

PERMEABILITY & CHARACTERIZATION STUDY OF  
(POLYLACTIC ACID) PLA-MODIFIED  $\text{Na}^+$  NANOCOMPOSITES  
FOR PACKAGING APPLICATION

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APPLICATION

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## **SUPERVISOR’S DECLARATION**

“I hereby declare that I have read this thesis and in my opinion this thesis has fulfilled the qualities and requirements for the award of Degree of Bachelor of Chemical Engineering”

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I declare that this thesis entitled “Permeability Study and Characterization Study of Polylactic acid) PLA – Modified Na<sup>+</sup> Nanocomposite for Packaging Application” is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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Date : .....

*To my beloved Mum, Rohaidah bt Abdul Kadir and Dad, Nor Effendi bin Nordin  
for always being there for me, and my wonderful and inspiring supervisor,  
Dr. Kamal Yusoh who never stops believe in and encouraging me.*

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## **PERMEABILITY & CHARACTERIZATION STUDY OF (POLYLACTIC-ACID) PLA-MODIFIED $\text{Na}^+$ NANOCOMPOSITES FOR PACKAGING APPLICATION**

### **ABSTRACT**

One of the most versatile polymers is poly-lactic acid (PLA) which is well known as its biodegradable, high molecular weight, aliphatic polyester derived from renewable resources which is environmentally benign and good processability. In this study, a series of PLA nanocomposite with a different percentage of modified  $\text{Na}^+$  with an addition of Polyethylene glycol (PEG) were prepared using the solution intercalation method. The modification of  $\text{Na}^+$  was done via an ion exchange method by using Copper (II) Chloride as an ion exchange solution with different type of solvent which are water, ethanol and methanol. The existence of the ion exchange between the modifications was confirmed through Atomic Absorption Spectrometry (AAS). The structure of the polymer was examined through X-Ray Diffraction (XRD) while their morphology was illustrated by Scanning Electron Microscopy (SEM). The modification of the  $\text{Na}^+$  for every type of solvent was found to be successful where they show their existence of the Transition Metal Ions (TMIs) through AAS and the highest d-spacing was obtained in methanol through XRD with  $d=14.74 \text{ \AA}$ . A barrier properties of the film were examined to investigate the amount of water vapor transmit per unit area and time. The permeability of the film was found to decrease with the increase of  $\text{Na}^+$  content since 3% of the clay content without an exhibition of Polyethylene Glycole (PEG) shows the lowest Water Vapor Transmission Rate (WVTR). An exfoliation behavior was also found in the structure of PLA with 3% of the clay without the presence of PEG with no peak was detected through XRD. This study indicates that PLA with a modified  $\text{Na}^+$  as a filler is better than pure matrix in terms of structure, barrier properties and configuration also could be served as effective nanocomposite for packaging application.

# **KETELAPAN & KAJIAN PENCIRIAN (POLYLACTIC ACID) PLA- DENGAN PENGUBAHSUAIAN CLAY NANOCOMPOSITES SEBAGAI APLIKASI PEMBUNGKUSAN**

## **ABSTRAK**

Salah satu daripada polimer yang paling versatil ialah polimer asid laktik (PLA) yang terkenal dengan berat molekul yang tinggi, boleh biodegradasi, poliester alifatik berasal daripada sumber-sumber boleh diperbaharui yang mesra alam dan mempunyai kebolehan untuk diproses dengan baik. Dalam kajian ini, satu siri PLA nanocomposite dengan peratus Na<sup>+</sup> berbeza diubah suai dengan tambahan Polyethylene glycol (PEG) disediakan menggunakan kaedah campuran interkalasi. Pengubahsuaian Na<sup>+</sup> telah dilakukan melalui kaedah pertukaran ion dengan menggunakan Copper (II) Chloride dengan pelbagai jenis pelarut seperti air, etanol dan metanol. Kewujudan pertukaran antara ion telah disahkan melalui Atomic Absorption Spectrometry (AAS). Struktur polimer telah diperiksa melalui Belauan Sinar-x (XRD) manakala morfologi telah diilustrasi oleh Scanning Electron Microscopy (SEM). Pengubahsuaian Na<sup>+</sup> menggunakan semua jenis pelarut didapati telah berjaya menunjukkan kewujudan Transition Metal Ions (TMIs) melalui AAS dan jarak-d tertinggi telah diperolehi dalam metanol melalui XRD dengan  $d=14.74 \text{ \AA}$ . Kajian terhadap ciri-ciri ketelapan filem terhadap jumlah wap air yang boleh melepasi setiap kawasan beserta unit dan masa telah dilakukan. Ketelapan filem didapati berkurang dengan peningkatan kandungan Na<sup>+</sup> dimana 3% kandungan Na<sup>+</sup> tanpa kehadiran Polyethylene Glycole (PEG) menunjukkan Water Vapor Transmission Rate (WVTR) terendah. Rawakan juga ditemui dalam struktur PLA dengan 3% Na<sup>+</sup> tanpa kehadiran PEG dengan tiada puncak dikesan melalui kajian XRD. Hal ini menunjukkan bahawa pengubahsuaian PLA dengan penambahan Na<sup>+</sup> lebih baik daripada matriks tulen dari segi struktur, ciri-ciri ketelapan dan tatarajah juga boleh digunakan sebagai nanocomposite berkesan dalam aplikasi pembungkusan.

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## LIST OF ABBREVIATION

AAS	-	Atomic Absorption Spectrometry
EDTA	-	Ethylenediaminetetraacetic acid
MMT	-	Montmorillonite
PEG	-	Polyethylene glycol
PLA	-	Poly-lactic Acid
SEM	-	Scanning Electron Microscopy
TMI	-	Transition Metal Ion
WVTR	-	Water Vapor Transmission Rate
XRD	-	X-Ray Diffraction

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Background Of Study**

Since the last few decades, polymers have been chosen as the main resource in the manufacturing field especially in a packaging application since they provide several desired features like softness, transparency and lightness. European Bioplastics (2008) states that in 2007, 260 million metric tonnes per annum polymers produced. Until today, polymers derived from petrochemical-based plastics such as polyvinyl chloride (PVC), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET), was produced on a large scale production because of their good mechanical performance. However, nowadays the productions of plastics from petrochemicals have to be restricted since they are not easily degraded in the environment and non-totally recyclable. Furthermore, recycling this material was extremely impracticable due to the high cost of consumptions. As a result, most of the plastic waste goes straight to the

landfills until today, our earth cannot afford further to receive any municipal waste (Richard et al, 2004). In order to overcome this problem, researchers have discovered the renewable sources based on biomaterials decomposed by natural resources. Currently, the most popular biodegradable polyester is aliphatic polyester. There are a series of biodegradable aliphatic polyesters used for commercial purpose. Among of them are Polyglycolide (PGA), Polycaprolactone (PCL) and Polylactic Acid (PLA). PLA is a biodegradable, low molecular weight, high transparency and good processability. Recently, PLA has been used as a short shelf life packaging product (Siracusa et al, 2008)

Nevertheless, PLA confront with cost and performance issues such as low ductility and brittleness. Singh et al. (2003) also mentioned that another limitation of PLA is its deficiency of gas barrier properties which are the important aspect to access the industry especially in the packaging production. Therefore, new technology has established the integration of polymer and layered silicate to produce nanocomposites to overcome these drawbacks (Okamoto, 2005). Nanocomposites technology is applicable to a wide range of application such as biomedical, transportation, and packaging.

There are three main techniques to be distinguished for preparing polymer nanocomposites which are in situ polymerization, solution intercalation and melt intercalation. In situ polymerization is a mixing of the nanoclay with the monomer then would be followed by polymerization. Melt intercalation consist of blending the organoclay with the polymer matrix in the molten state while solution intercalation can

be done by mixing the organoclay in a solution of a polymer in a specific solvent followed by solvent evaporation.

The research in this study represents an effort on modification of the surface of nanoclay to disperse as a filler within PLA to form a nanocomposites by using an ion exchange method. The nanocomposites must chemically be modified to increase the interlayer space between the clay layers in order to maximize the opportunity of an exfoliation structure happened during the formation of polymer. The existence of the ion exchange method was confirmed through AAS. After that, the modified nanoclay will be intercalated with PLA during the formation of polymer nanocomposites. The structure of PLA in this study was confirmed through X-ray diffraction study (XRD) whereas the impact on the resulting morphology PLA/clay nanocomposites were measured by using SEM. Besides, the permeability of the film will be evaluated through ASTM E 95-96 by wet cup test method.

## **1.2 Problem Statement**

New findings of renewable sources of biodegradable Polylactic acid (PLA) by natural resources gave a huge impact to overcome the environmental issues. This polymer however, is too much brittle and ductile in strength and even has a limitation to gas barrier properties. Nevertheless, the PLA properties can improve by adding nanoparticle fillers in pure matrix to offer an additional surface to interact with the pure matrix. In this study, a series of PLA nanocomposite with a different percentage of modified Na<sup>+</sup> were prepared by using the solution intercalation method perhaps to provide an improved structure and better barrier properties of polymers.

## **1.3 Objectives**

The objectives of this study are:

- To modify Sodium Cloisite organoclay using metal ion solution (ion exchange method)
- To produce PLA nanocomposite with good barrier properties.

## **1.4 Scopes Of Study**

In order to achieve the objectives of this study, there are four scopes of this study defined which are:

- Modification of organoclay to improve the properties of the nanocomposite by using the ion exchange method. In order to achieve that, Atomic Absorbance Spectrometer (AAS) has been used to verify the existence of the ion exchange in the solution.
- Characterized the structure and morphological of PLA through SEM and XRD
- Fabrication of PLA nanocomposites by solution technique
- Testing the barrier properties of the PLA via the wet cup test method described by ASTM E95-96.

## **1.5 Rationale & Significance**

This study has been done in order to improve the properties of the PLA nanocomposites in terms of permeability also the structure of PLA. In addition, it was done to prove the enhance of the brittleness and ductility of the nanoclay with an addition of a modification of nanofiller within the PLA structure. Consequently, it provides an environmental benign and safe to users.

The nanoclay also achieved the standard performance expected in the packaging application where they concern about the protection of the food quality from the environment and this study has verified its improvement in barrier properties.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Current Perspectives and Future Prospects: An Overview**

The discovery of an era nanotechnology has begun since 1985 when the Toyota Company created the first polymer clay nanocomposite (Usuki et al., 1993). Since that, compounding of polymers with inorganic fillers and fibers was developed leading to novel polymeric materials with tailored thermal and mechanical properties at a lower cost. The field of materials science has lately begun to focus on the quest for composite materials that exhibit the positive characteristics of their initial components. Worldwide, there has been a new and strong desire to modify the structure and composition of materials on the nanometer scale. Thus, we are seeing the foreword of a new and improved class of composites, called as the nanocomposites.

## **2.2 Polymer Nanocomposite**

According to Jordan et al. (2005), nanocomposites is defined as a composite material which at least one dimension of the component is in the nanometer scale ( $< 100$  nm). Nowadays, the term nanocomposites are already common in our daily life where it gains attention from worldwide for current research and development in basically all technical disciplines. The numbers of commercial applications of nanocomposites have been growing at a rapid rate encompass biomedical, transportation, packaging, also electrical and electronic applications.

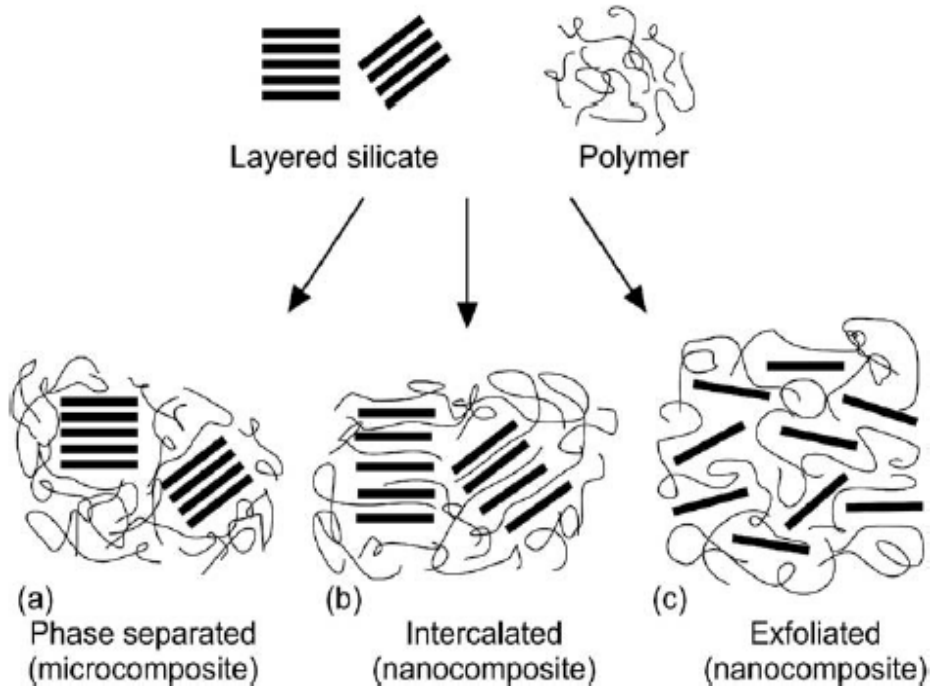
Naturally, the clay layers tend to bond strongly together, which makes the dispersion of the clay and the polymer matrix are difficult. By inserting the nano-sized inorganic compounds to the polymer matrix, the properties of polymers such as thermal stability and mechanical properties such as adhesion resistance, flexural strength, toughness and hardness can be enhanced and hence this has a lot of applications depending upon the inorganic material present in the polymers. Apart from that, Venkataraman (2005) also concludes that the polymer nanocomposites will increase modulus and strength, outstanding barrier properties, improved solvent and heat resistance and decreased flammability.

Polymer nanocomposites consist of a polymeric material such as thermoplastics, thermosets, or elastomers with reinforcement of nano-particles. Most commonly used nano-particles include montmorillonite organoclays (MMT), Carbon nanotubes (CNT)

as well as graphene. While the thermoplastic or thermosets is used as a matrix in preparation of nanocomposites such as PLA and nylon.

### **2.2.1 Structure of Polymer Nanocomposites**

Most of the packaging industries has focused on clay and silicates as they provide low cost, simple process ability, versatility, and significant improvement (Azeredo, 2009). There are three types of nanocomposites can be obtained depending on the preparation method, polymer matrix, organic cation and layered clay (Alexandre and Dubois, 2000). These methods are phase separated polymer-nanoclay composite, intercalated clay, and exfoliated clay (Blumstein, 1965), (Okamoto, 2005), and (Liu et al., 2006). **Figure 2.1** illustrated the type of nanocomposites structure. However, most of the polymer nanocomposite material's structure does not only have one kind of structure such as simply exfoliated or just intercalated but they usually have a plenty of the mixture of the structure (Huang et al., 2000).



**Figure 2.1** : Type of composite derived from the interaction between clays and polymers : (a) Phase – separated microcomposite, (b) intercalated nanocomposite (c) exfoliated nanocomposite

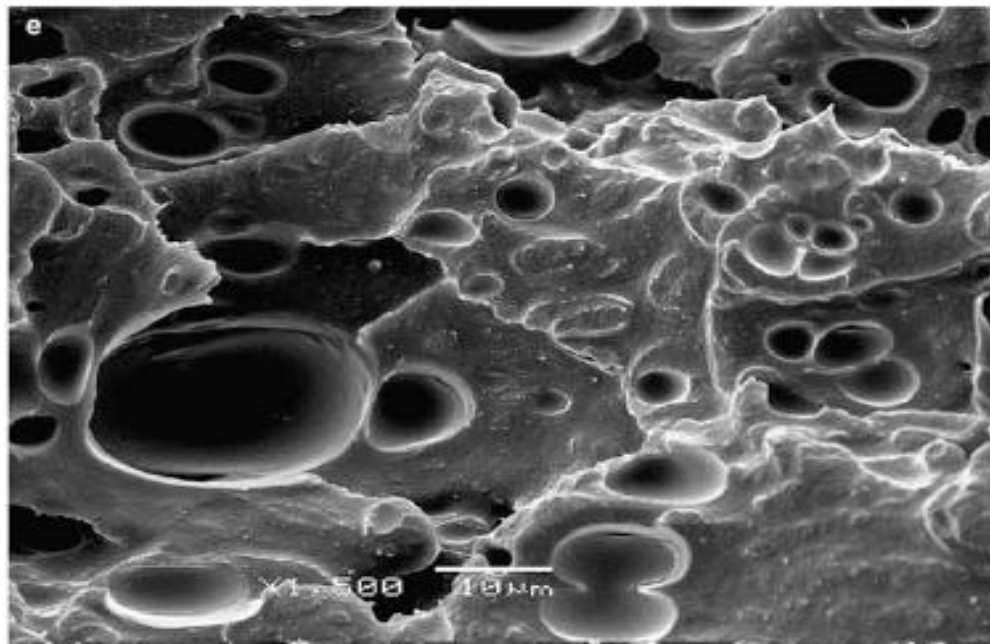
(Source : Alexandre and Dubois, 2000)

### Phase Separated Nanocomposites

This structure happened when the polymer is unable to disperse between the clay layers and it becomes flocculated. In other words, the layers stick together within the polymer matrix.

The morphology and thermo-mechanical behaviour of nanocomposites formed by a polycarbonate (PC) matrix and polyhedral oligomeric silsesquioxane with phenethyl substituents (Ph-POSS) have been studied by Soto et. al. (2009). They study

about the relationship between 0% and 15% Ph-POSS loadings with PC by melt blending. They found that at higher loadings micron-sized aggregates were observed in the nanocomposites by scanning electron microscopy. Increasing of Ph-POSS content lead to phase separation, agglomeration and low values of the final properties. **Figure 2.2** shows the SEM image of 15% Ph-POSS loadings with PC. From the micrographs it can be appreciated that at very low POSS loading small aggregates of sub-micrometric size are formed.



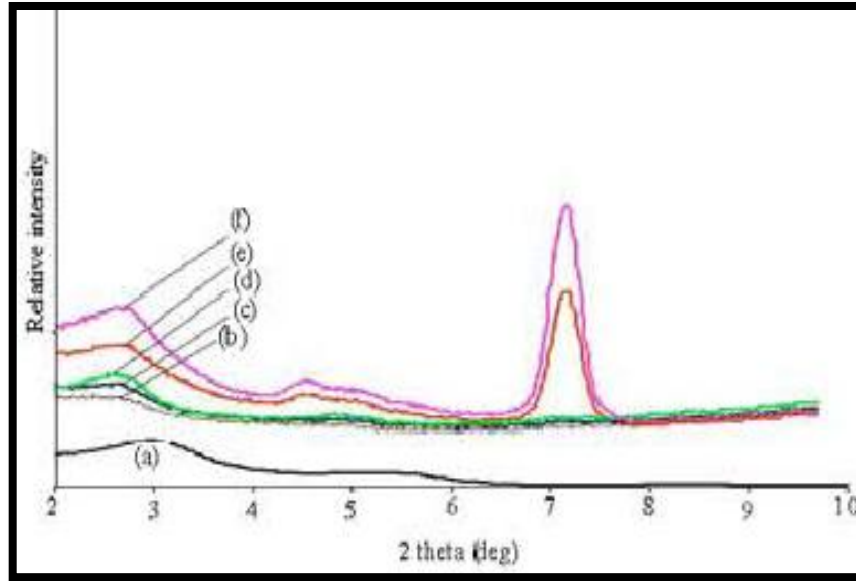
**Figure 2.2 :** SEM image of 15% Ph-POSS loadings with PC

(Source : Soto et. al., 2009)

## Intercalated Nanocomposites

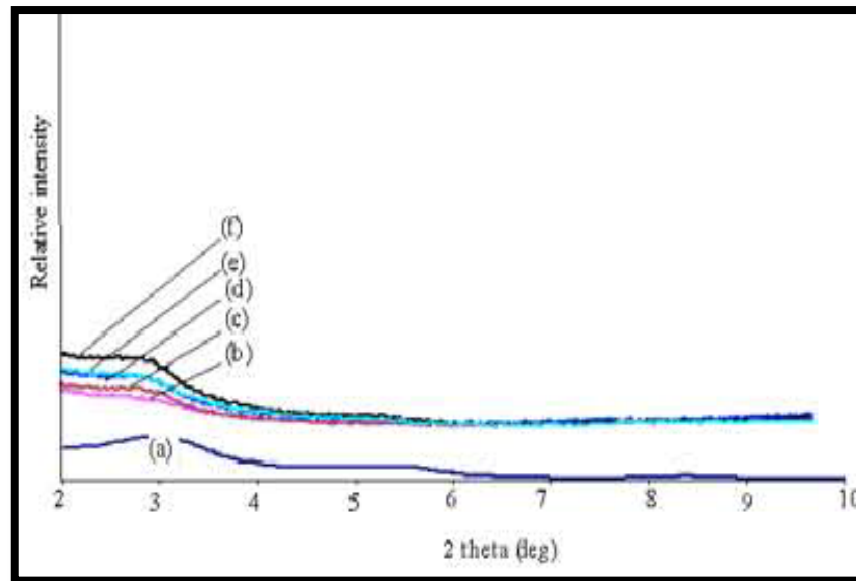
Intercalated form is a resulting from the dispersion of polymer chains within the interlayer space of the clay thus, produced a well-ordered multilayer structure of alternating polymeric and inorganic layers at a repeated distance. Intercalation causes less than 20 – 30 Å separation between the layers (Alexandre and Dubois, 2000).

Hoidy et. al. (2010) have come out with their research about the preparation and characterization of polylactic acid/polycaprolactone clay nanocomposites. In their studies, PLA/PCL-OMMT nanocomposites were prepared by both melt blending and solution casting of PLA, PCL and OMMT using ODA and FHA as modifiers of clay. The XRD result of PLA/PCL-ODA-MMT nanocomposites with 1, 2, 3, 4 and 5 php of ODAMMT in solution casting method show shift to lower angles between  $2\theta$  of 3.0-2.89 correspond to the basal spacing between 29.86 – 31.02 Å. While in melt blending process, the XRD result shows the  $2\theta$  value is between 2.80 – 2.61 correspond to the basal spacing between 32.04 – 33.61 Å. Based on **Figure 2.3** and **Figure 2.4**, their XRD results indicate that the material formed intercalated nanocomposites for both preparation methods.



**Figure 2.3 :** XRD patterns of (a) ODA-MMT, (b) PLA/PCL/1% ODA-MMT, (c) PLA/PCL/3% ODA-MMT, (d) PLA/PCL/4% ODA-MMT, (e) PLA/PCL/5% ODA-MMT by solution casting

(Source : Hoidy et. al., 2010)

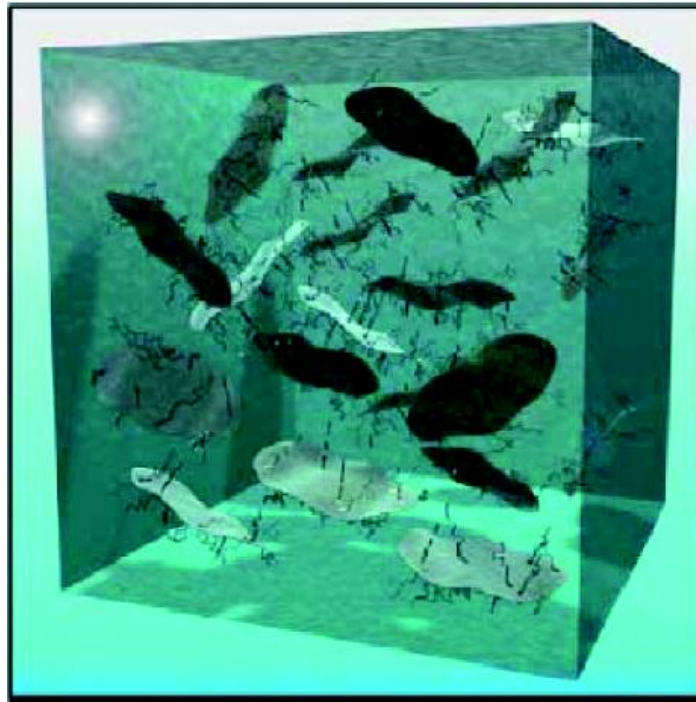


**Figure 2.4 :** XRD patterns of (a) ODA-MMT, (b) PLA/PCL/1% ODA-MMT, (c) PLA/PCL/3% ODA-MMT, (d) PLA/PCL/4% ODA-MMT, (e) PLA/PCL/5% ODA-MMT by melt blending

(Source : Hoidy et. al., 2010)

## Exfoliated Nanocomposites

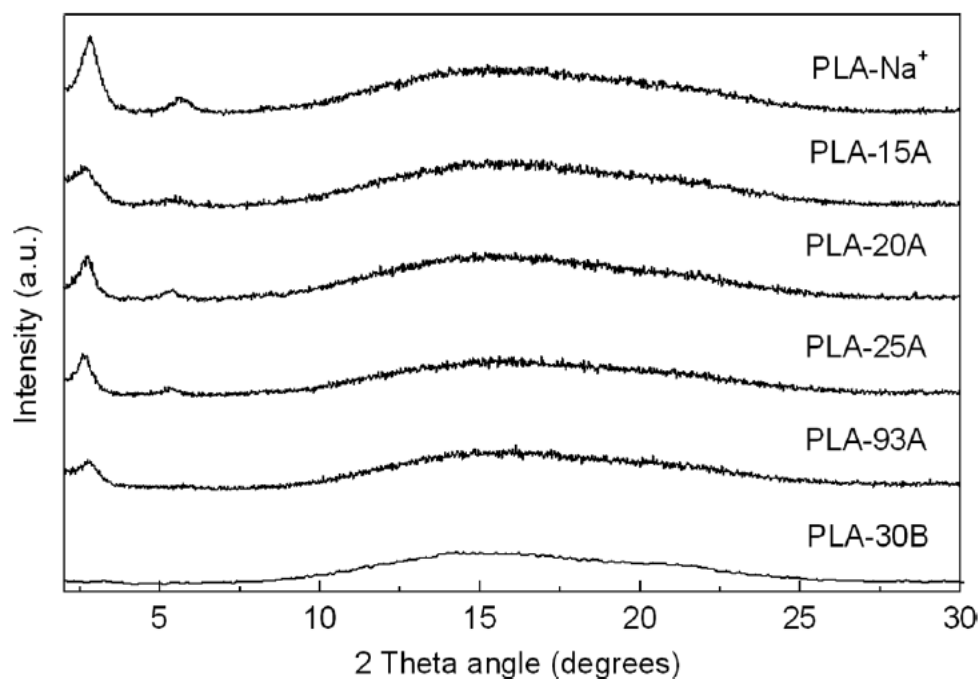
Exfoliated nanocomposites involve an extensive polymer distribution within the the polymer and the individual layers are dispersed within the polymer matrix when the polymer chain was inserted to the clay galleries. Among those three structures of nanocomposites, exfoliated structure has found to be the desired one during the preparation of nanocomposites (Ludueno and Leandro, 2007). Schematic picture of a polymer-clay nanocomposite material with completely exfoliated was shown in **Figure 2.5**.



