A STUDY OF INTERLAYER GALLERY OF MODIFIED SODIUM MONTMORILLONITE (MMT) NANOFILLER USING ION EXCHANGE AND SURFACTANT METHOD

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I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Thesis submitted in partial
fulfillment of the requirements for the award of the
degree of Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

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Dedicated to my parents

Mohamed Yatim Bin Awang Mohd and Mrs Fatimah Binti Omar,

My beloved family and My dearest friends.

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A STUDY OF INTERLAYER GALLERY OF MODIFIED SODIUM MONTMORILLONITE (MMT) NANOFILLER USING ION EXCHANGE AND SURFACTANT METHOD

ABSTRACT

Polymer/layered-silicate hybrid nanocomposites have attracted strong interest in today's materials research, as it is possible to achieve impressive enhancements of material properties compared to the pure polymers. This study aim is to modify the clay surface using ion exchange and surfactant methods before proceeding with fabrication of polymer nanocomposites. The polymer that used is Polylactic acid (PLA) because of its biodegradability characteristic. Organoclay will characterize by using Atomic Adsorption Spectrometry (AAS) and Fourier Transform Infrared Spectroscopy (FTIR). PLA-Nanocomposites were prepared by using solution casting and characterized by X-Ray Diffraction Analysis (XRD), Scanning Electron Microscopy (SEM). AAS analysis showed there is a transition metal ion in the interlayer of sodium montmorillonite (MMT) and it is confirmed with SEM analysis. The FTIR analysis for surfactant organoclay shows the presence of TEOS surfactant in the organoclay properties. The XRD analysis proved that the modification happens by the increasing of clay interlayer basal spacing. The XRD analysis for PLA-Nanocomposites showed that PLA is intercalated the interlayer gallery of organoclay to similar extents and also increased the d-spacing. The structure of polymer nanocomposites that came out of this research is intercalated and exfoliated nanocomposites.

Keywords: surface modification, ion exchange method, surfactant method, PLA-nanocomposites.

KAJIAN TENTANG MODIFIKASI STRUKTUR DALAMAN TANAH LIAT DENGAN MENGGUNAKAN KAEDAH PERTUKARAN ION DAN SURFAKTAN.

ABSTRAK

Pada waktu ini, kajian tentang polimer nano komposit telah menarik minat ramai penyelidik bahan kerana ia memberi banyak kelebihan berbanding komposit biasa. Target kajian ini adalah memodifikasi struktur dalaman tanah liat dengan menggunakan kaedah pertukaran ion dan surfaktan. PLA digunakan sebagai polimer kerana sifatnya yang mudah terurai. Ciri-ciri organoclay akan ditentukan dengan menggunakan Atomic Adsorption Spectrometry (AAS) dan Fourier Transform Infrared Spectroscopy (FTIR). PLA-Nanokomposit dihasilkan dengan menggunakan kaedah solution casting dan X-Ray Diffraction Analysis (XRD), Scanning Electron Microscopy (SEM) digunakan untuk menentukan ciri-ciri nya. AAS analisis menunujukkan kehadiran ion besi didalam struktur dalaman organoclay dan ia disahkan oleh analisis SEM. Analisis FTIR yang dijalankan keatas sampel organoclay surfaktan menunjukkan kehadiran surfaktan TEOS didalam struktur organoclay. Analsis XRD membuktikan bahawa modifikasi menyebabkan jarak antara dua struktur dalaman tanah liat bertambah. Analisis XRD pada sample PLA-Nanokomposit menunjukkan PLA meresap kedalam struktur dalaman tanah liat dan menyebabkan pertambahan jarak antara dua struktur dalaman tanah liat.

Kata kunci: modifikasi permukaan, kaedah pertukaran ion, kaedah surfaktan, PLA-Nanokomposite.

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CHAPTER 1

BACKGROUND OF THE RESEARCH

1.1 Introduction

Polymer/layered-silicate hybrid nanocomposites have attracted strong interest in today’s materials research, as it is possible to achieve impressive enhancements of material properties compared to the pure polymers (Strawhecker et. al., 2000). These composites exhibit superior strength, modulus, thermal resistance and heat distortion temperature (Joshi et. al., 2004). The first step before proceed with fabrication of polymer nanocomposites is to modify the surface of nanoclay.

The main reason of surface modification of nanoclay is to ensure that nanoclay is compatible with polymer matrix. According to Qian et. al. (2008), in his experimental work, he looks forward to focusing on how to modify the surface of nanoclay that enhancing the interaction between clay surface and polymer chain and by using a sol-gel modification approach, it combines the surface properties of mesoporous silica and nanoparticles with layered clay, while inheriting the structural properties of the pristine clay such as further intercalation with organic compounds and polymers. One of the drawbacks of clays is the incompatibility between hydrophilic clay and hydrophobic polymer, which often causes agglomeration of clay mineral in the polymer matrix. Therefore, surface modification of clay minerals is the most important step to achieve polymer nanocomposites. Upon organic treatment, clays become hydrophobic and hence compatible with the polymers (Zheng et. al., 2005)

Clay is the most common layer solid that are used widely. Based on Zheng et. al. (2005), there is many types of layered solids such as graphite, metal phosphates, etc. But the most common used in researches and industry are a clay mineral because of the uniqueness of its structure and properties. There are many types of polymer that can be used and Poly (lactic acid) polymer (PLA) is chosen in this study. Vahik et. al. (2003) state that Poly (lactic acid) polymer (PLA) is one of example of polymer that commonly used for packaging because of its biodegradability and for sure is ecologically friendly. According to McLauchlin et. Al. (2009), PLA is produced by fermenting dextrose derived from maize.

In surface modification of clay, the sodium montmorillonite have a hydrophilic interlayer characteristic while polymer has a hydrophobic interlayer characteristic. So, by using an organic treatment, the clay will be treat into hydrophobic characteristics to make sure it's compatible with polymer. According to Zheng et. al. (2005), it is important to change the inorganic clay to organic clay in the modification of nanocomposites in order to get a perfect compatibility with the polymer. Nowadays, many researchers focus on how to increase the exfoliation of the clay platelets in polymer matrixes by enhancing interaction between clay surface and polymer chains (Qian et. al, 2008). There two types of surface modification that we study here is ion exchange and surfactant method.

In the ion exchange method, the hydrophilic silicate of clay needed to be converted into hydrophobic in order to layer silicates miscible with most polymer matrices. This can be done by ion exchange modification with cationic surfactants. Clay layer is stacked together with van der Waals to form a gallery. By substituting lower valent metallic ion for Si, Al, or Mg in the layer will generate negative charges that are counteracted by the alkali and alkaline cation within the galleries as according to Liu et. al. 2006. Nawani et. al. (2007) said that the ion exchange method can be done by react the pristine clay with the Transition Metal Ion salt (TMIs) in the presence of solvent as shown in **Table 1.1.**

Table 1.1: TMI Salts and Solvents Used in the Modification Procedure (Pranav et. al, 2007)

Type of clay	A solvent used	TMI salt used	Concentration [M]
Sodium Montmorillonite (Pristine clay)	Water	Copper (II) sulfate	0.3
	Methanol	Copper (II)chloride	0.3
	Ethanol	Copper (II)chloride	0.3
	Dioxane	Copper (II) Nitrate	0.3

Different with surfactant method, Na^+ MMT will be modified with cationic surfactants (eg:, alkylammonium cation) to lower the surface energy and improve wetting characteristic of clay. So, intercalation is possible. This cation also provides a functional group that can react with polymer matrix or initiate polymerization to strengthen the interface between inorganic filler and an organic polymer matrix (Liu et. al., 2006).

For the dual surfactant method, recent studied by Andrew et. al. (2009) highlighted that mineral needs to modify with a thermally stable surfactant (eg: - aminopropyl-POSS

(AP-POSS)). For example, in dual surfactant method, poly (butylenes terephthalate) (PBT) and ditallowdimethylammonium chloride is sequentially modified with sodium montmorillonite (Na^+MMT) by the ion exchange reaction that will give a dual-surfactant organoclay (OC) (Andrew et, al., 2010).

1.2 Problem Statement

The main problem in polymer-organoclay nanocomposites is incompatibility between polymer and clay. This is due to clay characteristic is hydrophilic while the polymer is hydrophobic. In order to solve this problem, clay characteristic has to be modified into hydrophobic before reacting with a polymer to form nanocomposite. This surface modification will increase the d-spacing of clay interlayer and form a perfect compatibility with the polymer.

1.3 Objective

The first objective of this study is to modify the surface of sodium montmorillonite (Na+ MMT) by using the ion exchange method and surfactant method. The second objective is to fabricate PLA-Nanocomposites by using organoclay from ion exchange and surfactant method with PLA polymer. The third objective is to study the interlayer properties, structure and morphology of organoclay and PLA-Nanocomposites by using these two methods.

1.4 Scope of Study

In order to achieve the objectives, the scope of study is narrowed down to the following:-

1) a) To modify the surface of Na^+MMT with Copper (II) Sulfate or Copper (II) Chloride TMI salt in the presence of methanol or ethanol solvent.
   b) To modify the surface of mineral clay, Na^+MMT by reacting it with Tetraethyl orthosilicate (TEOS) / alkylammonium to form an organoclay.
2) To study which type modification of nanoclay that can provide a good interlayer d-spacing for polymer attachment and also more compatible with polymer.
3) To fabricate pla-nanocomposite using solution casting method.
4) To compare the structure of pla-nanocomposite from ion exchange method organoclay and surfactant method organoclay by using Scanning Electron Microscopy (SEM) and X-ray diffraction (X-RD).

1.5 Rational and Significant

The point of this experiment is to find out the most compatible surface modification method that can provide a suitable condition for the polymer chain to fill the interlayer space of organoclay because the problem that the issues here is PLA and Na^+MMT are not compactable. Using the following methods, ion exchange and surfactant modification show an improvement on interlayer structure or properties of Na^+MMT. Ion exchange shows improvement by increasing the d-spacing of the interlayer. While surfactant method makes an improvement by providing functional group to interact polar region of PLA chain. The structure of PLA-Nanocomposites shows that exfoliation is occurring.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Nanoclay and Polylactic acid (PLA).

2.1.1 Nanoclay/ Pristine Clay/ Sodium Montmorillonite.

One general way to prepare a polymer nanocomposite is by the intercalation chemistry of layered inorganic solids in which polymer is inserted into the interlayer space. There are many types of layer inorganic solid such as graphite, clay minerals, transition metal dichalcogenides, metal phosphates and phosphonates, etc. The common type of layer inorganic solid that used today in industries is clay mineral. The reason of clay mineral widely used in industries is because of its unique structure and properties. Clay minerals have a higher intercalation chemistry ability as compared to other layered inorganic solid when applied with polymer to form polymer nanocomposite. In details, clay mineral's unique layered structure and high intercalation capabilities that allow them to chemically modified to compactable with polymer and became clay-based polymer nanocomposites.

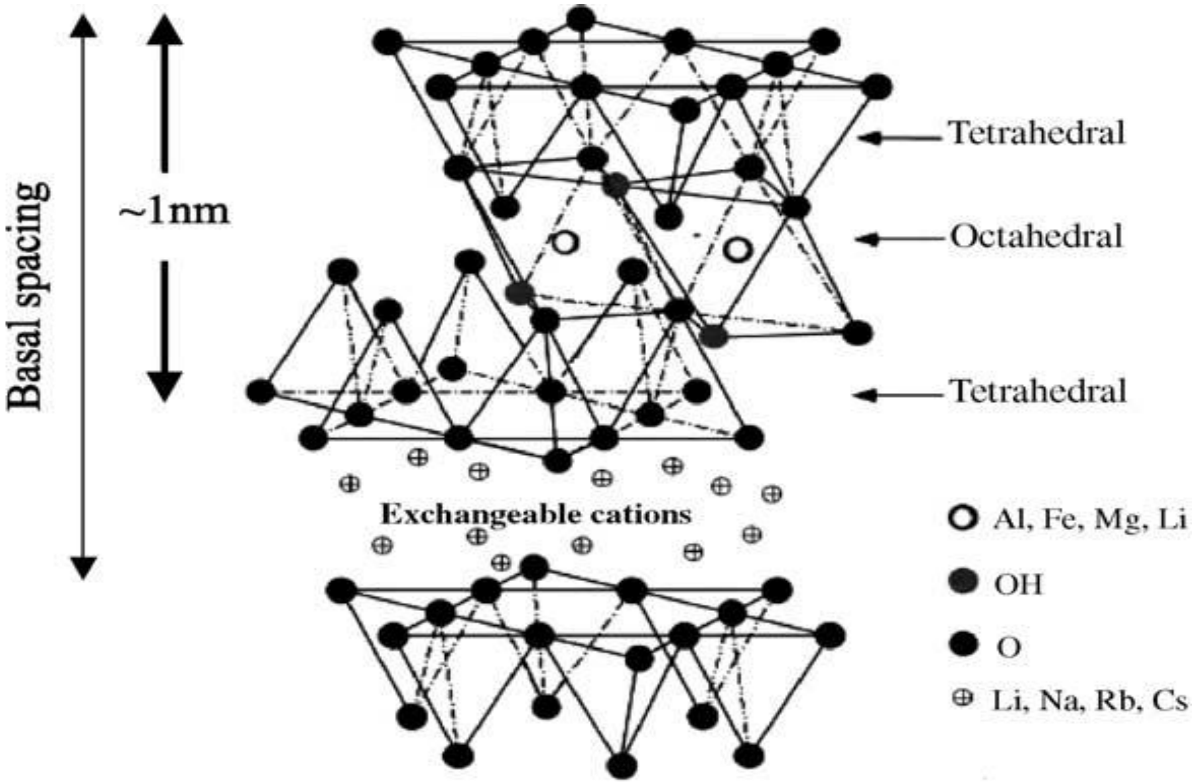


Figure 2.1: Structure of layered silicates (Giannelis, 1999)

As shown in the **Figure 2.1**, clay mineral structure is consisting of interlayer or gallery and this interlayer is caused by the van der Waals force between the layer gaps. This layer gap is made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. There is an isomorphic substitution within the layer for (e.g., Li, Na, Rb and Cs) and also a relatively layer charge. Clay mineral has a relatively low layer charge which is between (x= 0.2-0.6). So, the force between the adjacent layer also relatively low and finally the interlayer is cations exchangeable and the intercalation of inorganic and organic cations and molecules into the interlayer space are accomplished. Other advantages of using clay as a layered inorganic solid is it can form a high strength and stiffness polymer nanocomposites and clay is abundance and easy to get and also cheaper compare to other layered organic solids.

Clay mineral can be divided into two types which is natural clay and synthesis clay. The commonly used clay mineral is natural clay. The two types of natural clay that widely used is montmorillonite and hectorite type.

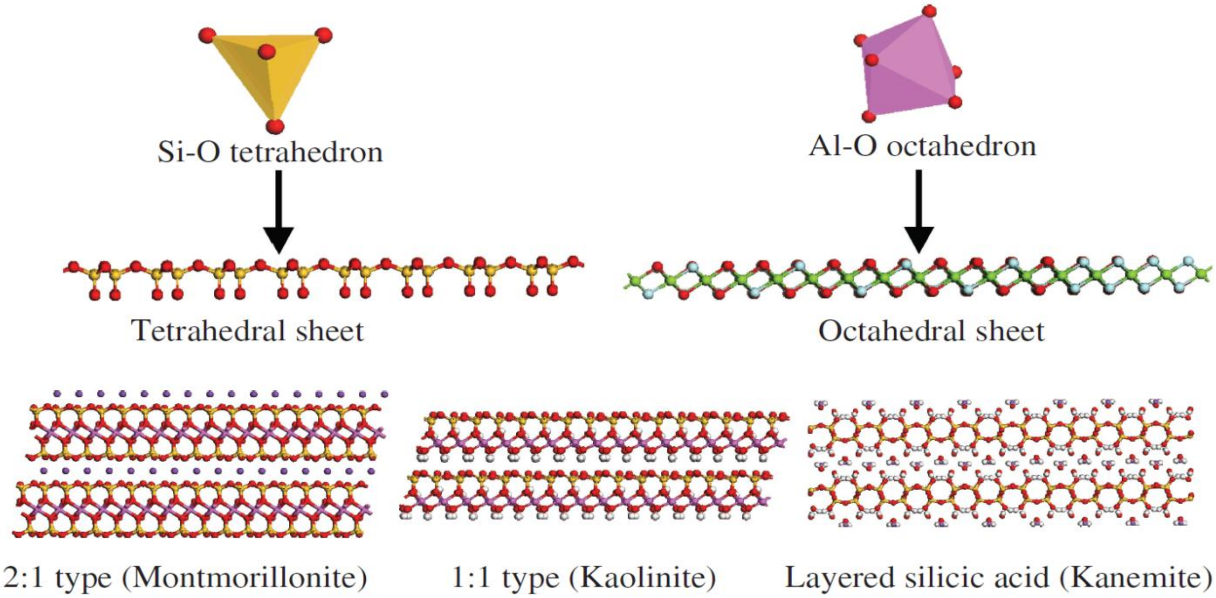


Figure 2.2: Structure of clay minerals represented by montmorillonite, kaolinite, and kanemite.

This two type of clay is falling under 2:1 type of clay. There is also 1:1 type and layered silicic acid type of clay **(Figure 2.2 and Table 2.1)**.

The 2:1 type has an aluminium octahedron sheet that sandwiched between two adjacent silicon tetrahedron sheets. Stacking of the layers leads to a van der Waals gap between this layers. Zeng et. al. (2005) mentioned that the isomorphic substitution of Al with Mg, Fe, Li in the octahedron sheets and/or Si with Al in tetrahedron sheets gives each three sheet layer an overall negative charge, which is counterbalanced by exchangeable metal cation residing the interlayer space, such as Na, Ca, Mg, FE, and Li.

The 1:1 type has a layer that made up of one aluminum octahedron sheet and one silicon tetrahedron sheet. The difference of this type of clay with 2:1 type is there was no isomorphic substitution in either octahedron or a tetrahedron. Water molecules the only ion that occupy the space between the layers. This layer is stacked together by hydrogen bonding between hydroxyl groups in the octahedral sheets and oxygen in the tetrahedral sheets of the adjacency.

The Layer Silicic Acids consists of silicon tetrahedron sheets with different layer thickness. Their basic structure composed of layered silicate networks and interlayer hydrated alkali metal cations. Layered silicic acids also are suitable to use for polymer nanocomposites because it has similar intercalation chemistry with 2:1 type clay. It also has high purity and structural properties that are complementary to smectie clays. They are built up from combinations of tetrahedral and octahedral sheets whose basic units are usually Si-O tetrahedron and Al-O octahedron, respectively. (Zeng et. al, 2005)

Table 2.1: Clay mineral used for polymer nanocomposites (Zeng et. al, 2005)

Type of clay	Origin	Substitution	Layer charge
2:1 type:			
MMT	Nature	Octahedral	Negative
Hectorite	Nature	Octahedral	Negative
Saponite	Nature	Tetrahedral	Negative
1:1 type:			
Kaoinite	Nature	NO	Neutral
Halloysite	Nature	NO	Neutral
Layered silicic acid:			
Kanemite	Natural/ Synthetic	Tetrahedral	Negative

2.1.2 Polylactic acid (PLA)

Today, plastic is produced by using fossil fuel and when this plastic is discarding into the environment, it will end up with waste that cannot be degraded spontaneously. In order to dispose this waste, incineration process need be done. This process actually will produce carbon dioxide that can harm the environment in which cause a global warming. Furthermore, incineration also releases toxic gases that also harm to human life (Donald, 2001).

According to the Municipal Solid Waste report issued by the U.S. Environmental Protection Agency (EPA) for the year 2008, 76.76 million tons of wastes were generated from packaging materials. This included 13.01 million tons of plastics with 4.89 million tons of plastic packaging in the form of films. Only 13.2% of this plastic packaging waste was recycled, while only 9.8% of plastic films were recovered; the rest was added to landfills (Samer et. al., 2011)

To solve this problem, researchers have found out that Polylactic acid (PLA) is suitable material to form a plastic because of its renewable resource and most important criteria is readily biodegradable. According to Ray et. al. (2003) this green polymer material did not need toxic component in manufacture and also can degrade in the natural composting process.

Polylactic acid (PLA) is made up of α-hydroxyl acids, which include polyglycolic acid or polymandelic acid. PLA falls under aliphatic polyesters family. PLA characteristic is thermoplastic, high strength, and high modulus. Major use of a PLA is for industrial packaging field or biocompatible or bio-absorbable medical device market. High molecular weight PLA is resistant to support bacterial and fungal growth in food packaging industries. PLA degradable is by simple hydrolysis of the ester bond and do not require an enzyme to speed up the rate of hydrolysis.

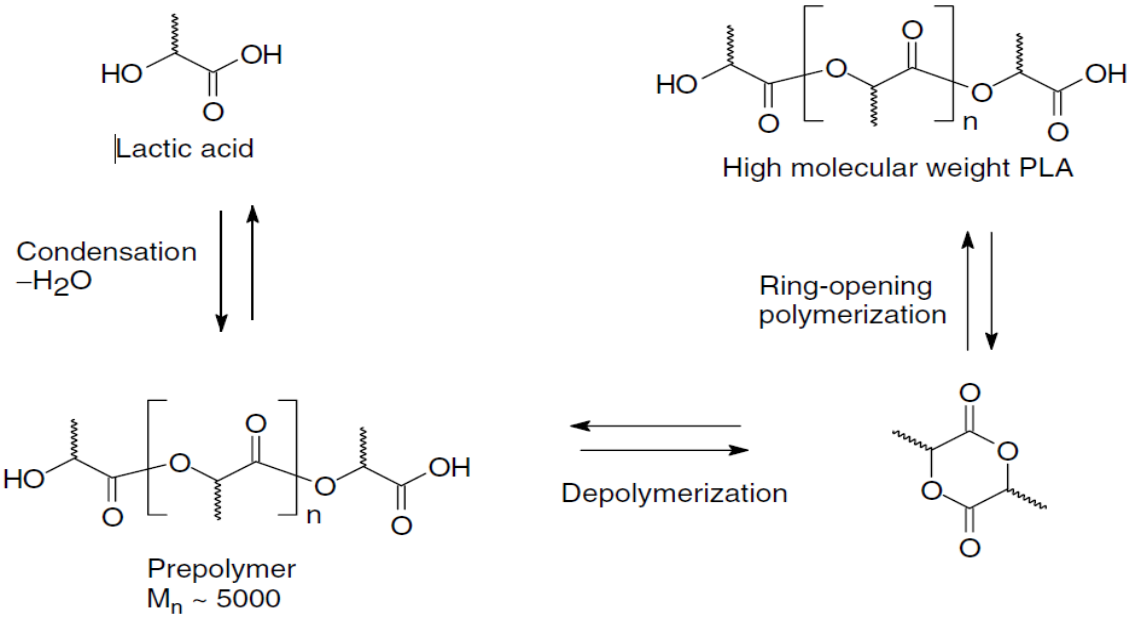


Figure 2.3: Schematic of PLA production via prepolymer and lactide. (Henton et. al, 2005)

PLA synthesis as shown in **Figure 2.3**, Henton et. al. (2005) said that the process starts with lactic acid produced by fermentation of dextrose followed by the continuous condensation reaction of aqueous lactic acid to produce low molecular weight PLA prepolymer. Later, the low molecular weight oligomers are converted into a mixture of lactide stereoisomer's using catalyst to enhance the rate and selectivity of the intramolecular cyclization reaction. The molten lactice mixture is then purified by vacuum distillation. Finally PLA high polymer is produced using an organo tin-catalyzed, ring-opening lactide polymerization in the melt, completely eliminating the use of costly and environmentally unfriendly solvent.

2.2 Type of Polymer Nanocomposites

The early history of polymer nanocomposites is begun by Ogata et. al.(1997) that resulting with micrometer-scale phase separation of the organoclay filler with the PLA (polymer) matrix without nanometer-range dispersion of silicate layers. In their research, they were using solution casting method to form a polymer nanocomposite.

