BIODEGRADABLE BEHAVIOUR OF POLYLACTIC ACID NANOCOMPOSITE BASED ON MODIFIED NANOCLAY

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Report submitted in partial fulfilment
of the requirements for the award of the degree of
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FACULTY OF CHEMICAL AND NATURAL RESOURCES ENGINEERING

I certify that the project entitled “Biodegradable behaviour of polylactic acid nanocomposite based on modified nanoclay” is written by Norayuni binti Azizi. I have examined the final copy of this project and in our opinion, it is fully adequate in terms of scope and quality for the award of the degree of Bachelor of Engineering. I herewith recommend that it be accepted in partial fulfilment of the requirements for the degree of Bachelor of Chemical Engineering.

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

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STUDENT’S DECLARATION

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

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Dedicated to my father, Mr. Azizi bin Khalid, my beloved mother, Mrs. Norsiah binti Meor Ahmad Ariffin, my brothers Asmaei bin Azizi and Afifi bin Azizi, my sister Noraimi binti Azizi and Noranati binti Azizi, my love one and last but not list to all my fellow friends

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ABSTRACT

Polylactic acid (PLA) is a unique polymer. Eventually, this polymer has the broadest range of application especially in biomedical field due to its biocompatibility characteristics. The main purpose of this research is to study on the biodegradable properties of PLA based on modified organoclay. The properties of PLA nanocomposite will be improved by adding nanoclay or Montmorillonite (MMT) and produce PLA nanocomposite. The MMT that used in this research is bis-(2-hydroxyethyl) methyl tallow alkyl ammonium cations (Cloisite B30). A series of PLA nanocomposite was classified by different percentage of compositions and the samples were analysed and compared with pristine PLA. PLA nanocomposite was produced by melt intercalation method using twin screw extruder. Then, the compounds were injection molded by injection molding method and formed dumbbell shape. Meanwhile, PLA nanocomposite is characterized by Scanning Electron Microscopy (SEM) and X–Ray Diffraction Analysis (XRD). However, SEM captures could not determine the dispersion of Cloisite B30 precisely nevertheless it illustrates that aggregates were formed in the images. XRD result supported an exfoliation nanocomposite was possible demonstrated as no diffraction peak was appeared in the XRD results. It also shows that the inter-galleries spacing of the Cloisite B30 between PLA matrixes is too wide. Subsequently, the samples were tested using accelerated weathering tester for biodegradable analysis. Finally, the samples before and after exposed in the accelerated weathering tester were examined by mechanical testing to determine mechanical properties such as ultimate strain, elastic modulus and ultimate stress using tensile strength testing. The most desired result of this research is based on the biodegradable testing. After a year observation, only pristine PLA was sustained in strength while the PLA nanocomposite is so brittle. Meanwhile for a year and half observation, all the samples were so brittle. It can be concluded that the pristine PLA is still remain sustain after a year but it start to degrade after a year and half. The result obtained for before exposing under accelerated weathering tester, the pristine PLA possesses good properties for ultimate strain and ultimate stress rather than elasticity behaviour.

Key words: Polylactic Acid, Polylactic Acid Nanocomposite, Weathering analysis, Biodegradability

ABSTRAK

Polylactic acid (PLA) adalah polimer yang unik. Akhirnya, polimer ini mempunyai kepenggunaan yang luas terutamanya dalam bidang bioperubatan disebabkan oleh ciri–ciri biokeserasiannya. Tujuan utama kajian ini adalah untuk mengkaji sifat-sifat terbiodegradasi PLA berdasarkan tanah liat yang telah diubahsuai. Ciri-ciri nanokomposit PLA akan dipertingkatkan dengan menambah tanah liat yang telah diubahsuai atau montmorilonit (MMT) dan menghasilkan nanokomposit PLA. MMT yang digunakan dalam penyelidikan ini adalah *bis-(2-hydroxyethyl) methyl tallow alkyl ammonium cations* (Cloisite B30). Siri nanokomposit PLA telah diklasifikasikan oleh peratusan komposisi yang berbeza dan sampel dianalisa dan dibandingkan dengan PLA asli. Nanokomposit PLA telah dihasilkan oleh kaedah interkalasi pencairan menggunakan extruder skru berkembar. Kemudian, sebatian dibentuk oleh kaedah pengacuan suntikan dan membentuk bentuk *dumbbell*. Sementara itu, nanokomposit PLA dicirikan oleh *Scanning Electron Microscopy* (SEM) dan *X–Ray Diffraction Analysis* (XRD). Walau bagaimanapun, gambaran dari SEM tidak dapat menentukan penyebaran Cloisite B30 dengan tepat namun ia menunjukkan bahawa agregat telah terbentuk. Keputusan XRD menyokong pengelupasan nanokomposit dengan menunjukkan tiada puncak pembelauan yang muncul dalam keputusan XRD. Ia juga menunjukkan bahawa jarak antara Cloisite B30 antara matriks PLA adalah terlalu luas.
Kemudian, sampel telah diuji menggunakan penganalisa cuaca untuk menganalisa siat terbiodegradasi terhadap sampel. Akhir sekali, sampel untuk sebelum dan selepas menggunakan pendedahan penganalisa cuaca telah diperiksa oleh ujian mekanikal untuk menentukan sifat-sifat mekanikal seperti sifat tarikan, modulus kekenyalan dan sifat tekanan menggunakan ujian kekuatan tegangan. Hasil yang paling dikehendaki bagi kajian ini adalah berdasarkan ujian terbiodegradasikan. Selepas setahun pemerhatian, hanya yang PLA asli kekal dengan sifat kekuatannya manakala nanokomposit PLA sangat rapuh. Sementara itu bagi pemerhatian satu tahun enam bulan, semua sampel sangat rapuh. Ia boleh disimpulkan bahawa PLA asli masih kekal sifatnya walaupun selepas setahun tetapi sifatnya mula merosot selepas satu tahun enam bulan. Keputusan yang diperolehi sebelum pendedahan penganalisa cuaca, PLA asli mempunyai sifat yang baik dari segi sifat tarikan dan sifat tekanan dan tidak pada sifat kekenyalannya.

Kata kunci: Acid Polilaktik, Nanokomposit Asid Polilaktik, Analisa Cuaca, Keupayaan Terbiodegradasi

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n	An integer
d	Inter–plane spacing
θ	The diffraction angle giving the primary diffraction peak
λ	The X-ray wavelength
H_2O	Water
CH_3	Methyl
O	Oxygen
H	Hydrogen
CO_2	Carbon dioxide

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
LA	Lactic acid
MMT	Montmorillonite
NPCC	Nano-sized Precipitated Calcium Carbonate
PET	Polyethylene Terephthalate
PLA	Polylactic acid
PP	Polypropylene
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
UVA	Acetyl Ultraviolet
UV	Ultraviolet
XRD	X – Ray Diffraction

CHAPTER ONE

INTRODUCTION

1.1 Research Background

Polymers have extremely high molecular weight compound made up of a large number of monomer (called simpler molecules). The process which is linked all the monomers together to form polymer is called polymerization. Monomer can have one or more substituted chemical groups. Variation of chemical groups can affect the chemical and physical properties of the polymer such as solubility, flexibility, strength, stress crystallized, thermally crystallized and etc. There are organic polymer and inorganic polymer in this world.

Since ten years before, nanocomposite based nano-layered silicates have attracted much attention due to its low cost, the availability ad non-isometric structure that derived from a high aspect ratio. Nowadays, conventional composite which is microcomposite is still used. Previous research has proved that nano-layered silicates in the polymer matrix significantly increase strength and heat resistance meanwhile decrease in gas permeability and flammability. However, good dispersion of organoclay in the polymer is crucial to achieve the improvement manner of polymer nanocomposite (Johanne *et. al.*, 2005). The intimate enclosure of nanoparticles in the polymer matrixes can change the properties of materials. The nanoparticles can serve as matrix reinforcement as well as transformation of material properties such as mechanical, chemical and morphological can be achieved. Nowadays, there are many researches based on the development of the polymer nanocomposite (Ujhelyioova, 2007).

Polymer degradation and erosion play crucial role for all polymer. The differences between degradable and non-degradable polymers is, hence, not clean-cut and is in fact arbitrary, as all polymers degraded. It is related on the time scale of degradation and the time scale of the application to compare the degradable and non-degradable polymers. Commonly known that degradable is refer to materials which degrade during their application or immediately after it while non-degradable require a substantially longer time degraded. Actually, the right definition of degradation is the chain scission process during polymer chains are cleaved to form oligomers and finally formed monomers. Meanwhile, erosion describes the loss of materials owing to monomers and oligomers leaving the polymer (Gopferish, 1996).

To improve the quality of polymer microcomposite, technology changes it into polymer nanocomposite. Polymer nanocomposite is the combination of one or more different components of nano-filler in order to obtain the desired properties of polymer composites. Nanoparticles are usually used as filler in polymer matrix nanoclay, metal, carbon nanotubes and etc. The development of polymer nanocomposite is speedily developed as a multidisciplinary research activity. The findings will resulted with a wide application to great benefit of many different fields (Gavitua *et. al.*, 2008).

Polylactic acid (PLA) usually is produced from corn, starch and sugarcanes. PLA derives from the polymerization of the lactide or lactic acid, which is a monomer produced in mammalian muscles during glycogenolysis and correlated with the Kreb cycle through piruvic acid and acetyl coenzyme (CoA) (Fambri, 1996). Meanwhile, lactic acid has different grade which is varying in purity depending on their application. PLA is a biodegradable polymer (Henton *et. al.*, 2005). PLA is not an acid but it is aliphatic polyester derived from renewable resources. Although PLA has been known for more than a century, it has a commercial interest in recent years because it’s biodegradable properties (Farrington *et. al.*, 2005).

This type of biopolymer is quite useful for nowadays. In the future outlook, PLA has potential to replace petroleum based plastic. It is regarding to its biodegradable properties. Their degradation occurs with simple hydrolysis of the ester bonds in an aqueous environment. Micro-organisms are metabolised the polymer chain into carbon dioxide and water as products. So that, if it used for biomedical field, there is no subsequent surgery to remove the implant. Hence, biodegradable polyesters are indicated for various devices, such as plates, pins and screws in bone, as well as for membranes for cell cultures and guided regeneration in soft tissue (Duek *et. al.*, 1998).

Usually, biodegradation studies are carried out in soil or compost, in particular, these materials may enhanced degraded in the presence of compost, a complex biological environment in which microbial diversity is relatively high. Therefore an increased degradation potential for polymeric compounds may result from the research (Kumar, 2010). However, biopolymer like PLA is not a danger material because it constituent passes into the environment (Pagga, 1997). PLA is being preferred alternative to its homologous poly (glycolic acid), due to its slow degradation rate (Fambri *et. al.*, 1996). Rudeekit *et. al.* (2008) also stated that PLA offer a possible alternative compared to the conventional non-biodegradable polymer especially when they are being recycled, it is non-economic.

To obtain toughened products, blending PLA with the other polymers presents a practical and economic measure. Blending PLA with other biodegradable polymers can retain the integrity of biodegradability is particularly interesting (Jiang, 2007). The degree of crystallinity of PLA depends on many factors such as molecular weight, thermal and processing history, temperature and time of annealing treatments (Fambri, 1996). Natural fibres have many benefits rather than synthetic fibres such as low weight, recyclable and biodegradable. Other than that, they are renewable and relatively high strength and stiffness besides cause no skin irritation (Oksman *et. al.*, 2003).

1.2 Problem statements

PLA microcomposite is usually used because of its biodegradability properties however biodegradation of PLA microcomposite is very low in toughness and it is brittle and stiff polymer with low deformation at break. Therefore, PLA nanocomposite is introduced to overcome those weaknesses.

1.3 Research objective

1.3.1 To study on the biodegradable properties of PLA based on organoclay

1.4 Scopes of research

In order to prove the improvement of characteristics of PLA, the scope of research is focusing on:

1.4.1 To produce PLA nanocomposite by melt intercalation method

1.4.2 To characterize PLA nanocomposite by Scanning Electron Microscopy (SEM) and X – Ray Diffraction Analysis (XRD)

1.4.3 To study on the biodegradable properties by using accelerated weathering testing

1.4.4 To study on the mechanical properties by using the tensile strength testing

1.5 Significance of research

PLA is produced from renewable resources has received much attention on their biodegradable properties in research of alternatives biodegradable polymer. PLA is one of the biopolymer that is, nowadays it is one of the most promising biodegradable polymers. In PLA principle, it can also be used as a matrix material in composites. Polymerization of lactic acid into PLA produces biodegradable thermoplastics polyester with good biocompatibility and mechanical properties, such as high tensile strength, thermoplasticity and fabricability. Nowadays, PLA is being developed into a variety of products included food packing, medical tubes, plastic bags of household, biodegradable agriculture films, biomedical application such as drug delivery system and controlled release matrices for fertilizers, pesticides and herbicides. Other than ecological concerns, PLA have resulted that resumed interest in renewable resources based products. In contrast, PLA fiber is derived from annually renewable crops, it is

100% compostable and its life cycle potentially reduces the Earth's carbon dioxide level. PLA are produced from renewable resources, it is by fermentation of carbohydrate. There has some contribution of PLA for environment because PLA is classified as an environmentally friendly polymer (Averous *et. al.*, 2008).

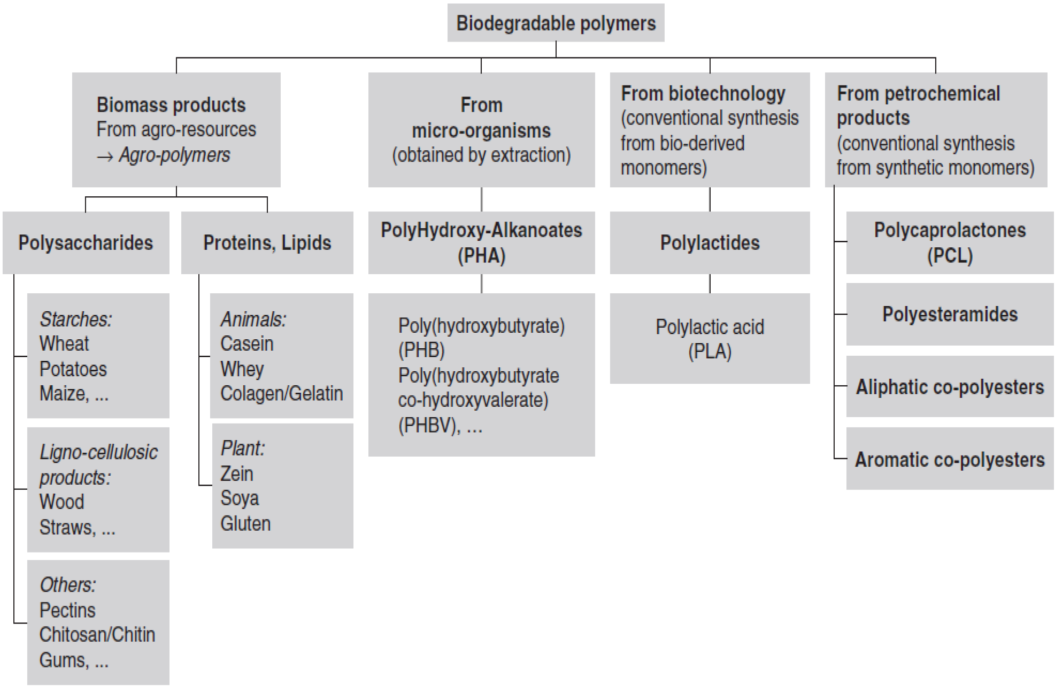


Figure 1.1: Classification of biodegradable polymer (Avérous, 2008)

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Polymer is made up of a large number of monomer and polymers could be divided into two categories: (1) matrix polymer and (2) natural polymer. A matrix polymer is a man-made polymer, while natural polymer is generated from chains of amino acids. A bio-composite is usually consisted of biodegradable polymers as host polymer and natural fibre as reinforcement filler. A polymers matrix and natural fibre are often used as reinforcement due to their good mechanical, chemical and natural properties.

2.2 Polymer

Natural polymer could be produced from natural resources such as starch, corn, cellulose, protein and etc. Polyethylene, polyester, polystyrene, nylon and etc are some of the example for synthetic polymers. However, a synthetic polymer is the most used by industrial and human due to the wide range of consumerism spectrum. A synthetic polymer is categorized into thermoplastic polymer and thermosetting polymer. The difference characteristic between thermoplastic polymer and thermosetting polymer is described in the table 2.1 below:

Table 2.1: Differences between thermoplastic polymer and thermosetting polymer

Thermoplastic polymer	**Thermosetting polymer**
Become soft when heated and hardens when cooled	Harden permanently when heated
High molecular weight polymers and consist of long molecular chains with no regular structure	Harder, more dimensionally stable, and more brittle
Weak Van der Waals forces	Cross-linked in a curing reaction which produces covalent bonds between them

A copolymer is polymerized from an intimate solution of different types of monomers. A copolymer is divided into three types of chain arrangement; block copolymer, blend/random copolymer and graft copolymer. A block copolymer is a constant pattern combination of polymeric components along a single carbon bonded chain and in contrast blend/random copolymer demonstrate a random mixture of polymeric molecules. The last structure arrangement of copolymer is a graft copolymer. In the graft copolymer arrangement type, component monomers with different chemical compositions are branched out from the primary chain (Xie *et.al*, 2003).

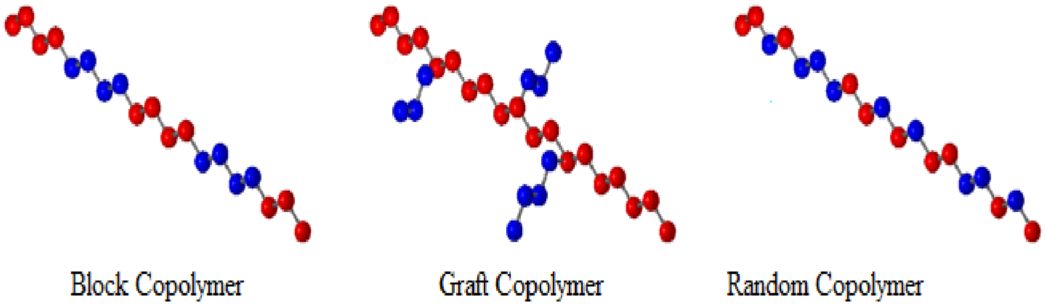


Figure 2.1: Different types of copolymer (Xie *et.al*, 2003)

2.3 Lactic acid

The lactic acid (LA) component of PLA is synthesised by using 100 % renewable resources through a fermentation process. In general, a PLA would degrade if exposed to the environmental setting at rapid rate. The excessive products of the degradation process possess very low toxicity since the products it selves are carbon dioxide and water (Blackburn *et.al*, 2005).

LA is one of the versatile polymers since LA is widely used as flavour and preservative in pharmaceutical, leather, food as well as in textile industries. LA is also used as for the production of base chemical and also polymerization to PLA. The production of the LA are recorded annually at about 80, 000 tonnes per year. At approximately 90% of PLA were produced via LA bacterial fermentation while the rest of PLA production is employed by using hydrolysis approach of lactonitrile (Karin *et. al.*, 1999). LA could be presented as the L-stereoisomer or D-stereoisomer.

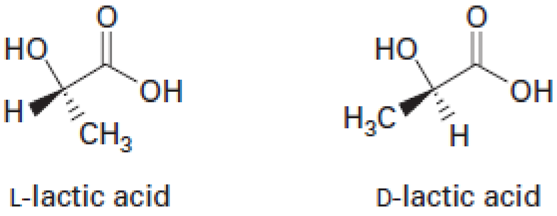


Figure 2.2: The stereoisomers of lactic acid (Farrington *et. al.*, 2005)

Lactic acid commercially produced by the bacterial fermentation of carbohydrate, using homolactic organism, for instance various optimized or modified strains of the genus *Lactobacilli*. The most of simple sugars that produced from agricultural by products also can be used. Amongst of the simple sugars are (1) glucose, maltose and dextrose gain from corn or potato starch (2) sucrose from cane or beet sugar and (3) lactose from cheese whey. Batch processing method is used to conduct the commercial fermentation, which takes three to six days to be completed (Garlotta, 2002).

Farrington *et. al.* (2005) summarized from the published study that energy from the sun is directly promotes photosynthesis mechanism by consuming carbon dioxide (CO_2) and water (H_2O) from the atmosphere and later is converted into starch. An enzymatic hydrolysis is used to extract the starch from the plant cells and consequently altered into a fermentation sugar after an enzymatic hydrolysis. The production of LA from renewable resources through fermentation could be described in the following steps: (1) pre-treatment of substrate including hydrolysis to sugar, (2) fermentation of sugar to LA, (3) separation of bacteria and solid particles from the broth (4) purification of LA.

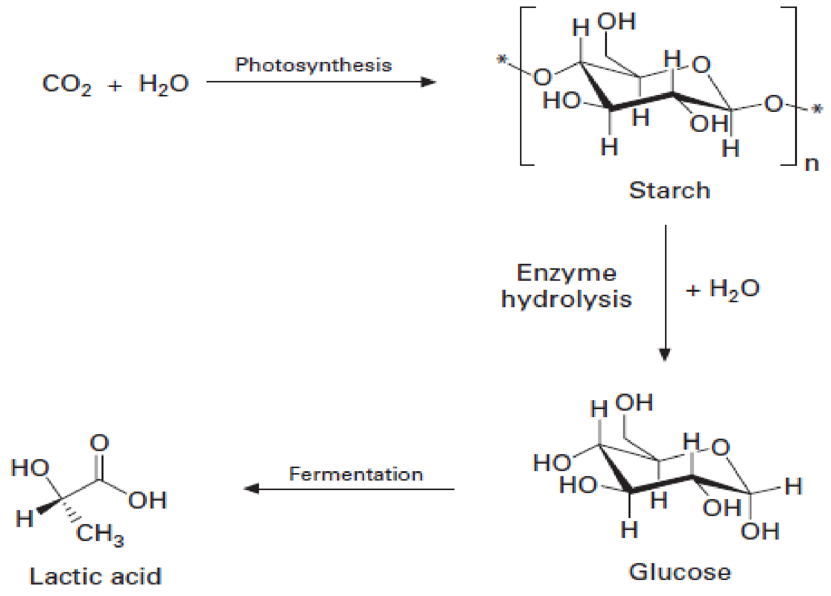


Figure 2.3: Production of lactic acid from renewable resources (Farrington *et. al.*, 2005)

2.4 Polymer nanocomposite

Polymer nanocomposite is defined as nanoparticles polymer bonded in order to produce an advanced materials properties. It has been known in existence for hundred years but is only used commercially nowadays (Butschli, 2004). A polymer nanocomposite is obtained by dispersing nanofiller particles into polymer matrix. PLA is produced through ring opening polymerization of lactides and lactic acid monomers themselves are obtained from the fermentation of sugar feed stocks (Chin, 2005).