**Figure 2.5** : Schematic picture of a polymer-clay nanocomposite material with completely exfoliated (molecular dispersed) clay sheets within the polymer matrix material

(Source : Fischer et al., 2003)

An exfoliation of a nanocomposites was found in a study by Krishnamachari et. al. (2009) where they make a comparison among PLA and several organically modified montmorillonites (nanoclays), namely Cloisite 30B, Cloisite Na<sup>+</sup>, Cloisite 25A, Cloisite 20A, Cloisite 93A, and Cloisite 15A. The XRD diffractograms for the PLA-clay nanocomposite samples of different clays are shown in **Figure 2.6** where it can be seen that PLA-30B nanocomposite did not show a peak corresponding to the d-spacing of the nanoclay (30B). In contrast to the PLA-30B nanocomposite, the other PLA-nanoclay nanocomposites, namely PLA-Na<sup>+</sup>, PLA-15A, PLA-20A, PLA-25A, and PLA-93A, were found to retain a Bragg peak corresponding to the clay d-spacing. It can be concluded that only PLA-30B nanocomposite achieved exfoliation.



**Figure 2.6 :** XRD Diffractograms : PLA with 1% (w/w) of Na<sup>+</sup>, 15A, 20A, 25A, 93A and 30A.

(Source : Krishnamachari et. al., 2009)

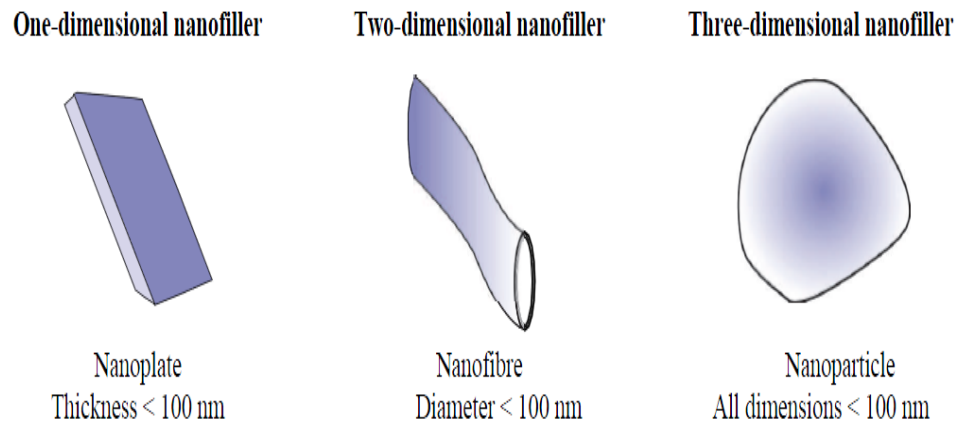
### 2.3 Nanofiller

The term “nanocomposites” was appeared in 1994 where an innovation to the nanofiller was first introduced by Usuki et al. (1993). Afterward, a lot of researches have started on various fillers in order to fulfill the demand for continual improvement in the performances of thermoplastic and thermoset polymer materials which has led to the emergence of these new technologies. Nowadays, the development of polymer nanocomposites is one of the most active areas of development of nanomaterials. The properties improved by the nanoparticles are various and focus particularly on strengthening the electrical conduction and barrier properties to temperature, gases and liquids as well as the possible improvement of fire behavior. Nanofillers can significantly improve or adjust the different properties of the materials into which they are incorporated, such as optical, electrical, mechanical, thermal properties or fire-retardant properties, sometimes in synergy with conventional fillers. The properties of composite materials can be significantly impacted by the mixture ratio between the organic matrix and the nanofillers. (Marquis et. al., 2011)

Besides, the materials can be in the form of solid or liquid. The appropriate selection of these materials is important in order to improve the properties such as processing and mechanical behavior. Nanofillers also can be considered as a nanocomposites can be distributed according to the nanofillers as highlighted in **Figure 2.7** where it consist of one, two and three dimensional nanofiller. One dimensional nanofiller was in a form of plates, laminas or shells where the thickness is below than

100 nm. Two dimensional nanofiller consist of nanofibres and nanotubes form which having a diameter lower than 100 nm. While, for three dimensional nanofiller is a isodimensional nanoparticle such as nanometric silica beads with the dimension of below than 100 nm.

According to Marquis et. al. (2011), nanofillers are introduced in polymer at rates from 1% to 10% (in mass). They are incorporated in addition to traditional fillers and additives, and eventually traditional reinforcement fibres such as glass, carbon or aramide fibres.



**Figure 2.7 :** Nano-objects used for nanocomposites, as defined in ISO/TS27687 (2008)

In terms of nanocomposites, there are 3 commons nanofiller that is always used in polymerization which are clay, metal and carbon nanotube. Among these three, the most widely used reinforcement is clay due to its natural abundance and its very high form factor. Samal (2008) investigated that polymer clay nanocomposites have been the

subject of many recent papers due to their excellent properties and commercialize in industrial applications. A studies by Patino Soto (2008) states that polymer-layered silicate nanocomposites enhanced the improvement of polymer properties, such as thermal and dimensional stability, lower gas permeability, better surface finish, improved biodegradability, and enhanced mechanical behavior. Marquis et. al. (2011) affirm that clays are classified according to their crystalline structures and also to the quantity and position of the ions within the elementary mesh. The elementary or primitive mesh is the simplest atomic geometric pattern, which is enough for duplicating the crystalline network, by repeating itself indefinitely in the three directions. **Table 2.1** presents the various natural and synthetic nanoclays available and used as fillers in polymers. The most common usage concerns organomodified Montmorillonite (MMT), a natural phyllosilicate extracted from Bentonite.

Raw formula of Montmorillonite is  $(\text{Na,Ca})_{0,3} (\text{Al,Mg})_2 \text{Si}_4\text{O}_{10} (\text{OH})_2, n\text{H}_2\text{O}$ . Montmorillonite clay is broadly used in industry because of its advantages in high ion exchange capacity, which allows modification of the interlayer spacing to achieve better compatibility with host polymer matrices also makes the clays are easy to go through the modification process. In addition, clay is easy to obtain from the natural resources also inexpensive (Ki Tak Gam, 2003). Other studies by Borchardt (1989), clays also exhibit high aspect ratio to give better reinforcement effect.

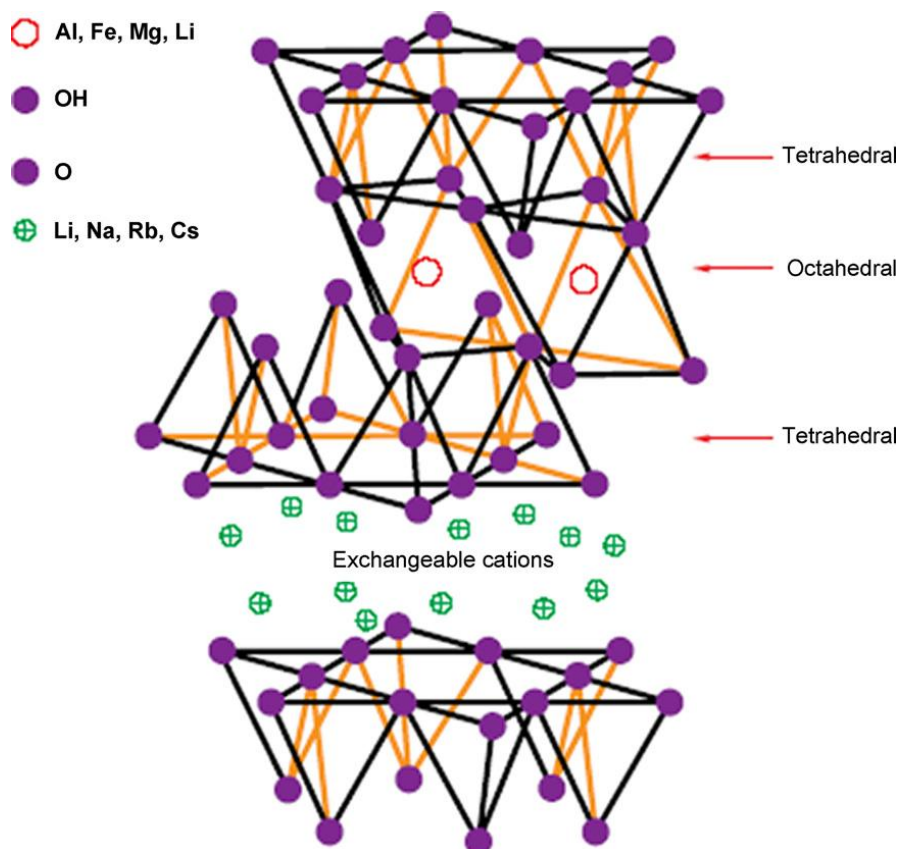
**Table 2.1 : Nanoclays identification.**

(Source : Marquis et. al., 2011)

Family		Group	Formula
<b>Phyllosilicates</b>	TO (1:1)	Kaolinite	The reference plate is from a tetrahedral plate T and an octahedral plate O. The thickness of the layer is about 0.7 NM. Kaolinite $Al_4Si_4O_{10}(OH)_8$
	TOT (2:1)	Smectite, (Talc, Mica, Montmorillonite, Sepiolite	Two tetrahedral plates T in both sides of an octahedral plate O form the reference plate. The thickness of the layer is about 1 nm. The group includes many minerals that are the major constituents of clays.
	TOT:O (2:1:1)	Chloride, Bentonite, Saponite.	The reference plate is formed of three plates TOT and another isolated O plate. The thickness of the layer is about 1.4 nm. Chloride di-tri $Al_2Mg_3Si_4O_{10}(OH)_8$
<b>Polysilicate</b>	Natural	Kenyaite, Magadiite, Kanemite, Ilerite, Silhydrite, Zeolite.	Magadiite ( $Na_2Si_{14}O_{29}H_2O$ )
	Synthetic	FluoroHectorite, Zeolite	
<b>Double lamellar hydroxide</b>	Synthetic	Hydrotalcite	Hydrotalcites $(Mg_6Al_2(OH)_{16})(CO_3^{2-})4H_2O$

### 2.3.1 Structure of Layered Silicate Organoclay

**Figure 2.8** shows the structure of MMT nanoclays. This material received a great attention because these nanoclays have a plenty structure with a thickness of one nanometer or less per unit and the lateral dimension may increase depending on the preparation technique. The aspect ratio of these layers is particularly high with values greater than 1000. Because MMT clay is hydrophilic, it is not friendly with most polymers and must be chemically modified to make its surface more hydrophobic. MMT exhibits a crystalline structure, described by two-dimensional layers that are composed of two tetrahedral sheets of silica surrounding an octahedral sheet of alumina or magnesia (Ray and Okamoto 2003).



**Figure 2.8 :** Structure of 2: 1 Layered Silicate

(Source : Okamoto, 2005)

### 2.3.2 Modification of Clay Layers

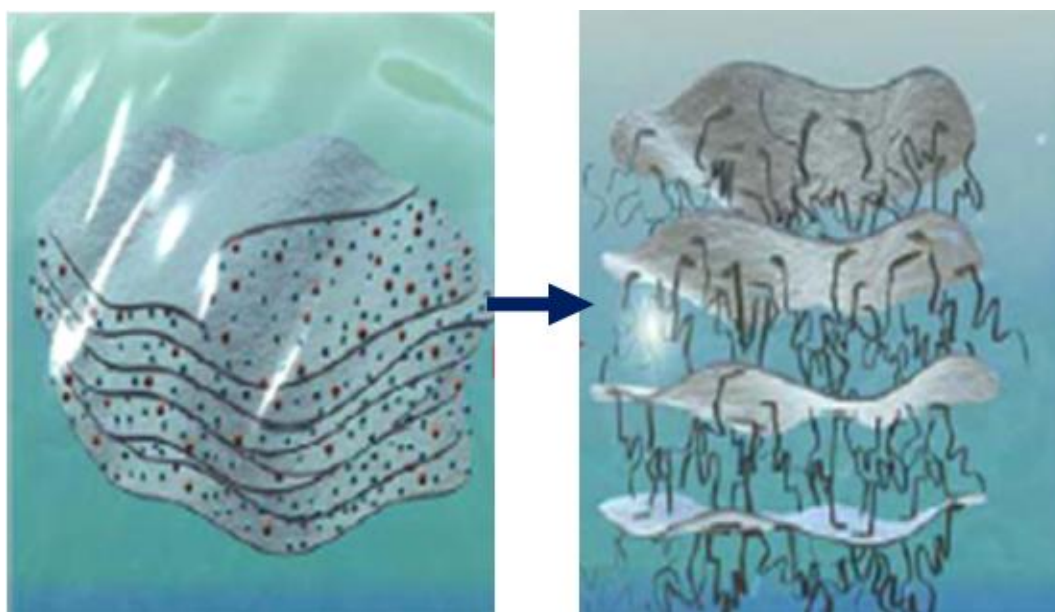
A good dispersion and distribution of clay layers within the polymer matrix by using a standard mixing of polymer and clay particles are impossible to happen due to the high sticking layers in agglomerated tested and their natural hydrophilic which makes them incompatible with the hydrophobic polymer. However, a study by Pavlidou and Papaspyrides (2008) states that some hydrophobic polymers can miscible with clay layers such as poly (vinyl alcohol), in order to render them miscible with other

polymers, one must exchange the alkali counter-ions with with a cationic organic surfactant.

A van de Waals chains of the hydrophilic clay layers and hydrophobic polymer acting as a barrier to the dispersion of clay nanolayers within the polymer matrix and causes to weak surface interaction. This difficulty prevents the exfoliated and a stable dispersion of nanocomposites with an enhanced properties. Thus, a modification of the clay must be done as it can reduce the surface energy of clay layers and match their surface polarity with polymer polarity consequently makes the clay layers more compatible with the polymer chain.

Generally, this can be achieved by ion-exchange reactions with cationic surfactants by replacing sodium and calcium cation present in the interlayer space by alkylammonium or alkyl phosphonium cations. Alkyl ammonium or alkylphosphonium cations in the organosilicates lower the surface energy of the inorganic host and improve the wetting characteristics of the polymer matrix, and resulting in an increasing of interlayer spacing (Giannelis, 1994) and (Okamoto, 2005). Additionally, the alkylammonium or alkylphosphonium cations can provide functional groups which interact with the polymer matrix, or in some cases initiate the polymerization of monomers to improve the strength of the interface between the inorganic and the polymer matrix (Blumstein, 1965).

Pavlidou and Papaspyrides (2008) explained about the mechanism of the ion exchange reaction as illustrated in **Figure 2.9** where the inorganic, relatively small (sodium) ions are exchanged against more voluminous organic onium cations. This ion-exchange reaction has two consequences. Firstly, the gap between the single sheets is widened, enabling polymer chains to move in between them and secondly, the surface properties of each single sheet are changed from being hydrophilic to hydrophobic.



**Figure 2.9 :** Schematic picture of ion exchange reaction

(Source : Pavlidou and Papaspyrides, 2008)

## **2.4 Polymeric Acid (PLA)**

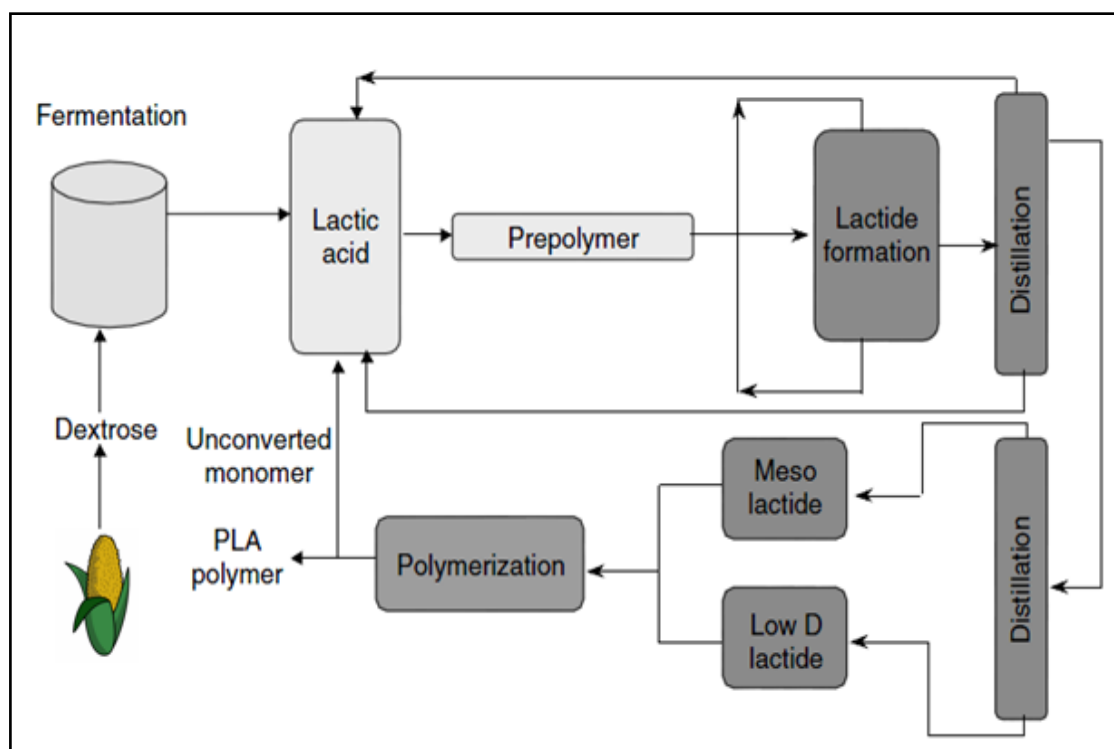
Polymeric acid (PLA) is a biodegradable polymer, a group of aliphatic polyester, derived from lactic acid. PLA is obtained from the controlled depolymerization of the lactic acid monomer obtained from fermentation of corn, wheat and sugar beets which are made from 100% renewable resources (Lunt, 1997). The polymer will also rapidly degrade in the environment and the by-products are of very low toxicity, eventually being converted to carbon dioxide and water. This renewable resource has been made to replace the petrochemicals- based product as they are environmentally unfriendly and higher cost of production. The starting material for polymeric acid is starch from a renewable resource such as corn. Corn is milled, which separates starch from the raw material. Unrefined dextrose is then processed from the starch. Dextrose turns into lactic acid using fermentation, similar to that used by beer and wine producers.

PLA is a versatile polymer where it behaves like PET, but also performs similar like polypropylene (PP). In addition, it has an extensive application because of its ability to be stress crystallized, thermally crystallized, impact modified, filled, copolymerized, and processed in most polymer processing equipment. Polymeric acid can be made with different mechanical properties suitable for specific manufacturing processes, such as injection molding, sheet extrusion, blow molding, and fiber spinning using more conventional techniques and equipment.

In spite of that, PLA deal with a big challenge in industrial application. One of the technical challenges is the difficulties to achieve mechanical and barrier properties comparable with the conventional synthetic polymers while maintaining their biodegradability (Nampoothiri et al., 2010). Singh et al. (2003) also mention that another limitation of PLA is its deficiency of gas barrier properties which are the important aspect to access the industry especially in the packaging production. Even though there are many limitations to its performance, this drawback can be overcome via new technologies development by making nanocomposites of PLA, blending with another polymer and modification of the properties. This new invention can make PLA are outstanding and compatible with the other petrochemical-based polymer such as PP and PVC.

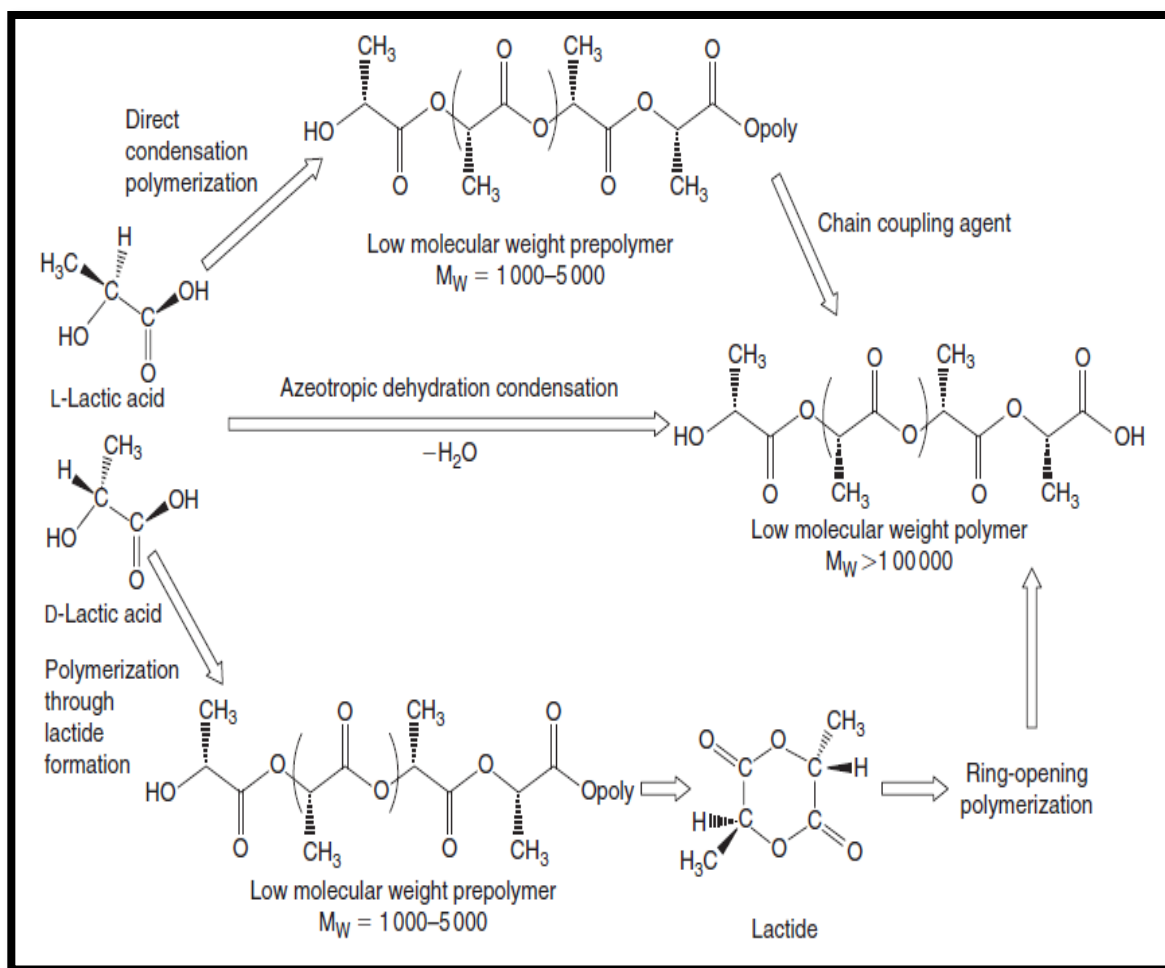
#### **2.4.1 Synthesis of Poly (Lactic Acid)**

The synthesis of PLA is a multistep process beginning from the production of lactic acid until the polymerization. **Figure 2.10** explain about this process.



**Figure 2.10** : Nonsolvent process to prepare polylactic acid.

During the process, it is important to obtain a high molecular weight of PLA. Method to produce high molecular weight of PLA can be followed by three main routes which are condensation polymerized, azeotropic dehydrative condensation of lactic acid and ring-opening polymerization (ROP) of lactide. The first step is by condensation polymerized to yield a low molecular weight and brittle polymer. This method this can only be used if an external coupling agent is added to increase the chain length. The second route is azeotropic dehydrative condensation of lactic acid. This route is better than the first one where it can be able to yield a high molecular weight of PLA without an external coupling agent. The last route is the main commercial process which is ring opening polymerization (ROP) where it can obtain a high molecular weight of PLA.



**Figure 2.11 : Manufacturing routes to PLA**

(Source : Avérous, 2008)

## 2.4.2 Properties of PLA

PLA is a thermoplastic resin derived from annually renewable resources and is specifically designed for use in food packaging applications. The other physical properties are transparent and high molecular weight biopolymer grade that processes

easily on conventional extrusion equipment. **Table 2.2** shows the permeability of PLA obtained from NatureWorks LLC.

**Table 2.2:** Permeability of PLA

(Source : NatureWorks LLC, n.d)

Permeability	PLA
Oxygen, cc-mil/m <sup>2</sup> .day.atm (ASTM D1434)	500
Carbon Dioxide, cc-mil/m <sup>2</sup> .day.atm (ASTM D1434)	3000
Water, g-mil/m <sup>2</sup> .day.atm (ASTM E96)	325

A research done by Auras et. al. (2003) about the mechanical, physical, and barrier properties of poly (lactide) films. In their work, they investigate mechanical, physical, and barrier properties two biaxially oriented poly (lactide) films which are 4030-D and 4040-D. **Table 2.3, Table 2.4** and **Table 2.5** below shows the results of this experiment.

**Table 2.3:** Mechanical properties of 4030-D, 4040-D, PS, and PET

(Source : Auras et. al., 2003)

	4030-D		4040-D		PS	PET
	MD	CD	MD	CD	Biaxial	
Tensile yield stress, MPa (kpsi)	72 (10.5)	65 (9.5)	84 (12.2)	74 (10.7)	55–82 (8–12)	275 (40)
Percent elongation at yield	4.7	4.5	3.4	4.2	–	~6
Percent elongation at break	10.7	5.5	78.2	96.9	3–40	60–165
Elastic modulus, GPa (kpsi)	2.11 (306.4)	2.54 (368.3)	2.31 (335.4)	2.87 (416.3)	3.2 (464)	2.8–4.1 (400–600)

**Table 2.4 :** DSC results for PLA, PS, and PET.

(Source : Auras et. al., 2003)

	4030-D	4040-D	PS (atactic)*	PET
$T_g$ (°C)	71.4	66.1	105	80
Relaxation enthalpy (J/g)	1.4	2.9	N/A	N/A
$T_m$ (°C)	163.4	140.8	N/A	245
Enthalpy fusion (J/g)	37.5	21.9	N/A	47.7
Percent crystallinity	40	25	N/A	38

\*PS used in packaging is atactic, so it cannot crystallize. Since it is an amorphous polymer, it does not have a defined melting point, but gradually softens through a wide range of temperatures.