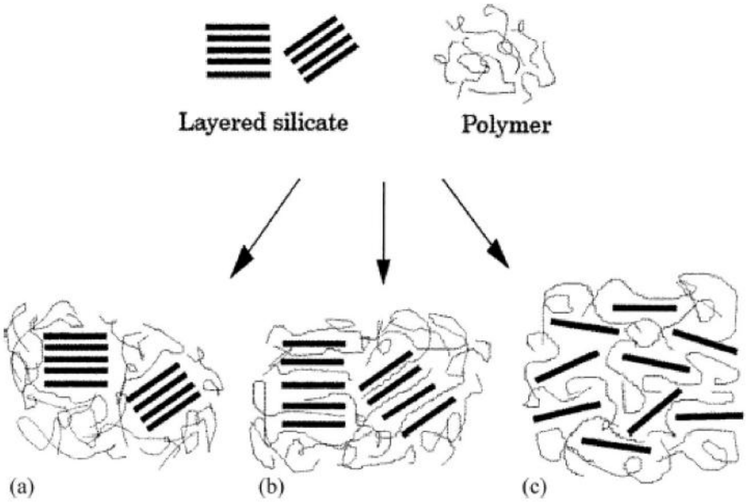


Figure 2.4: Schematic of three main types of polymer/layer structure composite morphologies: (a) microcomposites, (b) intercalated nanocomposites, and (c) exfoliated nanocomposites. (Liu et. al, 2006)

According to **Figure 2.4**, Polymer nanocomposite is achieved when layered clays are filled into a polymer matrix. The product can be either conventional composite or nanocomposite and that depending on the nature of the component and the processing condition. Conventionally, two idealized structure of polymer/layer structure nanocomposite morphologies may observe which are intercalated nanocomposites and exfoliated nanocomposites (Yenice et. al., 2008).

Intercalated nanocomposites form when several polymer chains are inserted between interlayer and intercalated structures are formed. Subsequently, the interlayer d-spacing is also expanded but limited between 20-30Å. According to Strawhecker et. al, 2000, in his experimental work, the structure of Poly(Vinyl alcohol)-Nanocomposites can be investigate by using Transmission Electron Microscopy (TEM) by focusing on the layered filler dispersion and changes of the polymer crystallity due to the inorganic layered filler.

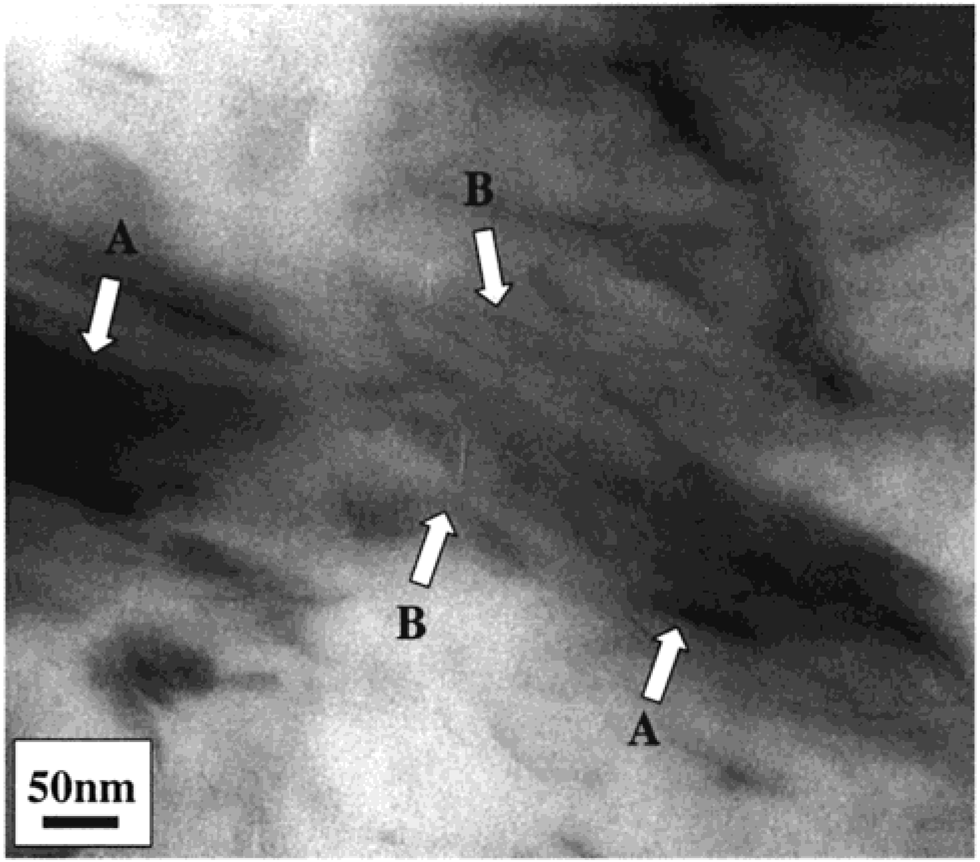


Figure 2.5: (A) TEM image of 20 wt % MMT/PVA nanocomposites revealed the coexistence of intercalated. (Strawhecker et. al, 2000)

From **Figure 2.5**, the A label shown a coexistences of silicate layered for the 20 wt % MMT nanocomposites and thus proven that there is an intercalated nanocomposites morphologies.

For Exfoliated nanocomposites, the idealized exfoliated structure consists of individual, nm-thick layers suspended in a polymer matrix, and is a result of the extensive penetration of the polymer and delineation of the layer structure (Liu et. al, 2006). The d-spacing of exfoliated nanocomposites is also greater than intercalated nanocomposite structure because the Van der Waals bond between adjacent layers is diminished. The d-spacing separation is about 10nm or more apart. That's why exfoliated nanocomposites are the researcher goals because of its dramatic improvement in mechanical, thermal properties and others that suitable for industries.

According to Fu et. al, 2000, in his experimental work, his study is focusing about the exfoliation of NaMMT in polystyrene matrix. To prove an exfoliation in the Vinylbenzyldimethyldodecylammonium chloride Nanocompsites (VDAC-NaMMT) is occurring in the polymerization. The XRD analysis is done in order to examine the crystal structure of polymer-clay nanocomposites.

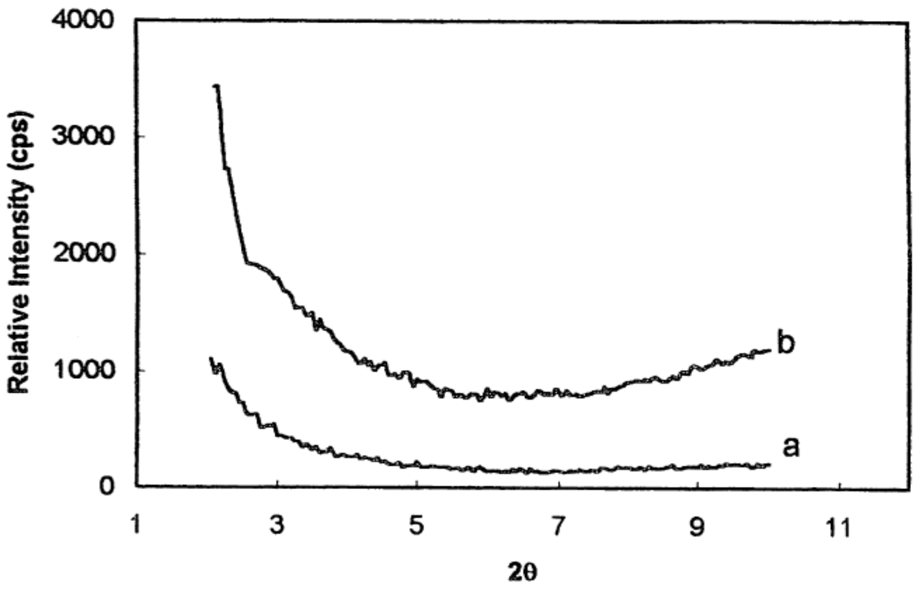


Figure 2.6: XRD pattern of polystyrene-clay nanocomposites: (a) 5.6 wt % VDAC-NaMMT. (Fu et. al, 2000)

From **Figure 2.6**, XRD pattern for 5.6 wt % VDAC-NaMMT shows that no characteristic NaMMT peak in the analysis. It means the VDAC-NaMMT is exfoliate into nanolayer in the polymer matrix.

2.3 Preparation of Polymer Nanocomposites

The intercalation of polymer in layered solid has been proven to be the most successful approach to fabricate polymer nanocomposites (Suprakas et. al, 2003). There are several methods to prepare a polymer nanocomposite which is Solution In, In Situ Intercalative Polymerization, Melt Intercalation and Template synthesis (Alexandre et. al., 2000). The formation of polymer nanocomposites is driven by different forces depending on the technique used, and each technique has its advantages and disadvantage. The polymers that have been studied so far cover almost the whole range of polymer, such as thermoplastic and biodegradable polymers (Zeng et. al, 2005).

2.3.1 Solution Intercalation

This method is based on a solvent system in which the polymer or prepolymer is soluble and the silicate layers are swellable. The layered silicates, owing to the weak forces that stack the layers together, can be easily dispersed in an adequate solvent such as water, acetone, chloroform, or toluene (Hussain et. al, 2006). First the layered host is exfoliated in a solvent, in which the polymer is soluble (water, toluene, etc.). The polymer is adsorbed onto the single-layer surfaces and after evaporation of the solvent or a precipitation procedure; the single layers are restacked, trapping the polymer and the hydrated/ solvated ionic species (Gacitua et. al., 2005).

According to Andrew et. al, 2009, in his experimental work, the fabrication of polymer nanocomposites is done by using the solution exfoliation method The organoclay is suspended in chloroform, the PLA (polymer) was stirred in chloroform to form a solution which was then added dropwise to the chloroform/clay suspension. After its well stirred, the solution of pla-organoclay-chloroform is poured into Petrie dishes and waited for chloroform to evaporated.

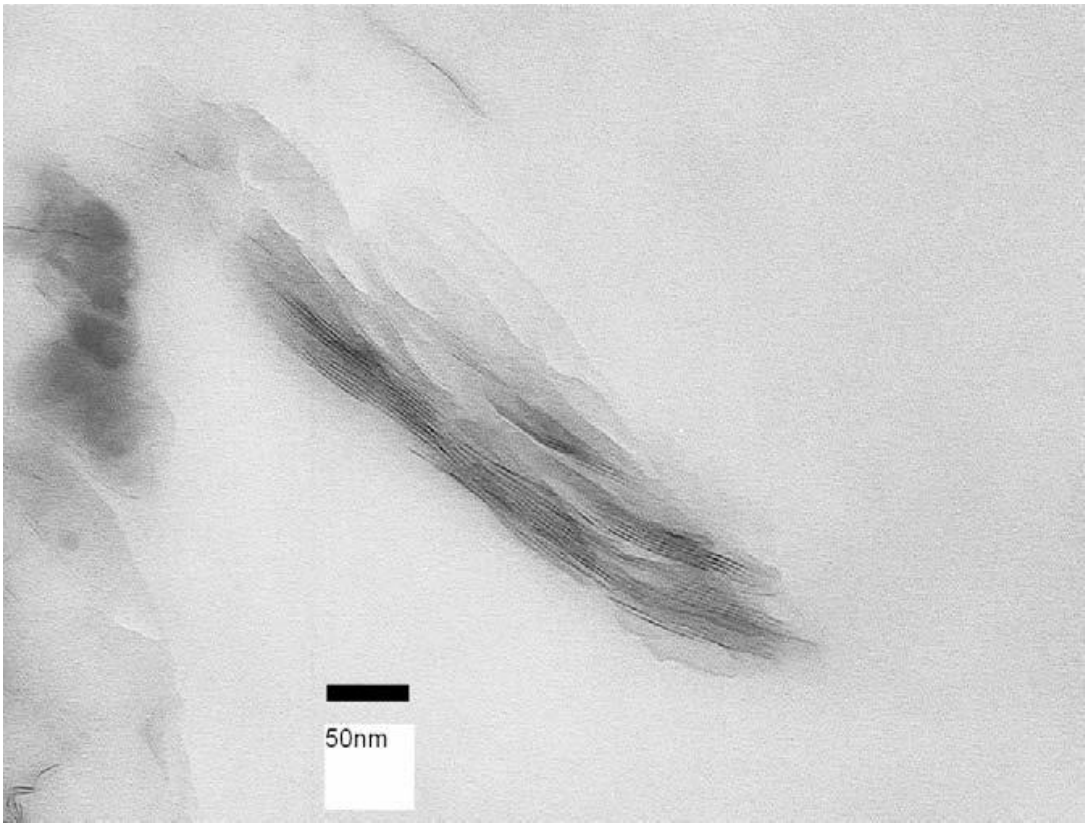


Figure 2.7: TEM image of PLA–CABmmt intercalated composite prepared by solution casting. (Andrew et. al, 2009)

By examining the TEM analysis (**Figure 2.7**), the result shows that an intercalated composite is formed by using solution intercalation. So, the advantages of using this method is it can form a well intercalated polymer nanocomposites while the disadvantages is using a large amount of solvent in the resin system.

2.3.2 In situ intercalative polymerization

In this technique, the layered silicate is swollen within the liquid monomer (or a monomer solution) so as the polymer formation can occur in between the intercalated sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator or by an organic initiator or catalyst fixed through the cationic exchange inside the interlayer before the swelling step by the monomer (Alexandre et. al., 2000).

According to Amiya et. al, 2002, in his experimental work, by using in situ polymerization to fabricate Poly(butylene terephthalate) Nanocomposites (PBT-NaMMT).

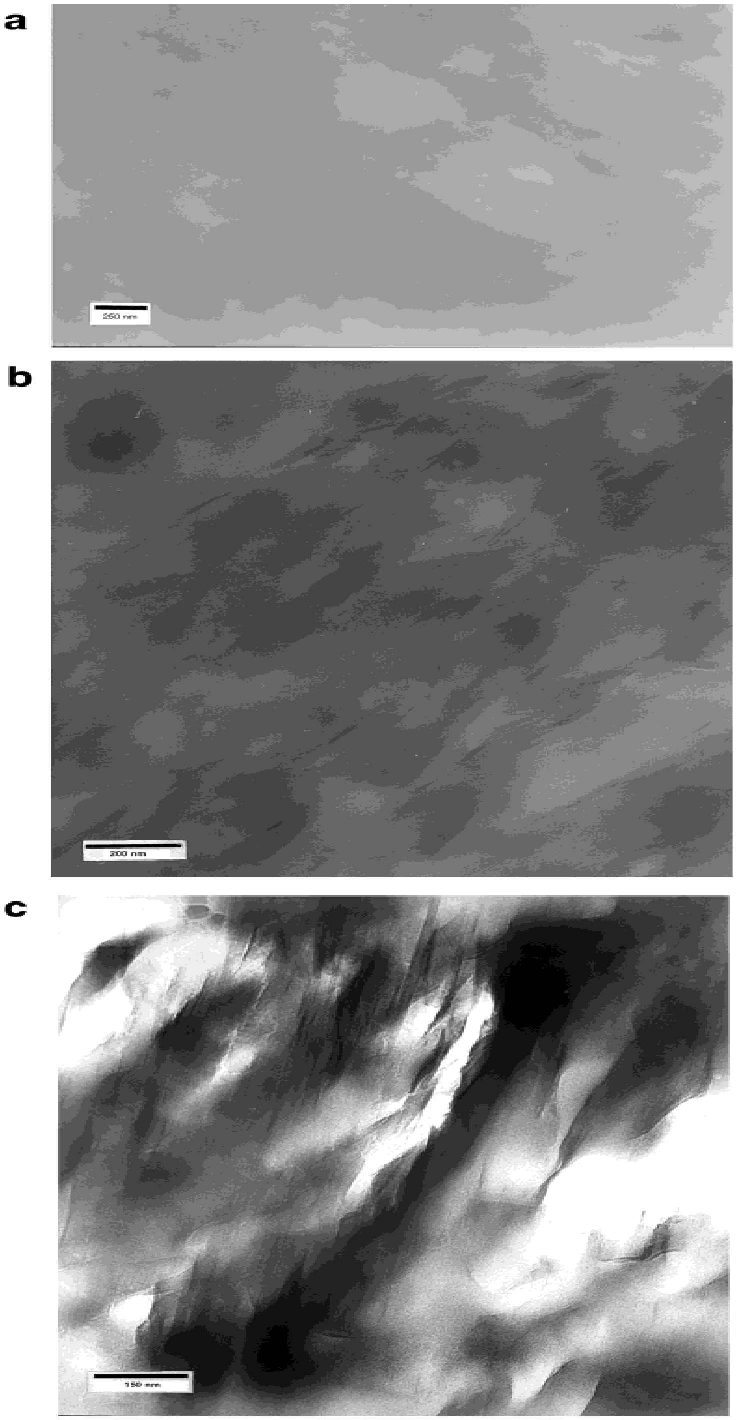


Figure 2.8: (a) TEM micrograph of PBT polymer. (b) TEM micrograph of NaMMT(c) TEM micrograph of PBT-NaMMT. (Amiya et. al, 2002)

According to TEM analysis by observing a nano-scale pattern of the PBT polymer matrix, **Figure 2.8 (a)** shows a smooth background of crystals originating from the PBT host. In **Figure 2.8 (b)**, there are individual silicate layers along with two, three and sometimes more layers stacked together that well dispersed in PBT host matrix. The TEM analysis for 20 wt% PBT-Nanocomposites is shown in **Figure 2.8 (c)**, it shows that both elements of exfoliation and intercalation of the clay layered. From the result of in situ polymerization method, we can conclude that clay exfoliation depends on the extent of clay swelling and diffusion rate of monomer in the gallery. Oligomer may be formed upon incompletely polymerization

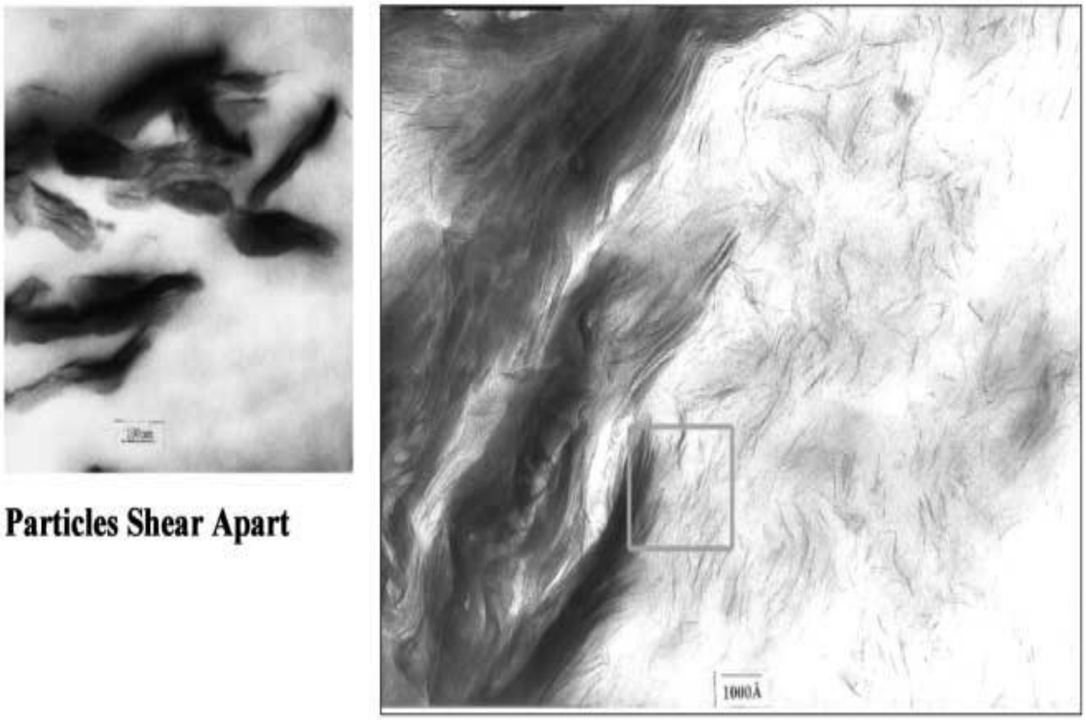
So, the advantage from this experimental work is it can form an exfoliated-intercalated type of polymer nanocomposites. Another advantage of in situ polymerization is it suitable for low or non-soluble polymer; A conventional process for thermoset nanocomposites. (Zeng et. al, 2005). The disadvantage of this method is it cannot form a well exfoliated polymer nanocomposite.

2.3.3 Melt Intercalation

In this technique, no solvent is required and the layered silicate is mixed within the polymer matrix in the molten state. A thermoplastic polymer is mechanically mixed with conventional methods such as extrusion and injection molding with organophillic clay at an elevated temperature. The polymer chains are then intercalated or exfoliated to form nanocomposites. This is a popular method for preparing thermoplastic nanocomposites. The polymers, which are not suitable for adsorption or in situ polymerization, can be processed using this technique (Hussain et.al., 2006).

According to Dennis et. al, 2001, in his experimental work, the degree of exfoliation and dispersion of layered silicate nanocomposites formed from polyamide 6 (polymer) by melt compounding is affected by both the clay chemical treatment and the type of extruder and its screw design. The other method to improve the exfoliation and dispersion is by increasing the mean residence time.

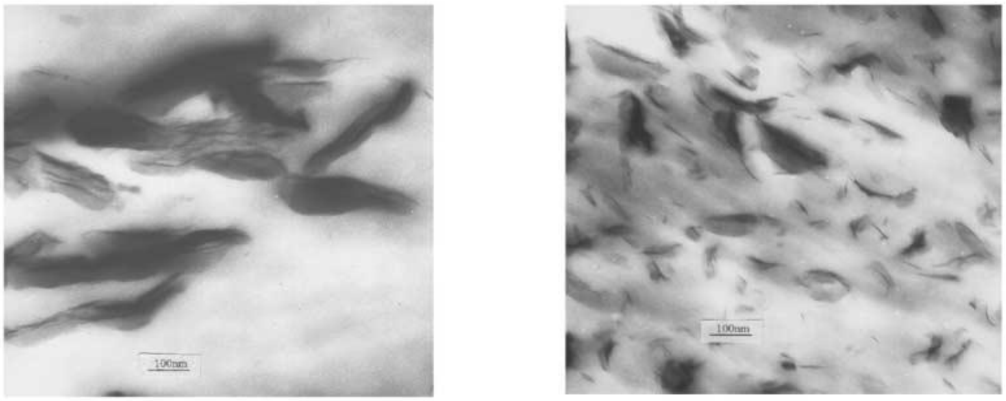
TEM can be used to study the morphologies of polymer nanocomposites using melt intercalation method. TEM is the best analysis instrument because it can monitor dispersion by monitoring on the clay platelets.



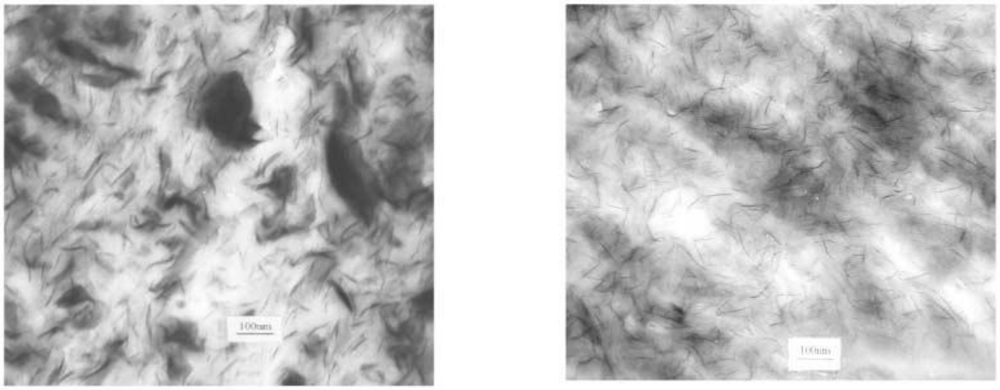
Particles Shear Apart

Platelets Peel Apart

Figure 2.9: TEM photomicrographs evidence for a process of peeling platelets apart during melt compounding. (Dennis et. al, 2001)



Single Screw **Co-Rotating, Low Shear**



Co-Rotating, Medium Shear **Counter-Intermeshing, Medium Shear**

Figure 2.10: TEM photomicrograph for selected nanoccomposites prepared using different extruder and screw configuration. (Dennis et. al, 2001)

Figure 2.9 shows an evidence for the process of peeling platelet apart during melt compounding. **Figure 2.10** shows the TEM photomicrographs for different extruder and screw configuration. The photomicrographs show that counter-rotating, non intermeshing medium shear extruder screw configuration gives the best dispersion and dilamination of polymer nanocomposites by using melt intercalation.

