

EFFECTS OF THE MODIFIER TYPES TO THERMAL, MECHANICAL AND  
BARRIER PROPERTIES OF POLYLACTIC ACID/MODIFIED NANOCCLAY  
NANOCOMPOSITE

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## ABSTRACT

Poly(lactic acid) (PLA) is a biodegradable polymer, derived from renewable sources, having either a semi-crystalline or amorphous structure. These characteristics make PLA an excellent candidate for food packaging. However, it has many weaknesses such as poor thermal properties, brittle in tensile behaviour, and limited water barrier properties. The introduction of nanoclay leads to the significant improvement of the mechanical, barrier and thermal properties to the samples provided that the clay platelets are well dispersed in the PLA matrix. In this work, the focus was on the modification of the nanoclay using three types of modifier namely CU, where the nanoclay was modified with Copper (II) Chloride, TEA, where the nanoclay was modified with triethylamine and TEOS, where the nanoclay was modified with Cocamidopropyl Betaine to assist the improvement of the properties. Upon characterising the modified nanoclay using X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Field Emission Scanning Electron Microscopy (FESEM), increased d-spacing of the modified nanoclays up to 39.9 Å has been seen confirming the success of the modification process. The fabrications of the nanocomposite films were performed by solution mixing method using dichloromethane as solvent creating nanocomposite samples using those three modified nanoclay and unmodified clay namely TEA, CU, TEOS and NA with 1, 2, and 3 wt% nanoclay. The nomenclatures of the samples were given by the name of modified nanoclay followed by the number of percent clay loading. The thermal properties of the films were tested on two areas that are thermal stability and melting temperature using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The results for thermal stability demonstrated both improvement and deterioration of thermal behaviour by knowing the values of the offset temperature. Increase in thermal degradation temperature up to 8.4% was demonstrated for TEA2 and 5.2% decreased by CU1. However, there was no significant change in the melting temperature, which 0.68% improvement was obtained in TEA2 and decrement of 1.38% of melting temperature for CU2 nanocomposite. All nanocomposite samples have shown improvement in water barrier property. Using a modified version of ASTM E96/E96M-12 wet cup test, the permeance value of TEA3 has shown the greatest improvement by exhibiting 44% less permeance. Universal testing machine has been used to perform the tensile test. In the study of mechanical properties, the most improved tensile stress is NA1 because 24% increment in tensile strength has been demonstrated. The most decreased tensile strength belongs to NA3 with a decrement of 51.5%. For the Young's modulus value, the most increased value was NA2 that has shown increment of 35% and the most decreased Young's modulus value was TEA1 with a decrement of 46%. With these results, it has been understood that different properties of nanocomposite have been greatly improved and some were even deteriorated by adding certain type of nanoclay with an optimum amount of filler. The most favoured nanocomposite in this study was TEA2 that has shown improvement in all properties tested.