The most common filler are utilized in the fabrication of nanocomposite is a clay class material called montmorillonite (MMT). Based on the natural characteristics of clay, it is hydrophilic while polymers are hydrophobic. To make the two components to be compatible, one of the components should be modified to make them interact successfully with each other (Hay, 2000; Ryan, 2003). The alternative way that could be employed to increase the interaction between the organic polymer and inorganic clay by modifying the surface properties of the clay. It can be done by exchanging organic ammonium cations for inorganic cations of the surface of the clay (Sherman, 1999).

There are many types of nanofillers that are commercially available according to market demand. There are carbon nanotubes, graphite platelets and carbon nanofibers. Carbon nanotubes are more expensive organoclay fillers compared to other organoclay fillers that are readily available. Other than that, carbon nanofibers offer excellent electrical and thermal conductivity properties. Southern Clay is the major suppliers for organoclay nanocomposite fibers (Alyssa, 2005).

In order to blend the polymer with nanofiller, there are three common methods; melt intercalation, in–situ polymerization and the solvent method. Melt intercalation process is being done using several machine; extruder, injection moulding and other processing machine. By utilizing in–situ polymerization approach, the filler is added directly into solution of monomer and would be followed by polymerization stage of polymer nanocomposite. In using solvent method, there are three solvents that can be used to undergo this method. The typically used solvents are toluene, chloroform and acetonitrile (Chen, 2004). The melt intercalation method and in–situ polymerization are more commercially used to produce polymer nanocomposite since the solvents method is not environmentally benign.

2.5 Polylactic acid

PLA is a biodegradable thermoplastic polymer with excellent mechanical properties that could be produced on a large scale beginning from fermentation of corn to produce lactic acid and subsequent polymerization process to synthesizing PLA. Most studies about the degradation of PLA are focused on abiotic hydrolysis due to the established role of PLA as biomedical implants (Shogren *et.al*, 2003). PLA could be either semi-crystalline or totally amorphous due to the characteristic of PLA as aliphatic polyester. It depends on the stereopurity of the polymer backbone. Other than that, PLA also is a unique polymer because it can perform like polyethylene terephthalate (PET), polypropylene (PP) and also polyolefin (Henton *et.al*, 2005).

Degradation occurs in two stages, whereas the first stage is diffusion of water into the polymer; hydrolysing the ester bonds and lowering its molecular weight followed by intracellular uptake of lactic acid into oligomers and humus. Li *et. al*. (1990) found that the carboxylic acid concentration was higher and hydrolysis process is occurred faster in the internal of a sample than on the outer surface due to leakage of the acidic PLA oligomers into the aqueous medium.

PLA has potential and is the most promising biodegradable polymer currently available in the market demands. PLA is a versatile polymer made from natural resources and renewable agriculture raw materials (Yusof, 2010). Moreover, PLA is used mainly to sustain the release of biologically active compounds and in the medical field; PLA is employed for the coating of a wide variety of therapeutic molecules (Onyari *et.al*, 2008).

Non-biodegradable polymers are normally disposed by incineration and as a result would release a large amount of carbon dioxides to the atmosphere. Besides that, it will contribute to global warming and content of toxic gases to the earth. That is the reason why the development of green polymeric materials that would not contribute to the pollution of the environment through toxic or noxious components, which are presence during the manufacturing process. The advantage offered by green labelled polymer is the biodegradability property which means that the degradation mechanism is succeeded through composting process. Although, in order to protect our environment to be in a good condition for our next generation, PLA has increased the commercial interest because it is one of the biodegradable polymers and it can be renewed (Suprakas *et. al*., 2003). The production of PLA is formed either by (1) direct condensation of lactic acid or (2) via a ring opening process.

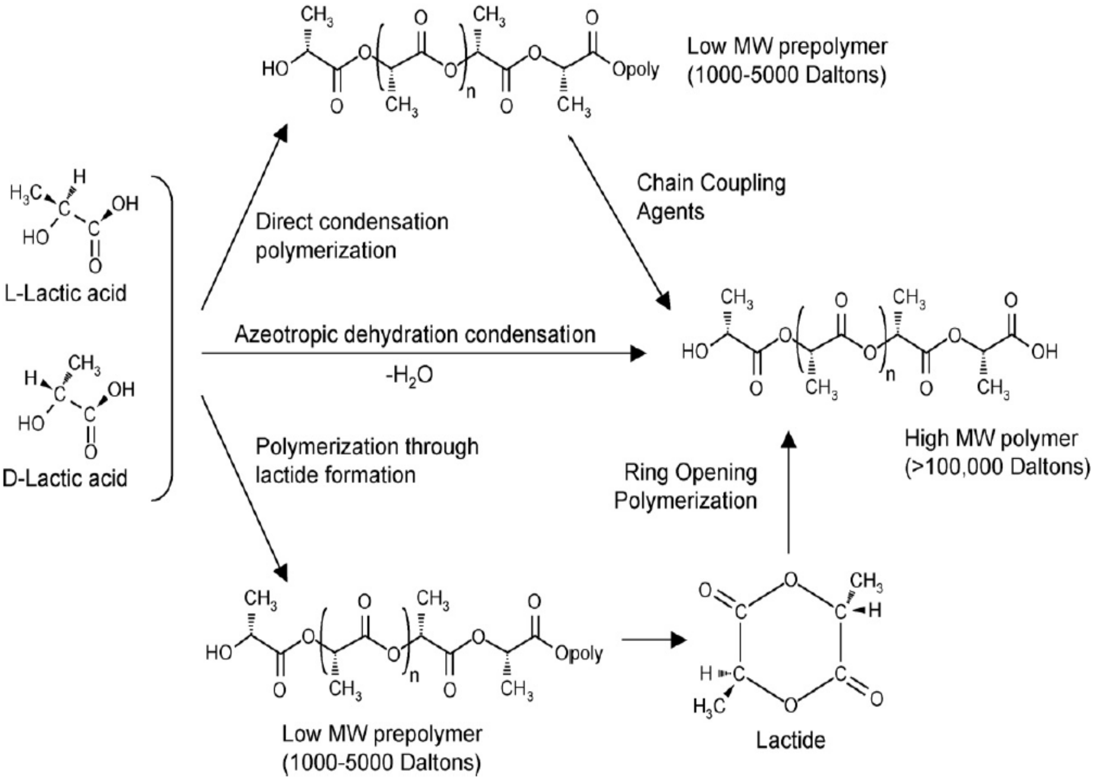


Figure 2.4: Synthesis of PLA from L-lactic acid and D-lactic acid (Auras *et. al.*, 2004)

Table 2.2: PLA properties and characteristic

Properties	**Characteristics**
Density (g/cm^3)	1.33
Melting Point (^{o}C)	169
Transition Glass (^{o}C)	45
Crystallization Temperature (^{o}C)	70 – 120
Crystallinity	0 – 1
Tensile Modulus (MPa)	2980
Tensile Yield Strength (MPa)	25.9
Tensile Elongation at Break (%)	8
Notched Izod Impact (J/m)	144
Flexural Strength (MPa)	44
Flexural Modulus (MPa)	2850
Thermal Conductivity (cal/cm sec ^{o}C)	Amorphous 3.1 x 10^{-4} Crystalline 4.5 x 10^{-4}
Specific Heat (cal/g ^{o}C)	Below T_g 0.29 Above T_g 0.51
Rockwell Hardness	84 – 115
Biodegradation (%)	100
Water Permeability	172
Surface Tension	50 N/m 37 gd 13 gp

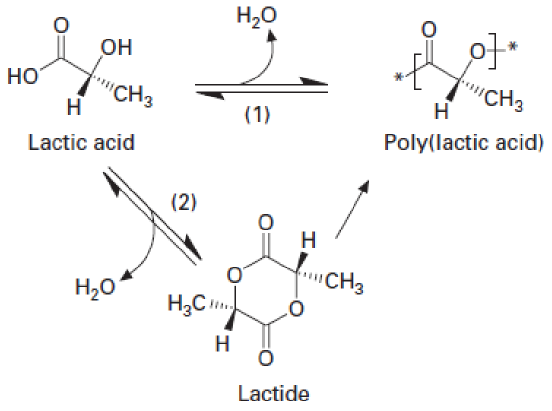


Figure 2.5: Direct condensation of lactic acid (Farrington *et. al.,* 2005)

Polycondensation of lactic acid process was discovered in 1932 by Carothers. It was about the ring opening polymerization of lactide. Then, the discovery has been continued by DuPont who improved purification techniques in 1954. The polycondensation process involves removing water by condensation. The used of solvent under high vacuum and temperature mainly due to the difficulties of removing water and impurities. This production is only for low to intermediate molecular weight polymers. The disadvantages of this process is usually involving large scale of reactor, requires evaporation process, recovery of the solvent and increased colour and racemisation (Garlotta, 2005)

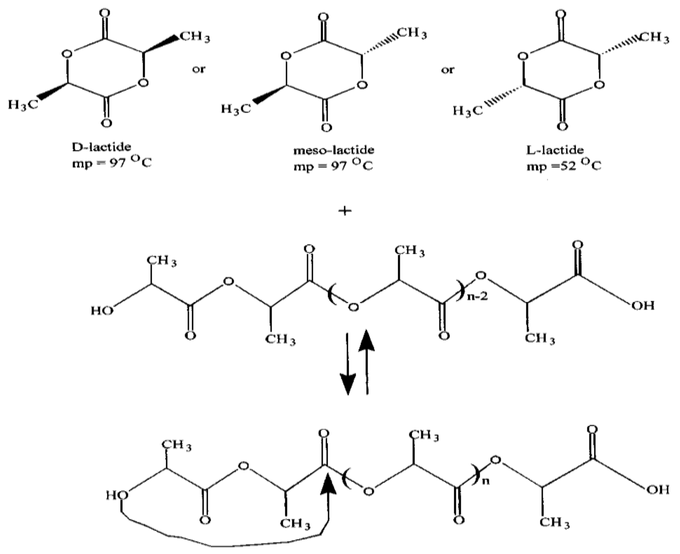


Figure 2.6: Lactide in formation (Garlotta, 2002)

Lactide purification is accomplished by vacuum-distillation of high temperature. After vacuum-distillation of L-lactide, ring opening polymerization resulting high molecular weight PLA with controlled optical and crystal purity. This method can be carried out using melt or solution intercalation method by cationic, anionic and coordination mechanism. Most method has focused on the ring opening polymerization to attain high molecular weight of PLA. This is due to the process is using high boiling point solvent to enforce removing water molecules in direct esterification process. The process is producing cyclic intermediate lactide dimer. It based on removing water components under milder condition. This monomer is ready to purify under vacuum-distillation. Production of cyclic lactide dimer will resulted three potential forms: the D,D-lactide (called D-lactide), L,L-lactide (called L-lactide) and the last one the D,L-lactide or L,D-lactide (called meso-lactide). The meso-lactide is not active because it has different properties (Jamshidian *et. al.*, 2005)

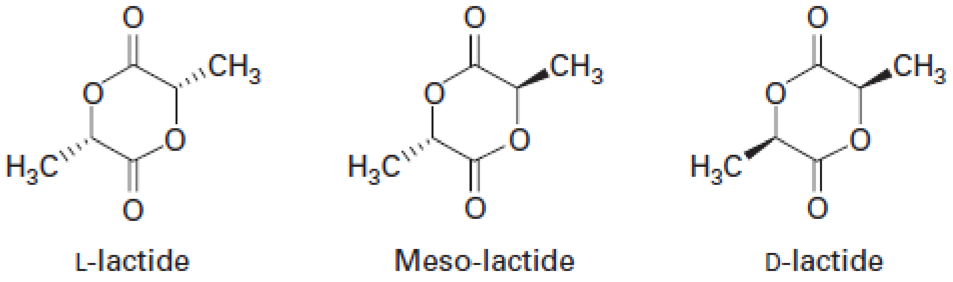


Figure 2.7: Dimer lactide isomers (Farrington *et. al.,* 2005)

Initially, the process is starting with producing low molecular weight pre-polymer PLA by continuous reaction of lactic acid. Pre-polymer PLA then converted into a mixture of lactide stereoisomers, undergo depolymerization using tin catalysis to form ring polymerization to enhance the rate selectivity of the intramolecular cyclization reaction. After ring polymerization is formed, the process is continued by purification process of molten lactide mixture using vacuum distillation. To produce high molecular weight of PLA, the ring opening polymerization is produced by melt intercalation method using a tin catalyst (Farrington *et. al.*, 2005)

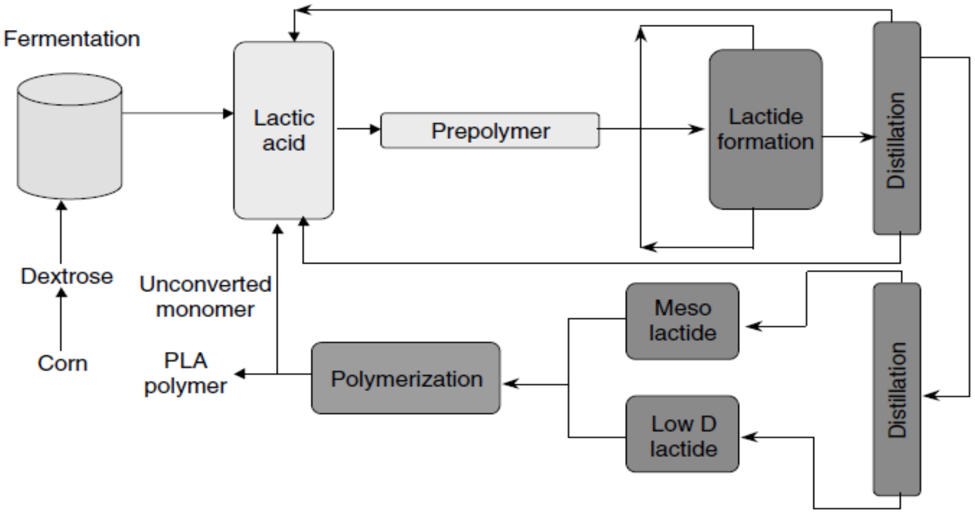


Figure 2.8: Non-solvent process to prepare PLA via prepolymer and lactide (Farrington *et. al.*, 2005)

2.6 Organoclay nanocomposite

Nanocomposite has same meaning with nanoparticles, which mean ultrafine particles in the size of nanometer order. ‘Nano’ is a prefix introducing the ninth power of ten, which is namely one billionth. Nanoparticles definition is wide; it is depending upon the materials, fields and application concerned. Features of nanoparticles are divided into two. It can be classified into activation of particles surface and increase of surface area. For activation of particles surface, all types of solid consist of atoms or molecules. As atoms and molecules are in nano-sized, they are affected on the materials characteristic and the properties are varies from those bulk solid of the same materials. Generally if the surface area is increased, it is proportionally reversible to the particle size (Hosokawa *et. al.*, 2007).

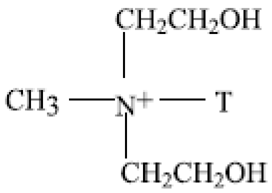
For instance, organoclay nanocomposite, calcium carbonate, calcium phosphate and hydroxyapatite are some examples of mineral fibres that usually used in industrial sector. Its purpose is to enhance the properties of polymer. There are many types of organoclay nanocomposite or montmorillonite (MMT) that commercially used as filler for preparing polymer nanocomposite. One common type of MMT is bis–(2–hydroxyethyl) methyl tallowakyl ammonium cations or Cloisite B30. The used of

Cloisite B30 has been proved by its ductility properties and polymer nanocomposite processing behaviour. Cloisite B30 tends to improve the surface characteristic, enhanced the crystallinity and at the same time raises the thermal behaviour of polymer nanocomposite. In other word, Cloisite B30 yields the best result in term of thermal stability and inter-galleries spacing dispersion between nanoclays (Paul, 2009).

Lewitus *et. al*. (2006) stated that, polymer nanocomposite based on organoclay layered have a great deal attraction because they exhibit improvement of physical properties if compared to the conventional pristine polymer. These improvements including enhanced of tensile modulus, increased of strength, toughness, heat resistance and gas retardancy, decreased permeability of gas and increased the degradation of polymer nanocomposite. Absence of organoclay layered relatively resulting poor tensile modulus as compared to the pristine polymer. Cloisite B30 is modification of natural MMT with quaternary ammonium salt. It functions as an additive to improve the various physical properties for plastics and rubbers.

Table 2.3: Properties of Cloisite B30 (Southern Clay Inc.)

Properties	**Characteristics**
Commercial name	Cloisite B30
Organic modified	Methyl, tallow, bis – 2 – hydroxyethyl, quartenary ammonium (MT2EtOH)
Modifier concentration	90 meq/100 clay
Moisture	< 2 wt%
Density	1.98 g/cm^3
Color	Off white
X – ray data	d_{001} = 18.5 Å



$$\begin{array}{c} CH_2CH_2OH \\ | \\ CH_3 - N^+ - T \\ | \\ CH_2CH_2OH \end{array}$$

Figure 2.9: Cloisite B30 chemical structural formula (Jiru *et. al.*, 2005)

Type of modified organoclay, Cloisite B30 and type of unmodified organoclay, Cloisite Na^+, were employed as inorganic phase. The polymer nanocomposite strength in the presence of Cloisite B30 was higher than the system of I.30 TC. This is due to the reduced of the chain mobility with introducing of Cloisite B30. In the other hand, the compatibility of Cloisite B30 with the matrix is better than I.30 TC. It is due to the hydroxyl group in the surface modifier, which is allowed better exfoliation to occur with the same amount of nanoclay concentration. It results the enhancement of the materials intensiveness based on Cloisite B30 as filler (Jiru *et. al.*, 2005).

2.7 Polylactic acid nanocomposite

The distribution of organoclay in PLA nanocomposite is proven to be well dispersed without introduce compatibilizing agents. This is due to the interaction of hydrogen bonding between ammonium groups in the inorganic ‘surfactant’ of the organoclay with the carbonyl group of PLA chain segments. There are also strong interactions between the PLA hydroxyl ends group and MMT platelet surfaces or the organically modified MMT, the hydroxyl groups of the ammonium surfactant (Balakrishnan *et. al.*, 2010).

The presence of organoclay represents as nucleation site. The nucleation site is function to ease the crystallization process of PLA. It produced small crystallites and lowers the crystallinity. Crystallinity controls the unique skin-core foam morphologies in PLA and PLA nanocomposite. Organoclay nanocomposite provides nucleation sites to generate foam morphology in PLA nanocomposite with high crystallinity (Liao *et. al.*, 2011)

2.8 Type of nanocomposite

Jiang *et. al.* (2007) defined that, to prepare polymer nanocomposite, it must use a co–rotating extruder equipped. The extruder with a gravimetric feeder and compound a strand of pelletizes of mixed polymer and organoclay. The temperature of the barrel of the extruder must be controlled properly to make sure the product yield of the polymer nanocomposite produce is in a well mixing composition. Before extrusion process, the pristine polymer and organoclay should be dried first to release the moisture trapped in the materials. The mixture of polymer and organoclay fed into the gravimetric feeder of extruder to melt compounding the materials. The extrudate is cooled in a water bath temperature and granulated by a pelletizer. Then, the compounded will be fed into injection molding to form desired shape.

The types of polymer nanocomposite are depending on the strength interfacial interactions between the polymer matrix and organoclay layered. The organoclay layeree that properly dispersed creates much higher surface area throughout the polymer matrix. There have three different types of dispersion of organoclay nanocomposite. It is intercalated nanocomposite, phase separated nanocomposite and exfoliated nanocomposite (Suprakas, 2003).

In figure 2.10 represents main types of nanocomposite structure for layered silicate materials. Phase separated nanocomposite structure will be obtained if the silicate sheets could not be penetrate between polymer matrix. The properties stay in the same range as dispersion in microcomposite. In an intercalated nanocomposite structure, silicate layers are dispersed between extended polymer chains. This will result a well-ordered multilayer morphology with alternating polymeric and inorganic layers. If the silicate layers are completely and constantly dispersed between the polymer matrixes, an exfoliated structure nanocomposite is obtained. The resultant of nanocomposite structure are significantly varies regarding to the physical properties (Hussain *et. al.*, 2006).

2.8.1 Intercalated nanocomposite

The insertion of organoclay structure into polymer matrix occurs in a crystallographically regular feature, regarding to the organoclay to polymer ratio. Normally, intercalated nanocomposite is interlayer by a few layers of organoclays between polymer matrixes. The properties of this type is typically resemble of ceramic tone (Suprakas *et. al.*, 2003).

2.8.2 Phase separated nanocomposite

Conceptually of this type of nanocomposite is almost same as intercalated nanocomposite structure. In addition, sometimes organoclay layers gather due to hydroxylated edge/edge intercalation (Suprakas *et. al.*, 2003).

2.8.3 Exfoliated nanocomposite

Exfoliated nanocomposite is a type of dispersion of organoclay nanocomposite that the organoclay layered structure is separated in a continuous polymer matrix that depends on organoclay loading by an average distance between organoclay and polymer matrix (Suprakas *et. al.*, 2003).

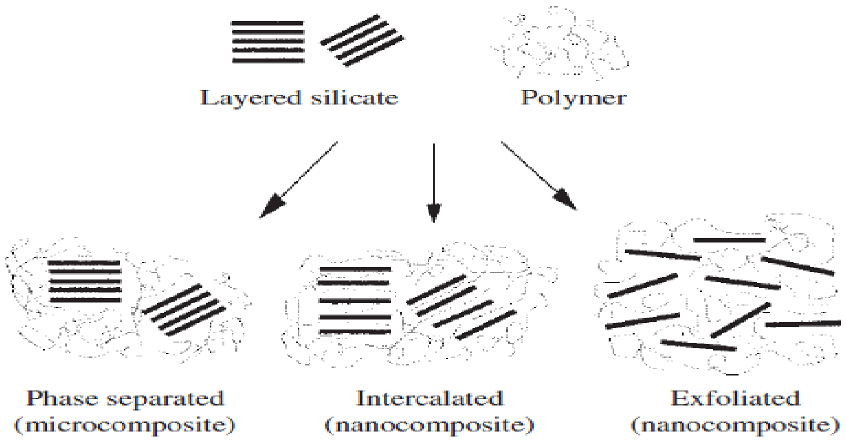


Figure 2.10: Scheme of three main types of layered silicates in polymer matrix (Hussain *et. al.*, 2006)

2.9 Type of intercalation polymerization

Intercalation polymerization is a method to mix together the polymer materials and organoclay nanocomposite. It has been successfully proven to synthesis polymer nanocomposite. The intercalation polymerization has been divided into three methods regarding to the processing techniques.

2.9.1 In-situ intercalation polymerization

In–situ polymerization is dispersion of organoclay which is called silicate layered particles. The silicate layered particles at first are dispersed in polymer matrixes and the mixture is polymerized. Typical silicate layered particles are commonly used is clay minerals such as MMT or originally large kaolin. Many laminated layers are in nanometers sized are formed by these silicate layered particles (Hosokawa *et. al.*, 2007).