From the above explanation, we can conclude that the advantages of melt intercalation are forming an exfoliated polymer nanocomposite. The other advantages are no solvent required and nanocomposites can be produced with conventional plastic extrusion and molding technology. The disadvantages of the melt intercalation method are the slow transport of polymer within the confined gallery (Zeng et. al, 2005).

To conclude, even though *In-situ* polymerization and melt intercalation are the most common methods to fabricate polymer/clay nanocomposites (Zhang et. al., 2008). The method that used in this study is a solution intercalated method because of its easy to run and not using any expensive equipment such as extruder that use in melt intercalation method. This method is suitable for lab scale testing because it uses a solvent to combine the polymer and organoclay. It's not suitable for large scale process because it need to use a lot of solvent in it process. In situ polymerization method is not suitable for this study because it gives an intercalated-exfoliated polymer nanocomposite but cannot give a well exfoliated polymer nanocomposite.

2.4 Modification of Na+ MMT

The main reason of modification sodium montmorillonite is because PLA/polymer is not compatible with pristine clay / Na^+ MMT. Therefore, Na^+ MMT need to organically modify to produce polymer-compatible clay / organoclay (OC). The characteristic of clay is hydrophilic but the characteristic of polymer is hydrophobic (Yoon et. al., 2007). So, by organic treatment, the clay characteristic will be change into hydrophobic characteristic to make it compatible with polymer. The surface modification process of nananoclay looks similar to the fiberglass treatment with silane coupling agent to ensure a perfect compatibility or chemical bonding polymers.

Ion exchange method is the most popular modification for clay. The hydrophilic silicate of clay needed to be converted into hydrophobic in order to layer silicates miscible with most polymer matrices. This can be done by ion exchange modification with cationic surfactants.

Clay layer is stacked together with van der Waals force to form a gallery. This force will attract a couple of adjacent interlayer in clay. In this layer, there is inorganic cations that can be replaced by an organic ammonium cation and by substitute lower valent metallic ion for Si, Al, or Mg in the layer will generate negative charges that are counteracted by the alkali and alkaline cations within the galleries (Liu et. al., 2006). Maiti et. al. (2004) mentioned in their research that Na+ ion present in the clay is fully replaced by phosphonium (P+) ion during the ion exchange process. So, from the CEC data, the amount of P+ (modifier) present in the silicate galleries is in the order smectite < MMT < mica.

By using the solution method for ion exchange method, Na^+MMT need to react with catalytically active transition metal ion salt (TMIs) with the presence of solvent. There is a combination between TMI salt and solvent. For example, methanol solvent with copper (II) sulfate TMI salt and dioxane solvent with copper (II) nitrate TMI salt. The other combination is shown in **Table 1.1**. The concentration that used is about 3M. Previous research by Pranav et. al. (2007), the by SEM morphologies shows that there was a TMIs ion between the clay interlayer.

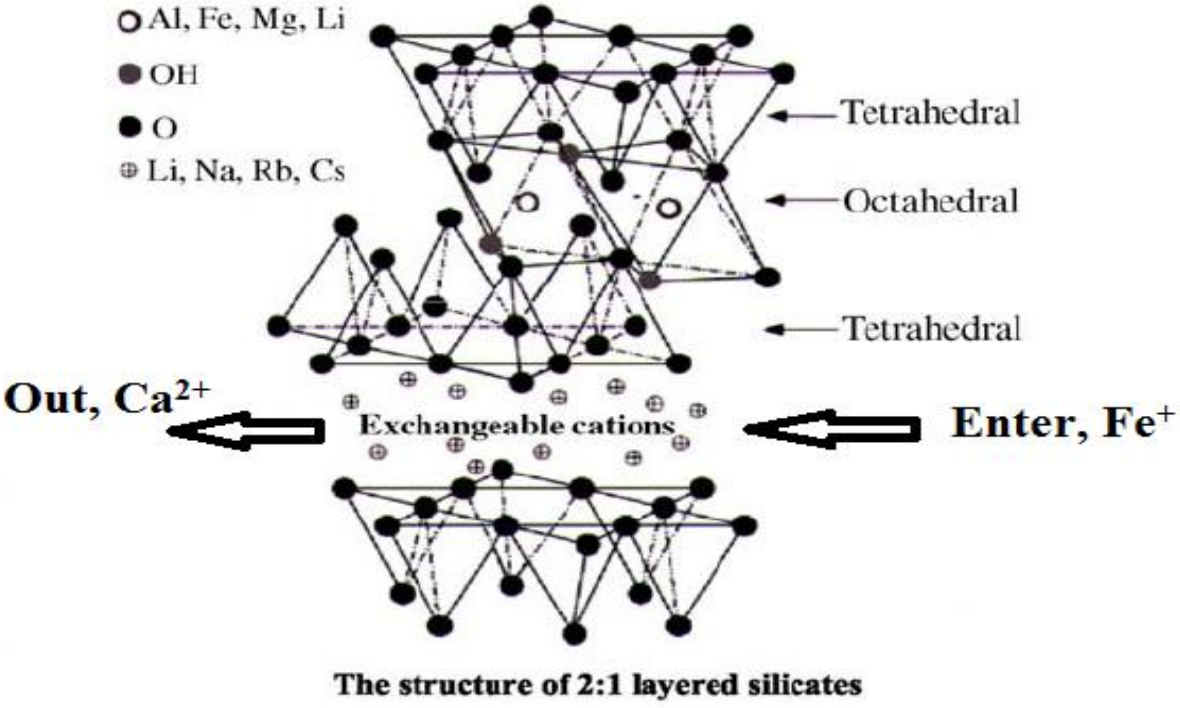


Figure 2.11: The ion replacement in interlayer of nanoclay.

Figure 2.11 can show more detail about the exchange of ion in the interlayer by the ion exchange method.

In surfactant method, Na^+ MMT will be modified with cationic surfactants (eg:, alkylammonium cation) in order to lower down the surface energy and improve wetting characteristic of clay so that the intercalation is possible. Benali et. al. (2008) said that the alkylammonium compound generally has a low thermal stability such that the degradation temperature of the organofiller can be close to that of the processing temperature of the polymer with the result that thermal degradation can cause the basal spacing of the clay to collapse under mixing condition. This cation also provides a functional group that can react with polymer matrix or initiate polymerization to strengthen the interface between inorganic filler and an organic polymer matrix (Liu et. al., 2006).

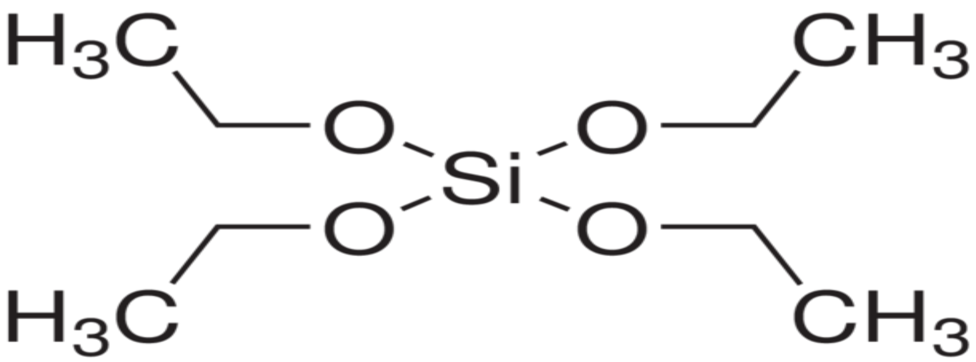


Figure 2.12: Structure of Tetraethyl orthosilicate (TEOS)

For the PLA nanocomposites, the surfactant that will be used is Tetraethyl orthosilicate (TEOS) (**Figure 2.12**). TEOS can provide second functionality or carboxyl group to the composite matrix by attaching on surface of layer silicate / interlayer of clay. So, this carboxyl group can interact with the polar region of PLA / polymer. Previous research by McLauchlin et. al. (2009) gives that the X-RD & TEM analysis shows PLA intercalated the gallery space of clay and increase of d-spacing of clay.

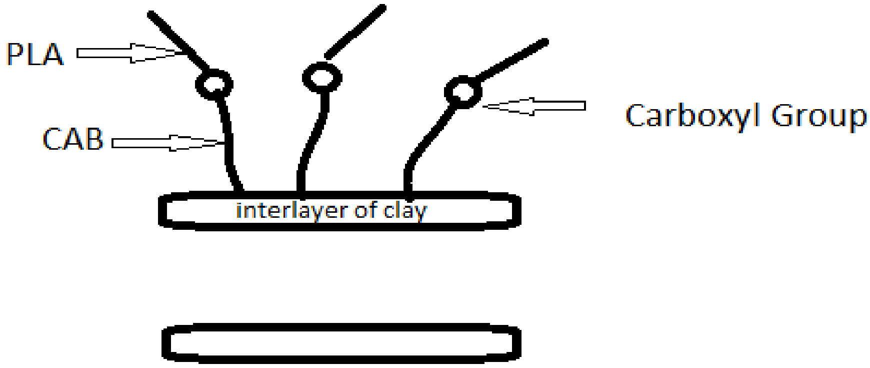


Figure 2.13: Modification CAB surfactant with PLA polymer.

Finally, the mechanical properties of PLA nanocomposites are improved dramatically. **Figure 2.13** will show more detail about this modification.

2.5 Properties of PLA and PLA-Nanocomposites

PLA is thermoplastic, height-strength, high modulus polymer that can be made from annually renewable resources to use in either industrial packaging field or the bicompactible/ bioabsorbable medical device market (Donald et. al, 2001). PLA different from others polymer because it can behave like PET and polypropylene (PP). It can use in a wide range of application because of its ability to be stress crystallized, thermally crystallized, impact modified, filled, copolymerized and processed in most polymer processing equipment (Henton et. al, 2005).

2.5.1 PLA Physical Properties

The physical characteristic of high molecular weight PLA is dependent on its transition temperature for common qualities such as density, heat capacity, and mechanical and rheological properties stereochemistry and thermal history can define either solid state PLA is amorphous or semicrystalline (Henton et. al, 2005). PLA is biodegradable and compatible and demonstrates good tensile strength and modulus. So, it is attractive for disposable biodegradable plastic product (Rui et. al, 2012).

According to Rui et. al, 2012, in his experimental work, the mechanical properties of neat PLA are studied by running a tensile test to get the stress-strain curve and properties of neat PLA. The tensile properties of neat PLA are shown in **Table 2.2**.

Table 2.2: Tensile Properties of Neat PLA.

Tensile Properties			
Strength (MPA)	Modulus (GPA)	Elongation %	Impact strength (J/m)
65.1 ± 0.6	3.47 ± 0.04	3.59 ± 0.14	11.3 ± 0.8

The result shows that the neat PLA have a good strength, modulus and elongation and impact strength.

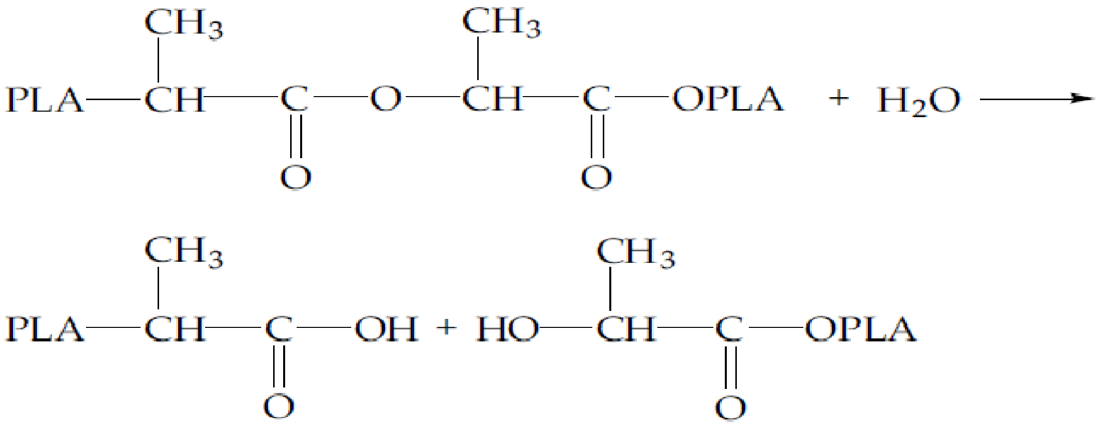


Figure 2.14: Degradation of PLA by hydrolysis of the ester linkages. (Henton et. al, 2005)

By referring the **Figure 2.14**, Henton et. al. (2005) said that the biodegrability PLA is caused by hydrolysis of the ester linkages that occur randomly along the backbone of the polymer with the presence of water. The rate of hydrolysis is also based on the intrinsic rate constant, water concentration, acid or base catalyst, temperature and morphology. The basic building block of PLA is lactic acid (2-hydroxy propionic acid). Lactic acid is the simplest hydroxyl acid with an asymmetric carbon atom and exits in two optically active configurations.

2.5.2 PLA-Nanocomposites Physical Properties.

According to De-Yi et. al, 2012, in his experimental work, it is proved that the PLA-Nanocomposites gives an improvement in thermal stability and mechanical properties. The thermal stability was improved and the glass-transition temperature also increases because of cross-linked structure under the electron beam treatment.

Table 2.3: Mechanical Properties of PLA-Nanocomposites.

Tensile properties			
Sample	Tensile strength (MPA)	Tensile modulus (Gpa)	Elongation at break (%)
PLA	60.7 ± 1.1	2.60 ± 0.07	9.2 ± 0.3
PLA-MMT-TAC	63.6 ± 0.5	2.08 ± 0.02	4.78 ± 5.6

Table 2.3 shows that the tensile properties of PLA-Nanocomposites are better than neat PLA in term of Tensile strength, modulus and elongation at break.

According to Huali et. al, 2003**,** for biodegradability test, the result of photo-degradation by FTIR observation shows that the degradation of PLA nanocomposites was greater than pure PLA composites after 200h of irradiation.

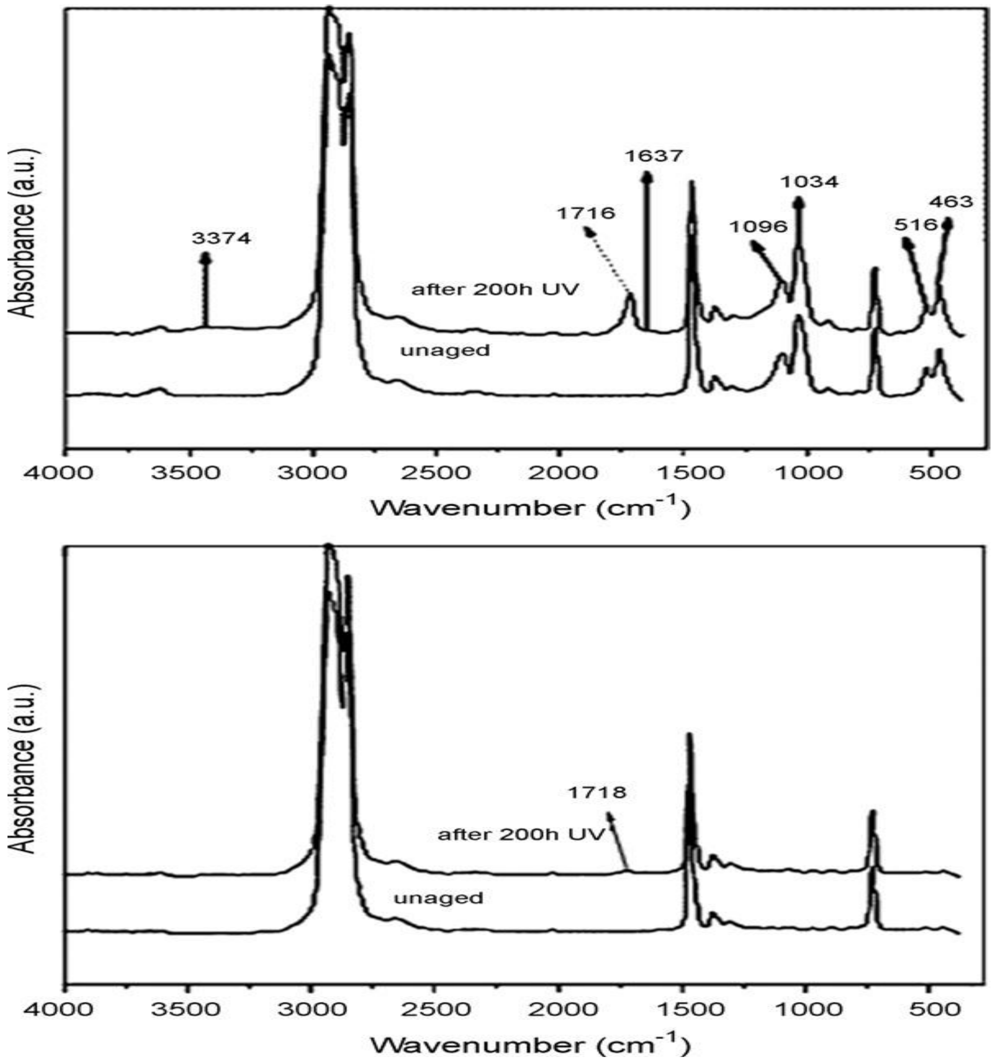


Figure 2.15: (a) FTIR spectra of PE/o-MMT nanocomposites before and after 200 h irradiation. (b) FTIR spectra of pure PE before and after 200 h UV irradiation. (Huali et al, 2003)

Figure 2.15 is illustrating the result for PE nanocomposite and pure PE composite. It is similar to PLA nanocomposites and pure PLA composites.

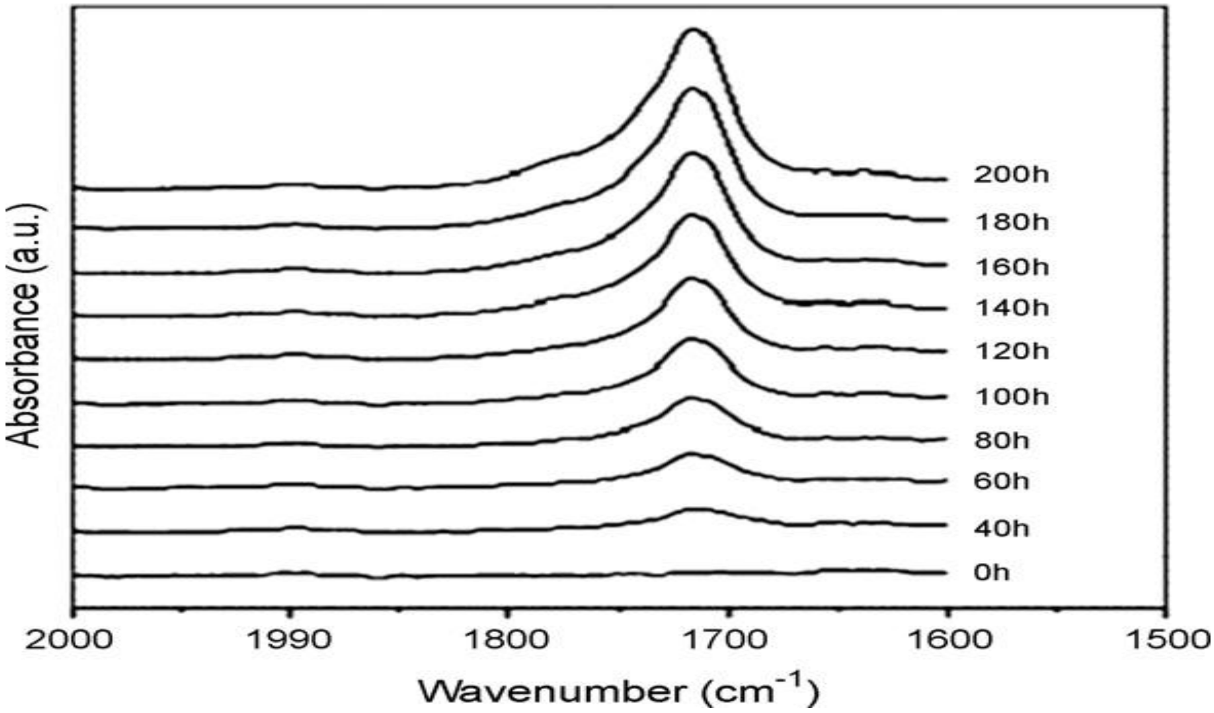


Figure 2.16: FTIR spectra of PE/nanocomposite at carbonyl region during photo-degradation. (Huali et al, 2003)

By referring **Figure 2.16**, it shows FTIR spectra in the carbonyl region upon UV irradiation. There was an increase in irradiation time in PE nanocomposites, which mean there was a degradation of nanocomposites. Pure PE composites show low intensity in the carbonyl region, which indicate less degradation.

2.6 Characterization and Testing of PLA-Nanocomposites

Generally, the structure of nanocomposites can be characterized by using XRD analysis and transmission electron microscopic (TEM) observation. Usually, XRD will be used to study the kinetics of the polymer melt intercalation. This method is based on monitoring the position, shape, and intensity of the basal reflection from the distributed silicate layer, and the nanocomposites structure (Intercalated or exfoliated).

In the other hand, TEM can be used to study morphology of the material. In more details, to allow a qualitative understanding of the internal structure, spatial distribution of the various spaces and views of the defect structure through direct visualization. Powder samples of clay were dispersed in water and 1–2 drops of the dilute solution were placed onto the carbon film-supported copper grids. TEM images were obtained using a JEOL JEM-2010 instrument with an acceleration voltage of 100 kV. SEM images were obtained on a JEOL S-4300F field emission scanning electron microscope at 15 kV. The nitrogen adsorption analysis was performed on an ASAP-2020 instrument at liquid nitrogen temperature. Prior to the adsorption, all samples were degassed at 100 1C for 6 h. The surface areas and pore size distributions were calculated using the Brunauer–Emmett–Teller (BET) method.

For X-ray diffraction (X-RD) data were collected on a MiniFlex Rigaku using graphite-filtered Cu Ka radiation (l¼ 1.542 nm). The diffractometer was controlled using Diffrac Plus XRD Commander and the raw data were manipulated using EVA software. The organoclay specimens were pressed into an aluminium holder where sufficient sample was available, otherwise they were spread on a silicon wafer and pressed to give a flat surface of the reference plane. The PLA–organoclay nanocomposite sheets were laid flat on an aluminium block, the height of which was always adjusted so that the sample surface was the reference plane of the instrument. Wide angle XRD patterns were obtained from a MiniFlex Rigaku with Cu Ka radiation (λ = 0.154 nm, 40 kV, 120 mA) at room temperature. The diffractograms were scanned in the 2y range of 1.5–401. The result will discuss later on result section.

CHAPTER 3

METHODOLOGY

3.1 Introduction

The objective of the research is to modify sodium montmorillonite as a filler in polymer nanocomposites in order to improve its properties. Verification of successful in changing pristine clay to organoclay need to be done by using FTIR, XRD, and SEM before proceed with the process of intercalation of organoclay with polymer.

3.2 Materials

3.2.1 Sodium Montmorillonite, NaMMT

Sodium montmorillonite is a type of layered silicates that was used to improve the polymer properties such as mechanical and thermal properties. The combination of specific polymer with sodium montmorillonite will form a polymer nanocomposites that have more properties improvement compare to neat polymer. The Sodium Montmorillonite were obtained from southern Clays, Texas, US and used as supplied. The properties of pure Sodium Montmorillonite are shown in the **Table 3.1**

.

Table 3.1: Properties of Sodium Montmorillonite.

Physical Properties	
CAS Number	1302-78-9
Physical State	Solid
Molecular Weight (g/mol)	540.46
Bulk Density (lb/gal)	50-70 lb/cu.ft at 20oC
pH	6-8 in 10% slurry
Color	Various
Odor	Odorless

3.2.2 Poly (lactic acid), (PLA)

PLA is a type of polymer and the reason of choosing PLA as a studied polymer is because of its ability to be stress crystallized, thermally crystallized, impact modified, filled, copolymerized and processed in most polymer processing equipment. We choose PLA as a studied polymer because of it is not hazardous polymer. It is produced from renewable resources and also biodegradable. Poly lactic acid (PLA) was obtained from Hycail B.V. The properties of PLA are shown in the **Table 3.2**.