**Table 2.5 :** Water vapor permeability coefficient and activation energy of PLA resins.

(Source : Auras et. al., 2003)

Resin	$P \times 10^{14} \text{ kg m/m}^2 \text{ s Pa}$				$E_P$ (kJ/mol)
	Temperature (°C)				
	10	20	30	37.8	
4030-D	2.20 ± 0.07	1.89 ± 0.08	1.65 ± 0.06	1.52 ± 0.05	−9.73 ± 0.27
4040-D	2.09 ± 0.12	1.79 ± 0.10	1.61 ± 0.07	1.48 ± 0.07	−10.11 ± 0.47

### 2.4.3 Properties of PLA Nanocomposites

A research done by Rhim et. al. (2009) about the tensile, water vapor barrier and antimicrobial properties of PLA/ nanoclay composite film. In their work, PLA-based composite films with different types of nanoclays such as Cloisite Na<sup>+</sup>, Cloisite 30B and Cloisite 20A were prepared via solution casting method by using chloroform as a solvent and the tensile, water vapor barrier and antimicrobial properties were tested. **Table 2.6** and **Table 2.7** below shows the results of this experiment.

**Table 2.6:** Tensile properties of neat PLA and various types of clay/ PLA nanocomposite films compounded with 5 parts of clay/100 parts of PLA.

(Source : Rhim et. al., 2009)

<b>Films</b>	<b>Thickness (<math>\mu\text{m}</math>)</b>	<b>Transmittance (%)</b>	<b>TS (MPa)</b>	<b>Elongation (%)</b>
Neat PLA film	$7.15 \pm 1.4$	$81.3 \pm 1.1$	$50.5 \pm 0.8$	$3.0 \pm 0.1$
PLA/Cloisite Na+	$80.6 \pm 4.4$	$16.7 \pm 1.0$	$40.8 \pm 1.1$	$2.5 \pm 0.3$
PLA/Cloisite 30B	$79.2 \pm 8.3$	$14.2 \pm 0.6$	$40.9 \pm 4.3$	$3.1 \pm 0.3$
PLA/Cloisite 20A	$84.1 \pm 4.6$	$68.0 \pm 1.0$	$45.3 \pm 1.3$	$2.7 \pm 0.3$

**Table 2.7 :** Water Vapor Permeability (WVP) of neat PLA and various types of clay/ PLA nanocomposite films compounded with 5 parts of clay/100 parts of PLA.

(Source : Rhim et. al., 2009)

<b>Films</b>	<b>WVP ( <math>\times 10^{-11}</math> g m/m<sup>2</sup>sPa)</b>	<b>RH<sub>1</sub> (%)</b>
Neat PLA film	$1.80 \pm 0.01$	$99.4 \pm 0.03$
PLA/Cloisite Na+	$2.08 \pm 0.01$	$99.3 \pm 0.02$
PLA/Cloisite 30B	$1.70 \pm 0.03$	$99.5 \pm 0.02$
PLA/Cloisite 20A	$1.15 \pm 0.02$	$99.6 \pm 0.07$

## **2.5 Preparation of PLA nanocomposites.**

An enhanced property of a polymer/clay was archived when the nanoparticle of the polymer can distribute and disperse well in a polymer matrix. In general, there are three main techniques to be distinguished for fabricating polymer silicate nanocomposites which are in situ polymerization (Usuki et al., 1993), solution intercalation and melt intercalation (Pavlidou and Papaspyrides, 2008)

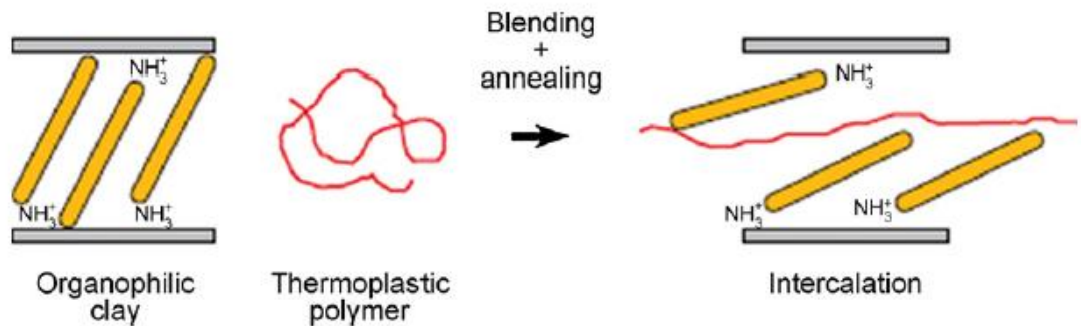
### **2.5.1 In-Situ Intercalation Method**

This technique was the first method used for the preparation of polymer/clay nanocomposite by the Toyota researches group in the preparation of Nylon-6 nanocomposite from caprolactam monomer (Usuki et al., 1993). 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. The in-situ polymerization technique has also been applied for the preparation of nanocomposites based on thermoplastic polymers other than polyamides (Pavlidou and Papaspyrides, 2008), polystyrene (PS) (Akelah and Moet, 1996) and has been widely used for the epoxies and styrenic polymer nanocomposites (Lan et al., 1995).

### 2.5.2 Melt Intercalation Method

The most versatile and environmentally benign method among all the methods of preparing polymer-clay nanocomposites are by melt intercalation method. In this method, a heated mixture of a polymer and layered silicate above the glass transition or melting temperature of the polymer was then mixed under shear forces in an extruder.

This method also involves annealing above the softening point of the polymer. While annealing, the polymer chains diffuse from the bulk polymer melt into the galleries between the silicate layers as shown in **Figure 2.12**. A range of nanocomposites with structures from intercalated to exfoliate can be obtained, depending on the degree of penetration of the polymer chains into the silicate galleries. Krishnamachari et al. (2009) have been using this method to produce PLA to study about the morphological, thermal and mechanical properties. As a result, they found an increase in thermal stability with a high loading level of 3% (w/w).



**Figure 2.12 :** The melt intercalation process

(Source : Pavlidou and Papaspyrides, 2008)

The advantages of using this method are it is quite appealing, more economical and simpler than in-situ polymer intercalation. It is also environmentally friendly due to the absence of an organic solvent (Ray and Okamoto, 2003). Based on a study by Hoidy et. al (2010), both PLA/PCL-ODA-MMT and PLA/PCL-FHA-MMT prepared by melt intercalation gave higher tensile strength and basal spacing compared with those of solution technique which proves that, this method are much better than the solution intercalation method. Yet, this method has a problem in controlling the distribution of the nanofiller compared to the solution intercalation method. After the preparation nanocomposites through this method, nanocomposites can be manufactured using an industrial process such as extrusion and injection molding.

### **2.5.3 Solution Intercalation Method**

The polymer solution technique is based on a solvent system where the polymer is soluble and silicate layers are swellable. In the beginning, the layered silicate is swollen in a solvent. But, after the polymer and clay are mixed, the polymer chain intercalate and displace the solvent between the clay layers. The final steps consist of removing the solvent, usually by evaporation or precipitation. During the solvent removal, the intercalated structure remains and forming a nanocomposite structure (Pavlidou and Papaspyrides, 2008). However, intercalation only occurs in a certain polymer/solvent pairs by this method. It is also appropriate for the intercalation of polymer low or even no polarity.

Ogata et al. (1997) applied the solution method for the production of PLA using montmorillonite modified with distearyldimethylammonium cations. The composite were prepared by dissolving PLA into hot chloroform with modified clay then was vaporized to produce a film. Though, under those conditions, it was found that no intercalation took place. They realized that the organo-modified clay rather formed a remarkable geometric structure in the filled polymers where tactoids consisting of several silicate monolayers form a superstructure in the thickness direction of the film. In spite of that, a different research work through this method for the preparation of poly ( $\epsilon$ -caprolactane) clay nanocomposite was claimed as successful where it shows an improvement in mechanical properties (Ludueno et al., 2007) also the biodegradability of the polymer (Wu et al., 2009). The major disadvantages of this technique is the large quantities of solvent usage make this method cannot be approached in industrial application where it is high cost and environmental unfriendly (Alexandre and Dubois, 2000). However, the solution intercalation method gives more advantages over melt intercalation on good dispersion of the clays in the polymer silicate matrix.

## **2.6 Plasticizers**

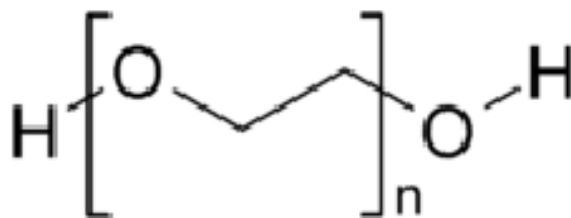
Plasticizers are widely used in the plastics industry to improve the process ability, flexibility, and ductility of glassy polymers. An addition of plasticizers within the PLA will reduce the brittleness and stiffness of the polymers by reducing the glass transition temperature of the polymer (amorphous regions), and thus improving its

mechanical properties and recovery (Almenar and Auras, 2010). A research about the Tributyl citrate oligomers as plasticizers for poly (lactic acid) by (Ljungberg and Wessle'n, 2003) have found that the plasticizer has decreased the glass transition temperature of the PLA and the reduction was the largest with the plasticizer having the lowest molecular weight. Further studies have been carried out by Boonfaung et. al. (2005) regarding the suitable plasticizer for PLA among Polypropylene glycol (PPG), Poly (ethylene glycol-ran-propylene glycol) (PEPG), Dioctyl phthalate (DOP), Tributyl citrate (TBC) and Adipic acid. In their findings, they found that PPG was a good plasticizer for PLA in which the tensile strength and Young's modulus of the plasticized PLA decreased, whereas its elongation at break increased dramatically. A negative aspect of plasticizer use is the potential decrease in barrier properties of PLA. Plasticizers such as water, polyethylene glycol, lactide, lactic acid, nontoxic citrates, glycerol, and sorbitol have been tested and reported as effective for PLA. (Almenar and Auras, 2010).

### **2.6.1 Poly (ethylene glycol)**

Poly (ethylene glycol) (PEG) is widely used as a plasticizer for PLA and monomeric and polymeric compounds which may be classified as plasticizers or, in some cases, as slow evaporating solvents. The following chemical formulas **Figure 2.13** describe the structures of these materials. The low molecular weight compounds up to 700 are colorless, odorless viscous liquids with a freezing point from -10 °C (diethylene

glycol), while polymerized compounds with higher molecular weight than 1,000 are wax like solids with melting point up to 67 °C for n = 180. (Wypych, 2004)



**Figure 2.13 :** Poly(ethylene glycol) chemical structure.

(Source : Wypych, 2004)

An addition of PEG has been reported to affect mechanical, physical, and barrier properties of the polymer. PEG content of 16.6% (w/w) can provide a favorable compromise between PLA barrier and mechanical properties (Sebastien et. al., 2006). Higher PEG contents results in a higher WVTR owing to progressive film plasticization that modifies the hydrophilic character of PLA film (Pitt et. al., 1992). The incorporation of PEG may decrease material cohesion by creating intermolecular spaces and thus increasing D for water. Siparsky et al.(1997) also reported higher WVP for PEG/PLA blends compared to that for PLA. This phenomenon was attributed to hydrogen bonding between water and the ester group of PEG, which leads to high solubility and P values. In addition, PEG is also soluble in many organic solvents including aromatic hydrocarbons (not aliphatics). They are used to make emulsifying agents and detergents, and as plasticizers, humectants, and water-soluble textile lubricants.

## 2.7 Structural Characterization Morphological Analysis

There are two methods used to characterize the nanostructure of polymer layered silicate nanocomposites in this research which are X-ray diffraction (XRD), Scanning Electron Microscopy (SEM)

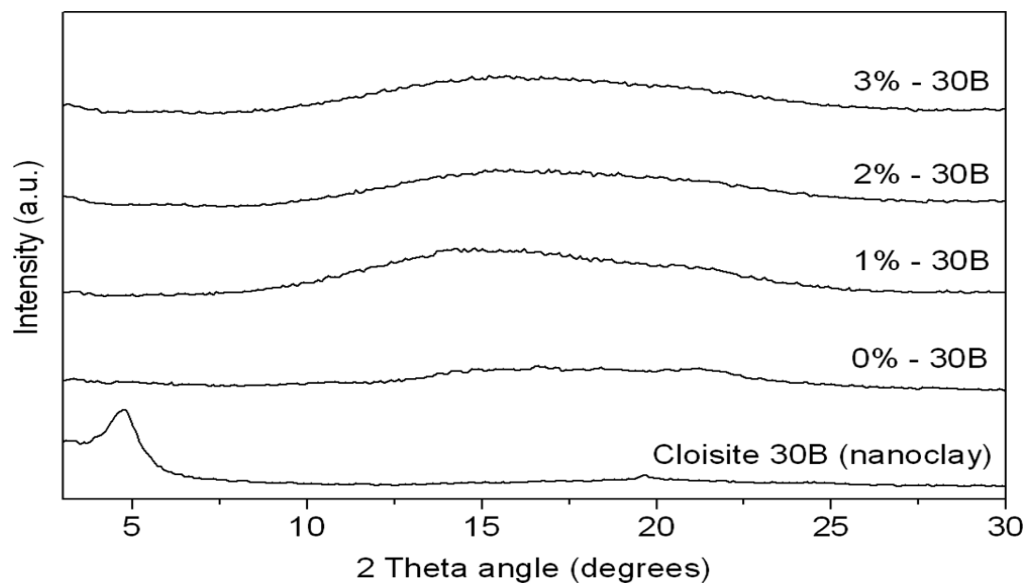
### 2.7.1 X-ray Diffraction (XRD)

The most straightforward is X-ray diffraction (XRD) because it is a simple way to evaluate the d-spacing between the silicate layers. The sample preparation is relatively easy and the XRD can be performed within a short time. However, one needs to be very careful with the interpretation of the results. Lack of sensitivity of the analysis and limits of the equipment can lead to misleading conclusions about the nanocomposite structure. The lack of peak at low angle is not a definite proof of nanocomposite structure.

Krishnamachari et al. (2009) declare that the common procedure to calculate the d-spacing for polymer-clay nanocomposites is by Bragg's equation using the XRD results. In their research, they used XRD to determine the d-spacing for the combination of PLA with a variable of Cloiste 30 B loadings as in **Figure 2.14**. The Bragg peak for the 30B nanoclay (without polymer) was located at  $2\theta = 4.9^\circ$ , which corresponds to the d-spacing of  $d_{001} = 1.8$  nm. For the PLA-30B nanocomposites of different nanoclay

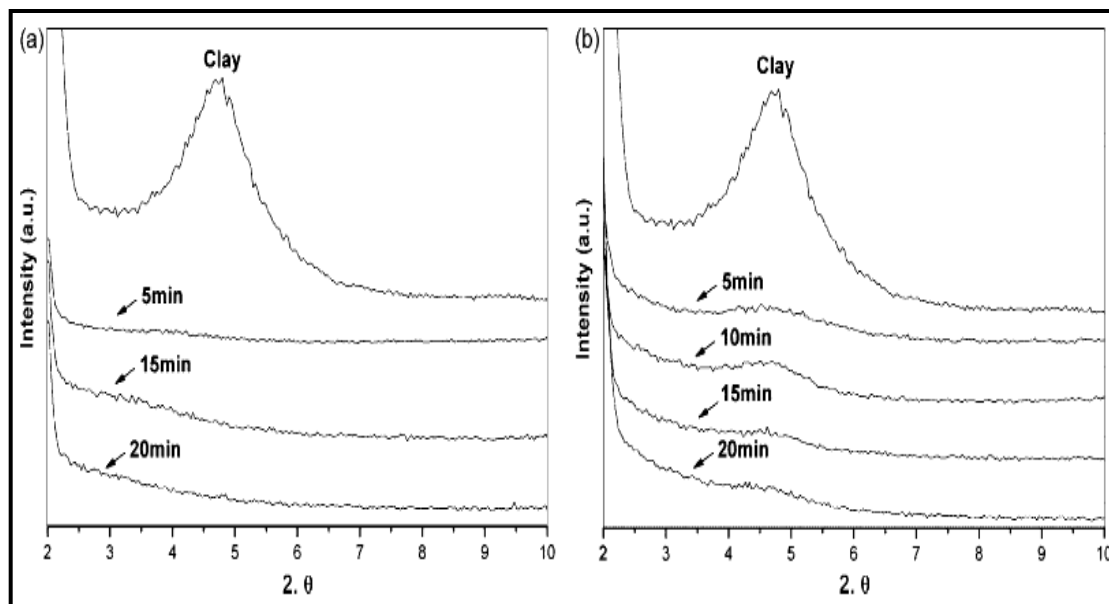
loading levels, there were no noticeable XRD peaks of 30B observed, confirming that the exfoliation of silicate layers of 30B in the PLA matrix was obtained

Another findings by Luduěna et. al. (2007) about the Processing and microstructure of PCL/clay nanocomposites where their studies about the morphology and mechanical properties of polycaprolactone/clay nanocomposite films prepared by two techniques (casting: exfoliation adsorption; intensive mixing) were also used XRD to revealed an intercalated–exfoliated mixed structure for both techniques. According to the **Figure 2.15**, shows that both clay structures, intercalated and exfoliated, coexisted in 5% C30B nanocomposites prepared with dichloromethane (a) and the mixture (50% v/v) of the two solvents (b) at all ultrasonic bath times, since there is no diffraction peak in comparison with the clay alone.



**Figure 2.14:** XRD Diffractograms: Cloisite 30B and PLA with 0%, 1%, 2% and 3% (w/w) of Cloisite 30B.

(Source : Krishnamachari et al., 2009)



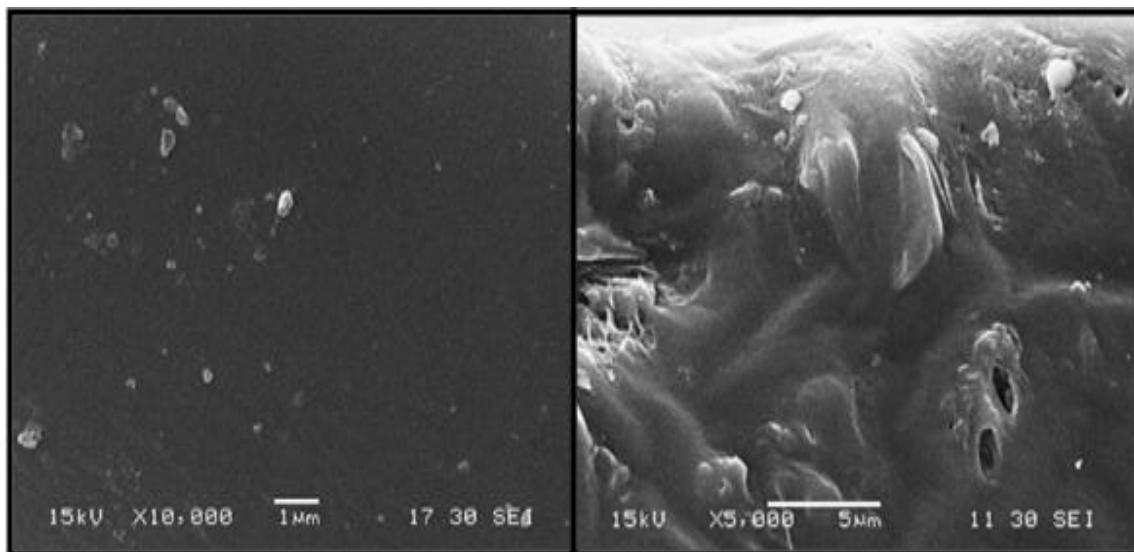
**Figure 2.15 :** X-ray diffractograms for 5C30B nanocomposites prepared by casting at different ultrasonic bath times: (a) dichloromethane and (b) mixing of solvents.

(Source : Luduēna et. al., 2007)

### 2.7.2 Scanning Electron Microscopy (SEM)

Apart from that, Scanning electron microscopy (SEM) is the most appropriate method to determine the microstructure of polymer-layered silicate nanocomposites. Alexandre and Dubois (2000) clarify that most of nanocomposites have a broadening of the diffraction peak which they must rely on the SEM examination to define the overall structure of nanocomposites.

**Figure 2.16** shows SEM micrographs of polycaprolactone/clay nanocomposite with 5 wt% of C30B nanocomposites prepared with (a) dichloromethane and (b) the mixture of solvents. In the case of dichloromethane, these pictures reveal the tendency of the solvent to leave holes into the matrix during its evaporation and the clay particles with a size range of 800–2100 nm was observed while for the mixing of solvents; even though clay particles were also observed, its size was lower (90–529 nm). It is expected that as far as particle size becomes lower, mechanical properties are better. (Luduěna et. al., 2007). However, the SEM analysis itself cannot verify the structure of the polymer either intercalated or exfoliated clay layers. Thus, the SEM results are usually being supported by XRD results as described in **Figure 2.15** in **Section 2.6.1**.



(a)

(b)

**Figure 2.16:** SEM micrographs of 5% C30B nanocomposite films thickness at 15 min ultrasonic bath: (a) mixing of solvents and (b) dichloromethane

(Source : Luduěna et. al., 2007)

## 2.8 Testing And Analysis

A brief literature on the testing and analysis, which were done in this study, are provided in this section. The description of the analytical equipments was also mentioned in order to describe their application in the analysis of the current study.

### 2.8.1 Barrier Properties Testing

The taste and the quality of a food from the production until the food is delivered to the consumers is a very important aspect to be concerned in the food manufacturing field. Duncan (2011) mention that the food must have a good packaging condition in

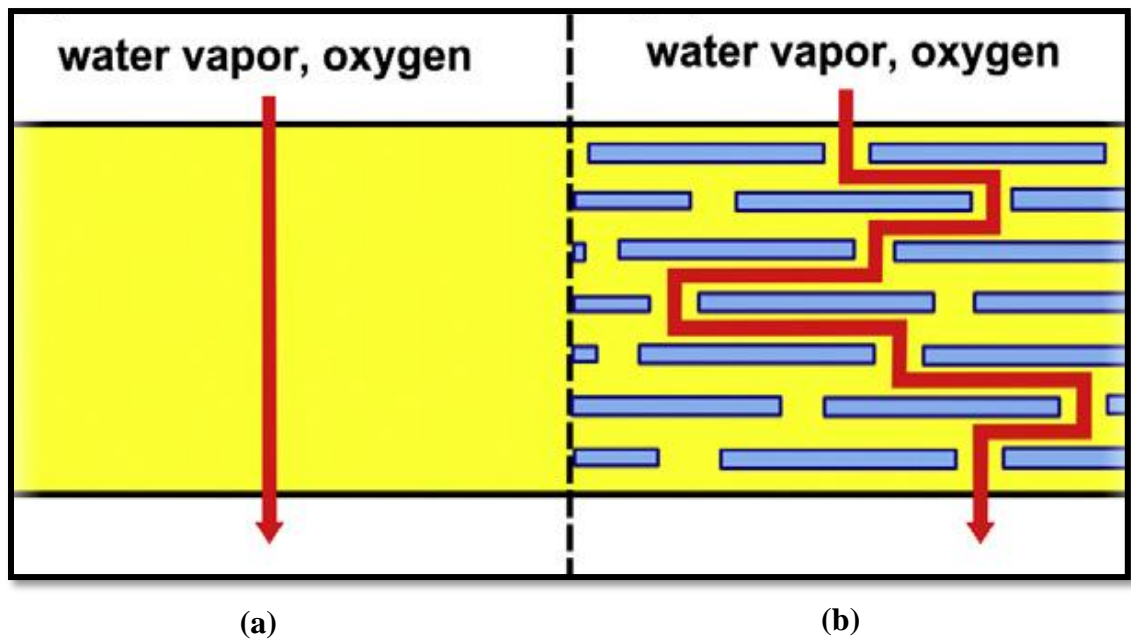
order to protect the food from dirt or dust, oxygen, light, pathogenic microorganisms, moisture, and a variety of other damage substance. A resistance to physical abuse, low cost, lightweight, recyclable or disposer and able to withstand with an extreme condition is the most desired feature of the packaging material (Albrecht et al., 2011).

One of the most critical issues in a polymer is its limitation to barrier properties. Thus, a new nanofiller technology has been introduced to overcome this weakness. Using this method, the properties of the polymer matrix has been improved by adding the polymer matrix with the silicate layers. Clay layers are naturally impermeable. Clays increase the barrier properties by creating a maze or tortuous path that retards the diffusion of gas molecules through the polymer matrix (Duncan, 2011). **Figure 2.17** shows the mechanism of the barrier properties before the addition of nanofillers also the improvement of barrier properties after the addition of nanofillers.

The presence of surfactants or other additives used to efficiently incorporate the filler into the matrix can also affect the diffusivity or solubility of permeants. The effects of the interfacial regions have been found to be particularly important in polymer matrices that possess very high native gas permeabilities, such as polyolefins. Furthermore, the degree of enhancement in the barrier properties depends on the degree of tortuosity created by clay layers in the diffusion way of molecules trough the enhancement in the polymer matrix. The tortuous factor is determined by the ratio of actual distance which diffusive molecule walks into the shortest distance to diffuse

(polymer film thickness). This factor is affected by the aspect ratio of clay dispersed in the matrix. (Ray et. al., 2003)

Yano et al.(2000) found that a 2% loading of synthetic mica and MMT gave drastic decreases in the coefficient of permeability. By looking at the dependence of the filler length on permeability coefficient, it was seen that as the length of the clay increases the permeability coefficient decreases dramatically. With 2% mica bringing the permeability coefficient of water vapor to a value that is less than one tenth of that of pure polyimide. In other words, the permeability is seen to decrease with increasing aspect ratio.

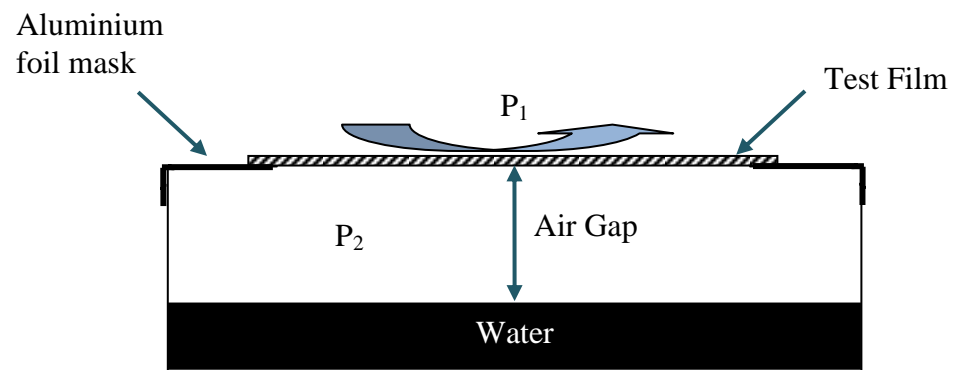


**Figure 2.17** : Mechanism of the barrier properties (a) before the addition of nanofillers and (b) improvement after the addition of nanofillers.