For this type of polymerization, organoclay is swollen within the polymer layers and the polymerization occurs between the intercalated layers. It can be initiated either by heating or radiation. Other than that, it also can be done by diffusion of suitable initiator or by organic initiator or catalyst fixed through cation exchanged inside the interlayer of polymer matrixes before start the swelling step (Bhattacharya *et. al.*, 2008).

2.9.2 Solution intercalation polymerization

Solution intercalation has two processes transportation, namely solvent diffusion and chain disentanglement. In effort to understand the physics of dissolution mechanism of glassy polymers, it has several models that have been proposed for this kind of effort. It can be categorized as phenomenological, external mass transfer, stress relaxation and molecular theories, anomalous transport models and scaling laws and molecular theories in continuum framework. Those approaches have incorporated phenomena as stress relaxation, polymer viscoelasticity and chain disentanglement, anomalous transport of solvent, chain reputation and external mass transfer limitations. Other than that, many experimental techniques have been done to characterize polymer dissolution behaviour and molecular properties of solvent and polymer matrix (Chou, 2002).

In other word, each polymers will soluble in specific solvent for instance chloroform, acetone, dimethyl chloroform, toluene or others meanwhile organoclay layers are swellable between the layers of polymer matrixes. The polymer chains intercalate and organoclay layer displaced the solvent after the mixing process of the polymer chain and organoclay solution is done. Actually this method is well used for non-polar or less polarity of the polymer chains. Silicate layered is facilitates into polymer matrixes and finally formed intercalated layer of polymer nanocomposite (Suprakas, 2003).

2.9.3 Melt intercalation polymerization

Nowadays, melt intercalation polymerization method is the best method amongst other polymerization method. This is due to this type of polymerization is environmental friendly. Melt intercalation polymerization is including blending and annealing process. It is not contain any organic solvents. In addition, melt intercalation polymerization also an economically favourable method for industries from waste perspective. Other than that, melt intercalation is compatible with current industrial process such extrusion and injection molding. This type of polymerization is able to replace other types of polymerization that is not eco-friendly. Melt intercalation leads to make new hybrids that previously inaccessible and it is highly specific for producing polymer nanocomposite (Suprakas, 2003).

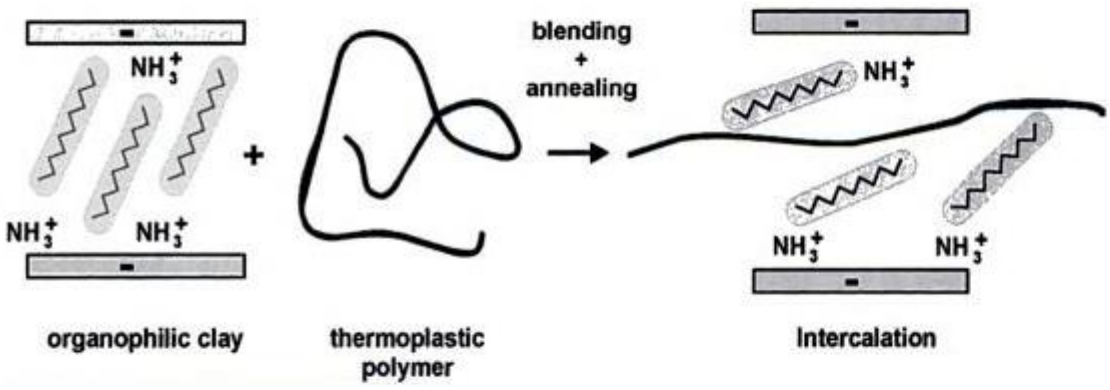


Figure 2.11: Melt intercalation polymerization method (Zaikof *et. al*, 2005)

2.10 Synthesis the samples

The polymer matrix and organoclay are mixed together using extrusion and injection molding. The mix compounds will be press using shear forces to make the compounds dispersed well while formed polymer nanocomposite (Brody, 2003; Chen, 2004).

2.10.1 Extrusion

Before processing, the samples (PLA and organoclay nanocomposite) are dried for duration 24 hours with temperature 90 ^{o}C. The mixed compounds are processed into extrusion machine with five heated zones and die end. The mixed composition ratios were maintained at composition as stated in table 2.4. (Ratto *et. al.*, 1999).

Table 2.4: Designation of materials and their compositions

Compositions	PLA (%)	B30 nanoclay (%)
Pristine Polylactic Acid	100	0.0
Polylactic Acid/B30 nanoclay	99.5	0.5
Polylactic Acid/B30 nanoclay	99.0	1.0
Polylactic Acid/B30 nanoclay	98.0	2.0

The polymer and organoclay is melting while being spun by using a twin screw extruder. This equipment will equipped with a cooling jacket to prevent the mix polymer nanocomposite become flake during melting process along the barrel zones. Initially, polymer spun through a single nozzle circular spinneret. Along the twin screw extruder, there are a few types of spinneret to blend the mixer. The heaters at every barrel are function to supply heat to melt the polymer and organoclay together. Then, at the end of the extrusion, the well mix polymer nanocomposite will be collected on a glass drum (Fambri, 1996).

2.10.2 Injection molding

The way to prepare samples without using solvent intercalation method is by using injection molding. This method is suitable to add any additives for accelerated degradation (Kumar, 2010). Injection molding is the most important method for thermoplastic polymers. Injection molding is widely used to change the polymer nanocomposite into different complex shapes and requires high dimensional precision. All types of injection molding consist of screw to plasticize the melted polymer. In contrast of standard extruder, the extruder unit in injection molding machine is designed as the polymer nanocomposite can be mixed to prepare for delivering the melted polymer into the mould cavities. This method is based on the ability of thermoplastic polymers can be melted by heat and harden while cooled. The process thus consisting heated cylinder that the polymers are cooled essentially and injected into the mould cavity under pressure, where the polymers harden after cooling. The melted polymers are carried out in separated barrel zones in the same injection molding machine (Chanda *et. al.*, 2006).

The beginner stages of injection molding process cycle is usually the mould closed. After the moulds clamp up, immediately the nozzle opens and the screws in the injection molding starts to move forward and ready for injecting the melted polymer into the mould cavities. The screw is maintained in the forward position by holding pressure inside the machine while the melted polymer is being cooled in the mould cavities. At the end of the holding phase, the nozzle is shut off and the screw begins to recover. To ensure that the part injected is in the stable enough withstand the opening stroke the moulds, sufficient cooling time is needed. In the process cycle, heat removal takes place predominantly during the fill, hold and cool phase (Lim *et. al.*, 2008).

Based on Jiang (2007) writing’s, standard tensile testing samples were moulded by using injection molding process. Barrel temperature from the feeding section to the nozzle was set in different temperatures setting. Meanwhile for mould temperature was 30 ^{o}C and cooling time was about 30 seconds. The pellets prepared by extruder were dried in a convection oven at temperature 90 ^{o}C for 24 hours.

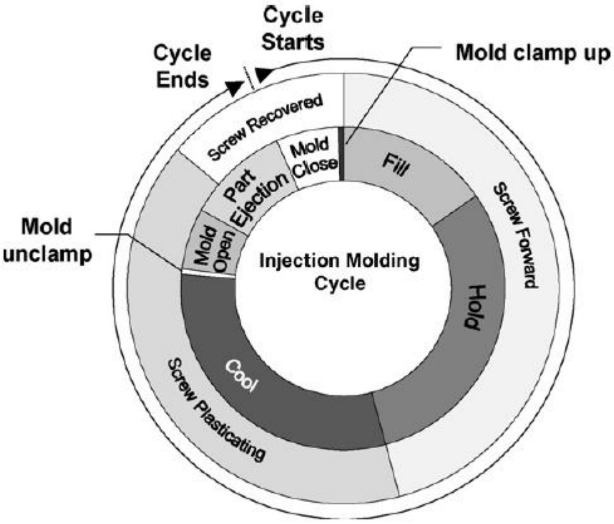


Figure 2.12: Typical cycle for an injection molding process (Lim *et. al.*, 2008)

2.11 Morphological analysis

The major components of polymer form are the polymer chains meanwhile the minor components are dispersed phase of organoclay. To analyse the morphology structure of polymer blends, equipment that usually used is Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Wide Angle X–ray Diffraction (XRD). The analysis has various average pore diameters with organoclay content for different compositions of polymer nanocomposite. A better dispersion and homogeneity of polymer nanocomposite arises from the formation of branched and crosslinked between the polymer and organoclay compound (Wu *et. al.*, 2005).

2.11.1 Scanning Electron Microscopy (SEM)

SEM is used to study the morphological structure of polymer nanocomposite. The views of SEM are on the fractured samples after tensile strength test. SEM function is to observe the dispersion of the organoclay between polymer matrixes. In addition, samples can be viewed in three dimensions. The SEM is different from the TEM. SEM is transmitting the beam to scan across the surface of the specimen. Then, the energy is increased by releasing the secondary electron from the specimen and then detected by a phosphor screen resulted the images shown (McMullan, 1993).

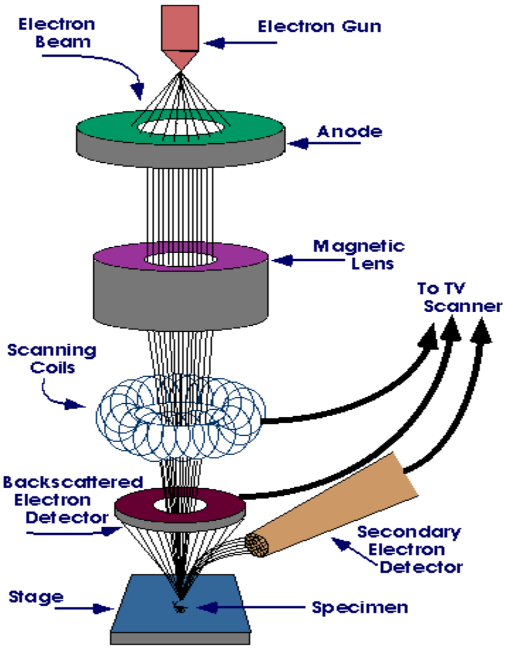


Figure 2.13: Schematic illustration of SEM procedure (Purdue University, 2010)

SEM is produced great images at low resolution. But the images of analysis is failed to give the detail required to determine the accurate of the exfoliation particles. However, the images provide a much better feel of the particles in 3D space. Figure 2.14 demonstrates the dispersion of the nanoparticles meanwhile figure 2.15 shows the resolution of the nanoclays dispersion using SEM is very difficult to determine even using the highest magnification (Snyder, 2007).

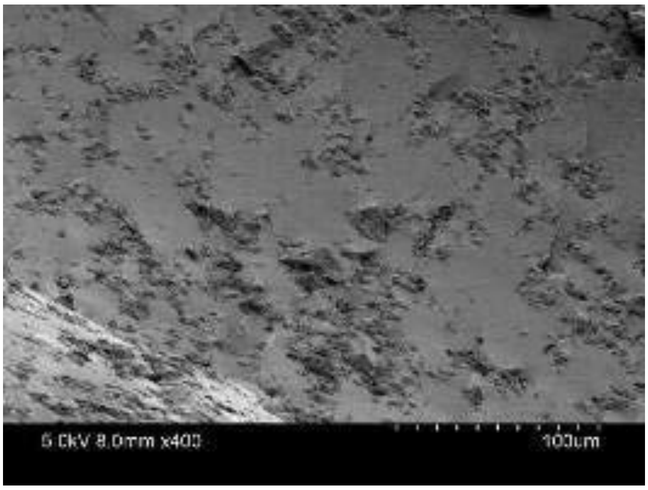


Figure 2.14: Dispersion of the nanoparticles (Snyder, 2007)

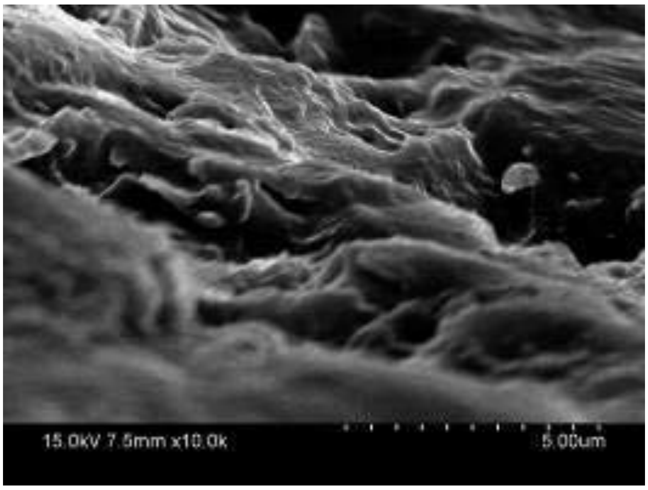


Figure 2.15: Resolution of the exfoliation of particles (Snyder, 2007)

2.11.2 Transmission Electron Microscopy (TEM)

TEM can observe a small portion of the samples, which may not representative by SEM resolution. The morphological analysis can be obtained by using TEM if quantitative bulk measurement is definitely preferred. Some bulks measurements have been used to complement TEM include small and ultra small angle X-ray scattering, infrared spectroscopy and rheological measurement. Low and high magnification micrographs of TEM can be presented.

The overall dispersion of organoclay can be emphasizes for low magnification micrographs emphasizes. Meanwhile the observations of the silicate layers are allowed to be observed by high magnification micrographs (Zhang *et. al.*, 2008). A TEM function is to analyze the polymer nanocomposite films which is the silicate layered between polymer matrix and hollow shells (Orozco *et. al.*, 2010). TEM is time intensive and gives qualitative information on the samples.

(a) (b) (c)

Figure 2.16: TEM images of three different types of nanocomposite (a) Intercalated nanocomposite structure (b) Phase separated nanocomposite structure (c) Exfoliated nanocomposite structure (Ray *et. al*., 2003)

2.11.3 X-ray Diffractometer (XRD)

XRD is the most basic method is function for characterizing the crystal structures of polymer nanocomposite. The properties of the materials might be affected by the structures of several to several hundreds nanometer scale meanwhile the arrangement of atoms are separated by 0.1 nm. Evaluation of crystal structure is generally important even for the nanoscale materials (Hosokawa *et. al.*, 2007).

Figure 2.2 represents different structure in organoclay layered in the polymer nanocomposite. It shows three maxima peak intensity for the Cloisite B30. For clay volume 0.5 %, there is no maximum intensity was observed. The maxima are poor for clay volume 1 % and 3 %.

Inter-galleries spacing, which is d-spacing was observed. The highest intensity value was noted for 20 % of organoclay concentration. This fact may indicate that the intercalation nanocomposite type was found in the clay structure, but if the concentration of the clay primary particles is too high, possibility exfoliation nanocomposite is formed. Comparing the polymer nanocomposite of 10 % and 20 % of Cloisite B30, 20 % Cloisite B30 demonstrates decreasing for interlayer distance (Kalendova *et. al.*, 2009).

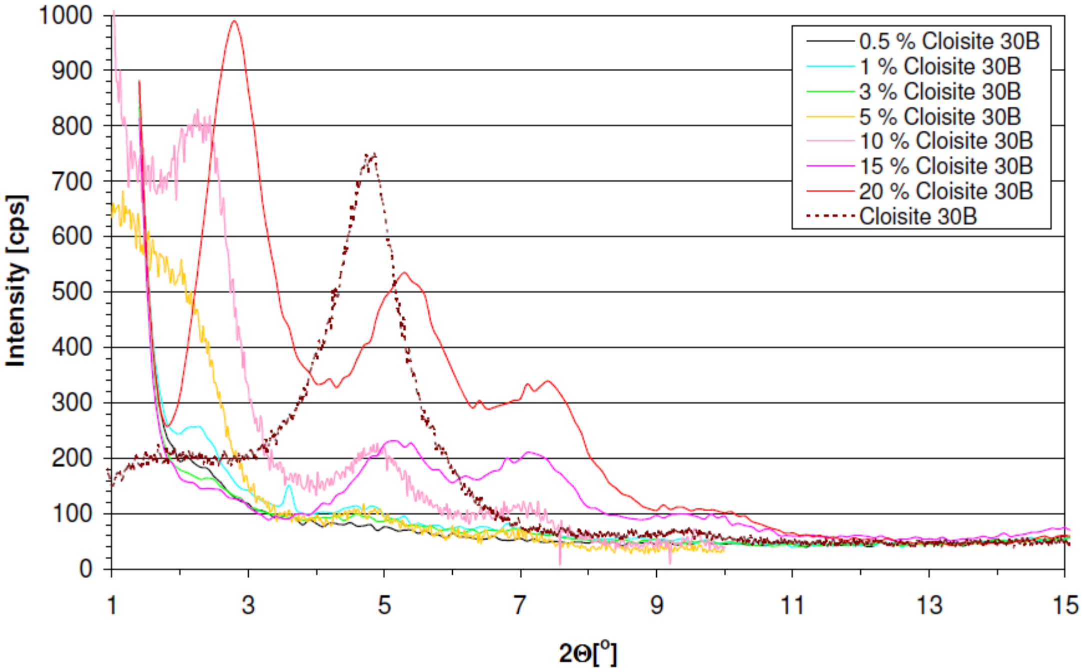


Figure 2.17: XRD Patterns Cloiste B30 / PVC (Kalendova *et.al.*, 2009)

2.12 Biodegradability analysis

This analysis is to examine the biodegradability rate of polymer nanocomposite sheet under several environments test. The aim of this analysis is to investigate the biodegradability of polymer nanocomposite after discarding in natural conditions such as real environments, water waste treatment, landfill conditions, composting plant conditions and controlled composting conditions in laboratory. The testing polymer nanocomposite sheets are visually inspected for colour and shape after the samples taken from the tested area for certain range of time (Rudeekit *et.al*, 2009).

The biodegradability of PLA nanocomposite is not only depends on their molecular weight. To lead the final mineralization of substances, it is depends on a huge different enzymes located in various species of microorganism, encoded in their genomes or plasmids in required for the numerous catabolic pathways. The test result will be different if the investigation is done in different methods. Using different inocula in the testing also can affect the result. But, normally test will produce similar test result if either easily or poorly biodegradable materials. Instead of the natural environments, biodegradable also occur to water or soil sediment situations. However, analytical reasons much more difficult to determine biodegradability compared to aquatic test (Pagga, 1997).

Degradation of polymer occurs step by step. Starting of the degradation, water molecules will diffused into the polymer nanocomposite materials. Then, it will hydrolysed ester bonds in the polymer nanocomposite and lowering the molecular weight of polymer nanocomposite followed by intracellular uptake of lactic acid oligomers and catabolism. Rate of hydrolysis increased with humidity and temperature and the chain catalyzed by free carboxyl groups of the hydrolyzed PLA ends (Shogren *et. al.*, 2002).

2.12.1 Accelerated weathering testing

The process of weathering involves the nature and agents. It can be classified into two types. It is mechanical weathering and chemical weathering. Types of mechanical weathering are exfoliation, abrasion, and freeze and thaw weathering. For the chemical weathering type is hydrolysis, oxidation, hydration, carbonic acid action (Ritter *et.al*, 2007).

According to the highest cost of the natural weathering in various climates, there are another alternative method to test the biodegradability of the polymeric materials using solar radiation. This testing is important to know how the material will react to extreme climate in the world. In the moderate climate zone off such as Central Europe, outdoor weathering will often be preferred to get a realistic idea of the material's characteristics and to keep the demands placed on resistance to weathering from driving up costs unexpectedly. For economic reasons, it is impossible to wait for years to obtain the results of the outdoor weathering. So, there is a reason for using accelerated weathering tester in the laboratory. This is purposing to identify and measure the same changes in the properties of polymeric materials that would apply under the same conditions as outdoor weathering during the normal service life of these materials. In connection of aging of the polymeric materials, the samples only absorbed the radiation that considerably causes the material heat up is the interest. The radiation only absorbed only by a small portion. This gives rise to primary processes, such as the formation of excited states, radicals and chain scission. Quantum yields for the chain scission of plastics have been measured in the range of 10^{-2} to 10^{-5}. Just one with scission will respond when 100 to 100,000 polymer molecules have absorbed the accelerated weathering radiation. Other than general practice, accelerated time testing is poses to the quite danger of radiation to initiate degradation processes on the polymeric materials, apart from the desired natural acceleration of aging processes. But, for the changes act on the materials outdoors might not same extent as the accelerated weathering (Roger Brown, 1999).

2.13 Mechanical analysis

Mechanical testing can be done by several testing such as Young' modulus, elongation, yield strength, Tensile and Brinell strength, twist and bending testing and hardness testing using Rockwell. All the testing were determined using samples of dumbbell sized, produce by the injection molding process and the samples are loaded by mechanical testing with the testing load. The testing is being done in room temperature with 50 % relative humidity (Lewitus, 2006).

2.13.1 Tensile strength testing

Several dumbbell shape samples of every composition of polymer nanocomposite films were used to be tested under several conditions. The films are exposed to different relative humidity for at least 14 days and some samples were dried at 55 ^{o}C for 24 hours. After removing the films from each condition, each film has been tested immediately for tensile strength testing (Ratto *et. al.*, 1999).

The strength and modulus increased if the organoclay is added into the PLA. If the organoclay is well dispersed in the polymer matrix it will result the increasing of tensile strength of the polymer nanocomposite. The organoclay is mainly attributed between the polymer matrixes. In the previous research, when the organoclay was introduced to the PLA, the result has no significance changes in tensile strength. Meanwhile, when the synthetic polyester was added as a carrier of the organoclay into the main polymer, the tensile strength of the polymer nanocomposite wil decrease compared to the pristine PLA. This due to the filler adding purpose, to increase the tensile strength and hardness of the polymeric materilas (Lewitus *et. al.*, 2006)

The pristine PLA samples broke without necking. For PLA nanocomposite or nano-sized precipitated calcium carbonate (NPCC) nanocomposite resulted with no necking with stress whitening across the whole gauge length. Yield stress decreased with NPCC loadings and visually observable stress whitening in the middle of the samples. Besides, with addition of NPCC, the samples showed a slight increase of Young's modulus. For PLA/MMT nanocomposite obtained a slight increase in yield stress. The samples showed intense stress whitening followed by necking. PLA/MMT nanocomposite broke in brittle manner without yield any whitening stress on the sample. The research found that if the concentration of MMT increased Young's modulus significantly increased too. Figure 2.18 shows the graph of tensile yield strength and Young's modulus of PLA/NPCC and PLA/MMT nanocomposite (Jiang *et. al.*, 2007).

