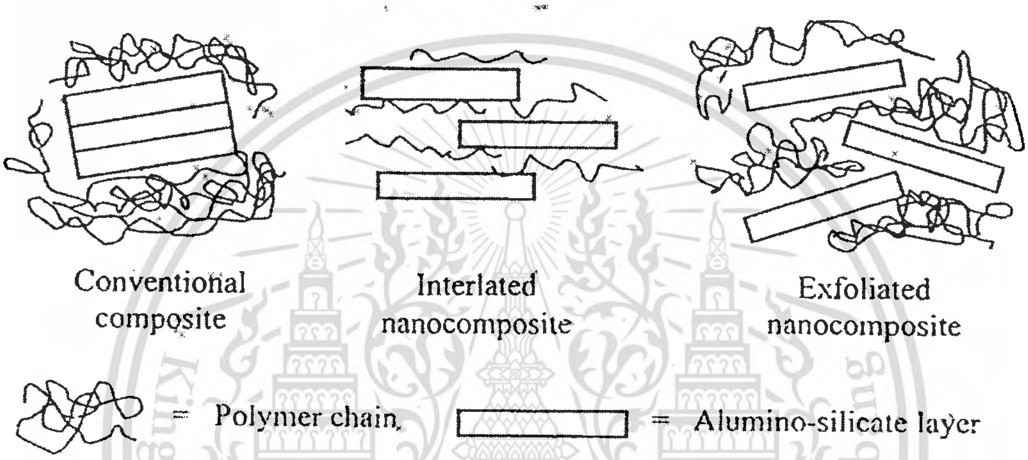


Fig. 2.3 Types of polymer-clay composites; (A) conventional composite, (B) intercalated nanocomposite and (C) exfoliated nanocomposite

The clay-containing polymeric nanocomposite performance is the extent of intercalation and exfoliation, X-ray diffraction (XRD) is the principal method that has been used to examine this [46]. The presence of multiple peaks in XRD spectra is quite common – it often originates from different organoclay structures and its incomplete change during incorporation in a polymeric matrix [11].

For the interlayer spacing, d_{001}, normally shown at low θ in the XRD pattern, is commonly determined from the XRD spectrum as arbitrary intensity versus 2θ. The spacing is then calculated from Bragg's law:

$$n\lambda = 2(d_{001})\sin\theta$$

Where n is an integer, θ is the angle of incidence (or reflection) of the X-ray beam, and λ is the X-ray wavelength most X-ray machines use Cu-$K\alpha_1$ radiation with $\lambda = 0.1540562$ nm. The peak position and the interlayer spacing related to the equation is one part of the information provided by XRD measurements. The intensity of the diffraction peak and its dependence on the concentration of scattering particles yields other information [10].

2.2.1. Nanocomposite Synthesis [12,29]

Nanocomposites can be synthesized by different routes. Most commonly used routes are:

- In-situ polymerization process
- Solution process

2.2.1.1. In situ polymerization process (In reactor polymerization) [32]

In-situ polymerization method is very useful method for the preparation of high performance polymer nanocomposites. In this method nanocomposite is synthesized by introducing the monomer, into the organically modified clay and then polymerizing it in-situ. After reaction completion the product was cooled and subjected to milling operation to obtain pellets.

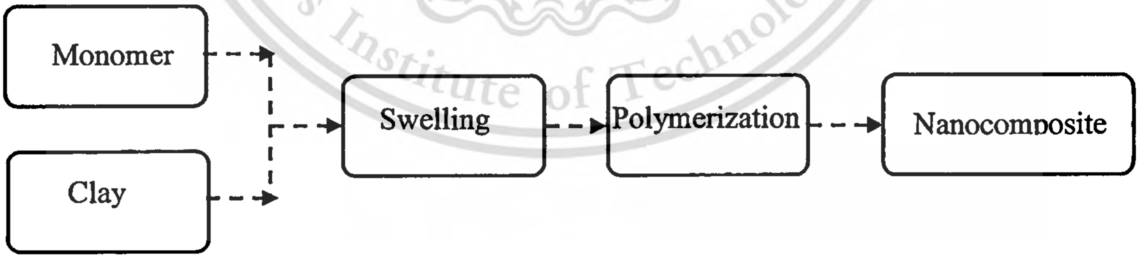


Fig. 2.4. Flow diagram for In- Situ polymerization process

2.2.1.2. Solution polymerization[32]

Organically modified clay is suspended in suitable solvent under vigorous stirring condition. Organoclay swells in the solvent. To this mixture monomer and initiator is added. The mixture is allowed to react while vigorous stirring condition is maintained. Reaction is then terminated. The product is separated and washed several times. It is then dried under reduced pressure to remove the washing solvent.

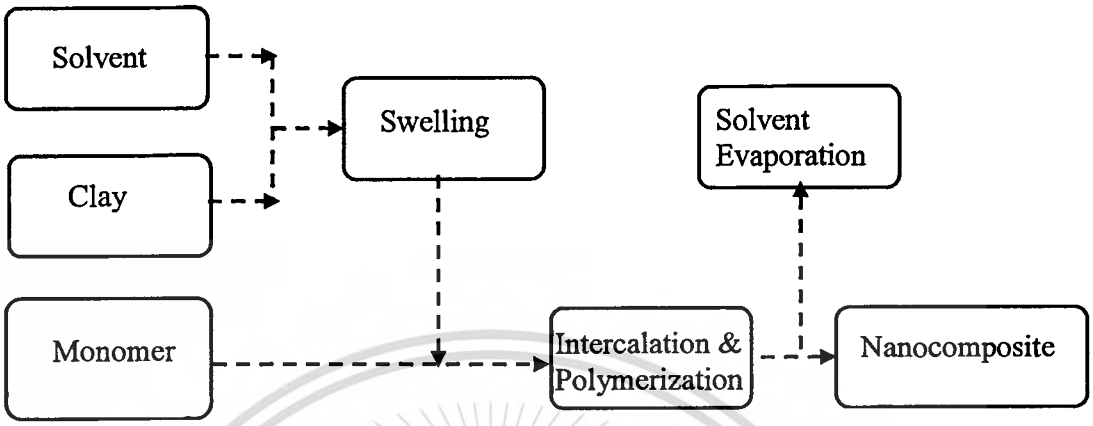


Fig. 2.5. Flow diagram representing the steps involved in the solution polymerization process.

2.3 Polymethyl methacrylate (PMMA) [38]

Poly(methyl methacrylate) (PMMA) is the synthetic polymer of methyl methacrylate. This thermoplastic and transparent plastic is sold by the trade names Plexiglas, Perspex, Plazcryl, Acrylite, Acrylplast, Altuglas, and Lucite and is commonly called acrylic glass or simply acrylic. Acrylic glass is nonpoisonous, weatherproof, unbreakable, lightweight and burns without residue. These favorable properties make it interesting for many uses: from construction to the automobile industry, in exhibition and retail construction, for furniture and household items, in lighted advertisements, for protective glass, displays and lab equipment.

Acrylic glass commonly serves as a substitute for glass. It is only about half as heavy, easier to handle and conducts light better [39]. The disadvantage, however, is that acrylic glass scratches more easily. It allows ultraviolet light and x-rays to pass through but holds back thermal radiation. For these reasons it is also used for greenhouses.

2.3.1 Properties of PMMA [38]

- Hard, rigid, transparent (very clear to see through)
- Softening point at 125 °C
- Tougher than polystyrene but less tough than ABS (acrylobutylstyrene) polymer
- Absorbs very little visible light but there is a 4% reflection at each polymer-air interface for normal incident light.
- A good electrical insulator at low frequencies but less satisfactory at higher frequencies
- Good water resistance
- PMMA prepared by free radical polymerization is amorphous and is therefore soluble in solvents with similar solubility parameters such as benzene, toluene, chloroform, methylene chloride, esters, ethyl acetate, and amyl acetate.
- PMMA has good resistance to alkalis (sodium hydroxide, etc.), aqueous inorganic salts (the Pacific Ocean) and dilute acids.
- PMMA has a better resistance to hydrolysis than PMA probably by virtue of the shielding of the methyl group.
- PMMA's outstanding good outdoor weather resistance is marketably superior to other thermoplastics.
- When heated about 200° C, decomposition becomes appreciable and at 350- 450 °C, a nearly quantitative yield of monomer is readily obtained. Thus, the recovery of monomer from scrap is feasible.
- It's a thermoplastic, it can be molten and molded (at 100 to 150 °C) into anything we want.
- A syndiotactic polymer can be polymerized. At lower temperatures, the stereochemistry of the polymer can be controlled by means of the solvent.

2.4 Polymerization

Polymerization is a process of reacting monomer molecules together in a chemical reaction to form three-dimensional networks or polymer chains.

Polymerizations have one thing in common: They all start with small molecules, and join them into big giant molecules. The properties of the polymer depend on how the kinds of monomers and how they are connected together. So we classify these polymerization reactions [13, 26-28].

2.4.1 Condensation Polymerization [14]

Condensation polymerization involves interaction of two similar (or different) monomers and generally eliminate liquid or gaseous by products (such as water, hydrochloric acid or nitrogen gas).

The monomers for condensation polymerization have two main characteristics:

⇨ Instead of double bonds, these monomers have functional groups (like alcohol, amine, or carboxylic acid groups).

⇨ Each monomer has at least two reactive sites, which usually means two functional groups.

2.4.2 Free Radical Polymerization [15]

A *free radical* is simply a molecule with an unpaired electron. The tendency for this free radical to gain an additional electron in order to form a pair makes it highly reactive so that it breaks the bond on another molecule by stealing an electron that molecule with an unpaired election (which is another free radical). Free radicals are often created by the division of a molecule (known as an *initiator*) into two fragments along a single bond. The following diagram shows the formation of a radical from its initiator, in this case benzoyl peroxide.

The *stability* of a radical refers to the molecule's tendency to react with other compounds. An unstable radical will readily combine with many different molecules. However a stable radical will not easily interact with other chemical substances. The stability of free radicals can vary widely depending on the properties of the molecule.

The *active center* is the location of the unpaired electron on the radical because this is where the reaction takes place. In free radical polymerization, the radical attacks one monomer, and the electron migrates to another part of the molecule. This newly formed radical attacks another monomer and the process is repeated. Thus the active center moves down the chain as the polymerization occurs.

There are three significant reactions that take place in addition polymerization: *initiation* (birth), *propagation* (growth), and *termination* (death). These separate steps are;

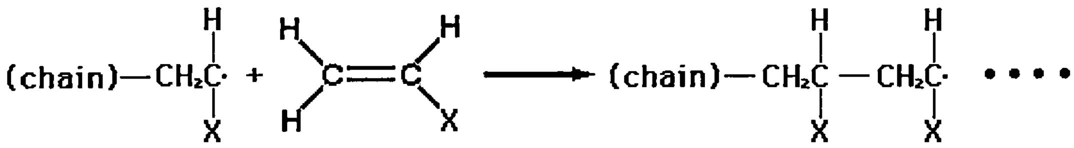
- *Initiation Reaction*

The first step in producing polymers by free radical polymerization is initiation. This step begins when an *initiator* decomposes into free radicals in the presence of monomers. The instability of carbon-carbon double bonds in the monomer makes them susceptible to reaction with the unpaired electrons in the radical. In this reaction, the active center of the radical "grabs" one of the electrons from the double bond of the monomer, leaving an unpaired electron to appear as a new active center at the end of the chain. Addition can occur at either end of the monomer. This process is illustrated in the following animation in which a chlorine atom possessing an unpaired electron initiates the reaction

In a typical synthesis, between 60% and 100% of the free radicals undergo an initiation reaction with a monomer. The remaining radicals may join with each other or with an impurity instead of with a monomer. "Self destruction" of free radicals is a major hindrance to the initiation reaction. By controlling the monomer to radical ratio, this problem can be reduced.