(Source : Duncan, 2011)

One of the techniques used to measure the water vapor transmission rate (WVTR) was a modification of the wet cup method described by ASTM E 96-95. In this method the test film covered a Petri dish filled with distilled water, as shown schematically in **Figure 2.18**. The mass of water lost from the dish was monitored as a function of time, and the WVTR was calculated from the steady-state region. Thickness measurements were obtained with a digital gauge at a minimum of nine positions on a test specimen (Hu et al., 2001).

Rhim et al. (2008) has emerged on a study about tensile, water vapor barrier and antimicrobial properties of PLA/nanoclay composite films among PLA-based composite films with different types of nanoclays, such as Cloisite Na<sup>+</sup>, Cloisite 30B and Cloisite 20A. In their studies, WVTR was determined gravimetrically using a modified ASTM Method E 96-95. The WVP of nanocomposite films compounded with organically modified nanoclays, which is Cloisite 20A and 30B, decreased, while that of films composite with unmodified natural nanoclay, Cloisite Na<sup>+</sup>, increased slightly. This result is mainly attributed to the hydrophobicity of organically modified nanoclays and hydrophilicity of unmodified nanoclay. The increase in water vapor barrier property of polymer/clay composite films is mainly attributed to the tortuous path for water vapor diffusion due to the impermeable clay layers distributed in the polymer matrix consequently increasing the effective diffusion path length.



Inside oven,  $T=35.5^{\circ}\text{C}$

**Figure 2.18 :** Schematic representation of the wet cup test.

(Source : Hu et al., 2001)

## **CHAPTER 3**

### **METHODOLOGY**

#### **3.1 Introduction**

The aim of this study is to modify sodium cloisite organoclay using metal ion exchange solution (ion exchange method). In this project, 6 samples of 3 different weight percentage of nanoclay at 1%, 2%, and 3% by weight with and without an existence of a plasticizer, polyethylene glycol (PEG) are produced to be tested. The modification of nanoclay has been done via solution dispersion method. A successful modification will be clarified through AAS and XRD testing. The highest inter layer spacing of modified clay obtained is then intercalated into polymer matrices and was tested again to determine its final properties via SEM testing and water vapor permeability.

## 3.2 Materials

### 3.2.1 Cloisite Na<sup>+</sup>

Cloisite Na<sup>+</sup> is a natural montmorillonite used as an additive for plastics to improve various plastic physical properties, such as reinforcement and barrier. It was obtained from Southern Clay Products, Inc. The physical properties of Cloisite Na<sup>+</sup> are as follows:

**Table 3.1:** Properties of Cloisite Na<sup>+</sup>

Physical Properties	
Physical states	Solid
Color	Off White
% Moisture	4-9%
% Weight Loss on Ignition	7%
Density	Density, g/cc = 2.86
X Ray Results:	d001 = 11.7Å

### 3.2.2 Copper (II) Chloride

Based on this experiment, Copper (II) Chloride also can be called as Cupric chloride has been used as the transition metal ion salts (TMI) in order to modify the pure Na<sup>+</sup> via ion exchange method where Copper (II) Chloride was purchased from SIGMA-ALDRICH. The physical properties of Copper (II) Chloride are as follows :

**Table 3.2:** Properties of Copper (II) Chloride

<b>Physical Properties</b>	
Physical states	Powder
Freezing / Melting Point	620 °C
Relative Density	3,386 g/cm <sub>3</sub> at 20 °C
Molecular Weight	134.45 g/Mol
Molecular Formula	CuCl <sub>2</sub>

### 3.2.3 Poly (lactic acid)

The type of poly (lactic acid) used for this research is Ingeo biopolymer 2003D, obtained from NatureWorks LLC. It is a thermoplastic resin derived from annually renewable resources and is specifically designed for use in fresh food packaging and food service ware applications.

**Table 3.3:** Properties of Poly(lactic acid)

<b>Physical Properties</b>	
Specific Gravity	1.24
Clarity	Transparent
<b>Mechanical Properties</b>	
Tensile Strength @ Break, psi (MPa)	7700 (53)
Tensile Yield Strength, psi (MPa)	8700 (60)
Tensile Modulus, kpsi (GPa)	500 (3.5)
Tensile Elongation, %	6.0
Notched Izod Impact, ft-lb/in (J/m)	0.3 (16)
Heat Distortion Temperature (°C)	55

### 3.2.4 Methanol and Ethanol

Ethanol and methanol were used as a solvent in modification of Na<sup>+</sup>, acquired from Fisher Scientific. The physical properties of ethanol and methanol are as follows:

**Table 3.4:** Properties of Methanol and Ethanol

Physical Properties		
Solvent	Methanol	Ethanol
Physical states	Liquid	Clear Liquid
Appearance	Clear, colorless	Clear, colorless
Odor	Alcohol-like – weak odor	Mild, rather pleasant, like wine or whis
Vapor Pressure	128 mm Hg @ 20°C	59.3 mm Hg @ 20°C
Vapor density	1.11 (air =1)	1.59 (air =1)
Viscosity	0.55 cP 20 °C	1.2 cP 20 °C
Boiling Point	64.7°C @ 760 mm Hg	78 °C
Melting Point	-98 °C	- 114.1 °C
Solubility	Miscible	Miscible
Specific Gravity/Density	7910 g/cm <sup>3</sup>	0.790 g/cm <sup>3</sup>
Molecular Formula	CH <sub>4</sub> O	C <sub>2</sub> H <sub>5</sub> OH
Molecular Weight	32.04	46.0414

### 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 as follows:

**Table 3.5:** Properties of Di-chloromethane

Physical Properties	
Physical states	Liquid
Appearance	Colorless Liquid
Odor	Ethereal odor
Vapor Pressure	350 mm Hg @ 20°C
Vapor density	2.9 (air =1)
Boiling Point	104 °F
Freezing / Melting Point	-142 °F
Solubility	Moderately soluble in water
Specific Gravity/Density	1.33 g/cm <sup>3</sup>
Molecular Formula	CH <sub>2</sub> Cl <sub>2</sub>

### 3.2.6 Polyethylene Glycole

Polyethylene glycol (PEG) is gained from Fisher Scientific. It is widely used as a plasticizer for PLA. The physical properties of Polyethylene glycol (PEG) are as follows:

**Table 3.6:** Properties of Polyethylene glycol (PEG)

Physical Properties	
Physical states	Liquid
Appearance	Clear
Odor	Odorless
Vapor Pressure	0.05 mm Hg @ 20°C
Vapor density	2.1 (air =1)
Boiling Point	195760 °C
Freezing / Melting Point	-13 °C
Solubility	Soluble in water, Di-chloromethane
Specific Gravity/Density	1.1200 g/cm <sup>3</sup>
Molecular Formula	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>

### 3.3 Modification of Nanoclay Using the Solution Intercalation Method

The main objective of the research is to use modified clay as filler in polymer nanocomposites in order to improve its permeability and configuration. The experiment begins with the modification of the organoclay.

### **3.3.1 Pre-treatment Phase of Nanoclay**

The clay sample was thoroughly washed first before the modification stages. This step was required to be done in order to remove an excess surfactants and impurities. In this process, clay sample was added into the solvent (ethanol) at a ratio 2g:40 mL. The suspension is then stirred exuberantly for 24 hours. During the stirring, the clay will be swell and changing the dispersion to become slurry. This slurry was kept in 1 M NaCl solution for 48 hours to ascertain the removal of exchangeable ion contaminants. The slurry was then being filtered and dried in an oven for 12 hours at 80 °C. The step was repeated by using methanol and water as a solvent (Nawani et al., 2007).

### **3.3.2 Preparation of Metal Ion Solution and Surface Modification Phase**

The dried clay was then being treated with 0.30 M of desired metal ion salts. In this experiment, Copper <sup>2+</sup> had been used as a metal ion. Copper was chosen because it has exceeded the CEC values from the previous studies by (Nawani et al., 2007).

Based on the molecular weight of the metal ion salts, the desired weight of material required to produce a 250 ml, 0.3M solution is determined as the table below,

**Table 3.7.**

**Table 3.7 :** Molecular weight and weight required for Copper (II) Chloride, CuCl<sub>2</sub>

Salt	Molecular weight (g/Mol)	Weight Required (g)
Copper (II) Chloride, CuCl <sub>2</sub>	134.5	10.09

The amount of salt needed as in a table above was weighed by using an analytical weight in **Figure 3.1**. Three types of solvent has been used in this experiment as a variable which are water, methanol and ethanol. Then the weighed salt was dissolved into a solvent. The solution is stirred for 1 - 2 hours at first in order to encourage the homogenous of the solution. For this experiment, 10g of pre-treated nanoclays was used for every 250 mL of metal ion solution. An organoclay subsequently was added into the solution and was stirred for 36 hours. As a prevention of solvent evaporation, the clay suspension was kept in a closed container throughout a stirring process. After the treatment, the samples were filtered, washed, and dried again in an oven for 12 hours at 80 °C (Nawani et al., 2007). Then, the clay was powdered by using mortar and pestle. The types of nanoclay employ, the various corresponding solvents and the transition metal ions used are summarized in **Table 3.8**.

**Table 3.8 :** Transition Metal Ion Salts, Solvents and Tyoes of Nanoclay used in the Modification Procedures.

Nanoclay	Solvent	Transition Metal ions
Na+	Water	Copper
	Methanol	
	Ethanol	



**Figure 3.1 :** Analytical Weight

### 3.4 Adsorption Intensity Testing Using Atomic Adsorption Spectrometry (AAS)

The intensity of adsorption of the transition metal ions onto the surface of nanoclay due to utilization of different solvents are tested at this stage. This step is done to prove the feasibility solvent to be used during the surface modification by solution intercalation phase. The sample must undergo a testing to verify the amount of the transition metal ions absorbed by the organoclay. In this study, AAS has been used as a medium to analyze the results as shown in **Figure 3.2**.



**Figure 3.2 : AAS Equipment**

### 3.4.1 Soil Leaching Phase

The initial step before the testing process has been taking place, is to prepare the sample. Since the AAS just only accepts a sample in a liquid form, all the samples needed to transform into a liquid phase. In order to prepare the sample, a soil leaching method has been chosen based on the journal written by Hwang, Park & Namkoong (2007). Ethylenediaminetetraacetic acid (EDTA) has been selected as the leaching solution because the recovery rate of heavy metals using this medium is approximately 97%. Hwang, Park & Namkoong (2007).

In this step, 0.05M EDTA was prepared by weighing 14.612g of EDTA powder based on its molecular weight which are 292.24 g/mol. The EDTA is then dissolved into 1000mL of ultrapure water.

Then, 3g of sample clay was weighed and placed in a Schott bottle and EDTA was added into it at a ratio of 10mL : 1g. The bottle is then be placed in an ultrasonic water bath (60 Hz) for 12 minutes to leach the adsorbed metal ions back out of the surface of nanoclay also to increase the treatment efficiency and shorten the time needed to extract the leach metal. After 12 minutes, the solution is then being filtered by using a vacuum filtration pump with 1  $\mu$ m filter paper. Afterward, the filtrate solution was collected and ready for the next stage.

### 3.4.2 Atomic Adsorption Spectrometry Testing

From the journal by Nawani et al. (2007), the testing began by filtering the sample using a 0.22µm syringe filter. This step must be done to remove any impurities and bubbles in the sample solution also to prevent damage to the AAS equipment. Then, 100µL of sample clay leachate is then diluted with ultra-pure water 10 mL, which is a dilution factor of 100. The standards for metal ions (Copper <sup>2+</sup> ) was prepared using several dilution methods with a variable concentration from 1.6 ppm until 0 ppm. The mother solution has a concentration of 1000ppm. So, calculation with the formulae below can be used to calculate the mother solution needed.

$$M_1 V_1 = M_2 V_2 \quad (1)$$

Where :

$M_1$  = Concentration of mother solution

$M_2$  = Concentration of the standard

$V_1$  = Volume of the standard needed

$V_2$  = Volume of mother solution needed

Then, from the stock solution, the standard for calibration with a differ concentration was prepared. The other calculation for a variety of concentrations are as in the table below:

**Table 3.9 :** Volume of mother solution needed for a range of concentration.

Calibration Standard (ppm)	Volume of mother solution needed, V <sub>2</sub> (μL)
1.6	1600
1.2	1200
0.8	800
0.6	600
0.00 (blank)	0

The summary of the standards and samples ran through AAS is shown in the table 3.10.

**Table 3.10 :** Summary of AAS Samples

Transition Metal Ions	Calibration Standard	Sample
Cu	1.6 ppm	Na+ in Ethanol
	1.2 ppm	
	0.8 ppm	Na+ in Methanol
	0.6 ppm	
	0.00 ppm (blank)	Na+ in Water

### 3.5 Fabrication of PLA Nanocomposites.

An outstanding outcome of modification process will be continued with the production of polymer nanocomposites by a solvent casting method with a specified procedure. The detailed composition of the film is presented in **Table 3.11**. At first, all ingredients were accurately weighed (0.4g  $\pm$  0.001g). The mixture is then poured into

20 mL of Dichlorometane in a conical flask. For the experiment with PEG, PEG was added together with 20 mL of Dichlorometane in a conical flask. Since this experiment is using a liquid PEG, 2 drops of PEG were added into the conical flask by using a dropper. The solution was then mixed well by using a stirrer for 30 minutes followed by an ultrasonic water bath 30 HT as in **Figure 3.3** for 20 minutes until the polymer was completely dissolved. The resultant solution was poured into a glass petri dish with a diameter 11 cm and 2 cm deep. The dichloromethane was allowed to evaporate and dry at a room temperature (Ahmed. J. et. al., 2010). A thin layer of nanocomposites is then formed called as a membrane as shown in **Figure 3.4**.

**Table 3.11** : Details of PLA-based material used in the experiment.

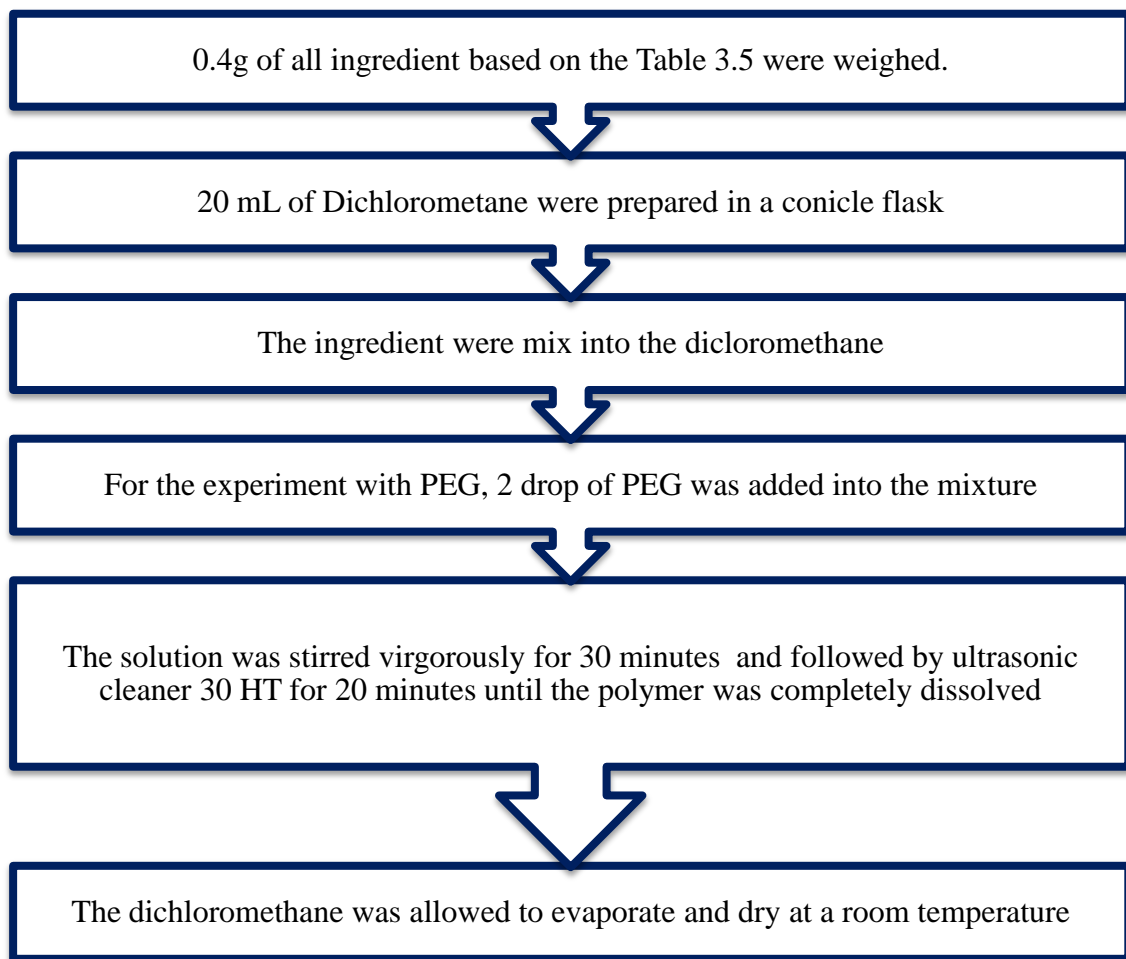
No	PLA		Modified Clay (Na <sup>+</sup> )		With PEG
	%	Weight (g)	%	Weight (g)	
<b>1</b>	99	0.396	1	0.004	X
<b>2</b>	98	0.392	2	0.008	X
<b>3</b>	97	0.388	3	0.012	X
<b>4</b>	99	0.396	1	0.004	√
<b>5</b>	98	0.392	2	0.008	√
<b>6</b>	97	0.388	3	0.012	√



**Figure 3.3 :** Ultrasonic water bath 30 HT.



**Figure 3.4 :** Formed of the thin layer film.



**Figure 3.5 :** Summary of the production of polymer nanocomposites.

### 3.6 Characterization of Polymer Nanocomposite

After the preparation of polymer nanocomposite has been done, the sample was go through some characterization and morphological testing such as SEM and XRD. The testing on permeability of the polymer nanocomposites was also done to achieve the objective of the studies.

#### 3.6.1 X-ray Diffraction Analysis (XRD)

The analysis by using XRD is to characterize the structure of the samples. also to identify and compare the d spacing of the modified clay. Based on the XRD result obtained, the best result of d spacing compared to the unmodified clay will be chosen to go through the next process which is the production of the polymer nanocomposites. After the formation of polymer, the film will be tested again with XRD analysis in order to analyze the structure of the clay inside the polymer.

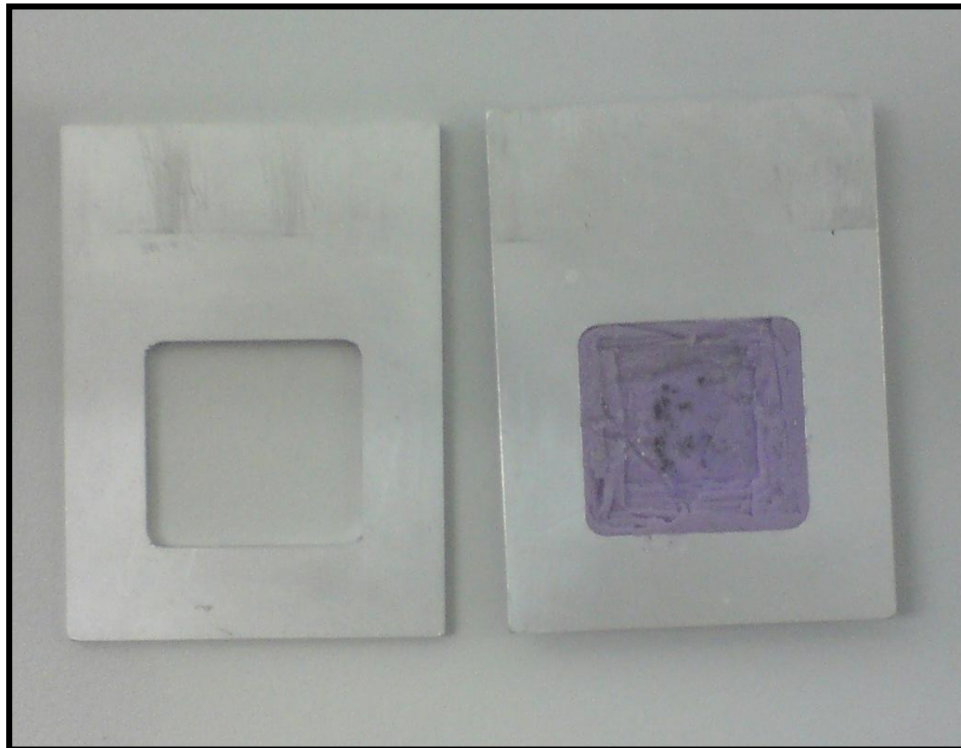
Before running the analysis of XRD, the preparation of the sample must be done first. The sample was prepared by placing a plasticine into the slot to cover the hole. Then, the top of the plasticine was covered by parafilm. Then, the sample was placed on top of the parafilm as in **Figure 3.6**. After that, the sample was transferred to XRD chamber. The samples are scanned in fixed step size, 0.02 with a step-time of 0.1 s in the range of  $3-80^{\circ}$ . Based on the scanning, an XRD diffractogram (intensity 20) is

obtained. Then, the d-spacing (d) of the interlayer gallery of Na<sup>+</sup> and the PLA based nanocomposites is calculated using Bragg's Law equation

$$d = \frac{n \lambda}{2 \sin \theta} \quad (2)$$

Where:

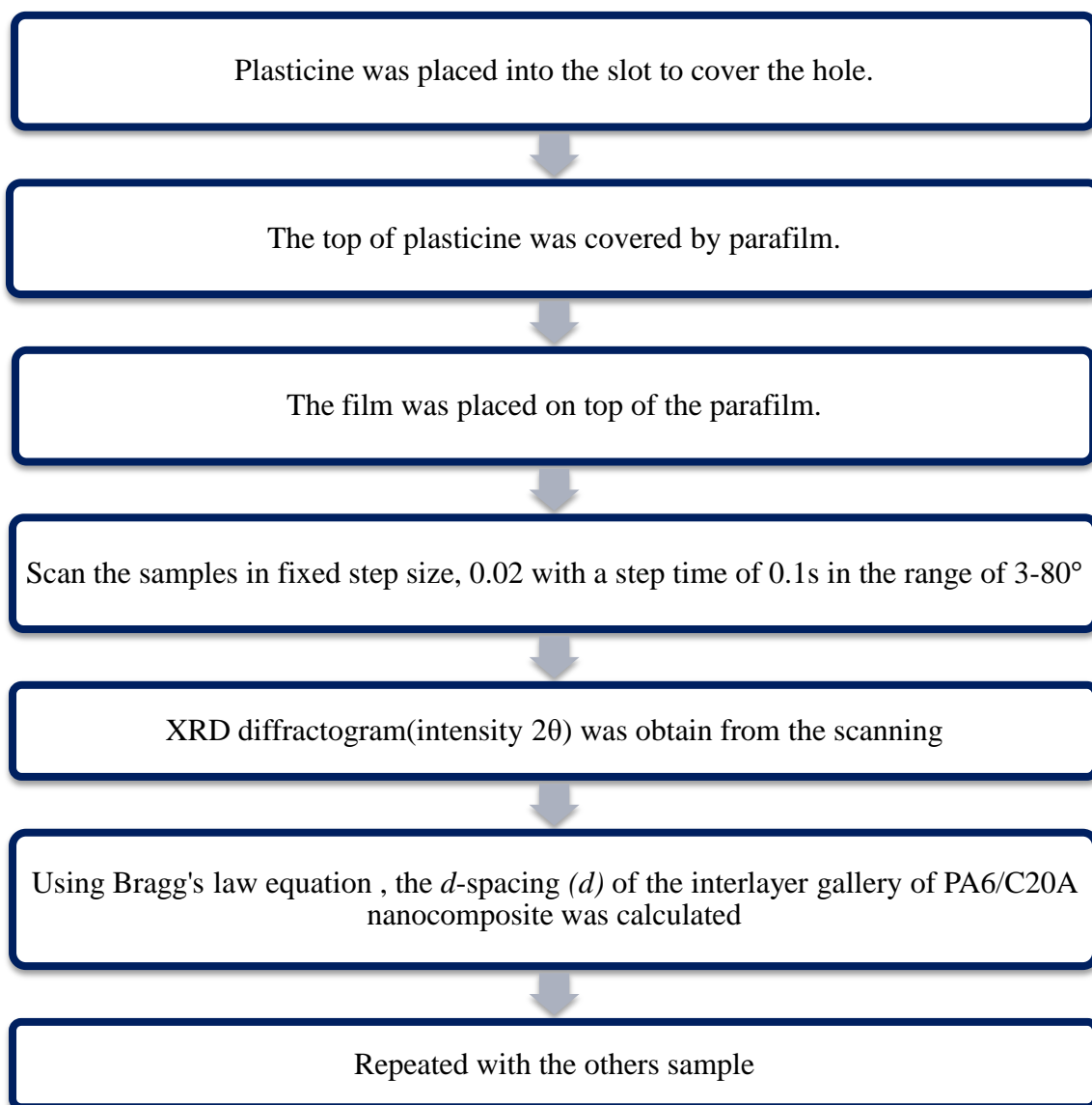
- d = Space between layers of the clay
- $\lambda$  = Wavelength of the X-ray which is 0.154nm
- $\theta$  = Angle at the maximum point of the first peak into a spectrum
- n = Order of diffraction



**Figure 3.6 :** Sample preparation : Left is the original sample slot and the right side is the sample slot with plasticine and paraffin on top of it.