## ABSTRAK

Asid polylactic (PLA) adalah polimer terbiodegradasi yang berasal daripada sumber-sumber yang boleh diperbaharui dan juga mempunyai ciri struktur sama ada semi-kristal atau struktur amorfus. Ciri-ciri tersebut menjadikan PLA satu pilihan yang terbaik untuk digunakan sebagai pembungkus makanan. Walau bagaimanapun, beberapa perkara penting yang perlu ditambah baikkan seperti sifat terma yang lemah, sifat mekanikal yang lemah, dan sifat halangan air yang terhad. Sawar nano boleh membawa kepada peningkatan yang ketara kepada sifat mekanikal, sifat kebolehtelapan dan juga sifat terma kepada sampel dengan syarat bahawa platelet sawar tersebar dengan baik didalam matriks PLA. Dalam karya ini, tumpuan adalah juga pada pengubahsuaian sawar nano menggunakan tiga jenis pengubahsuai iaitu CU dimana sawar nano telah di ubahsuai menggunakan kuprum (II) klorida, TEA yang mana sawar nano telah di ubahsuai menggunakan trietilamina dan TEOS dimana sawar nano telah di ubahsuai menggunakan Cocamidopropyl Betaine untuk membantu dalam peningkatan sifat-sifat. Keputusan dipamerkan oleh pembelauan sinar-X (XRD), Spektroskopi inframerah transformasi Fourier (FTIR) dan Pancaran Medan Mikroskopi Elektron Pengimbasan (FESEM) menunjukkan peningkatan dalam jarak dsawar nano yang diubah suai sehingga  $39.9\text{\AA}$  lalu mengesahkan kejayaan proses pengubahsuaian. Fabrikasi filem-filem nanokomposit telah dilakukan dengan kaedah tuangan menggunakan diklorometana sebagai pelarut sampel untuk mencipta nanokomposit daripada tiga sawar nano yang diubahsuai dan satu yang tidak diubahsuai iaitu TEA, CU, TEOS dan NA dengan peratusan berat 1, 2, dan 3%. Penamaan sampel telah di tentukan dengan nama jenis-jenis sawar nano terubahsuai dengan peratusan sawar nano yang telah digunakan. Sifat terma filem-filem tersebut telah diuji ke atas dua bidang iaitu kestabilan terma dan suhu lebur dengan menggunakan Analisis Termogravimetri (TGA) dan Kalorimeter Pengimbasan Perbezaan (DSC). Keputusan bagi kestabilan terma menunjukkan kedua-dua peningkatan dan kemerosotan sifat terma dengan mengenalpasti nilai suhu ofsetnya. Peningkatan suhu degradasi terma sehingga 8.4% telah ditunjukkan oleh TEA2 dan penurunan sebanyak 5.2% oleh CU1. Bagi suhu lebur, tiada perubahan yang ketara terhadap sifat lebur, menunjukkan peningkatan hanya 0.68% dimiliki oleh TEA2 dengan penurunan suhu lebur 1.38% untuk nanokomposit CU2. Semua sampel nanokomposit telah menunjukkan kemajuan dalam sifat ketelapan air. Menggunakan ujian cawan basah ASTM E96/E96M-12 yang telah di ubah suai, nilai ketelapan daripada TEA3 telah menunjukkan perkembangan yang paling besar dengan mempamerkan 44% kurang ketelapan. Mesin ujian universal telah digunakan untuk melaksanakan ujian mekanikal. Dalam pengajian sifat mekanikal, tegasan tegangan yang paling baik menunjukkan peningkatan 24% oleh NA1. Bagi yang paling menurun adalah tegasan tegangan dimiliki oleh NA3 dengan mencatatkan 51.5% pengurangan. Untuk nilai modulus Young, 35% peningkatan telah direkodkan oleh NA2 dan nilai modulus Young yang paling menurun adalah TEA1 dengan 46% pengurangan. Dengan keputusan ini, ia telah difahami bahawa berlainan sifat-sifat nanokomposit telah ditambah baikkan dan ada yang juga merosot dengan penambahan jenis sawar nano yang tertentu dengan jumlah yang pengisian yang optimum. Di dalam kajian ini, nanokomposit yang paling di gemari adalah TEA2 yang telah mempamerkan peningkatan di dalam kesemua sifat-sifat yang telah di uji.

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**LIST OF ABBREVIATIONS**

PLA	Polylactic Acid
MMT	Montmorillonite
NA	Unmodified Nanoclay
TEA	Triethyleamine modified nanoclay
CU	Copper (II) Chloride modified nanoclay
TEOS	Cocamidopropyl Betaine modified nanoclay
hr	Hour
°C	Degree Celsius
ml	Millilitre
g	Gram
%	Percent
L	Litre
wt	Weight
CEC	Cation Exchange Capacity
M	Molar
mm	Millimetre
pH	Power of hydrogen
XRD	X-ray Diffraction
TGA	Thermogravimetric Analysis
DSC	Differential Scanning Calorimetry
SEM	Scanning Electron Microscopy
WVTR	Water Vapour Transmission Rate
PNC	Polymer Nanocomposite
PLS	Polymer Layered Silicate
PET	Polyethylene terephthalate
PCL	Poly (3-caprolactone)