- *Propagation Reaction*

After a synthesis reaction has been initiated, the propagation reaction takes over. In the propagation stage, the process of electron transfer and consequent motion of the active center down the chain proceeds. In this diagram, (chain) refers to a chain of connected monomers, and X refers to a substituent group (a molecular fragment) specific to the monomer. For example, if X were a methyl group, the monomer would be propylene and the polymer, polypropylene.



$$\text{(chain)}—CH_2\overset{H}{\underset{X}{C}}\cdot + H_2C{=}CHX \longrightarrow \text{(chain)}—CH_2\overset{H}{\underset{X}{C}}—CH_2\overset{H}{\underset{X}{C}}\cdot \;\cdots$$

In free radical polymerization, the entire propagation reaction usually takes place within a fraction of a second. Thousands of monomers are added to the chain within this time. The entire process stops when the termination reaction occurs.

- *Termination Reaction*

In theory, the propagation reaction could continue until the supply of monomers is exhausted. However, this outcome is very unlikely. Most often the growth of a polymer chain is halted by the termination reaction. Termination typically occurs in two ways: *combination* and *disproportionation.*

Combination occurs when the polymer's growth is stopped by free electrons from two growing chains that join and form a single chain. The following diagram depicts combination, with the symbol **(R)** representing the rest of the chain.

$$(R)\text{—}CH_2\underset{X}{\overset{H}{C}}\bullet + \bullet\underset{X}{\overset{H}{C}}CH_2\text{—}(R) \longrightarrow (R)\text{—}CH_2\underset{X}{\overset{H}{C}}\text{—}\underset{X}{\overset{H}{C}}CH_2\text{—}(R)$$

Disproportionation halts the propagation reaction when a free radical strips a hydrogen atom from an active chain. A carbon-carbon double bond takes the place of the missing hydrogen. Termination by disproportionation is shown in the diagram.

$$(R)\text{—}CH_2\underset{X}{\overset{H}{C}}\bullet + \bullet\underset{X}{\overset{H}{C}}CH_2\text{—}(R) \longrightarrow (R)\text{—}CH_2\underset{X}{\overset{H}{C}}\text{—}H + \underset{X}{\overset{H}{C}}\text{=}CH\text{—}(R)$$

Disproportionation can also occur when the radical reacts with an impurity. This is why it is so important that polymerization be carried out under very clean conditions.

2.4.3 Polymerization Techniques

Bulk (Mass) Polymerization

The polymerization of a monomer in the absence of any medium other than a catalyst or accelerator. The monomers are usually liquids, but the term also applies to the polymerization of gases and solids in the absence of solvents [16].

Advantages:

- Minimum contamination of product

Disadvantages:

- R_t decreases at high conversion due to the Trommsdorf effect, making the reaction hard to control.
- R_p and ν increase as conversion increases, broadening the molecular weight distribution.
- Viscosity increases as conversion increases, making heat removal and processing more difficult.

Solution Polymerization

A polymerization process in which the monomers and the polymerization initiators are dissolved in a nonmonomeric liquid solvent at the beginning of the polymerization reaction. The liquid is usually also a solvent for the resulting polymer or copolymer[17].

Advantages:

- Solvent acts as a diluents and aids in removal of heat of polymerization.
- Solvent reduces viscosity, making processing easier.
- Thermal control is easier than in the bulk.

Disadvantages:

- Chain transfer to solvent occurs, leading to low molecular weights.
- Difficult to remove solvent from final form, causing degradation of bulk properties.
- Environmental pollution due to solvent release[18].

Suspension (Bead or Pearl) Polymerization

A polymerization process in which the monomer, or mixture of monomers, is dispersed by mechanical agitation in a liquid phase, usually water, in which the monomer droplets are polymerized while they are dispersed by continuous agitation. Used primarily for PVC polymerization [19].

Advantages:

- Low viscosity due to the suspension
- Easy heat removal due to the high heat capacity of water
- Polymerization yields finely divided, stable latexes and dispersions to be used directly in coatings, paints, and adhesives.

Disadvantages:

- Cannot be used for polymers whose glass transition temperature is less than the polymerization temperature, or else aggregation will occur.
- Must separate and purify polymer, or accept contaminated product.

Emulsion polymerization [22-24]

Emulsion polymerization is a type of radical polymerization that usually starts with an emulsion incorporating water, monomer, and surfactant. The most common type of emulsion polymerization is an oil-in-water emulsion, in which droplets of monomer (the oil) are emulsified (with surfactants) in a continuous phase of water. Water-soluble polymers, such as certain polyvinyl alcohols or hydroxyethyl celluloses, can also be used to act as emulsifiers/stabilizers. The name "emulsion polymerization" is a misnomer that arises from a historical misconception. Rather than occurring in emulsion droplets, polymerization takes place in the latex particles that form spontaneously in the first few minutes of the process. These latex particles are typically 100 nm in size, and comprise many individual polymer chains. The particles are stopped from coagulating with each other because each particle is surrounded by the surfactant ('soap'); the charge on the surfactant repels other particles electrostatically.

2.5 Literature Reviews

Nehal Salahuddin and Mohamed Shehata[33] ,[2001] studied to prepare of polymethylmethacrylate–montmorillonite composites for improve the mechanical, characterization properties. They were solving a problem of polymerization shrinkage in acrylic resin polymethylmethacrylate (PMMA) material. By using the organophilic montmorillonite (claytone) that was added up to 1% by weight to one commercial type of PMMA powder to form PMMA–MMT composite. Acrylic specimens were processed by the conventional heat curing method following manufacturer's instructions. Thermogravimetric analysis data indicates that polymer–clay composites exhibit significant increase in thermal stability with very small amount of inorganic content. The morphology of the composites was verified using scanning electron microscopy revealing the absence of large mineral aggregates. Interlamellar spacing was measured from wide angle X-ray diffraction. Overall, this research is increase in thermal stability with very small amount of inorganic content and the significant decrease of warpage and linear dimensional changes between PMMA specimens and that of PMMA–MMT composite materials.

Yuanqing Xiang [34] [2006] concerned in a new polymer/clay nano-composite hydrogel with improvement of response rate and tensile mechanical properties. They was prepared by introducing fibrillar attapulgite into poly(2-hydroxyethyl methacrylate-co-poly(ethylene glycol) methyl ether methacrylate-co-methacrylic acid) network, in which the nanosized attapulgite fibril worked as the cross-linker instead of conventional chemical cross-linker. The results showed that the nano-composite hydrogels had much greater equilibrium-swelling ratio, much faster response rate to pH and significantly improved tensile mechanical properties. As the content of AT increased, the tensile strength, effective cross-link chain density and glass transition temperature increased, while the equilibrium swelling ratio, deswelling rate and elongation at break decreased.

Metin Tanoğlu[35],[2006]concerned in effect of the Porous nanocomposites prepared from layered clay and PMMA [poly(methyl methacrylate)]. They contain clay (montmorillonite, MMT) platelets as reinforcements within the cell walls of the porous structure. To render the clay layers organophilic, MMT was surface treated by an ion exchange reaction between interlayer cations of the clay and ammonium ions of a surfactant. Clay/PMMA based porous nanocomposites were prepared by polymerization of water-in-oil emulsions with and without clay addition. The microstructure and compressive mechanical behavior of the nanocomposites were investigated. The results of mechanical tests showed that the porous systems with the addition of 1 wt. % of organoclay (OMMT) exhibited a 90% and 50% increase of collapse stress and elastic modulus values, respectively, as compared to neat porous PMMA.

Sanit Sirapanichart, Suraluck Macksasitorn and Suwicha Buakheio[36] [2007] studied to prepare of organophosphate modified montmorillonite/Poly(Methyl Methacrylate) nanocomposite. They concerned in preparation and properties of Tetrabutylphosphonium bromide (TBPB) that was intercalated into swelled montmorillonite (S-MMT) by cation exchange reaction using 2 modification techniques, i.e., mechanical agitation and sonication. The Phosphonium MMT (P-MMT) was characterized by X-ray diffractometer (XRD), X-ray fluorescence spectrometer (XRF) and thermogravimetric analysis (TGA). The absorbance of PMMA/P-MMT film was high in the UV region, especially in UV-A and UV-B, suggesting the potential to be used as the UV-screening film for the windscreen and the glasses lens.

Tapanut Leelaphat and Tepagorn Jarutawesub[37] [2007] research the preparation of poly(methyl methacrylate/montmorillonite nanocomposites (PMMA/MMT). PMMA/MMT compsites were preparation by *in-situ* polymerization using benzoyl peroxide (BPO) as initiator at 85 °C incompression molding. The ratio of methyl methacrylate and acrylic acid (MMA:AA) were varied in the ration of 100:0, 95:5 90:10 and 85:15 by weight. Amount of MMT was varied in the range of 0-2 wt%. It was found that the PMMA/MMT composites were intercalate nanocomposite because the d-spacing (d_{001}) of PMMA/MMT composites was higher than that of MMT. When the mount increased, the PMMA/MMT composites processed higher tensile strength and Young's modulus, better thermal stability and UV protection than PMMA. For P(MMA-*co*-AA), tensile strength and Young's modulus decreased with increasing AA content. When 1% MMT was added to P(MMA-*co*-AA), the P(MMA-*co*-AA)/MMT nanocomposites had higher tensile strength and Young's modulus than pure P(MMA-*co*-AA)

Chapter 3

Experiment

3.1 Chemicals

1. Methyl methacrylate monomer, (MMA) ($C_5H_8O_2$, Molecular weight = 100.12, Density = 0.963 g/ml), Aldrich, Analytical grade
2. Acrylic acid (AA), Thai Mitsui Specialty Chemicals CO., LTD.
3. Methanol (CH_3OH), Fisher, Commercial grade
4. Hydroxy *ethyl methacrylate* (HEMA), Thai Mitsui Specialty Chemicals CO., LTD.
5. Methyl methacrylic acid (MAA), Thai Mitsui Specialty Chemicals CO., LTD.
6. Clay (Montmorironite, MMT), Thai Nippon Chemical Industry
7. Toluene(C_7H_8), LAB SCAN, Analytical grade
8. Benzoyl peroxide (BPO), CARLO ERBA, Analytical grade
9. Sodium hydroxide (NaOH), LAB scan, Analytical grade
10. Sodium chloride (NaCl), CARLO ERBA, Analytical grade
11. Anhydrous sodium sulfate (Na_2SO_4), CARLO ERBA, Analytical grade
12. Nitrogen gas (N_2)
13. Distilled water

3.2 Apparatus

1. Glassware
2. Magnetic stirrer
3. Ultrasonic bath, ULTRAsonik, Fisher Scientific Worldwide
4. Compression molding
5. Balance, TC – 254, Denver instrument
6. Oven, Isotemp, Fisher Scientific
7. Water bath
8. Clear sheet
9. Universal testing machine, LR5K, LLOYD Instrument
10. Mold
11. X-ray diffractometer (XRD), D8 Advance, Bruker AG
12. UV-Visible Spectrometer (UV-vis), He λ ions α, Thermo Electron Corporation
13. Gel permeation Chromatography, water 150-cv, Milipore

3.3Methods

3.3.1 X-ray diffraction analyses (XRD)

X-ray powder diffraction (XRD) is analytical technique used for phase identification of a crystalline material.

Analysis test condition:

2θ to analyst	1°-25°
Step size	0.040°
Step time	5 sec

3.3.2 UV-visible spectrometer

UV-Visible absorption spectrophotometer

Analysis test condition:

Wave range	190-1100 cm^{-1}

3.3.3 Gel permeation chromatography (GPC)

Analysis test condition:

Column	: PLgel 10 µm Mix B 2 columns size 78x300 nm was analyzed molecular weight range 500-10,000,000 gram per mole. Polymer standard was polystyrene.
Eluent	Tetrahydrofuran (THF) HPLC grade.
Column temperature	30 °C
Injection temperature	30 °C
Solvent/pump temperature	30 °C
Flow rate	1 ml/min
Injection time	22 min
Detector	Reflective index

3.3.4 Tensile testing

Tensile testing by Universal testing machine was tested tensile properties measure the tensile strength, %elongation at break and Young's modulus of various thermoplastics polymers.