Table 3.2: Properties of Poly(lactic acid)

Physical Properties	
CAS Number	26100-51-6
Molecular Formula	-(C6H8O5)-
Physical state	Solid
Specific Gravity (g/cm3)	1.23-1.30
Flash Point (oC)	121
Color	White Color
Odor	No odor
Tensile Strength @ Break, psi (MPa)	7700 (53)
Tensile Yield Strength, psi (MPa)	8700 (60)
Tensile Modulus, kpsi (GPa)	500 (3.5)
Tensile Elongation, %	6

3.2.3 Copper (II) Chloride

Based on this experiment, Copper (II) Chloride has been choosing as the transition metal ion salts (TMI) in order to modify the pristine clay in ion exchange method. In this experiment, the pristine clay was modified by using Copper (II) Chloride and Copper (Cu) atom act as a catalytically active TMI ion. The reason of this TMIs selection is when using Cu as a solvent, the Cu atom content in modified clay exceeds the CEC values. In details, the overall amount of absorbed Cu ions combined with residual surfactant seemed to exceed the overall ion exchange capacity. This Copper (II) Chloride was purchased from SIGMA-ALDRICH. The physical properties of Copper (II) Chloride are shown in **Table 3.3**.

Table 3.3: Properties of Copper (II) Chloride

Physical Properties	
CAS Number	7447-39-4
Molecular Formula	CuCl2
Physical state	Powder
Molecular Weight (g/Mol)	134.45
Relative Density (g/cm3)	3,386 at 20oC
pH	3 (50 g/L aq.sol (20°C))
Boiling Point	993 deg C @760mmHg (1,819.40°F)
Freezing / Melting Point	498 deg C (928.40°F)

3.2.4 Methanol

The amount TMI salt absorbs into the interlayer gallery of pristine clay depend on the type of solvent. Methanol and ethanol act as a solvent in this experiment because it can give better overall contents of TMI in organically (Pranav et. al, 2007). Methanol and Ethanol are acquired from Fisher Scientific. The physical properties of methanol and ethanol are shown in **Table 3.4** and **Table 3.5** respectively.

Table 3.4: Properties of Methanol

Physical Properties	
CAS Number	67-56-1
Molecular Formula	CH4O
Color	Colorless
Odor	Weak odor

Physical state	Liquid
Vapor Pressure (mm Hg)	128 at 20oC
Viscosity (cP)	0.55 at 20oC
Solubility	Misicble
Molecular Weight (g/Mol)	32.04
Vapor Density (g/cm3)	1.11 (air =1)
Boiling Point	64.7oC @ 760 mm Hg
Melting Point	-98 oC

Table 3.5: Properties of Ethanol

Physical Properties	
CAS Number	64-17-5
Molecular Formula	C2H5OH
Color	Colorless
Odor	Milk odor
Physical state	Liquid
Vapor Pressure (mm Hg)	59.3 at 20oC
Viscosity (cP)	1.2 at 20oC
Solubility	Misicble
Molecular Weight (g/Mol)	46.0414
Vapor Density (g/cm3)	1.59 (air =1)
Boiling Point	78oC @ 760 mm Hg
Melting Point	-114.1 oC

3.2.5 Di-chloromethane

Di-chloromethane was used as a solution during the formation of polymer and obtained from Fisher Scientific. The physical properties of Di-chloromethane are shown in **Table 3.6**.

Table 3.6: Properties of Di-chloromethane

Physical Properties	
CAS Number	75-09-2
Molecular Formula	CH2Cl2
Color	Colorless
Odor	Ethereal odor
Physical state	Liquid
Vapor Pressure (mm Hg)	350 at 20oC
Solubility	Moderately soluble in water
Molecular Weight (g/Mol)	46.0414
Vapor Density (g/cm3)	2.9 (air =1)
Specific Gravity/Density (g/cm3)	1.33

3.2.6 Tetraethyl orthosilicate (TEOS)

Tetraethyl orthosilicate (TEOS) is a type of surfactant that used to modify pristine clay by using surfactant method. TEOS can provide second functionality or carboxyl group to the composite matrix by attaching on surface of layer silicate / interlayer of clay. So, this carboxyl group can interact with the polar region of PLA / polymer (Andrew et. al, 2009). TEOS is obtained from Sigma Aldrich and its properties are shown in **Table 3.7**.

Table 3.7: Properties of Tetraethyl orthosilicate (TEOS)

Physical Properties	
CAS Number	78-10-4
Molecular Formula	Si(OC2H5)4
Color	Colorless
Odor	Ethereal odor
Physical state	Liquid
Vapor Pressure (mm Hg)	< 1 at 20oC
Boling Point	168 oC (lit)
Molecular Weight (g/Mol)	208.33
Vapor Density (g/cm3)	7.2 (air =1)
Density (g/mL)	0.933 at 20oC (lit)

3.3 Modification of Sodium Montmorillonite / Na^+ MMT

3.3.1 Ion Exchange Method

The main objective of the research is to modify Na^+ MMT that acts as filler in polymer nanocomposite in order to improve their final properties. The flow diagram below shows the step of the ion exchange method of pristine clay using catalytically active transition metal ion salt (TMIs).

The purpose of surface modification of pristine clay is the incompatibility between hydrophilic clay and hydrophobic polymer. This different characteristic often causes agglomeration of clay mineral in the polymer matrix. By using the ion exchange method to treat the pristine clay, its characteristic will change to hydrophobic and hence compatibility with the specific polymer.

According to Pranav et. al, 2007, in his experimental works, the advantages of using the ion exchange method is the surface modification can be done using a variety of solvent and TMI salt. The type of solvent and TMI salt combination are shown in **Table 1.1**. The other advantages of the ion exchange method is the surface modification is it can give an improvement in the aspect fire retardant (FR) of polymer. The presence of TMI salts in the clay interlayer gives FR properties improvement of polymer material.

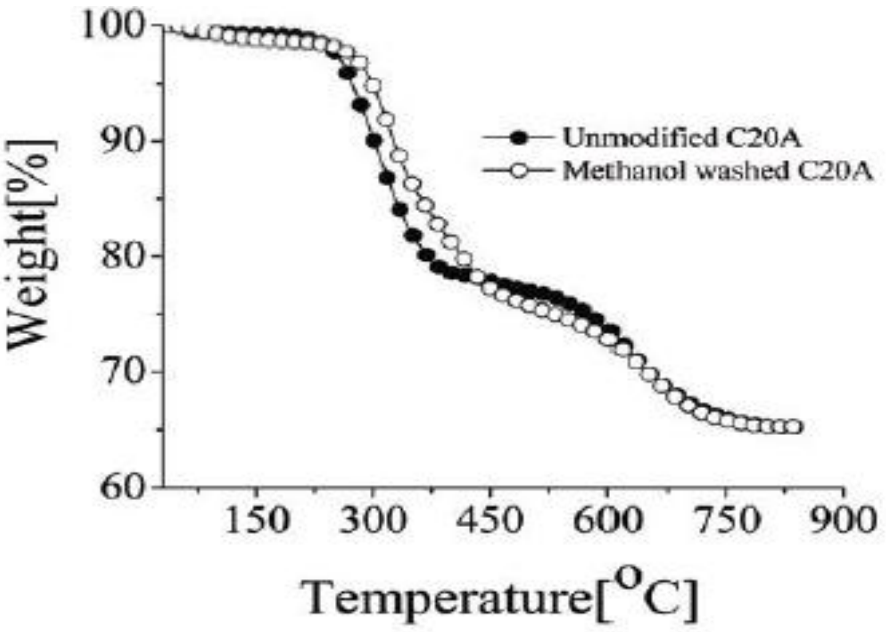
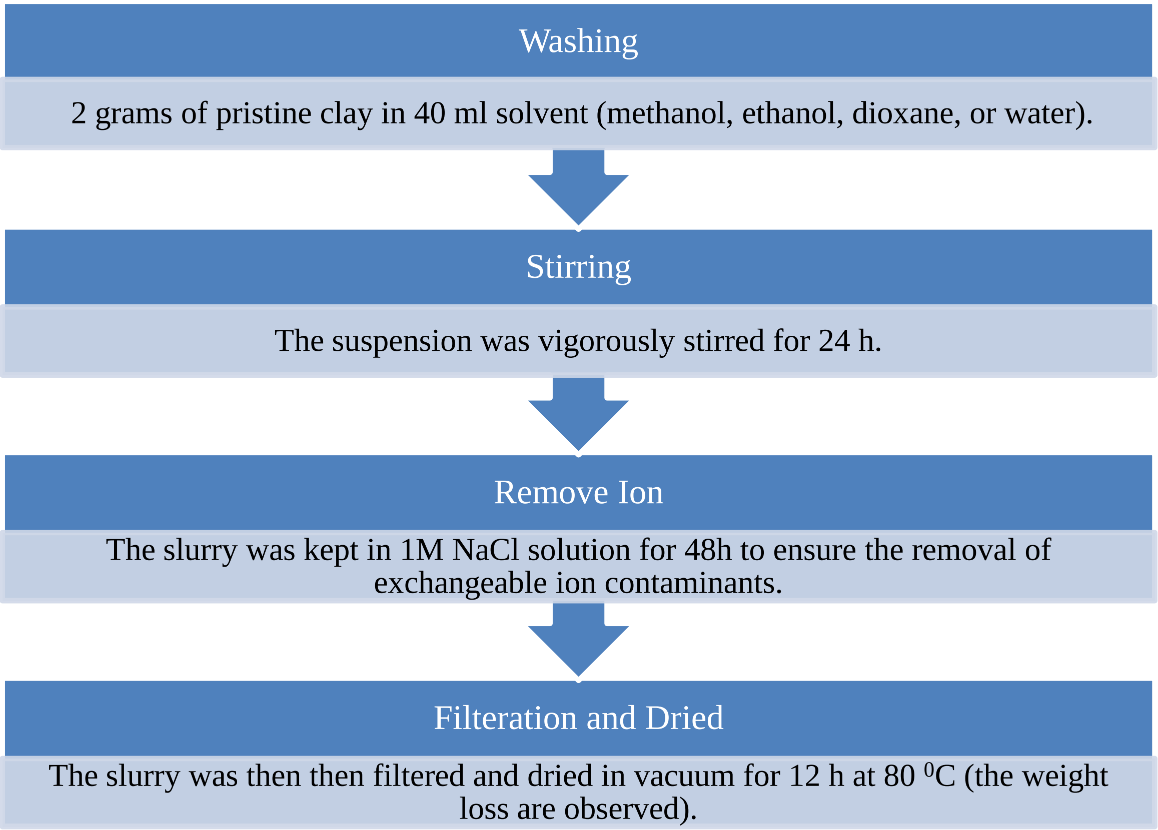


Figure 3.1: Thermograms of organoclay in the air for Unmodified C20A and Methanol washed C20A.

By referring **Figure 3.1**, the TGA result showed that the treatment significantly shifted the onset temperature of thermal degradation toward a higher value, thus increasing the thermal stability of organoclay in the air.

3.3.2 Pre-treatment Phase of Nanoclay for Ion Exchange Method

The pristine clay sample needs to be through a washed process before proceeding with the treatment. The reason for doing this modification is to remove excess surfactant and impurities in the pristine clay (Pranav et. al, 2007).


Washing

2 grams of pristine clay in 40 ml solvent (methanol, ethanol, dioxane, or water).

Stirring

The suspension was vigorously stirred for 24 h.

Remove Ion

The slurry was kept in 1M NaCl solution for 48h to ensure the removal of exchangeable ion contaminants.

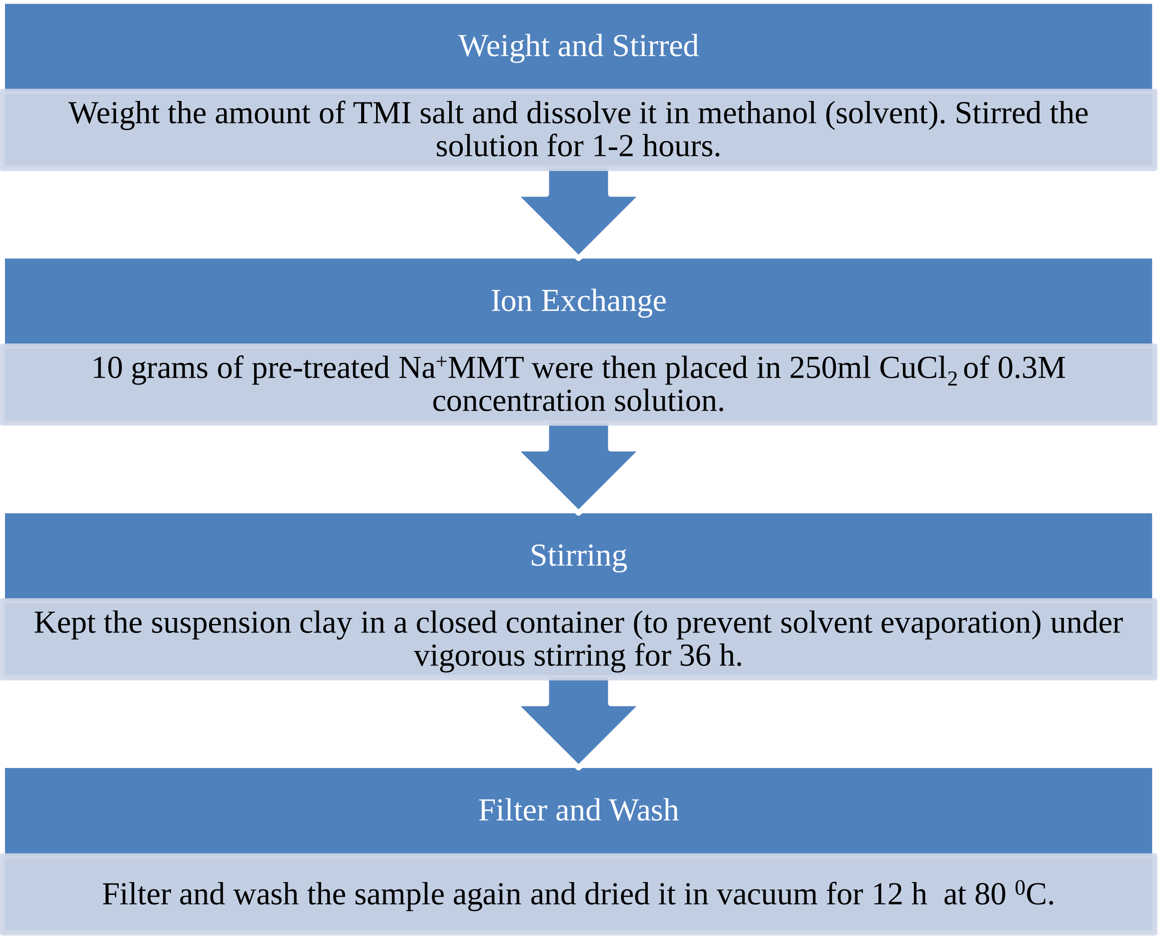
Filteration and Dried

The slurry was then then filtered and dried in vacuum for 12 h at 80 ^{0}C (the weight loss are observed).

Figure 3.2: Methodology for Pre-treatment Phase of Nanoclay For Ion Exchange Method

3.3.3: TMI salt Modification for Ion Exchange Method

Once the clay has been dried, it is ready to be treated with catalyst active TMI salt. The TMIS that used here is Copper (II) chloride, $CuCl_2$ and the solvent is methanol. Refer to **Table 1.1** for other combination of TMIs and Solvent. Based on the molecular weight of $CuCl_2$ / metal ion salts M_r =134.5g/mol, the desired weight to produce a 250ml, 0.3M solution is W= 10.09grams.



Weight and Stirred

Weight the amount of TMI salt and dissolve it in methanol (solvent). Stirred the solution for 1-2 hours.

Ion Exchange

10 grams of pre-treated Na^+MMT were then placed in 250ml $CuCl_2$ of 0.3M concentration solution.

Stirring

Kept the suspension clay in a closed container (to prevent solvent evaporation) under vigorous stirring for 36 h.

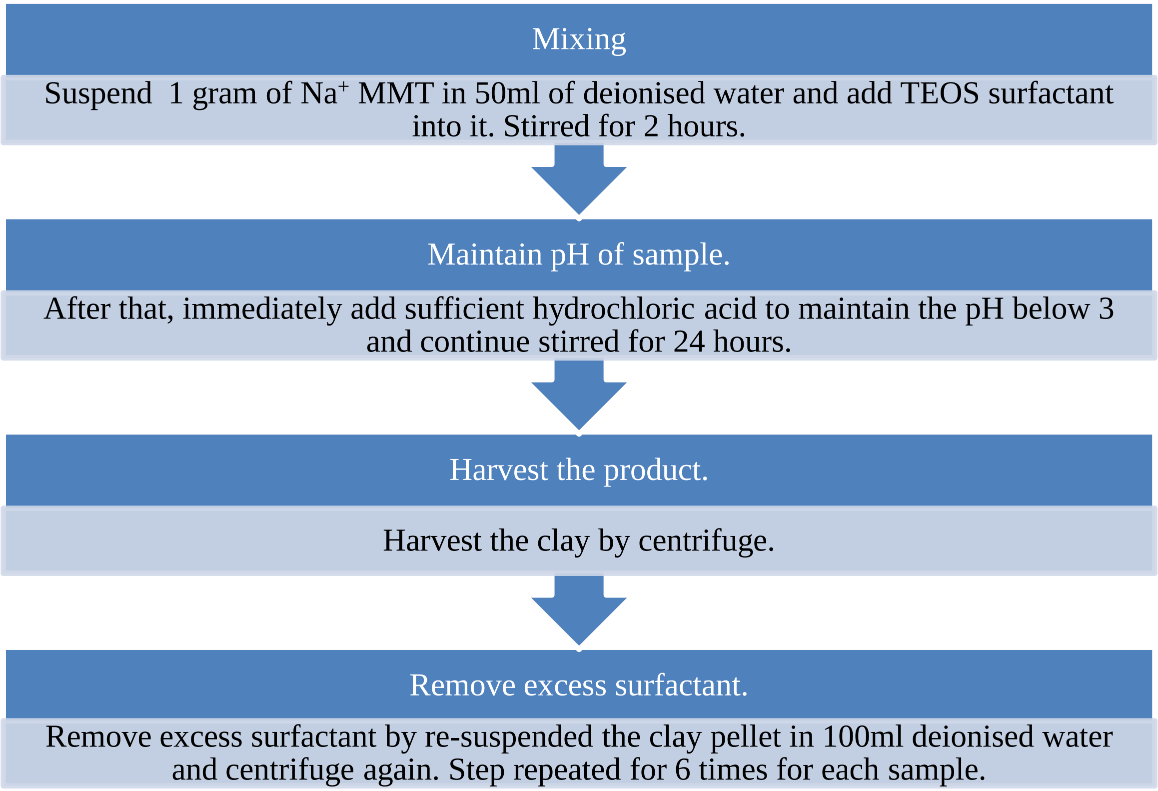
Filter and Wash

Filter and wash the sample again and dried it in vacuum for 12 h at 80 ^{0}C.

Figure 3.3: Methodology for TMI salt Modification For Ion Exchange Method

3.3.4 Surfactant Method

For surfactant method, TEOS surfactant is reacted to pristine clay/ Na^+ MMT / Cloisite-Na before us mixing it with polymer /PLA. We used 1 gram of Cloisite-Na and 50ml and 100ml of deionised water. The process flow is shown bellow.



Mixing

Suspend 1 gram of Na^+ MMT in 50ml of deionised water and add TEOS surfactant into it. Stirred for 2 hours.

Maintain pH of sample.

After that, immediately add sufficient hydrochloric acid to maintain the pH below 3 and continue stirred for 24 hours.

Harvest the product.

Harvest the clay by centrifuge.

Remove excess surfactant.

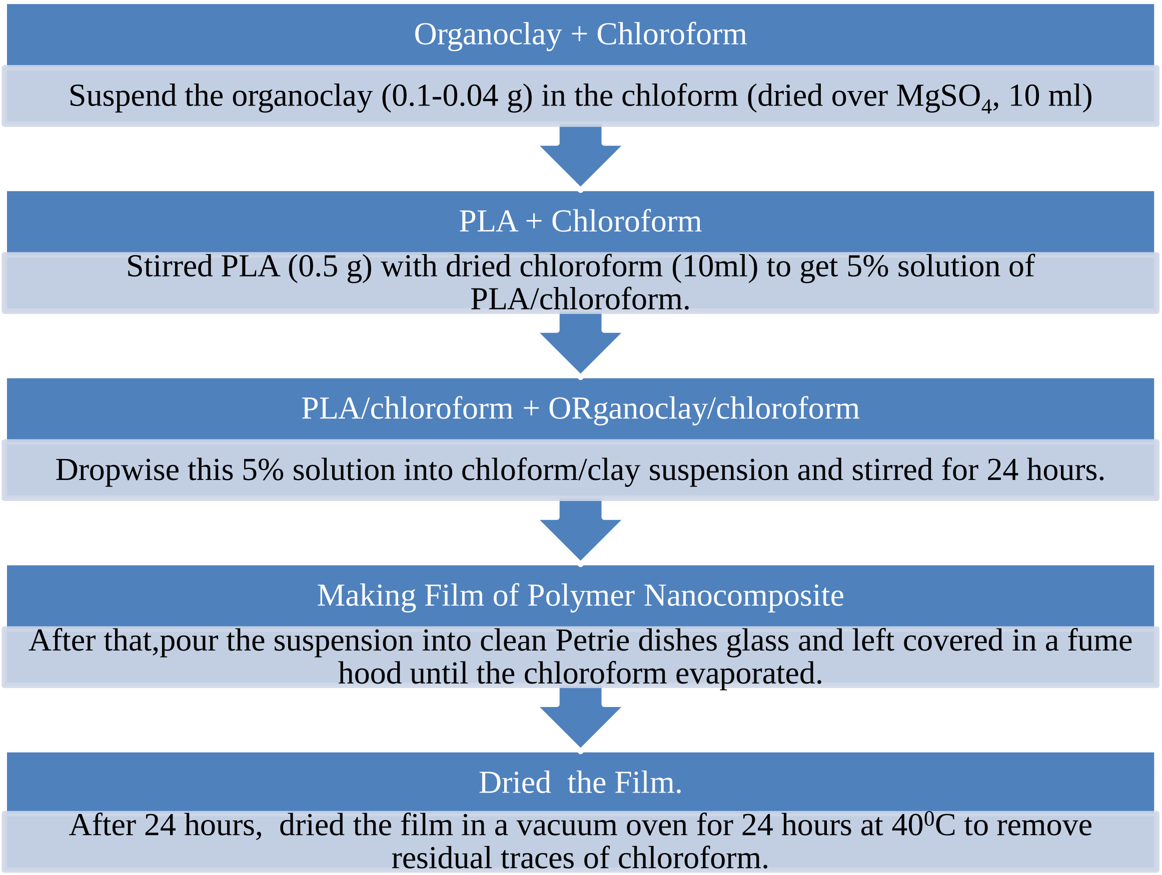
Remove excess surfactant by re-suspended the clay pellet in 100ml deionised water and centrifuge again. Step repeated for 6 times for each sample.

Figure 3.4: Methodology for Surfactant method

A range of sample was prepared by varying the amount of surfactant relative to the weight of clay calculated on a charge basis; assume one positive charge per molecule of betaine. The range was from 0.2 to 16 times the cation exchange capacity (CEC) of the clay which was given as 92 miliequivalents per 100 grams by the manufacturer.

3.4 Fabrication of PLA Nanocomposites.

After finishing with modification Na^+ MMT, we proceed with the process of intercalation of organoclay with polymer /PLA. The process flow of solution exfoliation methods is shown below.



Organoclay + Chloroform

Suspend the organoclay (0.1-0.04 g) in the chloform (dried over $MgSO_4$, 10 ml)

PLA + Chloroform

Stirred PLA (0.5 g) with dried chloroform (10ml) to get 5% solution of PLA/chloroform.

PLA/chloroform + ORganoclay/chloroform

Dropwise this 5% solution into chloform/clay suspension and stirred for 24 hours.