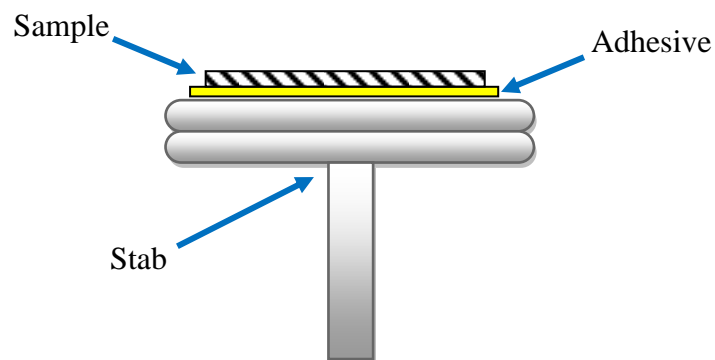
**Figure 3.7 : XRD Equipment**



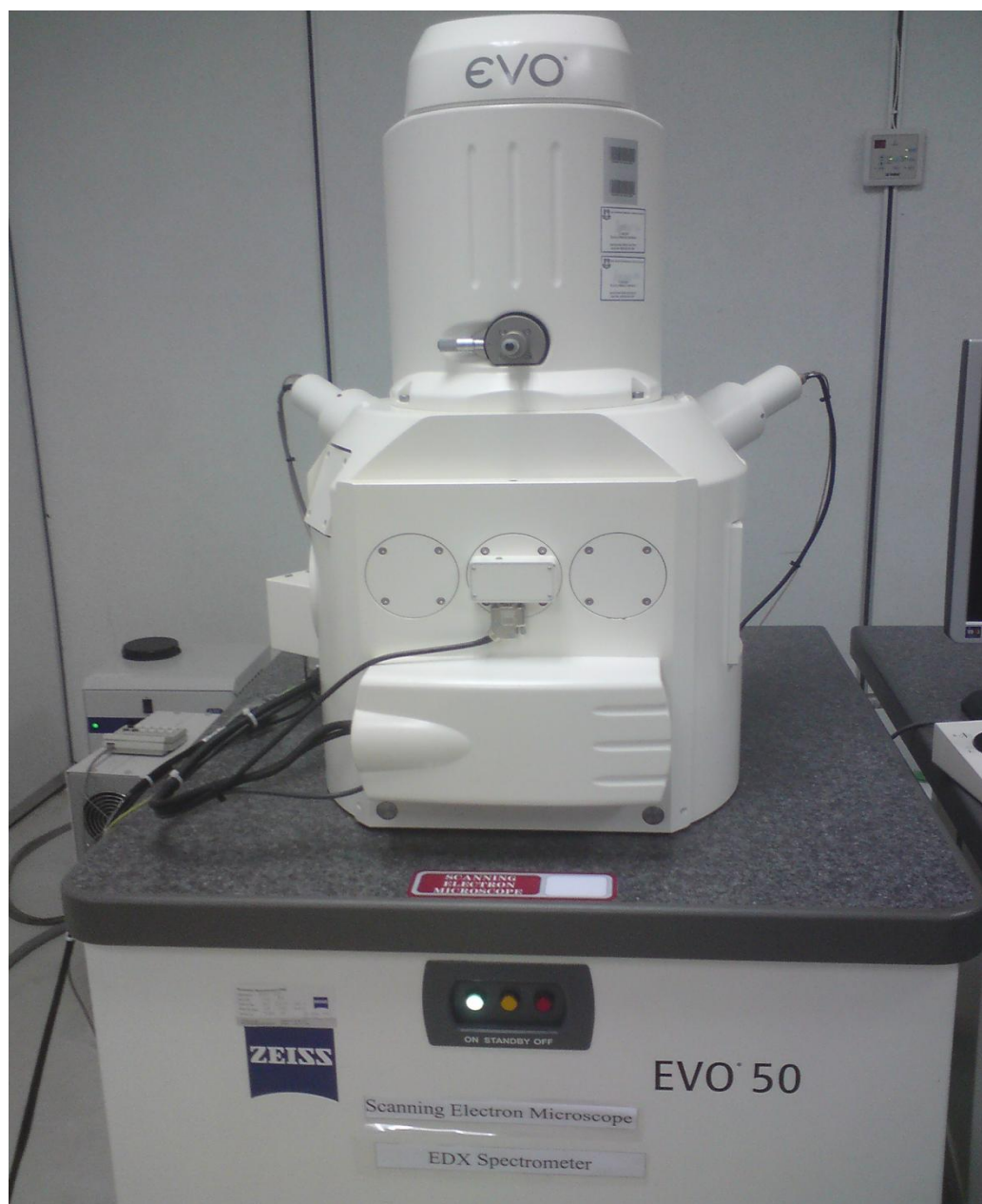
**Figure 3.8 :** The summary of XRD analysis from preparation until analysis procedure.

### 3.6.2 Morphology and Structure Determination through Scanning Electron Microscope (SEM)

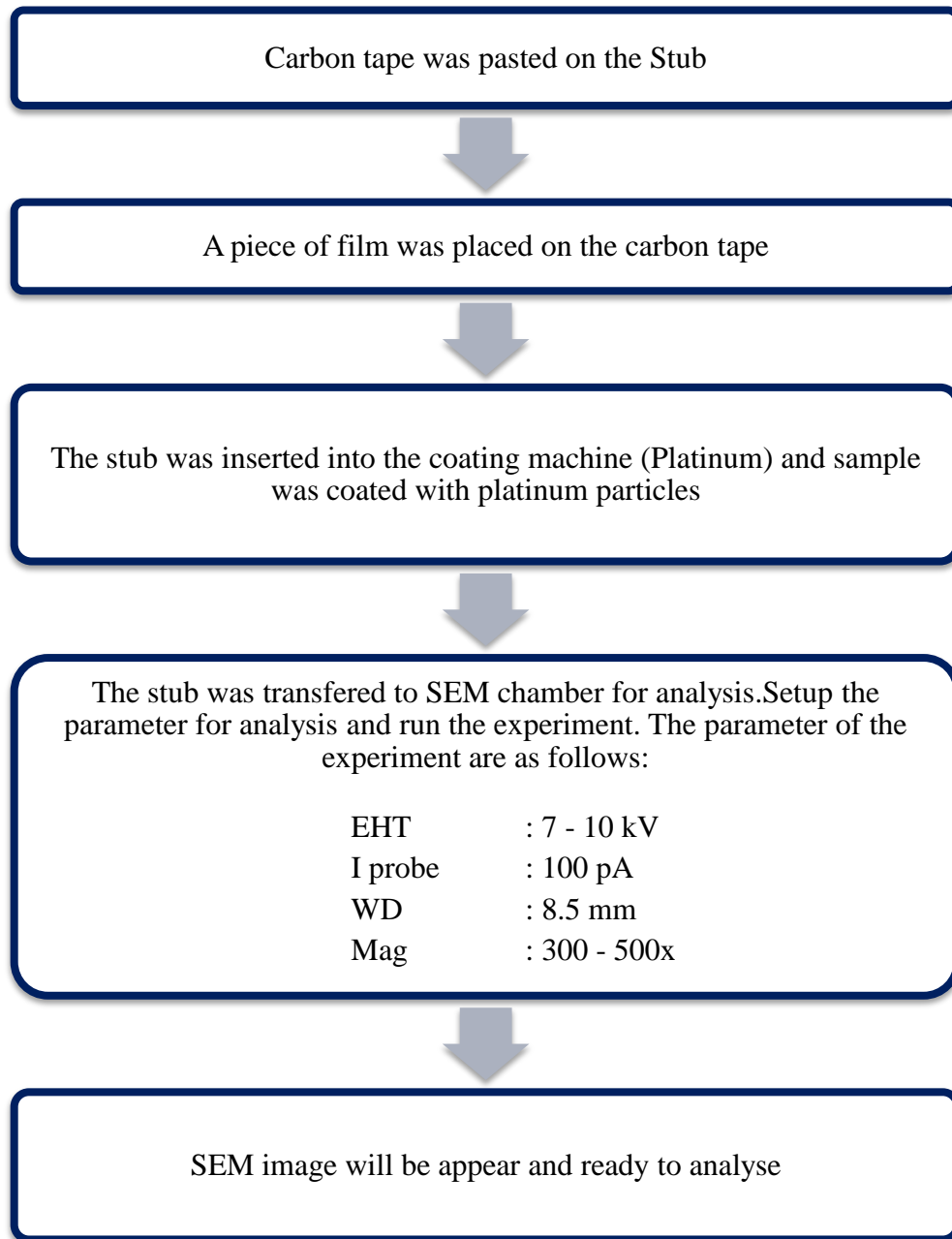
The surface of the film polymer nanocomposite can be verified by using SEM equipment. The specimen was initially cut into a small piece. Then, the specimen is coated on a specimen holder (stub) with a coating machine and sample was coated with platinum particles. Usually stubs are aluminum pegs with a flat surface. The specimen was attached to the stubs with a conductive adhesive where in this experiment, they are using a carbon tape as an adhesive. **Figure 3.9** shows the rough figure of stub with the specimen. Afterward, the samples are ready to be tested. The SEM image will be taken using backscattering detector. An example of SEM equipment can be seen in **Figure 3.10**



**Figure 3.9** : The stub with an attachment of a sample.



**Figure 3.10: SEM Equipment**



**Figure 3.11 :** The summary of SEM analysis from preparation until analysis method.

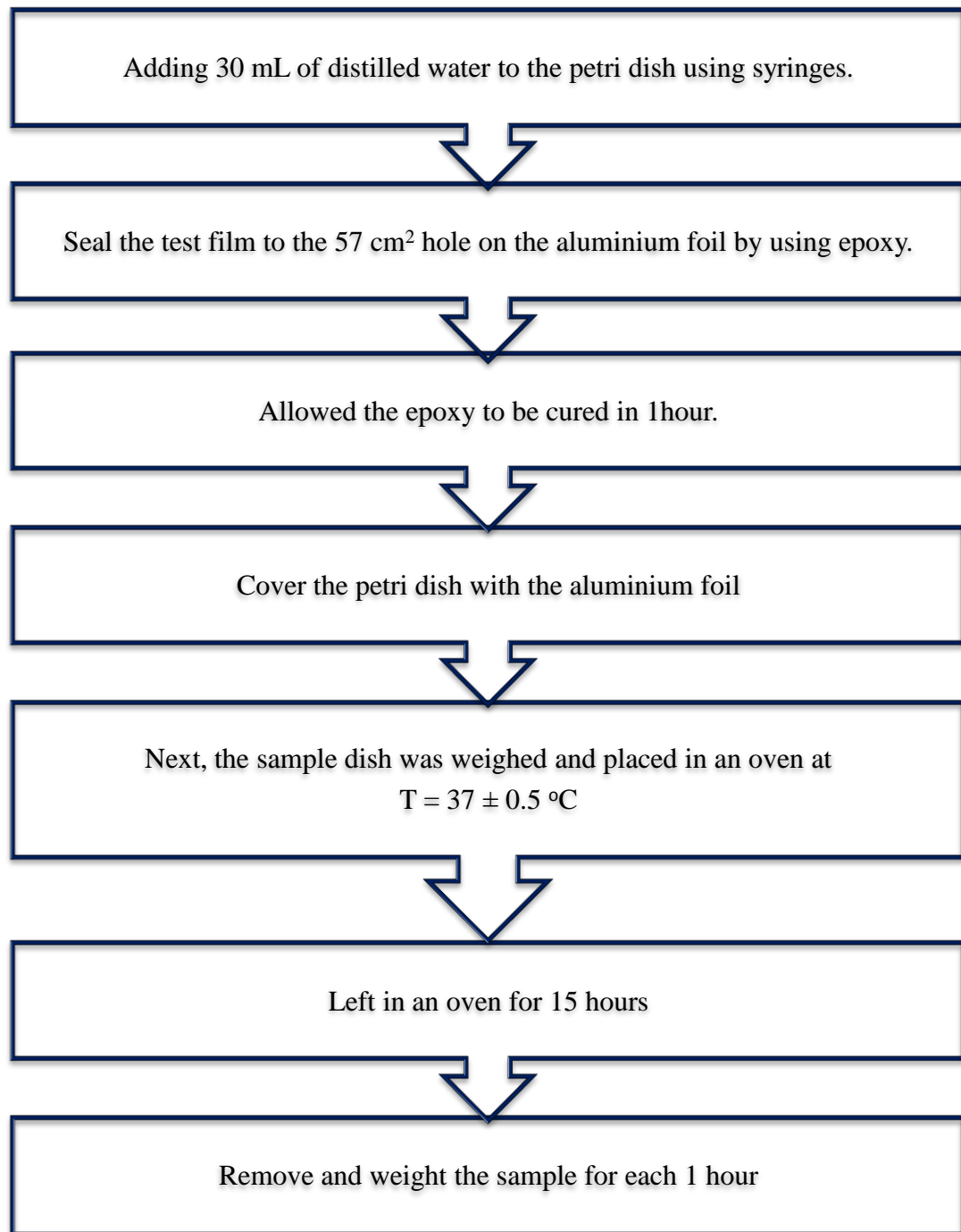
### 3.7 Permeability Studies

Measurement of water vapor transmission rate (WVTR) is based on the wet cup method described by ASTM E 96-95 (Hu et al., 2001). Using this method, distilled water was filled inside the petri dish followed by covering the petri dish with the test film.

The first step begins by 30 mL of distilled water was added to the petri dish using syringes. The surface of the petri dish was covered by the aluminum foil mask with an opening area (with or without test film)  $57\text{ cm}^2$  at the center of the aluminum foil. For the method using the test film, the test film was sealed to the aluminum foil using an epoxy. With 30 mL of water in the petri dish, the air gap will be 6 mm between the surface of the water and the test film. Then, the epoxy was allowed to be cured in 1 hour. Next, the sample dish was weighed and placed in an oven at  $37 \pm 0.5\text{ }^{\circ}\text{C}$ . It was left in an oven for 15 hours before being removed to be weighed as in **Figure 3.12**. This step is vital to confirm that this procedure did not disturb the weight loss. After 15 hours, the sample dish was removed and weighed for each 1 hour. This test was run in 5 – 6 hours. This method was repeated with an open area without the test film. The mass of water lost from the dish was monitored as a function of time and the WVTR was calculated from the steady state region.

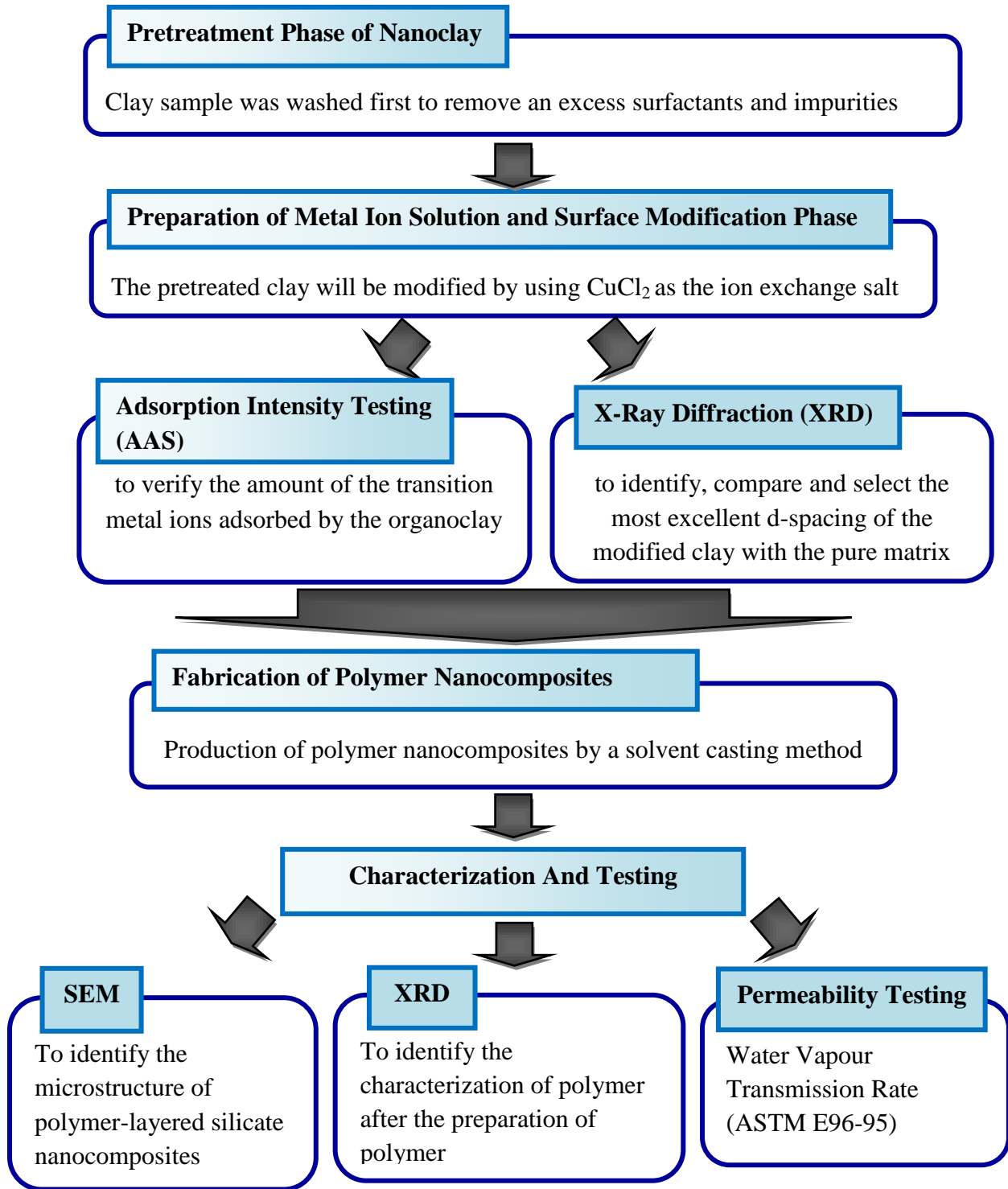


**Figure 3.12 :** The test sample was placed in an oven.



**Figure 3.13 :** Summary of the water vapor transmission rate testing

### 3.8 Overall Process Of The Research Work



**Figure 3.14 :** The overall process flow of this research

## **CHAPTER 4**

### **RESULT AND DISCUSSION**

#### **4.1 Introduction**

This section will review about the result from the test were made. The effect of the modification process before and after the preparation of polymer will be analyzed and discuss. The characterization by AAS, SEM, and XRD after the modification and the polymer preparation takes place will be discussed Apart from that, the data of each sample are plotted on the graph for better comparison and discussion. The effect of the fillers on permeability of the PLA will be compared among a different percentage of filler with and without the existence of polyethylene glycol.

## 4.2 Modification of Nanocomposites.

### 4.2.1 Introduction

Montmorillonite clay is commonly used as a filler of polymer-clay nanocomposites because layered silicate platelets of the clay can exfoliate as nanoparticles. However, the surface of the silicate platelets is originally hydrophilic and thus it must be modified chemically to make the platelet compatible with the polymer. In this study, montmorillonite clay (organoclay) has been modified with Copper (II) Chloride by using ion exchange method with different types of solvent used during pretreatment stage which are water, ethanol and methanol. The rate of success of the modification phase can be determined by using AAS.

### 4.2.2 Atomic Absorption Spectrometry

In this research, the pure MMT was modified using copper <sup>2+</sup> as a transition metal ion (TMI) with a variety solvent including ethanol, methanol and water. Thus, an analysis by using Atomic Absorption Spectrometry (AAS) was carried out in order to find out the amount of TMIs absorbed by the nanoclay. **Table 4.1** shows the result of AAS analysis of the TMI content in modified nanoclay.

**Table 4.1 :** AAS analysis of the TMI content in modified nanoclay.

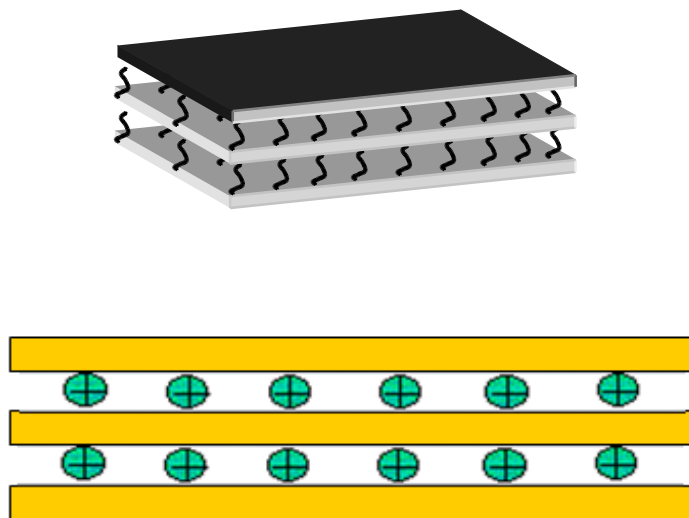
Sample	TMI content (mg/L)
Copper <sup>2+</sup> modification in methanol as a solvent	14.08
Copper <sup>2+</sup> modification in ethanol as a solvent	13.90
Copper <sup>2+</sup> modification in water as a solvent	14.09

Based upon the result, it shows the TMI content for each sample, where the Copper<sup>2+</sup> modification in water as a solvent gives the highest value which is 14.09 mg/L followed by using methanol as a solvent with 14.08 mg/L and finally ethanol as a solvent which is 13.09 mg/L.

As a conclusion, the AAS result shows that the modification of the nanoclay via copper<sup>2+</sup> as a transition metal ion (TMI) with an existence of varying types of solvent such as ethanol, methanol and water are successfully done where all the sample shows the existence of a copper<sup>2+</sup> in nanoclay content.

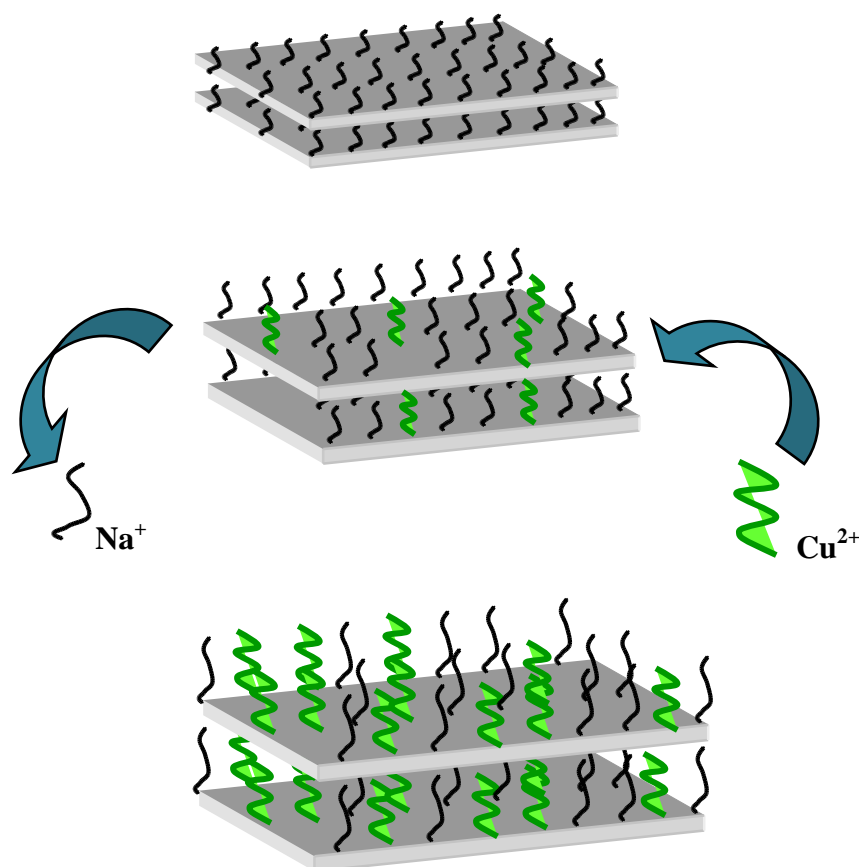
### 4.2.3 Proposed Mechanism of Modification Process

Montmorillonite, and other layered silicate clays, are naturally hydrophilic. This makes them poorly suited to mixing and interacting with most polymer matrices. Moreover, the stacks of clay platelets are held tightly together by electrostatic forces. As **Figure 4.1** shows, counterions are attracted to the net negative charge within the clay platelets. The counterions can be shared by two neighboring platelets, resulting in stacks of platelets that are tightly held together.



**Figure 4.1** : Stacks of platelets that are tightly held together.

During the modification process, the metal ions lower the surface energy of the silicate surface and improve wetting with the polymer matrix. Moreover, the long organic chains of such surfactants, with positively charged ends, are tethered to the surface of the negatively charged silicate layers, resulting in an increase of the gallery height. It then becomes possible for  $\text{Cu}^{2+}$  ions to diffuse between the layers and the surface properties of each single sheet are changed from being hydrophilic to hydrophobic. (Pavlidou & Papaspyrides, 2008). Figure 4.2 below illustrates the mechanism of the process occur.