Analysis test condition:

Test speed	50 mm/min
Gage length of	25 mm
Load cell	100 N

3.4 *Preparation of polymethyl methacrylate (PMMA) and preparation of sample.*

3.4.1. The purified of montmorillonite

Before being used for preparation of MMT composites, the as – received MMT was purified by dispersion of MMT in distilled water and sonication for 2 hours. The well suspension of MMT (upper part), S-MMT, was separated and dried at 100°C. The dried MMT was sieved through by 400-mesh sieve.

3.4.2. Extract inhibitor from methyl methacrylate monomer

1. Methyl methacrylate monomer (MMA) 10 ml was mixed with a 10% solution of *sodium* hydroxide 10 ml using separatory funnel.
2. The mixture was shaken vigorously and left for several minutes while the layers separate out and settle down. The lower layer is sodium hydroxide.
3. The sodium hydroxide layer (lower layer) was removed.
4. Step 1-3 was repeated.
5. Methacrylate monomer (MMA) layer was plenty washed with 10 ml of distilled water until no change in the color of the litmus paper (red ➤ blue).
6. Saturated sodium chloride was added into a mixture.
7. After remove sodium chloride layer, anhydrous sodium sulfate was added to remove water.
8. Sodium sulfate was filted off. The clear methyl methacrylate monomer (MMA) was kept in a refrigerator before use.

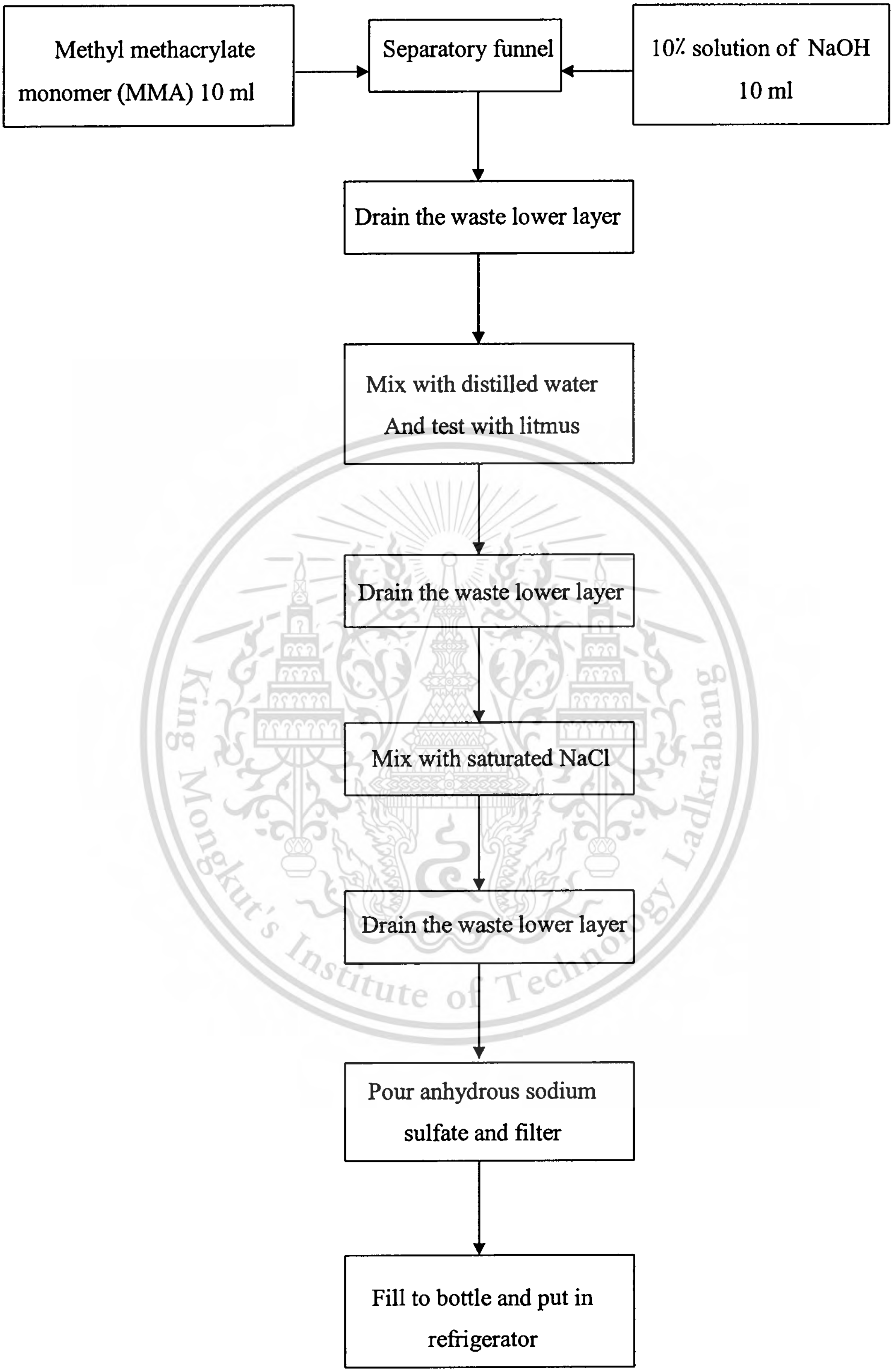


Fig. 3.1 Flow diagram for extracted inhibitor from methyl methacrylate monomer

*3.4.3. S*olution polymerization of methyl methacrylate

1. Inhibitor-free methyl methacrylate monomer 10 ml was poured into 250 ml round bottom flask.
2. Benzoyl peroxide (BPO) 0.01 g was dissolved in toluene 40 ml. The solution was added to monomer portion in the round bottom flask.
3. Nitrogen gas was purged into the solution for 15 minutes. The equipment was connected as shown in figure 3.2
4. The equipment was put into water bath at 85°C for 24 hours.
5. After cooling down, the slightly viscous solution was added drop wise into methanol with vigorous stir during which time. Then, white solid PMMA was precipitated.
6. The white solid product was filtered off and dried in oven at 60°C for 24 hours.
7. The polymer was grinded, the molecular weight was determined by Gel permeation chromatography (GPC).

Figure 3.2 The equipment used for polymerization of methyl methacrylate.

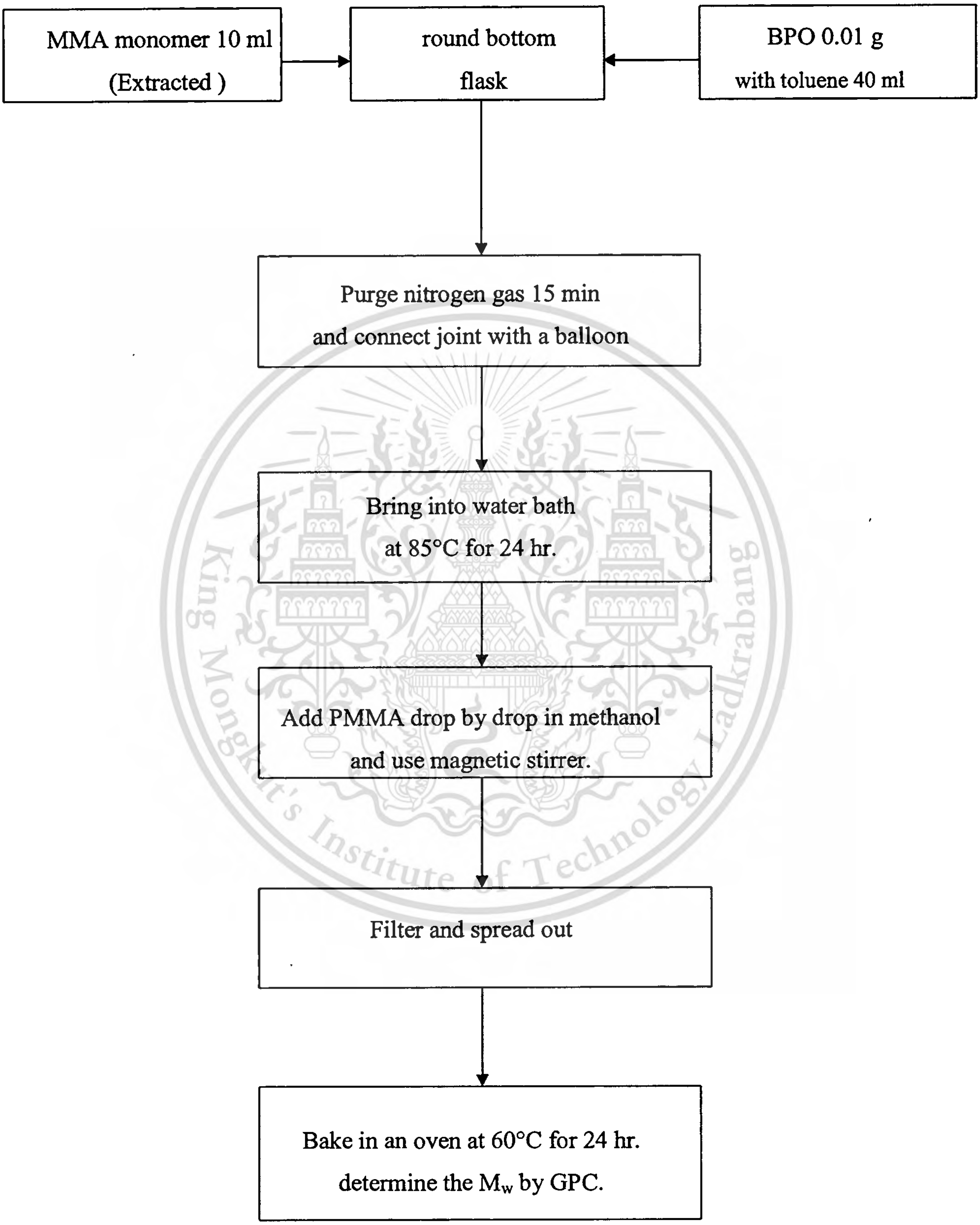


Fig.3.3 Flow diagram for solution polymerization of methyl methacrylate.

3.3.5 Swell test

1. The montmorillonite (MMT) and appropriate monomer (see a table 3.1) was mixed into test tube.
2. The montmorillonite (MMT) was dispersed in the monomer by sonication for 30 minutes at room temperature.
3. The results were observed and recorded.

Table 3.1 Preparation of The montmorillonite (MMT) and appropriate monomer for swell test.