## **CHAPTER 1**

### **BACKGROUND OF RESEARCH**

#### **1.1 INTRODUCTION**

The word nanocomposite is defined from two phases of words describing the dispersion behaviour and the size of the material in nanometre. The term is used basically in two material science's fields namely ceramics and polymers. In the subject of polymer, nanocomposites are usually derived from polymer reinforced by nanofillers from various types such as silica beads (Pu et al., 1996), cellulose whiskers (Helbert et al., 1996, Hajji et al., 1996), zeolites (Frisch and Mark, 1996) and other types of nanofillers (Godovski, 1995). Since a group of researchers from Toyota has made a discovery of the nanocomposite formation from an organophilic clay and polymer (Okada et al., 1989), the interaction between polymer and clay has been widely studied. The properties for their materials based on polyamide 6 and montmorillonite showed outstanding improvements at low clay content.

Nanoclay such as montmorillonite is hydrophilic in nature. Having a nature of this sort causing it to be poorly suited for mixing with most polymer that are normally hydrophobic in nature (Jordan, 1949, Van Olphen, 1963, Giannelis, 1996). Besides having a hydrophilic nature, the structure of the montmorillonite platelets itself are tightly held by electrostatic force causing difficulties for the monomer to enter the interlayer gallery of the clay. These factors made the treatment of the nanoclay to be essential for the effectiveness of the material to be used as filler for the hydrophobic polymer. There are several methods of modification but usually the most used

modification technique is by using traditional technique of ion exchange. Due to the weak bond of the cation to the surface of the clay, clay can be modified by various types of cations in order to ensure the compatibility of clay with the polymer and at the same time promote the formation of an intercalated and exfoliated nanocomposite. The studies of organically modified montmorillonite have been widely analysed. There are ammonium surfactant modified nanoclay by incorporating short aliphatic chain and benzoyl group to the clay (Vaia et al., 1994a, Xie et al., 2001b, Li and Ishida, 2005). There are also the usage of phosphonium surfactant in the formation of the organoclay (Zhu et al., 2001). Recently the work of modification has focused on quaternary ammonium compound nanoclay based on the hydrogenated tallowalkyls that are derived from animal fat (McLauchlin and Thomas, 2009) satisfying the specification of this study that is to modify the nanoclay using several methods available in order to compare the effectiveness of the nanoclay with the properties of the nanocomposite.

In order to prepare the nanocomposite, there are several methods that are available for the samples fabricating. Those are in-situ intercalative polymerisation, melt intercalation method, and intercalation of polymer or pre polymer from solution (Alexandre and Dubois, 2000, Sinha Ray and Bousmina, 2005). Every method has its own advantages and weaknesses. In this study, the focus is on the thermal properties and therefore the method that is suitable for the nanocomposite forming is solution method because other method such as melt intercalation has been known to be degrading the polymer in terms of the thermal stability (VanderHart et al., 2001). For the method in-situ polymerisation method, it involved the act of swelling the organoclay directly inside the solution containing monomer that are also sometimes using some heat to process the nanocomposite. Therefore the method that is chosen in this study is the solution method.

The usage of plastic has gained its popularity throughout the world. Besides having a low cost compared to other materials such as metals. It also can withstand a satisfactory amount of heat for plastics as some polymer is used as cooking utensil. One of the major problems for this material is most plastics are not environmentally friendly. It can even release toxic fumes when incinerated. That is why the interest on biodegradable and biocompatible polymer has increased, the most popular biodegradable polymers that have been produce commercially are polylactic acid (PLA)

and poly (3-caprolactone) (PCL). Recent study has showed that PLA can be produced from renewable resources(Ozkoc G. , 2009). The interest in PLA has increased dramatically compared to other synthetic polymers which are produced from mostly from petroleum derived chemical. These types of polymers are not easily degraded in the environment due to its low recovery and reproduction rates. PLA is thermoplastic polyester with rigid properties. The polymer backbones of the PLA determine the structure of the polymer to be either amorphous or semicrystalline. This special polymer is produced from natural renewable sources such as sugarcane, corn starch and tapioca starch. PLA unique properties enable it to be applied as compost bags and agricultural films. PLA is also used in medical applications for surgical implants, wound closure, tissue culture, and resorbable sutures (Kulkarni et al., 1966). Interest in this polymer has grown significantly due to the biodegradability and biocompatibility behaviour of the polymer with the ability to crystallise under stress or heat besides it also can be filled and copolymerised. These capabilities of the polymer have enabled it to be applied in wide range of usage. Even though the polymer is considered as special in term of its ability, this polymer has several weaknesses as for the application in food packaging.

