A STUDY OF MORPHOLOGICAL AND THERMAL PROPERTIES OF POLYLACTIC ACID (PLA) MODIFIED MMT (ION EXCHANGE METHOD) NANOCOMPOSITE

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NANOCOMPOSITE

WAN SITI NOORHASHIMAH BINTI WAN KAMARUZAMAN

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequade in terms of scope and quality of the award of degree of Bachelor of Chemical Engineering.

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Dedication to my beloved father, Wan Kamaruzaman Bin Wan Hassan, my mother, Endok Jenik bt Haji Tantu, my supportive siblings, my legendary friends, all faculty members and who gave me everlasting inspiration, never ending encouragements and priceless support towards the success of this research.

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In the name of Allah, the most Grateful, the most Merciful

A STUDY OF MORPHOLOGICAL AND THERMAL PROPERTIES OF POLYLACTIC ACID (PLA) MODIFIED MMT (ION EXCHANGE METHOD) NANOCOMPOSITE

ABSTRACT

Polylactic (PLA) is a thermoplastic aliphatic polyester produced by the ring opening polymerization of lactide. PLA is more suitable because it is made from renewable sources and its properties are friendly to the environment. A series of biodegradable PLA nanocomposites using modified organoclay. The type of modication is by ion exchange method and were prepared by melt compounding using a Brabender twin screw extruder. Then, the morphology of exfoliated PLA modified nanocomposite was observed using X-ray Diffraction (XRD) analysis and Scanning Electron Miscoscpy (SEM) analysis. By modification of PLA will affect the structure of nanocomposite from agglomerates to become intercalated nanocomposite or exfoliated nanocomposite. Besides that, the melting temperature of PLA modified nanocomposite should be increase after modification from original temperature 160℃ to become 170℃.

Keywords : PLA modified MMT, Sodium Montmorillonite, PLA Nanocomposite

KAJIAN SIFAT MORFOLOGI DAN THERMAL DARI POLILAKTIK ACID (PLA) MODIFIKASI (ION EXCHANGE METODE) NANOKOMPOSIT MMT

ABSTRAK

Polilaktik (PLA) adalah poliester alifatik termoplastik yang dihasilkan oleh pempolimeran pembukaan cincin lactide. PLA adalah lebih sesuai kerana ia dibuat dari sumber yang boleh diperbaharui dan sifat-sifatnya yang mesra alam sekitar. Satu siri nanocomposites PLA terbiodegradasikan menggunakan organo diubahsuai. Jenis modication adalah dengan kaedah pertukaran ion dan telah disediakan oleh pengkompaunan mencairkan degan menggunakan Brabender extruder skru berkembar. Kemudian, morfologi exfoliated PLA diubahsuai komposit nano telah diperhatikan dengan menggunakan pembelauan sinar-X (XRD) analisis dan Mengimbas Miscoscpy Elektron (SEM) analisis. Dengan pengubahsuaian PLA akan menjejaskan struktur komposit nano dari aglomerat untuk menjadi komposit nano intercalated atau komposit nano exfoliated. Selain itu, suhu lebur komposit nano diubahsuai PLA perlu meningkat selepas pengubahsuaian dari suhu asal 160℃ untuk menjadi 170℃.

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LIST OF SYMBOLS

%	-	Percentage
wt%	-	Weight percent
g	-	Gram
mg	-	Milligram
ml	-	Milliliter
ppm	-	part per minute
nm	-	nanometer
μL	-	miuliter
H_2O	-	Water
CO_2	-	Carbon Dioxide
℃	-	Degree Celsius
Li	-	Lithium
Na	-	Natrium
Rb	-	Rubidium
Si	-	Silicon
Al	-	Aluminium
Mg	-	Magnesium
Fe	-	Ferum
Ca	-	Calsium
T_g	-	Glass Transition Temperature
T_m	-	Melting Temperature
X_c	-	Degree of Crystallinity
T_c	-	Crystallization Temperature

LIST OF ABBREVIATIONS

CuSO$_4$		Copper (II) Sulphate
CuCl$_2$		Copper (II) Chloride
DNA		Deoyribonucleic Acid
PLA		Polylactic Acid
RH		Relative Humidity
OLA		Oligomerilactic Acid
XRD		X-ray Diffraction
SEM	-	Scanning Electron Microscope
DSC		Differential Scanning Calorimetry
TGA		Thermogravimetric Analysis
AAS		Atomic Absorption Spectroscopy
TEM		Transmission Electron Microscopy
Na+ MMT		Sodium Montmorillonite
2C$_{18}$ MMT		Ammonium Modified MMT
TMI		Transition Metal Ion
OMLS		Organically Modified Layered Sillicates
WAXD		Wide Angle X-ray Diffraction
SAXS		Small Angle X-ray Scattering
OC		Organoclay
PCL		Polycaprolactone
LNR		Liquid Natural Rubber

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CHAPTER 1

INTRODUCTION

1.0   Background of Proposed Study

Polymer is a chemical compound or mixture of compounds consisting of repeating structural units created through a process of polymerization and connected by covalent chemical bonding. The polymer used naturally is like cotton, starch protein and wool. Polymer's popular usage is plastic and polymer itself is refer to a large class of natural and synthetic material with a wide variety of properties. Due to the extraordinary range of properties of polymeric materials, polymer is an essential role in everyday life, ranging from familiar synthetic plastic and elastomers to natural biopolymer such as protein and DNA.

Nanotechnology is now recognized as one of the most promising areas for technological development in the 21st century. Nanotechnology has currently received an exceptional interest of researchers, technology incubators and commercial organizations to step forward in introducing the materials having nanocomposite structure and new performance standards. In materials research, the development of polymer nanocomposite is rapidly emerging as a research activity that could broaden the application of polymer for a benefit

of many different industries. Polymer nanocomposites are polymer which are themoplastics, thermoset or elastomers that have been reinforced with small quantities.

According to Ciprari, 2004, nanoscale interactions have significant implications on the macroscopic behaviour of materials as every structural level contributes to the mechanical stability and durability of the resulting materials. It has become increasingly importand to understand and manipulate materials for engineering and other application. Nanocomposite materials can show significant improvement of mechanical properties, (Khudyakov, David Zopf & Turro, 2009).

Polylactic acid can be produced in different ways either using chemical or biological process. Under biological process, it is by fermentation of carbohydrate from lactobacillus. The enantiomeric monomers (D and L) are polycondensed via its cyclic dimmer (lactide) by ring-opening polymerization (ROP) to a high molecular weight polymer. Compared to the other biodegradable polyesters, PLA is the product that at the present has one of the highest potentials due to its availability in the market. Based on this lactide intermediate method, NatureWorks LLC has developed a patented, low cost continuous process for the production of lactic acid based polymer (Gruber,2000). PLA has a number of characteristics that are similar to many other thermoplastics fiber such as controlled crimp, smooth surface and low moisture regain. One of the unique properties of PLA in comparison is that it is the only melt-processable fiber from anually renewable natural resources.

PLA can shows crystalline polymorphism which can lead to different melting peaks with a main transition at 152°C for the D, L-PLA. Furthermore,

PLA can be plasticized using oligomericlactic acid (OLA). The effect of plasticization increases the chain mobility and then favors the PLA organization and crystallization. After plasticization, a cristallinity ranging between 20 and 30%. PLA presents a medium water and oxygen permeability level comparable to polystyrene. These different properties associated with its tunability and its availability favour its actual developments in different packaging applications. McCarthy (1999) showed that PLA presents a soil degradation rate much slower compared to PBSA.

PLA is presumed to be biodegradable although the role of hydrolysis v's enzymatic depolymerization in this process remains open to debate. Composting conditions are found only in industrial units with a high temperature (above 50°C) and a high relative humidity (RH) to promote chain hydrolysis. But, according to Tuominen *et al*. (2002), PLA biodegradation does not exhibit any eco-toxicological effect.

In these recent years, increasing interest has been shown in the realm of nanocomposites. A general conclusion has been drawn that nanocomposite show much improved mechanical properties over their micro-sized similar systems. Because of their small size, nanoparticle have a high surface to volume ratio and provide high energy surfaces. Nanocomposites are family of materials, consisting of a continuous matrix reinforced with a fiber, platelet, or particle having at least one dimension in the nanometer scale. Therefore, new technology has established the integration of polymer and layered silicate to produce nanocomposite to overcome these drawbacks. Nanocomposite 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 nanocomposite which are in situ polymerization, solution intercalation, and melt intercalation. In situ polymerization is a mixing of the nanoclay with the monomer than would be followed by polymerization. Solution intercalation can be done by mixing the nanoclay in a solution of a polymer followed by solvent evaporation. While, melt intercalation consist of blending the organoclay with the polymer matrix in molten state.

The research in this study represents an effort on modification of nanoclay to disperse within PLA to form nanocomposite by using the ion exchange method. The structure of PLA in this study was confirmed through X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Besides that, the resulting in thermal of PLA/clay nanocomposite were also measured by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA).

1.1 Problem Statement

This problem it will be outcome from the environmental problem. PLA made from renewable sources and generally its properties are friendly to the environment. But, PLA that used in industries are offered in low strength, and low thermal stability of material. Therefore, PLA nanocomposite is introduced because it has attracted huge advantages to overcome those weaknesses.

1.2   Objectives

1.2.1   To modify Sodium Cloisite organoclay using metal ion solution (ion exchange method)

1.2.2   To fabricate of PLA-Modified MMT nanocomposite with good in morphology and thermal properties

1.3   Scope of Research

This research is focusing on PLA nanocomposite which is a biodegradable aliphatic polyester that can be synthesized from renewable resources. The scope of this research is as below:

1.3.1   To modify the surface of MMT by the ion exchange method

1.3.2   To produce PLA modified nanocomposite using an extruder from fabrication process of PLA

1.3.3   To characterize PLA and PLA modified nanocomposite using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM)

1.3.4   To testing the PLA and PLA modified by thermal testing using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA).

1.4   Significance of Research

This study has been done in order to improve the PLA nanocomposite. The aim of this research is to study the morphological and the optimum temperature amount would be the best for PLA after modification. Hence, the expected outcome would be an increase in properties of thermal. And it can used as material of plastics in the industry now.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Recently, the varieties of plastics, are produced mostly from fossil fuels, then consumed and discarded into the environment, finally ending up as undegradable wastes. By disposal of these materials by incineration process, it produces CO_2 and contributes to global pollution. For these reasons, there is an urgent need for the development of "Green polymeric materials" that do not involve the use of toxic components in the manufacture. For that issue, the polymer or other materials as more environmentally to substitute and also to overcome the environmental. Therefore, much attention has been lately posed on biodegradable polymers such as starch, cellulose, polylactides, polycaprolactone or blends of other biodegradable polymers.

2.2   Polylactic Acid (PLA)

2.2.1   Synthesis of PLA

Polylactic (PLA) is an aliphatic polyester made up of lactic acid (2-hydroxy propionic acid) building blocks. It is also a biodegradable and compostable thermoplastic derived from renewable plant sources such as starch and sugar. Although PLA existed for several decades, the used of PLA was limited to biomedical applications such as implants and biologically active controlled release devices due to its high cost (Auras *et. al.,* 2010). PLA is degraded by simple hydrolysis of ester bonds without the presence of enzyme of catalyst. The degradation rate depends on the size and shape of the particle, the isomer ratio and also the temperature of hydrolysis (Garlotta, 2002).

Recent studies and findings of the PLA had proven that PLA is good in terms of mechanical properties, thermal plasticity and biocompatibility and also in fabricating. PLA is identical to polystyrene which is brittle and stiff polymer with low deformation at break (Balakrishnan *et. al.,* 2010). There are two methods for manufacturing PLA from lactic acid. The first method uses the cyclic lactic acid dimer called lactide as an intermediate stage. And the second method is the direct polymerization of lactic acid. The method using the lactide intermediary yields PLA with greater molecular.
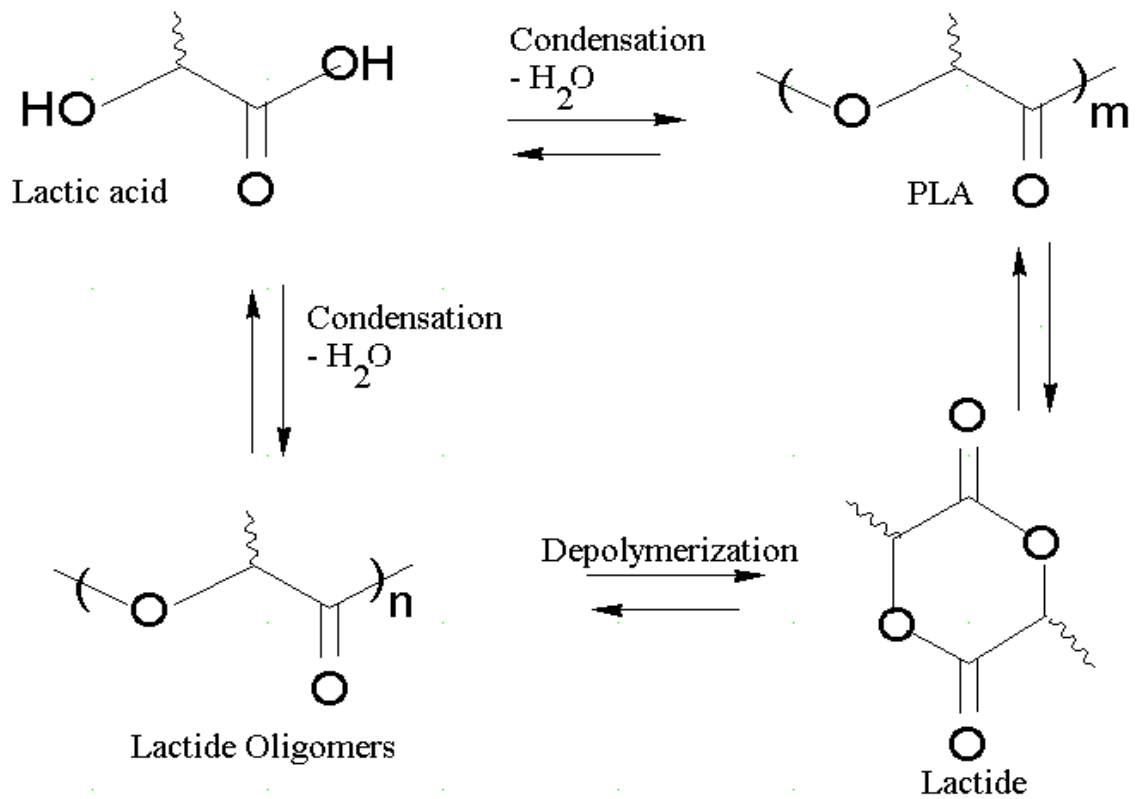
Figure 2.1   The method production of PLA

(Sources: www.googleimage.com.my)

Table 2.1: Mechanical Properties of PLA

Properties	Values
Young's Modulus (MPa)	3600
Tensile Strength (MPa)	70
Elongation at break (%)	2.4
Flextural Strength (N/mm^2)	98
Impact Strength (kJ/m^2)	16.5
Notched Impact Strength (kJ/m^2)	3.3
MFI (g/10min)	3-6
Density (g/cm^3)	1.25
Moisture Absorption (%)	0.3

(Material datasheet by Biomer for L9000)

2.2.2 Polylactid acid (PLA) nanocomposite

Biodegradable polymers are defined as polymers that undergo microbially induced chain separation that leads to mineralization, (Yixiang, 2009). The increased availability of PLA stimulated an increased in its research and development activities towards the use bio-based polymer. Balakrishnan *et. al*., has discovered that linear low density polyethylene improved the impact of the strength of PLA nanocomposites with a sacrifice of tensile and flextural strength. In his work, the PLA had proven that PLA is good in terms of mechanical properties, thermal plasticity and biocompatibility and also in fabricating. PLA is identical to polystyrene which is brittle and stiff polymer with low deformation at break Besides that, the crystallization temperature and glass transition temperature decreased gradually while the thermal stability of PLA improved with the addition of MMT in PLA nanocomposite.

Ogata *et. al.* (1997), first prepared PLA/OMLS blends by dissolving the polymer in hot chloroform in the presence of dimethyl distearyl ammonium modified MMT ($2C_{18}MMT$). In the case of PLA/MMT composite, WAXD and results showed that the silicate layers could not be intercalated using solution method. In other words, the clay existed in the form of tactoids, consisting of several stacked silicate monolayers. These tactoids are responsible for the formation of particular geometrical structures in the blends, which lead to the formation of superstructures in the thickness of the blended film. This kind of structural features increase the Young's modulus of the hybrid.

2.3   Nanofillers

2.3.1 Nanoclay/ Pristine Clay/ Sodium Montmorillonite.

There are many types of layer inorganic solid such as graphite, clay minerals, metal phosphates and phosphonates. The common type of layer inorganic solid that used today in industries is clay mineral. The reason of clay mineral widely used in industries is because of its unique structure and properties. Clay minerals have higher intercalation chemistry as compare to other layered inorganic solid when applied with polymer to form polymer nanocomposite. In details, clay mineral's unique layered structure and high intercalation capabilities that allow them to chemically modified to interact with the polymer and became clay –based polymer nanocomposites.

As shown in the **Figure 2.2**, the clay mineral structure is consisting of interlayer or gallery and this interlayer is cause by the van der Waals force between the layer gap. This layer gap is made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. There is an isomorphic substitution within the layer for (e.g., Li, Na, Rb) and also a relatively layer charge. Clay mineral has a relatively low layer charge which is between ($x = 0.2$-0.6). So, the force between the adjacent layer also relatively low and finally the interlayer is cations exchangeable and the intercalation of inorganic and organic cations and molecules into the interlayer space are accomplished.

The polymer nanocomposite also have high strength and stiffness when applied to clay mineral. By inserting the nano-sized inorganic compound into 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, (Sinha Ray *et al.*, 2003) also conclude that the polymer nanocomposite will increase modulus and strength, outstanding barrier properties, improved solvent and heat resistance and decrease flammability. The other reason clay mineral is widely used is because it is economical which mean inexpensive as compare to other layered inorganic solids.
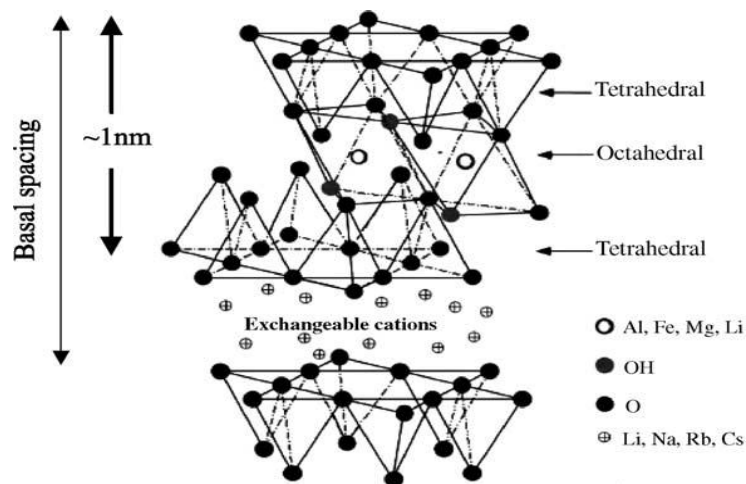
Figure 2.2 Structure of layered silicates

(Source: Sinha Ray, 2003)

2.3.2` Types of Clays

Clay mineral can be divided into two types which is natural clay and synthesis clay. The commonly used clay mineral is natural clay. The two types of natural clay that widely used is montmorillonite and hectorite type. This two type of clay is falling under 2:1 type of clay. There is also 1:1 type and layered silicic acid type of clay.

One of the type of clay is 2:1 type. This type of clay consists of two-dimensional layers where a central octahedral sheet of alumina is fused to two external silica tetrahedral by the tip, so that the oxygen ions of the octahedral sheet also belong to the tetrahedral sheets. The layer thickness is around 1nm and the lateral dimensions may vary from 300A to several microns and even larger depending on the particulate silicate, the sources of the clay and the method of preparation.

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

Layer silicic acids, this clay consist of silicon tetrahedron sheets with different layer thickness. Their basic structure composed of layered silicate networks and interlayer hydrated alkali metal cations. Layered silicic acids also are suitable to use for polymer nanocomposites because it has similar intercalation chemistry with 2:1 type clay. It also has high purity and structural properties that are complementary to smectite clays.
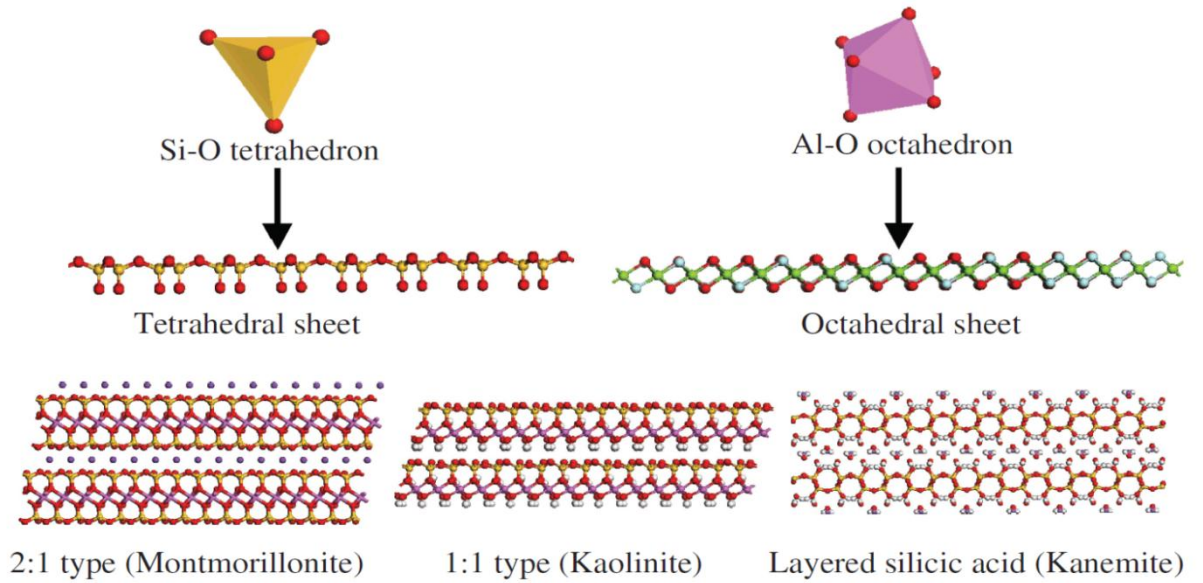
Figure 2.3 Structure of clay minerals represented by montmorillonite, kaolinite, and kanemite. Its built up from combinations of tetrahedral and octahedral sheets whose basic units are usually Si-O tetrahedron and Al-O octahedron, respectively.

(Source: Micheal Alexander, 2000)

2.4 Modification of Na+ MMT

The main reason of modification sodium montmorillonite is because PLA/polymer is not compatible with pristine clay / Na$^+$MMT. Therefore, Na$^+$ MMT first need to modify to produce polymer-compatible clay/organoclay (OC). The characteristic of clay is hydrophilic but the characteristic of polymer is hydrophobic. So, by organic treatment, the clay became hydrophobic to make sure it's compatible with polymer. It is important to change the inorganic clay to organic clay in the modification of nanocomposites. The surface modification process of nananoclay looks similar to the fiberglass treatment with silane coupling agent to ensure a perfect compatibility or chemical bonding polymers.

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In ion exchange method is the most popular modification for clay. The hydrophilic silicate of clay needed to be converted into hydrophobic in order to layer silicates miscible with most polymer matrices. This can be done by ion exchange modification with cationic surfactants. According to (Krishnamoorti et. al., 1996), the alkyl ammonium or alkylphosphonium cation can provide functional groups that can react with the polymer matrix, or in some cases initiate the polymerization of monomer to improve the strength of the interface between the inorganic and the polymer matrix.

Clay layer is stacked together with van der Waals force to form a gallery. This force will attract a couple of adjacent interlayer in clay. In this layer, there is inorganic cations that can be replaced by an organic ammonium cation and by substitute lower violent metallic ion for Si, Al, or Mg in the layer will generate negative charges that are counteracted by the alkali and alkaline cations within the galleries as according to (Liu *et. al*, 2006). By using the solution method for ion exchange method, pristine clay need to react with catalytically active transition metal ion salt (TMIs) with the presence of solvent. There is a combination between TMI salt and solvent. For example, methanol solvent with copper (II) sulfate, TMI salt and dioxane solvent with copper (II) nitrate.
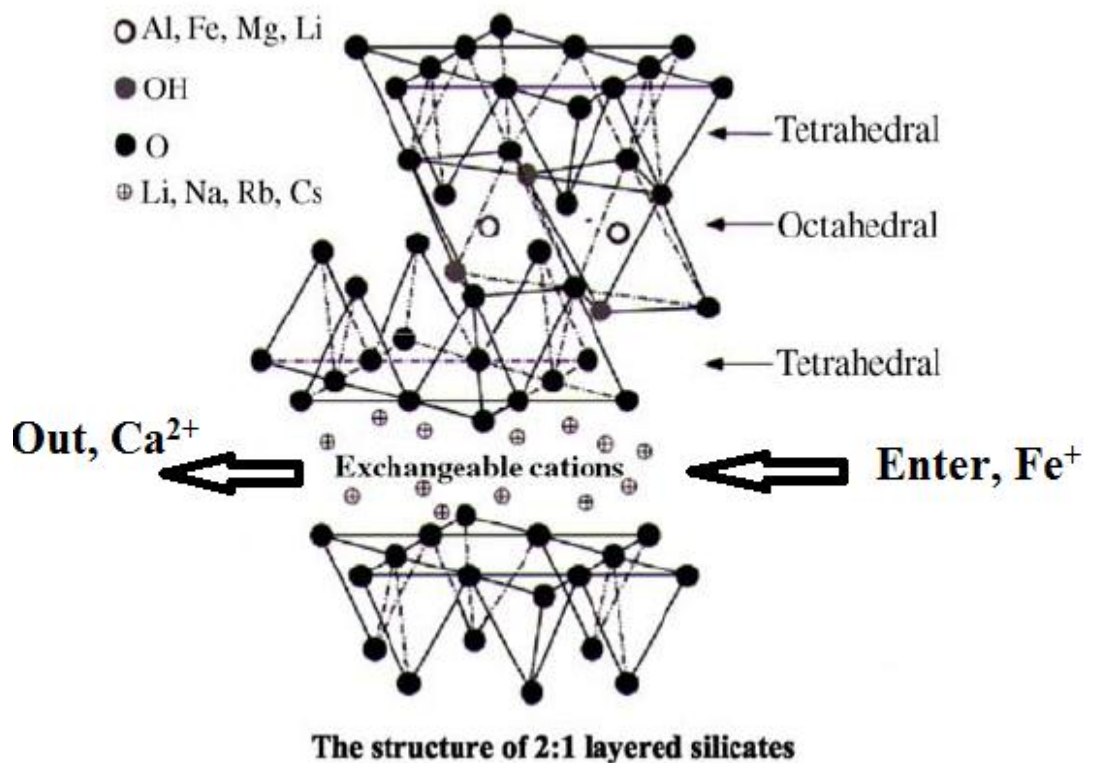
Figure 2.4   The ion replacement in interlayer of nanoclay.