Making Film of Polymer Nanocomposite

After that,pour the suspension into clean Petrie dishes glass and left covered in a fume hood until the chloroform evaporated.

Dried the Film.

After 24 hours, dried the film in a vacuum oven for 24 hours at 40^0C to remove residual traces of chloroform.

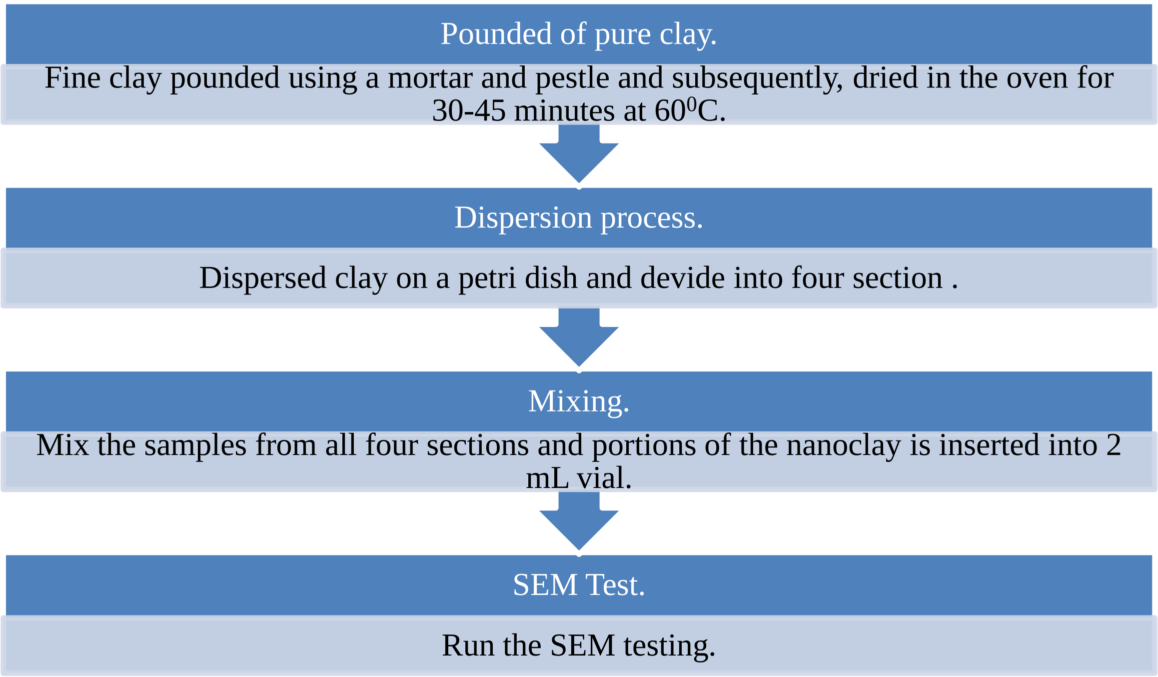
Figure 3.5: Methodology for Fabrication of PLA Nanocomposites

3.5 Characterization

We run all kinds of the characterization process to know the morphology of the sample and to prove that the modification of pristine clay and also polymer nanocomposite that we try to make is happen. There are three types of method that we can use to characterize the structure of our sample and shown below.

3.5.1 Scanning Electron Microscopy (SEM)

By running SEM testing, we will get the morphological image of organoclay (Hsiang et. al, 2003). SEM images will be taken using a backscattering detector.



Pounded of pure clay.

Fine clay pounded using a mortar and pestle and subsequently, dried in the oven for 30-45 minutes at 60^0C.

Dispersion process.

Dispersed clay on a petri dish and devide into four section .

Mixing.

Mix the samples from all four sections and portions of the nanoclay is inserted into 2 mL vial.

SEM Test.

Run the SEM testing.

Figure 3.6: Methodology for Scanning Electron Microscopy (SEM).

3.5.2 FTIR Testing of Modified Nanoclay

For FTRR testing, the test is running using SMART collector (Diffuse Reflection) head. The sample that we used is in powder form. The backgrounds of the sample were all in KBr standard. The readings of the sample are taken after the background was complete. Powder sample is making sure to be in line with the read beam to ensure accurate readings. The graph that generated shows the different level of absorbance between various peaks.

3.5.3 X-ray Diffraction (X-RD) Testing of Modified Nanoclay

For X-ray diffraction (X-RD) data were collected on a MiniFlex Rigaku using graphite-filtered Cu Ka radiation (l¼ 1.542 nm). The diffractometer was controlled using Diffrac Plus XRD Commander and the raw data were manipulated using EVA software (Wonho et. al., 2006). The organoclay specimens were pressed into an aluminium holder where sufficient sample was available, otherwise they were spread on a silicon wafer and pressed to give a flat surface of the reference plane. The PLA–organoclay nanocomposite sheets were laid flat on an aluminium block, the height of which was always adjusted so that the sample surface was the reference plane of the instrument (Morad et. al., 2008).
The *d*-spacing (*d*) of the interlayer gallery of Cloisite B30 and the PLA based nanocomposites is calculated using Bragg's equation:

$$d = \frac{n\lambda}{2d \sin \Theta}$$

d = spacing between layers of the clay

λ = wavelength of the X-ray which is 0.154nm

Ɵ = angle at the maximum point of the first peak in the spectra

n = order of diffraction

Figure 3.7: XRD Miniflex (Rigaku)

Figure 3.8: SEM JEOL 7500F-1

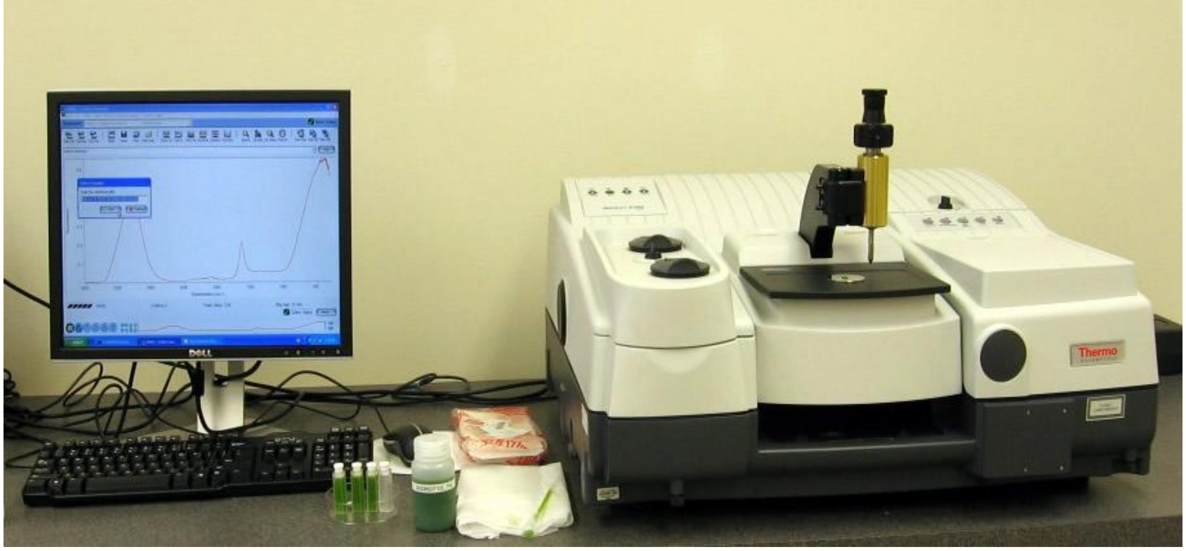


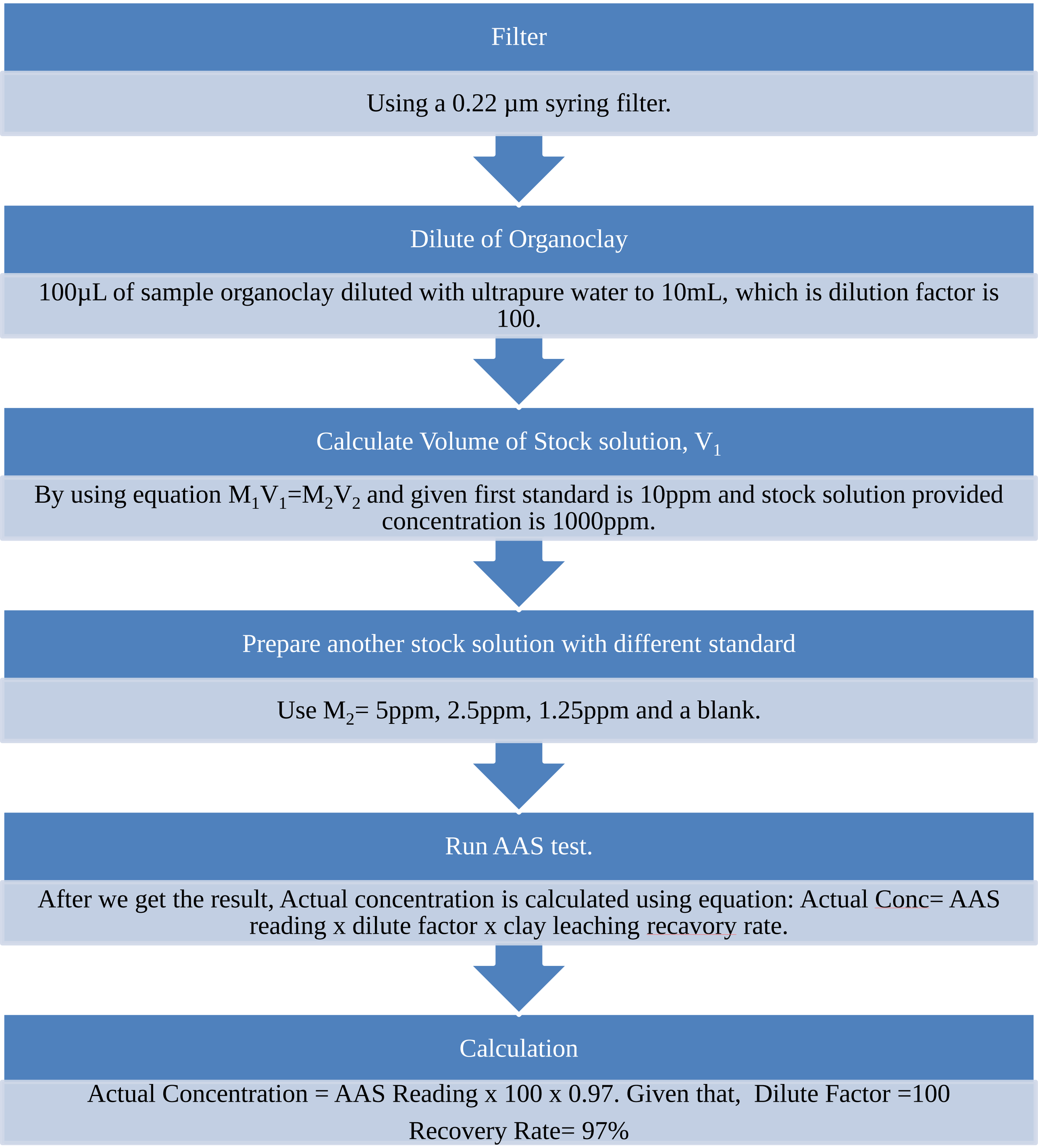
Figure 3.9: Nicolet 6700 FT-IR Spectrometer

3.5.4 Atomic Adsorption Spectrometry Testing.

The main reason we use AAS testing because it can detect the presence of Transition Metal Ions (TMIs) in the interlayer of modified nanoclay. The first thing need to be done before running AAS testing is to prepare stock solutions (V_1) with deference standard and the methods shown below.

By using equation M1V1 = M2V2, the volume of stock solution, V1 is calculated. Given that the first standard is 10ppm and stock solution provided concentration is 1000ppm.

M_1 = Conc of stock solution
V_1 = Volume stock solution need
M_2 = Conc of the first standard
V_2 = Volume of standard need



Filter

Using a 0.22 µm syring filter.

Dilute of Organoclay

100µL of sample organoclay diluted with ultrapure water to 10mL, which is dilution factor is 100.

Calculate Volume of Stock solution, V_1

By using equation $M_1V_1=M_2V_2$ and given first standard is 10ppm and stock solution provided concentration is 1000ppm.

Prepare another stock solution with different standard

Use M_2= 5ppm, 2.5ppm, 1.25ppm and a blank.

Run AAS test.

After we get the result, Actual concentration is calculated using equation: Actual Conc= AAS reading x dilute factor x clay leaching recavory rate.

Calculation

Actual Concentration = AAS Reading x 100 x 0.97. Given that, Dilute Factor =100

Recovery Rate= 97%

Figure 3.10: Methodology for AAS analysis.

Figure 3.11: Atomic Adsorption Spectroscopy.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

Polymer nanocomposites have attracted the attention of many researchers due to their improvement in mechanical, thermal,molecular barrier, flame retardant and corrosion protection properties. According to Yuan et. al, 2003, in his experimental works, he studies about the thermal and mechanical properties of polymer nanocomposites. The TGA analysis shows that neat poly(vinyl alcohol) (PVA) have a weaker thermal properties compare to PVA-Nanocomposites. The thermal decomposition of PVA-Nanocomposites shift slightly toward the higher temperature range than neat PVA. **Figure 4.1** shows the TGA curve for neat PVA and PVA-Nanocomposites.

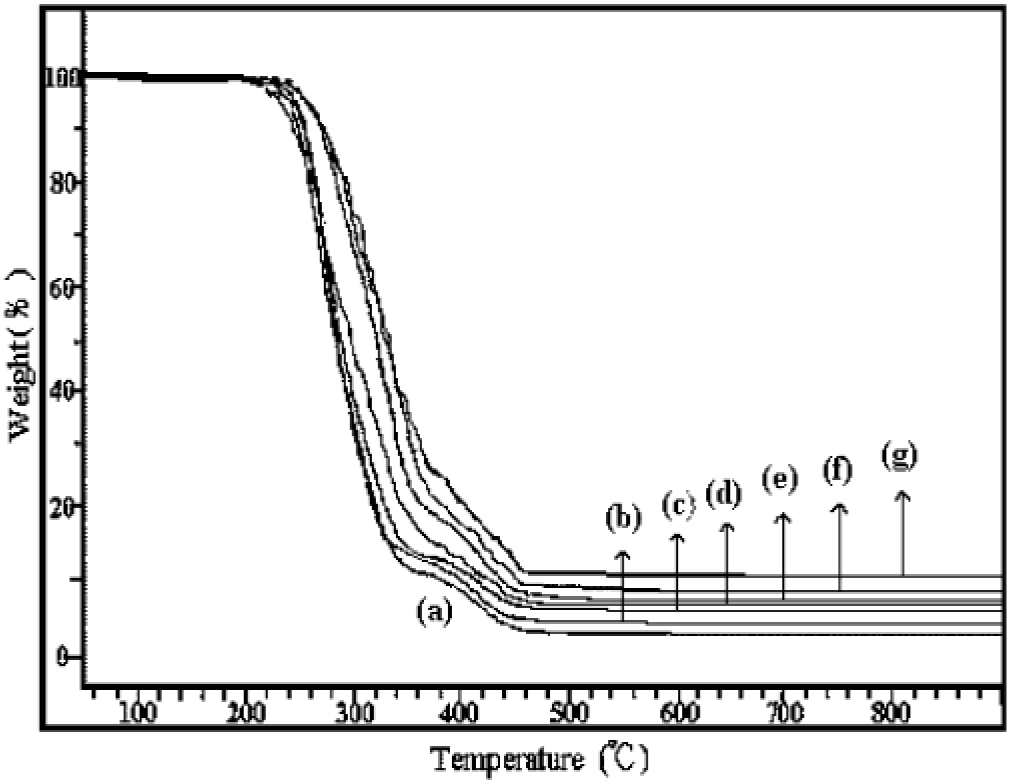


Figure 4.1: TGA curves of (a) PVA (b) CLVA0.15 (c) CLVA0.3 (d) CLVA1 (e) CLVA1.5 (f) CLVA3 (g) CLVA5.

4.2 Proposed Mechanism of Ion Exchange Method

The mechanism of surface modification of surface modification of pristine clay is illustrated in the **Figure 4.2**, **Figure 4.3** and **Figure 4.4**.

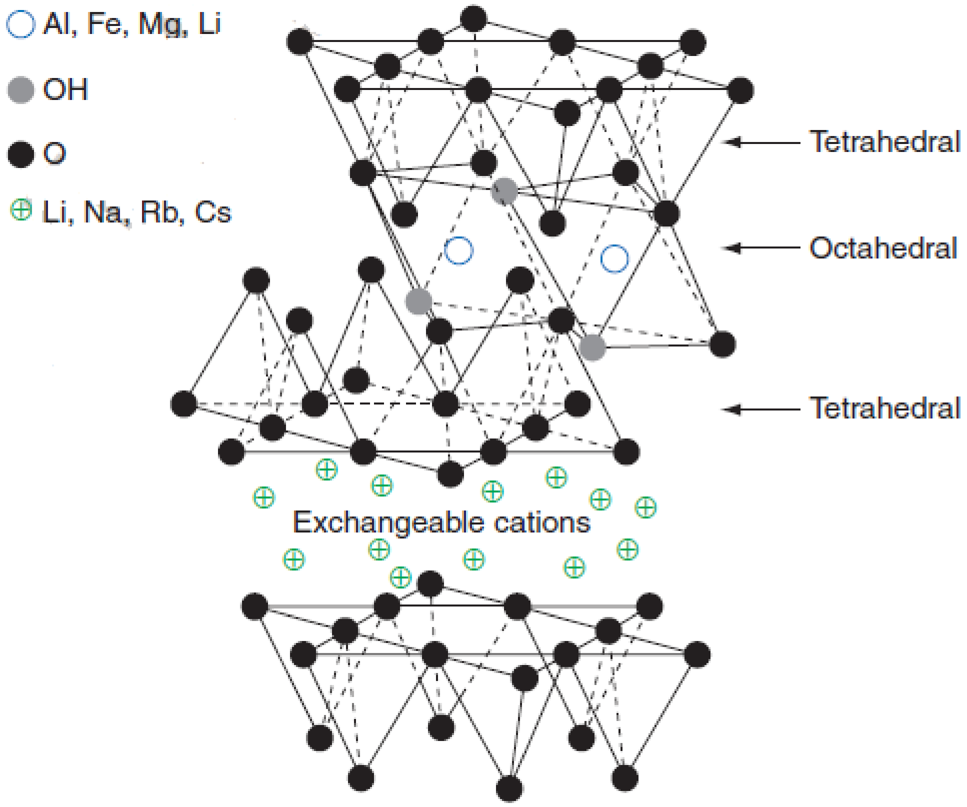
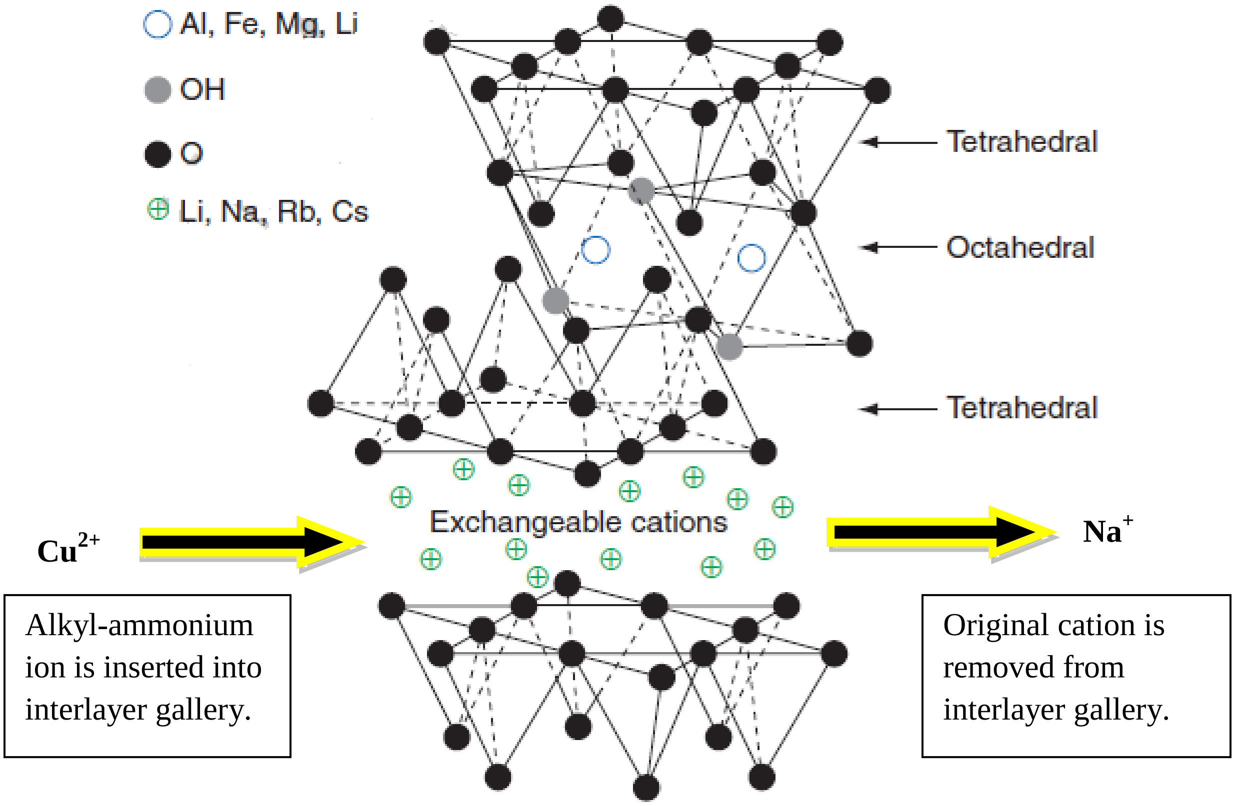


Figure 4.2: Structure of 2:1 layered silicates.

Layered silicate that was used in this experiment is sodium montmorillonite. **Figure 4.2** shows the structure of 2:1 layered silicates and as we can see here, it consist of two silica tetrahedral sheets that stacked together by weak Van der Waals force. The interlayer spacing of this adjacent layer is approximately 1nm thickness.

The interlayer spacing of two adjacent layers is quiet hydrophilic while the polymer characteristic is hydrophobic. This difference characteristic cause incompatibility between clay and polymer and intercalation-exfoliation polymer nanocomposites cannot be happening. So, by using the ion exchange method, the interlayer spacing between two adjacent layers will transform to hydrophobic characteristic.



Alkyl-ammonium ion is inserted into interlayer gallery.

Original cation is removed from interlayer gallery.

Figure 4.3: Ion exchange in 2:1 layered silicates.

Figure 4.3 shows that the cation exchange reaction in the clay interlayer gallery. The Na^+ ion is replaced by alkyl-ammonium cation which is Cu^{2+} in order to change the interlayer gallery characteristic of pristine clay and also cause the interlayer d-spacing of clay increase.

Table 4.1: The clay d-spacing differences before and after surface modification

Solvent	**2θ**	**d-spacing, Å**			
		Initial, Å	**After,Å**	**Different,Å**	**Different,nm**
Methanol	5.99	10.81	14.74	3.93	0.393
Ethanol	8.72	10.81	10.06	-0.75	-0.075
Water	7.7	10.81	11.47	0.66	0.066

Note: 1 Å = 0.1 nanometer

Table 4.1 shows the differences d-spacing of clay interlayer gallery before and after the surface modification by using a different type of solvent. This result is come out from the XRD analysis and will discuss more details in Structure, Morphologies of Modified Clay subtopic.