The properties of PLA such as thermal, mechanical and barrier are considered as weak (Murariu et al., 2010). Several approaches have been known to improve the properties of the polymer such as copolymerisation and fillers technique. The most discussed technique for the properties improvement is fillers technique due to the cost of the process is lower compared to the other method. That is why the method has been chosen to be used in this study in order to cope with the recent development of polymer advancement. Nanoclay filler were used in this study to form nanocomposites and there are several methods to prepare the nanocomposite. The popular methods of preparing the nanocomposites are melt intercalation method, in-situ polymerisation and solution intercalation. Since this study emphasises on the properties of the nanocomposites films, the method chosen for this study is solution method due to the simplicity of the process and the samples produced by this method are in film form. The samples can be used right after the production without undergoing other process to form films compared to the other two methods which require expensive machine and complicated process route to form the nanocomposite. The nanocomposites formed by mixture of nanoclay and PLA will have different structures depending on the compatibility of the nanoclay with

the polymer matrix. Potentially, there are three types of nanocomposite structure that can be achieved by the samples. Those are intercalated structure, exfoliated structure and agglomerated structure. The effectively interacted clay-PLA structure is found out to influence the properties of the PLA. These changes made by the nanoclay to the properties of the PLA can be used to alter the weak properties possessed by the pristine PLA to our advantage by improving the mechanical, thermal and barrier properties of the polymer.

## **1.2 PROBLEM STATEMENT**

In the production of polymers nowadays, many have concern of its limitation that has become a serious problem to the world. The produced polymers are mainly contributed to the increasing plastic waste that has becoming a difficult problem to overcome. The usage of biodegradable polymer such as PLA is one of the solutions for the problem but with a little drawback(Sinha Ray and Bousmina, 2005). The need of biodegradable material with strong properties is essential for the packaging application to ensure the quality of the food is at its best.

Thermal, mechanical and barrier properties of the PLA should be improved and in order to make it happen, fabricating polymer nanocomposite (PNC) from PLA is one of the means for the improvement. According to Sinha Ray et. al (2002) , the best polymer layered silicate nanocomposite is to blend with 2:1 layered phyllosilicate type which is called montmorillonite (MMT). However, the problem with this type of filler is the incompatibility of both MMT and PLA where it is in need of some modification to the MMT using ion exchange reaction in order to make it compatible by changing the nature of the MMT from hydrophilic to hydrophobic. By performing this act, the modifier is introduced between the interlayer spacing of the MMT resulting to the varied values of the interlayer spacing (d-spacing) for the modified MMT. This condition will eventually promote exfoliation due to the entrance of the PLA monomer into the d-spacing.

However, the types of modifier also play an important role in assisting the degradation process of the nanocomposite. According to Wu et.al (2006), one of the

reasons that promote the degradation of the PNC is the degradation of organic modifier within nanoclay used to fabricate the PNC. Therefore in this research, three types of modification have been made to the nanoclay in order to study the effect of the modifier types to the properties of the nanocomposite. The first modifier type is transition metal ion where in this study, Copper (II) Chloride has been used as the reactant of the ion reaction. Second, involves the use of amphoteric surfactant as a modifier to the MMT. This type of modification involves the use of Cocamidopropyl Betaine which is derived from coconut oil and having a long chain that is inferred to be causing the d-spacing of the MMT to be increased. Third is the modification using aliphatic ammonium compound as a modifier that are reacted from triethyleamine. The significance of these modifications is to compare which types of modifier could produce the most improved PNC properties besides proving the presence of Hofmann elimination process during the thermal degradation of the PNC.