**Figure 4.2 :** Mechanism of the modification of clay

### 4.3 Characterization of Nanocomposites Structure

#### 4.3.1 X- Ray Diffraction (XRD)

The analysis by using XRD is to characterize the structure of the samples where the interlayer spacing of the sample will be determined. The samples are scanned in fixed step size, 0.020 with a step-time of 0.1 s in the range of 3-80°. Based on the scanning, an XRD diffractogram (intensity  $2\theta$ ) is obtained. Then, the d-spacing (d) of the interlayer gallery of Na<sup>+</sup> and the PLA based nanocomposites is calculated using Bragg's Law equation

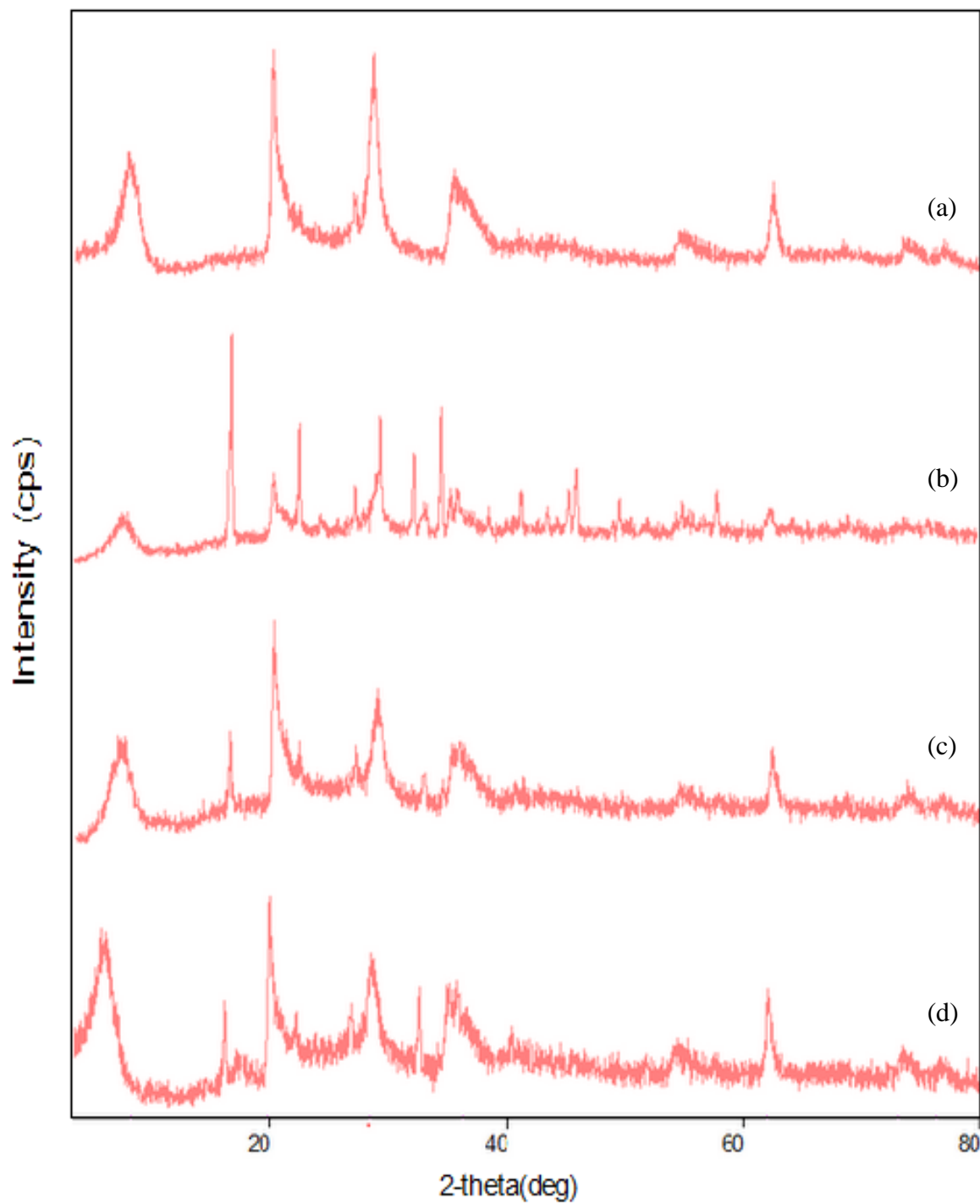
$$d = \frac{n \lambda}{2 \sin \theta} \quad (2)$$

Where:

- d = Space between layers of the clay
- $\lambda$  = Wavelength of the X-ray which is 0.154nm
- $\theta$  = Angle at the maximum point of the first peak into a spectrum
- n = Order of diffraction

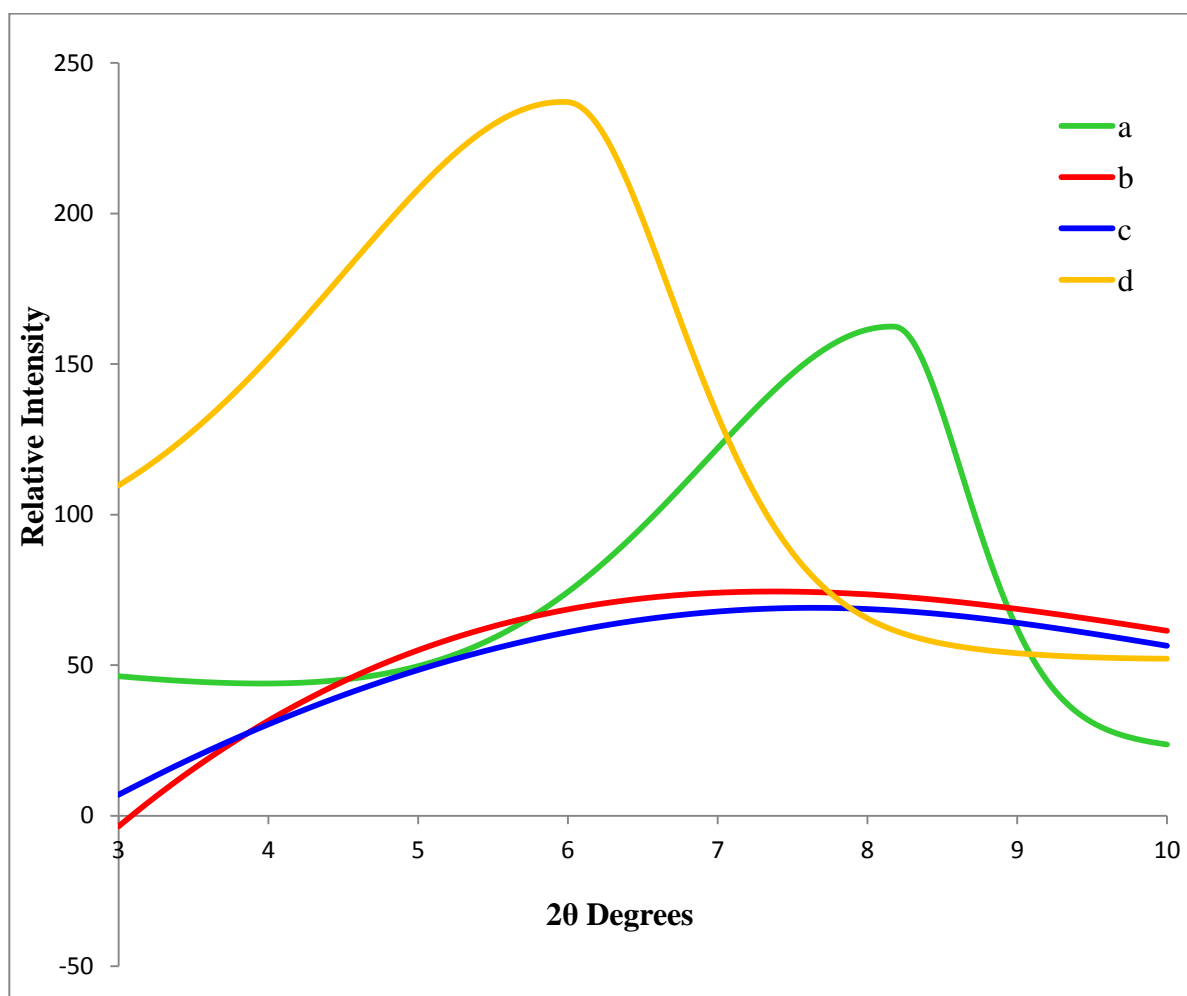
### **Comparison of the XRD Result Between Unmodified MMT with Pure MMT**

As mentioned before, in chapter 3, section 3.6.3, XRD analysis was done after the modification of the organoclay takes place. Clays will show a characteristic peak in XRD analysis due to their regular layered structure. The peak is indicative of the platelet separation or d-spacing in clay structure. According to the Braggs law, increasing of d-spacing results to the broadening and shifting the XRD peak towards the lower diffraction angle ( $2\theta$ ). **Figure 4.3** shows the data obtained from XRD for each type of samples with a diffraction angles from  $3^\circ$  to  $80^\circ$ .



**Figure 4.3 :** XRD result for each type of samples of (a) Pure MMT (b) Modified MMT with H<sub>2</sub>O + CuCl<sub>2</sub> (c) Modified MMT with Ethanol + CuCl<sub>2</sub> (d) Modified MMT with Methanol + CuCl<sub>2</sub> with a diffraction angles from 3 ° to 80°

While **Figure 4.4** shows a comparison of X-ray diffraction data of unmodified MMT and modified MMT with methanol, ethanol, and water as the solvent during purification for a better understanding. This sample was plotted on a graph of a relative intensity versus  $2\theta$  from the step size  $3^\circ$  to  $10^\circ$ .



**Figure 4.4 :** XRD patterns of (a) Pure MMT (b) Modified MMT with Ethanol + CuCl<sub>2</sub> (c) Modified MMT with H<sub>2</sub>O + CuCl<sub>2</sub> (d) Modified MMT with Methanol + CuCl<sub>2</sub>

Based on the **Figure 4.4**, the characteristic peak of pure MMT has been appearing at  $2\theta = 8.17$  corresponding to the inter layer space of 10.81 Å. Modification of neat MMT via an ion exchange method with  $\text{CuCl}_2$  as the metal ion gives a significance change towards the peak and inter layer spacing compared to the unmodified MMT. The interlayer spacing of modified MMT with ethanol and water together gives a decreasing in inter layer spacing where they both gives 3.101 Å and 5.361 Å with a characteristic peak appeared at  $2\theta = 28.77$  and 16.522. This result signified that the modified MMT with ethanol or water are tend to be intercalated or agglomerated after the film of PLA nanocomposite has been prepared. However, it is clear that the X-ray data for modified MMT with methanol shifted to left into the smaller angel compared with the unmodified MMT where the peak has been appearing at  $2\theta = 5.99$  corresponding to the inter layer space of 14.74 Å. An increase in d-spacing indicates that the  $\text{CuCl}_2$  chains intercalates into the gallery of MMT and have a tendency to form an intercalated or an exfoliated structure after the formation of PLA nanocomposites.

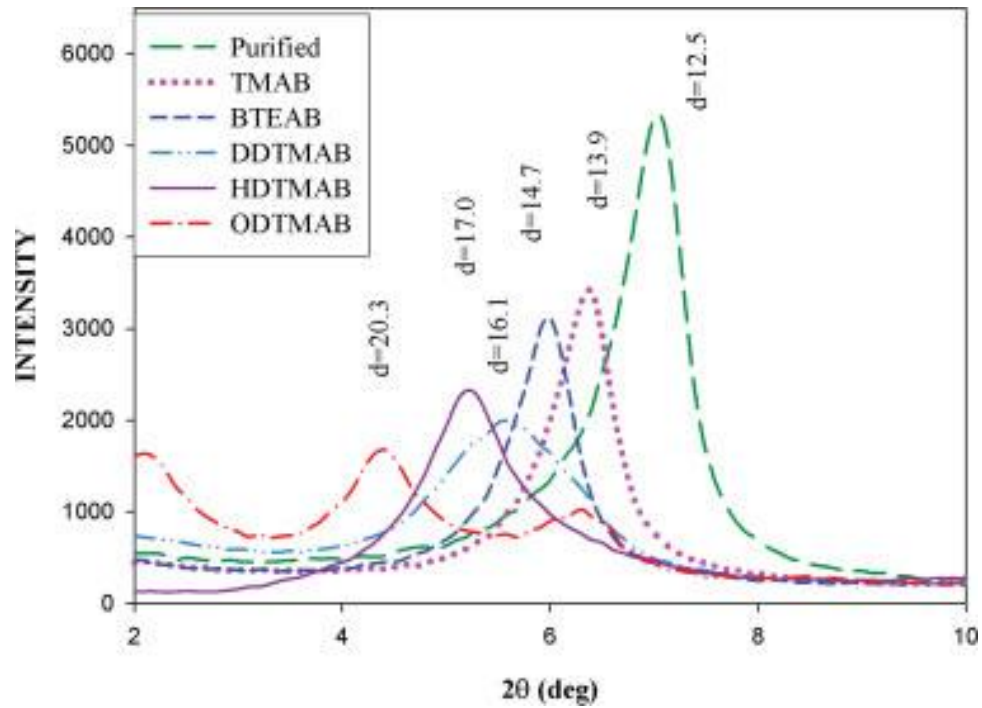
The experimental peak position ( $2\theta$ ) and related calculated clay layer spacing obtained from XRD spectra of pure clay and modified clays are summarized in **Table 4.2**

**Table 4.2 :** XRD data and inter layer space of pure MMT and modified MMT.

Sample	2 $\theta$ (°)	d (Å)
Pure MMT	8.17	10.81
Modified MMT with Ethanol + CuCl <sub>2</sub>	28.77	3.101
Modified MMT with H <sub>2</sub> O + CuCl <sub>2</sub>	16.522	5.361
Modified MMT with Methanol + CuCl <sub>2</sub>	5.99	14.74

Nakas and Kaynak (2008) states that a modification of clay will improve the interlayer spacing. In their studies, the clay surface was modified with different alkyl ammonium salts after the purification process to obtain the improvement in the wetting of clay layers by the polymer. In their work, they found that the interlayer spacing was increased by surface modification. **Figure 4.5** shows a different modifier used as the the d-spacing values are increased from 12.5 to 20.3 Å °. By comparing the result obtain from this research, it was found that only a modified MMT with methanol + CuCl<sub>2</sub> gives the increment in d-spacing when compared to modified MMT with ethanol + CuCl<sub>2</sub> and modified MMT with H<sub>2</sub>O. This probably happens due to some error made during the modification phase such as impurities.

Thus, the modified MMT with methanol + CuCl<sub>2</sub> have been selected as the filler for the next stage which is the formation of the polymer nanocomposite via solution casting method.



**Figure 4.5 :** X-ray diffractograms of the purified clay and then surface modified with different alkyl ammoniums

(Sources : Nakas and Kaynak, 2008)

#### **XRD Result of the Polymer Nanocomposites film.**

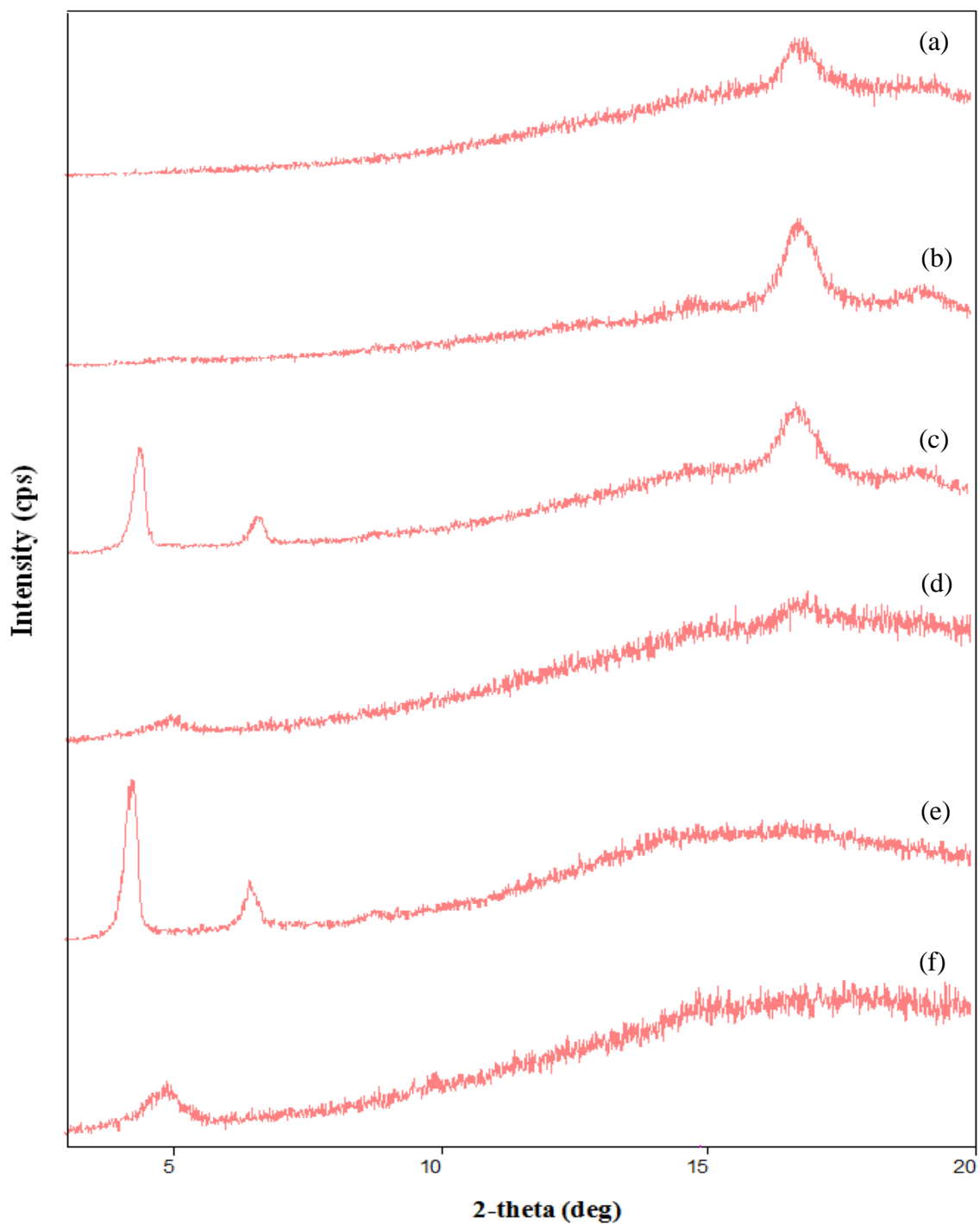
After the formation of polymer nanocomposites, the film is being tested again with XRD analysis in order to identify the structure of the nanoclay inside the polylactic acid either exfoliation or intercalation.

**Figure 4.6** shows the data obtained from XRD for each type of samples with a diffraction angles from  $3^{\circ}$  to  $20^{\circ}$ . While **Figure 4.7** shows a comparison of X-ray diffraction data of 1% modified clay (with and without PEG) + PLA, 2 % modified clay

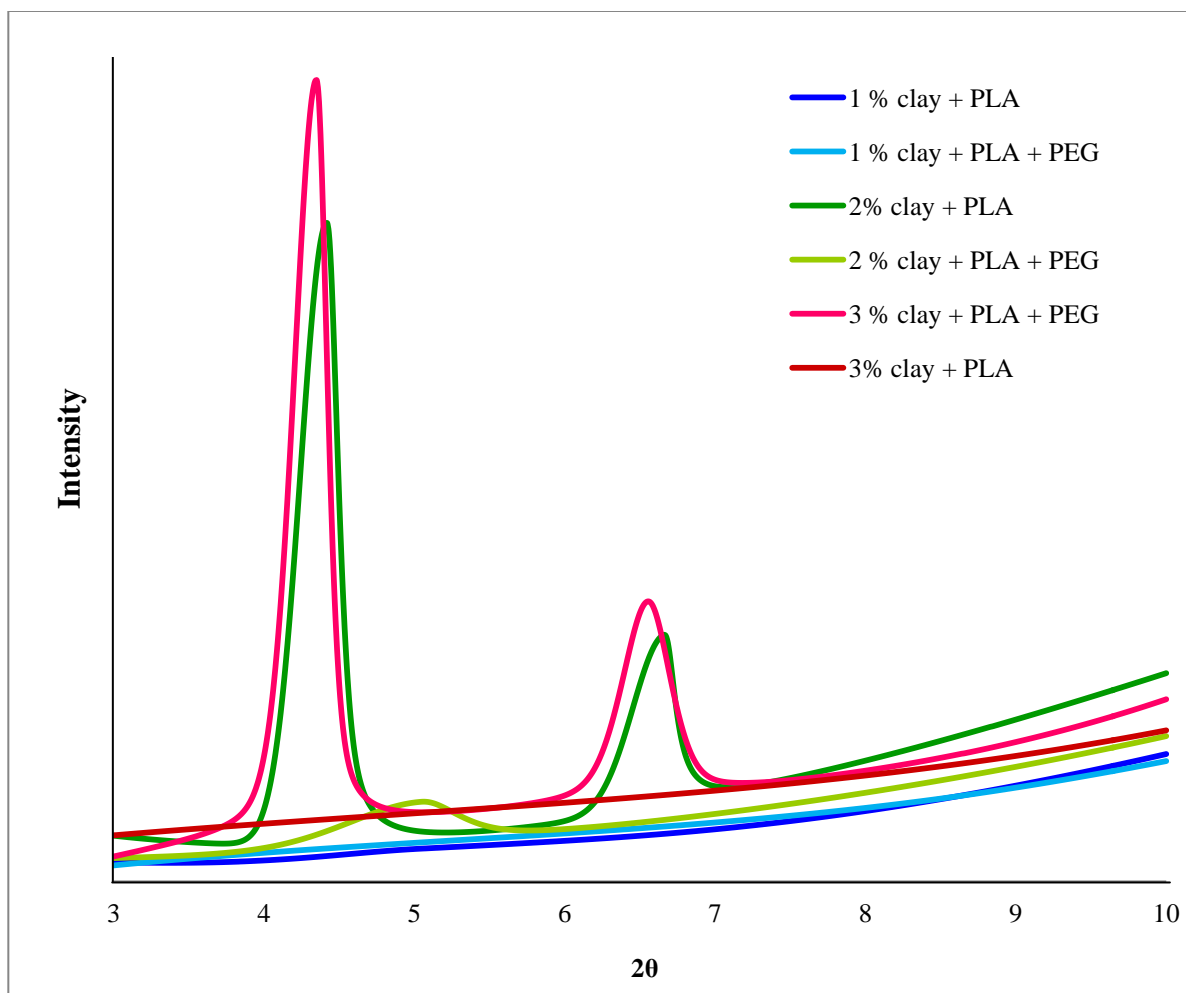
(with and without PEG) + PLA and 3 % modified clay (with and without PEG) + PLA for a better understanding. This sample was plotted on a graph of a relative intensity versus  $2\theta$  from the step size  $3^\circ$  to  $10^\circ$ . Besides, **Table 4.3** summarizes the XRD data and the inter layer space of the variable composition.

**Table 4.3 :** XRD data and inter layer space of the variable composition.

Sample	$2\theta$ ( $^\circ$ )	d ( $\text{\AA}$ )
1 % clay + PLA	-	-
1 % clay + PLA + PEG	-	-
2 % clay + PLA	4.415	20.00
2 % clay + PLA + PEG	5.04	17.50
3 % clay + PLA	-	-
3 % clay + PLA + PEG	4.345	20.32



**Figure 4.6 :** XRD result for each type of samples (a) 1% clay + PLA, (b) 1 % clay + PLA + PEG (c) 2 % clay + PLA (d) 2 % clay + PLA + PEG (e) 3 % clay + PLA + PEG (f) 3 % clay + PLA

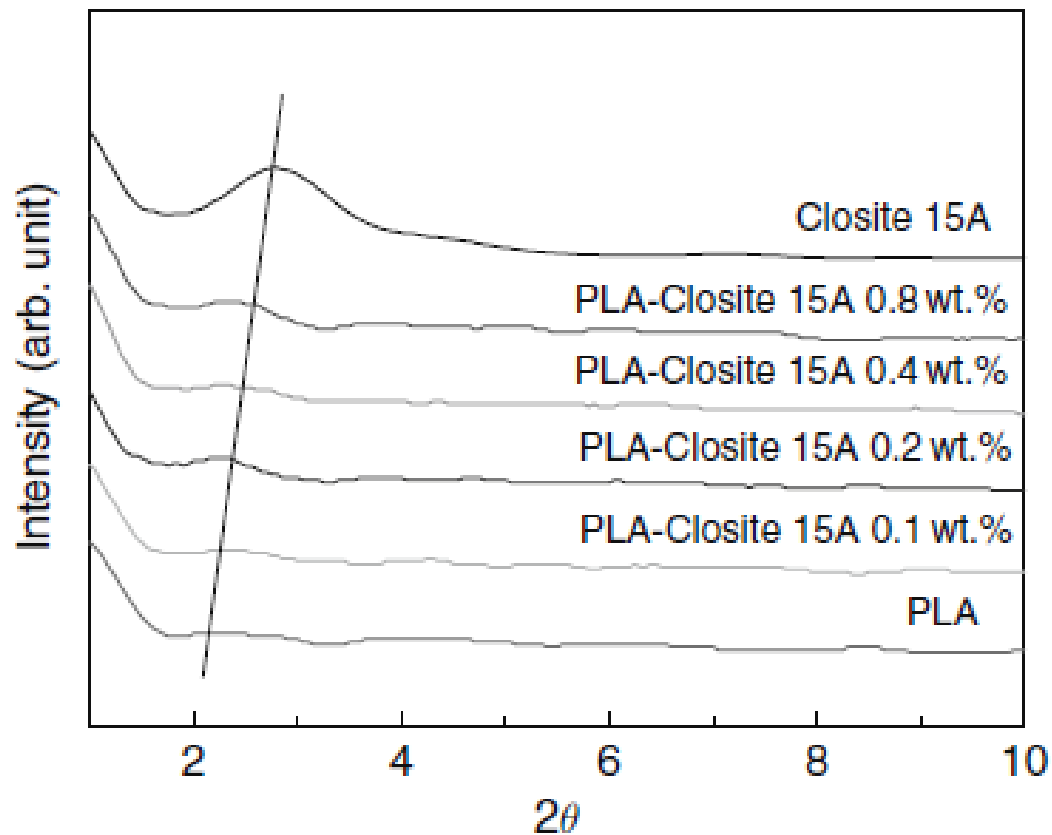


**Figure 4.7 :** XRD result for each type of samples from a step size  $3^\circ - 10^\circ$ .

If the nanoclay retains its original layered structures and the original d-spacing when it is dispersed inside the polymer matrix, the position of the Bragg peak corresponding to the d-spacing in the XRD diffractogram will remain unchanged. If the layered structure is maintained and the d-spacing is increased, the Bragg peak will remain and it will be shifted to the left (lower value). If the layered structure is disrupted, the Bragg peak will disappear. It can be seen from **Figure 4.7** that 1 % clay + PLA, 1 % clay + PLA + PEG and 3 % clay + PLA did not show a peak. In contrast to the 2 % clay + PLA, 2 % clay + PLA + PEG and 3 % clay + PLA + PEG were found to retain a Bragg peak corresponding to the clay d-spacing. It can be concluded that except for 1 % clay + PLA, 1 % clay + PLA + PEG and 3 % clay + PLA, none of the other PLA-nanoclay combinations achieved exfoliation. The rest, 2 % clay + PLA and 2 % clay + PLA + PEG gives 20.00 Å and 17.50 Å with a characteristic peak appeared at  $2\theta = 4.415$  and  $5.04$  while 3 % clay + PLA + PEG has an interlayer spacing of 20.32 with  $2\theta = 4.345$  indicates an intercalation behavior from an observation on the graph.

According to Koh et. al. (2008) on their studies about the biodegradable polymer/layered silicate nanocomposite membranes, the x-ray diffraction patterns of poly (lactic acid) and organoclay (Cloisite 15A), as shown in **Figure 4.8**, demonstrates the characteristic peak of Cloisite 15 A with the layer distance  $d_{(0\ 0\ 1)} = 32.36$  Å moved to, 39.23 Å caused by the intercalation of PLA matrix into the clay gallery. The peak intensity of the intercalated clay increased gradually with addition of organoclay, which was caused by more diffracted X-ray from platy groups of the additionally intercalated clay. Their result obtained are quite similar with the result of this experimental work

where an increase of clay loading caused an increase the intercalation between the gallery where it produce more good structure of polymer nanocomposites. However, the disappearance of the Bragg peak of 1 % clay + PLA and 1 % clay + PLA + PEG obtained in this experiment are contrast with the experimental work from Koh et. al. (2008). Nevertheless, it can also be due to too little clay in the sample that is below the detection limit of the XRD apparatus. This might happen to 1 % clay + PLA and 1 % clay + PLA + PEG since no peak has been detected.