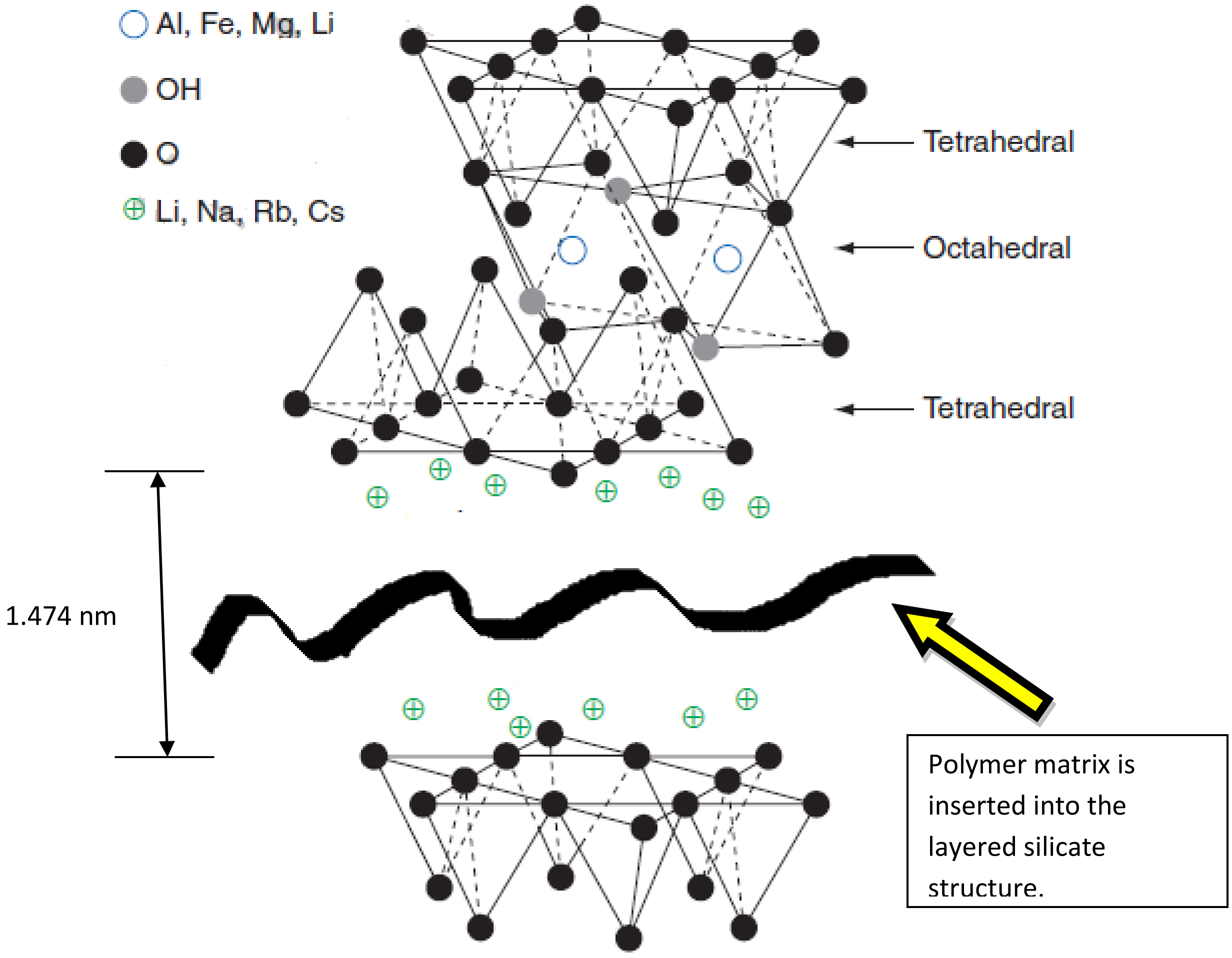


Figure 4.4: Insertion of polymer matrix into layered silicate structure.

Figure 4.4 shows the d-spacing or interlayer gallery increases up to 4.7826 nm after modified using methanol solvent and there is a polymer matrix is inserted into the layered silicate structure. This insertion will form an intercalation polymer nanocompsite structure.

4.3 Characterization of TMIs in Modified Clays.

Before preceding the fabrication of polymer nanocomposites, it is important to make sure that the modification of pristine clay by using the ion exchange method is achieved. In ion exchange modification, the inorganic cation that located in the interlayer of clay will be replaced with a catalytically active transition metal ion (TMIs) to play a role in the charring process of polymer nanocomposites.

In this experiment, the pristine clay was modified by using Copper (II) Chloride and Copper (Cu) atom act as a catalytically active TMI ion. The reason of this TMIs selection is when using Cu as a solvent, the Cu atom content in modified clay exceeds the CEC values. In details, the overall amount of absorbed Cu ions combined with residual surfactant seemed to exceed the overall ion exchange capacity.

To detect the presence of Cu / Transition Metal Ions (TMIs) in the interlayer of modified nanoclay, an Atomic Adsorption Spectrometry analysis need to be done. After diluting the sample, and also prepare the standard and stock solutions, the AAS test is run. The result of this analysis is shown in **Table 4.2**.

TABLE 4.2: AAS Analysis of the Cu/ TMI Content in Modified Nanoclay.

Sample	Mean Sample Cu Concentration, mg/L	Mean Standard Cu Concentartion, mg/L	SD
$CuCl_2$ Methanol/ D	14.13	14.13	0.039
$CuCl_2$ Ethanol/ A	13.66	13.66	0.552
$CuCl_2$ Water/ B	13.94	13.94	0.015

Based on the **Table 4.2**, every sample has a Cu ion in their interlayer gallery. The highest mean Cu ion concentration is in sample $CuCl_2$ Methanol with 14.13 mg/L and followed by $CuCl_2$ Water and $CuCl_2$ Ethanol with 13.94mg/l and 13.66mg/L respectively. Based on this analysis, we also can identify that the concentration of TMIs in organoclay also dependent on the type of solvent used. So, the best solvent that should be used in the ion exchange modification is methanol compare to water and ethanol.

The presence of TMIs in organoclay also can be proven by using Scanning Electron Microscopy (SEM), to get morphology images of organoclay. Organoclay containing TMIs, if precipitated from organic solvent or water, could form distinct crystallites, which would appear in SEM micrograph as a bright spot. Their shape would depend on the crystal structure of TMI (Pranav et. al, 2007). **Figure 4.5** shows an SEM image for pristine clay while **Figure 4.6** shows an SEM image for modified clay.

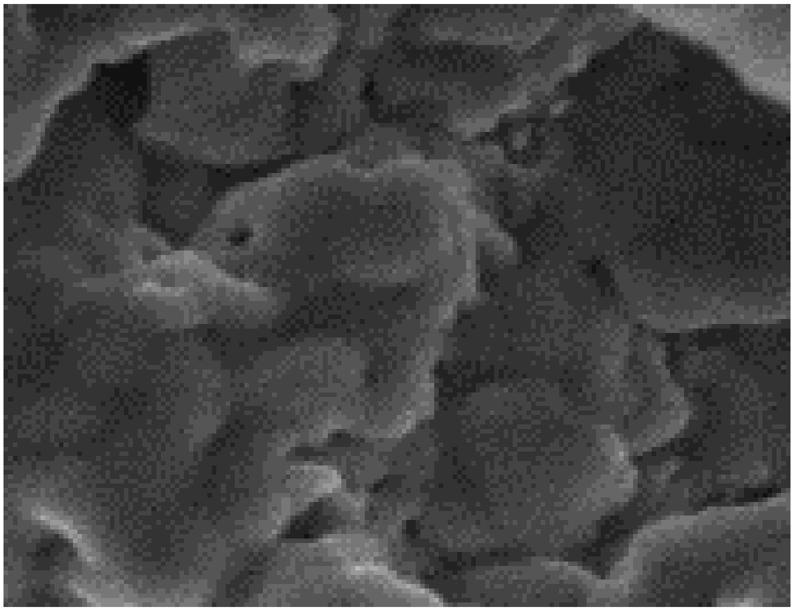
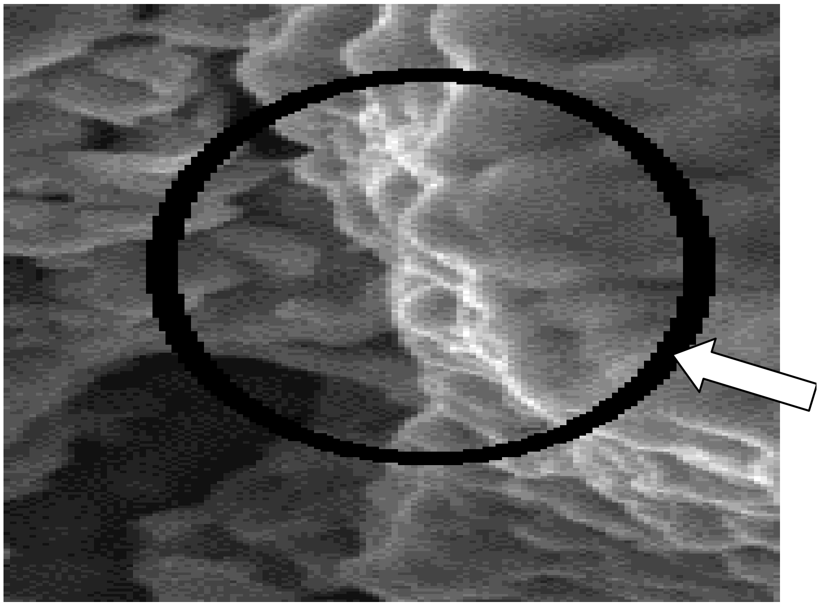


Figure 4.5: SEM image for pristine clay.



Copper ion / bright spot.

Figure 4.6: SEM images of pristine clay modified with Copper.

Based on **Figure 4.5**, the morphology of pristine clay shows only a little bright spot, while **Figure 4.6** shows a high density of bright spot (circle) in their morphology. This has happened when Copper ions are absorbed into the interlayer gallery of pristine clay and form distinct crystallites. After the presence of TMIs ion in the interlayer gallery of organoclay is proven, the study of organoclay interlayer gallery d-spacing can be proceed by using XRD analysis.

4.4 Structure, Morphologies of Organoclay Using Ion Exchange Method.

After modifying the structure of pristine clay by using the ion exchange method and surfactant method, the basal spacing of interlayer galleries of pristine and modified clay need to be analyzed in order to study the global morphology in reciprocal space and also to make sure that the modification using the ion exchange method and surfactant method are achieved. In this ion exchange experiment, the TMI salt used is 0.3M Copper (II) Chloride with three varieties of solvent which is methanol, ethanol, and water. To analyze the d-spacing of organoclay, a XRD analysis needs to be done. By referring **Figure 4.7**, its shows the summary of XRD pattern for pristine clay and organoclay that have modified with water, ethanol, and methanol solvent. **Table 4.3** shows the value of organoclay d-spacing before and after the modification by using ion exchange method in nanometers units (1Å = 0.1 nm). Note that, the initial value is base on XRD analysis for pristine clay that shows at peak $2\theta = 8.17^{o}$, the d-spacing value is 1.081 nm.

The method that uses to calculate the d-spacing of clay interlayer is by using Bragg's equation:

$$d = \frac{n\lambda}{2\sin\Theta}$$

d = spacing between layers of the clay

λ = wavelength of the X-ray which is 0.154nm

Ɵ = angle at the maximum point of the first peak in the spectra

n = order of diffraction

For the average basal spacing for pristine clay, at peak d001, $2\theta = 8.17^{o}$ and by substituting these value into Bragg's equation, the d-spacing value or average basal spacing is 1.081 nm.

$$d = \frac{1(0.154\text{nm})}{2\sin(\frac{8.17}{2})}$$

= 1.081 nm

The average basal spacing values for ion exchange method that using methanol solvent at peak d001, 2θ = 5.99^o is 1.474 nm.

$$d = \frac{1(0.154\text{nm})}{2\sin(\frac{5.99}{2})}$$

= 1.474 nm

For the surface modification that using ethanol solvent, the peak d001 is at 2θ = 8.78^o. So the average basal spacing for this organoclay is 1.006 nm.

$$d = \frac{1(0.154\text{nm})}{2\sin(\frac{8.78}{2})}$$

= 1.006 nm

The average basal spacing for modification using water at peak d001, 2θ = 7.7^o is 1.147 nm.

$$d = \frac{1(0.154\text{nm})}{2\sin(\frac{7.7}{2})}$$

= 1.147 nm

The increasing of d-spacing of pristine clay before and after modification is calculated and table in **Table 4.3**.

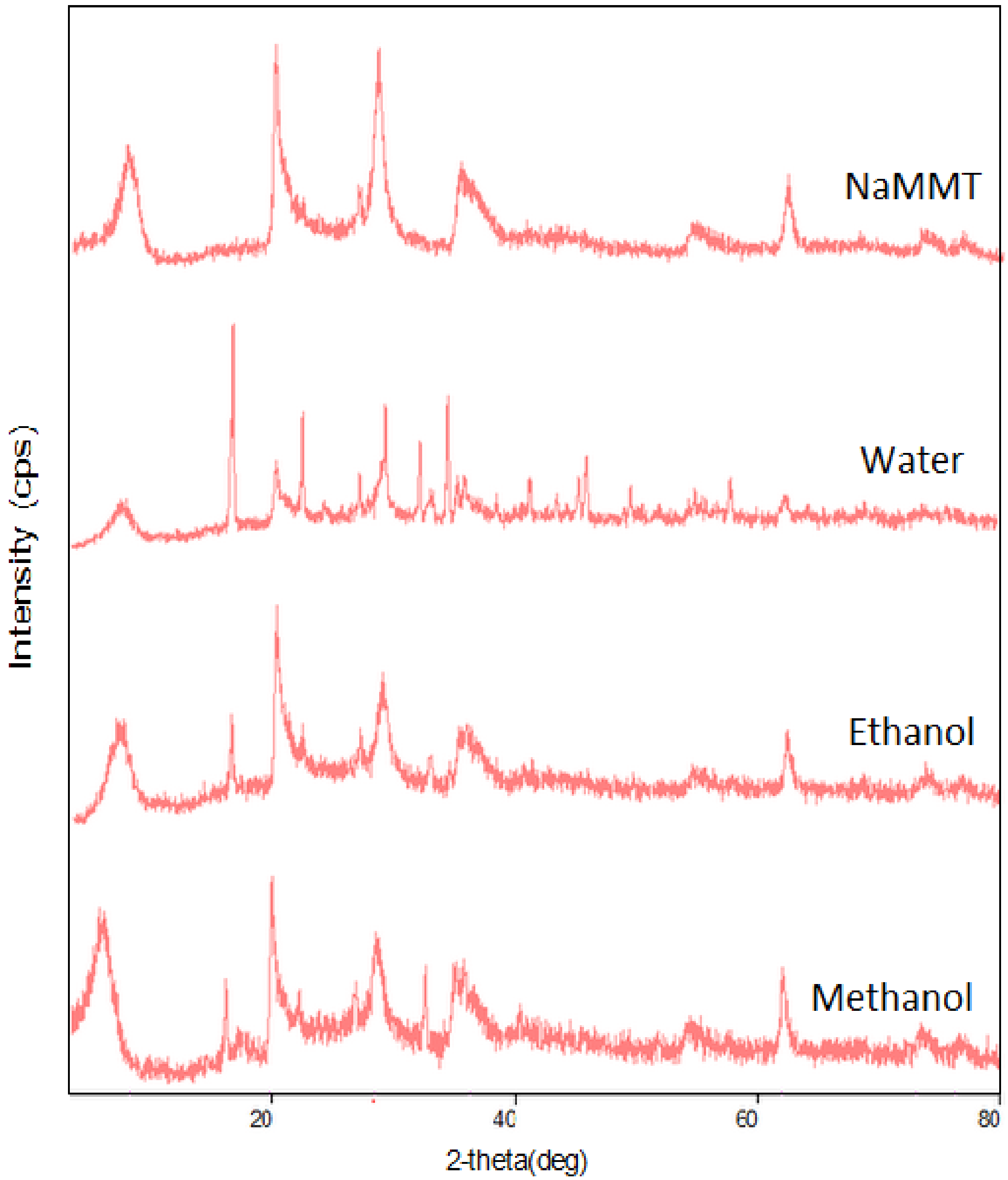


Figure 4.7: XRD pattern of pristine clay and pristine clay after surface modification using methanol, ethanol and, water as a solvent.

Table 4.3: The clay d-spacing differences before and after surface modification

Solvent	**2θ**	**d-spacing, nm**		
		Initial	**After**	**Different**
Methanol	5.99	1.081	1.474	0.393
Ethanol	8.72	1.081	1.006	-0.075
Water	7.7	1.081	1.147	0.066

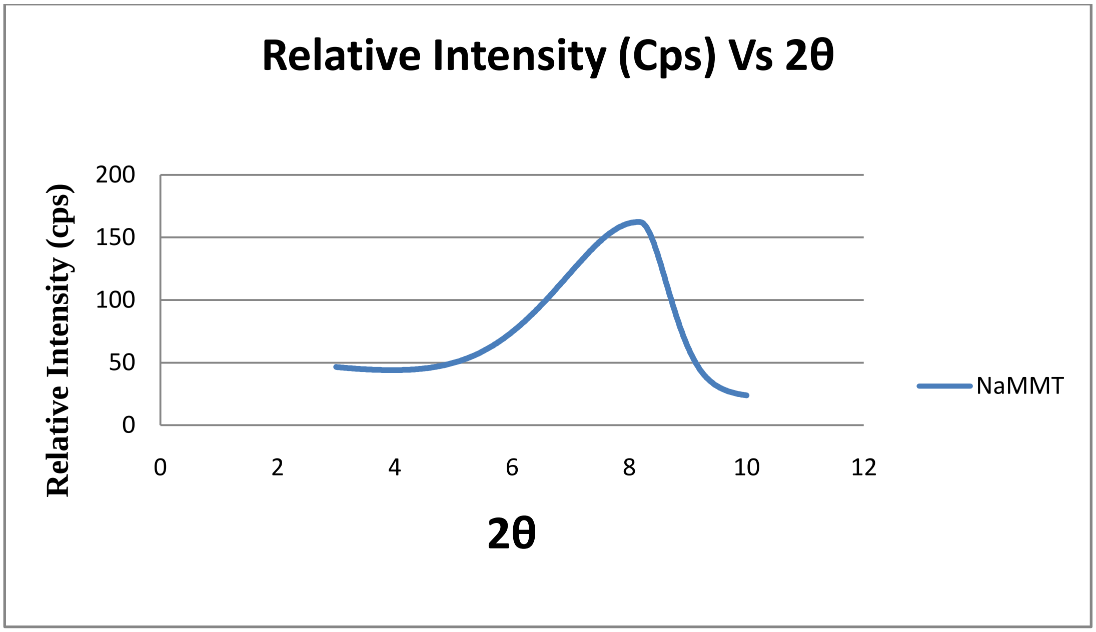


Figure 4.8: Intensity Vs 2θ for NaMMT

Figure 4.8 shows the X-ray diffraction pattern of the pure NaMMT and a diffraction pattern peak d_{001} at $2\theta = 8.17^{o}$, which correspond to the average basal spacing of 1.081 nm From the analysis, the three different solvent that used for ion exchange modification of pristine clay give a different average basal spacing compared to the pristine clay XRD pattern.

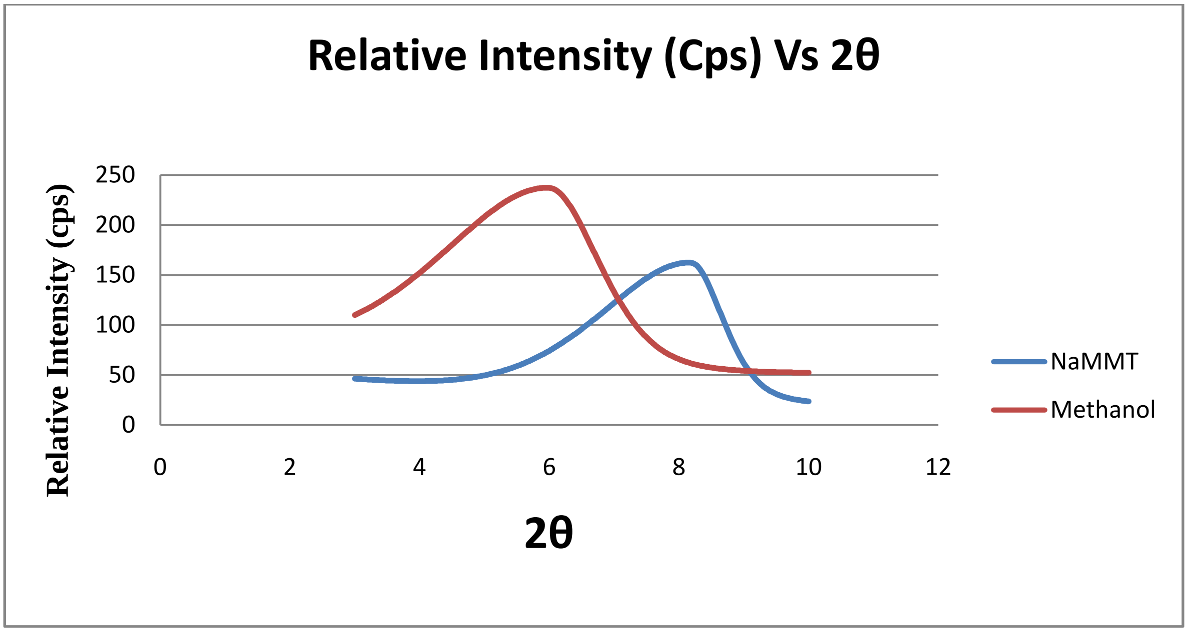


Figure 4.9: Intensity Vs 2θ for pristine clay modification using methanol solvent.

By referring **Figure 4.9**, for pristine clay that modified by using methanol as a solvent, the analysis shows that a diffraction pattern peak d_{001} at $2\theta = 5.99^o$, which correspond to the average basal spacing of 1.474 nm. The diffractograms of pristine clay and the modified clay (Methanol) shows that the original basal spacing of pristine clay increases from 1.081 nm to 1.474 nm after ion exchange modification. So, there was an expanding of the clay interlayer spacing with an increasing of up to 0.393 nm and the modification objectives are achieved.

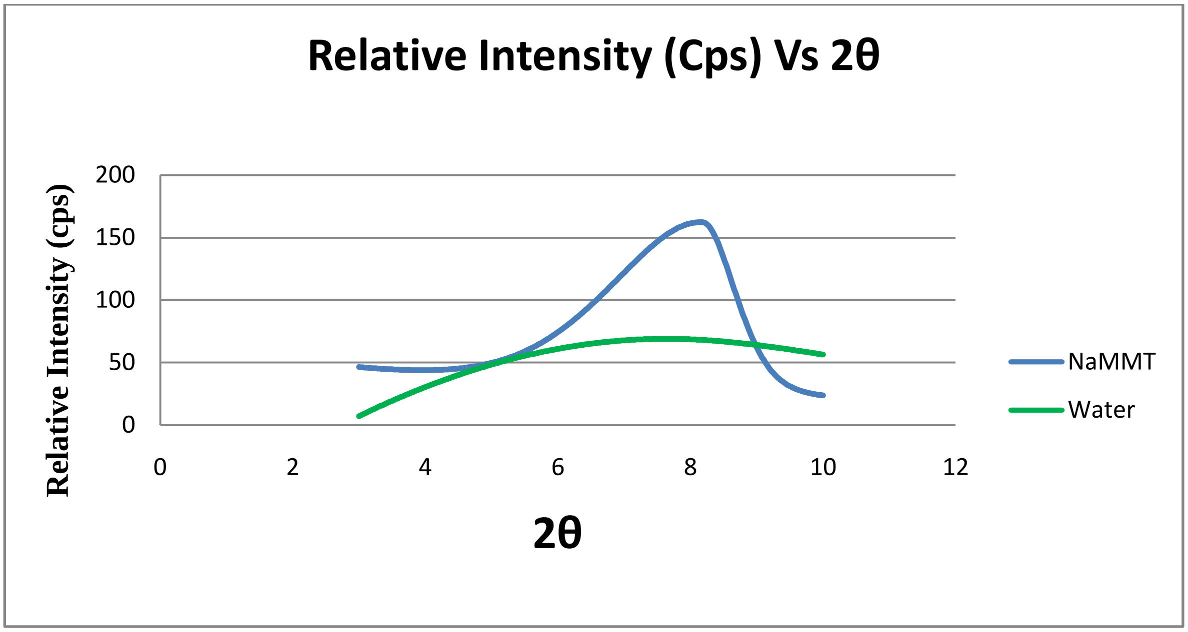


Figure 4.10: Intensity Vs 2θ for water and NaMMT

For pristine clay modification that using water as their solvent, the XRD analysis from **Figure 4.10** shows that a diffraction pattern peak d_{001} at 2θ = 7.7^{o}, which corresponding to the average basal spacing of, d-spacing = 1.147 nm. From the analysis, it is shown that the spacing of clay interlayer is increased up to 0.066 nm. So, the modification of pure clay by using water as a solvent also achieved.