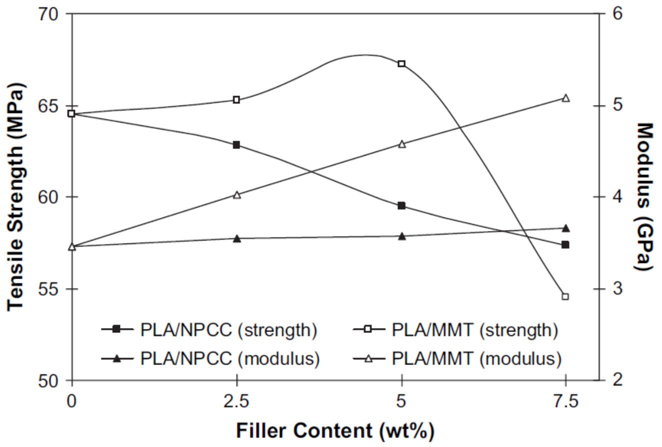


Figure 2.18: Tensile yield strength and Young's modulus of PLA/NPCC and PLA/MMT nanocomposite (Jiang *et. al.*, 2007)

CHAPTER THREE

METHODOLOGY

3.1 Introduction

In order to form, characterize, analyse and testing PLA nanocomposite, there were several methods that should be followed. The PLA nanocomposite will be prepared by melt intercalation method using twin screw extruder. Then, the PLA nanocomposites are being characterized by using TEM and XRD. To analyze the biodegradability of PLA nanocomposite, biodegradability test is conducted using accelerated weathering test and the samples are examined by mechanical testing. The samples before and after accelerated weathering test are compared to gain the result for biodegradable degradation.

3.2 Materials

PLA trade name is 2100D and Cloisite B30 is the main material used for this research. PLA (molecular weight, Mw; 74500 g/mol, density; 1.33 g/cm^3, index of polydispersity, M_w/M_n; 2.0, L/D isomer ratio of 96/4, melting point; 169 ^oC) is obtained from NatureWorks LLC, USA meanwhile Cloisite B30 (ignition temperature; 190 ^oC, melting point; decomposes at approximately 200 ^oC, specific gravity; 1.9 – 2.1 g/cc) is obtained from Southern Clay Products Inc., USA.

3.3 Nanocomposite Preparations

For the experimental purpose, both of PLA and Cloisite B30 were dried at constant temperature, 90 ^{o}C in an oven for duration of 24 hours. After the preparation, the samples were kept in the desiccator to prevent PLA adsorb humidity from the surrounding. The weight percentage ratio of the PLA and Closite B30 are as followed:

Table 3.1: Designation of materials and their compositions

Compositions	PLA (%)	B30 nanoclay (%)
Pristine Polylactic Acid	100.0	0.0
Polylactic Acid/B30 nanoclay	99.5	0.5
Polylactic Acid/B30 nanoclay	99.0	1.0
Polylactic Acid/B30 nanoclay	98.0	2.0

Figure 3.1: The PLA was kept in the desiccator

According to Table 3.1, the PLA compound was direct melt mixed by incorporating both of the components simultaneously using Thermo Scientific Prism EUROLAB 16 Twin Screen Extruder. The barrel partition temperature profile during mixing of all the components was configurated at 190 ^{o}C, 200 ^{o}C, 200 ^{o}C, 200 ^{o}C and 180 ^{o}C while the dies temperature was set to 170 ^{o}C. The speed of the screw rotation was maintained consistently at 35 rpm and the barrel pressure was held at 26 bars.

Figure 3.2: Thermo Scientific Prism EUROLAB 16 Twin Screen Extruder

In order to produce samples for later mechanical test, the pelletized PLA nanocomposite were processed by using the NS 20 Nessei injection molding machine with a barrel temperature range from 180 °C to 200 °C with a pressure of the machine is valued at 50 %, injected volume at 8 %, cooling time duration for 20 seconds, loading time for 1.8 seconds as well as total cycle time which is 0.5 seconds.

The samples were produced in dumbbell shape with the dimension of 3.96 mm thick and the middle width of 2.96 mm. All the obtained samples must be stored under ambient conditions for at least 48 hours prior to testing. This step is necessary to be done in order to prevent PLA from absorbing humidity in the air and indirectly affected its mechanical strength due to the biodegradable properties of the polymer. In general, this method of storage is conducted solely to ensure precision of the mechanical testing result.

Table 3.2: Barrel temperature profile for PLA nanocomposite for injection molding

Barrel section	Temperature profile (°C)
Rear	185
Middle	190
Front	183
Nozzle	177

Table 3.3: Setting for PLA nanocomposite injection profile

Type of setting	Time (s)
Injection time	1.80
Cooling time	20.00
Cycle system time	0.50
Filling time	2.25
Plasticity time	5.17

Figure 3.3: NS 20 Nessei injection molding machine

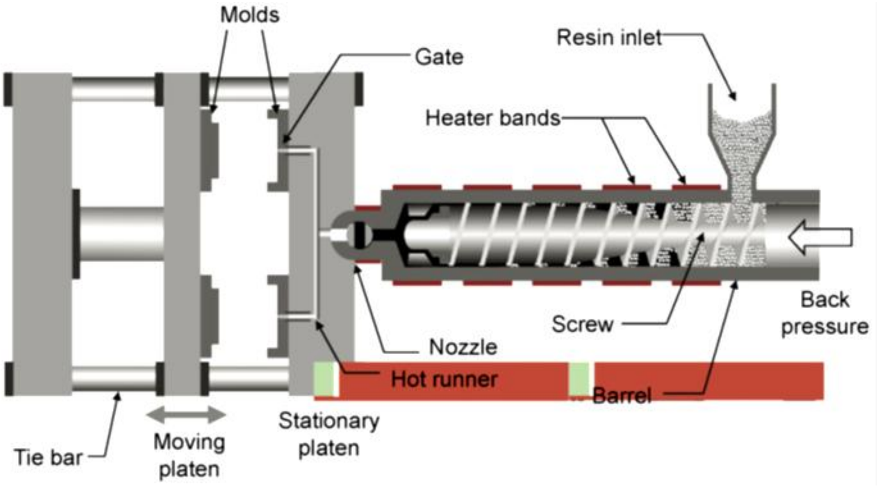
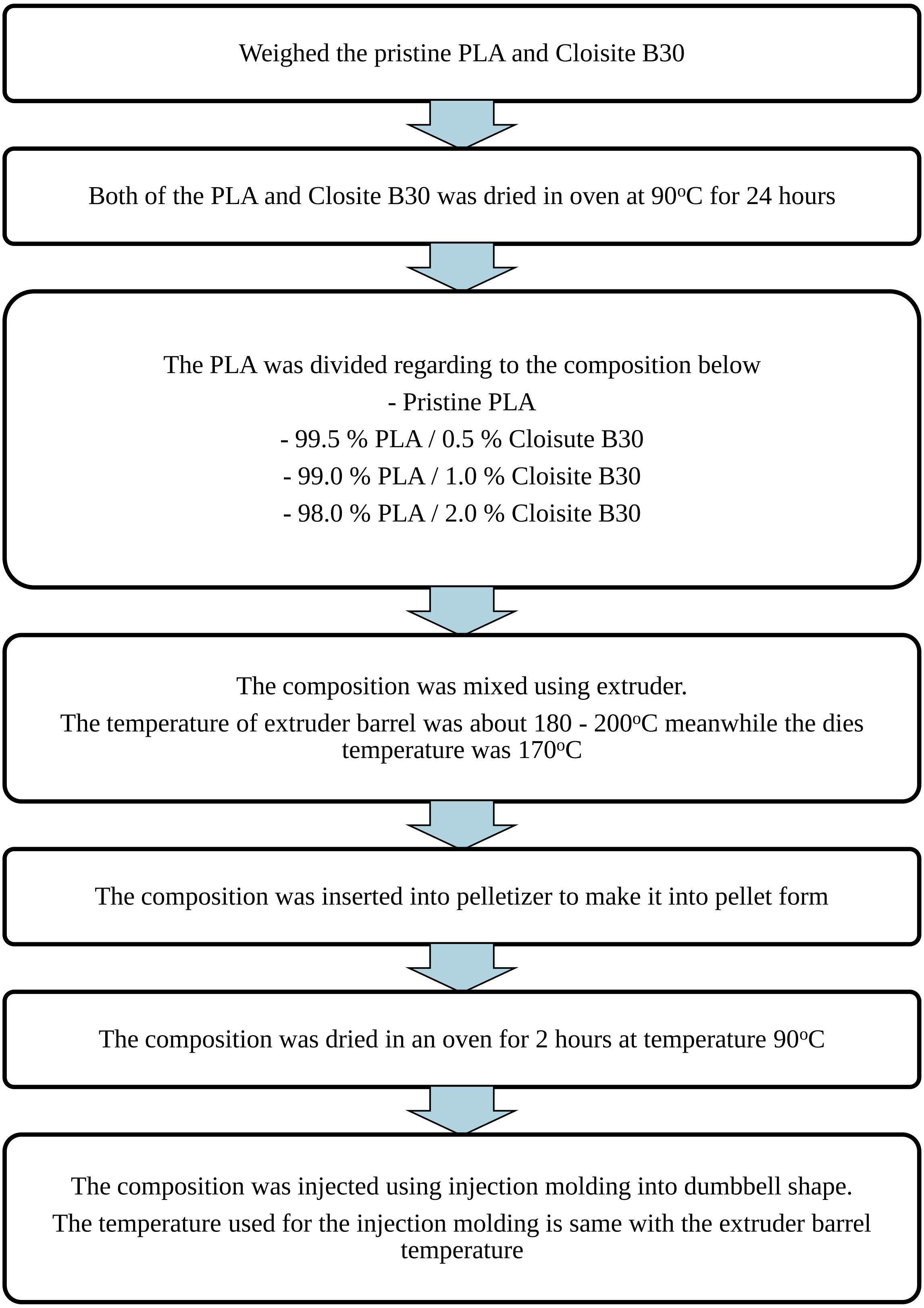


Figure 3.4: Major components of an injection molding machine (Lim *et. al.*, 2008)



Weighed the pristine PLA and Cloisite B30

Both of the PLA and Closite B30 was dried in oven at 90°C for 24 hours

The PLA was divided regarding to the composition below

- Pristine PLA
- 99.5 % PLA / 0.5 % Cloisute B30
- 99.0 % PLA / 1.0 % Cloisite B30
- 98.0 % PLA / 2.0 % Cloisite B30

The composition was mixed using extruder.

The temperature of extruder barrel was about 180 - 200°C meanwhile the dies temperature was 170°C

The composition was inserted into pelletizer to make it into pellet form

The composition was dried in an oven for 2 hours at temperature 90°C

The composition was injected using injection molding into dumbbell shape.

The temperature used for the injection molding is same with the extruder barrel temperature

Scheme 3.1: Step to prepare PLA nanocomposite

3.4 Morphological studies

3.4.1 X–ray Diffraction Analysis (XRD)

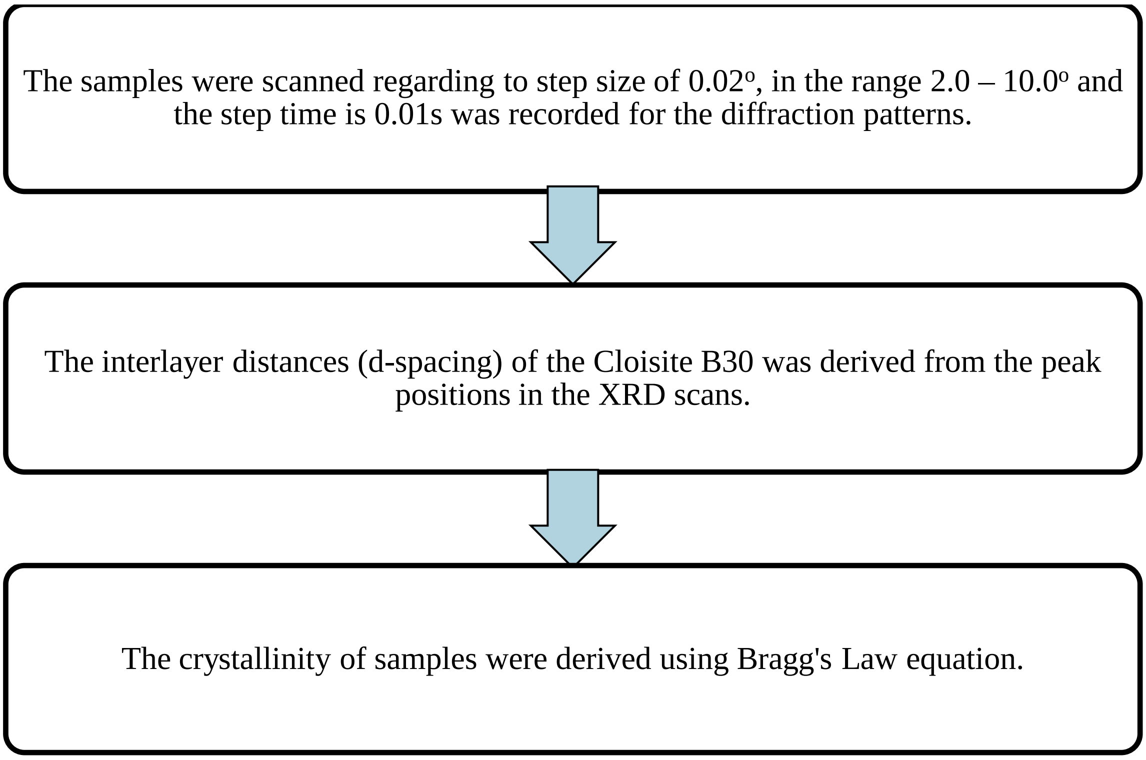
X–ray diffraction relies on the spacing of the scattering bodies and wavelength of the incident radiation. The diffraction that was stated by the Bragg's law was only can be observed when the incoming x–ray beam was emitted on a set of planes make a specific angle. The size of the molecules which is built up the structure can be determined by the angle that depends on the inter-plane spacing, d.

Rigaku Miniflex 2 Diffractometer was used to analyse the crystallinity of the polymer structure. The samples were scanned regarding to step size of 0.02^{o}, in the range 2.0 till 10.0^{o} and the step time 0.01s was recorded for the diffraction patterns. The interlayer distances (d-spacing) of the Cloisite B30 was derived from the peak positions in the XRD scans, according to Bragg's Law equation:

$$n\lambda = 2d\sin\theta \qquad -(1)$$

where n = an integer
d = inter–plane spacing
θ = the diffraction angle giving the primary diffraction peak
λ = the X-ray wavelength

Figure 3.5: XRD Miniflex by Rigaku model



The samples were scanned regarding to step size of 0.02^{o}, in the range 2.0 – 10.0^{o} and the step time is 0.01s was recorded for the diffraction patterns.

The interlayer distances (d-spacing) of the Cloisite B30 was derived from the peak positions in the XRD scans.

The crystallinity of samples were derived using Bragg's Law equation.

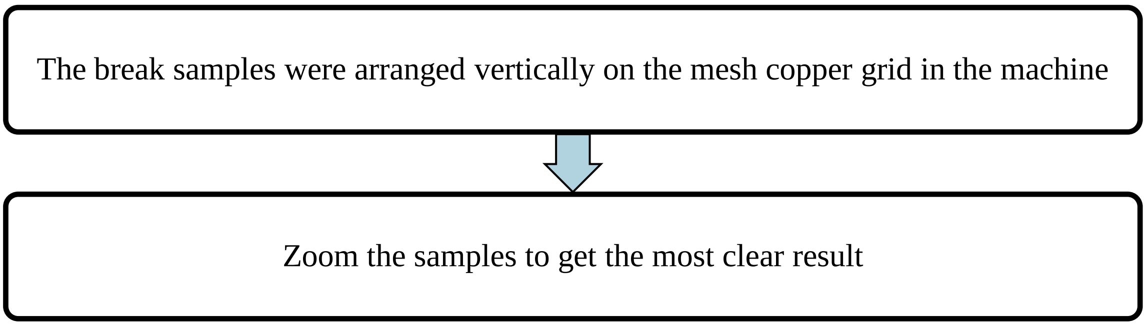
Scheme 3.2: The step for XRD analysis

3.4.2 Scanning Electron Microscopy (SEM)

The break samples were arranged vertically on the mesh copper grid in the machine. SEM was taken with a CARL ZEISS EVO Analytical Field Emission Scanning Electron Microscope. The views were taken for 1000x and 2500x magnification.

Figure 3.6: CARL ZEISS EVO Analytical Field Emission Scanning Electron Microscope

There are three principles for SEM analysis. SEM is the means of a focusing beam of electron and an electron gun on the specimen. Thus, the electron beam diameter about 5 to 10 nm was demagnify using a system of electron magnetic lenses across the specimen. For the last principle is detecting the response from the specimen and a display system.



Scheme 3.3: Flow for morphological testing

3.5 Biodegradability testing

3.5.1 Accelerated weathering testing

Figure 3.7: QLAB Accelerated Weathering Tester Model QUV/Spray with Solar Eye Irradiance Control

Q – LAB Accelerated Weathering Tester Model QUV/Spray with Solar Eye Irradiance Control is used to determine the degradation of the samples according to weather outdoor. The samples were the produced by injection molding machine. The PLA nanocomposite samples were attached to the aluminium panels to make array of the samples. For accelerated weathering test, the samples are tested on the UV alone, spray alone and condensation that represent the weather outdoor.

Figure 3.6 shows the accelerated weathering tests schematic. The power supply is electrical supply for the UVA lamp. The UVA lamp can be assume as UV solar by the sunlight. The samples were placed at the aluminium panels for exposing the samples to the UVA lamp. The samples condition must face the UVA lamp. To make sure there will be no accident while using the instrument, the power supply should be switching off before open the lid of the instrument. The direct UVA light can cause blindness.

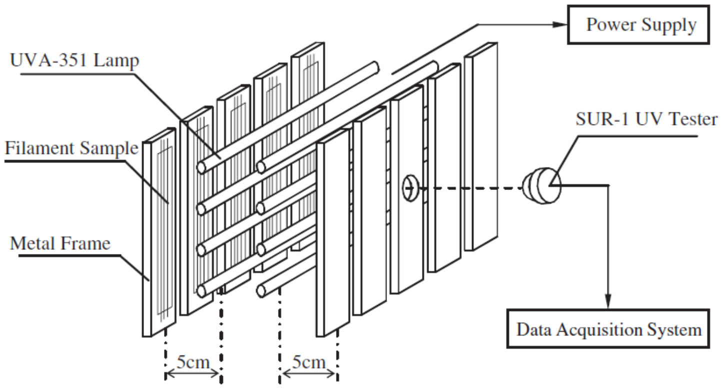


Figure 3.8: Schematic of the testing setup of accelerated weathering tests (Q – LAB Accelerated Weathering Tester brochure)

The samples produced by injection molded

The samples were attached to the aluminum panels to make arrays of the samples

The samples are tested on the UV alone, spray alone and condensation that represent the weather outdoor

Scheme 3.4: Flow work for accelerated weathering test

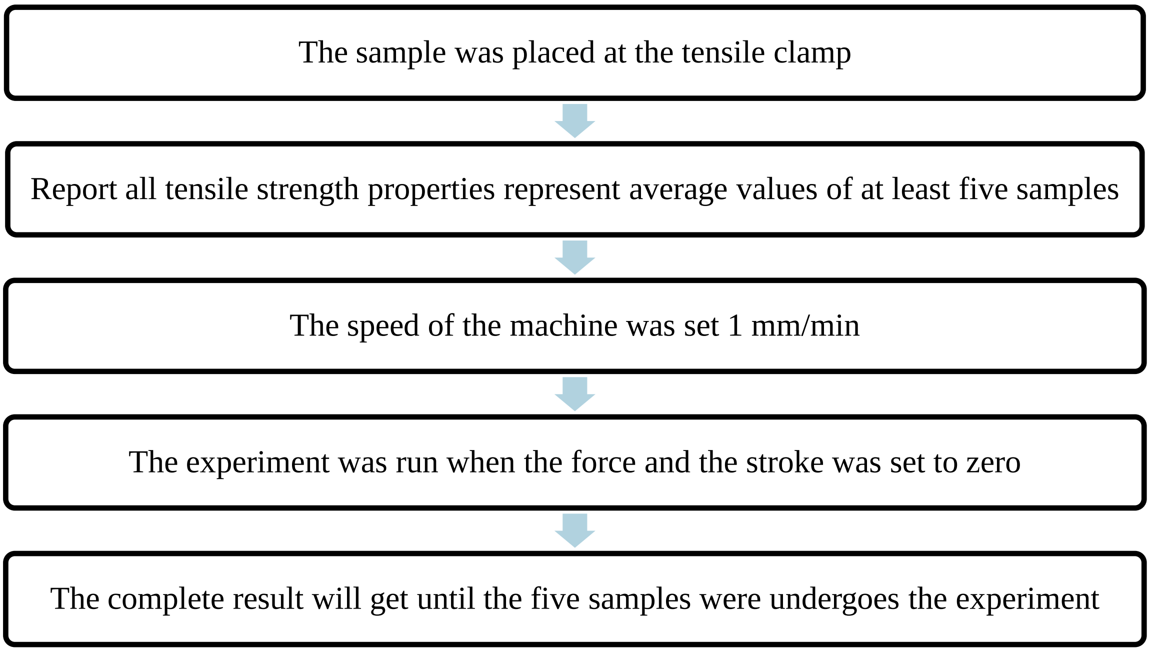
3.6 Mechanical studies

3.6.1 Tensile strength testing

Tensile strength on the PLA nanocomposite were carried out at the room temperature under ambient condition using Shimadzu Universal Testing Machine with cross – head speeds of 1 mm/min. Specimens with a gauge length 24.08 mm, middle width 2.96 mm and thickness 3.96 mm is follows the standard D638V as recommended in room temperature with 50 % relative humidity. The samples were placed at the tensile clamp and at the end of one segment will pull the samples until it break down. Then, the tensile strength analysis of the samples can be determined by the pull off force. A fracture line always occurred approximately in the centre of the samples.

The purpose of this test is mainly to measure the tensile strength, toughness and Young's modulus by exerting pull force onto one segment of the samples. PLA nanocomposite properties such as elasticity and plasticity behavior could be demonstrated by using this approach. During the tensile strength testing, the samples will be pulled to maximum elongation point at which the sample would initially experience a fracture and finally the sample will be broken into two segments.

Six samples were needed to determine the average values of tensile strength properties of PLA nanocomposite. Hence, six measurements were taken for each sample and the data were averaged to obtain a mean value. The speed of the machine was set at 1 mm/min. As the value of the force and stroke reach zero, the mechanical testing is initiated. The same described procedure was used to test the samples after the weathering effect.