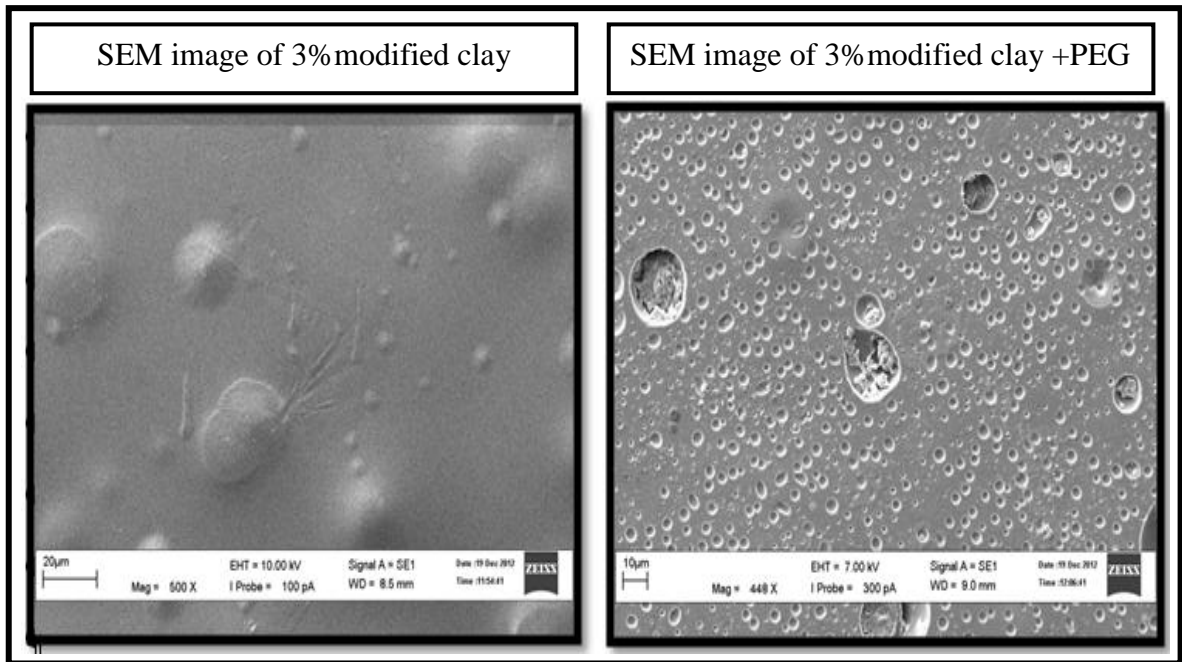
**Figure 4.8 :** X-ray diffraction patterns of organoclay and PLA/Closite115A nanocomposite membranes

(Sources : Koh et. al., 2008)

#### 4.3.2 Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. Through this analysis, the morphological difference of the samples can be determined and classified.

For this purpose, 2 types of film which are 3% modified clay and 3% modified clay by the existence of PEG has randomly been selected to differentiate the structure between the film with plasticizers and without plasticizer.



**Figure 4.9 :** SEM image of 3% modified clay and 3% modified clay +PEG

The SEM micrographs for both 3% modified clays with and without PEG are shown in **Figure 4.9**. The bright spot represents the clay particle while the dark spot represents the PLA. The micrographs of the sample without PEG shows a uniform distribution of clay particles where it can be intercalate or some of them exfoliate whereas there are so many agglomeration has happened in a sample with the exhibition of PEG. The clay does not distribute well and gathered at a certain area. The small bubble can be seen everywhere which they have probably been the effect of the trapped air during the evaporation of di-chlorometane. It is also can be happen due to some error might occur during the experimental work such as a contamination since PLA is very sensitive to any impurities.

## **4.4 Permeability Studies**

### **4.4.1 Introduction**

A permeability studies of this experiment were measured according to ASTM E 95-96 method using the wet cup test method. This experiment has been conducted in order to achieve the objective of this research work. By following ASTM E 95-96 method, the mass of water lost from the dish was monitored and weighed as a function of time for every 1 hour to 5 hours.

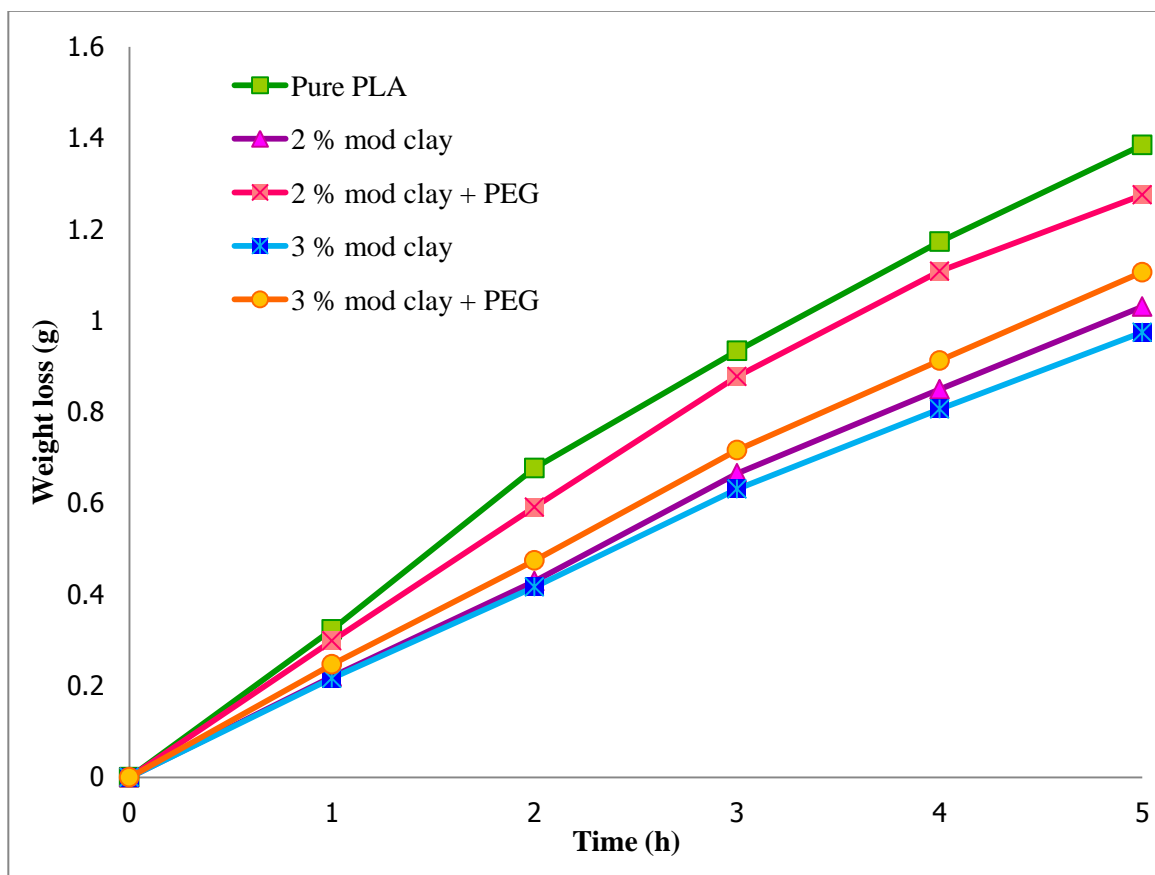
For a comparison, the testing has been carried out among 6 types of sample which are, pure PLA as well as 2% and 3% modified clay with and without an addition of PEG. However, an experiment of 1% modified clay sample with and without PEG cannot be completed due to some error such as the film is crack.

### **4.4.2 Weight Loss**

The water loss was recorded and tabulated in **Table 4.4**. **Figure 4.10** illustrates the weight loss as a function of time for better understanding.

**Table 4.4 :** Total weight of water loss (kg) for every 1h - 5h.

Sample	Time (h)				
	1	2	3	4	5
Pure PLA	0.0003237	0.0006772	0.000934	0.0011732	0.001385
2 % MeOH	0.0002203	0.0004297	0.000666	0.0008498	0.0010309
2 % MeOH + PEG	0.0002989	0.0005917	0.000878	0.0011085	0.0012757
3 % MeOH	0.0002167	0.0004168	0.000631	0.0008065	0.0009745
3 % MeOH + PEG	0.0002474	0.000475	0.000717	0.0009127	0.0011061



**Figure 4.10 :** Weight loss as a function of time in the wet cup test.

#### 4.4.3 Water Vapor Transmission Rate (WVTR)

Water Vapor Transmission Rate (WVTR) is the steady water vapor flow in unit time through unit area of a body, normal to specific parallel surfaces, under specific conditions of temperature and humidity at each surface. Based on the result of the weight loss as a function of time, the WVTR was calculated from the steady state region using the equation as in equation (4.2) and the result is tabulated in **Table 4.5**

Water vapor transmission rate :

$$WVTR = \frac{\text{mass } H_2O \text{ lost}}{\text{time} \times \text{area}} = \frac{\text{flux}}{\text{area}} \quad (4.2)$$

Where the the constant variable are:

Area, A : 0.0057 m<sup>2</sup>

Time, t : 18000 s

Temperature : 37.5 °C

**Table 4.5** : Effect of variable type of sample with WVTR

Sample	Flux (kg/s)	WVTR (kg/m <sup>2</sup> s)	Ratio
			WVTR <sub>PLA</sub> / WVTR <sub>mod clay</sub>
Pure PLA	7.69444E-08	1.3499E-05	1
2 % mod clay	5.72722E-08	1.00478E-05	1.34
2 % mod clay + PEG	7.08722E-08	1.24337E-05	1.09
3 % mod clay	5.41389E-08	9.49805E-06	1.42
3 % mod clay + PEG	6.145E-08	1.07807E-05	1.25

#### 4.4.4 Water Vapor Permeability (WVP)

Water Vapor Permeability is the time rate of water vapor transmission through unit area of flat material of unit thickness induced by unit vapor pressure difference between two specific surfaces, under specified temperature and humidity conditions (ASTM E-95/96). The WVP can be calculated from the steady state region using the equation as in equation (4.3) and the result is tabulated in **Table 4.6** and **Table 4.7** summarized the result obtain for permeability studies.

Water vapor transmission rate :

$$WVP = \frac{WVTR \times l}{\Delta P} \quad (4.3)$$

Where:

$\Delta P$  : Pressure difference ( $P_2 - P_1$ ), Pa

$l$  : The thickness of the film, m

**Table 4.6 :** Water Vapor Permeability of the PLA based film.

Sample	WVP (Kg.m/m <sup>2</sup> .s.Pa) x 10 <sup>-21</sup>
Pure PLA	2.48
2 % modified clay	1.85
2 % modified clay + PEG	2.2
3 % modified clay	1.75
3 % modified clay + PEG	1.98

**Table 4.7 :** Relationship between weight loss, WVTR and WVP.

Sample	Weight Loss (Kg)	WVTR (kg/m <sup>2</sup> s) x 10 <sup>-5</sup>	WVP (Kg.m/m <sup>2</sup> .s.Pa) (10 <sup>-21</sup> )
Pure PLA	0.001385	1.3499	2.48
1 % modified clay	-	-	-
1 % modified clay + PEG	-	-	-
2 % modified clay	0.0010309	1.00478	1.85
2 % modified clay + PEG	0.0012757	1.24337	2.2
3 % modified clay	0.0009745	0.949805	1.75
3 % modified clay + PEG	0.0011061	1.07807	1.98

Generally, from an observation on the **Figure 4.9**, the weight lost by the water was increased from 0 hours to 5 hours for each type of sample. Pure PLA gives the highest weight loss when compared to the others followed by 2% and 3% modified clay with an addition of PEG and finally 2% and 3% modified clay without the existence of PEG.

Theoretically, one of the criteria needs to be considered for a selection of a packaging material are depends on how much the water can permeate through the material. The lower WVP is the better where it will reduce the amount of water can pass through the film at a certain time. This will result in increasing the food protection.

**Table 4.7** describes the relationship between weight loss, WVTR and WVP. Based on the results, it shows that, as the weight loss increase, the WVTR values are also increasing and WVP values are proportional to the weight loss and WVTR values where when they both increased, WVP values are also increased. By comparing pure PLA with an addition of clay (with and without PEG), it shows that the weight loss, WVTR, and WVP of PLA is higher than others followed by 2% and 3% modified clay with an addition of PEG and finally 2% and 3% modified clay without the existence of PEG. The decrease in water vapor barrier property of PLA/clay composite films is mainly attributed to the tortuous path for water vapor diffusion due to the impermeable clay layers distributed in the polymer matrix consequently increasing the effective diffusion path length.

Among 2% and 3% clay (with or without PEG), 3% clay have the lowest weight loss, WVTR and WVP rate. This verifies that an addition of clay loading has increased the barrier properties of a film. This result proves the report made by Tang et. al. (2008) where in their studies regarding the barrier properties of starch-clay nanocomposite films with a clay content (0–9 wt% MMT), they found that an increase in clay content, lower (22–67%) water vapor permeability (WVP) were obtained. **Table 4.8** shows the results of their experimental work.

**Table 4.8 :** Effects of Clay Type on WVP of Corn Starch-Based Films.

(Sources : Tang et. al. ,2008)

Clay Content	WVP (g x mm/kPa x hr x m <sup>2</sup> )	
	Starch-MMT	Starch-130E
0% clay	1.61 ± 0.08a	1.61 ± 0.08 ae
3% clay	1.42 ± 0.04b	1.63 ± 0.12 e
6% clay	1.06 ± 0.09c	1.58 ± 0.08e
9% clay	0.77 ± 0.04d	1.56 ± 0.14e

On the other hand, the samples of a modified clay without PEG gives the best significant result compared with the modified clay with an addition of PEG sample. However, the result obtained did not match with a study by Pitt et. al. (1992) where they clarify that higher PEG contents result in a higher WVTR owing to progressive film plasticization that modifies the hydrophilic character of PLA film. Regarding the result obtain, this could be attributed to low exfoliation of the films. Furthermore, the PEG

used are in a liquid form where the concentration of the PEG might be different than what has been used in their studies.

Nevertheless, a research work by Ahmad et. Al. (2010) about the theological, thermal and barrier properties of PLA/PEG/clay through solution casting method was having the same outcome as this experimental work where they found that the addition of PEG did not show a statistically significant difference on water barrier. Addition of PEG and clay has only increased the variability of the WVTR values measured but did not reduce the WVP. **Table 4.9** shows the result obtained from their research work.

**Table 4.9 : Water Vapor Permeability of PLA-based film.**

(Sources : Ahmad et. al., 2010)

Composition	Water Vapor Permeability (kg.m/m <sup>2</sup> .s.Pa) (10 <sup>-14</sup> )
PLA	1.69 ± 0.28
75% PLA + 25% PEG	3.50 ± 0.93
67% PLA + 23% PEG +10% clay	3.58 ± 2.37

The result obtains in this experimental work are slightly different when compared to the result obtained by (Ahmad et. al., 2010). Their result obtain is in range  $1.69 \times 10^{-14}$  -  $3.58 \times 10^{-14}$  but this experimental work have a result range in  $1.75 \times 10^{-21}$  -  $2.48 \times 10^{-21}$ . This is probably because the material used is different where they used PLA grade P6463B compared to PLA grade Ingeo 2300D used in this experimental work. Furthermore, the method for barrier testing are also diverse since they measured

the WVP according to ASTM F 1249 method by using Permatran<sup>TM</sup> C3/C31 Water Vapor Permeation Measurement System compared to this research work which are using ASTM E95/96 (wet cup test method).

Leakage was also a potential source of error, either in the attachment area of film and aluminium foil with an adhesive or an existence of a hole on the film. As the result obtain among 2% and 3% modified clay, it shows that the 3% modified clay has the lowest weight loss. Theoretically, it can be concluded that as the filler percentage inside the polymer are increasing, the amount of weight loss will decrease. Nevertheless, the filler contain must be lower than 5% to maintain the filler in a nano size. (Ray & Okamoto, 2003). The decrease in water vapor barrier property of PLA/clay composite films is mainly attributed to the tortuous path for water vapor diffusion due to the impermeable clay layers distributed in the polymer matrix consequently increasing the effective diffusion path length. (Duncan, 2011). During the experimental work, there might be some error occurs for example, the air circulation in an oven might affect the result of the experiment. The higher air circulation give a consequence in transmission rate where it will rapidly increase. Since the air circulation cannot be controlled, this error is possible to be happen. Furthermore, the thickness of the film as well will have an effect on the WVTR and WVP value. The thicker the film, the lesser WVTR or WVP. However, in this experiment, the thickness of the film can be considered as the same for each type of sample, so, the thickness effect can be neglected.

## 4.5 Conclusion

This research is made to study the permeability of PLA nanocomposite also to observe its characterization and morphological analysis. From the results and discussion included in this section, it can be concluded that the attendance of the filler which is  $\text{Na}^+$  in poly-lactic acid matrix exhibit a significant improvement in terms of properties, structure and permeability of PLA perhaps will benefit the further researches as well as in polymer industries since the studies about PLA is the most popular topic recently because PLA with a renewable resource can be used to reduce the environmental pollution mostly in packaging applications.

## **CHAPTER 5**

### **CONCLUSION & RECOMMENDATION**

#### **5.1 Conclusion**

Poly (lactide) polymers have attracted the attention of industry as a packaging material because in addition to their biodegradability characteristics, they show good mechanical, physical, and barrier properties. However, there is a need to better understand the properties of this family of plastics before it can be fully adopted by the packaging industry. In this research work, the effect of the modified clay, the processing conditions for the preparation of a polymer, and the final properties of PLA-clay nanocomposites also its permeability were examined. The objective of this research work have been successfully achieved. The first objective is to modify Sodium Cloisite organoclay using metal ion solution (ion exchange method). This objective has already successfully implemented where the clay was effectively being modified with a different type of solvent via an ion exchange method by using copper <sup>2+</sup> as the metal ion. The

morphological observation and quantification of the modification of clay by XRD revealed that the largest interlayer spacing of clay increased is by using methanol as a solvent with  $d = 14.74 \text{ \AA}$ . From there, the modified MMT with methanol as a solvent has been selected to be used in the preparation of the polymer.

The second objective of this research work is to produce PLA nanocomposite with good barrier properties. In this work, the polymer nanocomposite was prepared by using solution casting method with or without the exhibition of PEG. The results indicate that montmorillonite clay can be incorporated into polylactide to make nanocomposites and films. PEG has been used to act as an effective plasticizer however it does not give a stimulate result of this experimental work. The measured water vapor permeability indicates that the incorporation of the modified clay with PLA without PEG provided the lowest permeability. It was found that an increase in clay content, the lower water vapor permeability (WVP) were obtained since 3% of the clay content without an exhibition of Polyethylene Glycole (PEG) shows the lowest Water Vapor Transmission Rate (WVTR). This results indicates that PLA with a modified  $\text{Na}^+$  as a filler is better than pure matrix in terms of structure, barrier properties and configuration also could be served as effective nanocomposite for packaging application.. Besides, the objective of this experiment has been succeed.

## **5.2 Recommendation**

From this research, some of consideration should be taken for further studies in understanding the improvement of the properties and permeability in polymer nanocomposites. Every aspect starting from the modification of clay until the testing and analysis should be considered because the each circumstance of the sample will affected the result in testing. During the preparation of polymer, any contamination must be avoided since PLA is very sensitive to impurities. For this purpose, before start the experiment, the apparatus condition must be clean from any contaminants such as water, excess film and dust. Besides, in preparing the sample for the permeability test, any leakage from the attachment between the sample film and the aluminum should be prevented in order to avoid any water loss that will affect the data obtain from the experiment (Hu et. al., 2000). It is believed that one of the main issues in preparing good polymer matrix nanocomposite samples is the good dispersion of the nanoparticles in a polymer matrix. The weakness of using this kind of method is, it is difficult to maintain the structure of the polymer since intercalation or exfoliation of the polymer are only occurring with some types of clay and solvent where one has to find the right match for this purpose. (Alexandre & Dubois, 2000).

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## APPENDICES

### APPENDIX A : AAS Result For Modification of Nanoclay

Sequence No.: 7					Autosampler Location:	
Sample ID: B					Date Collected: 11/8/2012 12:03:01 PM	
Analyst:					Data Type: Original	
Replicate Data: B					Analyte: Cu 324.75	
Repl	SampleConc	StndConc	BlncCorr	Time	Signal	Stored
#	mg/L	mg/L	Signal			
1	13.90	13.90	2.219	12:03:03 PM	Yes	
	Sample concentration is greater than that of the highest standard.					
2	13.94	13.94	2.226	12:03:07 PM	Yes	
	Sample concentration is greater than that of the highest standard.					
3	13.97	13.97	2.230	12:03:12 PM	Yes	
	Sample concentration is greater than that of the highest standard.					
Mean:	13.94	13.94	2.225			
SD:	0.036	0.036	0.0057			
%RSD:	0.26%	0.26%	0.26			
	Sample concentration is greater than that of the highest standard.					

**Figure A-1 : AAS data for modification of nanoclay by using ethanol as a solvent**

Sequence No.: 6					Autosampler Location:	
Sample ID: A					Date Collected: 11/8/2012 12:02:15 PM	
Analyst:					Data Type: Original	
Replicate Data: A					Analyte: Cu 324.75	
Repl	SampleConc	StndConc	BlncCorr	Time	Signal	Stored
#	mg/L	mg/L	Signal			
1	13.99	13.99	2.233	12:02:17 PM	Yes	
	Sample concentration is greater than that of the highest standard.					
2	13.98	13.98	2.231	12:02:21 PM	Yes	
	Sample concentration is greater than that of the highest standard.					
3	13.03	13.03	2.080	12:02:25 PM	Yes	
	Sample concentration is greater than that of the highest standard.					
Mean:	13.66	13.66	2.181			
SD:	0.552	0.552	0.0882			
%RSD:	4.04%	4.04%	4.04			
	Sample concentration is greater than that of the highest standard.					

**Figure A-2 : AAS data for modification of nanoclay by using ethanol as a solvent**

```

=====
Sequence No.: 9
Sample ID: D
Analyst:
Autosampler Location:
Date Collected: 11/8/2012 12:04:11 PM
Data Type: Original
=====

```

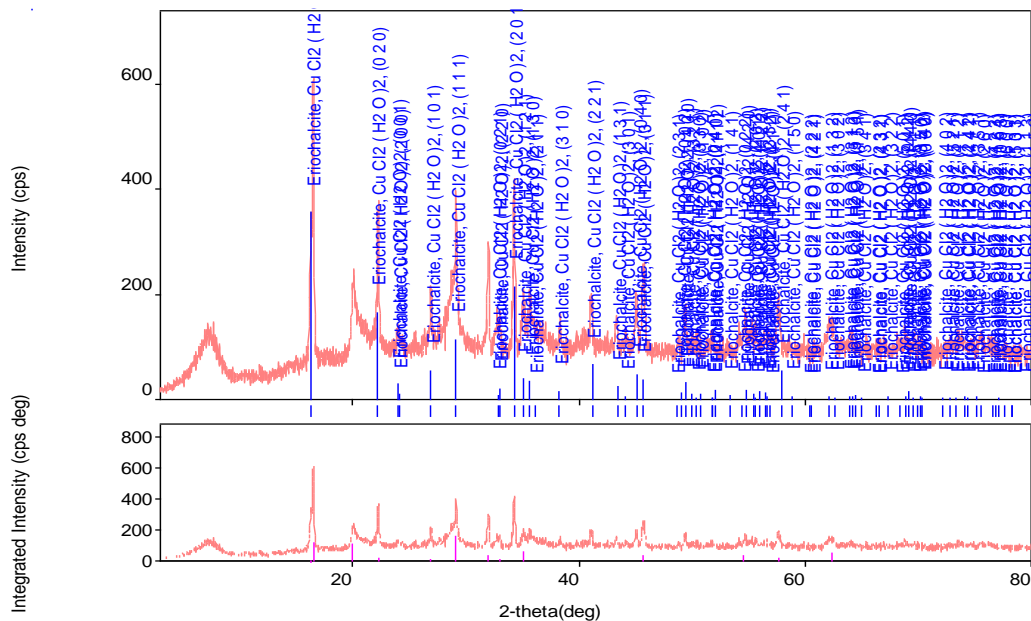
```

=====
Replicate Data: D
Analyte: Cu 324.75
Repl  SampleConc  StndConc  BlnkCorr  Time  Signal
#      mg/L       mg/L      Signal    Stored
1      14.09      14.09     2.250     12:04:12 PM  Yes
Sample concentration is greater than that of the highest standard.
2      14.11      14.11     2.253     12:04:17 PM  Yes
Sample concentration is greater than that of the highest standard.
3      14.17      14.17     2.262     12:04:21 PM  Yes
Sample concentration is greater than that of the highest standard.
Mean:  14.13      14.13     2.255
SD:    0.039      0.039     0.0062
%RSD:  0.27%     0.27%     0.27
Sample concentration is greater than that of the highest standard.
=====

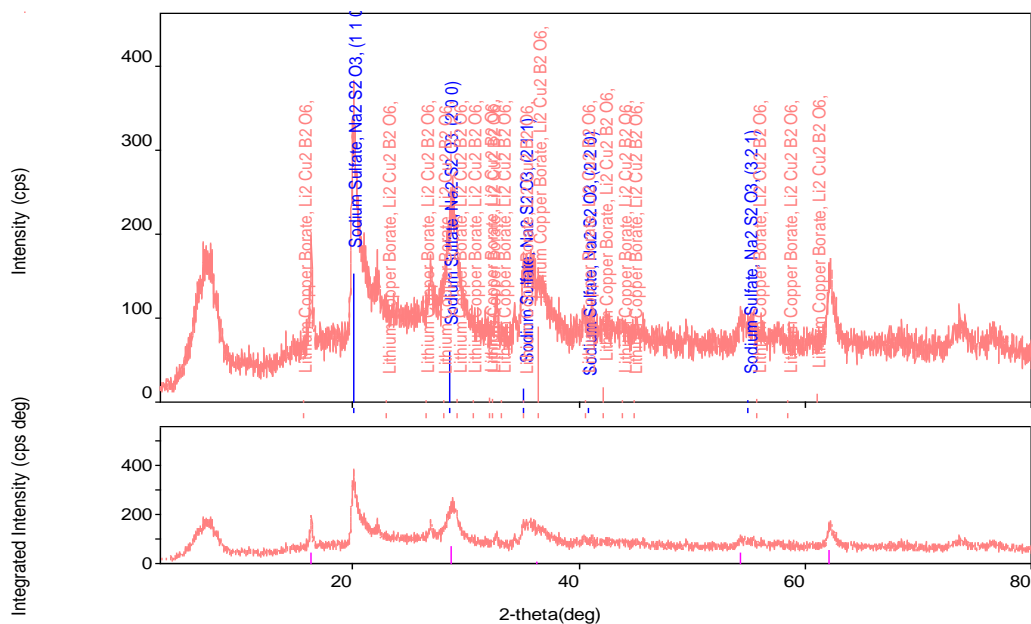
```