(Source: Sinha Ray, 2003)

2.5   Polymer Nanocomposite

2.5.1 Synthesis of PLA Nanocomposite

A polymer nanocomposite is a combination of polymer matrix and a strong reinforcing phase that called filler. Polymer nanocomposites provide desirable properties unavailable in a matrix of filler materials alone. A polymer nanocomposite is a polymer matrix with a reinforcing phase containing one dimensional nano-sized particle. Nanocomposites are polymers with a particle-filled which at least one dimension of the dispersed particle is in nanometer scale, (Kashiwagi*et. al*., 2003). The polymer nanocomposites also defined as polymer matrix containing nanostructure of inorganic matter (Frechette & Reed, 2007).

In order to enhance the performance of polymer especially a rubber, the fillers of polymers are introduced. According to Ciprari's (2004), a general conclusion has been drawn that nanocomposite show that the improvement of mechanical properties. By (Fornes *et. al*., 2003), the rigid fillers are naturally resistant to straining due to their high moduli. Therefore, when a relatively softer matrix is reinforced with such fillers, the polymer particularly that adjacent to the filler particles becomes highly restrained mechanical. In most conventionally filled polymer systems, the modulus increase linearly with the filler volume fraction, whereas for nanocomposite much lower filler concentration increase the modulus sharply and in much larger extent (Sinha Ray *et al*., 2003)

Beside that, by the increase of polymer, the toughness also considers as improvement of properties of polymer nanocomposite, (Kudyakov*et al.,* 2009). In other hand, polymer with nanoscale additive shown an improvement in flammability properties because one of the weak aspect of polymer is they are combustible under certain condition but its provide a possible alternative to conventional flame retardants (Kashiwagi *et. al.,*2003).

Devaprakasam *et .al.* state the nanoparticle with uniform packing density in the polymer matrix results in homogenous mechanical properties compared to microcomposite, that is heterogeneous mechanical properties. It is due to high energy dissipation and big particles with the weak interfacial bonding of micronanocomposite. The clay based nanocomposite always obey the continuum mechanics prediction there. They can exhibit properties not expected with larger scale particulate. The wear resistance of the

nanocomposite is enhanced as the strong interfacial bonding between the nanoparticles and matrix due to the high specific area of the nanoparticle.

2.6   Types of structure of nanocomposite

Nanoparticles are commercially available from different sources. The types of nanocomposite are phase separated nanocomposite, intercalated nanocomposite and exfoliated nanocomposite. However, the nanocomposite is depending on the preparation method and the nature of the components used including the polymer matrix. From this three nanocomposites, the exfoliated nanocomposite is the most desired nanocomposite.

2.6.1 Phase separated nanocomposite

Micronanocomposite are formed when the polymer chain is unable to intercalate into the silicate layer and therefore phase separated nanocomposite is formed. This structure happened when the polymer unable to disperse between the clay and it becomes flocculated. In the other words, the layer sticks together within the polymer matrix.

2.6.2 Intercalated nanocomposite

Intercalated nanocomposite is obtained when the polymer chain is inseted between clay layer such that the interlayer spacing is expanded but the layers still bear a well defined spatial relationship to each other. The insertion of a polymer matrix into the layered silicate structure occurs in a crystallographically regular fashion, regardless of the clay to polymer ratio. Intercalated nanocomposite are normally interlayer by a few molecular layers

of polymers. Properties of the composites typically resemble those of ceramic materials.

2.6.3 Exfoliated nanocomposite

Exfoliated nanocomposite are formed when the layers of the clay have been completely separated and the individual layer are distributed throughout the organic matrix. The exfoliated configuration is particular interest because it maximize the polymer-clay interactions making the entire surface of layers available or polymer. This should lead to the most significant change in mechanical and physical properties.

The exfoliated give better mechanical properties than intercalated ones. The complete dispersion of clay nanolayers in a polymer optimizes the number of available reinforcing elements for carrying an applied load and deflecting cracks. (Chin I-J *et. al*., 2001).
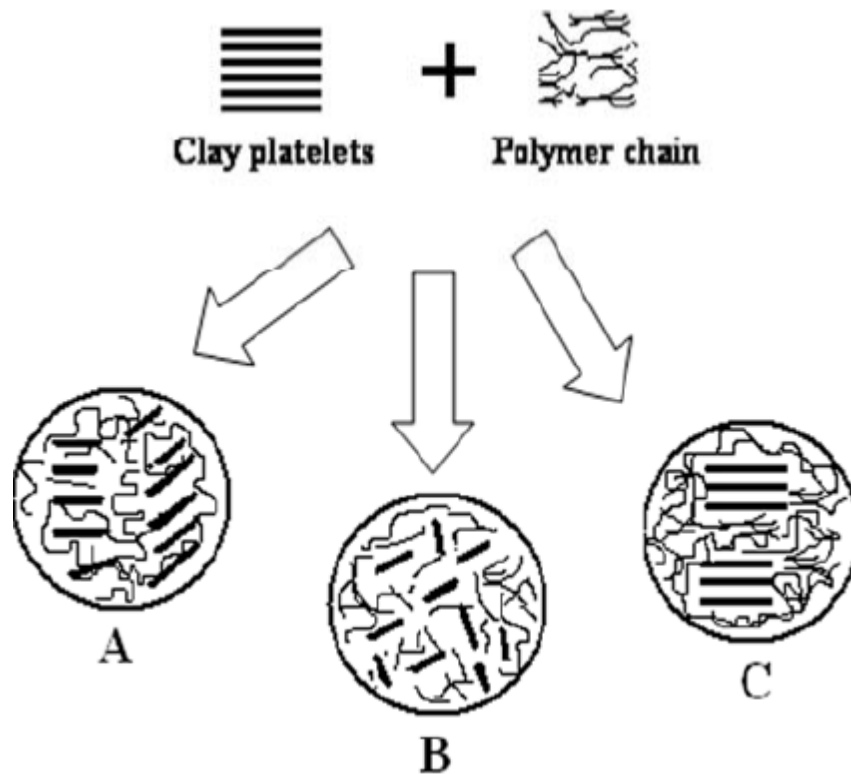
Figure 2.5   Schematic illustration types of nanocomposites. (A) intercalated, (B) exfoliated (C) phase separated polymer nanocomposite

(Source: Bhat *et. al*., 2008)

2.7   Preparation of Polymer Nanocomposite

In principle, nanocomposites can be formed from clay and organoclays in a number of ways. There are in-situ polymerization, solution intercalation and lastly melt intercalation

2.7.1   In-situ polymerization

In the in-situ polymerization method, the layered silicate is swollen within the liquid monomer or monomer solution so the polymer formation between the layered silicates. In this process, the monomer migrates into the galleries of the layered silicate, so the polymerization reaction can occur between the intercalated sheets. The reaction can be initiated by heat or

radiation, by the diffusion of a suitable initiator or by an organic initiator or catalyst fixed through cation exchange inside the interlayer before the swelling step by monomer thus allowing formation of polymer chains between the intercalated sheets. (Bhattacharya, Kamal & Gupta, 2008).
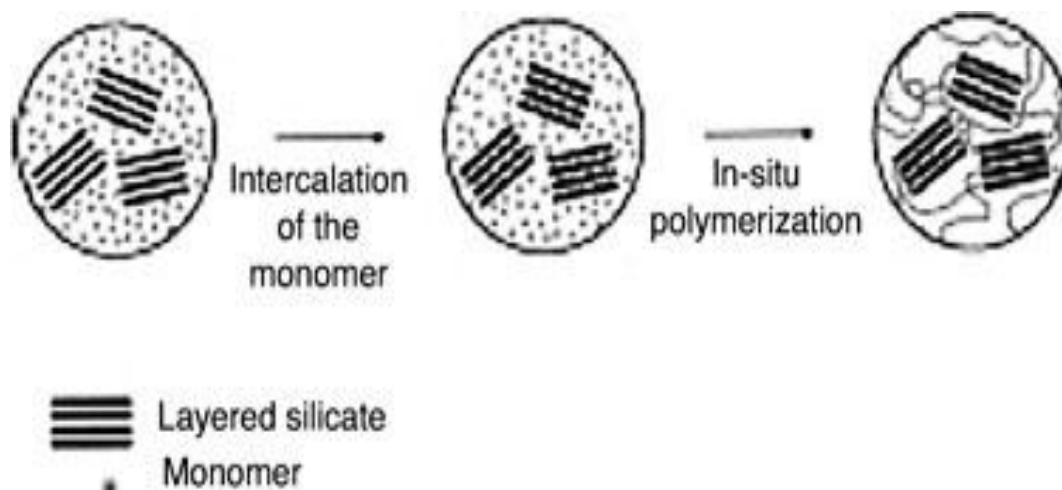
Figure 2.6: Schematics representation of polymer nanocomposite obtained by in-situ polymerization

(Source: Bhattacharya, 2008)

2.7.2 Solution Intercalation

This is based on a solvent system in which the polymer or pre-polymer is soluable and the silicate layers are swellable. The layered silicate is first swollen in a solvent such as water, chloroform or toluene. Using this technique, the layer silicate is exfoliated into single layer using a solvent in which the polymer is soluble. In layer silicated, the weak forces that stack the layers together can be easily dispersed in adequate solvent. After the organoclay has dispersed in the solvent, the polymer is added into the solution and intercalates between the clay layers. One of the advantages by using this method is the intercalated nanocomposite can be synthesized based

on the polymer with low or even no polarity. But, it is not suitable used in the industry owing to problems associated with the used of large quantities of solvents.
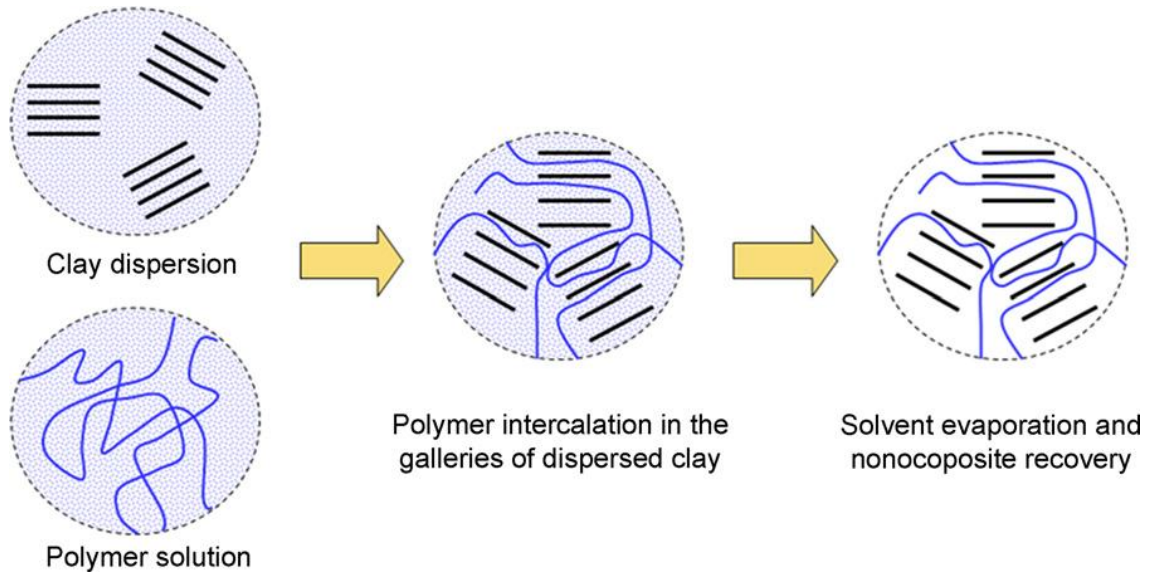
Figure 2.7: The schematic represents of PLS obtained by intercalation from solution.

(Source: Pavlidou, 2008)

2.7.3   Melt Intercalation

The melt intercalation technique is the suitable method in the most industrially viable approach that can lead to commercialized process especially in the plastics industry. The absence of solvent makes it an economically and environmentally. This technique has become the standard preparation of polymer-layered silicate nanocomposite. In this method, a polymer and layered silicate mixture is heated under either batch or continuous shear (in an extruder) above the softening point of the polymer. During the heating process, polymer chains diffuse from the molten polymer into the silicate

galleries to form either intercalated or exfoliated depending on the degree of penetration of the polymer chains into the silicate galleries.

The screw configuration and the nature of the extruder are crucial to achieve good organically dispersion. Long residence times in the extruder favor better dispersion. In some cases, dispersion can be achieved by melting a higher viscosity because of the higher stresses that can be imposed on the clay. However, this effect is not universally observed (Paula & Robeson, 2008).

The blending process under shear action of a twin screw between dry mixture of the polymer and then nanoclay powder. As the result of the modification, the clay are intercalated with alkyl ammonium cations bearing long alkyl chain to increase the interlayer spacing and improved the compatibility of nanoclay with the polymer matrix. It is also helping to facilitate the diffusion of the polymer chain from the bulk polymer melt into the galleries between the silicate layers of nanoclays.
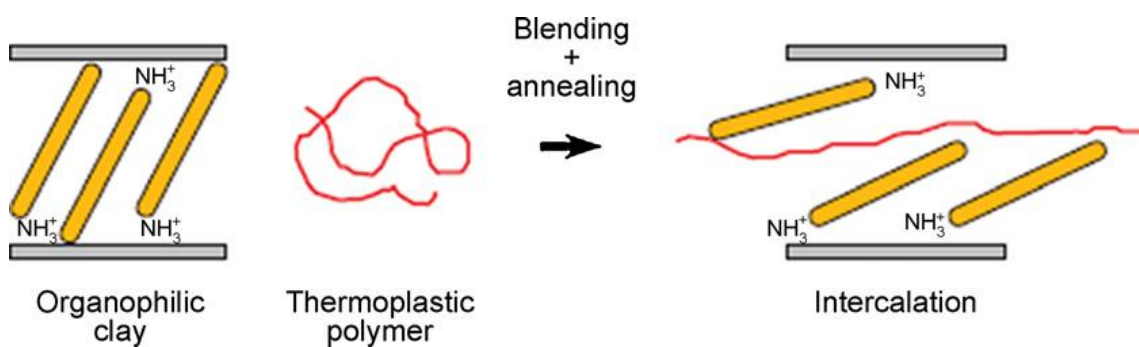
Figure 2.8: Melt Intercalation Process

(Source: Beyer G., 2002)

2.8   Morphological using PLA/ PP

The studies on morphology of the polymer blend are of paramount importance for determining the structure and property relationship. The morphology characterization will provide insights, among others, such as particle size, distribution of the rubbery impact modifiers in a polymer matrix, the distribution of components in a binary blend, the effect of interfacial addition on the particle size, the crystalline phase, dispersion / agglomeration of particles, as well as distribution of fillers in the polymer blend. The **Figure 2.9** illustrate the SEM micrograph examined from the tensile fracture surfaces for neat PLA/PP and PLA/PP/LNR blends respectively. It can be seen that there was a phase separation between the PLA and PP particles as shown in the figure. However, when LNR was added, the morphology of the blend showed a more homogenized and refined structure as evident. This can be explained by the role of LNR in compatibilizing the PLA and PP phases which resulting the better elongation at break, flexural and impact strength as discussed earlier. Liquid natural rubber is a chemically modified NR generated via oxidative degradation of NR.
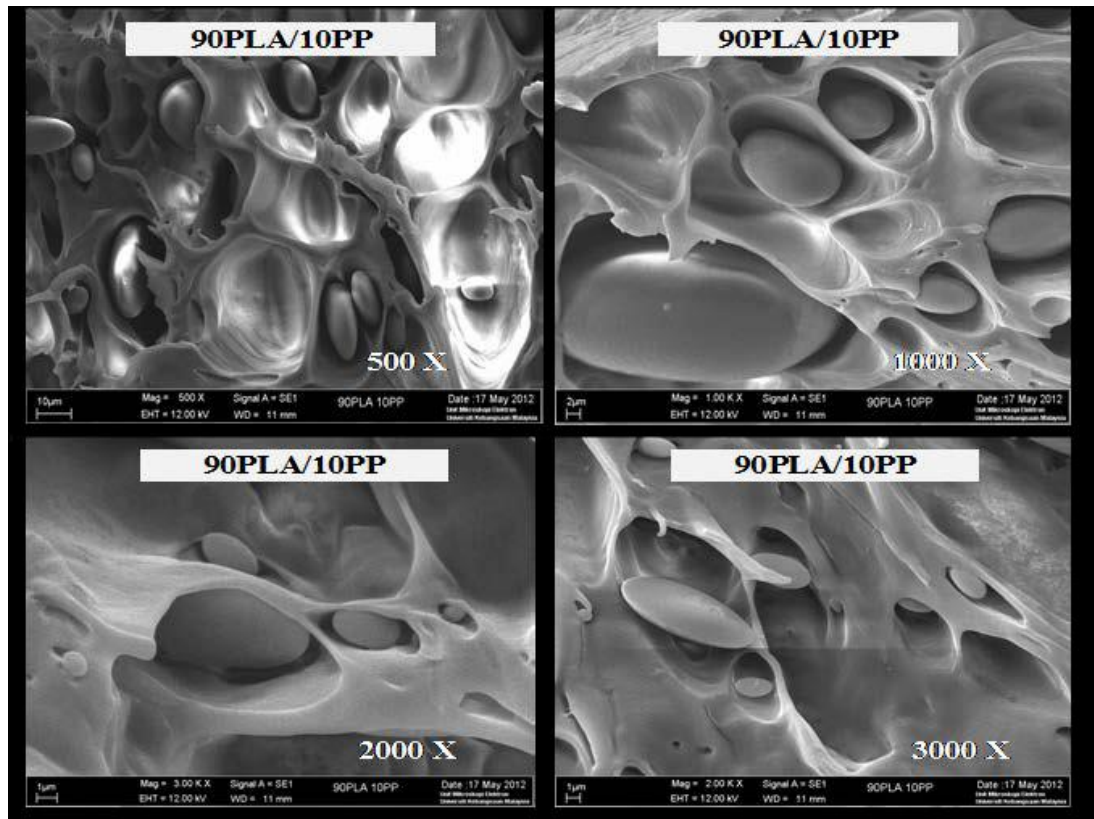
Figure 2.9: SEM micrographs of tensile fractured specimens for PLA/PP (90/10) blends.

(Sources: Rasal, 2010)

2.9 Mechanical and Thermal Properties using PLA/ PNC

In recent times, blending was the main approach to improve the mechanical properties of PLA by using different plasticizers and polymers to reach desired mechanical properties. PLA, which is a glassy polymer at room temperature, has a poor elongation at break (Rasal *et al*., 2008). Various biodegradable and non-biodegradable plasticizers were used to lower the glass transition temperature (Tg), improve processibility, and increase flexibility (Mascia *et al*., 1992). These aspects were carried out by modifying some of the plasticizer properties, polarity, molecular weight, and end groups.

Glycerol, citrate ester, polyethylene glycol, and oligomeric lactic acid were used to plasticize PLA and found that oligomeric lactic acid and low molecular mass polyethylene glycol gave finest results while glycerol was found to be the least competent plasticizer (Martin and Avérous, 2001). Citrate esters were found to be miscible with PLA at all compositions. Elongation at break was significantly improved accompanied with considerable loss of tensile yield strength (Labrecque *et al*., 1997).

PLA–biodegradable polymer blends were studied and extensively investigated more than PLA–non-biodegradable polymer blends due to their property improvements without compromising biodegradability. For instance, polyhydroxyalkanoates (PHA) produced by bacteria from biodegradable aliphatic homo or copolyesters with over 150 unlike kinds composed of dissimilar monomers (Steinbüchel and Lütke-Eversloh, 2003). Poly(3-hydroxybutyrate) (PHB) and its copolymers with 3-hydroxyvalerate (PHBHV), 3-hydroxyoctanoate (PHBHO), and 3-hydroxyhexanoate (PHBHHx) units are among the largely employed PHAs (Bluhm *et al*., 1986; Doi *et al*., 1988; Noda *et al*., 2004). The high crystallinity of PHB homopolymer results in a hard and brittle material, inconvenient to blend with PLA.

Polycaprolactone (PCL) is another extensively studied biodegradable PLA blend system. PCL as a rubbery polymer, has a low Tg and degrades by hydrolytic or enzymatic pathways. Broz *et al*. (2003) observed changes in modulus, elongation at break and tensile strength by blending PCL with PLA. Elongation at break increased only above 60 wt% PCL. However, the elongation at break improvement was not significant and resulted in a large modulus and tensile strength loss. The addition of a small quantity of

surfactant (copolymer of ethylene oxide and propylene oxide) did not lead to any significant elongation at break improvement for PLA/PCL blends (Chen *et. al.*, 2003). However, addition of a small amount of PLA–PCL–PLA tri-block copolymer (4%wt) to PLA/PCL (70/30, w/w) blends enhanced the dispersion of PCL in PLA and improved the flexibility of the resultant blend.

According to (Pluta *et. al.,* 2006), investigated the properties of PLA modified by thermal treatment, filling with MMT and plasticization with 10% of PEG. The researches showed the melt filling of PLA by organomodified nanoparticle had led to the formation of an intercalated nanostructure. They also observed that an intercalated nanostructure formed in plasticized PLA nanocomposite as the molecule of PEG stimulated in the intercalation process. The presence of inorganic clay particles reduces the crystallization of PLA and this effect was more pronounced in nanocomposites due to the intercalated nanostructure with provides higher surface area of interaction. Besides that, the addition of plasticizer facilitates the crystallization process of both plasticized PLA and plasticized PLA nanocomposite. The crystallization process by heating up from the glassy amorphous state led to the formation of the same crystalline modification in PLA. They also observed a reinforcing effect of MMT in the intercalated plasticized PLA nanocomposites as the storage modulus from DMA analyses registered higher value for MMT filled plasticized PLA compared to the unfilled plasticized PLA. The observed increase in modulus contributes to the rigidity of the material.

Lately, Jiang *et. al.* (2007), investigated the reinforcing effects and toughning mechanism by comparison of PLA/nano-sized calcium carbonate and PLA/MMT nanocomposite. They reported that the semicrystalline PLA exhibits

high tensile strength and modulus but very low at break and toughness. The researches also revealed the intercalation on MMT by PLA and good dispersion of both MMT and NPCC nanoparticles were achieved when the filler concentration was lesser than 5wt%. However, more large agglomerates were observed with increasing concentration of the filler. The strain at break of PLA increased with NPCC concentration ranging from 0 to 7.5wt%, whereas it only increased with MMT concentration up to 2.5wt% and decreased at higher concentrations and it was observed that the tensile strength of PLA nanocomposite also decreased with MMT content up to 5wt%. Interestingly, stress yielding was noted in PLA/MMT nanocomposites at 2.5wt% MMT with significant necking but with 5 and 7.5wt% MMT, however the strain at break was dramatically reduced and the nanocomposites fractured in completely brittle manner without yielding. They also concluded that the different reinforcing effect of MMT and NPCC could be mainly attributed to the diffrences in microstructure and interactions between the nanoparticles and PLA in the respective nanocomposites. It was observed that the MMT stacks located between the microvoids and prevented their coalescence, allowing large scale shear yielding but at higher MMT concentration. However, the agglomerates of MMT induced premature material failure occured before the shear yielding was able to start.

2.10   Characterization

One of the most challenging parts in this characterizing is to quantify the levels of dispersion and exfoliation. Atomic Absorption Spectroscopy (AAS), X-ray Diffraction (XRD), Tranmission Electron Microscopy (TEM) and

Scanning Electron Microscopy (SEM) analysis is the one of the most reliable and currently most often used to examine clay containing nanocomposites. However, the combination of TEM analysis and XRD appears more global method to quantify levels of dispersion and exfoliation when they couple with TEM analysis for image confirmation (Snyder, 2007).

2.10.1 Toughness and strain

The brittle behaviour often exhibited by nanocomposites probably originated from the formation of microvoids due to debonding of clay platets from the polymer upon failure. This is testified through careful inspection of fracture and its also correlated to observations by in situ deformation experiments using TEM.
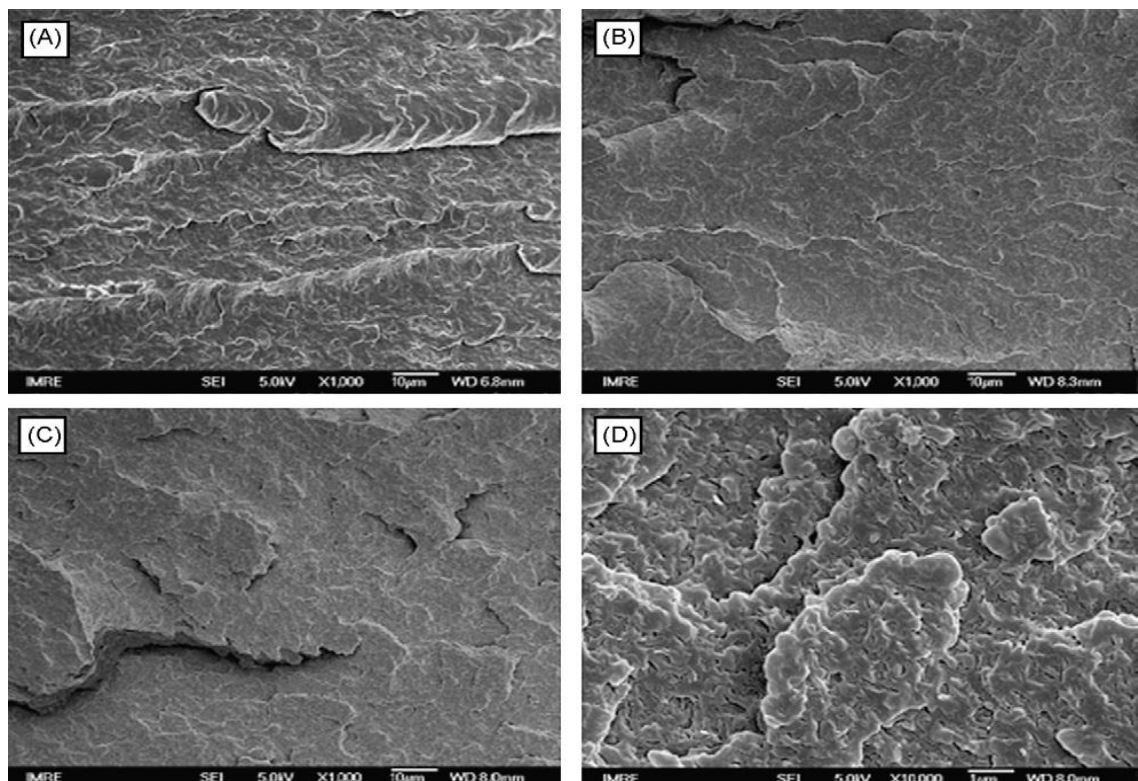
Figure 2.10 SEM images showing fracture surface after impact test. (a) Neat PA12 : (b) and (c) PA12 nanocomposites containing 1 and 5wt% clay respectively: (d) high magnification of (c)

(Source: Pavlidou, 2008)

2.11   Thermal Analysis

The term of thermal analysis refers to a collection of analytical techniques that is designed to provide information of materials. The materials can be obtained by observing the structure and property changes that occur with changes in temperature. Thermal analysis can be used in a variety combination. This technique is widely used for polymer because these methods are sensitive to structural change which are suitable for the substance that composed of large and extended molecules. The most common combination is Thermogravimetric analysis (TGA) with Differential Scanning Calorimetry (DSC).