Sample	Clay (Montmorironite, MMT)	Acrylic acid (AA)	Hydroxy *Ethyl Methacrylate* (HEMA)	Methyl methacrylic acid (MAA)
1	0.1 g	1 ml	-	-
2	0.1 g	-	1 ml	-
3	0.1 g	-	-	1 ml

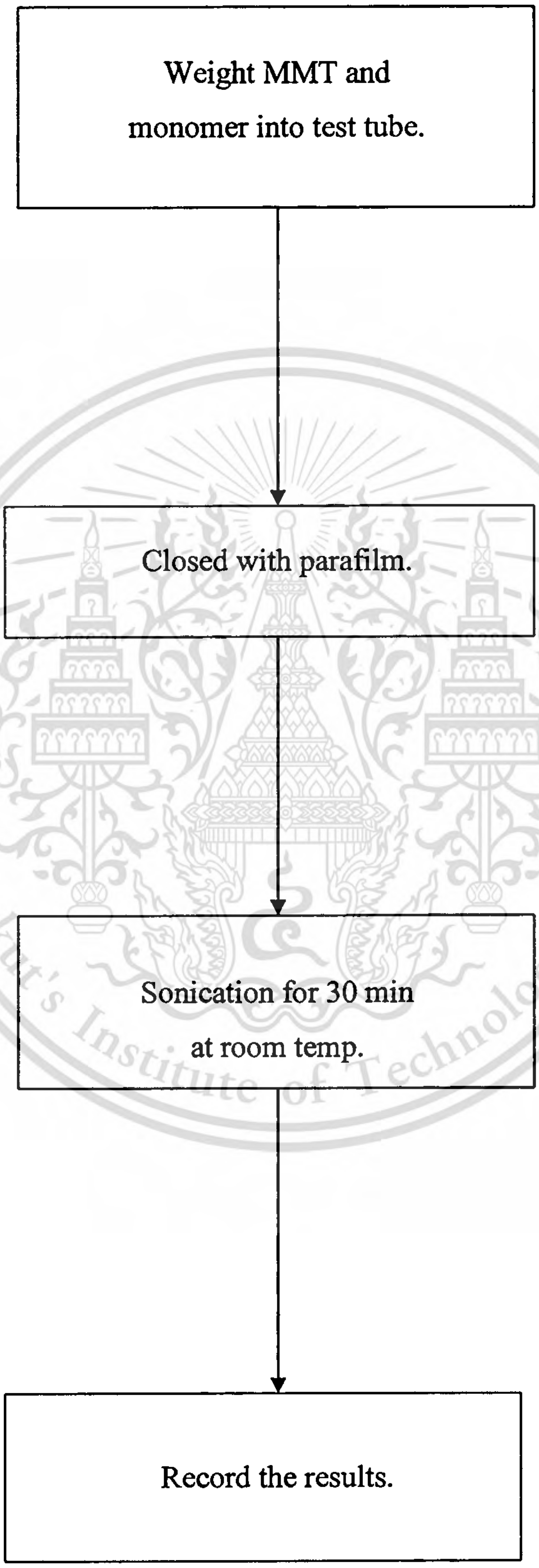


Fig.3.4 Flow diagram for the swell test

3.4.5. Preparation of nanocomposite sheet

1. Polymethacrylate (PMMA) (3 part by weight) was dissolved in methyl methacrylate monomer (MMA) (5 part by weight) into beaker and using magnetic stirrer.
2. Recipes as shown in Table 3.2 were mixed as follows:
3. The montmorillonite (MMT) was added into AA and the mixture was sonicated for 30 minute.
4. Hydroxy ethyl methacrylate (HEMA) or Methyl methacrylic acid (MAA) was added and the mixture was sonicated for 10 minute.
5. Benzoyl peroxide (BPO) was added and allowed to dissolve.
6. Portion 2 was added into portion 1 and then mixed well.
7. The mixture was shaped into clear plastic mold with the thickness 0.05 mm.
8. Condition for compression is 85 °C for 12 minutes.
9. Then, the mold was post cured in oven 60 °C for 1 hour.
10. The obtained clear sheet was characterized and tested by UV-Visible absorption spectrophotometer, X-ray diffraction analyses (XRD), and tensile testing.

Table 3.2 Preparation of chemical used for nanocomposite sample[33-37]

Sample	Clay (Montmorironite, MMT) % w/v	Acrylic acid (AA) part by weight	Hydroxy *Ethyl Methacrylate* (HEMA) part by weight	Methyl methacrylic acid (MAA) part by weight	Benzoyl peroxide (BPO) % w/v of monomer
1.	-	-	-	-	3
2.	-	1	1	-	3
3.	-	1	-	1	3
4.	-	2	-	-	3
5.	0.5	1	1	-	3
6.	-	1	-	1	3
7.	-	2	-	-	3
8.	1	1	1	-	3
9.	-	1	-	1	3
10.	-	2	-	-	3
11.	2	1	1	-	3
12.	-	1	-	1	3
13.	-	2	-	-	3

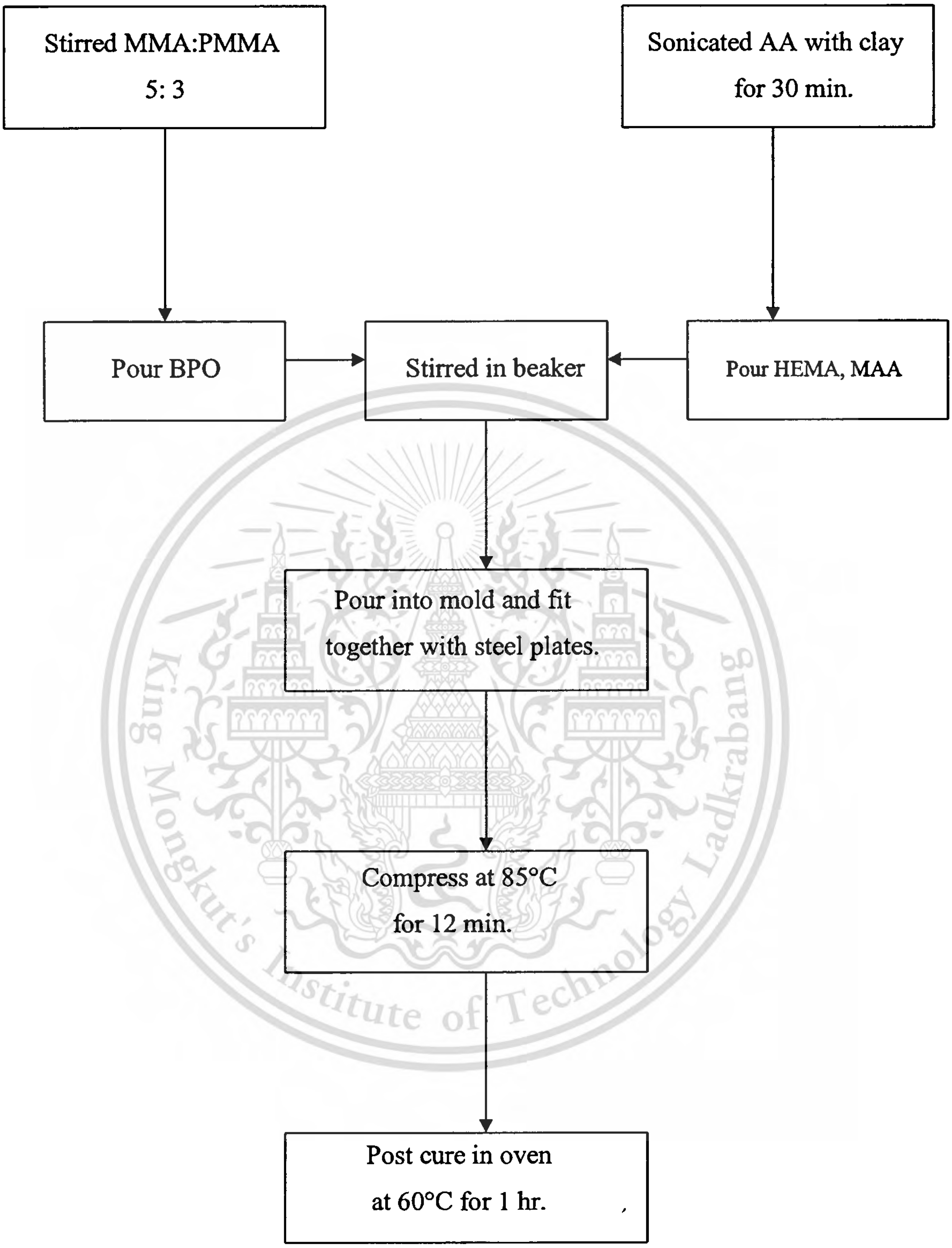


Fig.3.5 Flow diagram for preparation of nanocomposite sheet

Chapter 4

Results and Discussion

4.1 Characterization of Montmorillonite

The XRD pattern of the purified montmorillonite (MMT) was showed in Fig. 4.1. The crystalline peak of d_{001} plane was observed at $2\Theta = 7.24$, corresponding to the basal spacing of 1.22 nm.

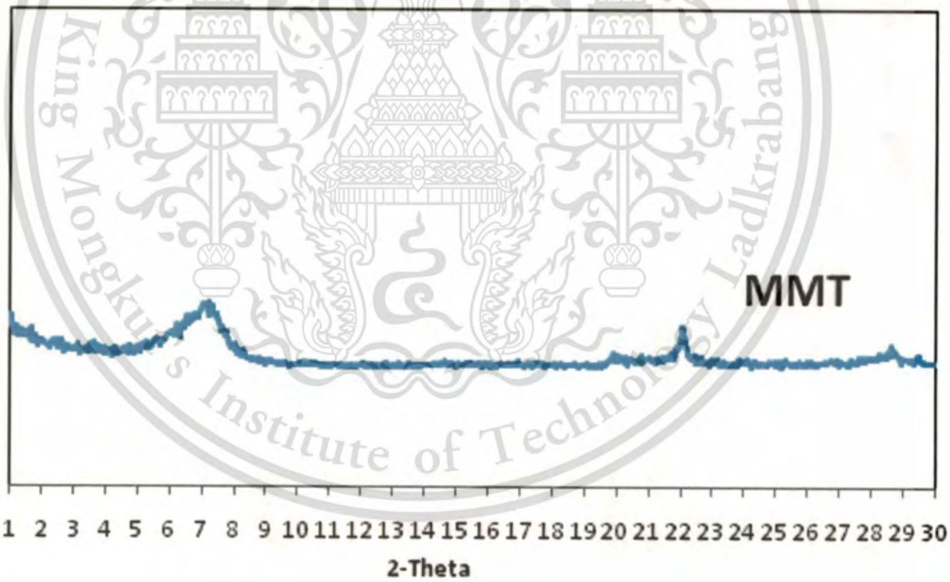


Fig 4.1 XRD pattern of MMT

The decomposition temperature and percentage of weight loss of the MMT were investigated by TGA under oxygen atmosphere. Figure 4.2 shows a long range of decomposition period (60 - 680 °C) was obtained with the weight loss of about 11%. The first decomposition (60 - 100 °C) region was due to the moisture content with the weight loss of about 7% by weight. The second region was the decomposition of the organic impurities in natural clay (580 -680 °C), in which it lost about 4.3% by weight.

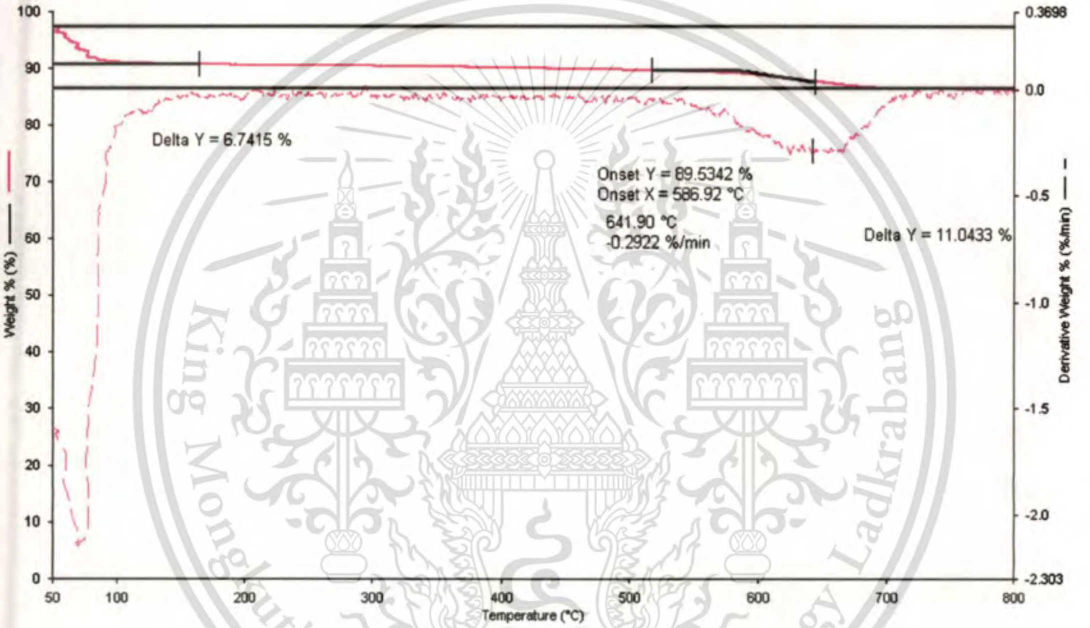


Fig 4.2 Thermogram of MMT

4.2 Synthesis of PMMA by solution polymerization

The PMMA was synthesized by solution polymerization in the range of 47-57 %. The molecular weight of the synthesized PMMA was determined by GPC technique. The results were found that $\bar{M}_n$ = 61,312g/mole, $\bar{M}_w$ = 123,461g/mole and MWD = 2.01

4.3 Swell test

The dispersion ability of MMT in monomer was investigated by swelling tests, in order to set up the monomer system for preparation of composites. The better swelling, the better dispersion of clay particle in polymer matrix will be obtained, resulting in the exfoliation structure of composite. Table 4.1 and figure 4.3 shows the result of selling test. The swelling ability of MMT in AA monomer was better than HEMA and MAA monomers. This result was because the AA monomer was similar polarity to MMT.