**Figure A-3** : AAS data for modification of nanoclay by using water as a solvent

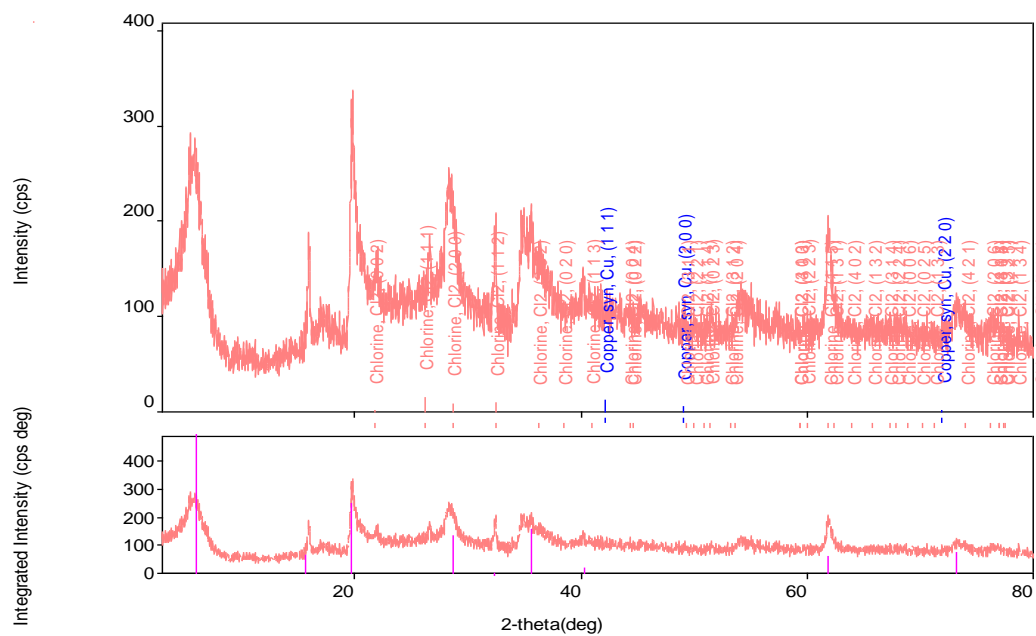
## APPENDIX B : XRD Result For Modification Phase



**Figure B-1 : Modification of Na<sup>+</sup> by water as a solvent**

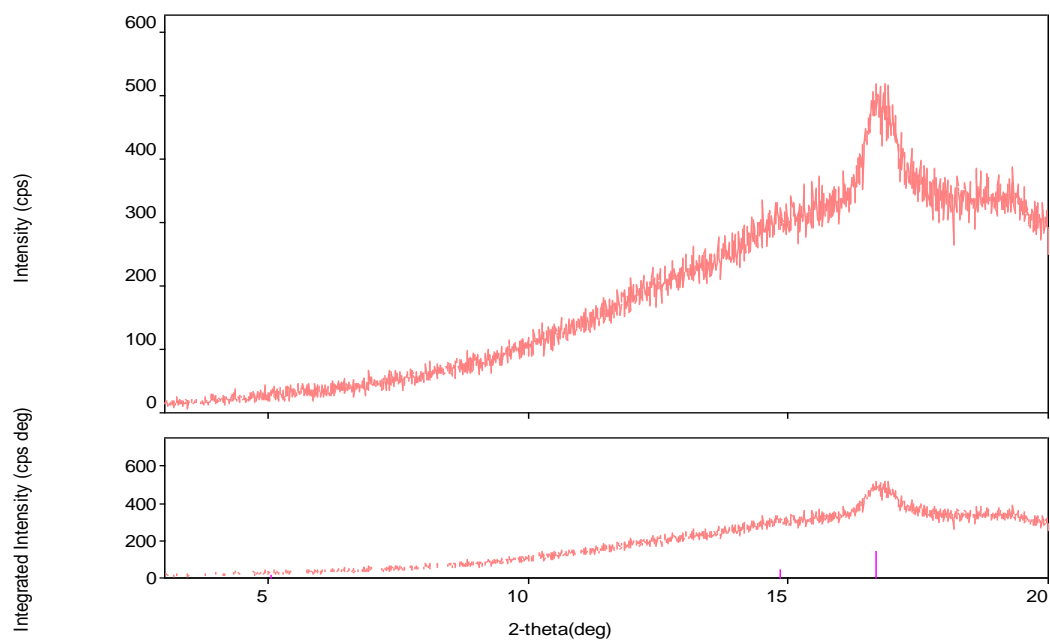


**Figure B-2 : Modification of Na<sup>+</sup> by ethanol as a solvent**

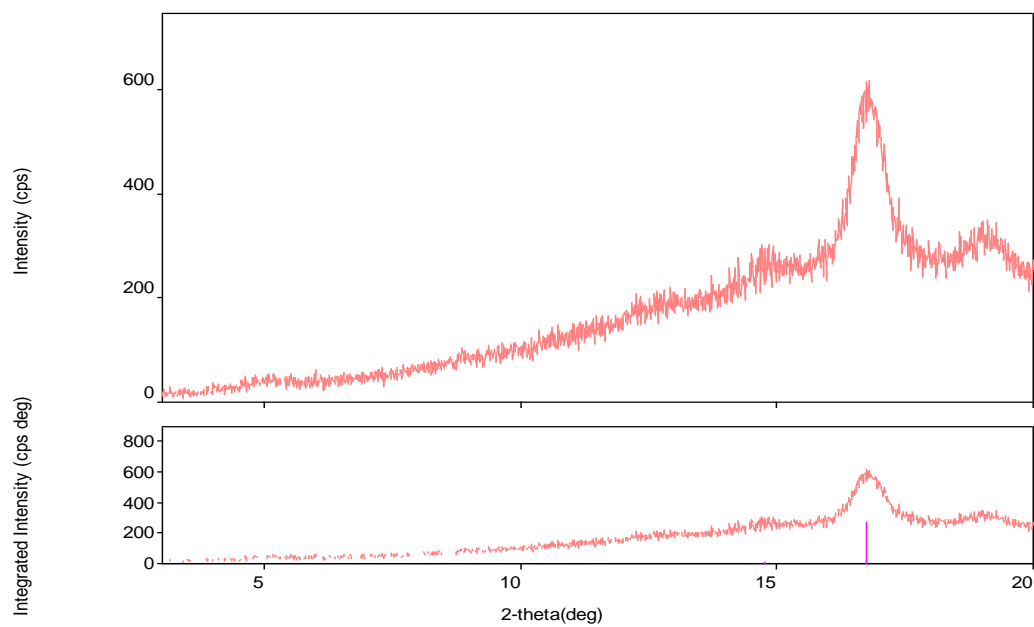


**Figure B-3 : Modification of Na<sup>+</sup> by Methanol as a Solvent**

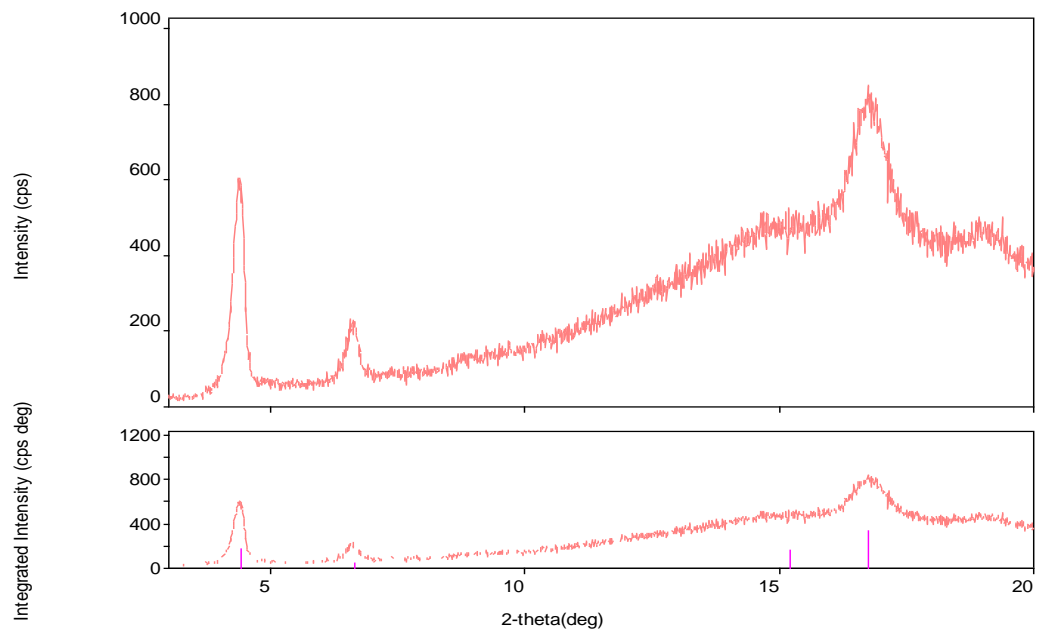
## APPENDIX C : XRD Result After the Formation of Polymer Nanocomposites.



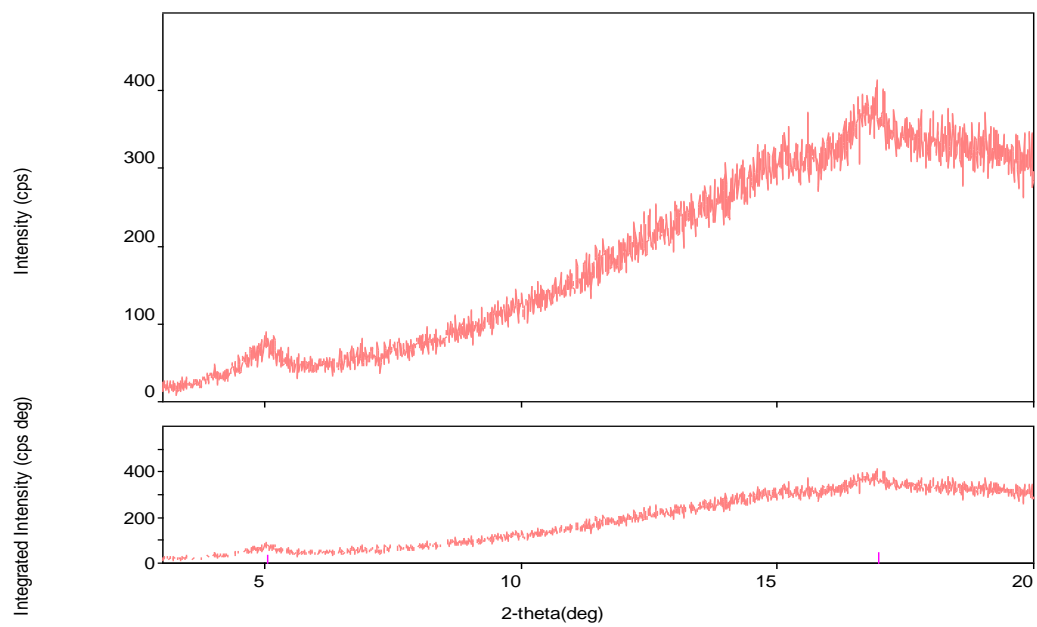
**Figure C-1 : 1% clay + PLA**



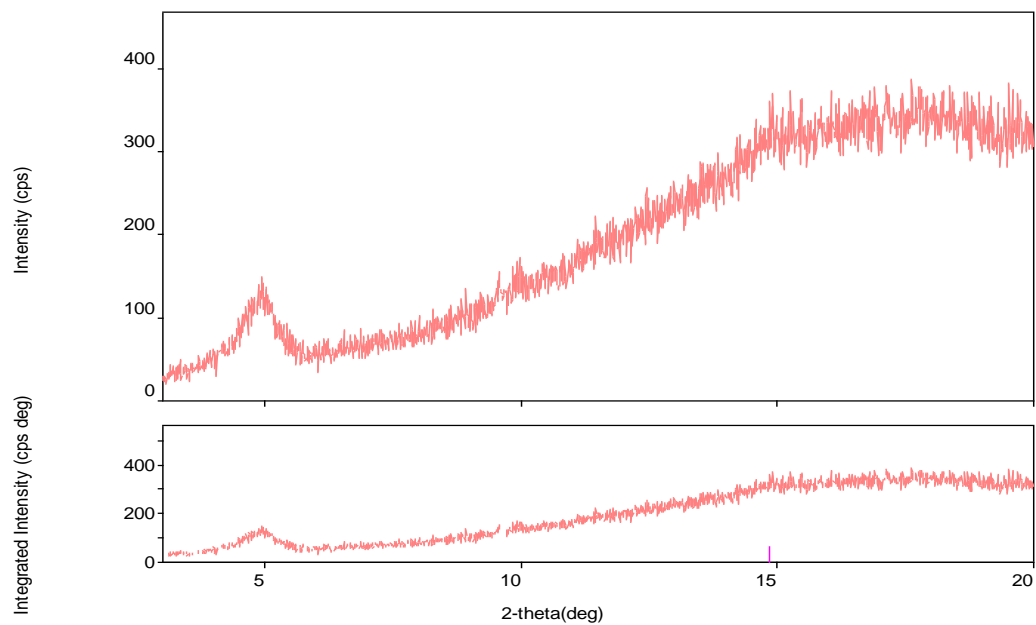
**Figure C-2 : 1% clay + PLA + PEG**



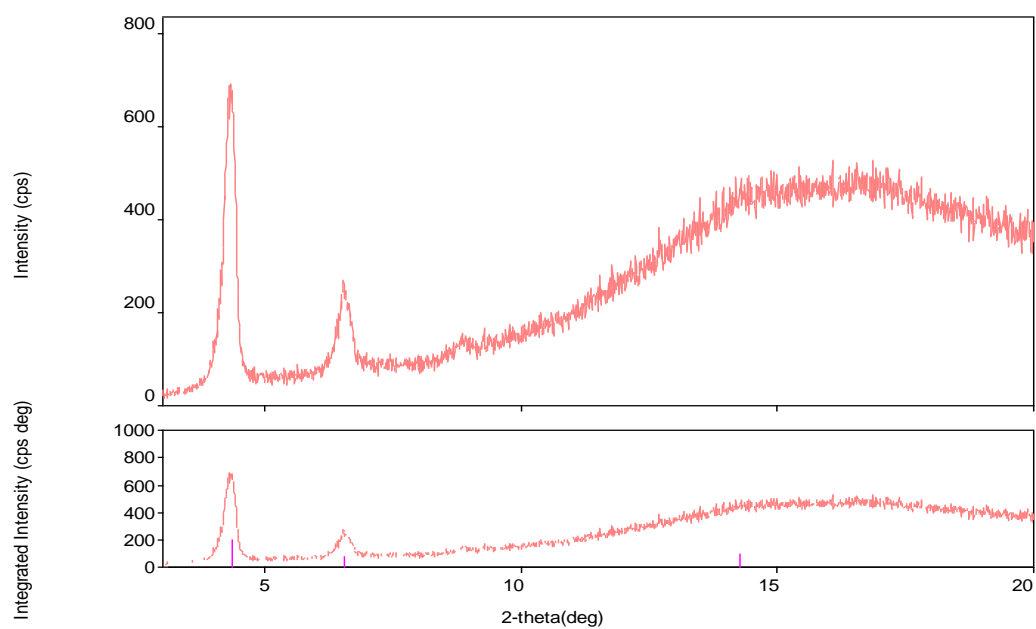
**Figure C-3 : 2% clay + PLA**



**Figure C-4 : 2% clay + PLA + PEG**



**Figure C-5 : 3% clay + PLA**



**Figure C-6 : 3% clay + PLA + PEG**

## APPENDIX D : Permeability Testing

**Table D-1 :** Data obtain from weighing the weight loss of water

Sample	Time					
	0 hr (g)	1 hr (g)	2 hr (g)	3 hr (g)	4 hr (g)	5 hr (g)
<b>Pure PLA</b>	59.4732	59.1495	58.796	58.5391	58.3	58.0882
<b>2 % MeOH</b>	65.0461	64.8258	64.6164	64.3804	64.1963	64.0152
<b>2 % MeOH + PEG</b>	58.7007	58.4018	58.109	57.7863	57.5424	57.3061
<b>3 % MeOH</b>	67.238	67.0213	66.8212	66.6066	66.4315	66.2635
<b>3 % MeOH + PEG</b>	64.6955	64.4481	64.2205	63.9789	63.7828	63.5894

**Table D-2 :** The total weight loss of water from 0 hr to 5 hr.

Sample	Time (h)					
	0 hr (kg)	1 hr (kg)	2 hr (kg)	3 hr (kg)	4 hr (kg)	5 hr (kg)
<b>Pure PLA</b>	0	0.0003237	0.0006772	0.000934	0.0011732	0.001385
<b>2 % MeOH</b>	0	0.0002203	0.0004297	0.000666	0.0008498	0.0010309
<b>2 % MeOH + PEG</b>	0	0.0002989	0.0005917	0.000878	0.0011085	0.0012757
<b>3 % MeOH</b>	0	0.0002167	0.0004168	0.000631	0.0008065	0.0009745
<b>3 % MeOH + PEG</b>	0	0.0002474	0.000475	0.000717	0.0009127	0.0011061

$\Delta P$  values were calculated by using an ideal gas equation as follows:

$$PV = nRT$$

$$P = \frac{nRT}{V} \quad (4.4)$$

Where :

$$R = 8314.34 \text{ m}^3\text{Pa/kg. Mol. K}$$

$$T = 35.5^\circ\text{C} = 308.5 \text{ K}$$

$$V_1(\text{Volume of air inside the oven}) = 0.161 \text{ m}^3$$

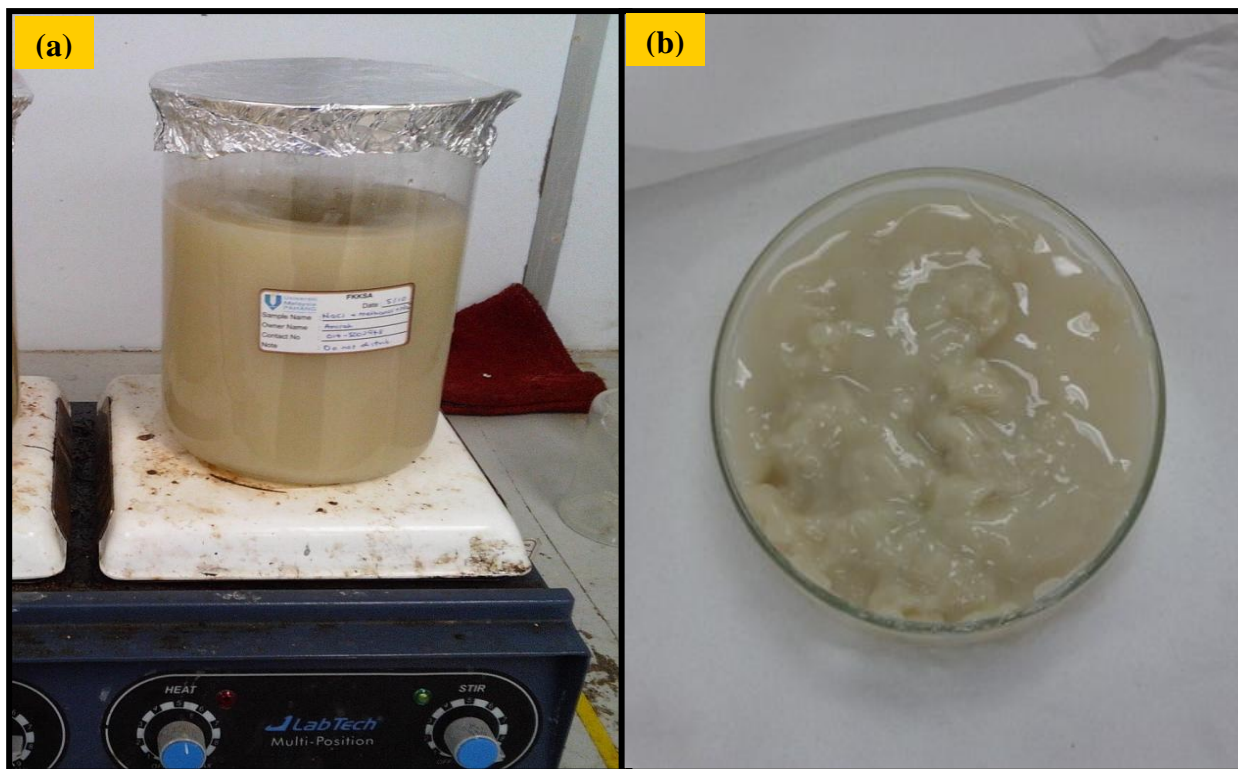
$$V_2(\text{Volume of air inside the petri dish}) = 4.71 \times 10^{-5} \text{ m}^3$$

$$P_2 = \frac{(1 \times 8314.34 \times 308.5)}{0.000047123} = 5.44 \times 10^{10} \text{ Pa}$$

$$P_1 = \frac{(1 \times 8314.34 \times 308.5)}{0.161} = 1.59 \times 10^7 \text{ Pa}$$

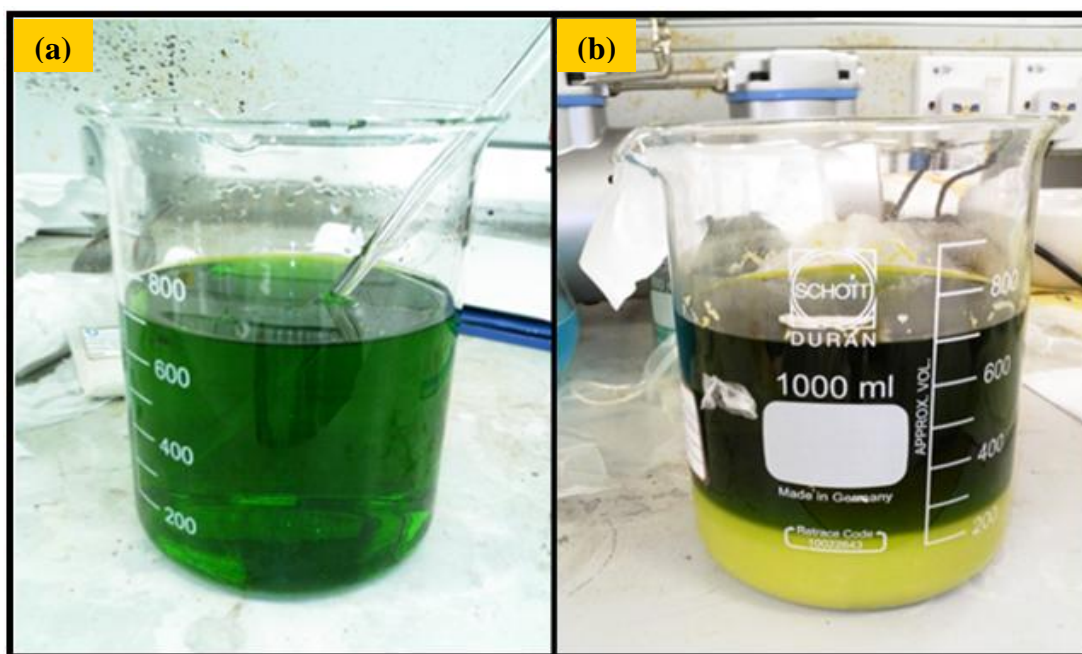
$$\Delta P = 5.44 \times 10^{10} \text{ Pa} - 1.59 \times 10^7 \text{ Pa} = 5.44 \times 10^{10} \text{ Pa}$$

## APPENDIX E : Pretreatment Of Nanoclay Phase

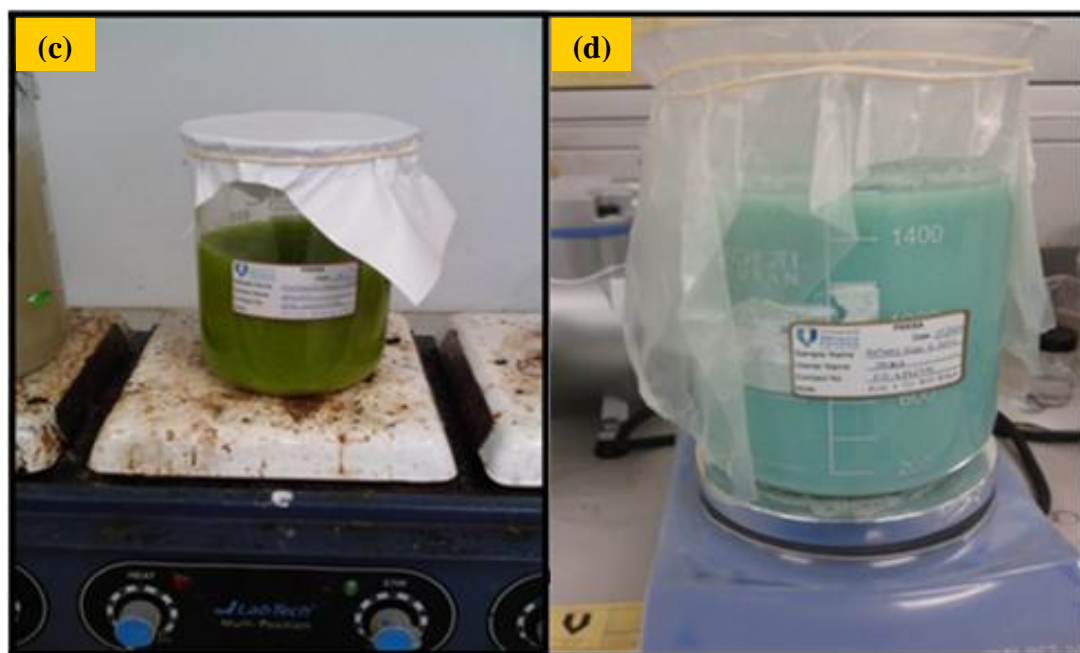


**Figure E-1 :** (a) Clay is stirred exuberantly for 24 hours and (b) The slurry obtained after filtration and ready to be dried in an oven

## APPENDIX F : Modification Of Clay



**Figure F-1 :** (a) Preparation of  $\text{CuCl}_2$  solution and (b) Addition of clay (pretreated with methanol) into  $\text{CuCl}_2$  solution



**Figure F-2 :** Stirring the solution of  $\text{CuCl}_2$  + clay (c) pretreated with methanol and (d) pretreated with  $\text{H}_2\text{O}$



**Figure F-3 :** Filtration of clay by using centrifugal pump



**Figure F-4 :** Powdering the dry clay by using mortar and pestle

## APPENDIX G : Preparation For Aas



**Figure G-1 :** Standard for calibration with a different concentration



**Figure G-2 :** Sample For AAS Teting

## APPENDIX H :Permeability Testing



**Figure H-1 :** The film was attached with epoxy on top of the aluminium foil