2.11.1 Thermogravimetric analysis (TGA)

TGA is an analytical method to utilize a sensitive balance to determine weight loss of the sample through a range of temperature. A sample is loaded onto a pan and then place in the balance. A furnace then encloses the sample and the temperature can be increased at given rates and given environment. The constituents of the sample will burn off at different rates making the weight percents of constituents determinable.

Neat PLA exhibited a one step decomposition profile with a single transition temperature, as demonstrated by TGA. The TGA peak temperature is the temperature at the beginning point of the most weight loss, while the final temperature at the end of the degradation. These two points can be determined easily using the derivate graph. Under conditions of high temperature and high humidity, as in active compost, PLA will degrade quickly and disintegrate within weeks to months. The primary mechanism of

degradation is hydrolysis, followed by bacterial by bacterial attack on the fragmented residues. The enviromental degradation of PLA occurs by a two-step process (Lunt, 1998).

During the initial phases of degradation, the high molecular weight polyester chains hydrolyze to lower molecular weight oligomers. The rate of hydrolysis is accelerated by acids or bases and is dependent on moisture content and temperature. Sample dimensions, crystallinity and blends will affect the rate of degradation. PLA products rapidly degrade in both aerobic and anaerobic composting conditions. However, under typical use conditions, PLA is very stable and will retain its molecular weight and physical properties for years.
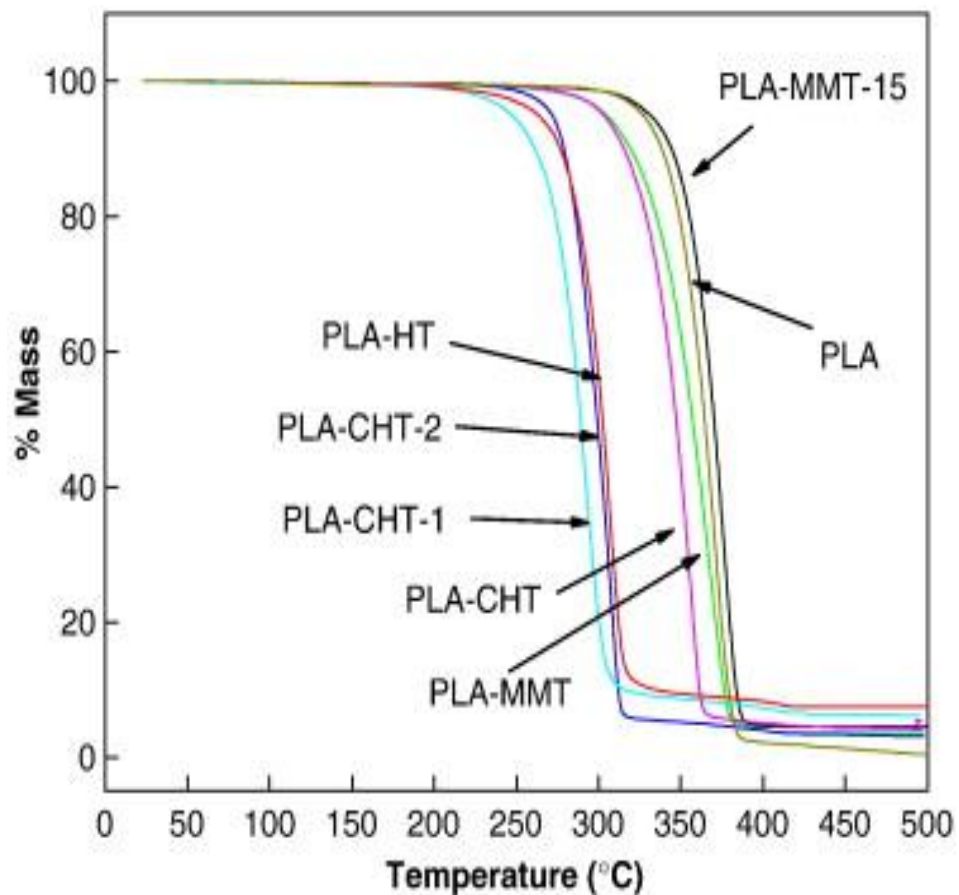
Figure 2.11   The example of TGA curve of PLA

2.11.2 Differential Scanning Calorimetry (DSC).

DSC is one of the analytical equipment that measures the change of differences in the heat flow in the sample and to a reference sample with the controlled temperature program. Glass transition depending on a number of factors such as chain flexibility, molecular weight, branching, cross linking, intermolecular interaction and stress effects.

Glass transition temperature (T_g) is a central property of polymers and importance in both fundamental polymer science as well as polymer engineering processing. And, this method to characterize a property of polymeric material. T_g is the temperature where the polymer goes from a hard, like rubber state. DSC defines the glass transition as a change in heat capacity as the polymer matrix goes from the glassy state of the rubbery state. It is a second order endothermic transition which requires heat to go through the transitions. Thus, in DSC the transition appears as a step transition and not peak such as might be being with a melting transition.
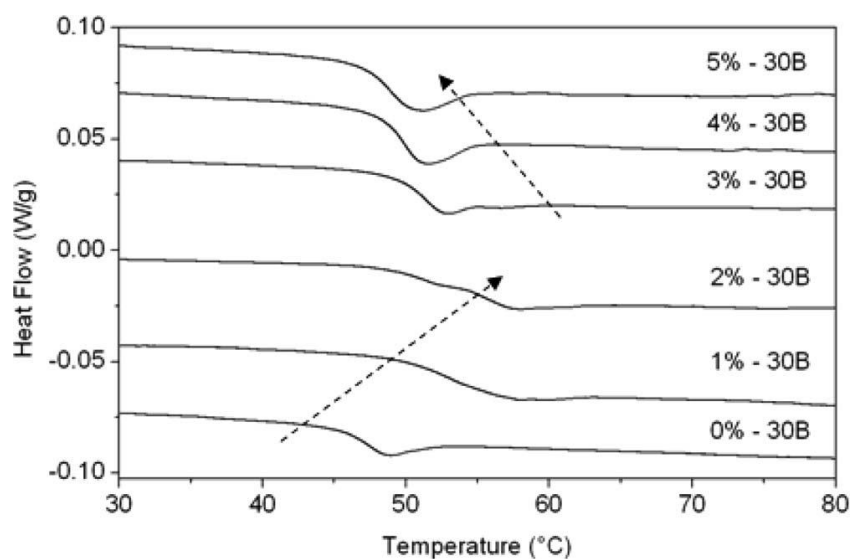
Figure 2.12 The DSC thermograms for PLA

(Source: Sinha Ray, 2003)

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Table 2.2 T_g values of various PLA- B30 nanocomposite

Nanocomposite (PLA-30B)	Glass transition temperature (℃)
0%-30B (control of PLA)	47.4
1%-30B	53.2
2%-30B	55.2
3%-30B	51.3
4%-30B	49.9
5%-30B	48.9

2.12   Conclusion

The conclusion of this research is for the study of the thermal and the mechanical properties of PLA-modified MMT nanocomposites. The composite were confirmed and characterized by XRD, and SEM. And other properties can defined with another much of the literature claimed.

CHAPTER 3

METHODOLOGY

3.1   Introduction

In order to prove the problem statement, there are a few methods that have to be followed. The first method is synthesizing PLA and PLA nanocomposite samples. Second, the TMI modification sample is tested by Atomic Absorption Spectroscopy (AAS). Third, the sample is characterized based on morphological analysis by using XRD and SEM.. Lastly, it is followed by thermal analysis which by using analytical tools that are TGA and DSC.

3.2   Materials

3.2.1 Sodium Montmorillonite (Na$^+$ MMT).

Table 3.1: Properties of Na$^+$ MMT

Appearance	Pale grey – brown granular powder, puggy when wet
Boiling Point	Not relevant
Vapour Presure	Not relevant
Bulk Density	1.2 – 1.6
Granular Density	1.8 – 2.4
Flash Point	Not relevant
Flammability	Not relevant
Auto-ignition Temperature	Not relevant
pH	8.5 – 10.5

3.2.2 Polylactic acid (PLA)

Table 3.2: Properties of PLA

Chemical Formula	-($C_6H_8O_5$)-
Appearance	White solid
Odor	No odour
pH	No data
Melting Point	130-170 ^{0}C
Flash Point	121 ^{0}C
Flammibility	Not flammable
Specific Gravity	1.30 g/cm^3
Solubility	Not soluable

3.2.3 Transition metal ion salt Copper (II) chloride.

Table 3.3: Properties of Copper (II) chloride

Physical State	Crystalline powder
Colour	Brown-fine
Odor	odorless
pH	3
Vapour Pressure	Not available
Viscocity	Not available
Boiling Point	993 ^{0}C
Melting Point	498 ^{0}C
Solubility in Water	620 g/l (20^{0}C)
Density	Not available
Molecular Formula	$CuCl_2$
Molecular Weight	134.45

3.2.4 The solvent either methanol, ethanol or distillate water.

3.3   Preparation of PLA nanocomposites

3.3.1   Ion Exchange Method

The main objective of the research is to modify Na+ MMT that acts as filler in polymer nanocomposite in order to improve their final properties. The flow diagram below shows the step of the ion exchange method of pristine clay using catalytically active transition metal ion salt (TMIs). The layered silicate are only miscible which hydrophilic polymer. In order to render them miscible with other polymer, one must exchange the alkali counter-ions with a cationic-organic surfantant.

Alkylammonium ions are mostly used. It is can be readily achieved through ion exchanged reaction that render the clay organophilic. Natural clay may contain divalent cations such as calcium and requires exchange procedures with sodium prior to further treatment with onium salts. The alkali cations as they are not structural can be easily replaced by other positively charged molecules and thus are called exchangeable cations (Xie W., 2001).

3.3.2 Pre-treatment Phase of Nanoclay

Pristine clay needs to be washed first before modification to remove excess surfactant and impurities in pristine clay by (Nawani *et. al.*, 2007)

Washing: 2g of pristine clay in 40 ml solvent (methanol, ethanol, or water).

Stirring: The suspension was vigorously stirred for 24h

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

Filteration and Dried : The slurry wasthen filtered and dried in vacuum for 12h at 80℃ (the weight loss are observed).
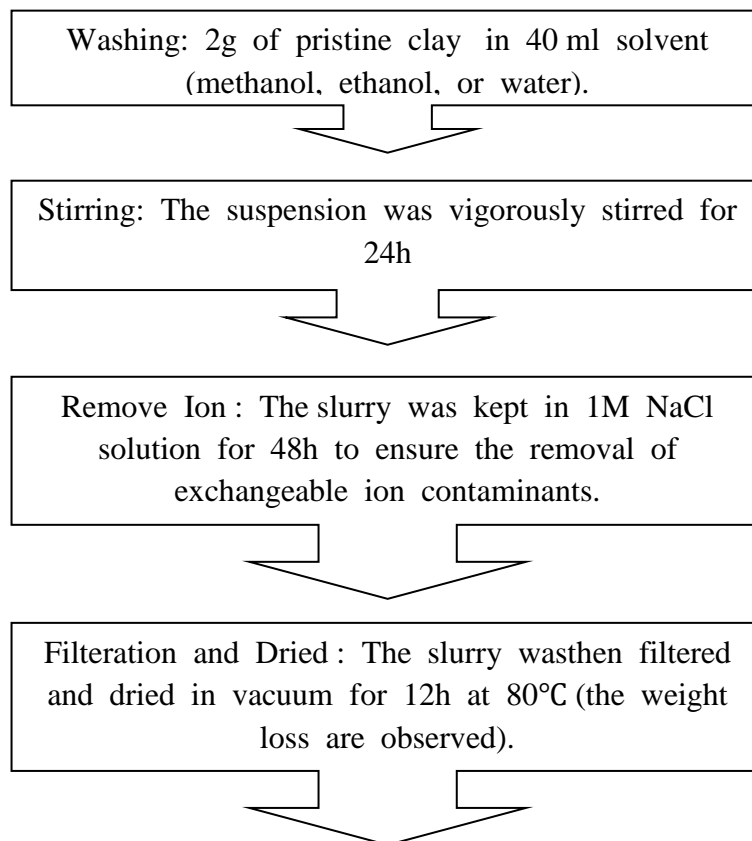
Figure 3.1 : Pre-treatment Phase of Nanoclay

Figure 3.2: Pre-treatment of Na$^+$ MMT

3.3.3 TMI salt Modification

Once the clay has been dried, it is ready to be treated with catalyst active TMI salt. The TMI that used here is Copper (II) Chloride, $CuCl_2$ and the solvent is water. Based on the molecular weight of $CuCl_2$, metal ion salts $Mr=170.48g/mol$, the desired weight to produce a 1550ml, 0.3M solution is $W= 79.27grams$, (Nawani *et. al.*, 2007)

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

Ion Exchange : 10g of pre-treated Na+MMT were then placed in 250ml $CuCl_2$ of 0.3M concentration solution.

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

Filter and Wash : Filter and wash the sample again and dried it in vacuum for 12h at 80 ℃

Figure 3.3 : Modification of Na$^+$ MMT

Figure 3.4: Modification of Na^+ MMT with $CuCl_2$

3.3.4 Characterization of TMI salt modification using Atomic Absorption Spectroscopy (AAS)

AAS is a spectroanalytical procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state. This technique is used for determining the concentration of a particular element (the analyte) in a sample to be analyzed. The variations in the intensity of adsorption of the transition metal ion into the surface of nanoclay due to the utilization of different solvents are tested at this stage. This step is done to prove that solvent to be used during the surface modification by solution intercalation phase. The method to characterize the $CuCl_2$ and $CuSO_4$ in Na^+ MMT is prepared by

soil leaching stage. And it has continued with AAS testing, (Hwang, Park & NamKong, 2007)

The medium is used is Ethylenediaminetetraetic acid, EDTA. The desired weight to produce a 500ml, 0.05M solution and the weight is needed is 7.306grams.

Weight of 7.306g of EDTA in 500 ml ultrapure water with 0.05M EDTA..

Weight of 5g of Na^+ MMT modified.

Mixed the solution EDTA 0.05M and 5g of Na^+ MMT modified

Put the mixer solution in the ultrasonic waterbath for 12min at power 60kW.

Filteration the EDTA mixer solution
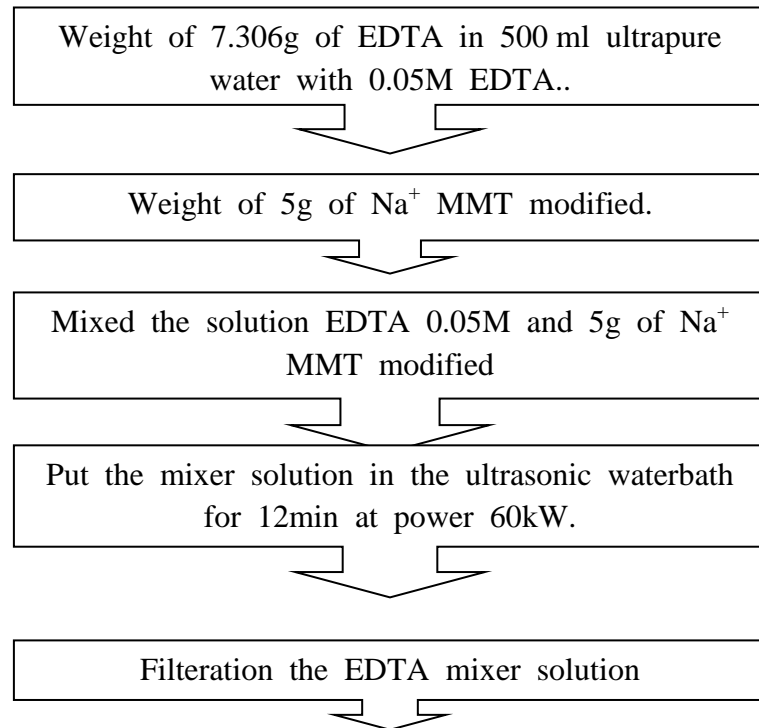
Figure 3.5: Soil Leaching Stage method

Prepared $100\mu L$ leachate to 10mL ultrapure water

Used $M_1V_1 = M_2V_2$ to prepared concemtration of stock solution of Copper (1000ppm).

Using the same equation,, prepare the stock solution for 100ppm, 1.6ppm, 1.2ppm, 0.8ppm and 0.6ppm.
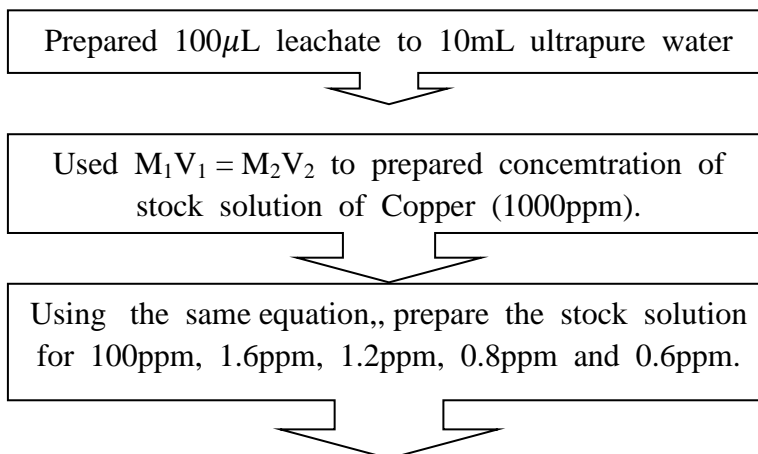
Figure 3.6: AAS Testing

Figure 3.7: AAS Equipment (AAS 7003M)

Type of filter: Syringe filter (Nylon & 0.22μm)

$$M_1V_1 = M_2V_2 \qquad\qquad\qquad\qquad \text{(Equation 3.1)}$$

M_1 : concentration of 1st standard

V_1 : volume of 1st standard

M_2 : concentration of stock solution

V_2 : volume of stock solution

a) From 1000ppm to 100ppm

$(100)(500) = (1000) V_2$

$V_2 = 50$mL

b) From 100ppm to 1.6ppm

$(1.6)(100) = (100) V_2$

$V_2 = 1.6$ml

c) From 100ppm to 1.2 ppm

$(1.2)(100) = (100) V_2$

$V_2 = 1.2$ml

d) From 100ppm to 0.8ppm

$(0.8)(100) = (100) V_2$

$V_2 = 0.8$ml

e) From 100ppm to 0.6ppm

$(0.6)(100) = (100) V_2$

$V_2 = 0.6$ml

3.4   Fabrication of PLA modified MMT

PLA pellets were dried in an oven at 90°C respectively for 24 hours. The nanocomposites were compounded by simultaneous adding all the components to Prism EUROLAB 16 Twin Screw Exruder (Thermo Scientific). PLA is prepared in weight percentage and Cloisite Na^+ is added as part per

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hundred together with PLA into the blends. The temperature for feed section for extruder during compounding all blends is set to $190^{\circ}C$ and decrease to $160^{\circ}C$ at the die head. The screw rotation speed is fixed at the rate 100rpm. The total weight for each sample is 570g, (Sinha Ray, 2002).

Table 3.4   Material designation and composition

Designation	PLA (%)	Weight (g)	Closite Na^+ (%)	Weight (g)
Neat PLA	100	570.00	0.0	0.00
PLA/ Na^+	99.7	568.29	0.3	1.71
PLA/ Na^+	99.5	567.15	0.5	2.85
PLA/ Na^+	99.3	566.01	0.7	3.99
PLA/ Na+	99.0	564.3	1.0	5.70
PLA/ Na^+modified	99.7	568.29	0.3	1.71
PLA/Na+modified	99.5	567.15	0.5	2.85
PLA/ Na^+ modified	99.3	566.01	0.7	3.99
PLA/ Na^+ modified	99.0	564.3	1.0	5.70

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┌─────────────────────────────────────────────────┐
│   Dry PLA pellets in an oven at 90⁰C respectively │
│                 for  24hours                     │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│         Prepare PLA in weight percentage         │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│   Add Cloisite Na⁺ as parts per hundred (phr)    │
│        together with PLA into the blends         │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│   Set the temperature for feed section of extruder │
│     during compounding all blends to 190⁰C      │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│   Decrease the temperature of extruder to 160⁰C at │
│                   die head                       │
└─────────────────────────────────────────────────┘
                        │
                        ▼
┌─────────────────────────────────────────────────┐
│   Set the screw rotation speed at rate of 200 rpm │
└─────────────────────────────────────────────────┘
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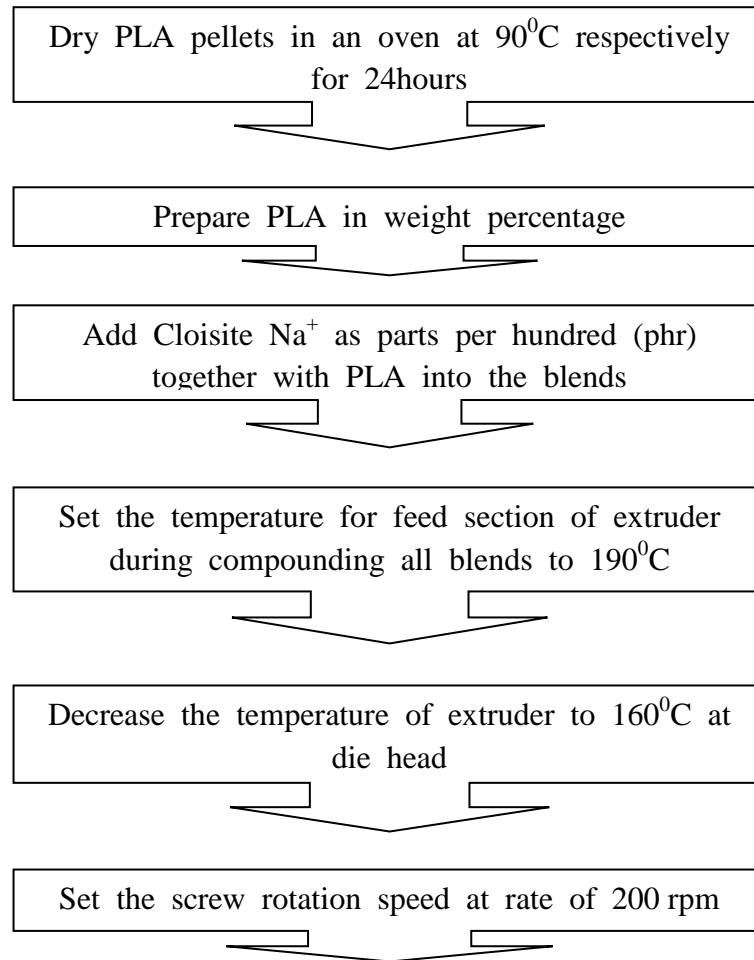
Figure 3.8   Fabrication of PLA nanocomposites
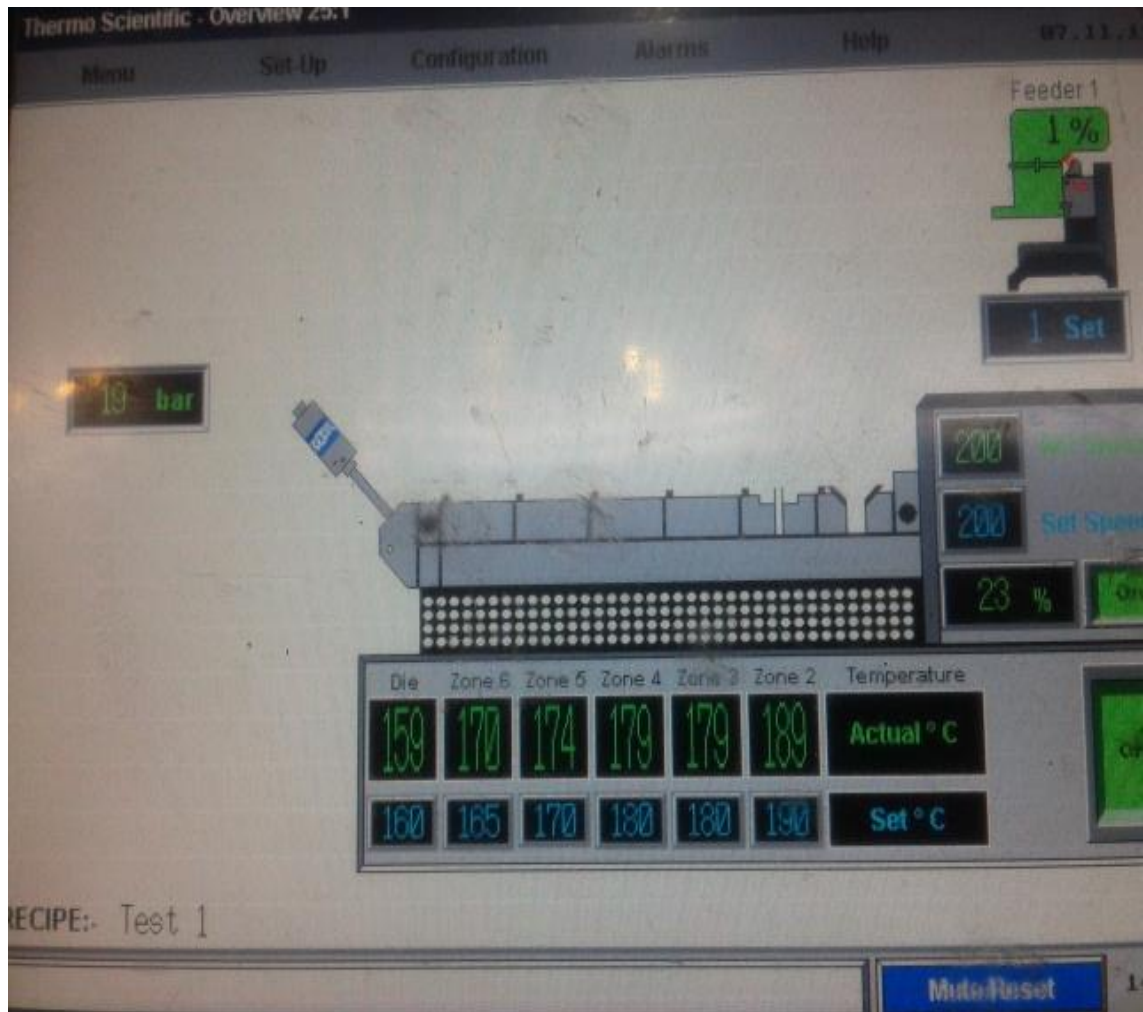
Figure 3.9: The temperature profile for extruder

3.5 Characterization

3.5.1 X-ray Diffraction Analysis (XRD)

The analysis is performed using XRD Miniflex by Rigaku to characterize the structure of the samples. The samples are scanned in fixed step size, 0.05 with a step -time of 0.1s in the range of $1\text{-}10^{o}$c. Based on the scanning, an XRD diffractorgram (intensity 20) is obtained. Then, the *d*-spacing (*d*) of the interlayer gallery of CloisiteNa+ and the PLA based nanocomposites is calculated using Bragg's equation:

$$d = \frac{n\lambda}{sin\theta}$$
(Equation 3.2)

d = spacing between layers of the clay

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

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

n = order of diffraction

Prepare the sample

Scan the sample in fixed step size, 0.05 with a step-time of 0.1s in the range of $1-10^0$C.