Using an extruder to fabricate the nanocomposite is considered as a favourable method. However, the involvement of heat during the fabrication could also assist the degradation process (Davidson et al., 1984). Therefore in this study, to avoid some inaccuracy during the evaluation process of the thermal degradation, the use of solution mixing method is essential to avoid any other external heat contributed to the samples during the fabrication process before the test. Indeed the melt compounding process is more simple and reliable but the focus in this study is to investigate the effect of the modifier to the thermal stability of the polymer nanocomposite (PNC). In the solution mixing method, the use of the solvent was applied in this research where dichloromethane was the name of the solvent. It proves that the type of the nanofiller used to the PLA have some effect to the properties of the nanocomposite as the cause of the low degradation temperature is related to the modifier used in the modified nanoclay.

As for the water barrier properties of the PLA, the formation of the polymer nanocomposites could improve the barrier properties of the PLA. Another challenge that mostly has overwhelmed some of the researchers in this field is the formation of the PNC structure. It is known that the structure of the nanocomposite is the reason for the change in the nanocomposite properties. In order to obtain excellent improvement in the properties of PNC, the structure has to be exfoliated and the attempt into producing one

is not an easy task where there are many factors affecting the formation of the structure. The factors include the types of filler, processing method, and the amount of the nanoclay used in forming the nanocomposite.

For the mechanical properties of the PLA it is well known for the brittleness that is causing it to be slightly hard to be applied in the food packaging industry. Therefore, a numbers of studies have been made to amend the mechanical properties of the PLA in order to make this material applicable. The challenge by far is the development of PLA samples that are strong in both tensile stress and modulus and in this study the approach of studying the effect of the nanoclay to the PLA in creating a sample that are applicable as food packaging material.

### **1.3 RESEARCH OBJECTIVES**

The aims of this project are to solve or minimise the problems experienced by the PLA as introduced in the problem statement. The approaches are to produce a nanocomposite with improved thermal, mechanical and barrier properties. This study is also made to improve the nanoclay by modifying it with several types of modifier to avoid Hofman's degradation of the modifier that will assist the PNC thermal degradation. These are the objectives of this study that have been divided into several aspects:

1. To fabricate PLA modified clay nanocomposite.
2. To characterise the PLA modified clay nanocomposite by means of XRD and FESEM.
3. To study the mechanical, thermal, and barrier properties of PLA modified clay nanocomposite.

### **1.4 SCOPE OF STUDY**

In order to achieve the objective of this study as have been stated in the previous sub chapter, several scopes of the study have been set up to assist the experimental work of the study. The scopes of this study consist of two phases that were introduced in detail as following:

Phase 1: Modification process of sodium montmorillonite ( $\text{Na}^+$ )

- i. The modification process of the nanoclay is conducted by using transition metal ion, aliphatic ammonium compound, and amphoteric surfactant involving ion exchange reaction into making three types of nanoclay that will be used further in the experiment.
- ii. Characterisation of the modified nanoclay using x-ray diffraction (XRD), FESEM and FTIR to assure the successfulness of the modification process before being used as filler to the PLA into forming PLA nanocomposite.

Phase 2: Formation and characterisation of the nanocomposites.

- i. Solution method is applied into making the nanocomposite and the solvent dichloromethane was used to cast the nanocomposite films.
- ii. The thermal properties of the samples were investigated by using thermogravimetric analysis (TGA) to obtain the thermal stability of the nanocomposite and differential scanning calorimetry (DSC) to study the melting temperature of the samples.
- iii. Mechanical properties of the samples were characterised by using universal testing machine where both maximum tensile stress and Young's modulus of the samples were listed.
- iv. Utilisation of modified ASTM E96/E96M to investigate the water barrier properties of the samples.
- v. The usage of XRD and scanning electron microscopy (SEM) to characterised the structure of the PLA nanocomposites.

It is hypothesised that the nanocomposite formed with TEA modified nanoclay were having the most improved properties. All of the nanoclay modifications have already been done by previous researcher but no study yet so far has used the modified nanoclay to be blended with PLA for the improvement of the nanocomposites' properties.