The sample was placed at the tensile clamp

Report all tensile strength properties represent average values of at least five samples

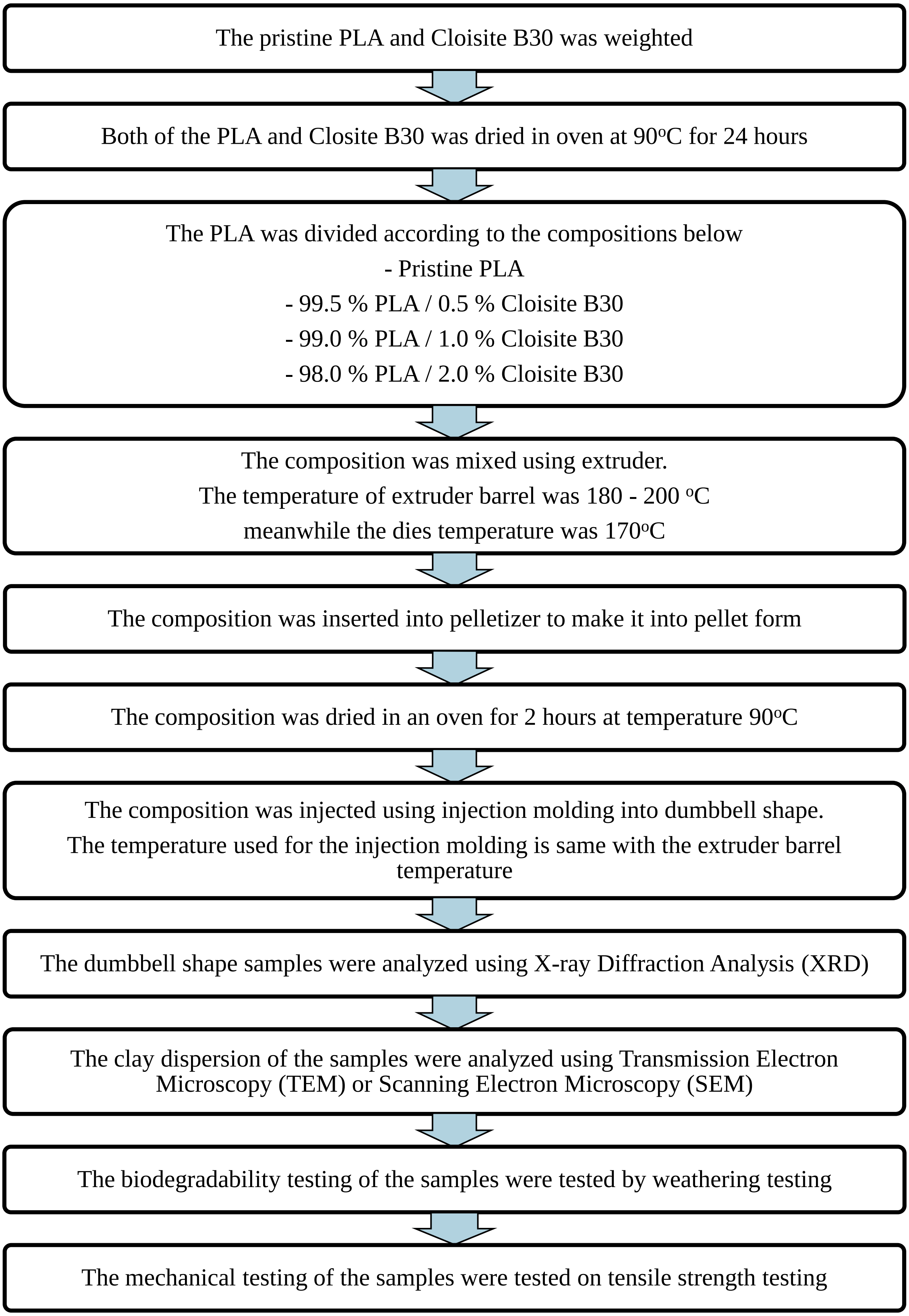
The speed of the machine was set 1 mm/min

The experiment was run when the force and the stroke was set to zero

The complete result will get until the five samples were undergoes the experiment

Scheme 3.5: Flow diagram for tensile strength testing

Figure 3.9: The samples was tested using Shimadzu Universal Testing Machine following ASTM D638V recommendation



Scheme 3.6: Overall flow diagram of the research

CHAPTER FOUR

RESULT AND DISCUSSION

4.1 Introduction

Nowadays, based on their facile availability and good biodegradability of PLA, it appears to be the most attractive biopolymer. PLA can be obtained by the petrochemical route process and available from renewable resources. PLA is commercially used for food packaging, biomedical, pharmaceutical industry and agricultural sector because of its biodegradable behaviour. That is the reason PLA has a great potential with respect to the application (Fukushima *et. al.*, 2008). PLA is a thermoplastic, high strength and high modulus polymer. It is easily processed on standard plastics equipment to yield moulded part. PLA is degraded by simple hydrolysis of the ester bond. The process does not require any enzymes to catalyze this degradation process. The rate of degradation is dependent on the size and shape of the products, the isomer ratio and the temperature of hydrolysis (Garlotta, 2002). This chapter will elaborate the result while the research was being conducted. The result based on the tensile strength testing, SEM analysis, XRD analysis and accelerated weathering test samples tested using tensile strength testing.

4.2 Morphological analysis

Morphological analysis is an analysis to view the structure and characteristic of the materials. There has interaction between the polymer matrix and silicate layered. This interaction had larger impact in polymer nanocomposite due to the large interfacial area between the silicates layered (Gacitua *et. al.*, 2004). At the end of this study, the type of nanocomposite can be determined. The most desired type is exfoliation nanocomposite since its characteristic is homogenous dispersion and separated in a continuous polymer matrix. The exfoliation nanocomposite has better physical properties such as stiffness and strength with far less inorganic content than the intercalation nanocomposite. It is rationalized that the greater enhancement of these properties was contributed by the higher degree of exfoliation in polymer nanocomposite.

4.2.1 Scanning Electron Microscopy (SEM)

SEM is to analyse fracture surfaces of broken samples of tensile test. SEM shows the magnified images to obtain the silicate layered dispersion between polymer matrixes and to observe the scattering images of the fracture samples. The images were viewed with magnification for 1000 and 2500 times taken. The SEM captures are at low resolution resulted great views but the images taken still could not confirm the dispersion of silicate layered precisely. Same goes as Yu *et. al.* (2006) findings, by SEM studies, there is no evidence of phase separation of the blends was observed exactly. The clearer observation of the dispersion of the silicate layered can be easily obtained in the TEM analysis. During running the research, TEM was not available.

The strength of interfacial interactions between the polymer matrix and silicate layered that usually obtained is intercalated nanocomposite and exfoliated nanocomposite. Intercalated nanocomposite is the insertion of the stacks of silicate layered into the polymeric materials structure occurs in a crystallographically regular dispersion and usually interlayers by a few molecular layers of polymer. Meanwhile, exfoliation nanocomposite is the individual organoclay dispersed in continuous polymeric materials by an average of the organoclay loading. Usually, the organoclay content of an exfoliated nanocommposite is lesser than intercalated nanocomposite (Suprakas *et. al.*, 2003).

For figure 4.1 (a) and (b), it is pristine PLA images. There is no any dispersion of the silicate layers in the polymeric materials shown. The images shown smooth captured and the crack scattering lines images are almost hard to be seen. In the images, there got bubbles. This may affect the mechanical properties. Thus, for figure 4.2 to 4.4

(a) and (b), the images show there are dispersion between PLA matrix and Cloisite B30. From observation of the images, it cannot be concluded the type of dispersion for the samples. The dispersion of silicate layers are not dispersed very well. This will result the mechanical properties of the samples. In addition, the presence of agglomerates in the interfacial interaction also can affect the mechanical properties of PLA nanocomposite. The samples might be more brittle and easily to crack due to the presence of agglomerates. It is supported by Tjong (2006), filler is recognized to agglomerate and can formed easily during the processing of polymer nanocomposite. This may lead to poor mechanical properties.

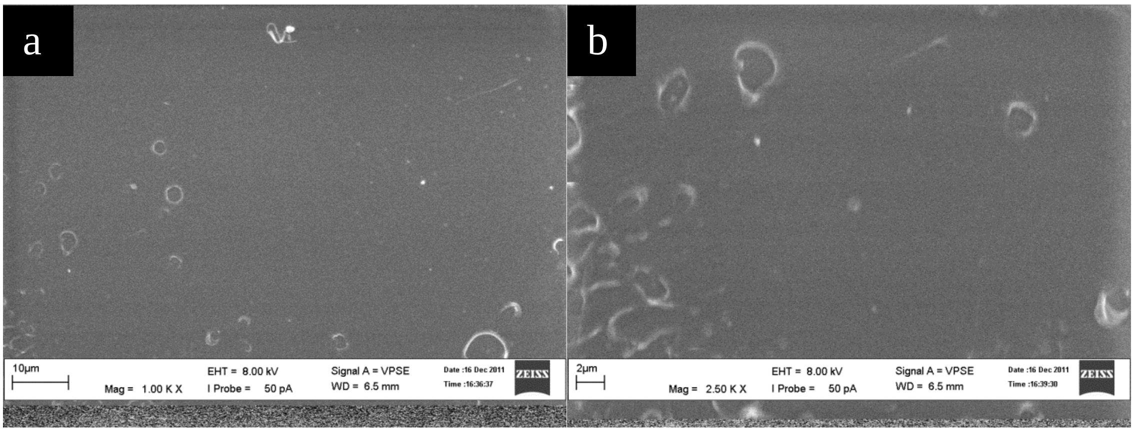


Figure 4.1: Pristine PLA for a) 1000x sample and b) 2500x sample

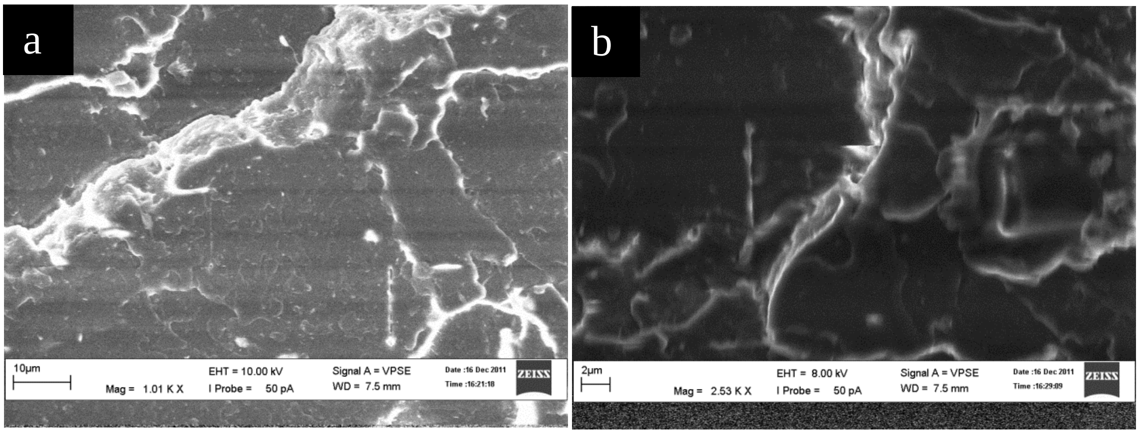


Figure 4.2: Composition of 99.5% PLA/0.5% Cloisite B30 for a) 1000x sample and b) 2500x sample

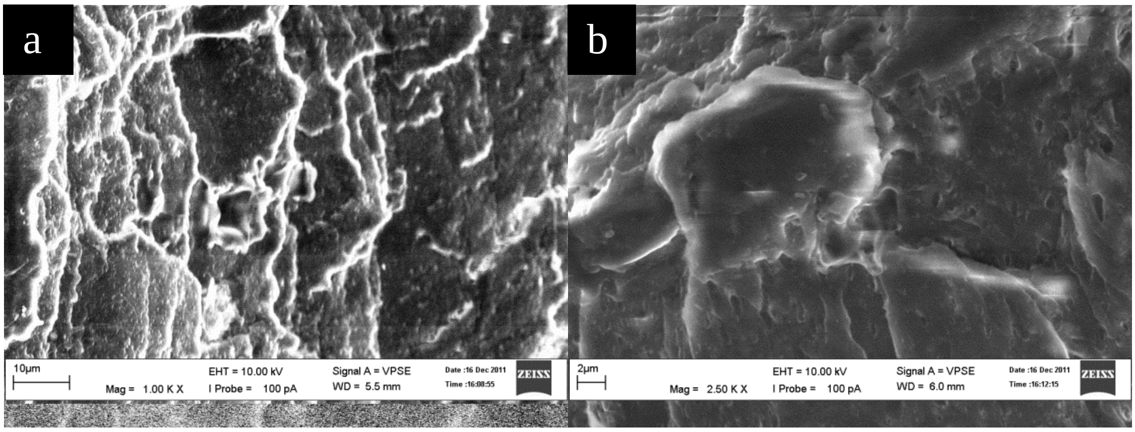


Figure 4.3: Composition of 99.0% PLA/1.0% Cloisite B30 for a) 1000x sample and b) 2500x sample

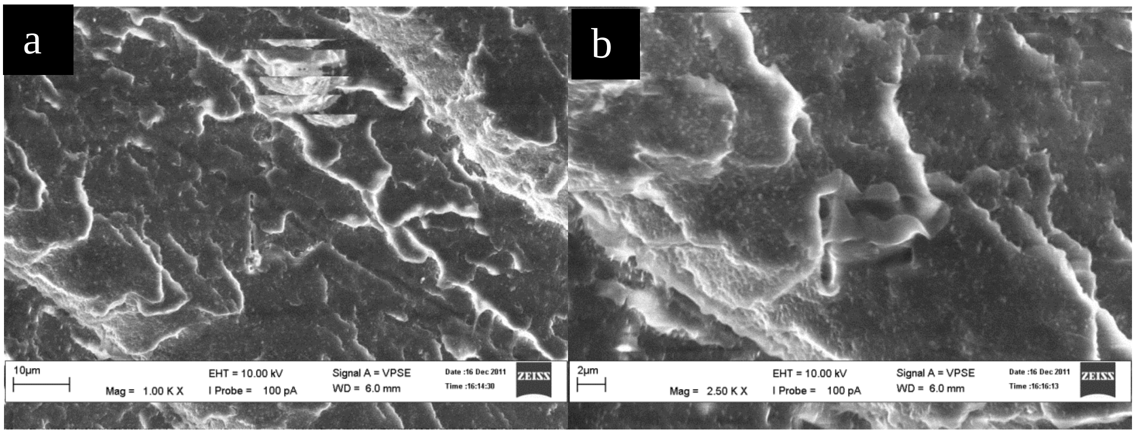


Figure 4.4: Composition of 98.0% PLA/2.0% Cloisite B30 for a) 1000x sample and b) 2500x sample

4.2.2 X-ray Diffraction (XRD)

XRD is a method an x-ray is projected onto the powder samples. The delamination of organoclay in the polymeric materials can be confirmed using XRD. Time resolved high temperature was used to investigate the expansion performance of the silicate layers during processing polymer nanocomposite (Suprakas *et. al.*, 2003). XRD pattern is like a fingerprint of the polymer nanocomposite and the powder diffraction method is used to suite for characterization and identification of polycrystalline phases (Scintag Inc). XRD analysis is a well-known method to characterize and identify polycrystalline phase of polymer nanocomposite and the most reliable technique to study the dispersion of organoclay in polymer nanocomposite and in this case, PLA nanocomposite. Inter-galleries spacing value can be determined by analyze diffraction peaks that shown in the XRD result. However, XRD result simply could not estimate the d-spacing of exfoliated due to its limitation in the dimension.

In the figure 4.5 to 4.8, shows no diffraction peak is possible to observe, which is correspond of the exfoliation structure of Cloisite B30 in the PLA matrix was established. No clear peak was observed in the XRD result, suggesting complete exfoliation of Cloisite B30 in the PLA matrixes (Misra *et. al.*, 2005). The absence of the diffraction peak recommended that the parallel of stacking of the organoclay was completely disrupted (Balakrishnan *et. al.*, 2010). This finding should be followed with the TEM images. TEM are frequently used to verify the exfoliated structure. Nevertheless, TEM images do not provide quantitative but only qualitative results (Seong *et. al.*, 2005). This result is no means confirm exfoliation structure. It could be disordered during compounding. The intercalation and exfoliation nanocomposite is explained by the silence of the x-ray intensity exhibit by the low concentration of the dispersion of organoclay. Twin screw extruder could contribute shear forces effect while processing to localized viscoelastic deformation similar to the sliding of organoclay between inter-galleries during melt processing and promote a disordered structure (Chen *et. al.*, 2002). Other than exfoliation structure, the orientation of organoclay also plays important role in the purpose to improve polymer nanocomposite properties (Galgali, 2003).

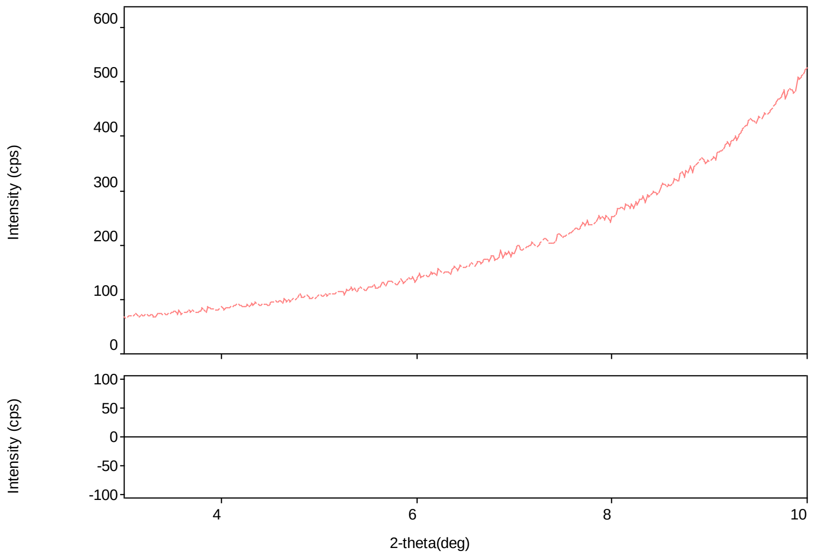


Figure 4.5: XRD result Pristine PLA

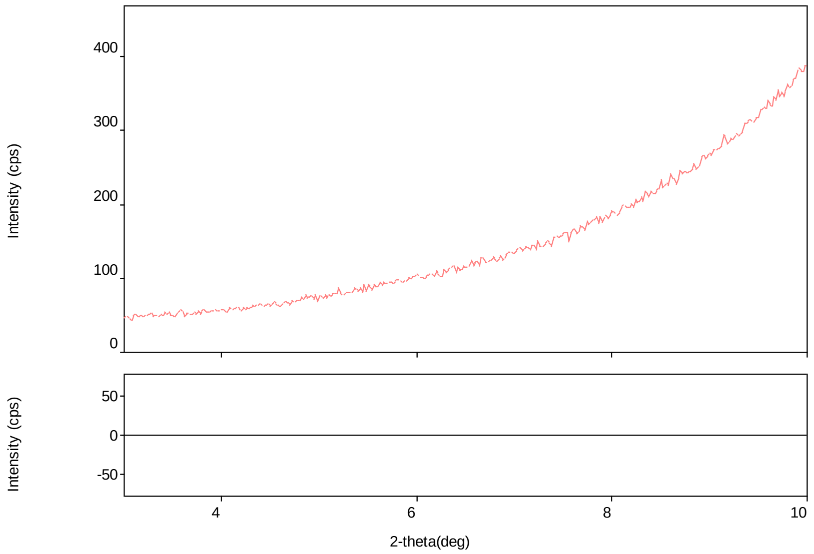


Figure 4.6: XRD result for 99.5% PLA/0.5% Cloisite B30

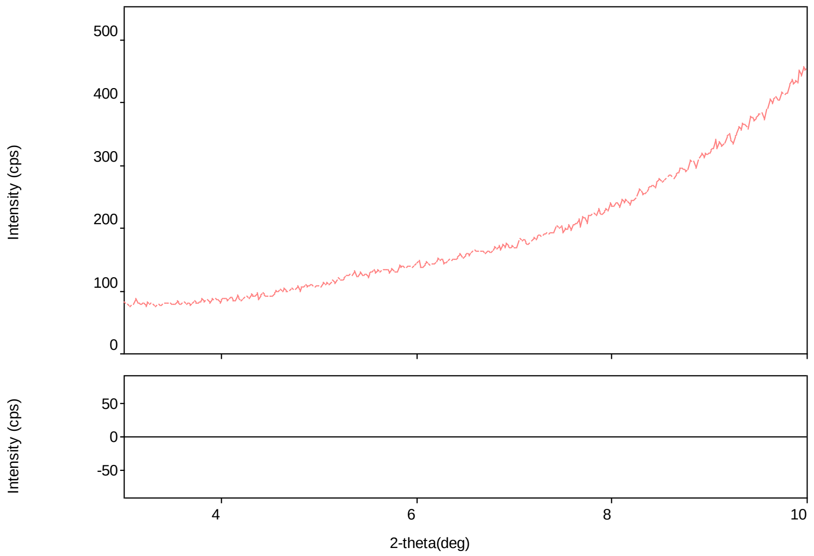


Figure 4.7: XRD result for 99.0% PLA/1.0% Cloisite B30

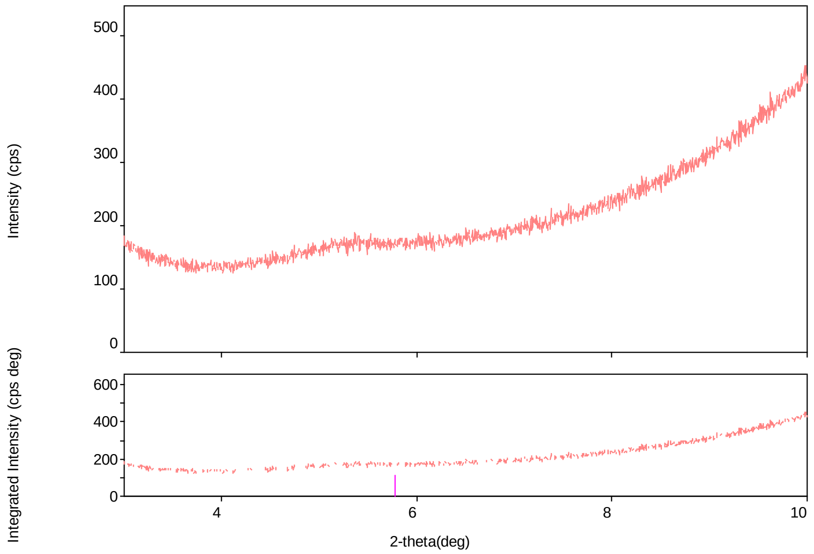


Figure 4.8: XRD result for 98.0% PLA/2.0% Cloisite B30

4.3 Biodegradability analysis

Recently, most of the study found that PLA is one of biodegradable polymer and much research is focus on PLA because it's special characteristic. It is produce from renewable resources with excellent properties comparable to many petroleum-based plastics and readily biodegradable (Balakrishnan *et. al.*, 2010). The degradation step is described as the chain scission process of long polymer chains is cleaved to form oligomers and finally monomers. Furthermore, degradation is significantly loss of molecular weight under the influence of UV-light (Yonghui, 2011). For this study, the accelerated weathering test method was used to determine the biodegradation of PLA and PLA nanocomposite. The tensile strength of the samples under accelerated weathering test condition was then measured. Meanwhile, the duration for the biodegradable analysis was taken for a year and a year and half.