Obtain XRD diffractorgram (intensity 20) from the scanning

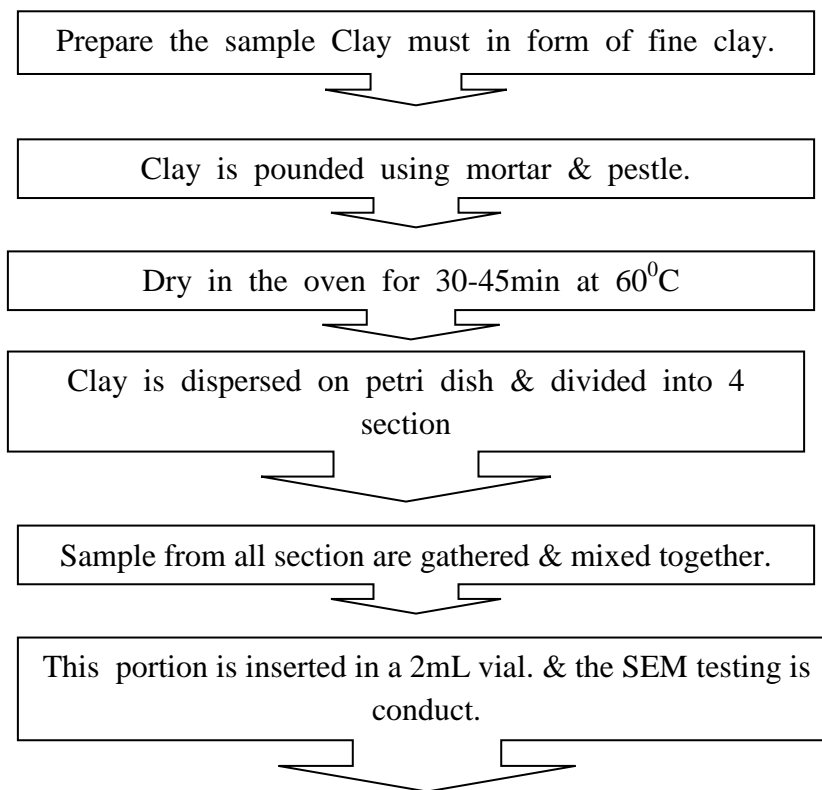| Calculate the (*d*) of the interlayer gallery of CloisitNa+ and the PLA based nanocomposites using Bragg's law equation |
| --- |
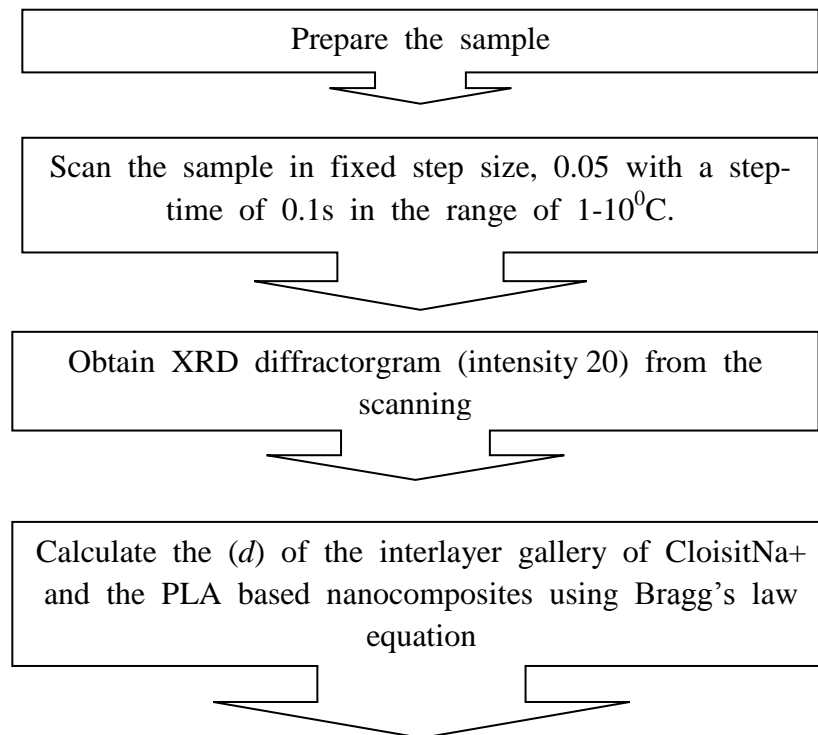
Figure 3.10: Characterization method using XRD

Figure 3.11: XRD Miniflex (Rigaku)

3.5.2 Scanning Electron Microscopy (SEM)

The morphological features of the particles were studied with Scanning Electron Microscopy (SEM). SEM test was carried out to check the surface of the modified nanoclay. An uncharacteristically rough surface is not suitable to be made commercially and proves the quality of modification is sub-par.

For this test, the clay must be in the form of fine clay. Therefore, the clay is pounded using a mortar and pestle and subsequently dried in the oven for 30-45minutes at 60^0C. Then the clay is dispersed on the petri dish and divided into four sections. Samples from all four sections gathered and mixed together. This portion of the nanoclay is then inserted into a 2mL vial. SEM testing was conducted by the central lab. SEM images will be taken using a backscattering detector.

Prepare the sample Clay must in form of fine clay.

Clay is pounded using mortar & pestle.

Dry in the oven for 30-45min at 60^0C

Clay is dispersed on petri dish & divided into 4 section

Sample from all section are gathered & mixed together.

This portion is inserted in a 2mL vial. & the SEM testing is conduct.

Figure 3.12: Morphological study by SEM

Figure 3.13: SEM Equipment (Merlin)

3.6   Thermal analysis
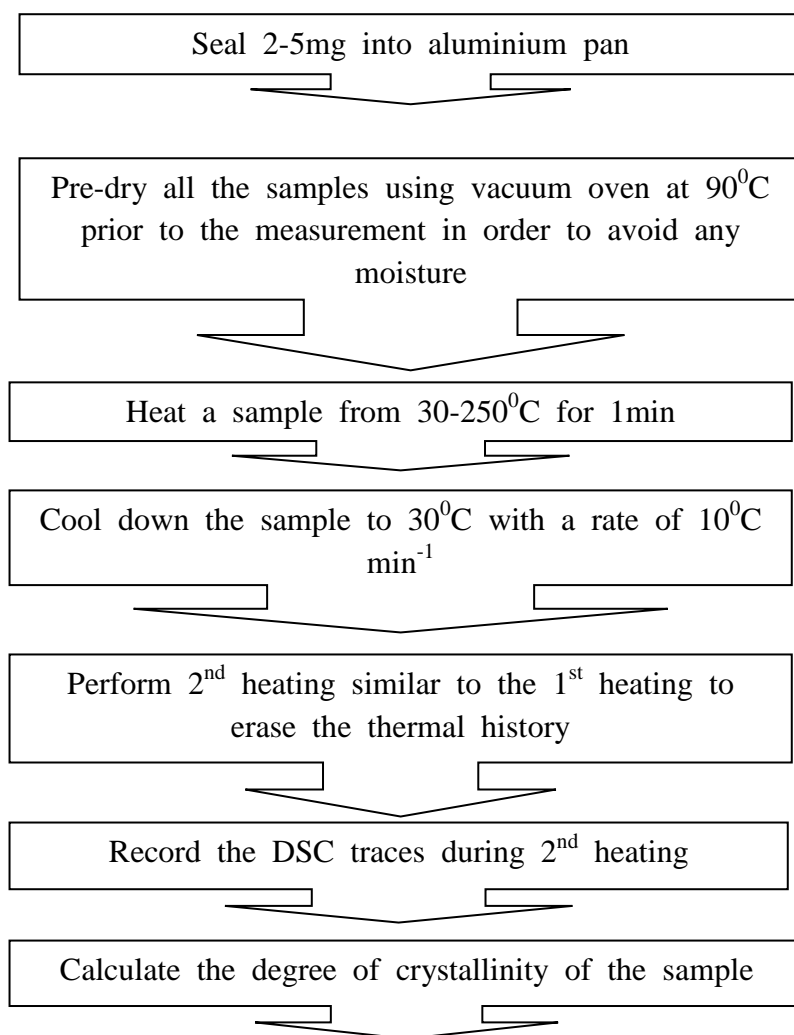
3.6.1 Differential Scanning Calorimetry (DSC)

DSC is used to determine the glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c) and degree of crystallinity (χ_c). The fabricated is carried out in Perlin Elmer DSC Q1000 under nitrogen atmosphere. 8-10g sample is sealed in an aluminum pan. All the samples were pre-dried using vacuum oven at 90^0C prior to the measurement in order to avoid any moisture. The sample is heated from 30-250^{0}C for 1 min, and cooled down the sample to 30^{0}C with a rate of 10^0C min^{-1}. Second heating is performed similarly to the first heating to erase the thermal history. The DSC traces are recorded during second heating. Then, the degree of crystallinity (χ_c) of the sample is calculated by comparing the heat of fusion obtain for the tested sample with that a reference sample with 100% crystalline by using an equation:

$$\chi_c = \frac{\Delta H_m - \Delta Hc}{93.6} X \ 100\%$$
(Equation 3.3)

Where ΔH_m = heat of fusion of the sample

ΔH_c = heat of crystallization

The crystallinity of PLA in the composite is calculated by setting the heat of fusion 100% crystalline PLA ($\Delta H_{f, PLA}$) equal to 93.6Jg