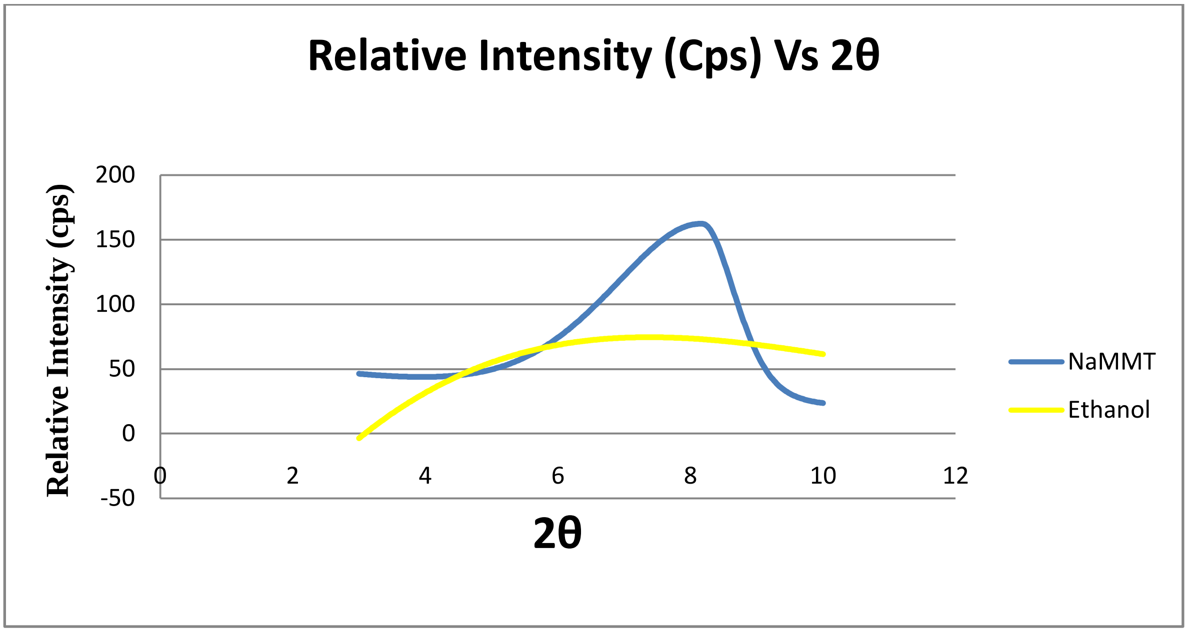


Figure 4.11: Intensity Vs 2θ ethanol and NaMMT

Figure 4.11 shows the analysis for modification of pristine clay with ethanol as a solvent. The diffraction pattern peak at 2θ = 8.72^{o}, which correspond to the average basal spacing of 1.006 nm. There was no clay interlayer expanding and this might happen because of some error during doing the experiment. According to Shipeng et. al, 2011, in his experimental work, XRD analysis of the ion exchange method using ethanol as a solvent shows there is an increasing of interlayer d-spacing up to 0.089 nm. It means, the real result of ion exchange modification using ethanol solvent should give an increase in their interlayer d-spacing.

Summary from **Figure 4.12** shows that only two types of solvent that used for pristine clay modification showed an improvement in increasing the interlayer gallery of clay. Methanol solvent gives the highest expand of clay interlayer spacing compared to the water and ethanol solvent with the increasing of 0.393 nm. The expanding of interlayer spacing of water is smaller than methanol solvent but higher than ethanol solvent with increasing of 0.066 nm. The surface modification that using ethanol as a solvent gives a negative result because of some error during the modification such as the weight % ratio between pristine clay and $CuCl_2$ are not followed the specification to form organoclay.

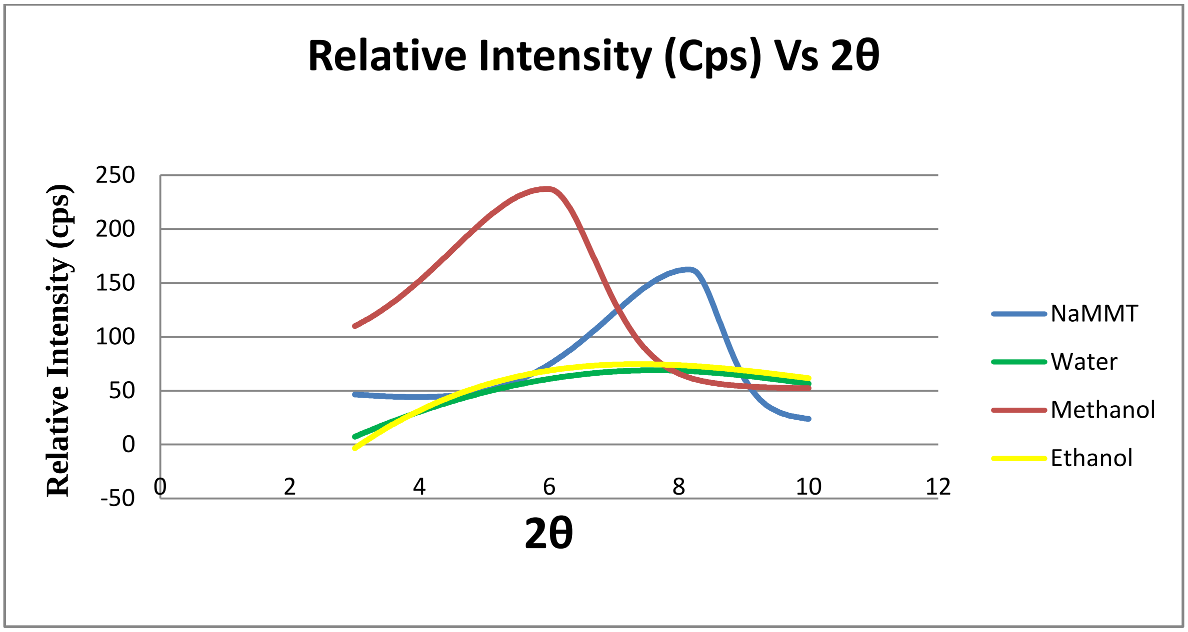


Figure 4.12: Summary XRD graph pattern of pristine clay and pristine clay after surface modification using methanol, ethanol and, water as a solvent.

Conclusion, the best solvent that should be chosen in an ion exchange method is methanol because it gives the highest average basal spacing because the reason of this modification is to make sure that the d-spacing interlayer gallery of pristine clay is highly increase to ensure that layered clay are filled into a polymer matrix to form intercalated or exfoliated nanocomposites. The XRD analysis of the ion exchange method supports the AAS analysis in term of choosing solvent and the modification of pristine clay is a success. This conclusion is supported by Pranav et.al, 2007, in his experimental works, he stated that the solvent choosing also important because it will affect the surface modification effectiveness.

After the modification of surface gallery using the ion exchange method is success and proven. Then, the fabrication of PLA-Nanocomposites is proceeding and the polymer nanocomposites is tested using XRD to check the nanostructure of PLA-Nanocomposites by comparing it XRD pattern with the pristine clay XRD pattern.

For the fabrication PLA-Nanocomposites, the fabrication used a different mass percentage ratio of organoclay and poly (lactic acid) which is 1%, 2%, 3% and 4% organoclay composition in the polymer nanocomposites. The modified clay that use in this experiment is the pristine clay that modified with methanol solvent because the previous analysis proved that this organically have higher average basal spacing compared to ethanol and water so that the percentage of polymer matrix to intercalate in the clay interlayer gallery is high. The example for 1% organically PLA-Nanocomposites experiment is the desired mass of PLA-Nanocomposites is equal to 4 grams. If the percentage of clay mass is 1% of the total mass, so the mass for organically is 0.04 g while the mass of PLA is 3.96 g.

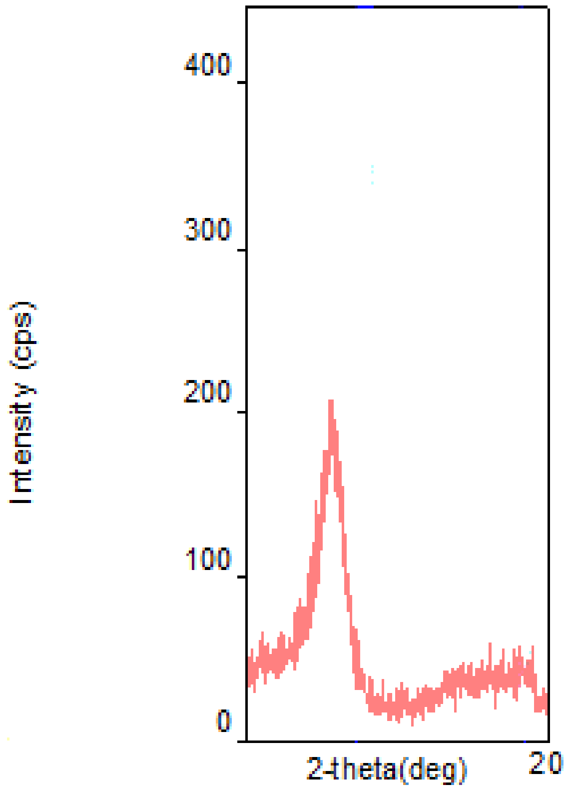
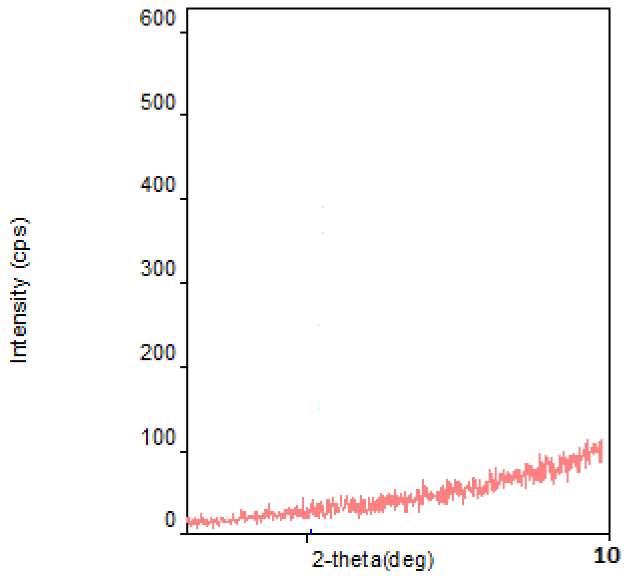
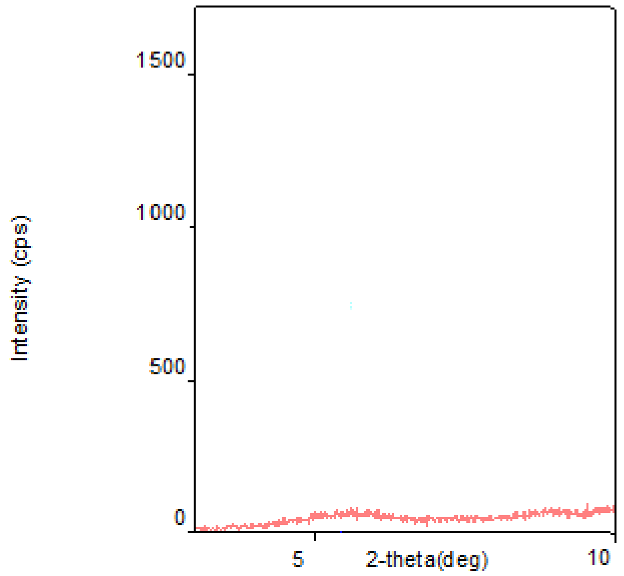


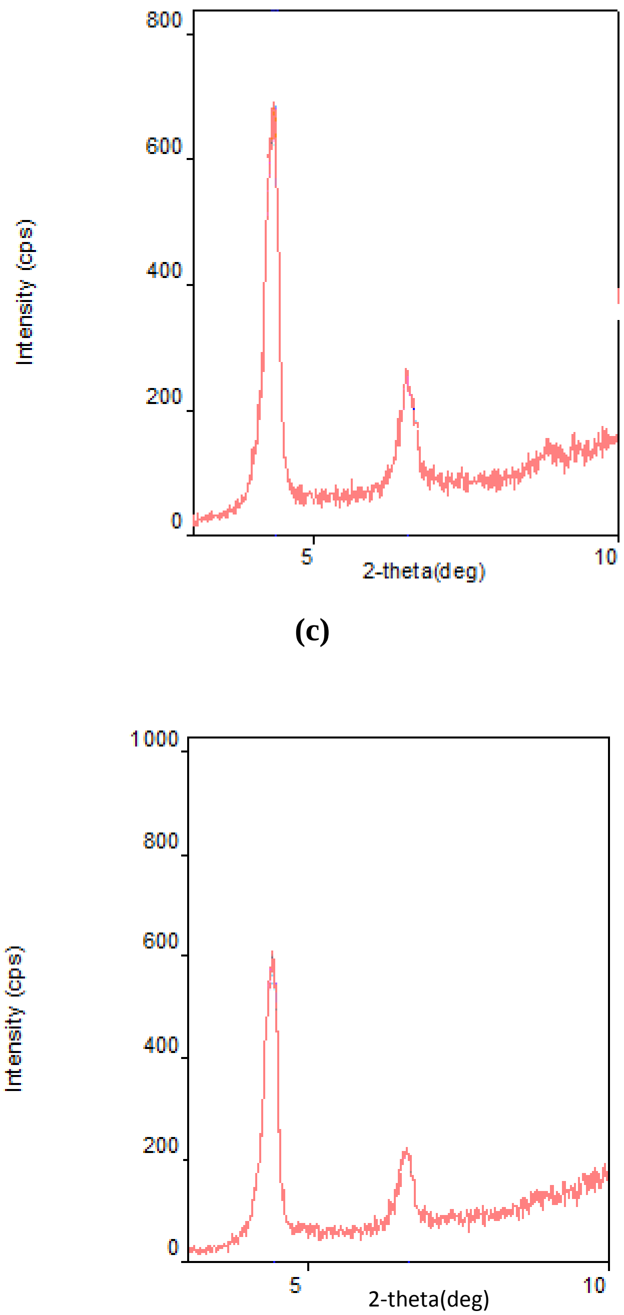
Figure 4.13: XRD pattern for pristine clay.


Intensity (cps)
600
500
400
300
200
100
0
2-theta(deg)
10

(a)


Intensity (cps)
1500
1000
500
0
5
2-theta(deg)
10

(b)



(c)

(d)

Figure 4.14: XRD pattern for (a) 1 wt % (b) 2 wt %, (c) 3 wt % and (d) 4wt % of organoclay PLA-Nanocomposites.

By comparing the XRD pattern of pristine clay with 1 wt % organoclay PLA-Nanocomposites, it shows that there is a diffraction pattern peak d_{001} for pristine clay (**Figure 4.13**) while there is no diffraction pattern peak d_{001} for 1 wt % organoclay PLA-Nanocomposites pattern (**Figure 4.14 (a)**). The standard range for diffraction pattern peak for XRD analysis is at $2\theta = 0^o$ until $2\theta = 10^o$. The 1 wt % PLA-NaMMT shows no diffraction pattern peak because the insertion of polymer matrix into a layered silicate structure cause the two adjacent layers in organoclay galleries separate and weaker or diminish the interlayer Van der Waals force.

In simple words there is no characteristic peak due to the regular stacking of the silicate layers in polymer matrix. In the end, the silicate layers are completely and uniformly dispersed in a continuous polymer matrix. According to Hussain et. al, 2006, this type of layered silicates is specified as exfoliated nanocomposites.

For the 2 wt % organoclay PLA-Nanocomposites result (**Figure 4.14 (b)**), the XRD analysis shows a quiet similar pattern with 1 wt % PLA-NaMMT. It means the 2 wt % NaMMT also has an exfoliated nanocomposites structure.

For the 3 wt % organoclay PLA-Nanocomposites **(Figure 4.14 (c))**, the XRD pattern shows the presence of diffraction pattern peak d_{001} at $2\theta = 4.345^o$, which correspond to the average basal spacing of 2.0312 nm. This average basal spacing is value is calculated using Bragg's equation.

$$d = \frac{1(0.154\text{nm})}{2\sin(\frac{4.345}{2})}$$

$$= 2.0312 \text{ nm}$$

The average basal spacing for pristine is 1.081 nm, so there was an expanding of the interlayer spacing of PLA-Nanocomposites which is 0.9502 nm. According to Ray et. al, 2003, the expansion of interlayer gallery is happening because the insertion of a polymer matrix into the layered silicate structure occurs in a crystallographically regular fashion, regardless of the clay to polymer ratio. Intercalated nanocomposites are normally interlayer by a few molecular layers of polymer. Properties of the composites typically resemble those of ceramic materials. This polymer nanocomposite is called as intercalated polymer nanocomposites structure.

For the 4 wt % organoclay PLA-Nanocomposites XRD analysis **(Figure 4.14 (d))**, the pattern shows there is also a presence of diffraction pattern peak d_{001} at $2\theta = 4.415^o$ which correspond to the average basal spacing of 2.0 nm. The d-spacing expansion of this polymer nanocomposite is about 0.919 nm which is smaller than d-spacing for 3 wt % organoclay PLA-Nanocomposites. It means the percentage polymer matrix for 4 wt % PLA-NaMMT that intercalate in the interlayer galleries of organoclay is smaller than 3 wt % PLA-NaMMT. This XRD analysis for 4 wt % PLA-NaMMT also shows an intercalated nanocomposites structure.

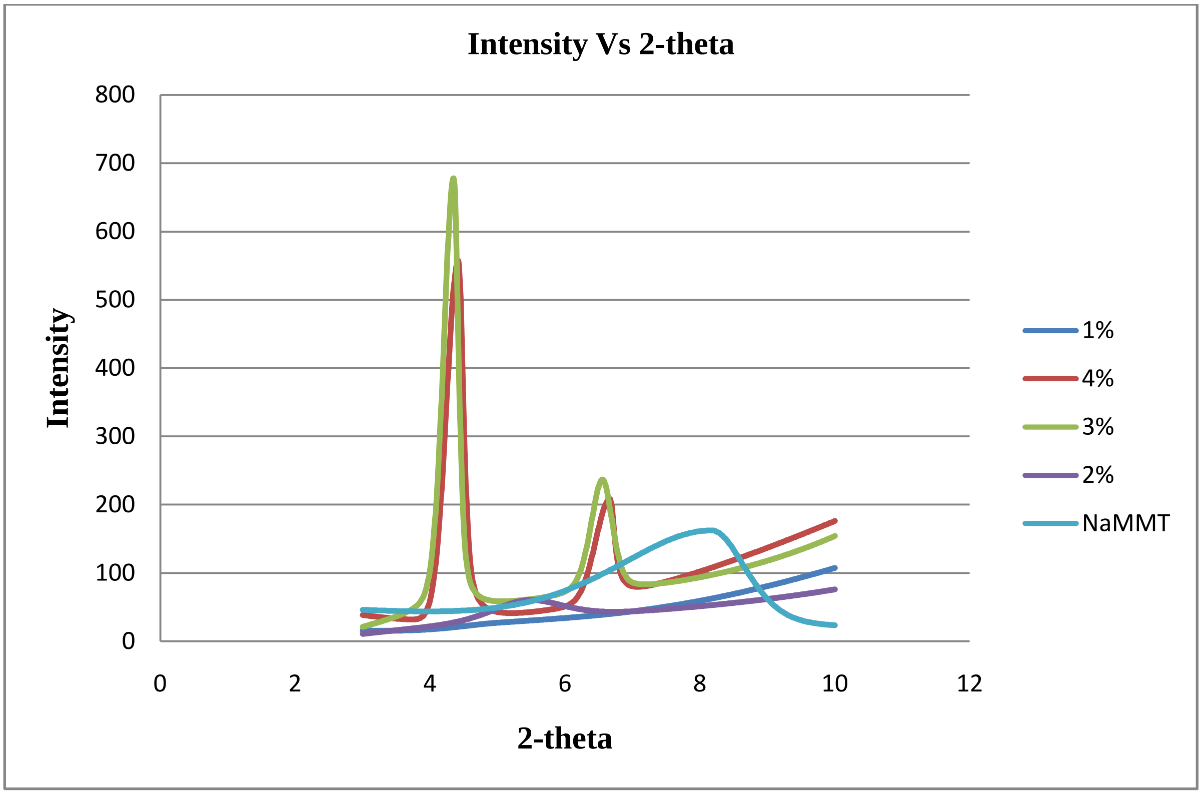
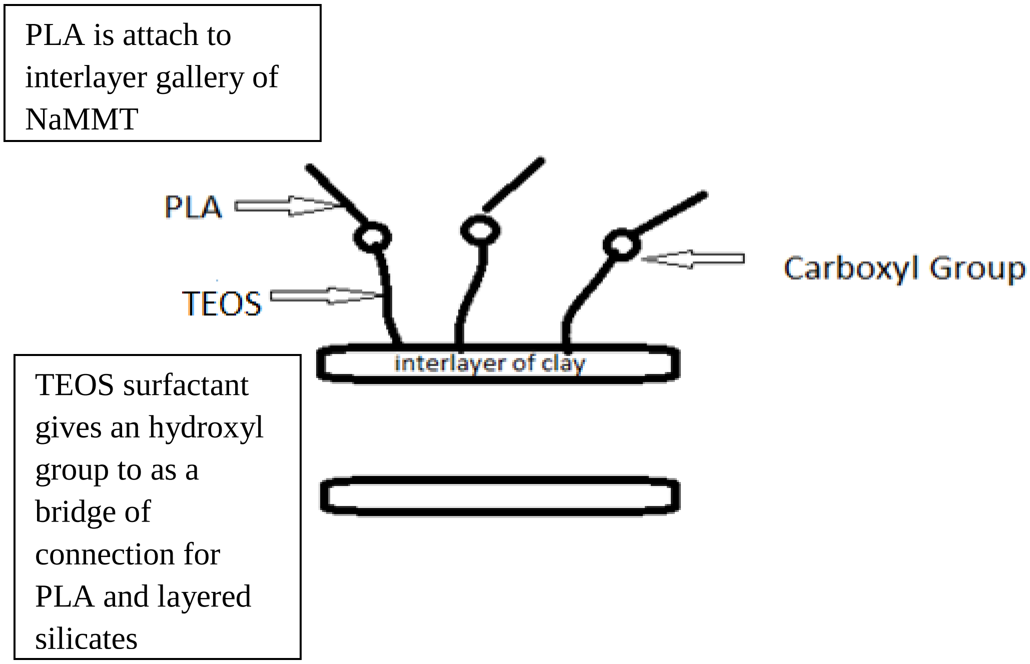


Figure 4.15: Summary XRD pattern.

Conclusion, the best organoclay weight % that should be used in fabrication of PLA-Nanocomposites is 1 wt %, followed by 2 wt %, 3 wt % and 4 wt %. The lowest usage of clay wt % in the fabrication of PLA-Nanocomposites gives the best polymer nanocomposites structure. In the previous study by another researcher, the best polymer nanocomposites structure is exfoliated, followed by intercalated nanocomposites structure. According to Liu et. al, 2006, exfoliation of polymer nanocomposites has been the ultimate goal of most researchers because this morphology is expected to lead to dramatic improvement in nanocomposites properties, with a much lower required loading of fillers than traditional composite. At the end, the second objective of this study which is to fabricate PLA-Nanocomposite using organoclay from ion exchange method with PLA-polymer is achieved.

4.5 Proposed Mechanism of Surfactant Method

Surfactant method is a direct grafting reaction in the covalent bond on the clay surface. By using TEOS as a surfactant in these studies, it will introduce a second functionality, namely the carboxyl group, into the nanocomposites matrix at the interface between the silicate surface and the polymer. This carboxyl group could interact with the polar regions of the PLA chain. Carboxyl groups have been shown to be protonated in the highly acidic environment of the interlayer space. It has also been shown that the carboxyl group in TEOS–MMT organoclay cans catalyst curing in epoxy resins (Andrew et. al, 2009). **Figure 4.16** shows the mechanism of surfactant method.