Table 4.1 Swelling test

Composition	**Result**
1% clay of 1 ml AA	Good swelling
1% clay of 1 ml HEMA	Partial swelling
1% clay of 1 ml MAA	Partial swelling

(a) (b) (c)

Fig 4.3 Dispersion and swelling of clay in various solvents; (a) AA, (b) HEMA and (c) MAA at the ratio of 1%w/v *(This picture was taken after the suspension was aged for 1 week)*

4.4 Characterization of PMMA with MMT films

4.4.1 X-ray Diffractometer (XRD)

Figure 4.4, 4.5 and 4.6 show the XRD patterns of P(MMA-co-AA), P(MMA-co-AA/HEMA), P(MMA-co-AA/MAA) films. The characteristic peak at MMT of acrylate polymer could not be observed in the XRD patterns of composite films. These results might be 2 main reasons, the first reason is low content of MMT in the composites caused the XRD signal of MMT was concealed by the amorphous signal of polymer matrix. The second reason was the tactoid of MMT was destroyed by penetrating of PMMA into the 001 plane of MMT layers.

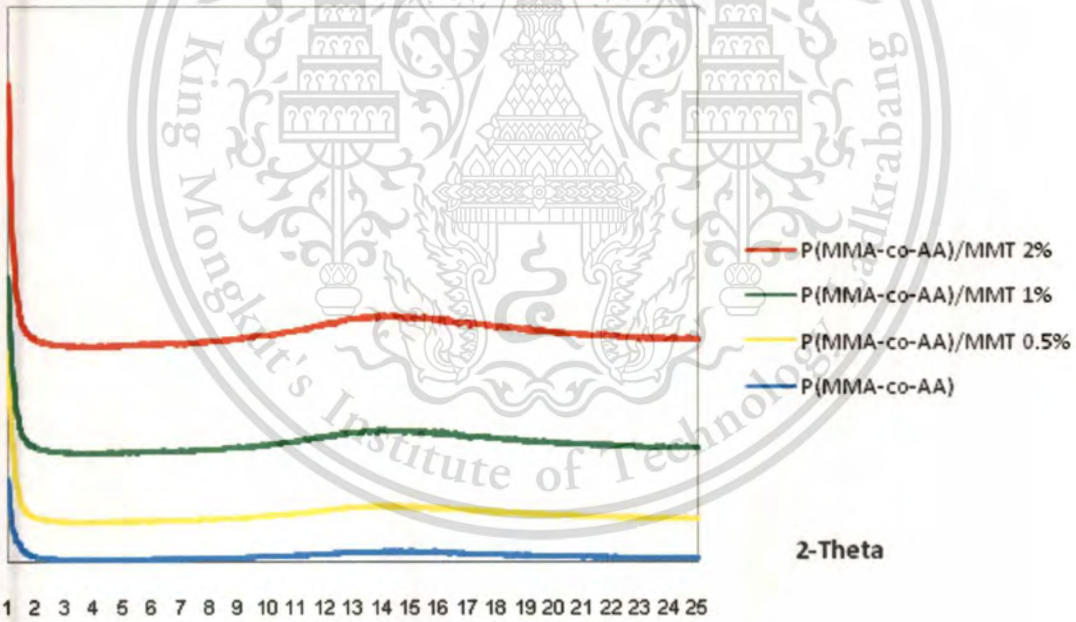


Fig 4.4 The XRD patterns of P(MMA-*co*-AA)/MMT contain 0, 0.5%, 1% and 2%

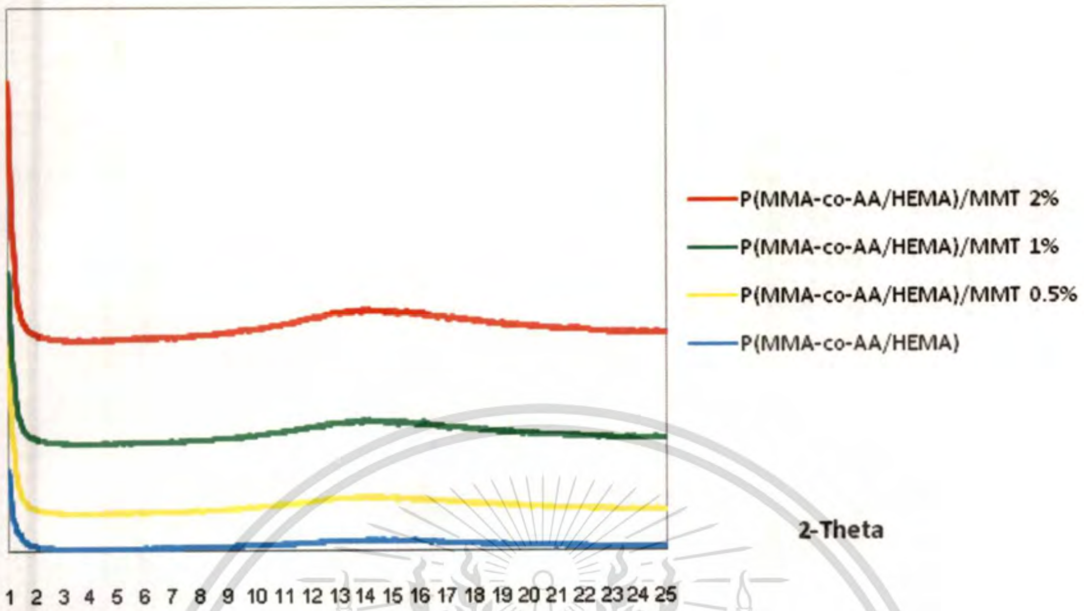


Fig 4.5 The XRD patterns of P(MMA-*co*-AA/HEMA)/MMT contain 0, 0.5%, 1% and 2%

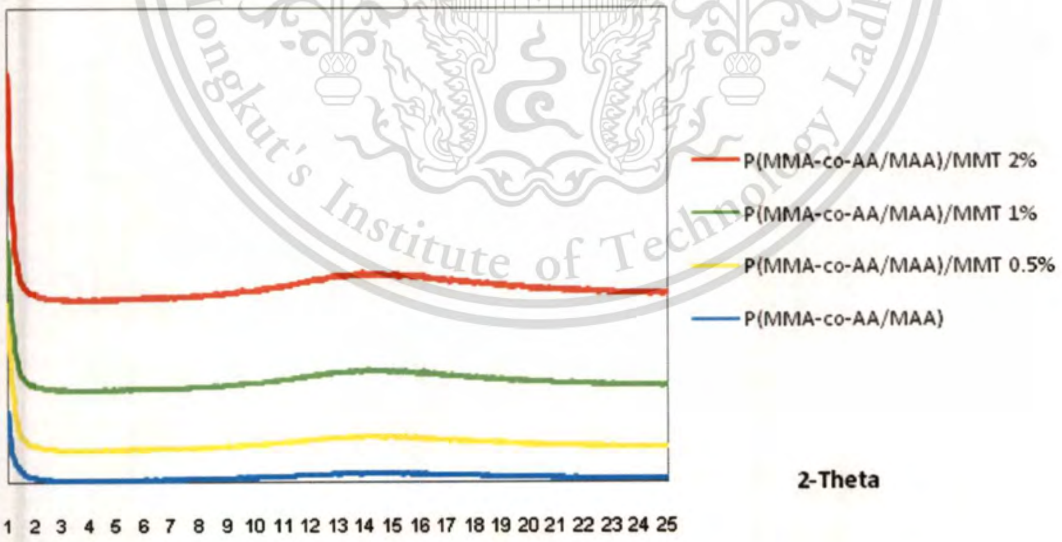


Fig 4.6 The XRD patterns of P(MMA-*co*-AA/MAA)/MMT contain 0, 0.5%, 1% and 2%

4.4.2 UV-vis Spectrometer

The percentage of transmittance of UV (190-400 nm) and visible light (400-600 nm) of PMMA with MTT film were measured. Fig 4.7 shows the UV-visible spectra of PMMA with MMT film.

From fig 4.7, it was seen that the %transmittance decreased when the amount of PMMA with MTT was increased. As if, the absorbance of these nanocomposite films was focused, it was found that their absorbance was higher in UV range, especially UV-A and UV-B.

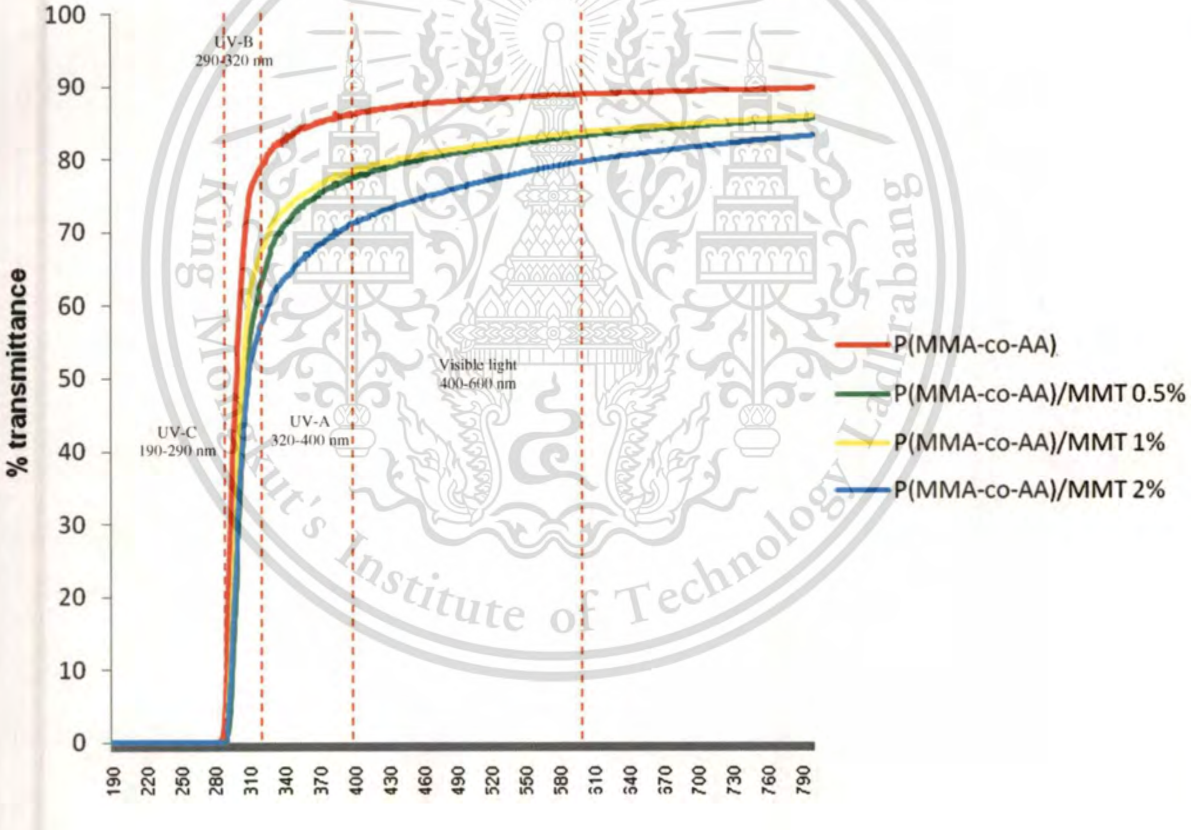


Fig 4.7 UV-visible spectra of P(MMA-co-AA) with MMT containing 0, 0.5%, 1% and 2% .