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┌─────────────────────────────────────────────────────┐
│           Seal 2-5mg into aluminium pan               │
└─────────────────────────────────────────────────────┘
                          │
                          ▼
┌─────────────────────────────────────────────────────┐
│  Pre-dry all the samples using vacuum oven at 90$^0$C │
│   prior to the measurement in order to avoid any      │
│                     moisture                          │
└─────────────────────────────────────────────────────┘
                          │
                          ▼
┌─────────────────────────────────────────────────────┐
│        Heat a sample from 30-250$^0$C for 1min        │
└─────────────────────────────────────────────────────┘
                          │
                          ▼
┌─────────────────────────────────────────────────────┐
│  Cool down the sample to 30$^0$C with a rate of 10$^0$C │
│                       min$^{-1}$                      │
└─────────────────────────────────────────────────────┘
                          │
                          ▼
┌─────────────────────────────────────────────────────┐
│   Perform 2$^{nd}$ heating similar to the 1$^{st}$ heating to │
│             erase the thermal history                 │
└─────────────────────────────────────────────────────┘
                          │
                          ▼
┌─────────────────────────────────────────────────────┐
│       Record the DSC traces during 2$^{nd}$ heating   │
└─────────────────────────────────────────────────────┘
                          │
                          ▼
┌─────────────────────────────────────────────────────┐
│   Calculate the degree of crystallinity of the sample │
└─────────────────────────────────────────────────────┘
```

Figure 3.14 Characterization method using DSC

Table 3.5: The composition of PLA

Composition	Weight Sample (mg)	Weight Lid (mg)	Weight Pan (mg)	Total Weight (mg)
PLA pure	2.1	9.1	10.6	21.8
0.3% unmodified PLA	2.2	9.1	11.0	20.1
0.5% unmodified PLA	2.5	9.2	11.0	22.7
0.7% unmodified PLA	2.5	8.5	10.6	21.2
1.0% unmodified PLA	2.7	9.3	10.9	22.9
0.3% modified PLA	2.2	9.1	11.0	20.1
0.5% modified PLA	2.8	9.2	10.6	22.6
0.7% modified PLA	2.5	9.0	11.2	22.7
1% modified PLA	2.7	9.0	11.3	20.3

Figure 3.15: DSC Equipment (Perlin Elmer)
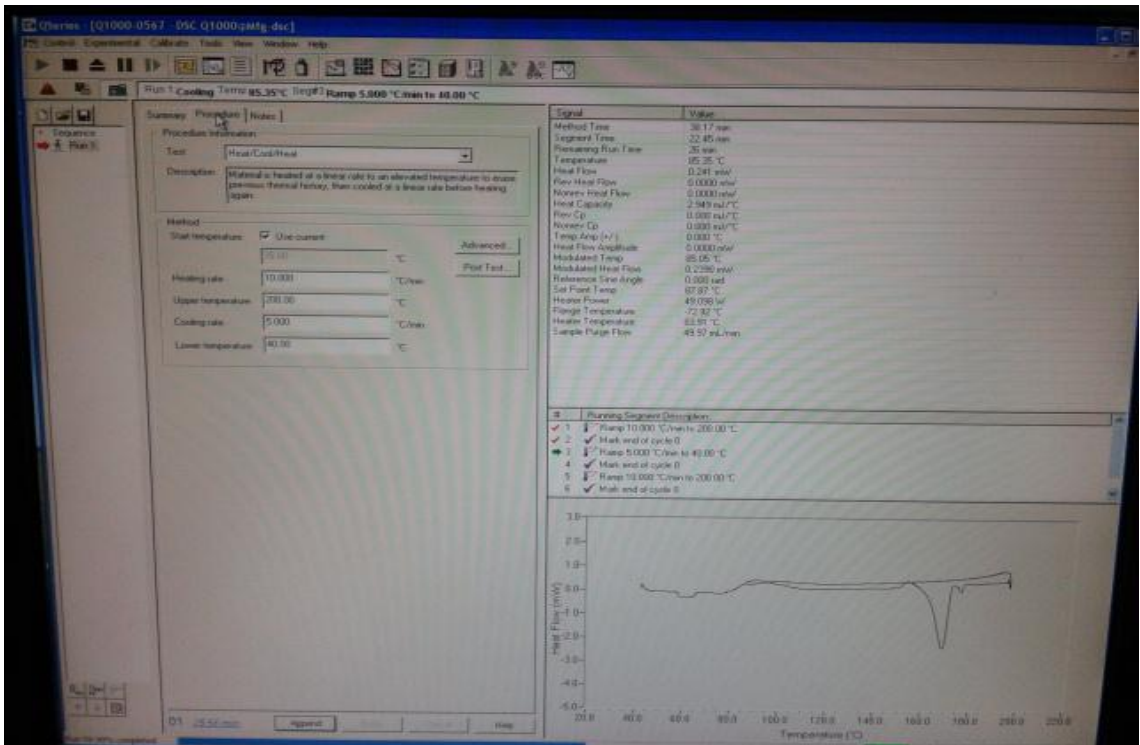
Figure 3.16: The temperature profile for DSC

3.6.2 Thermogravimetric Analysis (TGA)

TGA is used to examine the thermal degradation of the behavior of the organic components in the PLA and PLA/ CloisiteNa+ blends. Using TGA Q500 (Perkin Elmer), heat the PLA and its nanocomposites from room temperature to 500^0C at a heating rate of 20^0C min^{-1} under nitrogen atmosphere. The resulting mass change versus temperature curve will provide the information of thermal stability for the samples.

Heat the PLA and its nanocomposites from room temperature to 500^0C at a heating rate of 20^0C min^{-1} under nitrogen atmosphere.

The resulting mass change versus temperature curve will provide the information of thermal stability for the samples.
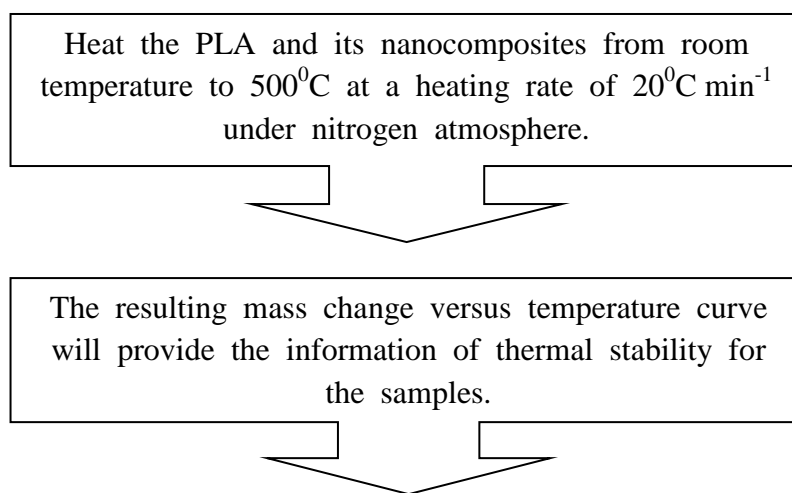
Figure 3.17 Characterization method using TGA

Figure 3.18: TGA Q500 (Perkin Elmer)

CHAPTER 4

RESULT AND DISCUSSION

4.1   Introduction

This chapter focus on the result, discussion and analysis of Atomic Absorption Spectroscopy (AAS), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC) and Thermogravimetri Analysis (TGA).

4.2   Pre-treatment Process

4.2.1 Introduction

The experiment will starting with pre-treatment process. In this process, the clay needs to be washed first before modification. The function of washing is to remove all the excess surfactant and the impurities in pristine clay. The solvent is normally used for washing are methanol, ethanol or water. After that, the experiment will continue by TMI salt modification and the result will be discuss in AAS result.

4.2.2   AAS Result

The main reason to modify the sodium montmorillonite is because the PLA is not compatible with clay. So, Na^+ MMT are modified to produce polymer compatible organoclay. And the characteristics of of clay will change from a hydrophilic to become hydrophobic to make sure it's compatible with polymer. The most popular modification for clay is an ion exchange method. By using the solution method for ion exchange method, the clay need to react with active transition metal ion salts, $CuCl_2$. The characterization of $CuCl_2$ in Na^+ MMT is determined by Atomic Absorption Spectroscopy (AAS).

Table 4.1: TMI modification result by AAS

No.	ID	Mean Signal (Abs)	Entered Concentration (mg/L)	Calculated Concentration (mg/L)	Standard Deviation	% RSD	Signal Stored
1.	Blank	0.000	0.0	0.0	0.0	0.31	Yes
2.	Calib Std 1	0.114	0.6	0.715	0.0	0.39	Yes
3.	Calib Std 2	0.139	0.8	0.868	0.0	0.25	Yes
4.	Calib Std 3	0.192	1.2	1.203	0.0	0.43	Yes
5.	Calib Std 4	0.240	1.6	1.504	0.0	0.78	Yes
6.	A	13.66	13.99	13.99	0.552	4.04	Yes, sample conc. is greater than of highest standard
7.	B	13.94	13.90	13.90	0.036	0.26	Yes, sample conc. is greater than of highest standard
8.	C	14.07	14.08	14.08	0.015	0.11	Yes, sample conc. is greater than of highest standard
9.	D	14.13	14.09	14.09	0.039	0.27	Yes, sample conc. is greater than of highest standard
10.	E	13.93	13.95	13.95	0.022	0.16	Yes, sample conc. is greater than of highest standard

Note:

A : Methanol modified $CuCl_2$

B : Ethanol modified $CuCl_2$

C: Methanol modified $CuCl_2$ (by Faiz)

D: Water modified $CuCl_2$

E: Water modified $CuSO_4$

The result from AAS, were used to calculate the amount of metal concentration in the unit mg/L. In the sample, our case is the copper concentration. From the result also, the TMI modification indicates the successful modification. This had proven based on the value between the amount of entered concentration and the amount of calculating concentration which shown a very high concentration. So, the metal ion, copper had attached itself to the surface of the nanoclay as well.

The value is 13.99mg/L in methanol modified $CuCl_2$, 13.90mg/L in ethanol modified $CuCl_2$. While in methanol modified $CuCl_2$ prepared by Faiz is 14.08mg/L. For water modified $CuCl_2$ is 14.09mg/L. And lastly, for water modified $CuSO_4$, the value is 13.95mg/L. All this value, is achieved the minimum value of copper. Besides that, from the signal stored in the **Table 4.1,** the result also shown the positive response where the metal is inside but the value of sample concentration is much more greater than the value of higher standard, so it's cannot shown in the graph of "Concentration VS Absorbance" of copper. The higher standard for copper for this AAS equipment is 1.6ppm.

4.2.3 Mechanism of Modification Process

A popular and relatively easy method of modification, making it compatible with an organic matrix is ion exchange method. The cations are not strongly restricted to the clay surface so small organic cations can replace the cations present on clay (Giannelis, 1996). If the cations were quarternary alkylammonium ions with long chains, clay would be much more compatible with an organic matrix. By exchanging sodium ions with various organic cations, MMT can be compatible with several different matrix polymer. They