PLA is attach to interlayer gallery of NaMMT

TEOS surfactant gives an hydroxyl group to as a bridge of connection for PLA and layered silicates

Figure 4.16: Proposed mechanism of surfactant method.

4.6 Structure, Morphologies of Organoclay Using Surfactant Method.

After modifying the structure of pristine clay by using the surfactant method, the Fourier Transform Infrared Spectroscopy (FTIR) analysis need to be done in order to justify the surface modification of pristine clay is achieved. The FTIR pattern is discussed below.

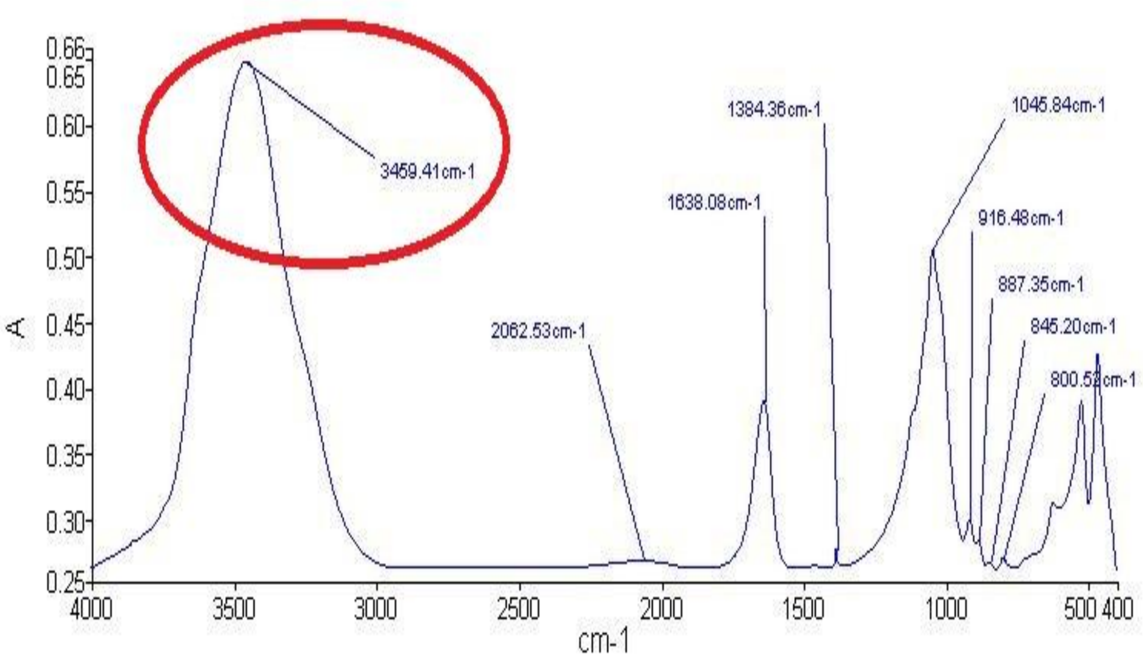


Figure 4.17 (a): FTIR pattern for pristine clay.

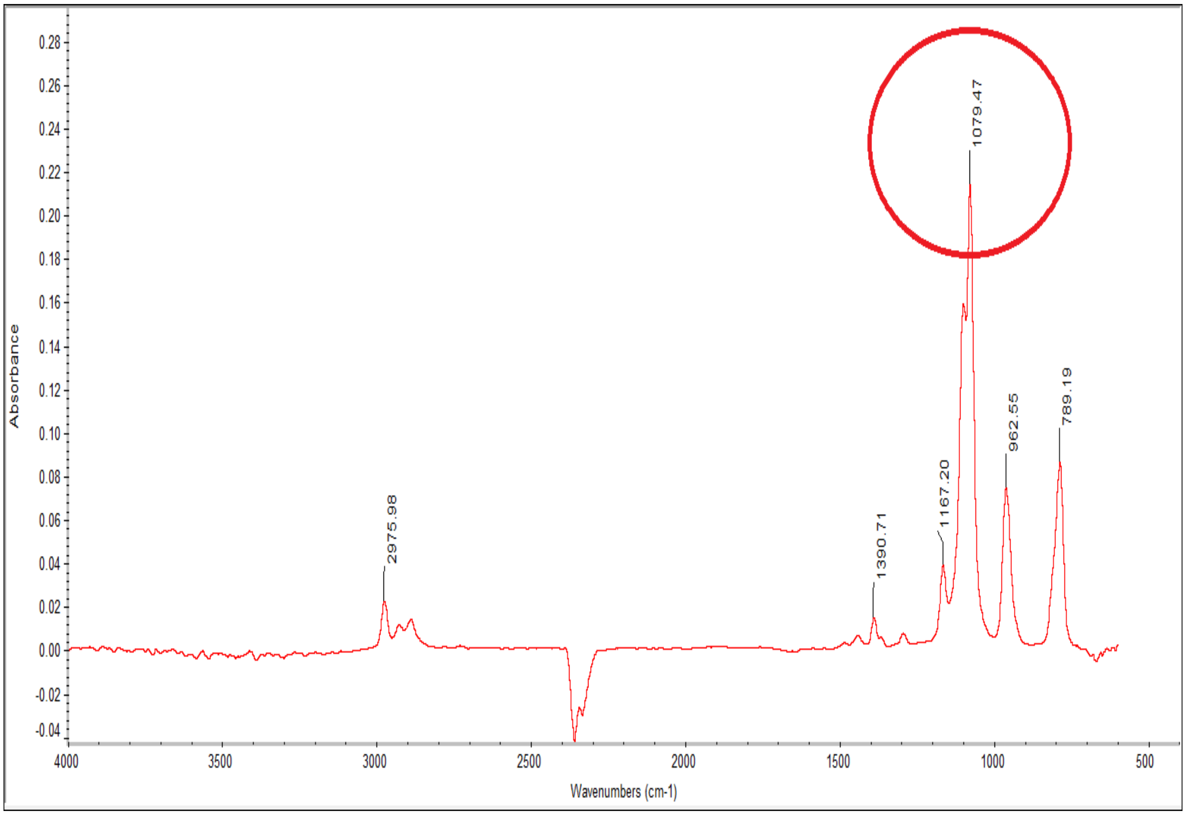


Figure 4.17 (b): FTIR pattern for TEOS surfactant.

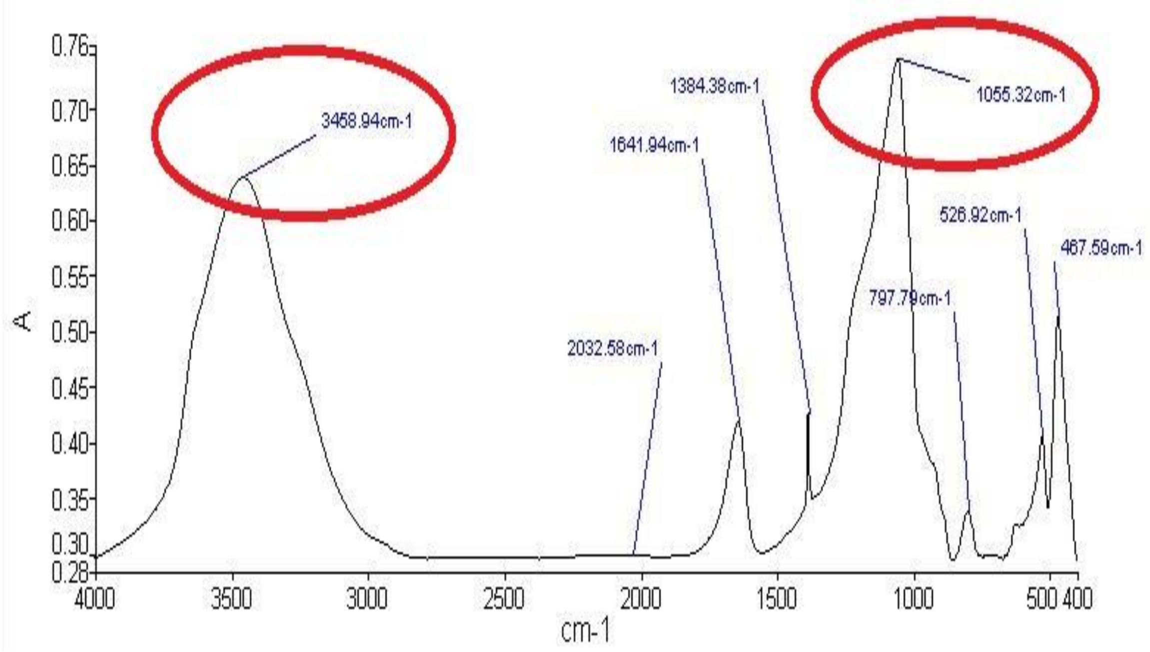


Figure 4.17 (c): FTIR pattern for modified clay using surfactant method.

Based on **Figure 4.17 (a)**, the FTIR pattern for pristine clay shows that the highest pattern peak at 0.65 A which correspond to the wave number of 3459.41 cm^{-1}. **Figure 4.17 (b)** shows the FTIR pattern for TEOS surfactant and the highest peak is at 0.23 A which correspond to the wave number 1079.47 cm^{-1}. After the highest peak for TEOS and pristine clay is identified, FTIR pattern for modified clay using surfactant method will be analyzed. From **Figure 4.17 (c)**, the FTIR pattern shows there is a presence of TEOS surfactant pattern peak in the clay morphologies and this proved that the modification using surfactant method is succeeding.

The other way to justify the modification is achieved is by doing XRD analysis and study the basal spacing of interlayer galleries of pristine and modified clay An XRD analysis is done and the result is discussed below.

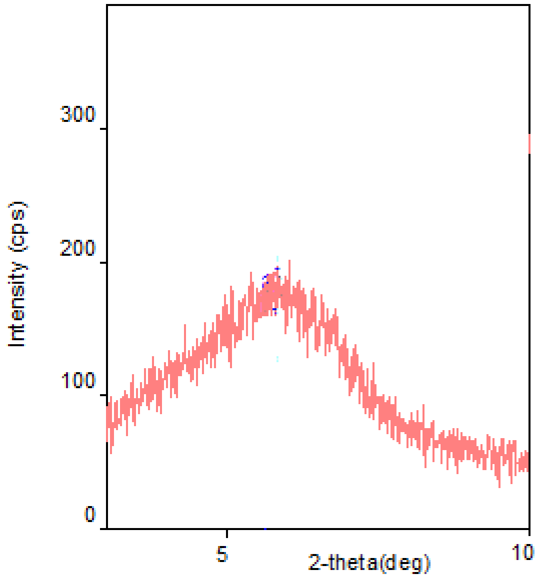


Figure 4.18: XRD pattern for NaMMT +TEOS.

Based Figure 4.18, the XRD pattern shows that the modification by using surfactant method is achieved. This is because the pattern shows there is also a presence of diffraction pattern peak d_{001} at $2\theta = 5.62^{o}$ which correspond to the average basal spacing of 1.57 nm. As mentioned before, in this study experimental work, the diffraction pattern peak d_{001} for pristine clay is $2\theta = 8.17^{o}$ which correspond to the average basal spacing of 1.081 nm. So there is an expansion in the spacing of clay interlayer with an increasing up to 0.489 nm.

This shows the first objectives of this study is achieved which is to modify layered silicates, clay by using surfactant method.

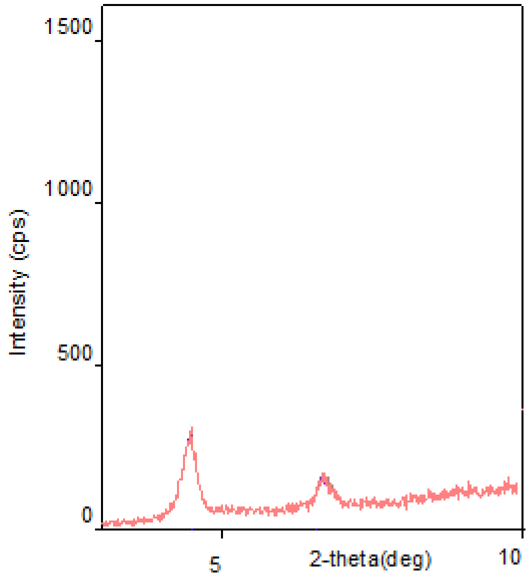


Figure 4.19: XRD pattern for 1 wt % organoclay PLA-Nanocomposites.

After the modification of pristine clay is successful, it's followed by an experiment to support a second objective which is to fabricate PLA-Nanocomposites by using organoclay from surfactant method with PLA polymer. For the 1 wt % organoclay PLA-Nanocomposites **(Figure 4.19)**, the XRD pattern shows the presence of diffraction pattern peak d_{001} at $2\theta = 4.488^o$, which correspond to the average basal spacing of 1.968 nm. This average basal spacing is value is calculated using Bragg’s equation. The average basal spacing for pristine is 1.081 nm, so there was an expanding of the interlayer spacing of PLA-Nanocomposites which is 0.887 nm. This result shows that this polymer nanocomposite contain of intercalated nanocomposites morphologies.

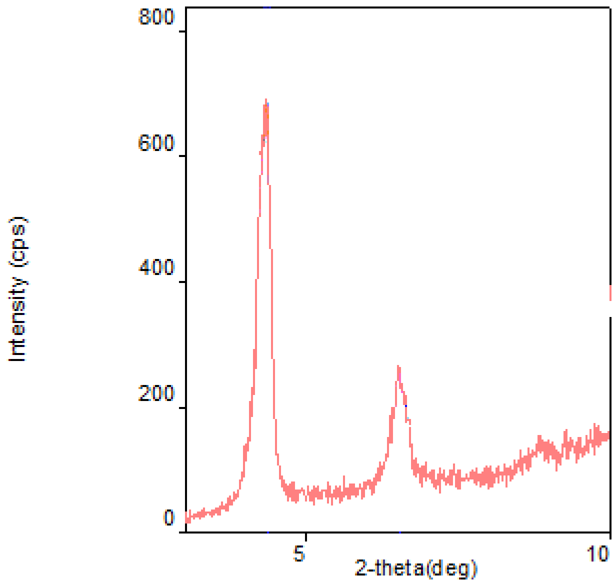


Figure 4.20: XRD pattern for 3 wt % organoclay PLA-Nanocomposites.

In **Figure 4.20**, the 1 wt % PLA-NaMMT shows no diffraction pattern peak because the insertion of polymer matrix into a layered silicate structure cause the two adjacent layers in organoclay galleries separate and weaker or diminish the interlayer Van der Waals force. So, the silicate layers are completely and uniformly dispersed in a continuous polymer matrix. It means the structure for these polymer nanocomposites is exfoliated nanocomposites type.

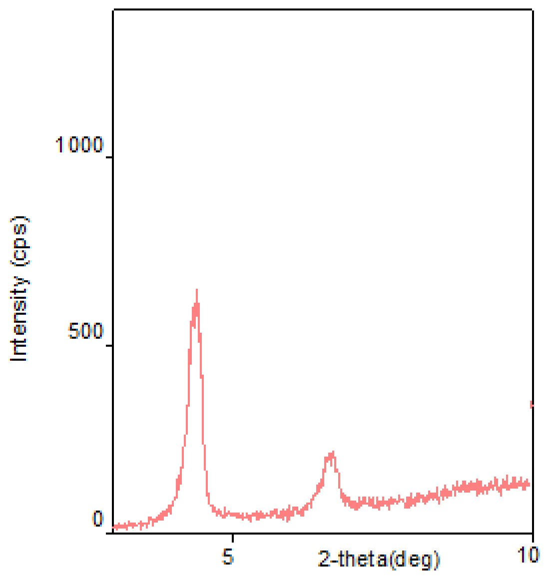


Figure 4.21: XRD pattern for 4 wt % organoclay PLA-Nanocomposites

For the 4 wt % organoclay PLA-Nanocomposites XRD analysis, the pattern shows there is also a presence of diffraction pattern peak d_{001} at $2\theta = 4.3915^o$ which correspond to the average basal spacing of 2.0 nm. So, there was an expanding of the interlayer spacing of PLA-Nanocomposites which is 0.887 nm. This pattern shows that the structure of polymer structure for 4 wt % PLA-NaMMT is in the intercalated nanocomposites category.

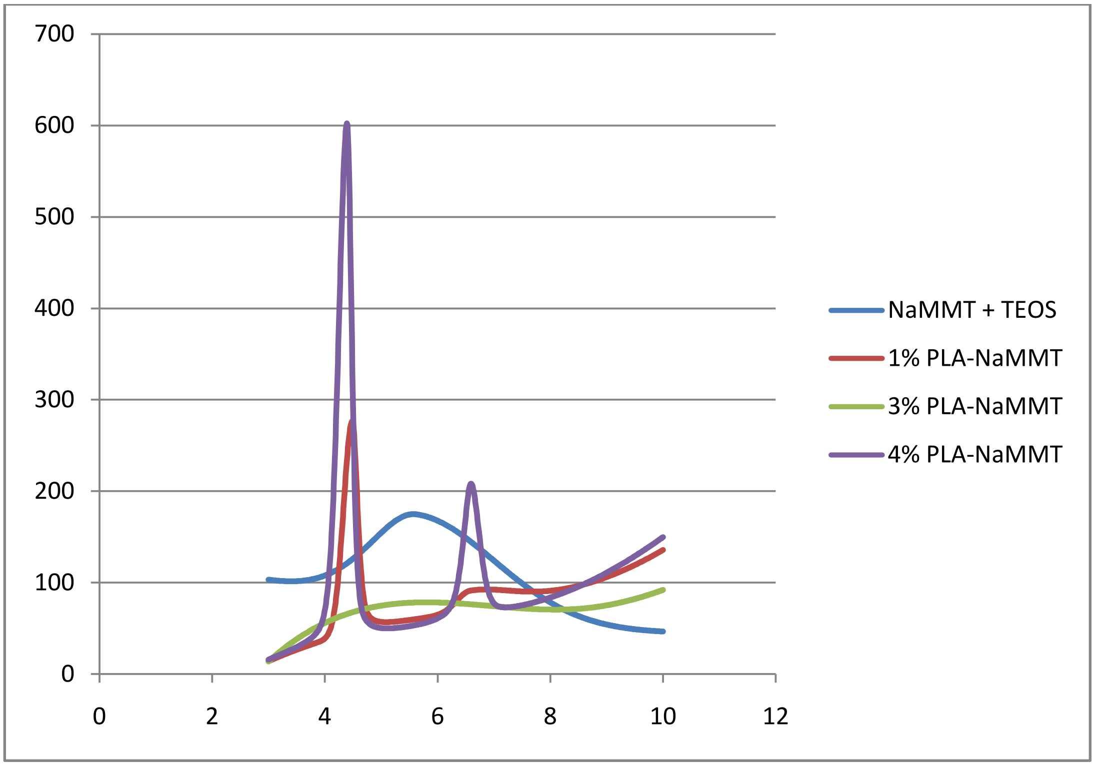


Figure 4.22: Summary XRD pattern for surfactant method.

Conclusion, the best PLA-NaMMT form is 3 wt %, followed by 4% and 1%. The percentage composition of organoclay in the fabrication of polymer is important in order to get exfoliated nanocomposites morphologies. According to Andrew et. al, 2009, the mechanical, thermal and other properties of PLA-NaMMT depended on the organoclay content, with the greatest improvement occurring at 4% organoclay content. The experimental work for 4% organoclay content might have some error because it should give an exfoliated nanocomposites structure. So, the higher percentages organoclay in polymer nanocomposites, the better structure that formed. The second objective is also achieved.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Introduction

In this thesis, the first chapter is focused on the background of the research and its discussing about the introduction of surface modification and polymer nanocomposites. The other element that discuss in the background of research is the problem statement, objectives, scope of study and rational and significant. The second chapter is the literature review. In this section, its focusing on the type of surface modification, type of layered inorganic solids and also the type of polymer chosen. The other element that discuss in the literature review is polymer nanocomposites morphologies, the method of preparation polymer nanocomposites and characterization and testing of PLA-Nanocomposites. In chapter three, it stated that the methodology for fabrication of PLA-Nanocomposites and the surface modification of pristine clay which is an ion exchange method and surfactant method. This chapter also discusses the methodology for characterization of organoclay and polymer nanocomposites by using SEM, XRD, FTIR and AAS. Chapter four mainly discusses about the result that collect from the characterization analysis of organoclay and polymer nanocomposites.

5.2 Conclusion

There are three objectives in this study and from the analysis result, we can conclude that the entire objective achieved and this study is a success. The first objective is to modify the surface of sodium montmorillonite by using the ion exchange method and surfactant method. This objective achieved when the analysis from X-ray diffraction (XRD) for modified clay shows that there is an improvement in increasing the interlayer gallery of clay and methanol solvent gives the highest expand of clay interlayer spacing compared to the water and ethanol solvent.

This result also supported by AAS analysis which is proven that every sample of modified clay has a Cu ion in their interlayer gallery. Based on this analysis, we also can identify that the concentration of TMIs in organoclay also dependent on the type of solvent used. So, the best solvent that should be used in the ion exchange modification is methanol compare to water and ethanol.

The successful of ion exchange modification also can be proven by using Scanning Electron Microscopy (SEM), to get morphology images of organoclay. Organoclay containing TMIs, if precipitated from organic solvent or water, could form distinct crystallites, which would appear in SEM micrograph as a bright spot. Based on **Figure 4.5**, the morphology of pristine clay shows only a little bright spot, while **Figure 4.6** shows a high density of bright spot in their morphology.

The XRD analysis for PLA-Nanocomposites shows there is an intercalated and also exfoliated nanocomposites structure. It means, the fabrication of PLA-Nanocomposites by using organoclay from the ion exchange method is successful. The lowest percentage clay that uses for fabrication of polymer nanocomposites, the better morphologies of nanocomposites will form.

For the modification by using surfactant method, the first objective is achieved when the XRD pattern shows that there is an increasing d-spacing of organoclay. The second objective also achieved when the XRD pattern for all PLA-NaMMT shows intercalated and exfoliated nanocomposite morphologies.

The third objectives which is to study the interlayer properties, structure and morphology of organoclay and PLA-Nanocomposites by using these two modification method is also achieved.

5.3 Recommendations

For the recommendation, this study can be proceed to another type of polymer nanocomposites research studies such as biodegradation, thermal properties , mechanical properties, and other research. Another recommendation is the limitation of equipment for experimentation and analysis should be overcome in order to get a better result and also save a time. For example, Transmission Electron Microscopy should be provided because this equipment can observe the nano size particle compare to the Scanning Electron Microscopy (SEM) that commonly used to observe micro particle. The limited apparatus for experimental work also gives a big problem in term of time management. Some experiment is extended because of no apparatus or equipment to run the experiment.

CHAPTER 6

GANT CHART

5.1 Semester II 2011/2012 (Undergraduate Research Project I)

Activities	**W3**	**W4**	**W5**	**W6**	**W7**	**W8**	**W9**	**W10**	**W11**	**W12**	**W13**	**W14**	**W15**	**W16**
PSM Topic Release.	🟨													
PSM Briefing By Supervisor.		🟫												
Literature Review.	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Preparation of Proposal Report.		🟪	🟪	🟪	🟪	🟪	🟪	🟪						
Submission of The presentation Approval Form To Coordinator.							🟥							
Presentation.								⬛						
Submission of Report.										🟧				
Preparation For PSM II And Research Work Started.										🟦	🟦	🟦	🟦	🟦
Submission and Correction of First Draft- Chapter 1 & 2.													🟪	🟪

5.2 Semester I 2012/2013 (Undergraduate Research Project II)

Activities	**W2**	**W3**	**W4**	**W5**	**W6**	**W7**	**W8**	**W9**	**W10**	**W11**	**W12**	**W13**	**W14**	**W15**	**W16**	**W17**	**W18**
Briefing on PSM II by Coordiator and Research Methodology Seminar II.	🟥	🟥															
Literature Review and Preparation of Thesis.	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
Submission and Correction of Second Draft- Chapter 2 and 3.					🟩	🟩											
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Submission of Dissertation, Technical Paper & Logbook (Hardbound & Softcopy).																⬛	⬛

CHAPTER 7

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