4.3.1 Accelerated weathering testing

Accelerated weathering test analysis is a testing to measure the degradation of materials under the UV-light exposure. There are decreasing of molecular weight and residual weight after the accelerated weathering test has been conducted. This study purpose is to evaluate the reinforcing benefits of organoclay in the polymer matrix. The accelerated weathering tester was operated at a temperature 50 ^{o}C and 24 hours and the amount of cumulative UV radiation were in the same range as outdoor weather (Ding *et. al.*, 2006). The intensity of the UV light in the accelerated weathering tester is much greater than the sunlight, whereas the intensity of the visible area is below half than sunlight. So that, the biodegradation rate under accelerated weathering tester is attained (Nagai *et. al.*, 2004). For this study, samples that were undergone accelerated weathering test were analysed using tensile strength test. This is because to determine the endurance of the materials towards force. The samples were compost with time. The time duration for accelerated weathering test is a year and a year and half. The increase amount of organoclay dispersion will increase the degradation rate of the polymer nanocomposite. The role of organoclay in the hybrid structure might influence the mechanical analysis before and after undergone accelerated weathering test (Lim *et. al.*, 2002).

After a year of observation, only pristine PLA sample was stay maintained in shape and able to be placed at the tensile clamp. For the rest composition samples, they were broken before the samples were placed at the tensile clamp. But the result for a year and half is quite differing than a year observation. All the samples including pristine PLA were easily to break. It is due to the materials were decomposed time by time. This means that the interaction between PLA matrix and Cloisite B30 were being degraded. Due to the PLA special characteristic, it is a biodegradable polymer and the most desired product for the biomedical field (Pandey *et. al.*, 2007). This kind of degradation gives an advantage due to easy to mix with filler and produce more surface area to promote further attack by microorganism (Suprakas *et. al.*¸ 2003). Hence, the biodegradable study period on PLA should be shortening to get the best result. It can be concluded that PLA is being degraded less than a year period. Table 4.1 shows the summary of tensile strength result after undergone accelerated weathering test while figure 4.9 to 4.11 represents the result for mechanical properties of the samples after exposed in the accelerated weathering tester.

Table 4.1: Summary of tensile testing results after accelerated weathering test

Sample	**Ultimate strain (%)**	**Ultimate stress (Mpa)**	**Elastic modulus (Mpa)**
Pristine PLA	3.206	1918.425	26.155
99.5% PLA/0.5% Cloisite B30	0	0	0
99.0% PLA/1.0% Cloisite B30	0	0	0
98.0% PLA/2.0% Cloisite B30	0	0	0

<u>Duration: A year</u>

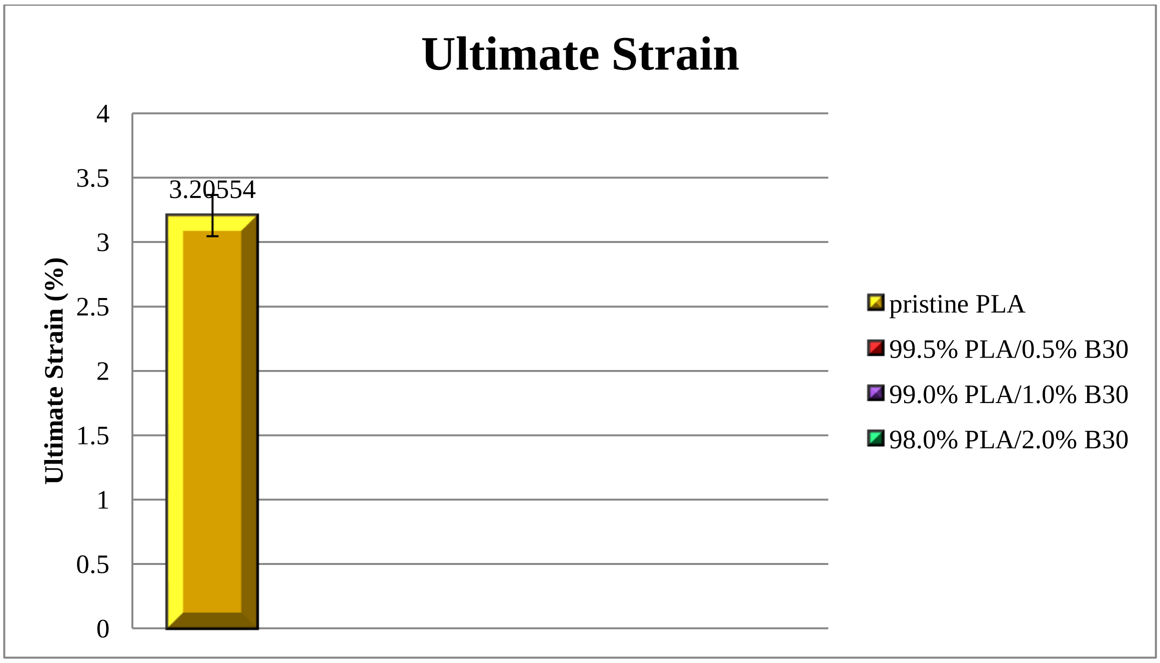


Figure 4.9: Ultimate strain analysis for the compositions after accelerated weathering testing

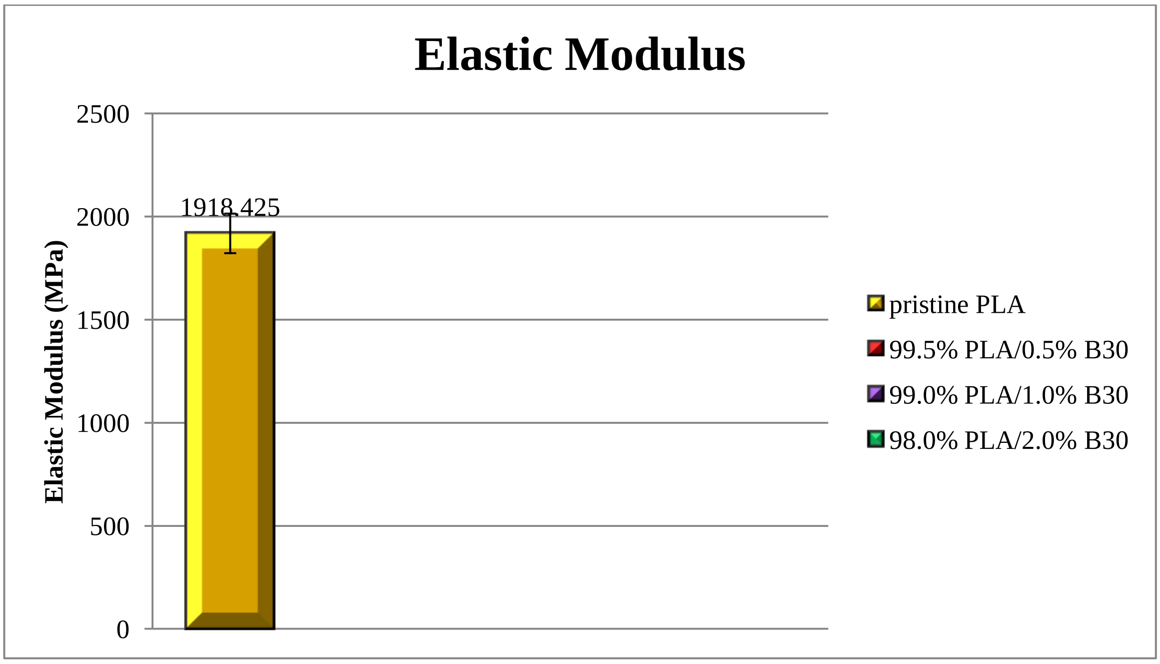


Figure 4.10: Elastic modulus analysis for the compositions after accelerated weathering testing

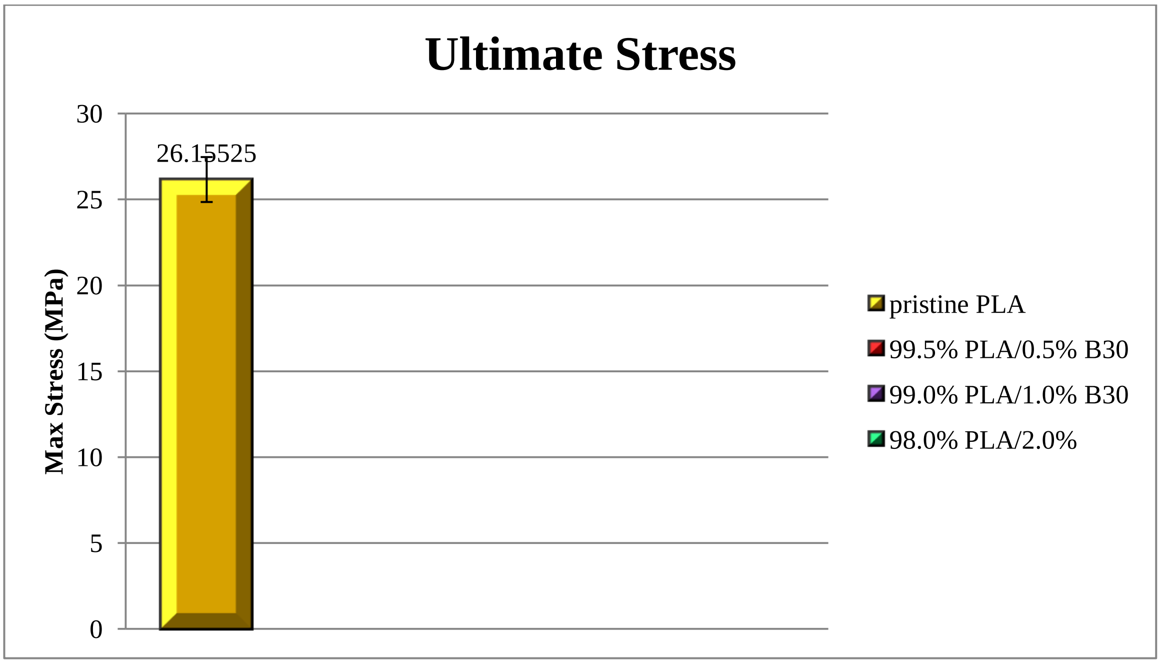


Figure 4.11: Ultimate stress analysis for the compositions after accelerated weathering testing

4.4 Mechanical analysis

Mechanical analysis is to test the strength of the samples towards the force resistance. Tensile properties purpose is to examine the clay loading dependence and determine the bulk mechanical properties of polymer nanocomposite. It revealed the dispersion of organoclay reinforcing characteristic that is the increment in strength and modulus with high aspect ratio. The decreased of tensile properties of the nanocomposite at high clay loading is due to the filler – filler interaction. This may resulted agglomerates and induced local stress concentration in the nanocomposite. At the same time, the organoclay aspect ratio is lead to reduce thereby the contact surface between the clay and the polymer matrix has been decreased (Nayak *et. al.*, 2010). Pristine polymer as a reference system to compared with polymer nanocomposite because aspects like molecular weight, tacticity and processing history will affect mechanical properties of the both samples (Ciprari, 2004).

4.4.1 Tensile strength testing

A tensile test is probably the most fundamental type of mechanical test can be performed on material. Tensile test is a simple, relatively inexpensive, and fully standardized. Thus, by pulling on the one side of the material, it can quickly determine how the material will react to force. As the material is being pulled, it will find its strength by analysing the data of the elongation of the materials. This type of analysis is to examine the ultimate strain, ultimate stress and elastic modulus for the samples. The table and charts below show the average results for the six samples. Table 4.2 is the summary of the result of tensile strength test.

Table 4.2: Summary of tensile testing results before accelerated weathering test

Sample	**Ultimate strain (%)**	**Ultimate stress (Mpa)**	**Elastic modulus (Mpa)**
Pristine PLA	4.6113	33.29	721.9222
99.5% PLA/0.5% Cloisite B30	3.52742	30.47	863.8041
99.0% PLA/1.0% Cloisite B30	3.34707	28.58	853.8812
98.0% PLA/2.0% Cloisite B30	3.41973	26.64	779.0089

Figure 4.12 shows ultimate strain for all the compositions. From the data, the pristine PLA is the strongest sample compared to the other compositions. It shows that the pristine PLA is a strong polymer even has no filler added. For the compositions of PLA nanocomposite, the interaction between PLA matrix and Cloisite B30 caused it is more brittle. At high Cloisite B30 volume percentage, the strength of PLA nanocomposite starts to decrease due to the insufficient filling of the PLA matrix. This is likely due to the degree of orientation of organoclay loads in the sample. The voids developed in the direction of the load, make the interaction between the polymer matrixes become weak and failed at last (Urocha *et. al.*, 2003). To accomplish high mechanical performance, both sufficient exfoliation of silicate layered and strong adhesion of polymer matrix are required. It is necessary for achieving high stiffness in the polymer nanocomposite (Yusuke *et. al.*, 2002). Other than that, the mechanical properties affected by exfoliation structure of organoclay is due to shear deformation

and stress transfer in the organoclay layered (Becker *et. al.*, 2002). Furthermore, the addition of organoclay to the PLA yielded decrease in strain at break value and also can change the stress-strain behaviour (Ozkoc *et. al.*, 2009).

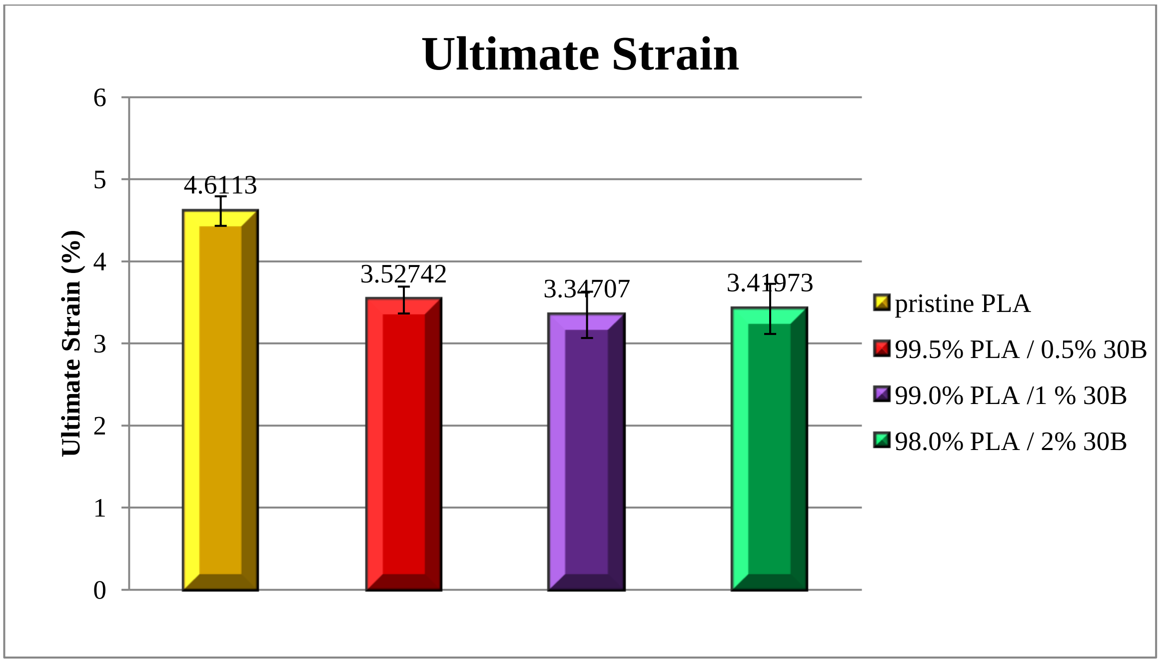


Figure 4.12: Ultimate strain analysis for all the compositions

However, figure 4.13, the highest elastic modulus is composition of 99.5% PLA/0.5% Cloisite B30 while the lowest elastic modulus is pristine PLA. It can be concluded that the dispersion for 99.5% PLA/0.5% Cloisite B30 compositions is good. The organoclay dispersed well between the polymer matrixes. High modulus of elasticity gives stiffness to the composite. Therefore, PLA matrixes are separated by Cloisite B30 and make a good interaction. The dispersion of Cloisite B30 attributed to the enhancement in strength and elastic modulus. Consequently, the benefit of organoclay reinforcement is not highly dependent on the magnitude of the organoclay silicate layered (Wang *et. al.*, 1998). That can be concluded that the dispersion of Cloisite B30 in PLA is dispersed well so that the elastic modulus is more effective in the PLA nanocomposite rather than pristine PLA (Zhao *et. al.*, 2004). In addition, the elastic properties of PLA nanocomposite influenced in indicating intercalated structure and also significantly enhance the glass transition temperature of PLA nanocomposite (Suprakas *et. al.*, 2003).

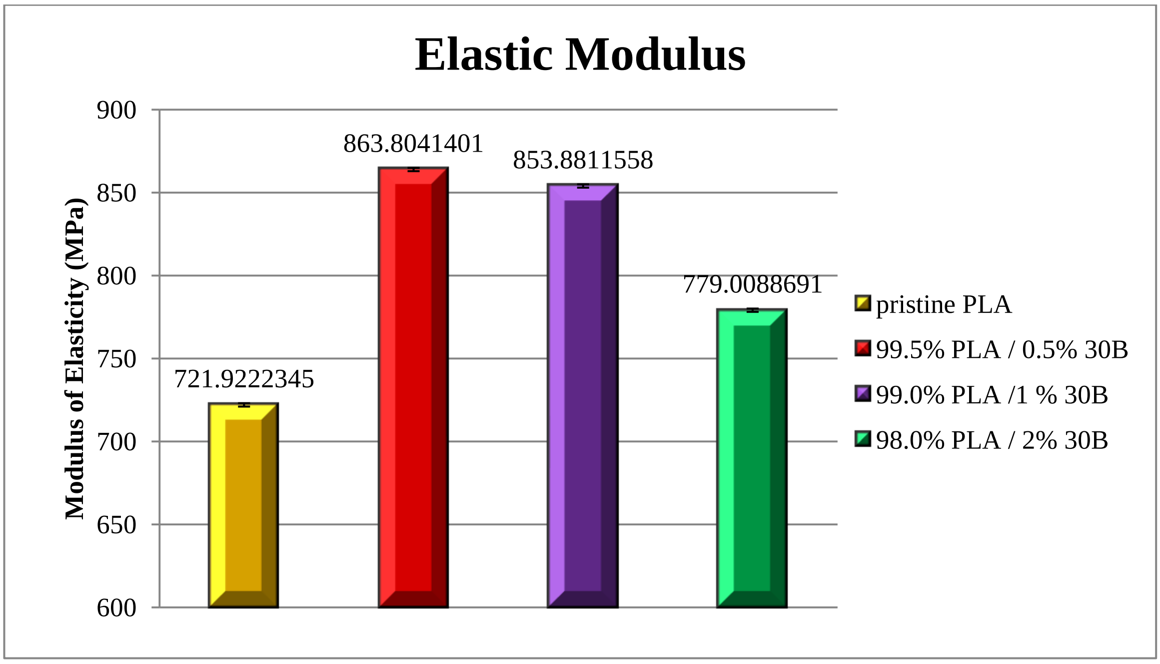


Figure 4.13: Elastic modulus analysis for all the compositions

Figure 4.14 shows the ultimate stress of the samples. The result shows that pristine PLA is the best force resistance. It can be concluded that pristine PLA behaviour is better than PLA nanocomposite in the ultimate stress analysis. This is might be related to the dispersion of the organoclay particles. Probably the inter-galleries spacing between Cloisite B30 is too large and make the interaction of the PLA matrixes getting weaker (Ciprari, 2004). As in Karabulut (2003), has stated that at high organoclay loading, the samples do not performed as stiff as low organoclay loading much due to potential of organoclay particles to agglomerate. This is might be correlated to the migration of the organoclay in the samples. Other than that, it is attributed to high level of exfoliation and lead to concurrent strengthening and toughening of PLA matrix (Lewitus *et. al.*, 2006). The elongation of PLA and PLA nanocomposite samples are due to the flexibility of the chain that introduced by the PLA matrix (Mythill *et. al.*, 2004). Previous study by Ahmed *et. al.* (2010) mentioned that the increased of mechanical strength is because the polymer chains swell and conduct to a well ordered dispersion of silicate layered in the polymer matrixes.

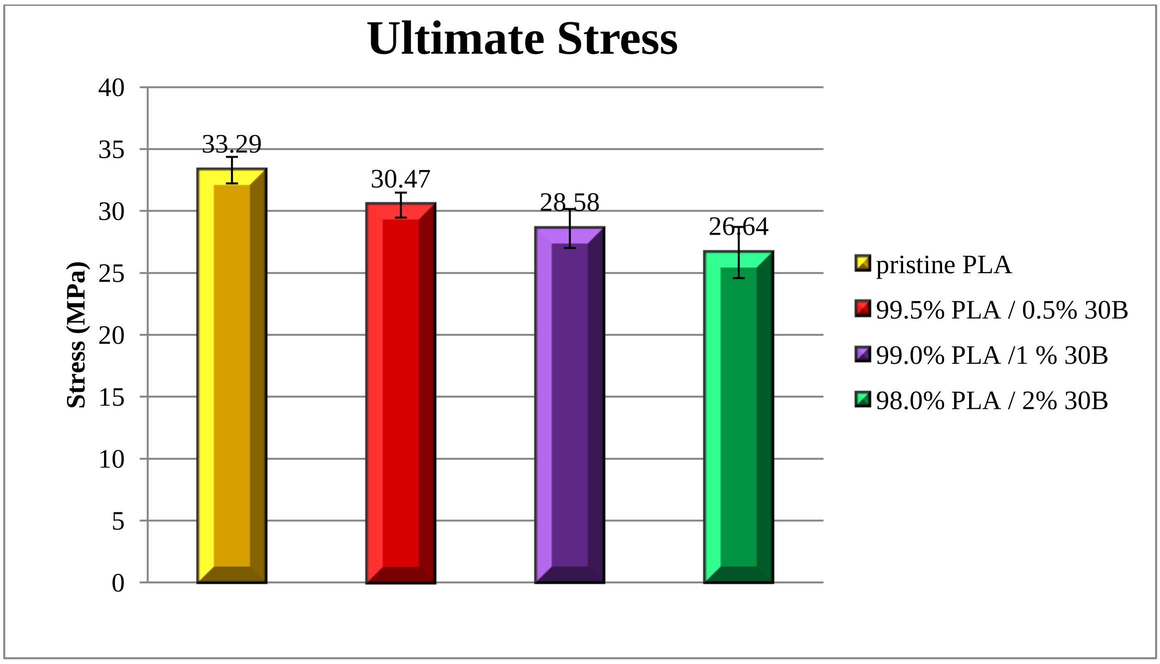


Figure 4.14: Ultimate stress analysis for all the compositions

4.5 Conclusion

This analysis purpose is to find out the effect of the interaction of Cloisite B30 in the PLA matrix. SEM results show great captures but have low limitation on giving the details of the type of Cloisite B30 dispersion in the PLA matrix. Unfortunately, the type of dispersion could not be confirmed exactly because the limitation on giving the precise images. This is due to lack of availability of equipment. The presence of aggregates might affect on the mechanical strength of the samples. However, it is believe that exfoliation dispersion is formed by analysing XRD result since there has no peak was observed for all samples. Accelerated weathering test was carried out to examine the biodegradable behaviour on the samples. Then, the samples were tested using tensile strength test and after a year, it resulted that the pristine PLA is the most sustainable rather than PLA nanocomposite. It is due to the materials were decomposed time by time. This means that the interaction between matrix and filler were being degraded. This gives an advantage to promote further attack by microorganism. Instead of the biodegradable test, the samples also were tested before undergone accelerated weathering test. The result obtained is the pristine PLA possesses good properties for ultimate strain and ultimate stress rather than elasticity behaviour.