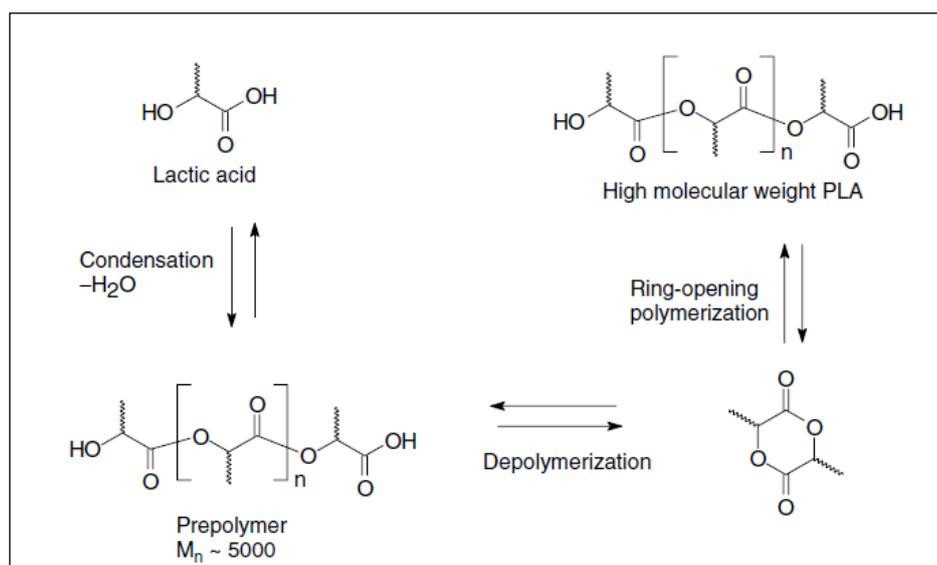
## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 POLYLACTIC ACID**

In 1845, Théophile-Jules Pelouze has done an experiment by condensing lactic acid by distillation of water to form some low-molecular weight polylactic acid and the cyclic dimer of lactic acid, lactide (Pelouze, 1845). Years later around 1894, an effort to optimise the usage and production of PLA has been done by Bischoff and Waden when they tried to polymerize lactide to PLA (Bischoff and Walden, 1894). Unfortunately the method is not suitable for practical use, as a review had done on Polylactic acid stated that this polymer has potential to be used as coatings and as constituent (Watson, 1948). As in 1986, PLA is identified as not viable or practically useful polymer due to lack of technology for proper processing of PLA at that time although it was described as having potential as a commodity plastic (Lipinsky and Sinclair, 1986). Initially, this polymer being produced by ring-opening polymerization of lactide monomer which is divided into two routes, those are direct condensation which involves solvent under high vacuum and formation of cyclic dimer intermediate (lactide) which is solvent free. In 1999, the method of fermentation of petrochemical feedstock had been used to produce monomer lactide. By this process, it produces optically inactive mixture of L- and D- enantiomers. Nowadays, polylactic acid is derived from lactic acid which is an organic acid found in various product of natural origin such as plant, animal and also microorganism in nature. Usually the production of lactide monomer is by bacterial

fermentation of corn starch and others (Drumright et al., 2000). A development in manufacturing monomer economically from agricultural product has placed PLA at the forefront of the biodegradable plastic industries (Vink et al., 2003). Usually, lactic acid is obtained by fermentation process of some group of lactic acid bacteria which can convert hexoses into lactic acid (Heriban et al., 1993). From lactic acid, polylactic acid can be produced by some process which is called, polycondensation, ring-opening polymerization, and post-polymerisation which is divided into three sections. Those three sections are melt modification, radiation induced cross-linking and degradation, and graft-copolymerisation. Normally, the PLA synthesis process begins with lactic acid which is produced by the fermentation of dextrose. This is followed by a continuous condensation reaction which will lead to the production of low molecular weight PLA prepolymer. Next, the low molecular weight prepolymer is then converted to high molecular weight polymers by using ring-opening polymerization. The process is described further in the following Figure 2.1.