can be more easily intercalated and exfoliated because this process helps to separate the clay platelets. Nanocomposite can then be formed by incorporating the intercalated or exfoliated clay in a matrix. The first commercial clay nanocomposite was prepared via ion exchanging process (Ray and Okamoto, 2003).

In ion exchange, certain ion are removed by the ion exhange solid. Since electro neutrality must be maintained, the solid releases replacement ions into the solution. The first ion exchange material were naturally occurring porous sands called zeolite, which are cation exchangers. Positively charged ion Cu^{2+} diffuse into the pores of the solid with the Na^+ ion in the minerals.
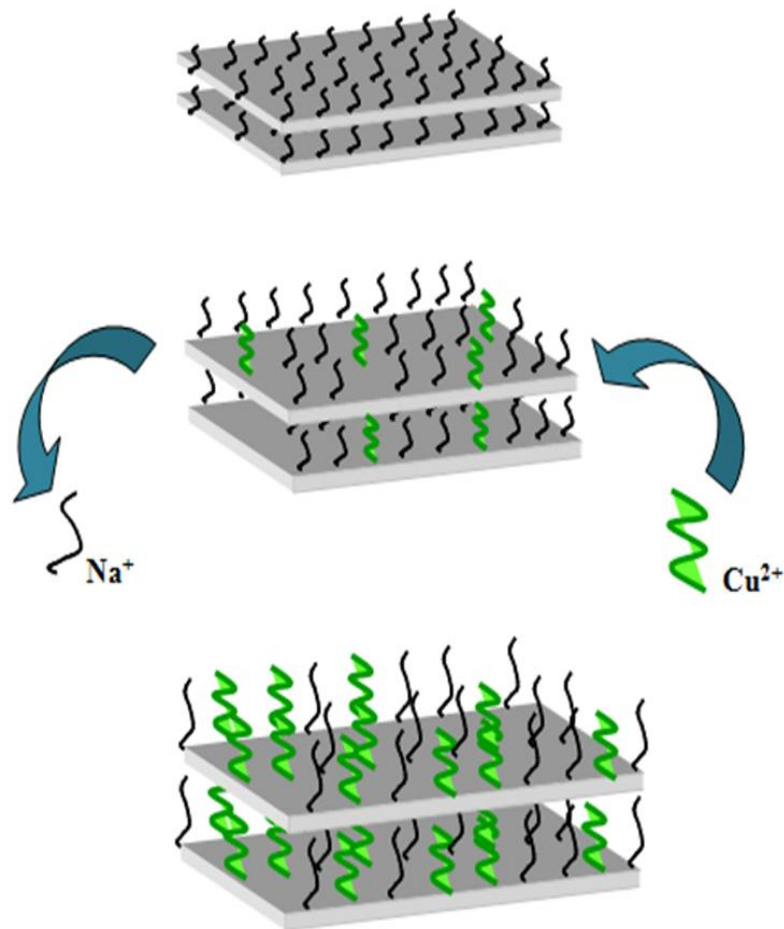
Figure 4.1: The mechanism of TMI salt modification

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4.3   Characterization

4.3.1   X-ray Diffraction Analysis (XRD)

The analysis is performed using XRD Miniflex by Rigaku to characterize the structure of the samples. The diffraction pattern was recorded with a step size of 0.02° from $2\theta = 2.0$ to 10.0. The interlayer distances (d-spacing) of the MMT in nanocomposite were derived from the peak positions (d001 reflections) in the XRD scans according to Bragg Laws.

$$d = \frac{n\lambda}{sin\theta} \qquad\qquad \text{(Equation 4.1)}$$

d = spacing between layers of the clay

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

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

n = order of diffraction, which is 1

a)   Na$^+$ MMT
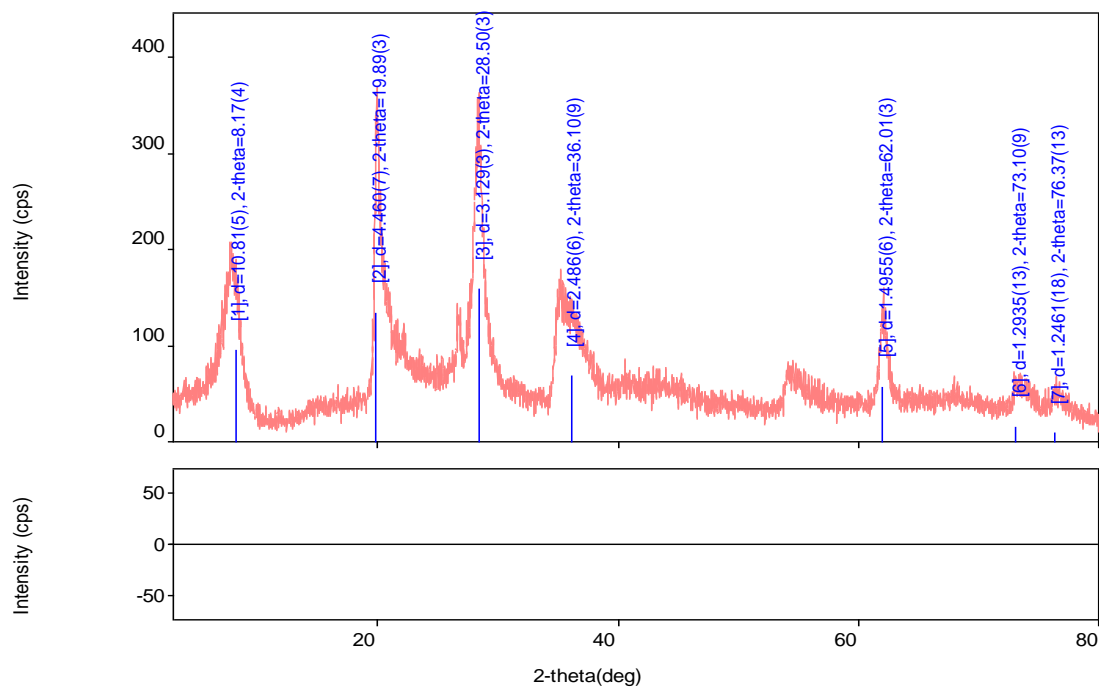
Figure 4.2: The graph of Na$^+$ MMT

b) Na$^+$ MMT modified by CuSO$_4$ (solvent: water)
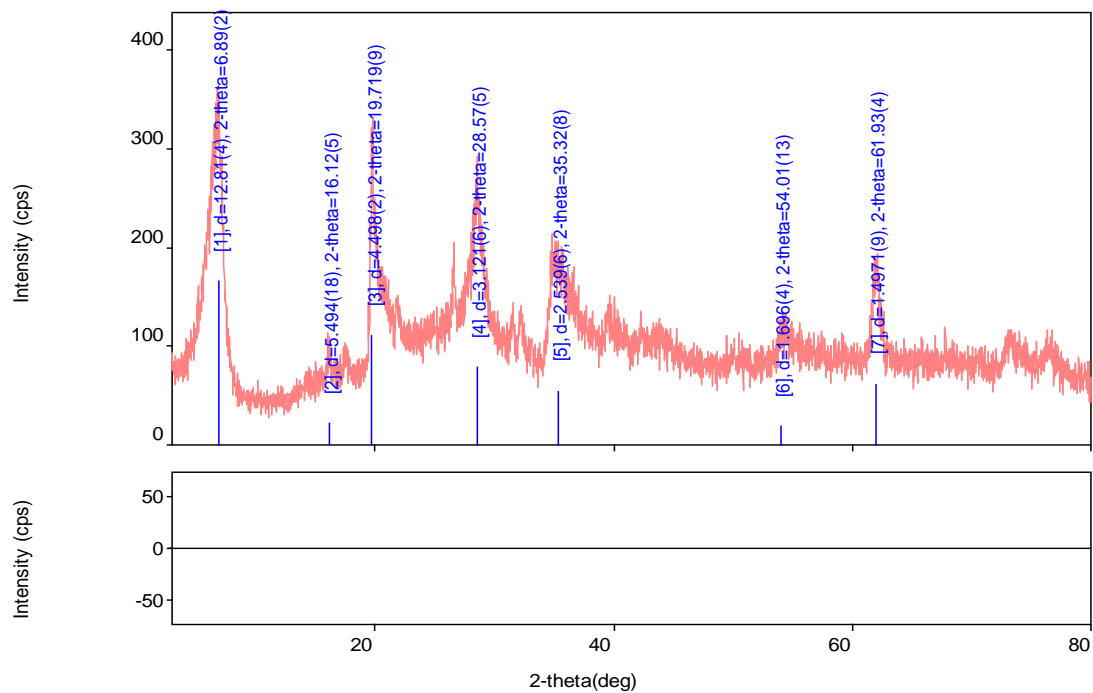
Figure 4.3: The graph of Na$^+$ modified by CuSO$_4$ (solvent water)

c) Na$^+$ MMT modified by CuCl$_2$ (solvent: ethanol)
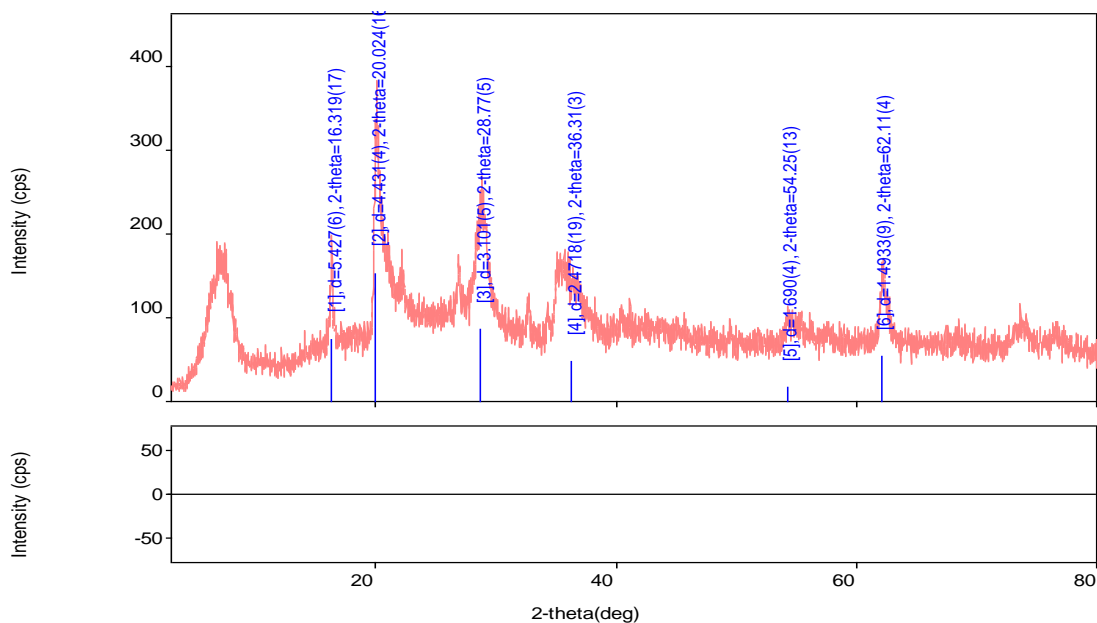
Figure 4.4: The graph of Na$^+$ MMT modified by CuCl$_2$
(solvent: ethanol)

d) Na$^+$ MMT modified by CuCl$_2$ (solvent: water)
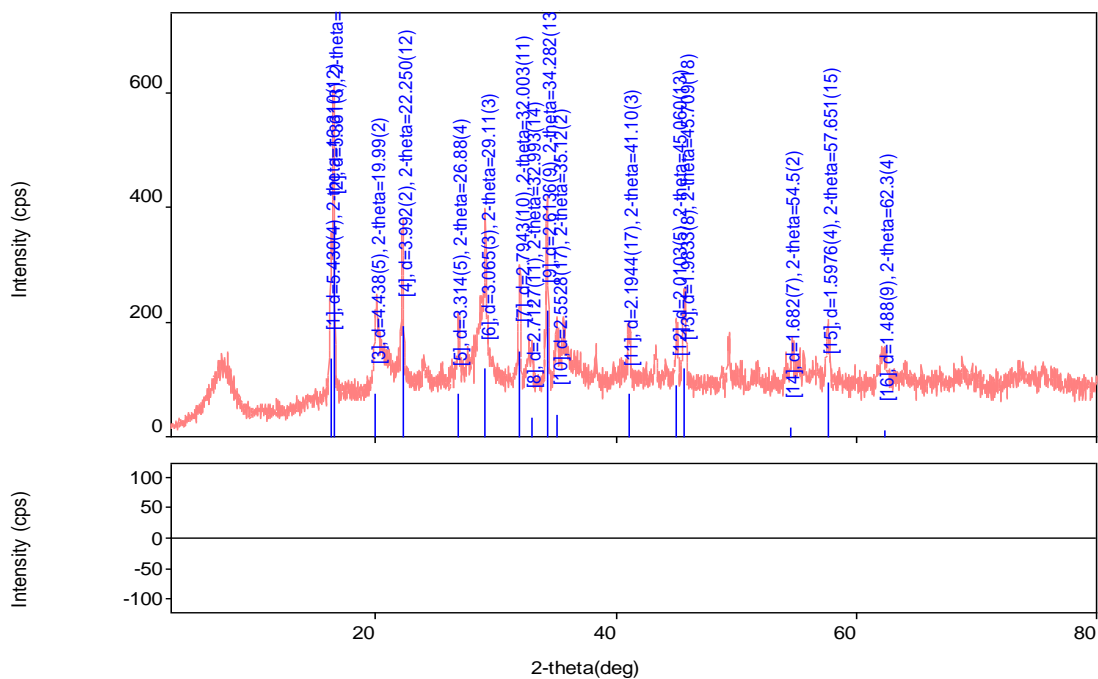
Figure 4.5: The graph of Na$^+$ MMT modified by CuCl$_2$
(solvent: water)

e) Na+ MMT modified by CuCl2 (solvent: methanol)
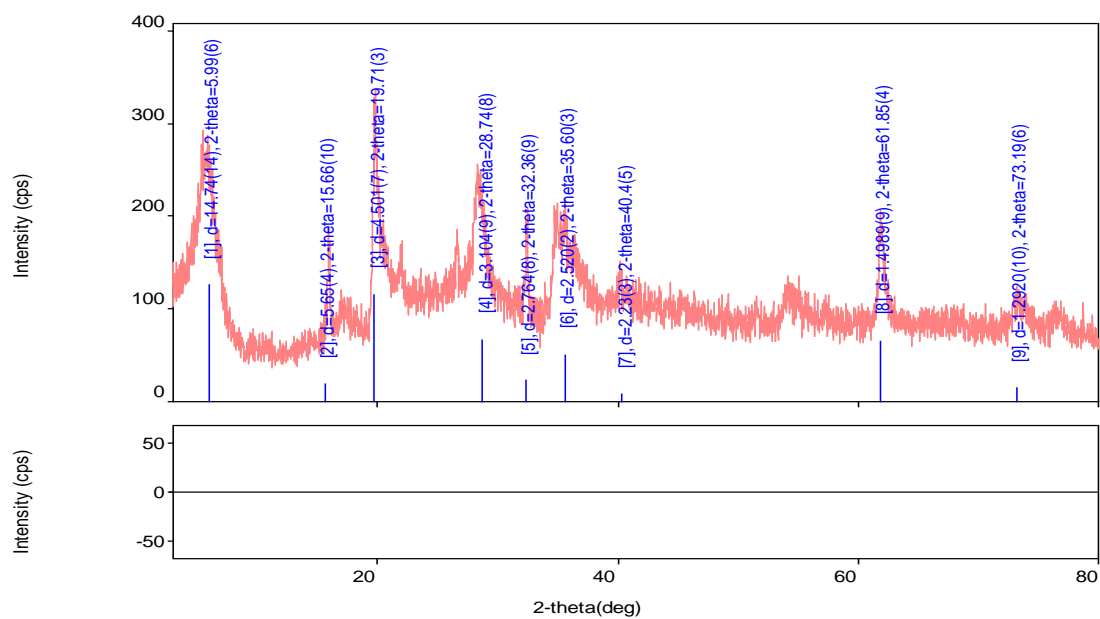
Figure 4.6: The graph Na+ MMT modified by CuCl$_2$
(solvent: methanol)
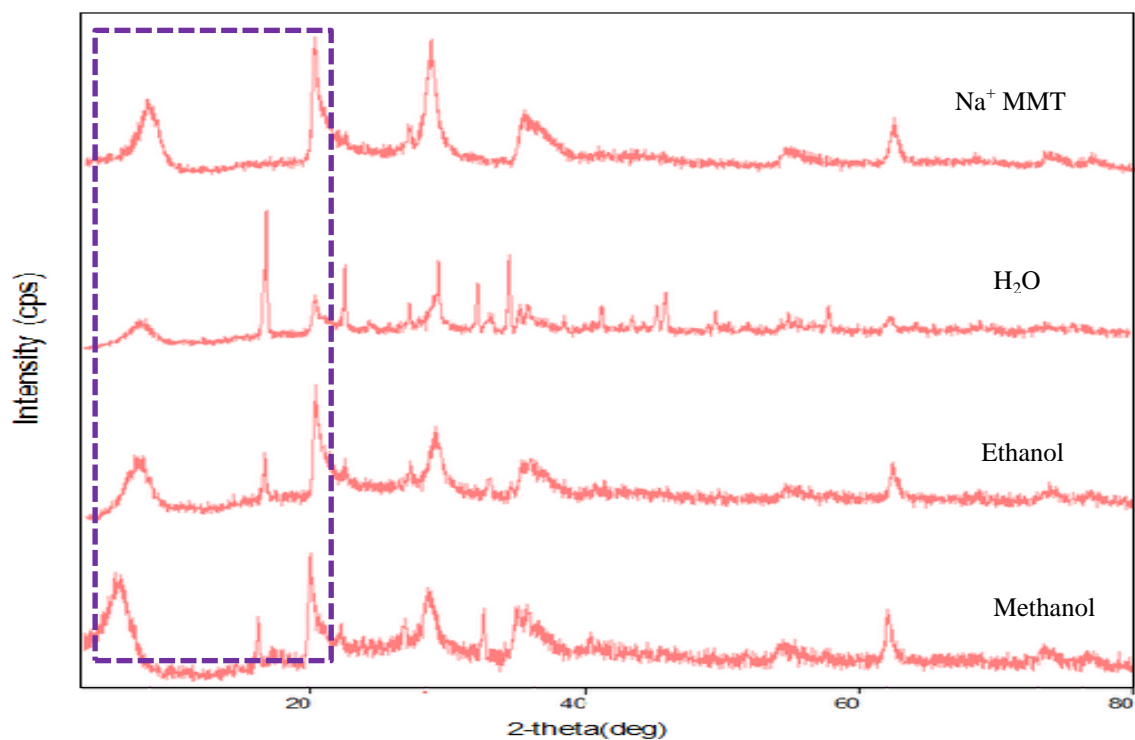
Figure 4.7: The combination graph of Na$^+$ MMT by different solvent

Due to the easiness and avaibility XRD is commonly used tool to probe nanocomposite structure (Ray *et. al.,* 2003). By monitoring the position, shape and intensity of the basal reflections from dispersed silicate layers, the nanocomposite structure either intercalated or exfoliated. XRD pattern is shown in **Figure 4.2** until **Figure 4.6** but in different solvent. The (001) diffraction in the **Figure 4.2**, for original Na^+ MMT, the d-spacing value only 10.81 at $2\theta= 8.17$ (d-spacing and diffraction angle, θ. is related through Bragg's relation). In the **Figure 4.3**, for Na^+ MMT modified $CuSO_4$, the d-spacing is 12.81 at $2\theta= 6.87$. While, in the **Figure 4.4**, for Na+ MMT modified $CuCl_2$ by ethanol, the d-spacing is 5.427 at $2\theta=16.319$. For Na+ MMT modified $CuCl_2$ of water in **Figure 4.5**, the d-spacing is 5.439 at $2\theta=18.31$. And lastly, at **Figure 4.6,** Na+ MMT modified $CuCl_2$ by methanol, the d-spacing is 14.74 at $2\theta=5.99$.

Table 4.2: The 2θ and d-spacing

| Composition	2θ	d-spacing (nm)
Na^+ MMT	8.17	10.81
Na^+ modified by $CuSO_4$ (solvent water)	6.87	12.81
Na^+ MMT modified by $CuCl_2$ (solvent: ethanol)	16.319	5.427
Na^+ MMT modified by $CuCl_2$ (solvent: water)	18.31	5.439 .
Na+ MMT modified by $CuCl_2$ (solvent:methanol)	5.99	14.74
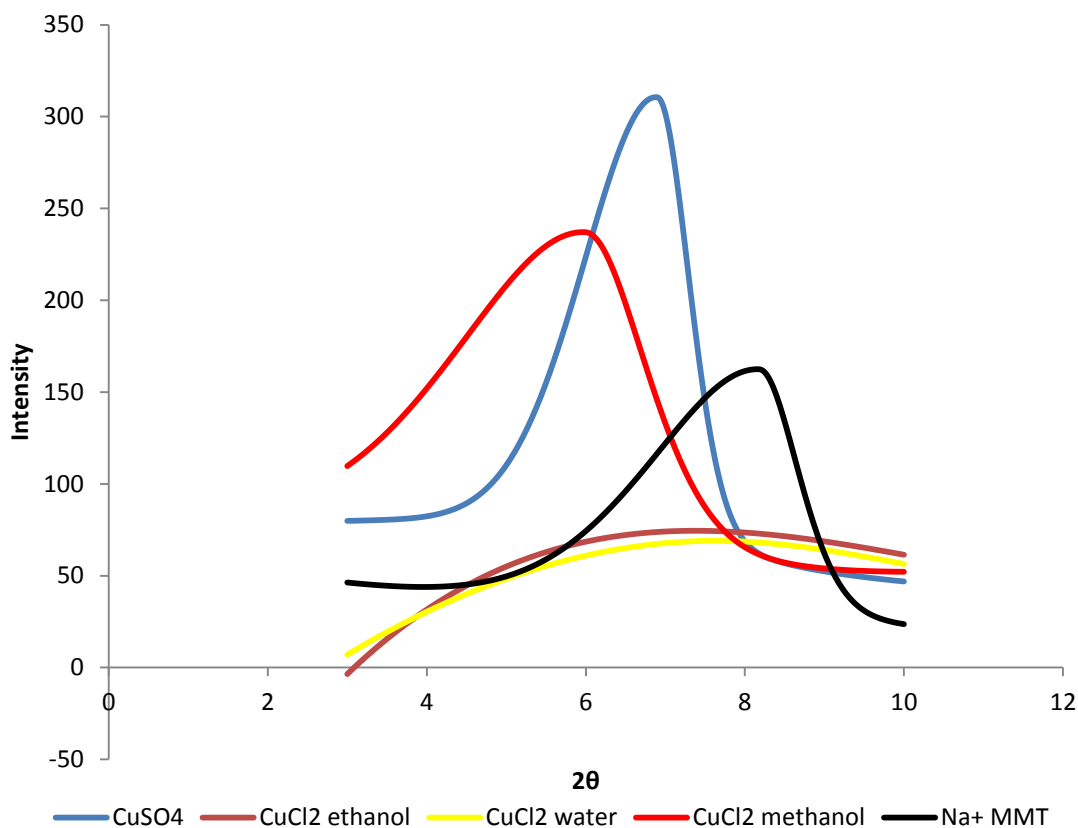
Figure 4.8: The graph of 2θ vs Intensity for all PLA modified

Based on the **Figure 4.8,** only the modification of Na^+ MMT by CuSO4 and the modification of Na^+ MMT by CuCl2 (methanol) just follow the pattern of the graph of original Na^+ MMT. At here, the modification occurs and success by increasing value of d-spacing in large amount. It is interesting to note that the XRD pattern of PLA nanocomposite with ethanol and water do not show (001) suitable peak at 2θ. This indicates the presence of interlayer distances is no regular periodicity. The absence of peak also suggests that the parallel form of stacking of the MMT was totally disrupted. This also shows the scattering and dispersion of the MMT nanolayer within the PLA matrix with the formation of exfoliated nanocomposite.

The increment in the interlayer spacing in methanol and CuSO$_4$ is evident that PLA polymer chain were intercalated in between the gallery of MMT. The increase in the interlayer spacing of MMT may be due to the organic modification of MMT which provides the possibility for PLA chains to diffuse between the layers during processing. The diffusion of PLA chains into MMT layer directly increase the intergallery distance and reduces the electrostatic attraction between adjacent platelets providing the possibility of PLA chains diffuse between the MMT layer during processing. A better dispersion of nanoparticle was achieved only when the filler concentration was <5wt% and larger agglomerates were observed with higher MMT content. (Jiang *et*. *al.,* 2007). The dispersion of MMT nanolayers with the PLA matrix leading to the formation of exfoliated nanostructure similar to previous reported studies (Pluta *et. al.,* 2006).

4.3.2 Scanning Electron Microscopy (SEM)

The morphological features of the particles were studied with Scanning Electron Microscopy (SEM). SEM test was carried out to check the surface of the modified nanoclay.
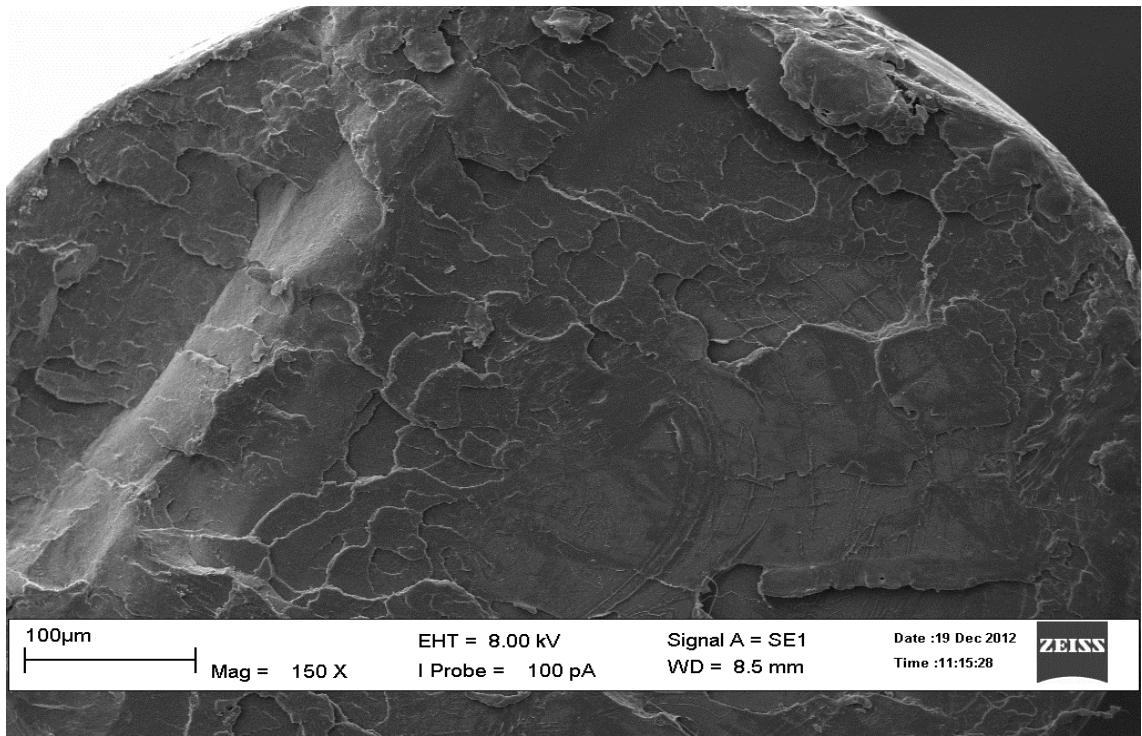
Figure 4.9: SEM picture at magnification (150x) of the 99.5% PLA & 0.5% Na$^+$ MMT modified
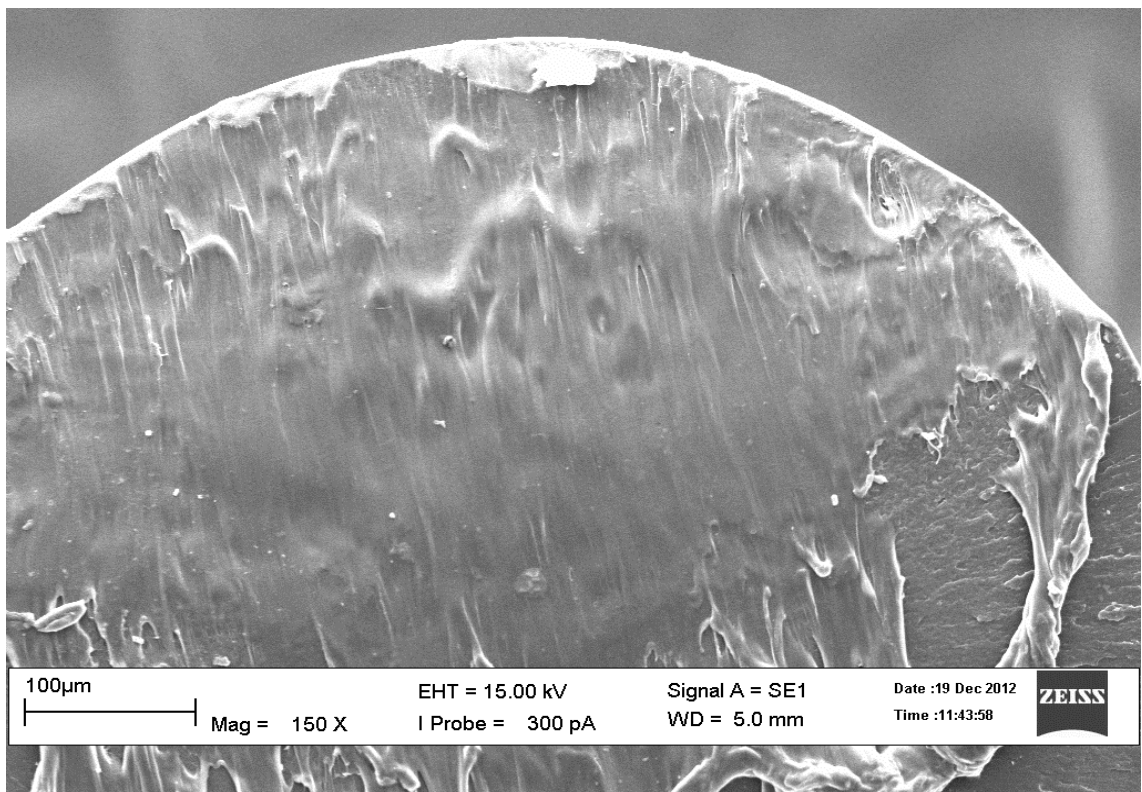
Figure 4.10: SEM picture at magnification (150x) of the 99.5% PLA & 0.5% Na$^+$ MMT unmodified

The types of nanocomposite are normally phase separated nanocomposite, intercalated nanocomposite and exfoliated nanocomposite. However, the nanocomposite is depending on the preparation method and the nature of the component. With the aim of assessing of extent of dispersion, **Figure 4.9** is shown exfoliated nanocomposite, while in **Figure 4.10** looks like intercalated nanocomposite. The exfoliated nanocomposite is the best particular interest it maximizes the PLA and Na+ MMT modified making the entire surface of layer and disperse very well.

From **Figure 4.10,** illustrates the dark fiber like objects are the stacks of MMT crystal platelets. Some stacks consisted of more platelets and appreared darker and thicker. The formation of agglomerates of MMT shows that the MMT layers are not exfoliated. The structure surface of nanocomposite which exhibited stress whitening and necking during tension, numerous fibrils was drawn out of the polymer, which cavities residing among them. The cavities were microvoids which initiated ligament shear yielding process during the tension. Thus, it can be said that MMT is still in the intercalated form.

According to Sinha Ray *et. al.,* (2002) showed similar agglomeration of MMT layers observed of PLA nanocomposites with increasing content of MMT up to 4 wt%. They reported that the terminal-hydroxy group in MMT contributed to the hydroxylated edge-edge interaction of silicate layers which cause the formation of much flocculate structure. They also stated that disk-disk interaction in MMT plays important role in determining stability of clay particles and hence the enhamcement of mechanical properties of PLA nanocomposite.