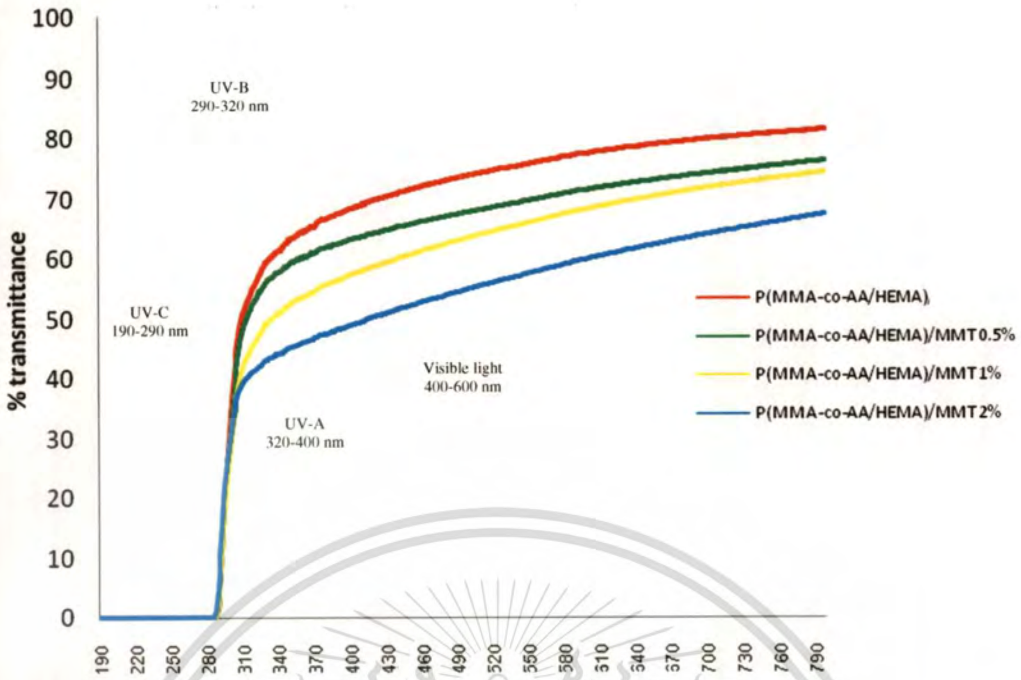


Fig 4.8 UV-visible spectra of P(MMA-co-AA/HEMA) with MMT containing 0, 0.5%, 1% and 2% .

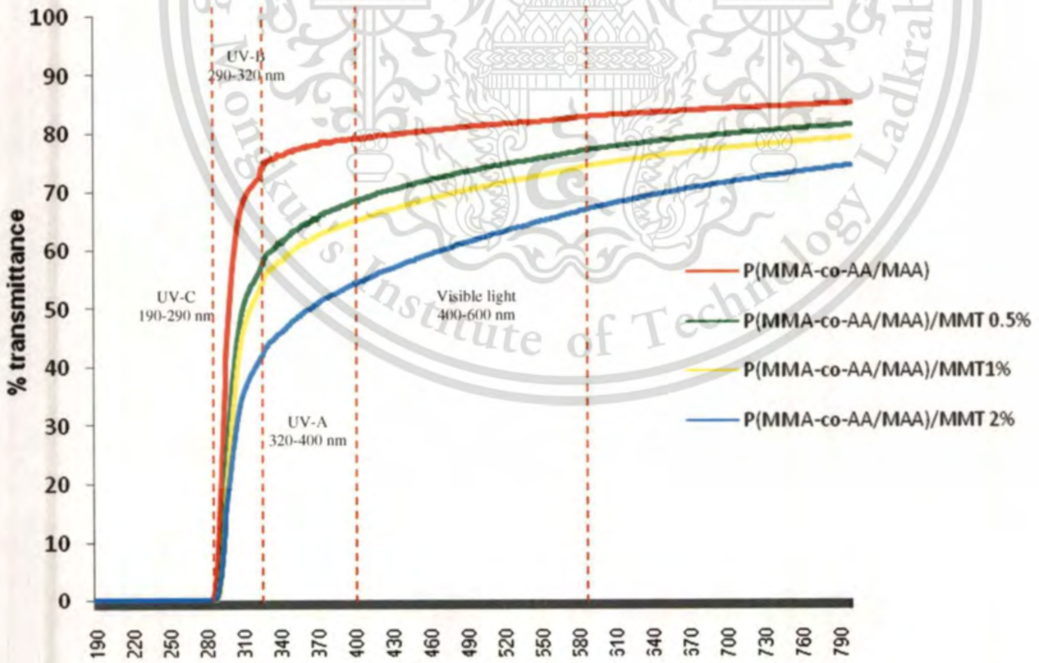


Fig 4.9 UV-visible spectra of P(MMA-co-AA/MAA) with MMT containing 0, 0.5%, 1% and 2% .

4.4.3 Mechanical properties of PMMA with MMT films

In the nanocomposite material, by adding the montmorillonite which affect to tensile strength, Young's Modulus and % elongation at break. From the fig.4.11, 4.12 and 4.13 we can discuss the factor that affecting to mechanical properties of product follows:

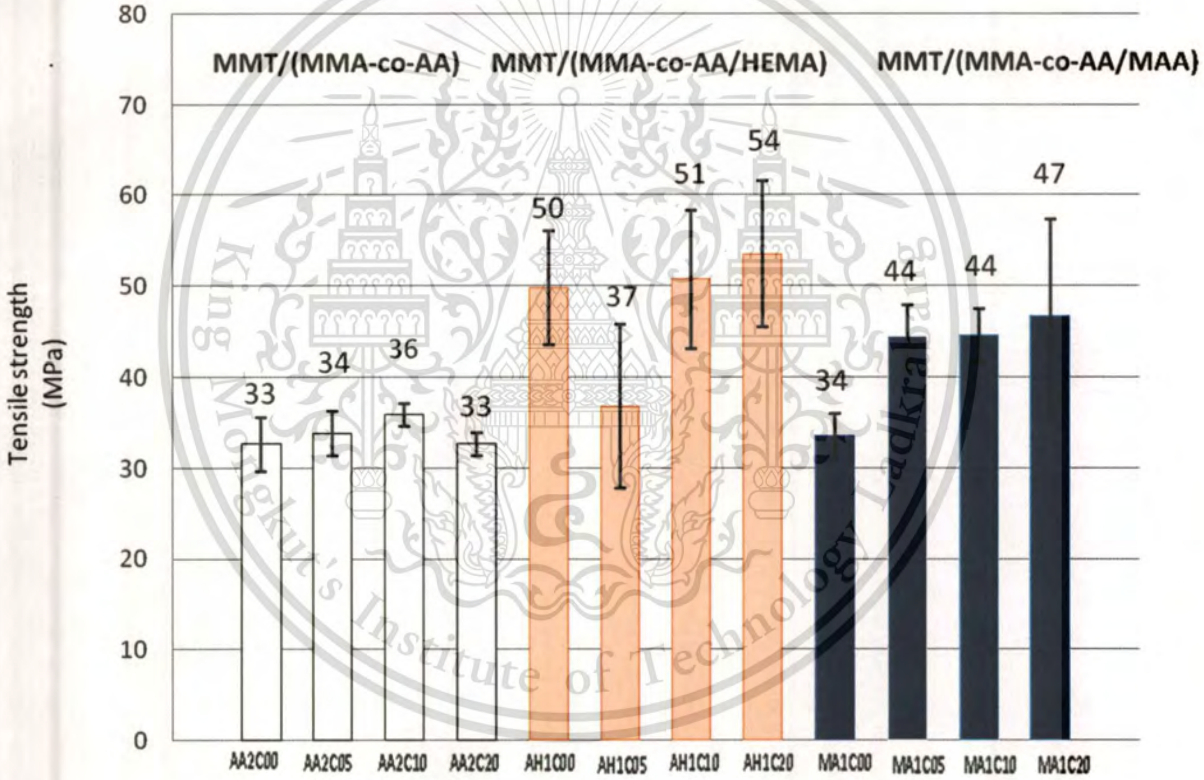


Fig 4.10 The tensile strength of acrylate/MMT nanocomposite film.

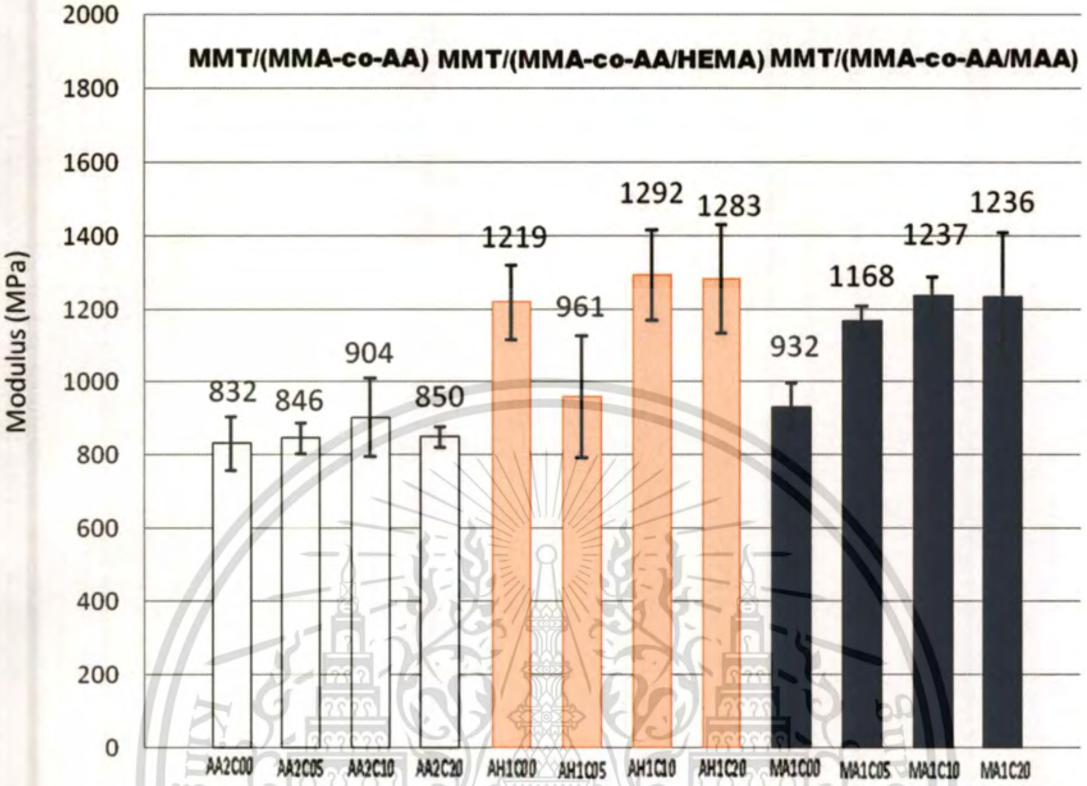


Fig 4.11 The Young's modulus of acrylate/MMT nanocomposite film.