CHAPTER FIVE

CONCLUSION

5.1 Introduction

Mostly plastics are produced from petroleum feedstock and ultimately end up as non-biodegradable waste after not being used. Deservedly, nowadays PLA and other aliphatic polyesters are increasing interest due to its biodegradable properties, compostability and also use as renewable feedstock. Meanwhile, this study was conducted to obtain the improvement the morphology, biodegradable and mechanical properties of PLA nanocomposite from the previous research. A literature review has been done to figure out the processing method to produce the polymer nanocomposite. Other than that, literature review purposes are to understand the concept of the type of dispersion and nature of the polymer nanocomposite. In this chapter will explain about the findings from this research. The samples were analyzed and characterized to test the biodegradable behaviour of the PLA and PLA nanocomposite. There is discussion on the biodegradability findings for PLA nanocomposite. After this research has been conducted, the result obtained has been compared with the previous research result.

5.2 Conclusion

The morphological, biodegradability and mechanical analyse result was obtained. For morphological analysis, this finding is supported by the result of XRD and the images of SEM. The result for XRD showed that inter-gallery spacing between nanoclays are too large. But, possibly the dispersion can describe as exfoliated dispersion of silicate layered of Cloisite B30 in the PLA matrix. Then, to support the exfoliation dispersion in the PLA nanocomposite, SEM analysis has been run. The view by SEM failed to determine the nanoclays dispersion in the PLA matrix exactly. Therefore, TEM is suggested for the further research because TEM able to observe the fracture more accurate than SEM. For mechanical test before undergoes biodegradable test, PLA nanocomposite resulted poor in ultimate strain and ultimate stress but more elastic than pristine PLA. Meanwhile, for the biodegradability testing, in this research found that the pristine PLA is more force resistance compare to the PLA nanocomposite. The PLA nanocomposite is more brittle after a year and a year and half observation. For the best result, the duration of testing is suggested to be lesser than a year. For tensile strength test, pristine PLA is the most sustainable in ultimate strain and ultimate stress with 4.61 % and 33.29 MPa. The PLA nanocomposite 99.5% PLA/0.5% Cloisite B30 composition is the most elastic samples with 863.80 MPa.

5.3 Recommendations

5.3.1 Before start the experiment, the PLA and Cloisite B30 should be dried first and keep the dried materials in the desiccator to prevent from the materials are being exposed to the humidity from the surrounding.

5.3.2 For extruder, there should have a thermogravimetric feeder that can figure the pellet insertion consistently into the barrel of the extruder. This method will affect the dispersion of the filler in the polymer matrix.

5.3.3 Make sure that the screw speed of the extruder not too fast because the nanoclay will degrade while extruding the mixture. In addition, the nanoclay also can be degraded if the residence time while in the extruder is too long.

5.3.4 After injecting the materials using injection molding, the samples must be examined directly using tensile strength test right after the injection molding process.

5.3.5 To prevent the samples from being be affected by the air and humidity. But if the samples were not used, it must be kept in the desiccator to maintain its properties.

5.3.6 In order to test the biodegradable properties of PLA nanocomposite, the samples should be tested for six months duration to get the desired result.

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APPENDIX

APPENDIX A1

Weighed the raw materials regarding to the percentage composition

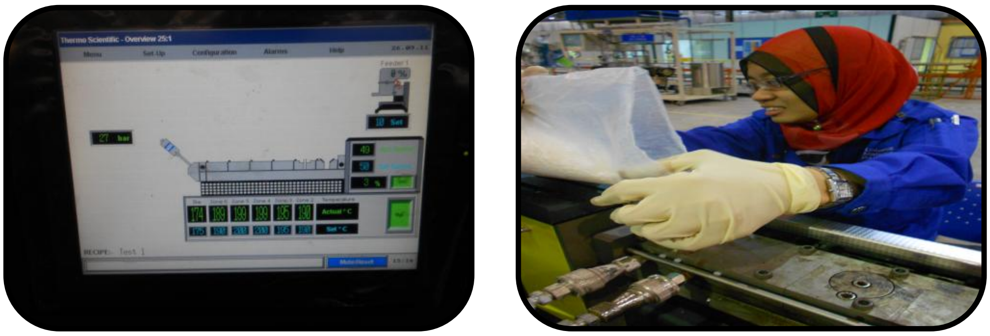
Prepared the raw materials to be dried in an oven

Dried the materials in the oven

Keep the dried raw materials in a desiccator

Figure 6.1: Preparation process before blending and mixing process

APPENDIX A2



Turn on heater and cooler and set the temperature profile for the PLA nanocomposite

Feed mixed PLA and organoclay in the hopper feeder manually

Collect the products that was being purged at the end of the dies

The products obtained after extruding process

The products were pelletized using pelletizer

Figure 6.2: Extruding and pelletizing process

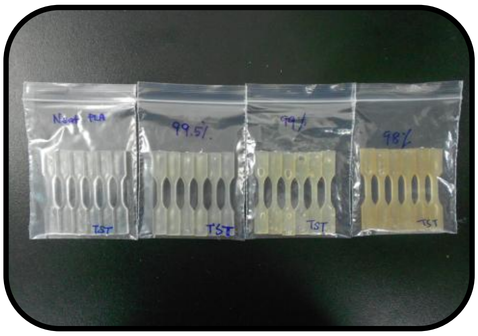
APPENDIX A3

Set the temperature profile for PLA nanocomposite and other setting for injection molding

Set the residence time for injection molding

Feed dried pristine PLA and PLA nanocomposite in the hopper feeder manually

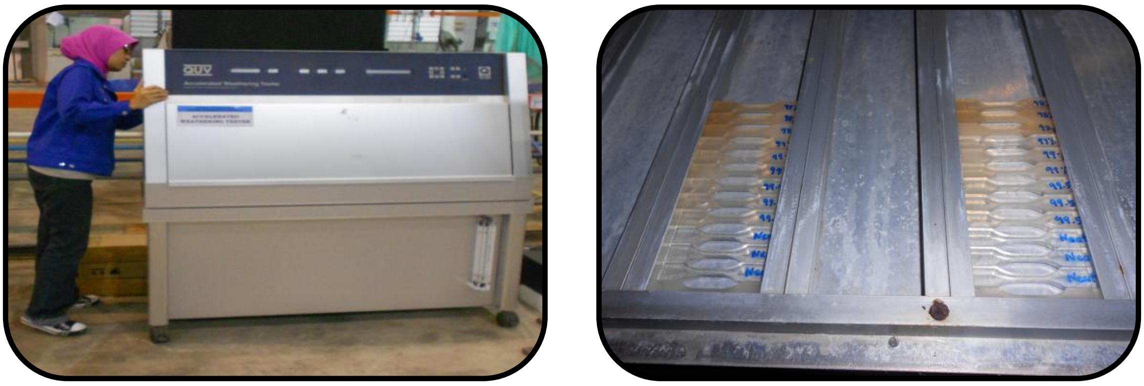
Collect the products that was being purged at the end of the dies



Dumbbell shape products produced by injection molding and arranged the products regarding to the compositions

Figure 6.3: Injection molding process

APPENDIX A4



Make sure that instrument has been switched off before open the lid

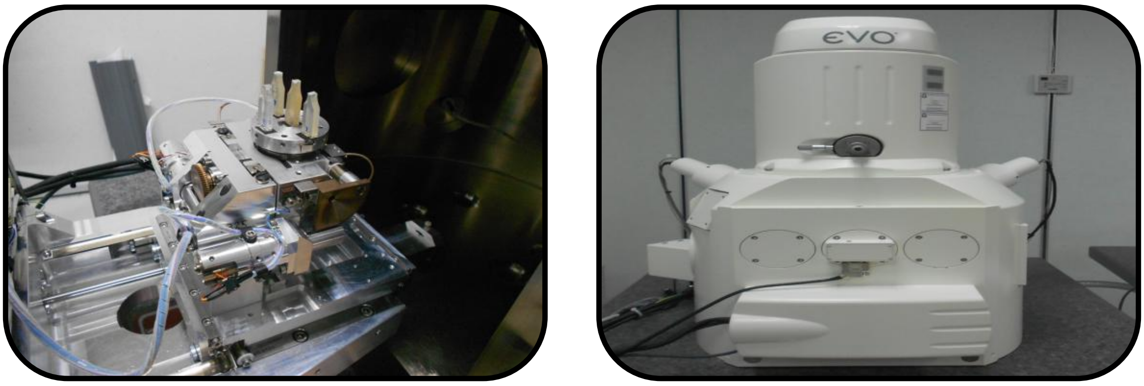
Arranged the samples on the aluminium panels for weathering test

Placed the aluminium panel and closed the instrument lid before switching on the instrument

Set the temperature to conduct the weathering test

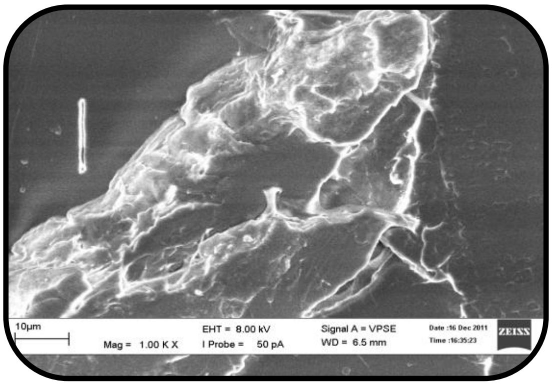
Figure 6.4: Preparation for weathering test

APPENDIX A5



Tapped all fracture samples on the samples holder in the SEM instrument

The morphological analysis was determined by SEM



The high resolution images were viewed until magnification of 2500 times and the views has been taken

Figure 6.5: The samples were analyzed by SEM

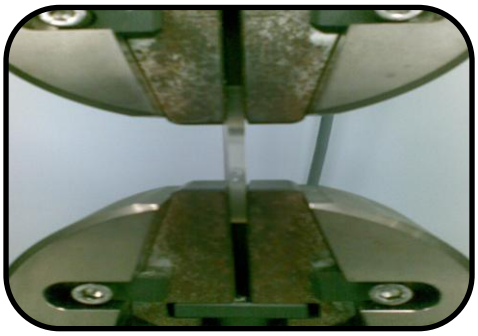
APPENDIX A6

Switched on the instrument

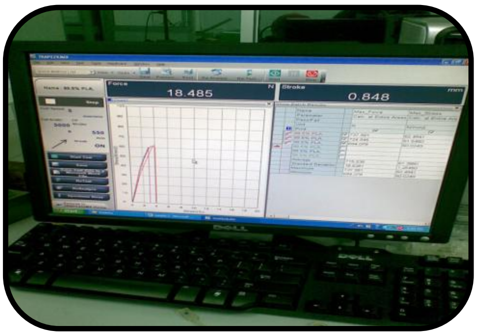
Set the instrument and make sure that force and stroke reach zero

Measured width, thickness and gauge length for every samples

Placed the samples on the tensile clamp



The samples were elongated and cracked after achieved the maximum force



The result wasshown right after the test completed

Figure 6.6: Mechanical testing for before and after weathering test

APPENDIX B1

Key Word		Product Name	100% PLA
Test File Name		Method File Name	Astm D638-03.xmak
Operator	Madieha	Report Date	2011/12/05
Test Date	2011/12/05	Test Mode	Single
Test Type	Tensile	Speed	5mm/min
Shape	Plate	No of Batches:	1
Qty/Batch:	6		

Name Parameters Unit	Max_Force Calc. at Entire A N	Max_Stress Calc. at Entire A N/mm2	Max_Strain Calc. at Entire A %	Break_Force Level(%/Max) 15 N
100% PLA	826.948	70.1945	5.24771	-10.245
100% PLA	768.488	64.7945	4.24557	18.4846
100% PLA	817.641	69.0575	4.80192	-2.6608
100% PLA	827.507	70.5968	4.42463	85.6996
100% PLA	825.946	69.7589	4.50183	0.87182
100% PLA	800.470	67.9470	4.44514	6.35624
Average	811.167	68.7249	4.61113	16.4177
Standard Devi	23.2907	2.13994	0.36043	35.2762
Maximum	827.507	70.5968	5.24771	85.6996
Minimum	768.488	64.7945	4.24557	-10.245

Name Parameters Unit	Break_Stress Level(%/Max) 15 N/mm2	Break_Disp. Level(%/Max) 15 mm	Break_Strain Level(%/Max) 15 %	Max_Disp. Calc. at Entire A mm
100% PLA	-0.8696	1.62310	5.78853	1.47146
100% PLA	1.55851	1.19990	4.27923	1.19046
100% PLA	-0.2247	1.43969	5.13441	1.34646
100% PLA	7.31125	1.44656	5.15893	1.24067
100% PLA	0.07363	1.41150	5.03388	1.26231
100% PLA	0.53954	1.50990	5.38479	1.24642
Average	1.39811	1.43844	5.12996	1.29296
Standard Devi	3.00860	0.13921	0.49648	0.10106
Maximum	7.31125	1.62310	5.78853	1.47146
Minimum	-0.8696	1.19990	4.27923	1.19046

Name Parameters Unit	EASL1_Stroke Force 1 N mm	Elastic Force 10 - 20 N N/mm2
100% PLA	0.00945	917.942
100% PLA	0.00917	1743.21
100% PLA	0.00919	2326.57
100% PLA	0.00958	1993.55
100% PLA	0.00944	2011.92
100% PLA	0.00928	1424.06
Average	0.00935	1736.21
Standard Devi	0.00016	501.560
Maximum	0.00958	2326.57
Minimum	0.00917	917.942

Table 6.1: Tensile strength test result for pristine PLA

APPENDIX B2

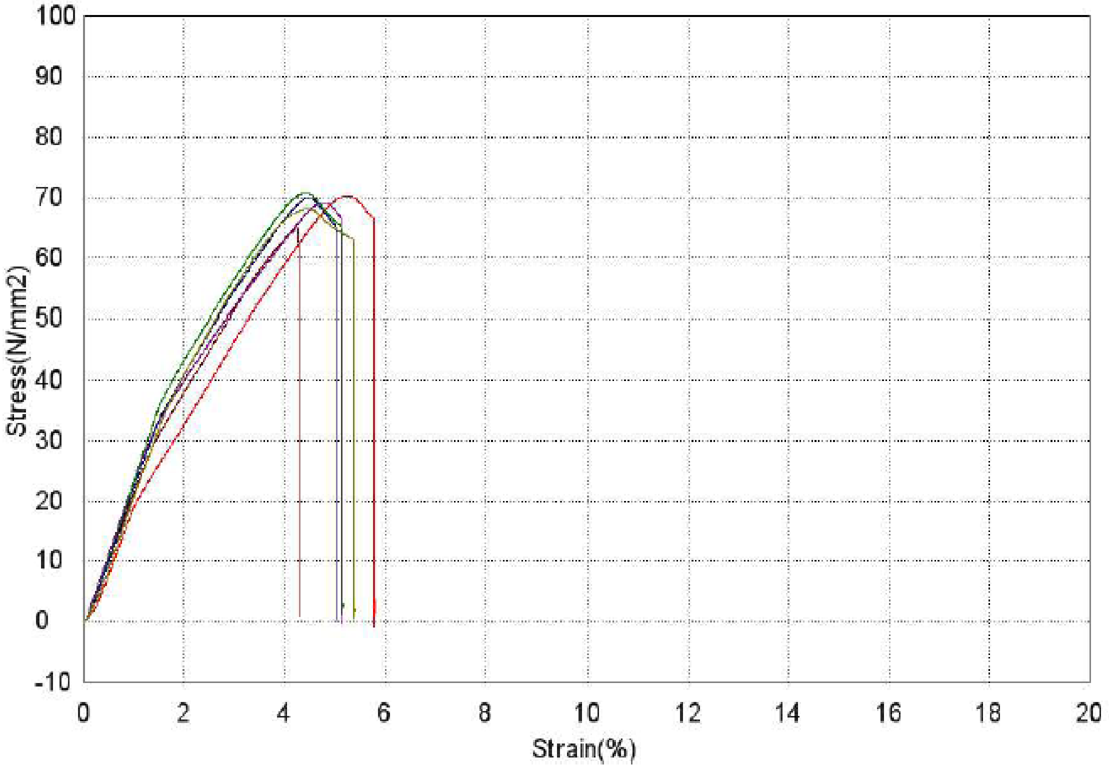
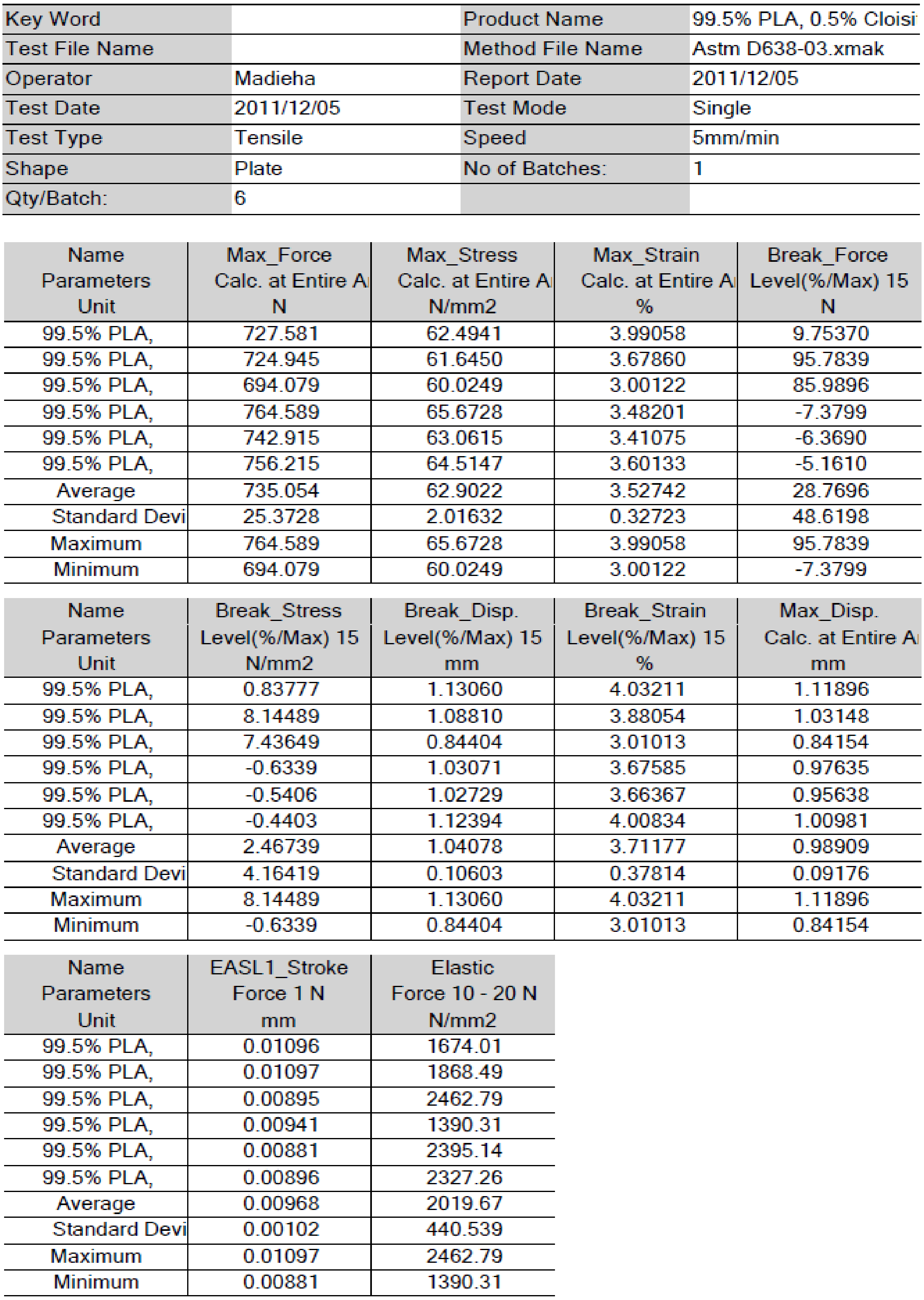


Figure 6.7: Graph of stress versus strain for pristine PLA

APPENDIX B3



Key Word		Product Name	99.5% PLA, 0.5% Cloisi
Test File Name		Method File Name	Astm D638-03.xmak
Operator	Madieha	Report Date	2011/12/05
Test Date	2011/12/05	Test Mode	Single
Test Type	Tensile	Speed	5mm/min
Shape	Plate	No of Batches:	1
Qty/Batch:	6		

Name Parameters Unit	Max_Force Calc. at Entire A N	Max_Stress Calc. at Entire A N/mm2	Max_Strain Calc. at Entire A %	Break_Force Level(%/Max) 15 N
99.5% PLA,	727.581	62.4941	3.99058	9.75370
99.5% PLA,	724.945	61.6450	3.67860	95.7839
99.5% PLA,	694.079	60.0249	3.00122	85.9896
99.5% PLA,	764.589	65.6728	3.48201	-7.3799
99.5% PLA,	742.915	63.0615	3.41075	-6.3690
99.5% PLA,	756.215	64.5147	3.60133	-5.1610
Average	735.054	62.9022	3.52742	28.7696
Standard Devi	25.3728	2.01632	0.32723	48.6198
Maximum	764.589	65.6728	3.99058	95.7839
Minimum	694.079	60.0249	3.00122	-7.3799

Name Parameters Unit	Break_Stress Level(%/Max) 15 N/mm2	Break_Disp. Level(%/Max) 15 mm	Break_Strain Level(%/Max) 15 %	Max_Disp. Calc. at Entire A mm
99.5% PLA,	0.83777	1.13060	4.03211	1.11896
99.5% PLA,	8.14489	1.08810	3.88054	1.03148
99.5% PLA,	7.43649	0.84404	3.01013	0.84154
99.5% PLA,	-0.6339	1.03071	3.67585	0.97635
99.5% PLA,	-0.5406	1.02729	3.66367	0.95638
99.5% PLA,	-0.4403	1.12394	4.00834	1.00981
Average	2.46739	1.04078	3.71177	0.98909
Standard Devi	4.16419	0.10603	0.37814	0.09176
Maximum	8.14489	1.13060	4.03211	1.11896
Minimum	-0.6339	0.84404	3.01013	0.84154