While in **Figure 4.9,** when the modification of MMT is added, a MMT percolation network was formed as evidenced by rheological. It can be noted that the layered MMT is well separated and exfoliated in PLA matrix. The finding with Pluta *et. al.,* (2006) who stated that the individu silicate nanoplatelets or small stacks of only a few silicate nanoplatelets in exfoliated system. The exfoliation is also possible due to hydrogen bonding interactions between the PLA hydroxyl end groups and the MMT platelet surfaces or the ammonium groups of the ammonium surfactant in the organically modified MMT as reported in previous study by Lee *et. al.* (2003). Cooperative chain motion was restrained by the network through the interaction between MMT and PLA chain. Besides, high concentration of MMT modification led to more agglomerates which could trigger premature material failure.

4.4   **Thermal Analysis**

4.4.1 Differential Scanning Calorimetry (DSC)

DSC is used to determine the glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c) and degree of crystallinity (X_c).
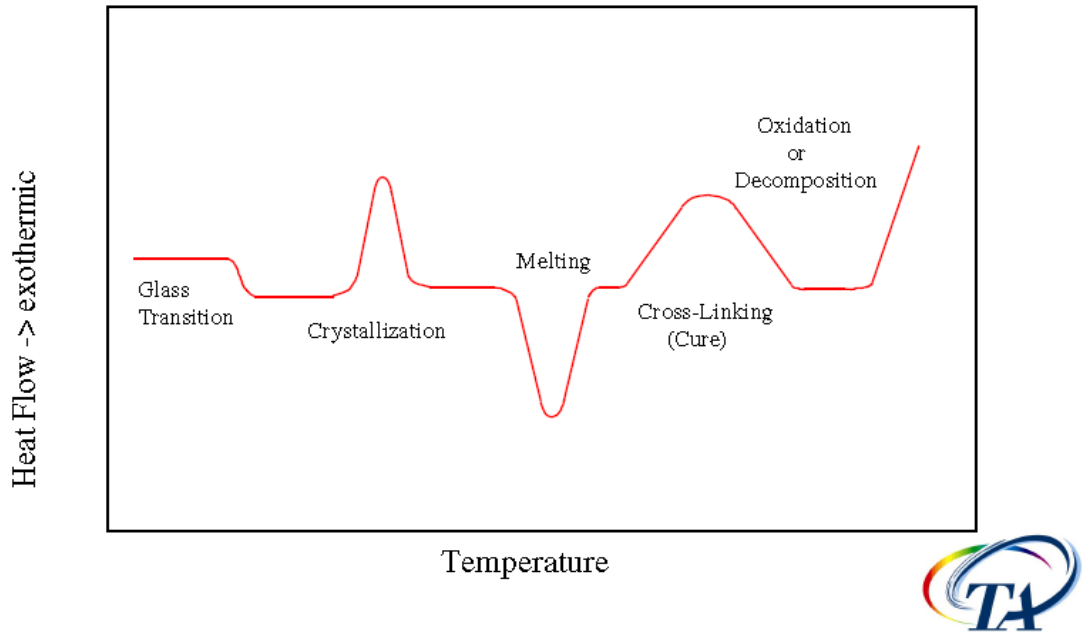
Figure 4.11: The graph pattern for DSC

DSC monitors heat effects associated with phase transitions and chemical reactions as a function of temperature. In a DSC the difference in heat flow to the sample and a reference at the same temperature, is recorded as a function of temperature. Glass transitions is a reversible change of the amorphous region of a polymer from, or to, a viscous or rubbery condition to, or from, a hard and relatively brittle one. The glass transition temperature is a temperature taken to represent the temperature range over which the glass transition takes place. Glass transition temperature is highly relevant for amorpheous material as it is a valuable indicator of stability.

Melting and boiling points is the endothermic transition upon heating from a crystalline solid to the liquid state. This process is also called fusion. The enthalpy of melting is the heat energy required for melting. The example is for breaking down the crystalline lattice. This is calculated by integrating the area of the DSC peak on a time basis. A sharp well defined melting

peak corresponds to at well defined crystal structure. Changes in melting temperature and energy gives information about for instance, content of amorpheous material. Thus, the melting endotherm can be used for determination of purity of the sample.

While for crystallization time and temperature, the melting is a one-step process while crystallization involves nucleation and crystal growth. Nucleation will be dependent on cooling rate, whereas the melting point is unaffected. Cooling at different rates might lead to discovery of new polymorphic forms.
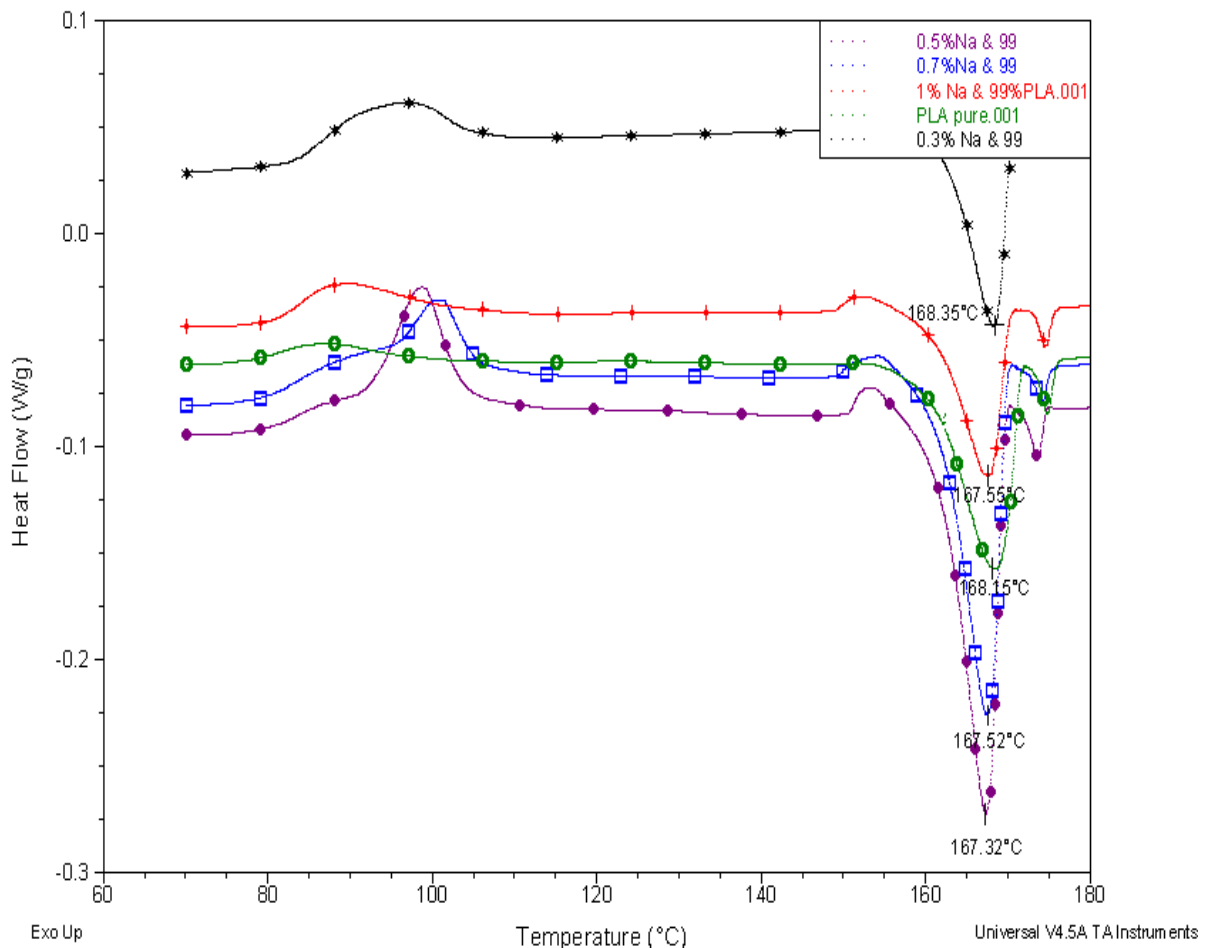
Figure 4.12: The graph of unmodified Na$^+$ MMT & PLA
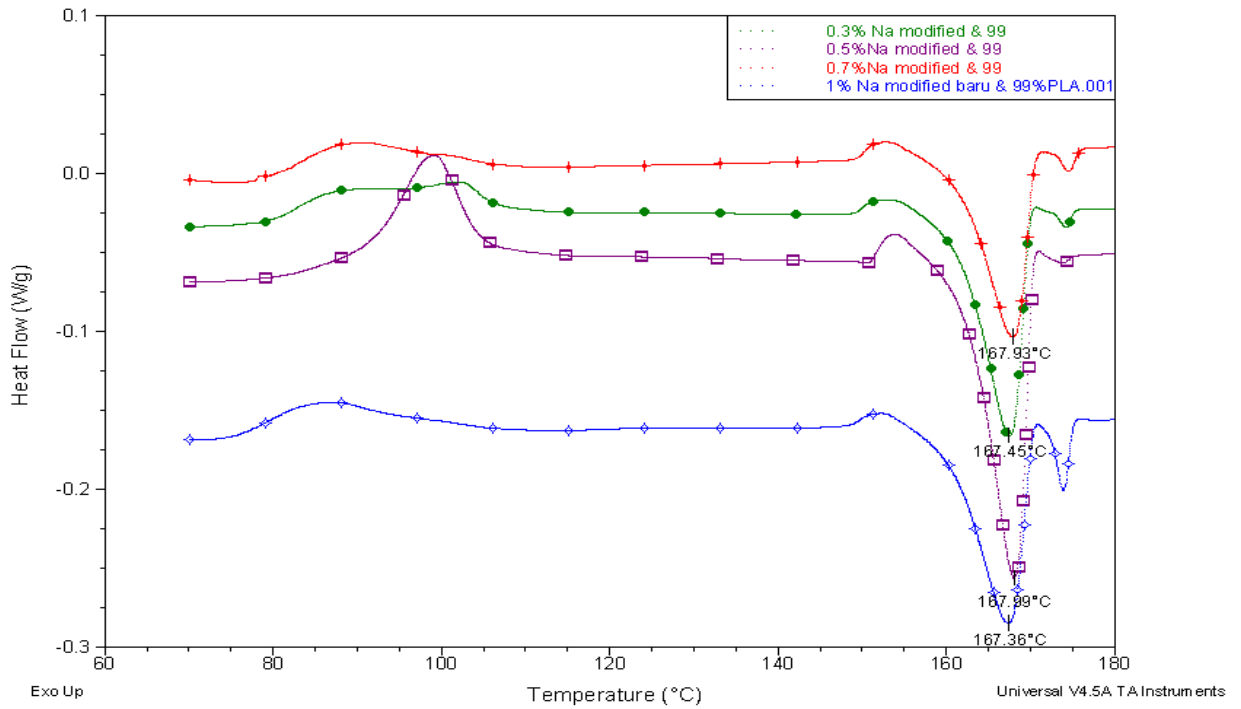
Figure 4.13: The graph of modified Na^+ MMT & PLA

Table 4.3: DSC resulting for PLA and PLA modified

Composition	Glass transition temperature , T_g (°C)	Melting temperature , T_m (°C),	Degree of crystallinity, $\mathcal{X}_c$ (J/g).
PLA pure	-	168.15	-
0.3% unmodified	85.02	168.35	0.6858
0.5% unmodified	93.61	167.32	1.803
0.7% unmodified	97.09	167.52	1.492
1.0% unmodified	82.13	167.55	0.4145
0.3% modified	97.67	167.93	1.140
0.5% modified	93.08	167.99	0.9639
0.7% modified	81.97	167.93	1.088
1% modified	78.10	167.36	1.184

Table 4.3 presents the glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c) and degree of crystallinity ($\mathcal{X}_c$) obtained from the differential scanning calorimetry (DSC) analysis for

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PLA unmodified nanocomposite and PLA modified nanocomposite. It is interesting to note that the T_c peak for PLA did not appear during cooling in PLA nanocomposite. It is similar observation had also been reported by (Shang and Kuen, 2008). It is believed that the main reason for this occurrence was due to a very slow crystallization rate of PLA during cooling.

It can be observed in **Table 4.3** that the majority of Tg value is decreased with increasing content of PLA modified. According to Pluta *et. al.,* (2006) where the Tg of PLA had dropped with increasing content of MMT. Lee *et. al.* (2003), also had observed a decrease in T_g with the addition of MMT in nanocomposite. The T_g depends primarily on chain flexibility, molecular weight, branching/crosslinking, intermolecular attraction and stearic effects. The intermolecular attractions of PLA segments seem to be interrupted by the charged MMT layers and subsequently the PLA backbone chains gained additionally segmental mobility. It can also be addressed that the MMT nanoparticles may provide stearic factors that seemingly increase the chain flexibility of PLA backbones. The decreased was attributed to plasticizing of PLA matrix by surfactant of MMT. The alkyl ammonium surfactant which was used to modify the interlayer distance of MMT by facilitating PLA's chain diffusion into the layer had resulted in plasticizing effect.

However, the DSC results revealed that the melting temperature, T_m remainined altered upon addition of MMT. This shows that the addition of MMT modified had little influence on the melting temperatures of nanocomposite. The melting enthalpy (ΔH_m) of pure PLA was 36.5J/g. The lower melting enthalpy is probably due to grafted branches that disrupt the regularity of the chain structure in PLA and increase the spacing between

chain. The references melting enthalpy of the 100% of crystalline polymer is 93.6J/g.

Based on the **Table 4.3,** the result of degree of crystallinity is not very well. The value of the result is not smooth like the observation from Nam *et. al.* (2003). He claimed that the crystallinity of PLA increased from 36 to 49.1% by the addition of 4 wt% MMT platelets. The degree of crystallinity depends on many factors such as molecular weight, thermal and processing history, temperature and time of annealing treatments. The crystallization of PLA based nanocomposite tends to shift to a higher temperature than PLA pure (not shown). Overall, the $\%\mathcal{X}_c$ of the PLA decreased with the addition of Na^+ MMT modified. $\%\mathcal{X}_c$ of the PLA used in this study is much lower than the reported in the literature.

Another strategy to increase the crystallinity of PLA is by incorporating nucleating agent in the polymer during extrusion. This lowers surface free energy barrier for nucleation and enables crystallization at higher temperature to take upon cooling. Maybe the talc can be added to PLA to effectively modify the crystallization rate of polymer.

4.4.2 Thermogravimetric Analysis (TGA)

TGA is used to examine the thermal degradation of the behavior of the organic components in the PLA and PLA/ CloisitNa+ blends.
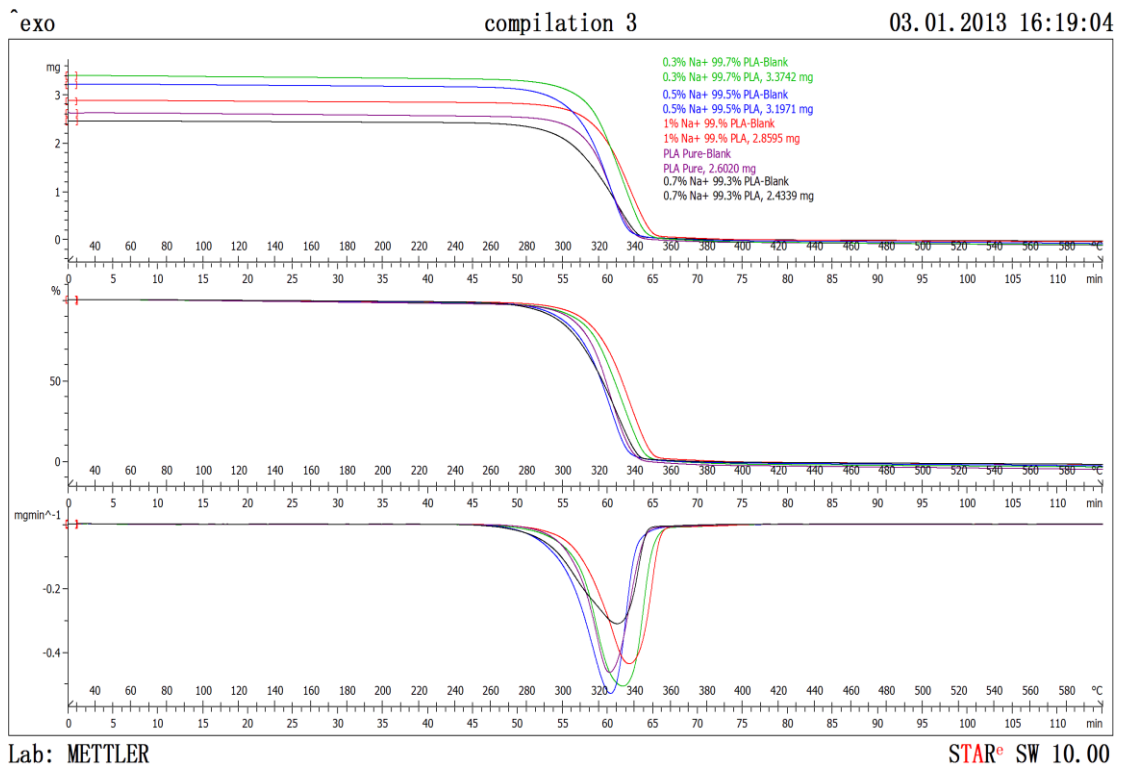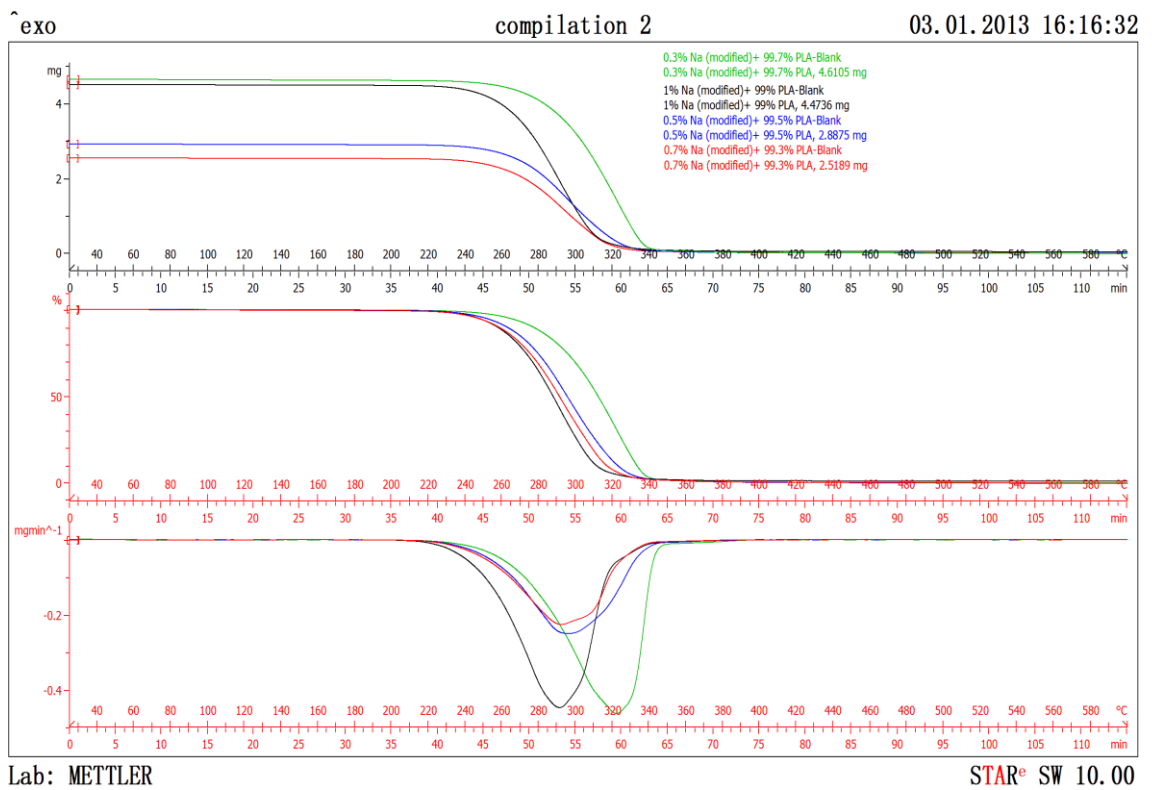
Figure 4.14: The graph all unmodified Na⁺ MMT

Figure 4.15: The graph all modified Na⁺ MMT

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Table 4.4 Data of Thermal testing (TGA)

Composition	Weight Sample (mg)	Step (%)	Onset Temperature (^{0}C)	Endset Temperature (^{0}C)	Residue (%)
PLA pure	2.6021	-98.3608	312.08	342.42	2.4387