**Figure 2.1:** Synthesis of Polylactic Acid (Schwach et al., 2008)

The interest in PLA has increased dramatically compared to other synthetic polymers which are produced from mostly petrochemical. Petrochemical based polymers are not easily degraded in the environment due to its low recovery and reproduction rates. By using PLA, the current problems that the world is having today

which is the growth of municipal waste, can be improved by using this renewable and biodegradable polymer as replacement. It is known that plastics from petrochemical based are very hard to biodegrade and it can even withstand incineration process. Therefore choosing PLA as a sample for this project is a very suitable decision due to its biodegradability. This special polymer is produced from natural renewable sources such as sugarcane, corn starch and tapioca starch. This thermoplastic aliphatic polyester has a lot of applications; it is used for making woven shirts, microwave resistant tray, and many other hot-fill applications. As being a heat resistant plastic, PLA unique properties enable it to be applied as compost bags and agricultural films. PLA is also used in medical applications for surgical implants, wound closure, tissue culture, and resorbable sutures (Sinha Ray and Okamoto, 2003). PLA is a thermoplastic group polymer that can be either semicrystalline or totally amorphous during in a solid state. PLA is a unique polymer that in some ways behaves similarly to PET, and it performs a lot like polypropylene (PP). Lactic acid (2-hydroxy propionic acid) is the most common form of the acid. Ultimately, it can be considered as the polymer with the broadest range of applications because of its ability to be crystallized, modified, filled, copolymerized, and processed in most polymer processing equipment. It can be fabricated into transparent films, fibres, or injection moulded into pre-forms like bottles (William Gacitua, 2005).

Besides having these tremendous advantages, it has its own weaknesses which are more costly compared to other petroleum derived plastics and the properties of this organic plastic are not as good as synthetic plastic. These problems have confined the usage of PLA and had created an issue for commercialization for PLA. These weaknesses cause some researchers to have some ideas for modifications of this polymer. There are many ways to modify this polymer; the most popular method of all is blending it with nanofiller which can improve the properties of this polymer (Pinnavaia, 2001). There are several methods of fabricating polymer nanocomposite. There are melt intercalation, in situ intercalative polymerization and template technology. But the best method to be applied for lab or even industrial scale is melt intercalation. Different types of nanofillers are used in fabricating nanocomposite. The most common are carbon nanotubes and montmorillonite. There are several papers that review the properties and characteristics of PLA in detail. The physical characteristics

of PLA are greatly dependent on its transition temperatures for common qualities such as density, heat capacity, and mechanical properties. When in the solid state PLA can either be amorphous or semicrystalline, depending on its stereochemistry. For amorphous PLAs, the glass transition ( $T_g$ ) determines the maximum usable temperature for commercial applications. When in the semicrystalline state, both the  $T_g$ , which is approximately 58 °C and the melting point,  $T_m$ , which ranges from 170-190°C are important when determining the usable temperature for various applications. Above the  $T_g$ , amorphous PLA will behave as a viscous fluid upon further heating.

## **2.2 NANOFILLERS**

### **2.2.1 Introduction**

Over the last few years, wealth of investigations has been made to improve the impact resistance and the mechanical properties of PLA. These efforts have made use of biodegradable and nonbiodegradable fillers and plasticizer or blending of PLA with other polymer (Martin and Avérous, 2001). Nowadays, various types of nanoreinforcements such as nanoclay, cellulose nanowhiskers, ultrafine layered titanate, nanoalumina, and carbon nanotubes have been used to improve the properties of polymers (Mohanty et al., 2003, Nazhat et al., 2001, Hiroi et al., 2004, Nishida et al., 2005, Mark, 2006, Kim et al., 2006). Though both carbon nanotubes and nanoclay are proven as very useful fillers for polymers, the project will be focusing on the usage and modifications of nanoclay (Cloisite  $\text{Na}^+$ ) rather than carbon nanotubes because of the cost of nanotubes in comparison with nanoclay which is actually slightly higher. The significantly lower cost of nanoclay will make it a more appropriate choice for it to be applied in the industrial scale.

There are many types of fillers that can be applied for polymer enhancement. Normally, these fillers are fibres, clay and carbon. But the most commercially used nowadays are all in nanosize particle. The most popular types of nanofillers are carbon nanotubes and nanoclay. It is known that carbon nanotube has a very stable structure and it is very strong in terms of mechanical properties or strength. Nanotubes or Carbon