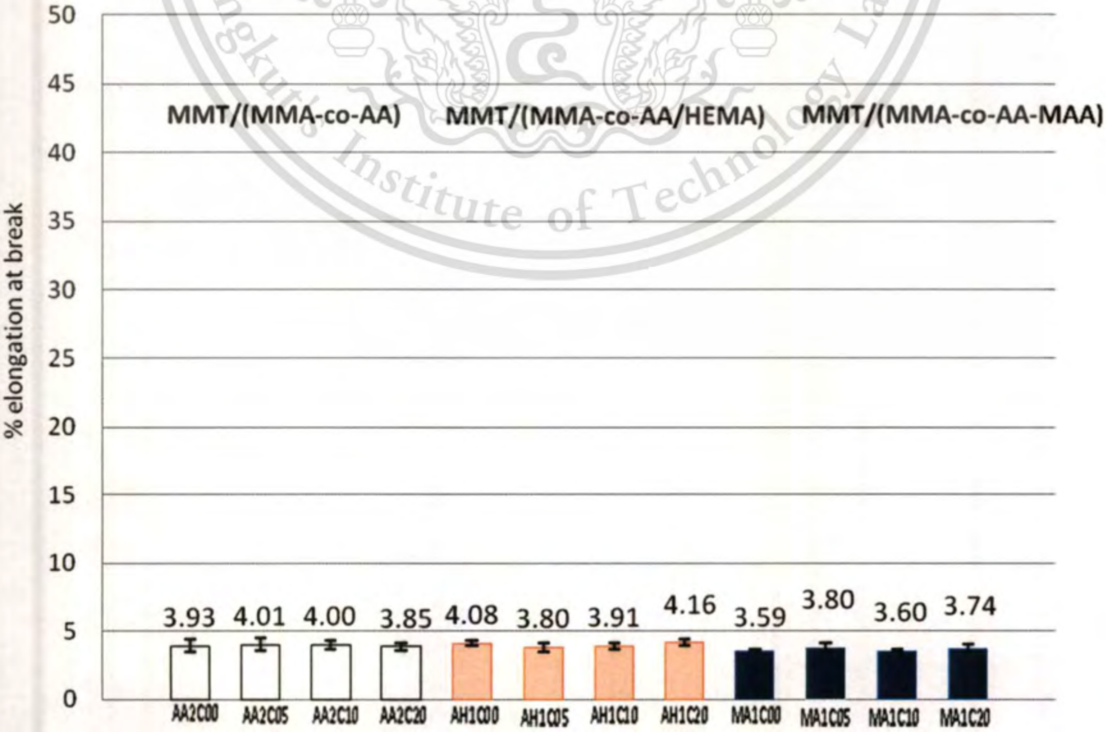


Fig 4.12 The % elongation at break of acrylate/MMT nanocomposite film.

Young's modulus, % elongation at break and tensile strength of the composites were obtained from tensile tests performed on rectangular samples film. The mechanical properties of composites depend on many factors, i.e. clay loading and monomer system.

The tensile strength of acrylate/MMT nanocomposite with various amounts of MMT was shown in fig. 4.10. It was seen that the tensile strength tended to slightly increase from AA2C00 (no MMT) to AA2C10 (MMT 1% by weight) and AH1C00 (no MMT) to AH1C20 (MMT 2% by weight). However, MA1C00 (no MMT) to MA1C20 (MMT 2% by weight) is a sharp increase. It can be explained that the rigid particle of MMT were well dispersed in the polymer matrix in nano level brought about the minimization of size of stress concentration, resulting in the increase in mechanical properties , especially, tensile strength.

However, the tensile strength of AA2C20 (MMT 2% by weight) and AH1C05 (MMT 0.5% by weight) slightly decreased due to deflect of film such as bubble or poor dispersion. This phenomenon caused the larger stress concentrator size, in which they because the weak point in the composite.

In comparison among these three composites, P(MMA-co-AA)/MMT had the lowest values. Because of the highest T_g than others. Therefore, they were more brittle and easier to break. P(MMA-co-AA/MAA)/MMT had lower T_g than P(MMA-co-AA)/MMT since the MAA contains methyl group, resulting in more flexible structure of polymer chain. This led to higher values of tensile strength than P(MMA-co-AA)/MMT. The highest tensile strength was obtained in P(MMA-co-AA/HEMA)/MMT composite systems. It might be because of the intermolecular and/or intramolecular bonding between the hydroxyl group on HEMA.

Fig. 4.11 showed Young's modulus of acrylate copolymer/MMT nanocomposites. As the same tend as tensile strength results, the higher the MMT contents, the higher Young's modulus were obtained.

In case of % elongation at break of acrylate copolymer/MMT nanocomposite, all sample shown the same % elongation at break of about 3.8.

The results were because all samples were the nanocomposites containing exfoliated structure of MMT.

Chapter 5

Conclusion and Recommendations

5.1 Conclusion

- The acrylate nanocomposites containing 0, 0.5%, 1% and 2% by weight of MMT could be prepared by ***in-situ*** polymerization technique. All composite systems had the exfoliate structures.

- The mechanical properties of composites depend on clay loading and monomer systems. The higher the clay loading the higher tensile strength and modulus were obtained all systems.

- The highest tensile strength and Young's modulus of composites were obtained in P(MMA-co-AA/HEMA) with MMT containing 2%

- The % transmittance of UV and visible light would decrease when the amount of MMT in acrylate polymer increased.

5.2 Suggestion for the future

1. The nanocomposite films can be prepared from other kinds of polymers, which have same polarity as acrylate polymers with MMT.

2. MMT might be modified with organic molecules such as long chain phosphonium or ammonium salt.

3. Characterization of sample by using other methods: impact strength, scratch resistance, TGA, DMTA.

4. The nanocomposite films can be prepared by other method such as vacuum.

Reference

[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://en.wikipedia.org/wiki/Clay

[4] Available online at http://en.wikipedia.org/wiki/Montmorillonite

[5] Available online at http://www.aquatechnologies.com/info_bentonite_clay.htm

[6] Available online at http://en.wikipedia.org/wiki/Clay_mineral

[7] Available online at http://www.galleries.com/minerals/silicate/kaolinit/kaolinit.htm

[8] Available online at http://www.galleries.com/minerals/silicate/montmori/montmori.htm

[9] Available online at http://en.wikipedia.org/wiki/Illite

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

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

[12] Available online at http://www.scribd.com/doc/518847/Polymner-Clay-Nanocomposite

[13] Available online at http://en.wikipedia.org/wiki/Polymerization

[14] Available online at http://www.materialsworldmodules.org/resources/polimarization/

[15] Available online at http://plc.cwru.edu/tutorial/enhanced/files/polymers/synth/synth.htm

[16] Available online at http://composite.about.com/library/glossary/b/bldef-b836.htm

[17] Available online at http://composite.about.com/library/glossary/s/bldef-s5018.htm

[18] Available online at http://www.stanford.edu/class/cheme160/lectures/lecture13.pdf

[19] Available online at http://composite.about.com/library/glossary/s/bldef-s5338.htm

[20] Amethyst Galleries. **"The Clay Mineral Group."** 2006. February 22, 2007.

[21] Bailey, S. W., 1980, **"Summary of recommendations of AIPEA nomenclature committee on clay minerals"**, American Mineralogist Volume 65, pages 1-7

[22] Available online at http://en.wikipedia.org/wiki/Emulsion_polymerization

[23] Odian, G, Principles of Polymerization, Wiley, New York

[24] Gilbert, R. G. **"Polymerization Techniques"**: a Mechanistic Approach Academic Press, London, 1996.

[25] Available online at http://www.mindat.org/min-2011.html

[26] R.J. Young Chapman & Hall, **"Introduction to Polymers"**. 1987 ISBN 0-412-22170-5

[27] International Union of Pure and Applied Chemistry, et al. (2000) **" Gold Book"**

Retrieved on 11 May 2007 from "IUPAC Gold Book" on http://goldbook.iupac.org/

[28] Clayden, J., Greeves, N. et al. (2000). **"Organic chemistry"** Oxford

[29] Bhupendra Singh Department of Chemical Technology University of Mumbai Matunga, Mumbai – 400 019

[30] W. Udo, K. Bernd, W. Dieter, G Thomas; German Offen. De. 10,002,997,(CL. CO8J3/20)(2001)

[31] Beyer, Fredrick L, Tan, Nora C, Beck; Mater. Res. Soc. Symp. Proc.; 628, CC4.5.1- CC4.5.6 (2001)

[32] L.Liu, Z. Qi, X. Zhu, J. Appl. Polymer. Sci., 71, 1133-1138 (1999)

[33] Nehal Salahuddin and Mohamed Shehata , **"Prepare of polymethylmethacrylate–montmorillonite composites for improve the mechanical"**, characterization properties, [2001]

[34] Yuanqing Xiang, **"A new polymer/clay nano-composite hydrogel with improvement of response rate and tensile mechanical properties"**, [2006]

[35] Metin Tanoğlu, **"Effect of the Porous nanocomposites prepared from layered clay and PMMA [poly(methyl methacrylate)]"** , [2006]

[36] Sanit Sirapanichart, Suraluck Macksasitorn and Suwicha Buakheio, **"Prepare of organophosphate modified montmorillonite/Poly(Methyl Methacrylate) nanocomposites"**, Project of KMITL.2007

[37] Tapanut Leelaphat and Tepagorn Jarutawesub, **"Preparation of poly(methyl methacrylate/montmorillonite nanocomposites (PMMA/MMT)"**,Project of KMITL.2007

[38] Available online at http://en.wikipedia.org/wiki/Acrylic_glass

[39] Kutz, Myer, "**Handbook of Materials Selection**". John Wiley & Sons 2002. pg 341

Appendices

Appendix-A

The Results of the molecular weight analysis of PMMA by GPC technique

Sample information

Sample Name: PMMA

Vial: 1

Injection: 1

Injection Volume: 100.00 ul

Run Time: 22.00 Minutes

Sample Type: Broad Unknown

Acq Method Set:

Y2008_methR_THF_30C_2

Processing Method:

Y2008_ProcR_THF_30C_2

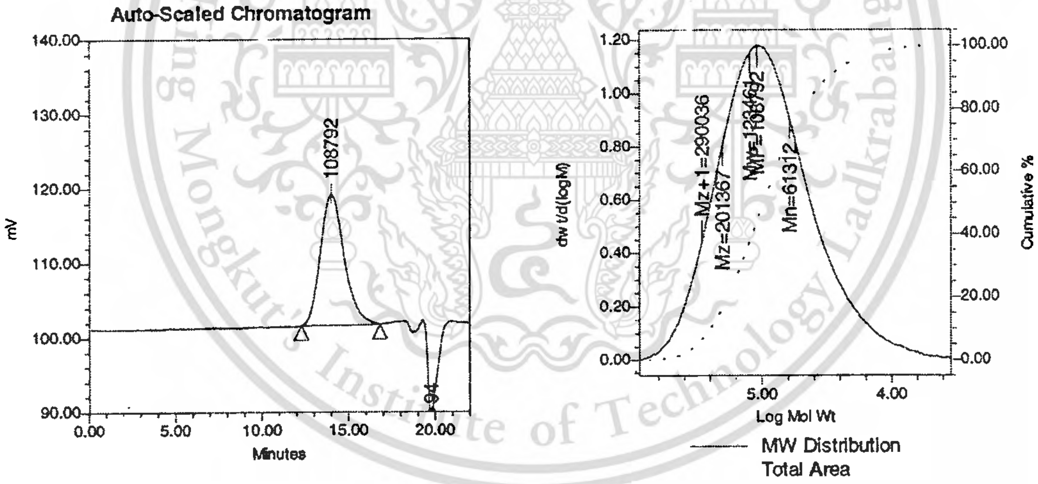


Fig. A-1 Chromatogram of PMMA

Table A-1 Peak Results form chromatogram of PMMA

	Name	MN (g/mole)	Mw (g/mole)	MP	Mz	Mz+1	Polydispersity (MWD)
1	Broad	61312	123461	108792	201367	290036	2.013632
2	Reference			94			