Name Parameters Unit	EASL1_Stroke Force 1 N mm	Elastic Force 10 - 20 N N/mm2
99.5% PLA,	0.01096	1674.01
99.5% PLA,	0.01097	1868.49
99.5% PLA,	0.00895	2462.79
99.5% PLA,	0.00941	1390.31
99.5% PLA,	0.00881	2395.14
99.5% PLA,	0.00896	2327.26
Average	0.00968	2019.67
Standard Devi	0.00102	440.539
Maximum	0.01097	2462.79
Minimum	0.00881	1390.31

Table 6.2: Tensile strength test result for 99.5 % PLA/0.5 % Cloisite B30

APPENDIX B4

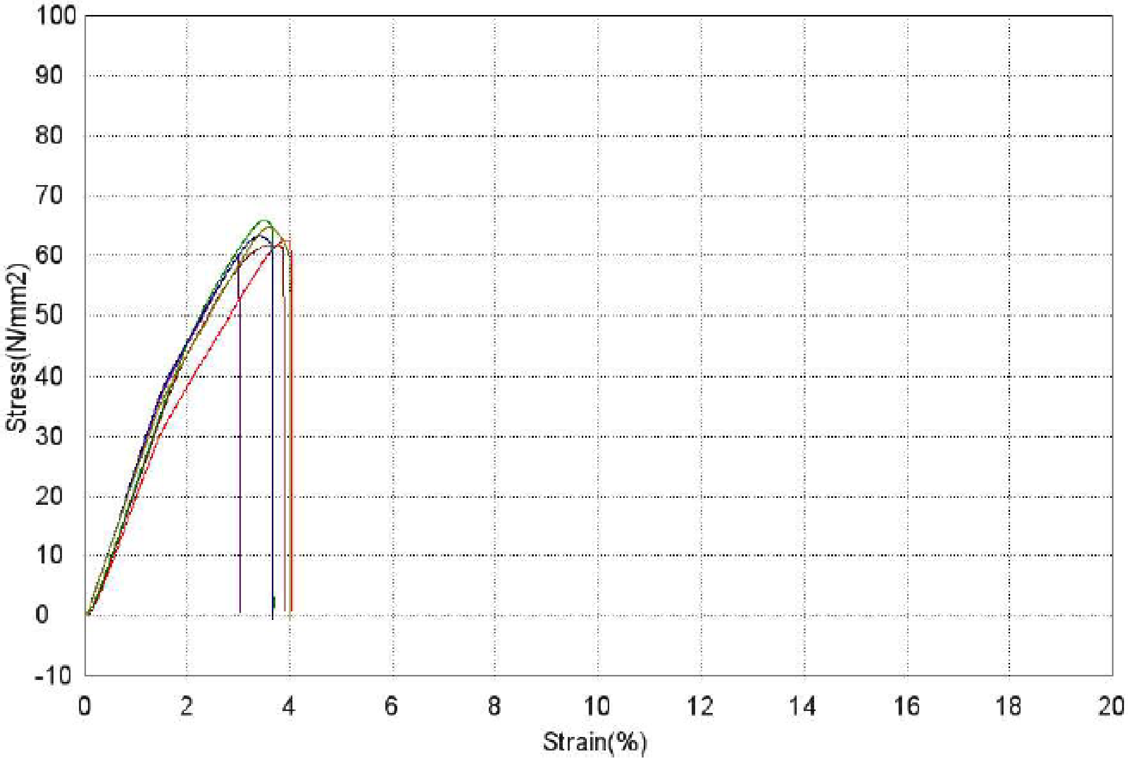
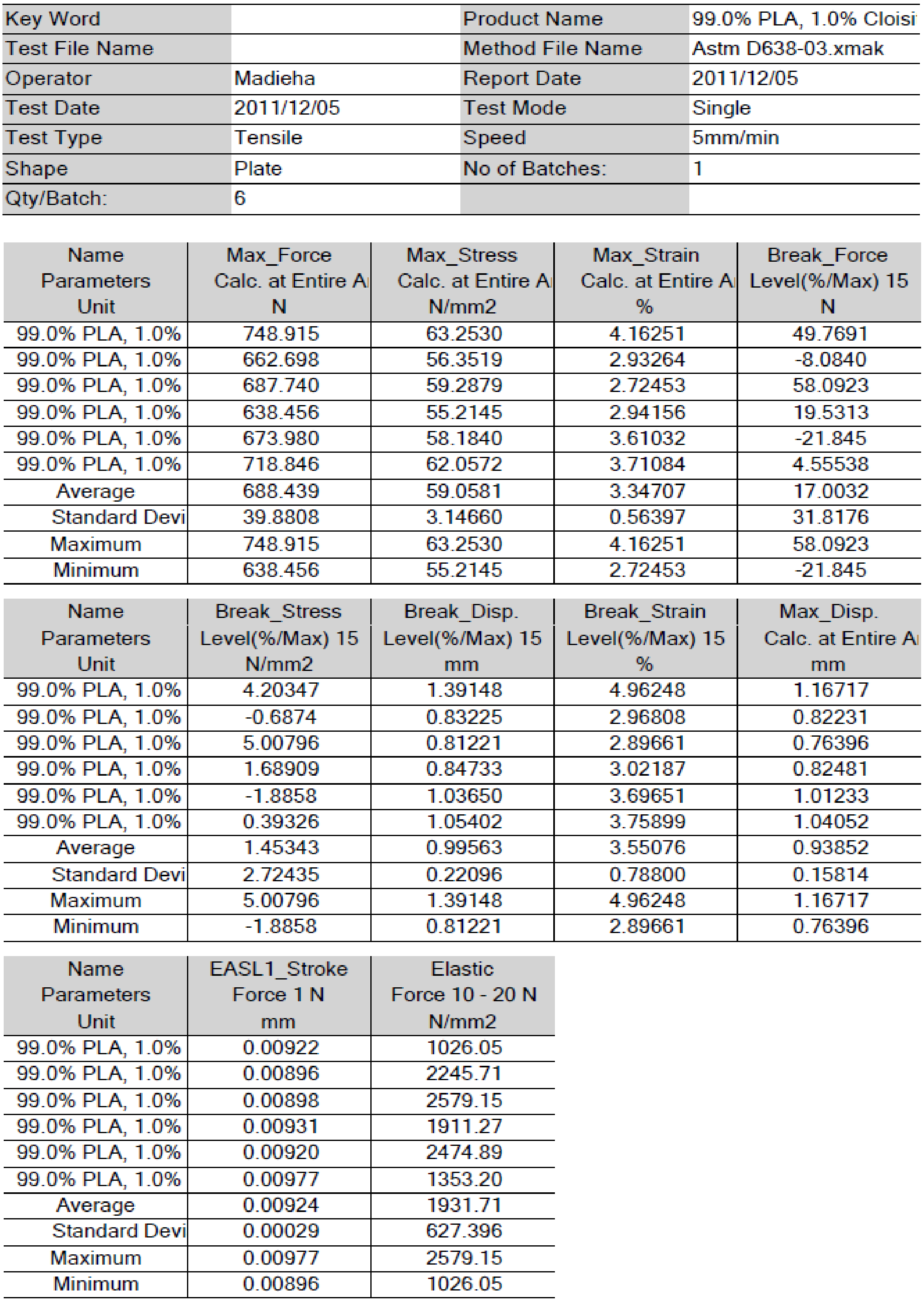


Figure 6.8: Graph of stress versus strain for 99.5 % PLA/0.5 % Cloisite B30

APPENDIX B5



Key Word		Product Name	99.0% PLA, 1.0% Cloisi
Test File Name		Method File Name	Astm D638-03.xmak
Operator	Madieha	Report Date	2011/12/05
Test Date	2011/12/05	Test Mode	Single
Test Type	Tensile	Speed	5mm/min
Shape	Plate	No of Batches:	1
Qty/Batch:	6		

Name Parameters Unit	Max_Force Calc. at Entire A N	Max_Stress Calc. at Entire A N/mm2	Max_Strain Calc. at Entire A %	Break_Force Level(%/Max) 15 N
99.0% PLA, 1.0%	748.915	63.2530	4.16251	49.7691
99.0% PLA, 1.0%	662.698	56.3519	2.93264	-8.0840
99.0% PLA, 1.0%	687.740	59.2879	2.72453	58.0923
99.0% PLA, 1.0%	638.456	55.2145	2.94156	19.5313
99.0% PLA, 1.0%	673.980	58.1840	3.61032	-21.845
99.0% PLA, 1.0%	718.846	62.0572	3.71084	4.55538
Average	688.439	59.0581	3.34707	17.0032
Standard Devi	39.8808	3.14660	0.56397	31.8176
Maximum	748.915	63.2530	4.16251	58.0923
Minimum	638.456	55.2145	2.72453	-21.845

Name Parameters Unit	Break_Stress Level(%/Max) 15 N/mm2	Break_Disp. Level(%/Max) 15 mm	Break_Strain Level(%/Max) 15 %	Max_Disp. Calc. at Entire A mm
99.0% PLA, 1.0%	4.20347	1.39148	4.96248	1.16717
99.0% PLA, 1.0%	-0.6874	0.83225	2.96808	0.82231
99.0% PLA, 1.0%	5.00796	0.81221	2.89661	0.76396
99.0% PLA, 1.0%	1.68909	0.84733	3.02187	0.82481
99.0% PLA, 1.0%	-1.8858	1.03650	3.69651	1.01233
99.0% PLA, 1.0%	0.39326	1.05402	3.75899	1.04052
Average	1.45343	0.99563	3.55076	0.93852
Standard Devi	2.72435	0.22096	0.78800	0.15814
Maximum	5.00796	1.39148	4.96248	1.16717
Minimum	-1.8858	0.81221	2.89661	0.76396

Name Parameters Unit	EASL1_Stroke Force 1 N mm	Elastic Force 10 - 20 N N/mm2
99.0% PLA, 1.0%	0.00922	1026.05
99.0% PLA, 1.0%	0.00896	2245.71
99.0% PLA, 1.0%	0.00898	2579.15
99.0% PLA, 1.0%	0.00931	1911.27
99.0% PLA, 1.0%	0.00920	2474.89
99.0% PLA, 1.0%	0.00977	1353.20
Average	0.00924	1931.71
Standard Devi	0.00029	627.396
Maximum	0.00977	2579.15
Minimum	0.00896	1026.05

Table 6.3: Tensile strength test result for 99.0 % PLA/1.0 % Cloisite B30

APPENDIX B6

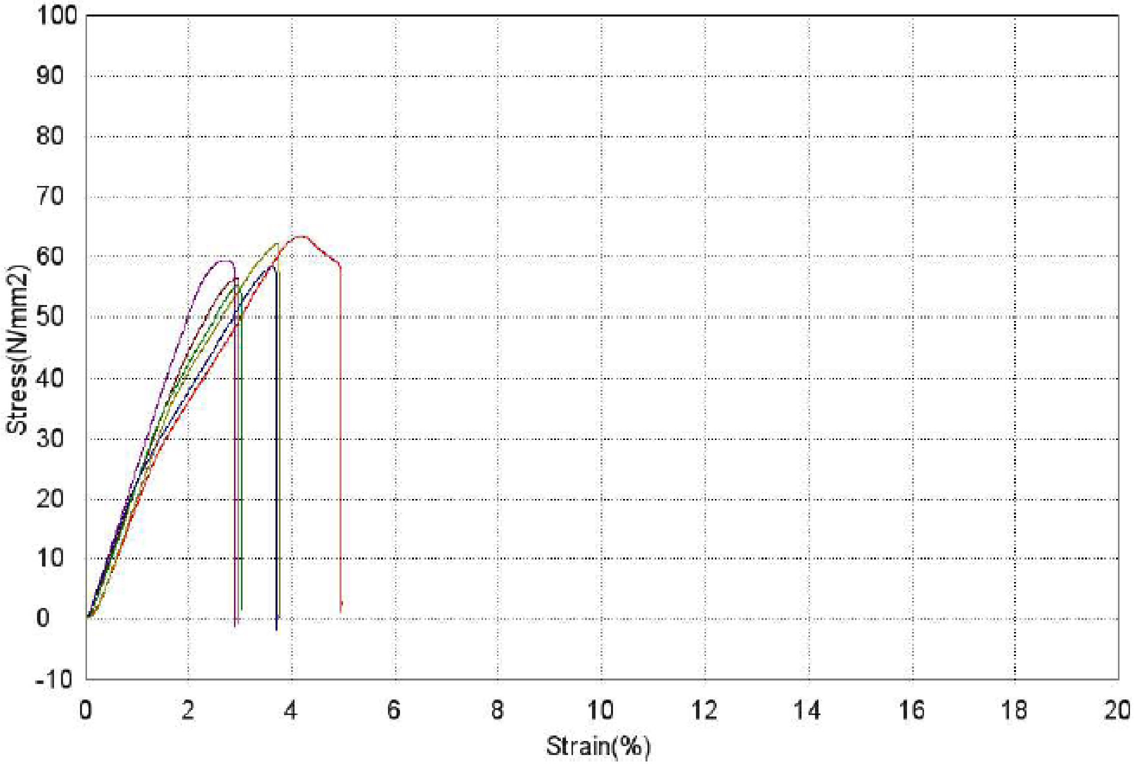


Figure 6.9: Graph of stress versus strain for 99.0 % PLA/1.0 % Cloisite B30

APPENDIX B7

Key Word		Product Name	98% PLA, 2.0% Cloisite
Test File Name		Method File Name	Astm D638-03.xmak
Operator	Madieha	Report Date	2011/12/05
Test Date	2011/12/05	Test Mode	Single
Test Type	Tensile	Speed	5mm/min
Shape	Plate	No of Batches:	1
Qty/Batch:	6		

Name Parameters Unit	Max_Force Calc. at Entire A N	Max_Stress Calc. at Entire A N/mm2	Max_Strain Calc. at Entire A %	Break_Force Level(%/Max) 15 N
98% PLA, 2	622.838	54.2352	2.96206	8.12928
98% PLA, 2	684.298	57.6960	4.02884	5.46376
98% PLA, 2	658.608	56.0041	3.52398	34.3903
98% PLA, 2	680.363	57.9466	4.00514	38.7089
98% PLA, 2	544.755	47.0281	2.46241	23.3165
98% PLA, 2	664.500	57.0759	3.53595	8.37167
Average	642.560	54.9977	3.41973	19.7301
Standard Devi	52.6589	4.13291	0.61058	14.5265
Maximum	684.298	57.9466	4.02884	38.7089
Minimum	544.755	47.0281	2.46241	5.46376

Name Parameters Unit	Break_Stress Level(%/Max) 15 N/mm2	Break_Disp. Level(%/Max) 15 mm	Break_Strain Level(%/Max) 15 %	Max_Disp. Calc. at Entire A mm
98% PLA, 2	0.70788	0.83979	2.99498	0.83056
98% PLA, 2	0.46067	1.13656	4.05336	1.12969
98% PLA, 2	2.92434	1.00056	3.56834	0.98813
98% PLA, 2	3.29684	1.13404	4.04437	1.12304
98% PLA, 2	2.01289	0.70071	2.49896	0.69046
98% PLA, 2	0.71907	1.00560	3.58632	0.99148
Average	1.68695	0.96954	3.45772	0.95889
Standard Devi	1.23517	0.17107	0.61009	0.17121
Maximum	3.29684	1.13656	4.05336	1.12969
Minimum	0.46067	0.70071	2.49896	0.69046

Name Parameters Unit	EASL1_Stroke Force 1 N mm	Elastic Force 10 - 20 N N/mm2
98% PLA, 2	0.00907	2280.13
98% PLA, 2	0.00979	1600.72
98% PLA, 2	0.01123	822.740
98% PLA, 2	0.00958	1748.21
98% PLA, 2	0.00873	1765.76
98% PLA, 2	0.00887	1683.07
Average	0.00954	1650.11
Standard Devi	0.00092	470.742
Maximum	0.01123	2280.13
Minimum	0.00873	822.740

Table 6.4: Tensile strength test result for 98.0 % PLA/2.0 % Cloisite B30

APPENDIX B8

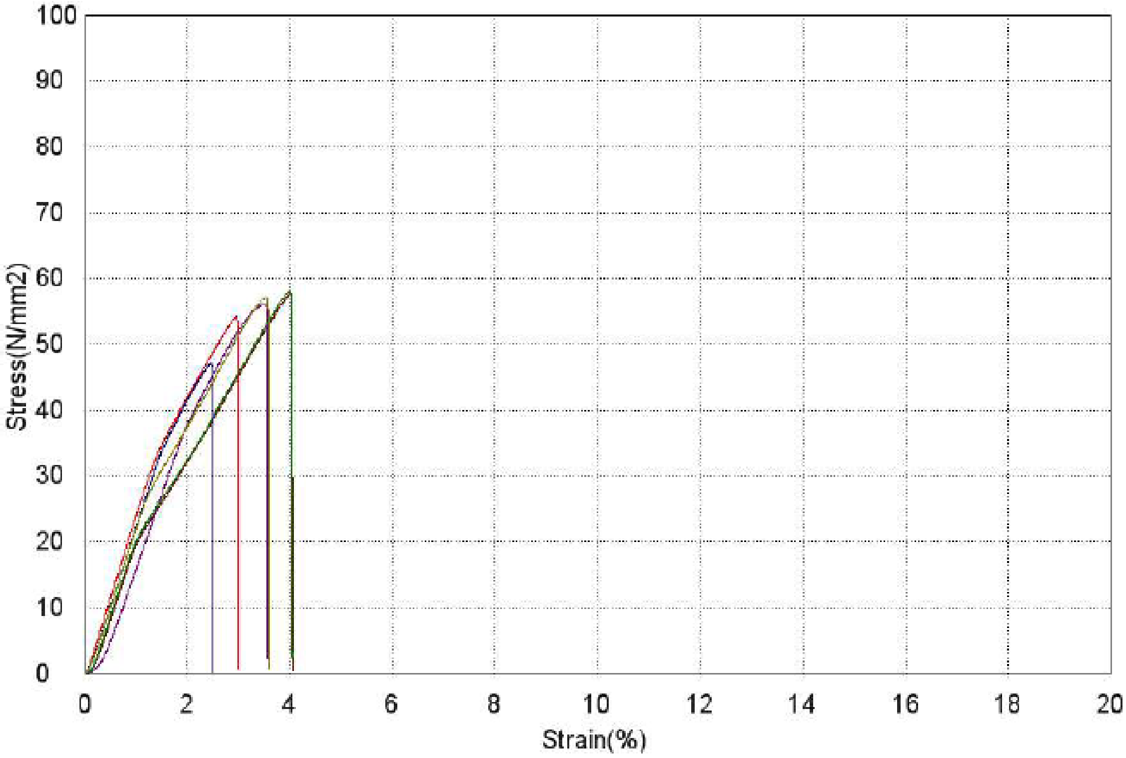
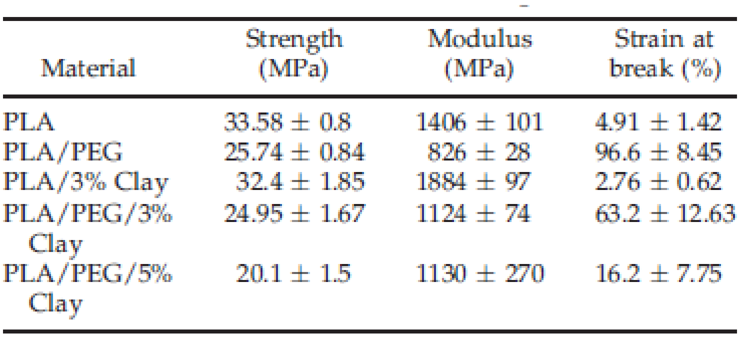


Figure 6.10: Graph of stress versus strain for 98.0 % PLA/2.0 % Cloisite B30

APPENDIX B9

Calculation for tensile testing speed correction

The speed used during tensile test is conducted is 5 mm/min which not following the ASTM standard for specimen D638 V. According to (Ozkoc & Kemaloglu, 2009), by using tensile speed of 2 inch/min or 50 mm/min, the result of tensile strength is as Table 6.5. The correction constant calculation is as follow:



Material	Strength (MPa)	Modulus (MPa)	Strain at break (%)
PLA	33.58 ± 0.8	1406 ± 101	4.91 ± 1.42
PLA/PEG	25.74 ± 0.84	826 ± 28	96.6 ± 8.45
PLA/3% Clay	32.4 ± 1.85	1884 ± 97	2.76 ± 0.62
PLA/PEG/3% Clay	24.95 ± 1.67	1124 ± 74	63.2 ± 12.63
PLA/PEG/5% Clay	20.1 ± 1.5	1130 ± 270	16.2 ± 7.75

Table 6.5: Mechanical test results of PLA, PLA/PEG, and their nanocomposites

Taking maximum stress of actual pure PLA value = 68.7249

$$\frac{68.7249}{33.58} = \frac{10k}{5}$$
$$k = 1.0233$$

For 99.5% PLA:

$$\frac{62.4941}{x} = \frac{10k}{5}$$
$$\frac{62.4941}{x} = \frac{10(1.0233)}{5}$$
$$x = 2.0466\ (62.4941)$$
$$x = 30.5356$$

The rest of the correction calculation were tabulated in Appendix B10

APPENDIX B10

No.	**100 %PLA**		**99.5 % PLA**		**99.0 % PLA**		**98 %PLA**	
	Actual Max stress (N/mm^2)	**Corrected Max stress (N/mm^2)**	**Actual max stress (N/mm^2)**	**Corrected max stress (N/mm^2)**	**Actual max stress (N/mm^2)**	**Corrected max stress (N/mm^2)**	**Actual max stress (N/mm^2)**	**Corrected max stress (N/mm^2)**
1	70.1945	34.2981	62.4941	30.5356	63.2530	30.9064	54.2352	26.5001
2	64.7945	31.6596	61.6450	30.1207	56.3519	27.5344	57.6960	28.1911
3	69.0575	33.7425	60.0249	29.3291	59.2879	28.9690	56.0041	27.3645
4	70.5968	34.4947	65.6728	32.0887	55.2145	26.9786	57.9466	28.3136
5	69.7589	34.0853	63.0615	30.8128	58.1840	28.4296	47.0281	22.9786
6	68.7249	33.5800	64.5147	31.5229	62.0572	30.3221	57.0759	27.8882
Ave	68.8545	33.6434	62.9022	30.7350	59.0581	28.8567	54.9977	26.8727

Table 6.6: Actual and corrected value of max stress for PLA and PLA nanocomposite