0.3% unmodified	3.3742	-98.5197	314.17	349.70	1.0475
0.5% unmodified PLA	3.1971	-97.7104	307.32	340.80	0.5132
0.7% unmodified PLA	2.4339	-96.9185	301.14	348.38	0.2081
1.0% unmodified PLA	2.8595	-97.3006	316.75	353.56	0.2940
0.3% modified PLA	4.6105	-96.2966	286.11	342.73	0.0287
0.5% modified PLA	2.8875	-97.4508	268.17	328.19	0.1114
0.7% modified PLA	2.5189	-99.1092	263.70	324.08	0.3049
1% modified PLA	4.4736	-96.2413	264.24	315.38	0.9285

Figure 4.14 and **Figure 4.15** show the for PLA unmodified MMT and PLA modified MMT nanocomposite with different ratio content. The initial thermal are characterized by onset temperature (the temperature start to degrade) and the endset temperature (the temperature finished degrade). All the result in **Table 4.4.** During thermal degradation, the TGA curves displayed double-step degradation processes for all of the sample. The sample weight in percentage decreased continuously to a residual level after mass losses had commenced. Incorporation of MMT, has resulted in a significant improvement in the initial stability expecially in PLA modified nanocomposite.

According to Pavlidou (2008), the organoclay shields the polymer from the action of oxygen, dramatically increase the thermal stability under oxidative conditions. From Bandyopadhyay (1999), the first improved thermal

stability of biodegradable nanocomposites that combines PLA and organically modified fluorohectorite or montmorillonite. They showed that the PLA intercalated between the galleries of FH or MMT clay resistant the thermal degradation under conditions that would otherwise completely degrade pure PLA.

The thermal stability of PCL based nanocomposite has also been studied by TGA. Generally, the degradation of PCL fits into two step mechanism. First, random chain scission through pyrolysis of the ester group, with the release of CO_2. H_2O and hexanoic acid and in the second step ε-caprolactone (cyclic monomer) formation as a result of an unzipping depolymerization process. It has been reported that the thermal stability of PCL/o-MMT nanocomposites systematically increase with increasely clay up to a loading of 5 wt% from Pavlidou, 2008.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Introduction

In the first chapter, the background of the research has been outline followed by the chapter two which is the literature review. In the literature review, the polymer, melt intercalation method and the purpose of doing characterization and thermal testing have been discussed. The preparation of PLA nanocomposite, characterization and sample testing is stated in chapter three. In chapter four, it's more focus about result, discussion and analyze for each characterization using AAS, XRD, SEM, DSC and TGA. While in this chapter, is focused on overall conclusion of this research.

5.2 Conclusion

Based on this research devoted to the study of morphological and thermal properties of PLA modified MMT nanocomposites, the following conclusion an be drawn:

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The modification of PLA have improved the mophological. SEM analysis revealed that dispersed modified MMT particles size in PLA and in exfoliated structure. The d-spacing of interlayer also increase by using a methanol as the best solvent. The thermal anaylsis through DSC revealed that the addition of modified MMT had effect the T_m and T_g. TGA revealed the the addition of modified MMT improved the thermal stability of PLA as the degradation temperature of PLA. Hopefully, this research can contribute new technology in polymer nanotechnology field. It is because the biodegradable properties of PLA can give the biggest impact to the environment as well to the nation.

5.3   Recommendation

In order to produce PLA modified nanocomposite by fabrication process using an extruder, the extruder is the main machine need to use. But, the extruder is very limited and the condition of the extruder is not very well, so need a time to repair a machine. The design of extruder is not suitable and it's very hard to control the sample to feed in the hopper. The design is supposed to be in longitudinal and auto controller. And maybe can change with the new machine of the extruder.

Besides that, a long time as needed to do the injection molding before do a mechanical testing. To get the best temperature profile for PLA nanocomposite in injection molding machine, the step try and error need to implement. And it's maybe taking a long time. Maybe the person in charge of the machine can provide or save the date of the temperature profile in the machine for each type of the polymer as a reference.

Majority the machine and equipment in the lab are very limited. So, the apparatus need to share with another person. Because of that, the duration time and the sample can disturb or contaminated from surrounding. For next time, maybe the capacity user in the lab can divide into a few groups with suitable time of the student. And hopefully, all the machine in the lab is in good conditions. And very make sure that the person that handling the machine get the enough training from instructor to avoid the machine from damaged and a big trouble with another person.

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APPENDIX A: Preparation of PLA Nanocomposite for pre-treatment phase of nanoclay.

Figure A.1: Apparatus for preparation PLA Nanocomposite
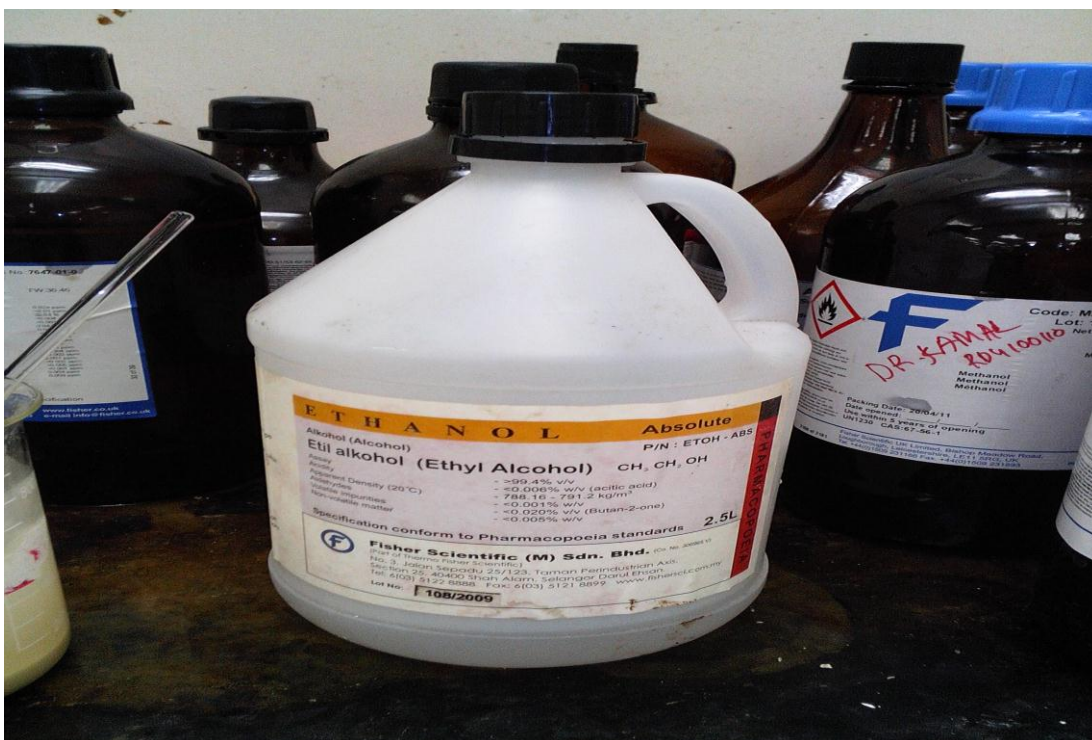
Figure A.2: The solvent (ethanol)

Figure A.3: The pristine clay

Figure A.4: The clay after pre-treatment

Figure B.1: The pristine clay, $CuCl_2$ and the solvent

Figure B.2: The TMI salt modification
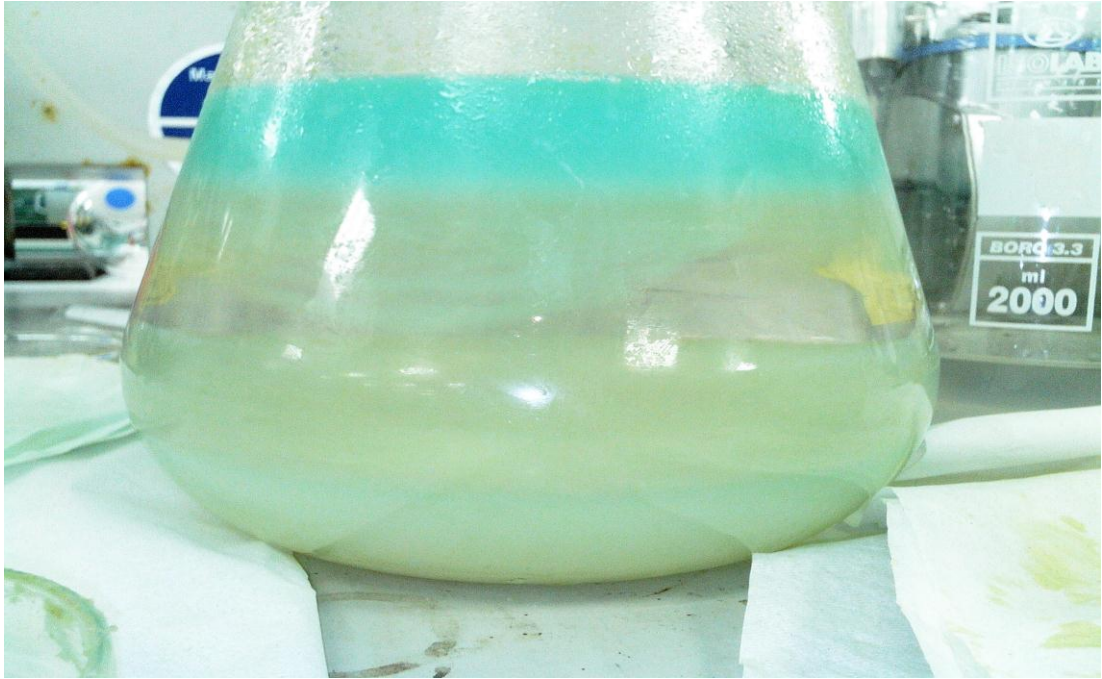
Figure B.3: The filtration of TMI salt modification
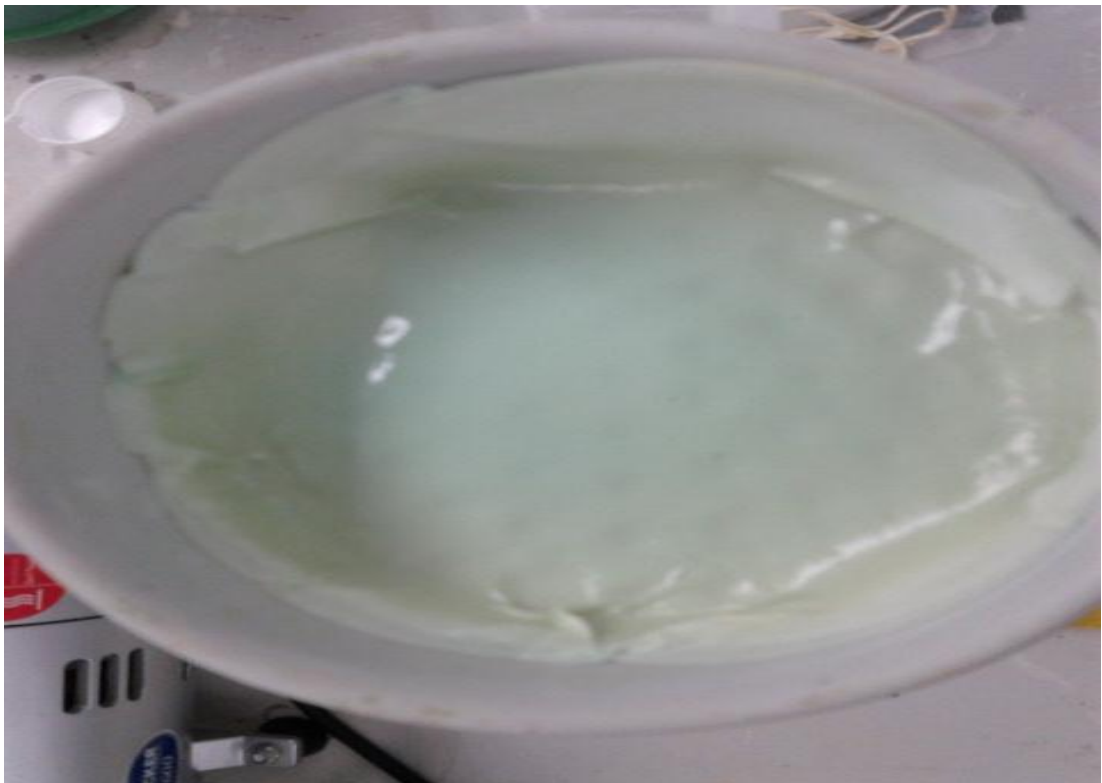
Figure B.4: The filtration of the sample
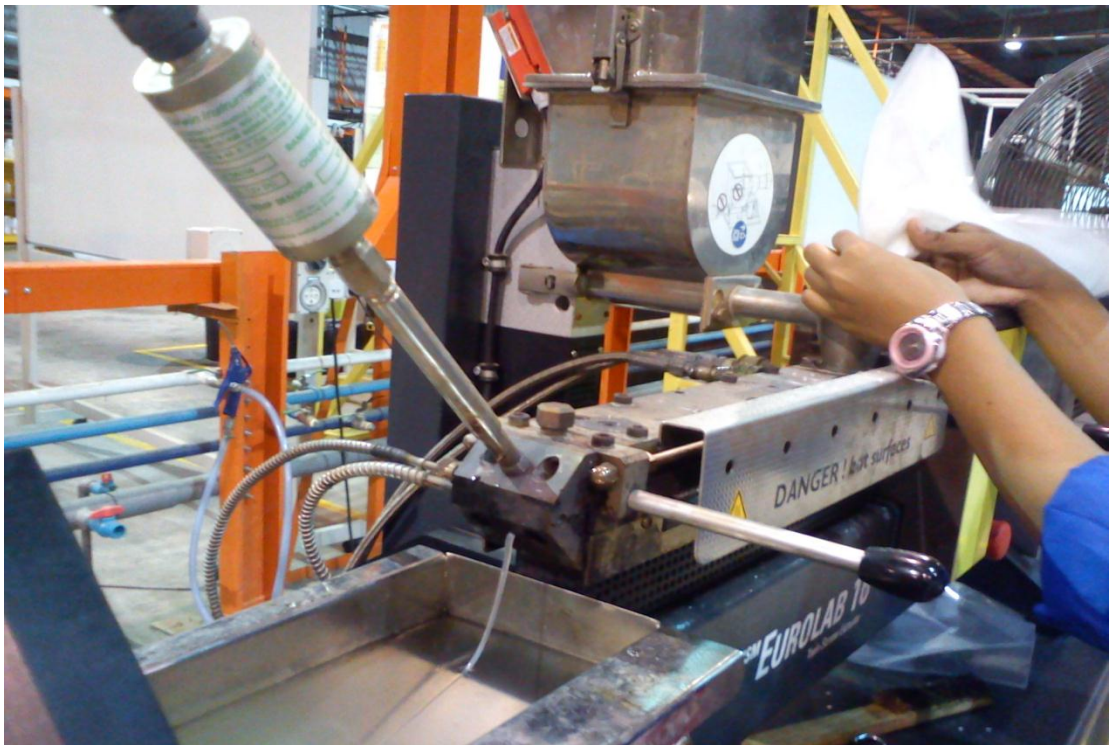
Figure C.1: The sample into the extruder
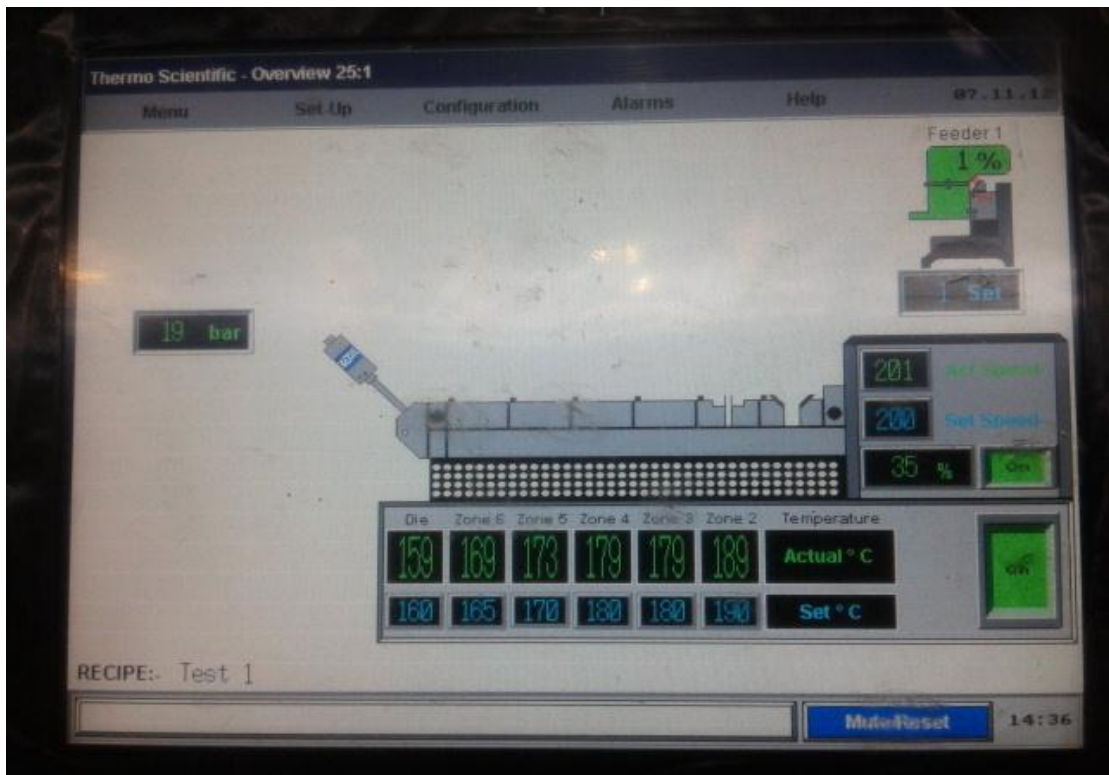
Figure C.2: The temperature profile of extruder
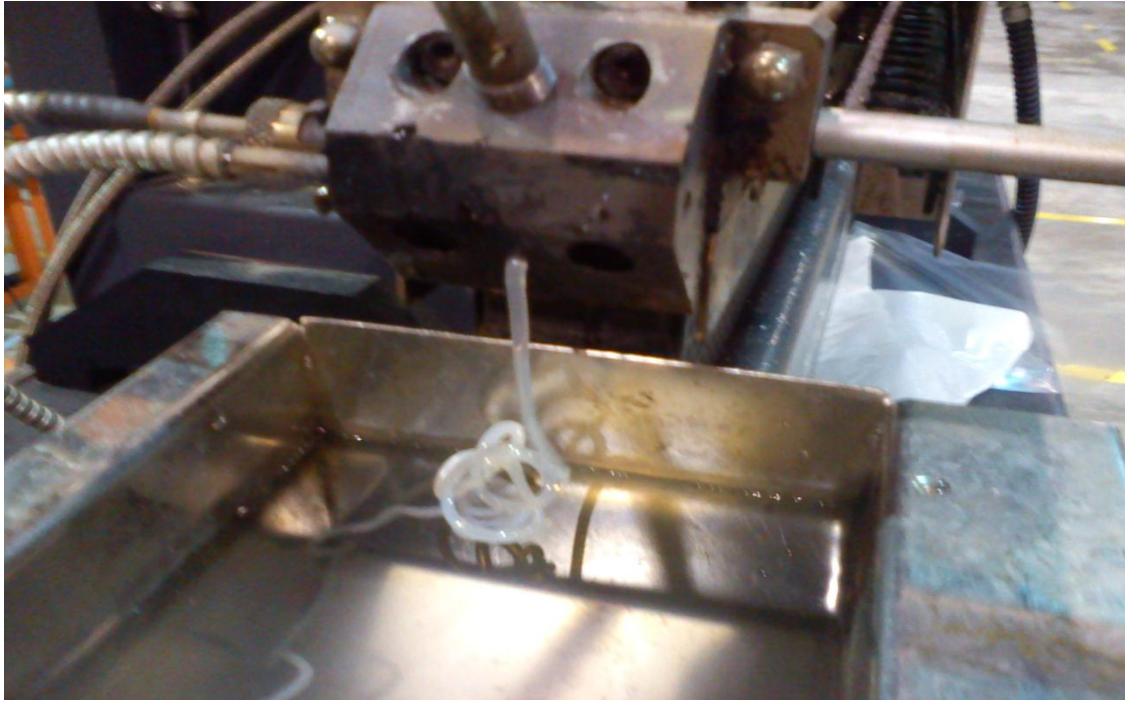
Figure C.3: The sample out from extruder

APPENDIX D: The result data for DSC Analysis
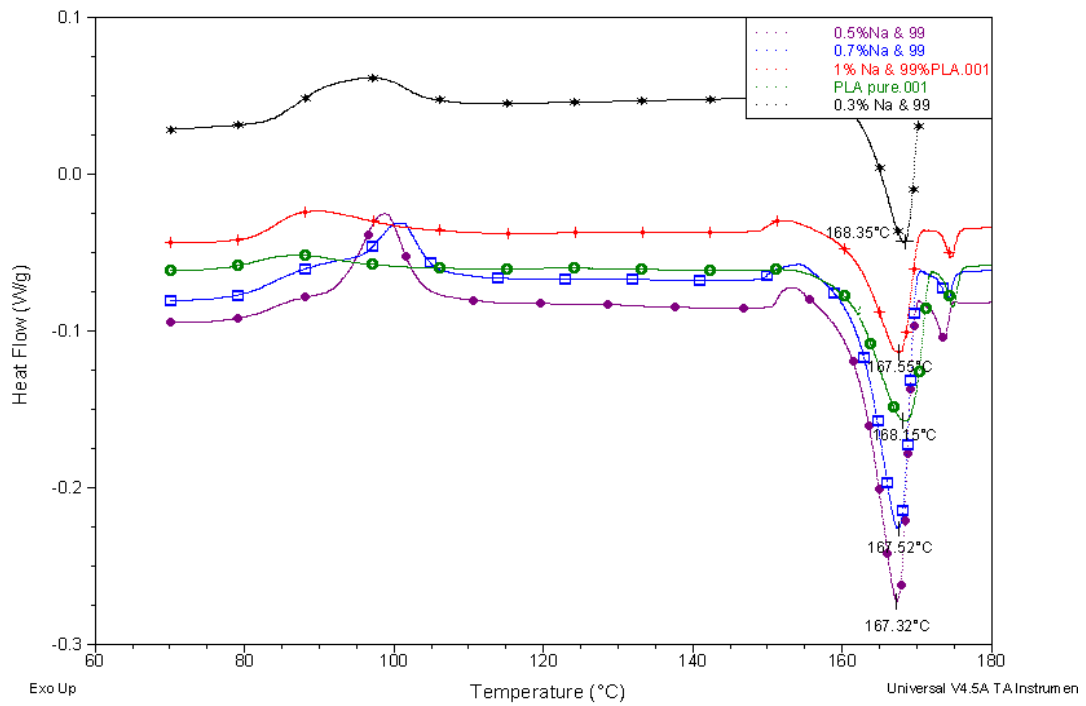
Figure D.1: The result data for all unmodified MMT
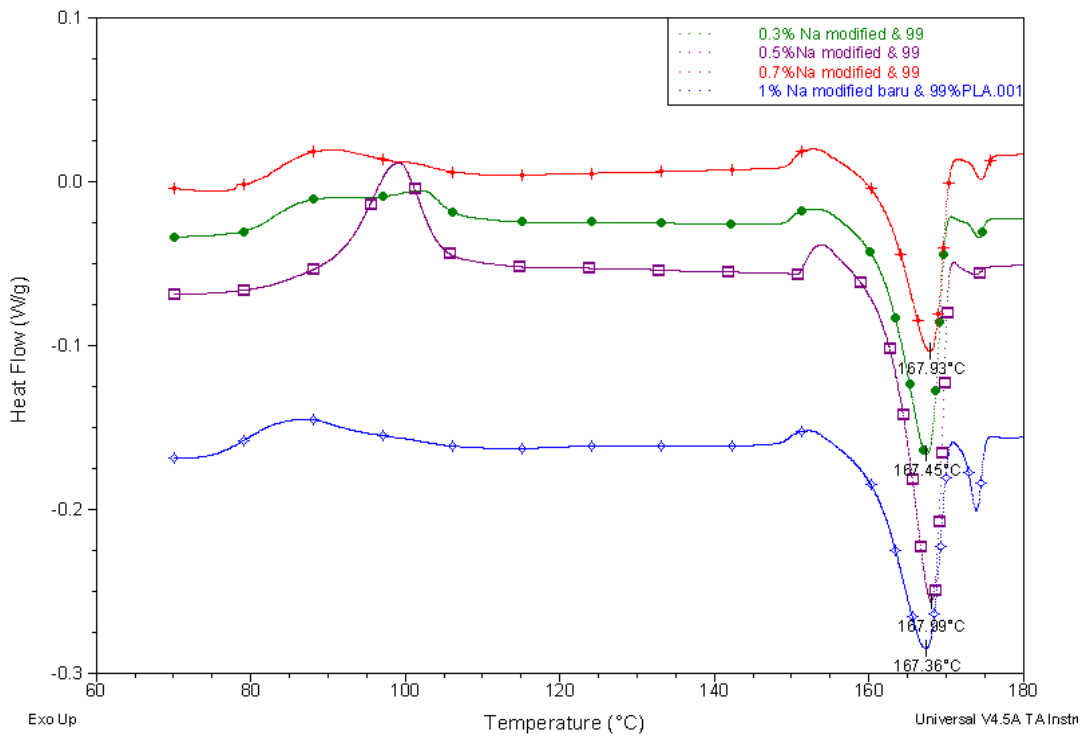
Figure D.2: The result data for all modified MMT
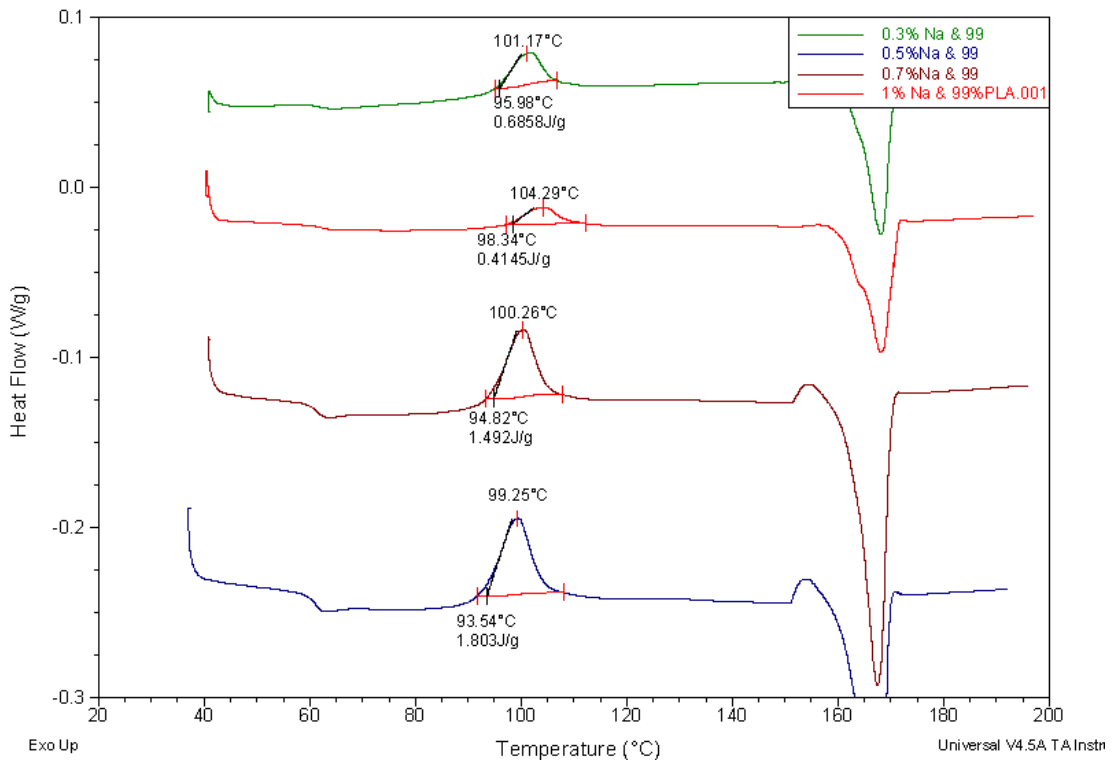
Figure D.3: The result of Tg for all unmodified MMT
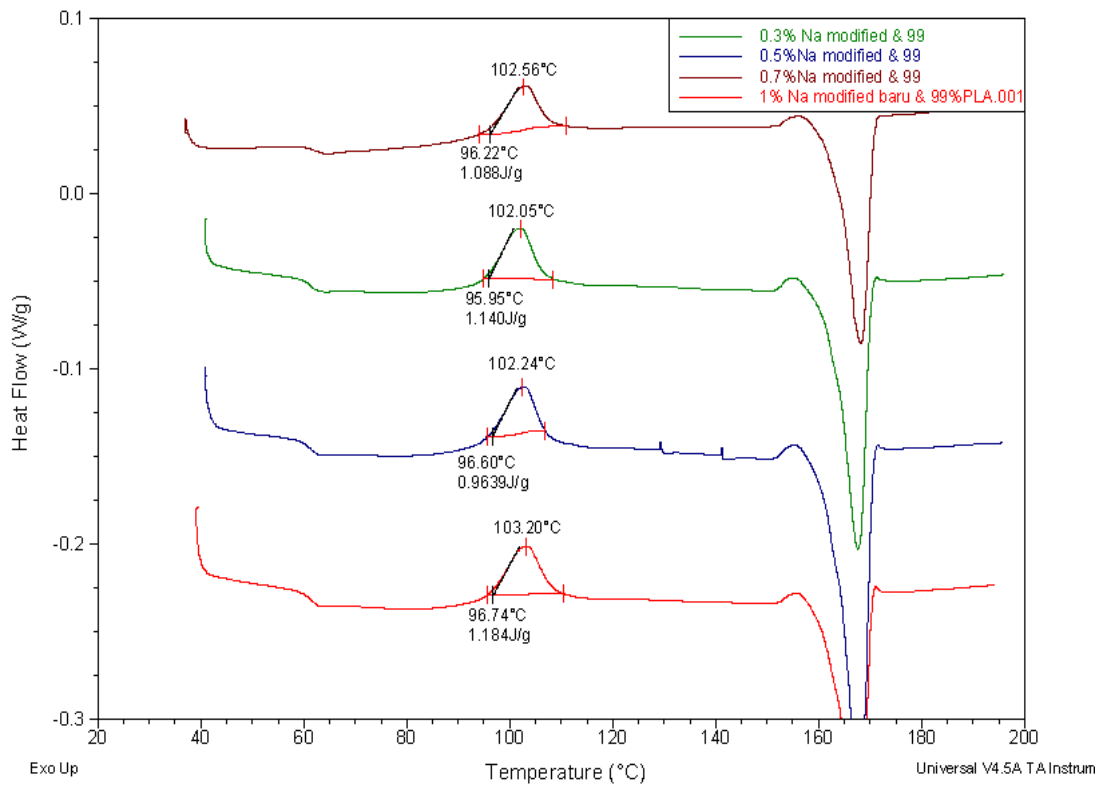
Figure D.4: The result of Tg for all modified MMT

93

APPENDIX E: The result data for TGA Analysis
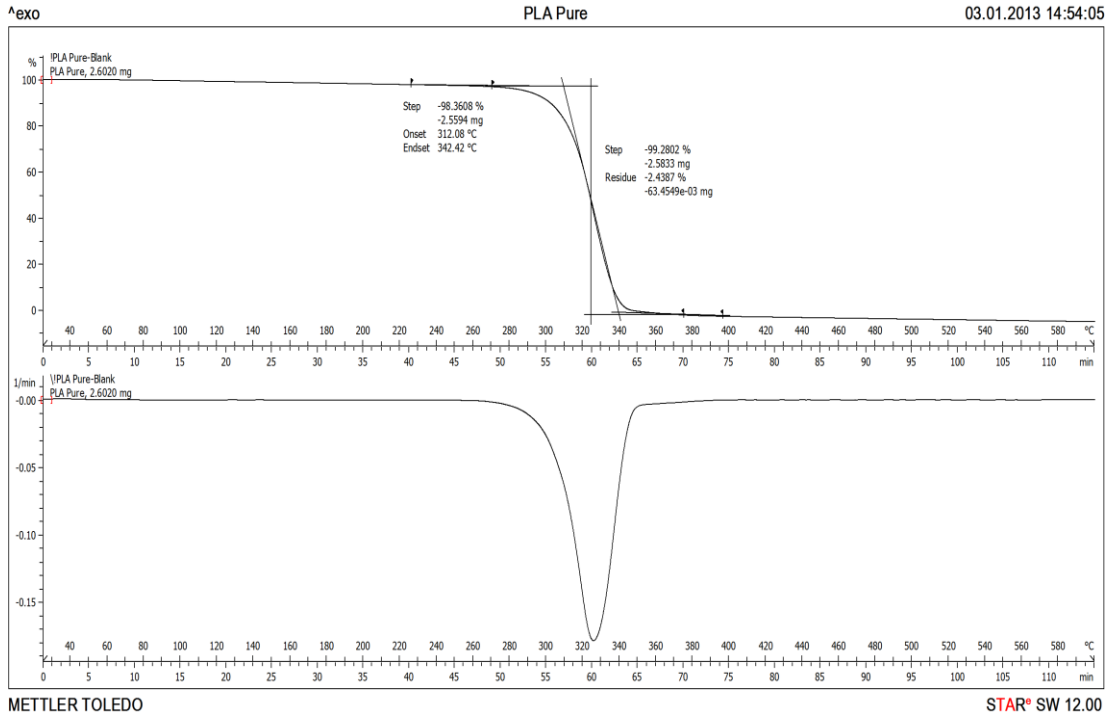
Figure E.1: The result for PLA pure
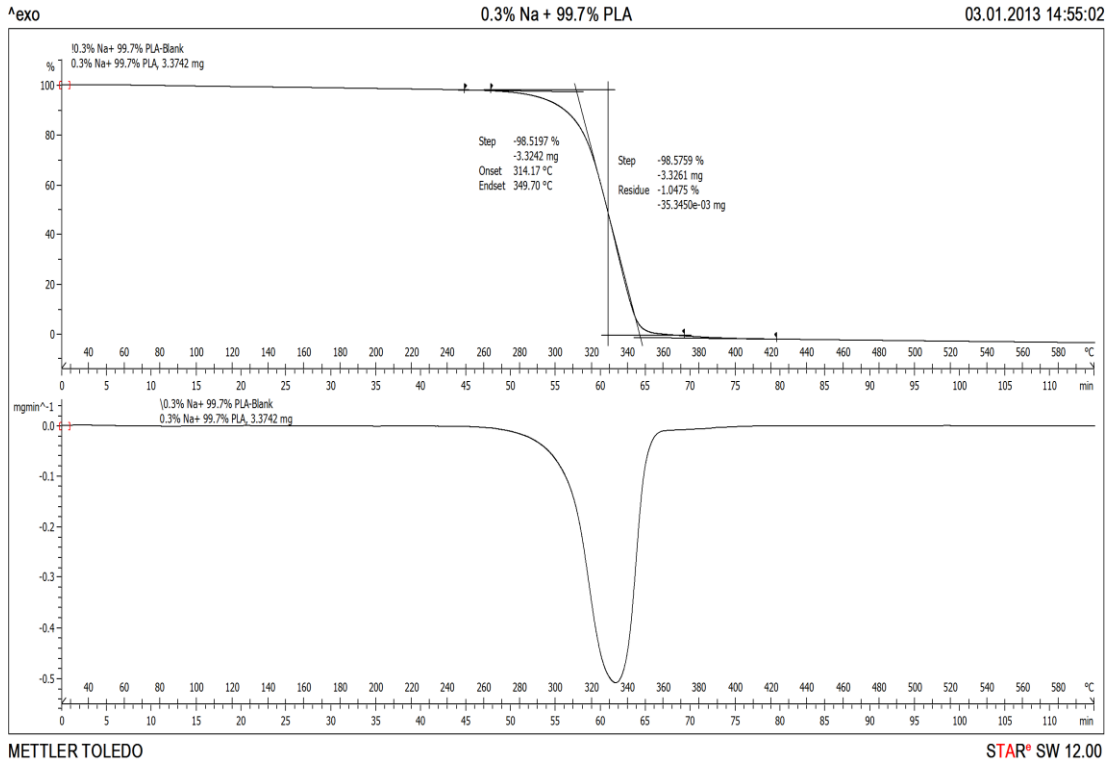
Figure E.2: The result for 0.3% Na$^+$ & 0.97% PLA
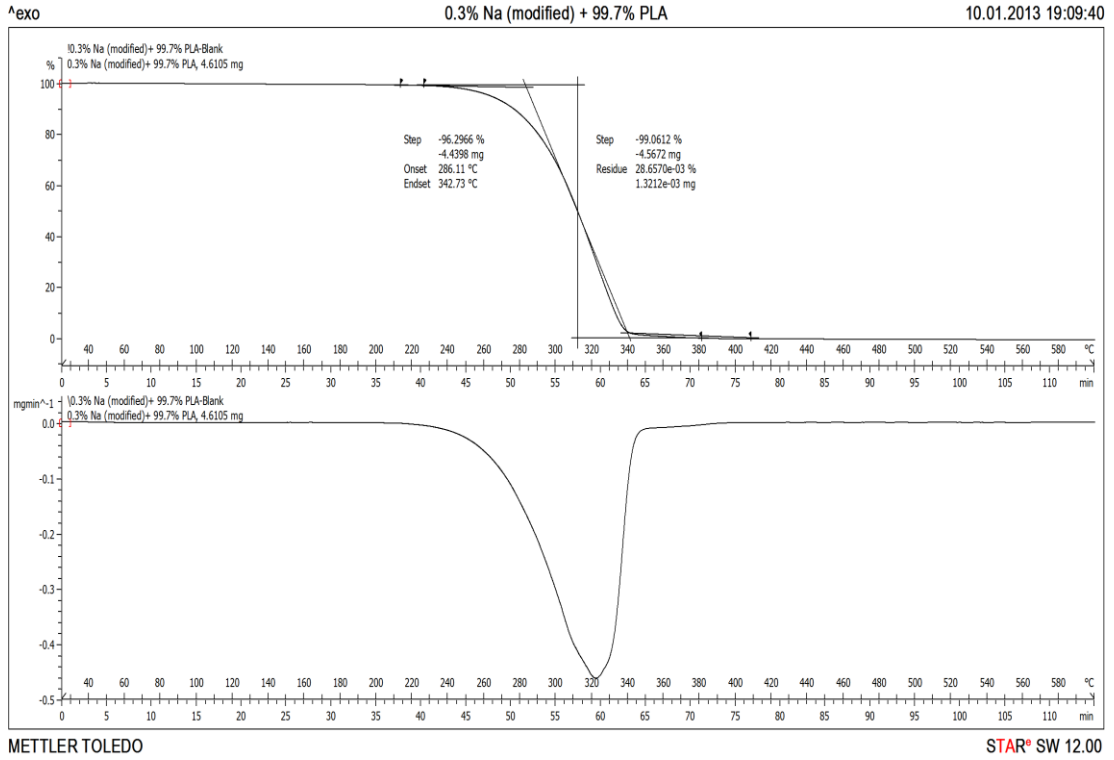
Figure E.3: The result for $0.3\%\text{Na}^+$ modified & 0.97% PLA
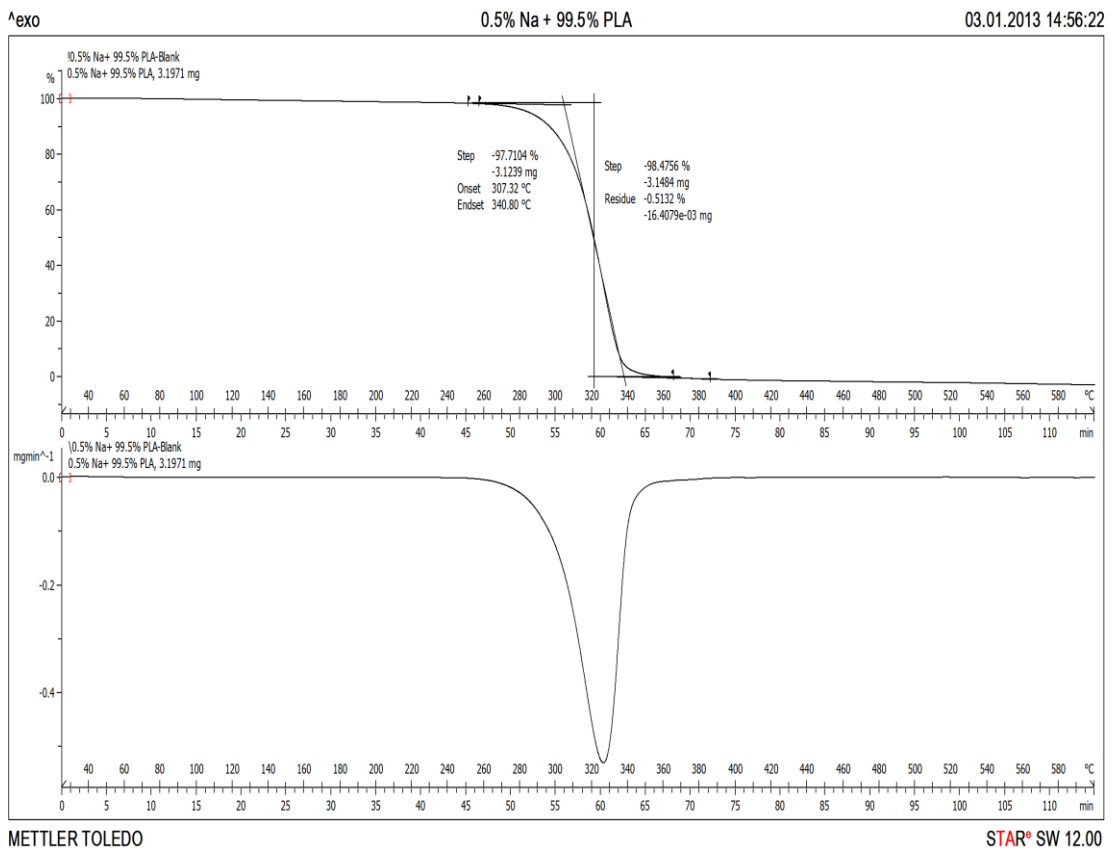
Figure E.4: The result for $0.5\%\text{Na}^+$ & 0.95% PLA
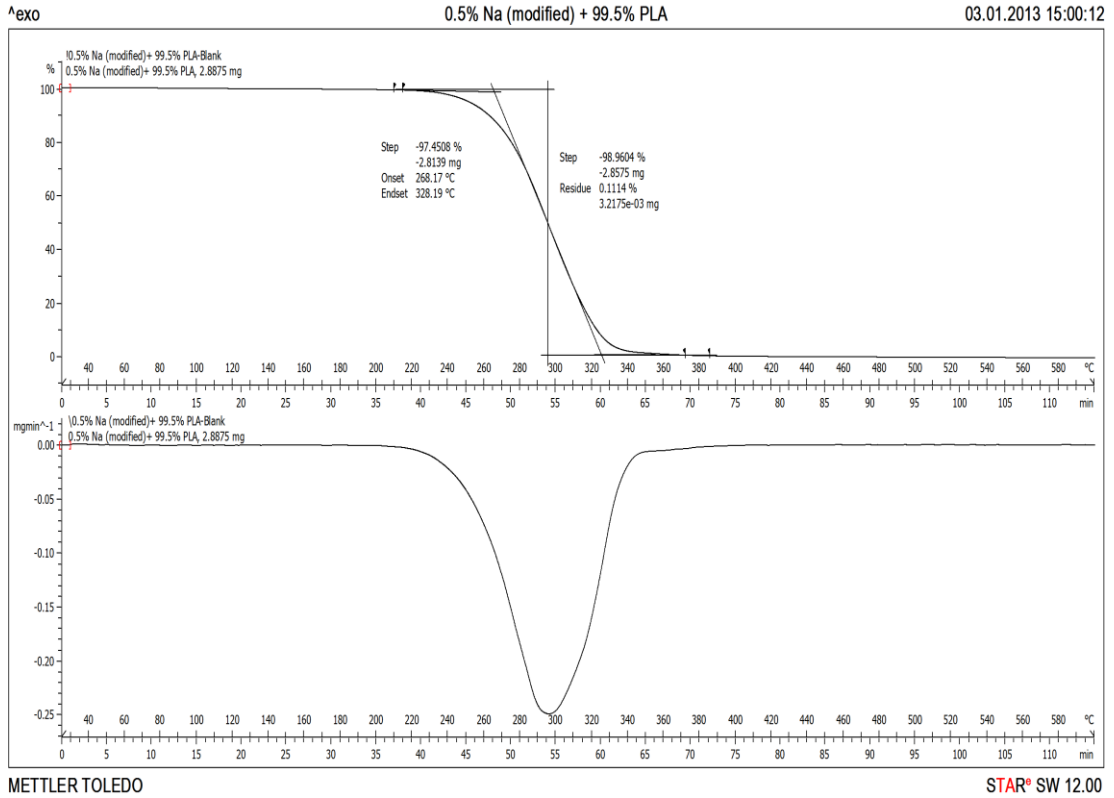
Figure E.5: The result for 0.5%Na$^+$ modified & 0.95% PLA
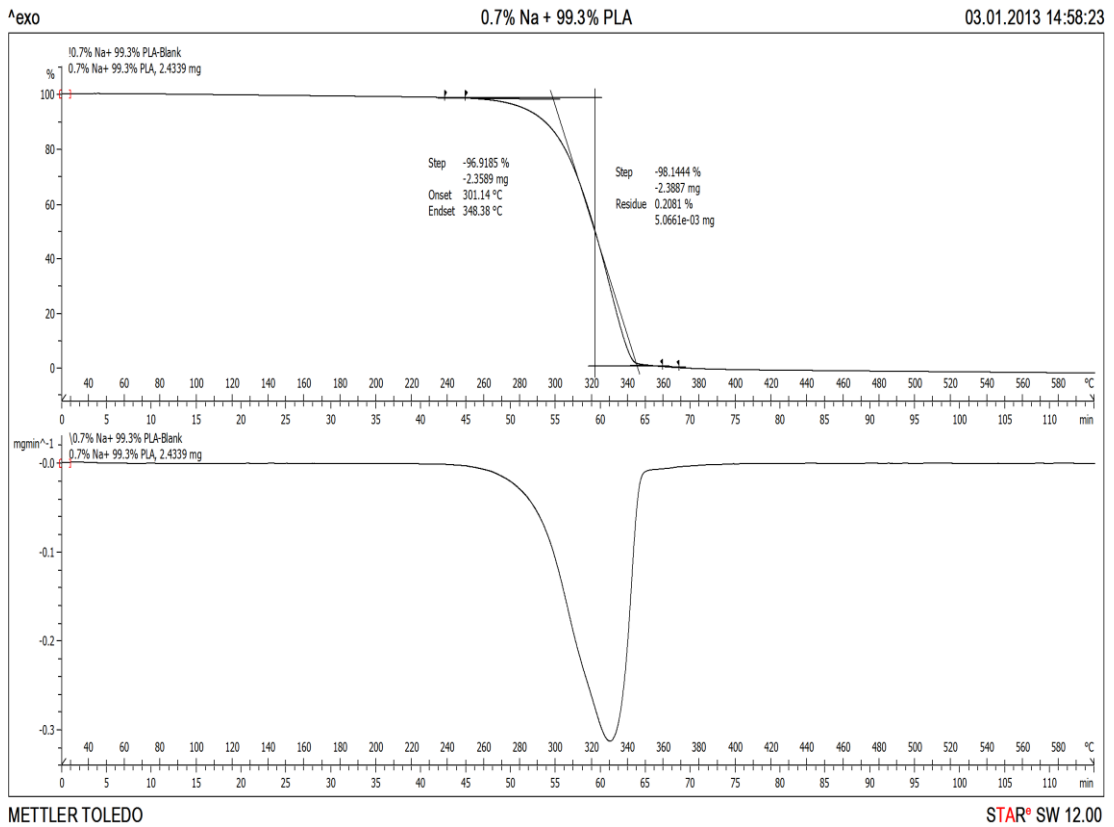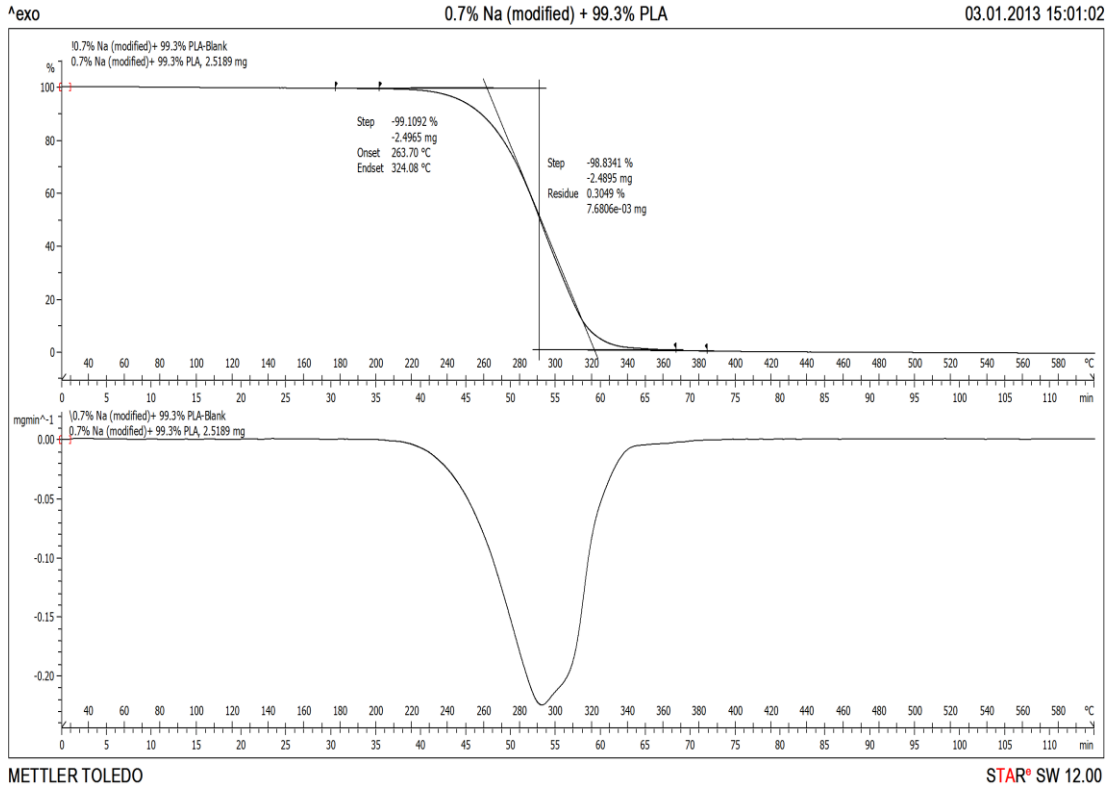

Figure E.6: The result for 0.7%Na$^+$ & 0.93% PLA

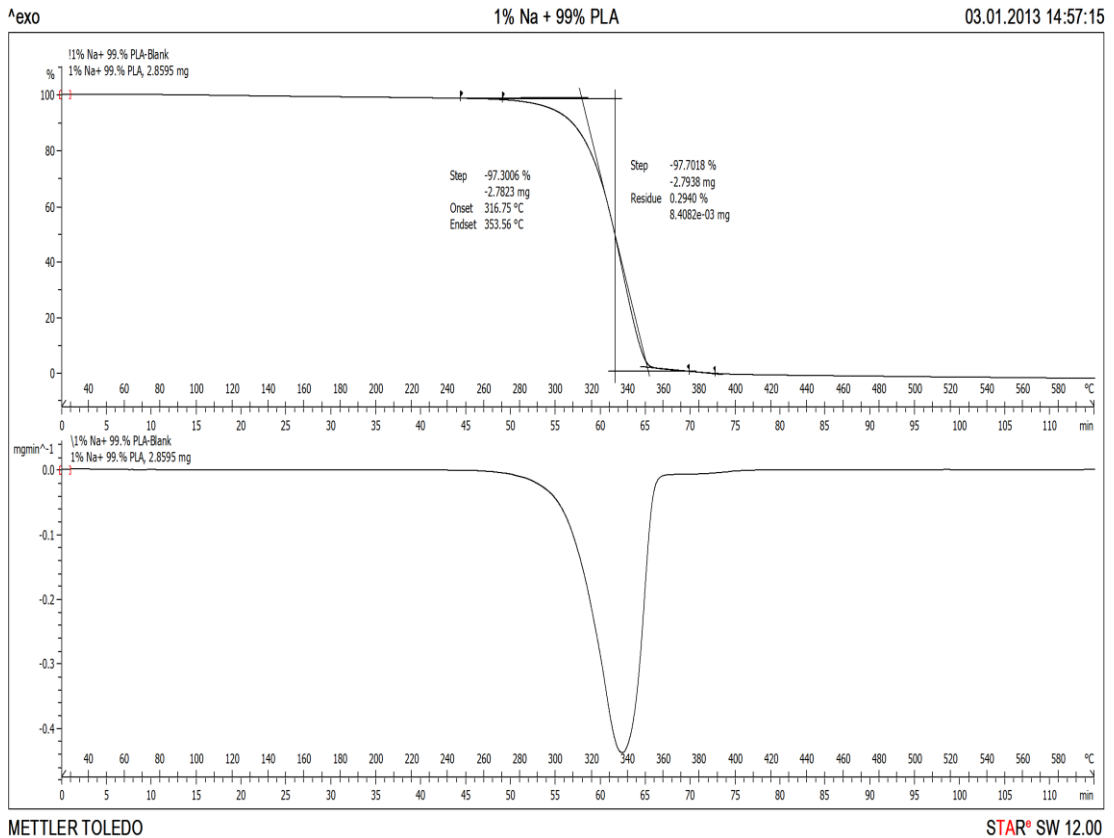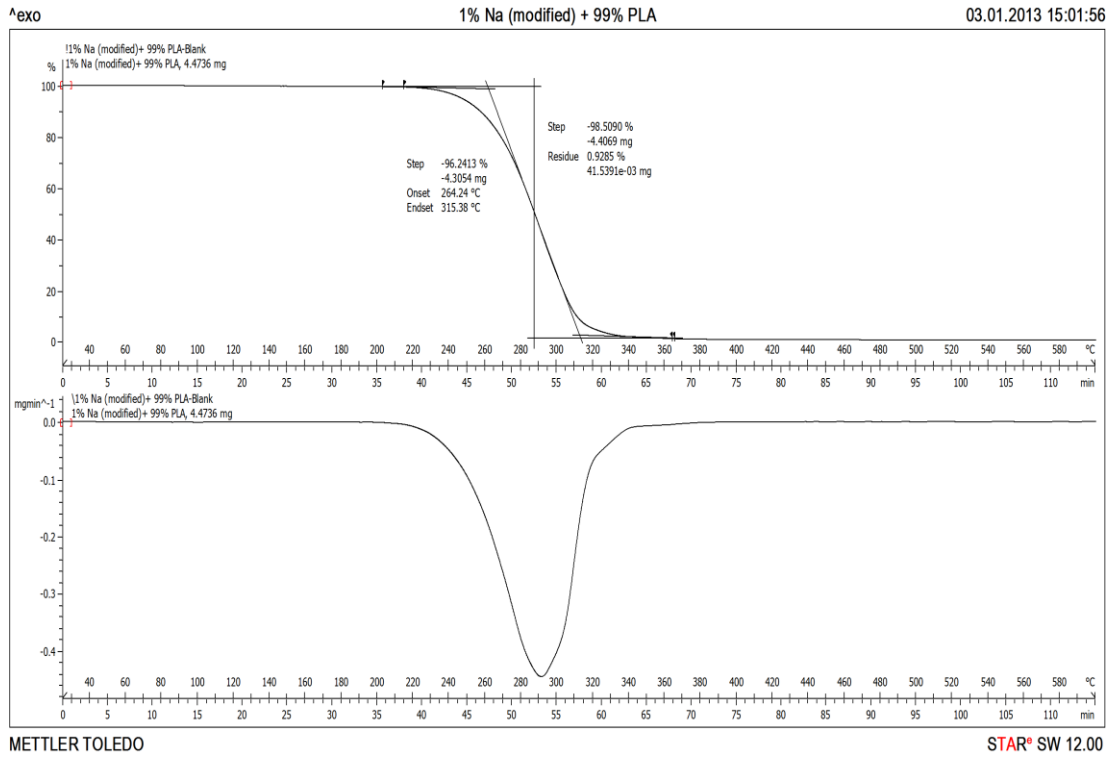**Figure E.7:** The result for 0.7%Na⁺ modified & 0.93% PLA

Figure E.8: The result for 1.0%Na⁺ & 0.90% PLA

Figure E.9: The result for $1.0\%\,\mathrm{Na^+}$ modified & 0.90% PLA