Appendix-B

Table B-1 Show mechanical properties of P(MMA-co-AA),(AA2C00)

	tensile strength	% elongation at break	modulus	sample width (mm)	sample thick (mm)
sample 1	33.06	4.045	817.3053152	19	0.37
sample 2	32.66	4.044	807.6162216	18	0.35
sample 3	31.39	4.019	781.0400597	20	0.37
sample 4	37.29	3.462	1077.12305	20	0.37
sample 5	33.72	4.1535	811.8454316	20	0.37
sample 6	29.89	3.455	865.1230101	19	0.38
sample 7	32.96	4.075	808.8343558	18.5	0.38
sample 8	34.86	4.162	837.5780875	18.5	0.36
sample 9	31.44	4.084	769.8334966	19	0.36
sample 10	33.46	4.006	835.2471293	20	0.38
sample 11	33.87	4.097	826.7024652	20	0.38
sample 12	24.35	3.073	792.3852912	18	0.37
sample 13	33.81	4.119	820.8302986	18	0.39
sample 14	34.06	4.239	803.4913895	19	0.37
mean	**32.63**	**3.93096**	**832.4968287**	**19.071427**	**0.371428**
SD	**2.946377**	**0.342683**	**74.405586**	**0.775913**	**0.010271**

Table B-2 Show mechanical properties of P(MMA-co-AA)/MMT 0.5% ,(AA2C05)

	tensile strength	% elongation at break	modulus	sample width (mm)	sample thick (mm)
sample 1	30.67	3.362	912.2546104	19	0.37
sample 2	36.27	4.389	826.3841422	18	0.35
sample 3	30.42	3.3645	904.1462327	20	0.39
sample 4	35.58	4.291	829.1773479	19	0.38
sample 5	36.04	4.382	822.4554998	20	0.37
sample 6	33.38	4.1065	812.8576647	20	0.39
sample 7	34.37	4.231	812.3375089	18	0.38
mean	**33.81857**	**4.018**	**845.65900**	**19.14285714**	**0.3757142**
SD	**2.449730**	**0.457396**	**43.25033**	**0.8997354**	**0.013972**

Table B-3 Show mechanical properties of P(MMA-co-AA)/MMT 1% ,(AA2C10)

	tensile strength	% elongation at break	modulus	sample width (mm)	sample thick (mm)
sample 1	36.15	4.132	874.8789932	17	0.37
sample 2	37.34	3.362	1110.648424	19	0.4
sample 3	35.42	4.141	855.3489495	20	0.38
sample 4	36.92	4.142	891.3568324	19	0.39
sample 5	34.85	4.1565	838.4458078	20	0.39
sample 6	37.91	3.472	1091.87788	18	0.38
sample 7	34.52	4.1065	840.6185316	19	0.39
sample 8	33.77	4.122	819.2624939	20	0.38
sample 9	36.04	4.031	894.0709501	20	0.4
sample 10	36	4.382	821.5426746	19	0.39
mean	**35.892**	**4.0047**	**903.8051537**	**19.1**	**0.387**
SD	**1.291844504**	**0.323295462**	**107.3772688**	**0.994428926**	**0.009486833**

Table B-4 Show mechanical properties of P(MMA-co-AA)/MMT 2% ,(AA2C20)

	tensile strength	% elongation at break	modulus	sample width (mm)	sample thick (mm)
sample 1	32.29	3.7685	856.8395913	18.5	0.37
sample 2	33.42	4.111	812.9408903	18	0.35
sample 3	32.81	3.813	860.4773145	20	0.36
sample 4	30.34	3.4005	892.2217321	20	0.38
sample 5	33.34	4.072	818.762279	18.5	0.38
sample 6	32.19	3.762	855.661882	20	0.39
sample 7	34.35	4.022	854.0527101	17	0.38
mean	**32.67714286**	**3.849857143**	**850.1366285**	**18.85714286**	**0.372857143**
SD	**1.26864382**	**0.246574653**	**26.8847922**	**1.180193689**	**0.013801311**

Table B-5 Show mechanical properties of P(MMA-co-AA-HEMA),(AH1C00)

	tensile strength	% elongation at break	modulus	sample width (mm)	sample thick (mm)
sample 1	44	3.9415	1116.326272	18	0.35
sample 2	55.21	4.1155	1341.513789	20	0.36
sample 3	54.18	4.1850	1294.623656	20	0.39
sample 4	43.89	3.9195	1119.785687	21	0.38
sample 5	54.49	4.2380	1285.747994	21	0.38
sample 6	58.39	4.3955	1328.40405	22	0.37
sample 7	44.2	3.9080	1131.013306	20	0.39
sample 8	44.2	3.9080	1131.013306	20	0.38
mean	**49.82**	**4.0764**	**1218.55351**	**20.25**	**0.375**
SD	**6.273773073**	**0.1855**	**102.1345**	**1.1650**	**0.0141**

Table B-6 Show mechanical properties of P(MMA-co-AA-HEMA)/MMT 0.5%,(AH1C05)

	tensile strength	% elongation at break	modulus	sample width (mm)	sample thick (mm)
sample 1	33.66	3.8220	880.6907378	19	0.38
sample 2	34.94	3.5390	987.2845437	19	0.37
sample 3	32.37	3.7620	860.446571	20	0.38
sample 4	31.17	3.5660	874.0886147	20	0.39
sample 5	33.52	3.6065	929.4329683	19	0.4
sample 6	33.77	3.6220	932.3578134	20	0.38
sample 7	36.04	4.1810	861.9947381	21	0.37
sample 8	58.71	4.3095	1362.339018	19	0.38
mean	**36.7725**	**3.8010**	**961.079376**	**19.625**	**0.38125**
SD	**8.9857025**	**0.2924464**	**167.9697623**	**0.744024**	**0.009910**

Table B-6 Show mechanical properties of P(MMA-co-AA-HEMA)/MMT 0.5%,(AH1C05)

	tensile strength	% elongation at break	modulus	sample width (mm)	sample thick (mm)
sample 1	41.06	3.6110	1137.081141	18	0.4
sample 2	43.89	3.6195	1212.598425	19	0.38
sample 3	53.69	3.8755	1385.36963	20	0.37
sample 4	47.05	3.8155	1233.12803	18	0.38
sample 5	45.14	3.9055	1155.805915	19	0.37
Sample 6	62.65	4.2395	1477.768605	20	0.36
sample 7	53.86	3.9220	1373.278939	19	0.38
sample 8	58.71	4.3095	1362.339018	19	0.38
mean	**50.75625**	**3.91225**	**1292.17121**	**19**	**0.3775**
SD	**7.647640042**	**0.254166987**	**123.6935568**	**0.755929**	**0.0116496**

Table B-7 Show mechanical properties of P(MMA-co-AA-HEMA)/MMT 1%,(AH1C10)

	tensile strength	% elongation at break	modulus	sample width (mm)	sample thick (mm)
sample 1	41.06	3.6110	1137.081141	18	0.4
sample 6	43.89	3.6195	1212.598425	19	0.38
sample 7	53.69	3.8755	1385.36963	20	0.37
sample 3	47.05	3.8155	1233.12803	18	0.38
sample 7	45.14	3.9055	1155.805915	19	0.37
sample 3	62.65	4.2395	1477.768605	20	0.36
sample 2	53.86	3.9220	1373.278939	19	0.38
sample 10	58.71	4.3095	1362.339018	19	0.38
mean	**50.75625**	**3.91225**	**1292.17121**	**19**	**0.3775**
SD	**7.647640042**	**0.254166987**	**123.6935568**	**0.755929**	**0.0116496**

Table B-8 Show mechanical properties of P(MMA-co-AA-HEMA)/MMT 2%,(AH1C20)

	tensile strength	% elongation at break	modulus	sample width (mm)	sample thick (mm)
sample 1	59.43	4.2270	1405.961	20	0.37
sample 2	47.7	4.2235	1129.395	20	0.37
sample 3	69.95	4.3845	1595.392	20	0.36
sample 4	51.21	4.0155	1275.308	18	0.37
sample 5	54.18	4.1850	1294.623	19	0.39
sample 6	43.89	3.9195	1119.785	19	0.38
sample 7	44.69	3.7380	1195.559	20	0.37
sample 8	56.39	4.3355	1300.657	20	0.39
sample 9	54.2	4.4080	1229.582	18	0.38
mean	**53.5155**	**0.83192**	**1282.918**	**19.3333**	**0.3755556**
SD	**8.09260**	**0.04520**	**147.4565**	**0.86025**	**0.0101379**

Table B-9 Show mechanical properties of P(MMA-co-AA-MAA),(MA1C00)

	tensile strength	% elongation at break	modulus	sample width (mm)	sample thick (mm)
sample 1	32.44	3.5865	904.503	19	0.37
sample 2	33.44	3.596	929.9221	19	0.37
sample 3	38.46	3.632	1058.921	18.5	0.37
sample 4	31.67	3.512	901.7654	19	0.37
sample 5	31.34	3.5335	886.9393	19	0.36
sample 6	33.46	3.6665	912.5869	20	0.38
mean	**33.46833**	**3.58775**	**932.44**	**19.08333333**	**0.37**
SD	**2.597648**	**0.05815561**	**63.54459**	**0.49159604**	**0.006325**

Table B-10 Show mechanical properties of P(MMA-co-AA-MAA)/MMT 0.5%,(MA1C05)

	tensile strength	% elongation at break	modulus	sample width (mm)	sample thick (mm)
sample 1	48.05	4.1655	1153.523	18	0.38
sample 2	41.06	3.6110	1137.081	18	0.4
sample 3	43.89	3.6195	1212.598	19	0.38
mean	**44.33333**	**3.798666667**	**1167.7**	**18.33333333**	**0.386667**
SD	**3.516025**	**0.317715412**	**39.71377**	**0.577350269**	**0.011547**

Table B-11 Show mechanical properties of P(MMA-co-AA-MAA)/MMT 1%,(MA1C10)

	tensile strength	% elongation at break	modulus	sample width (mm)	sample thick (mm)
sample 1	43.37	3.5365	1226.354	18.5	0.37
sample 2	49.03	3.7275	1315.359	18	0.35
sample 3	43.96	3.6255	1212.522	20	0.36
sample 7	41.03	3.4775	1179.871	18	0.35
sample 8	47.96	3.6865	1300.963	20	0.36
sample 9	43.23	3.5775	1208.386	18	0.35
sample 10	43.15	3.5505	1215.322	20	0.36
mean	**44.53286**	**3.59735**	**1237**	**18.92857**	**0.357143**
SD	**2.873144**	**0.08787**	**50.820**	**1.017700**	**0.007559**

Table B-12 Show mechanical properties of P(MMA-co-AA-MAA)/MMT 2%,(MA1C20)

	tensile strength	% elongation at break	modulus	sample width (mm)	sample thick (mm)
sample 1	68.23	4.3205	1579.215	19	0.37
sample 2	45.94	3.7555	1223.273	21	0.35
sample 5	41.03	3.5225	1164.798	18	0.35
sample 8	40.96	3.6865	1111.081	20	0.36
sample 9	43.23	3.6215	1193.704	18	0.35
sample 10	40.15	3.5070	1144.853	20	0.36
mean	**46.59**	**3.735583**	**1236.2**	**19.33333**	**0.356667**
SD	**10.8082**	**0.301861**	**172.4702**	**1.211060**	**0.008165**