PREPARATION AND CHARACTERIZATION OF POLY(LACTIC ACID) / POLYOXYMETHYLENE (POM) BLENDS

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PREPARATION AND CHARACTERIZATION OF POLY LACTIC ACID(PLA)/POLYOXYMETHYLENE(POM) BLENDS

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Thesis submitted in partial fulfilment of the requirements
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DEDICATION

In The Name of Allah, Most Gracious, Most Merciful

Love special dedicated to

Special inspiring and special encouraging of my lovely parent: Nizulkeman Bin Mohamed and Rosmawati Binti Yaacob,

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I would like to take an opportunity to reveal my gratitude towards my parents, Mr. Nizulkeman Bin Mohamad and Mrs. Rosmawati binti Yacoob for their prayers, supports and love that never breaks. I appreciate their sacrifice, patient and moral support throughout my research and my studies.

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ABSTRACT

Plastics are important material in producing goods, for example electronic casing, plastic bag, diapers, groceries apparatus and automotive parts. Many researches have been conducted that polylactic acid (PLA) was produced as a biodegradable thermoplastic polyester from lactic acid. However, PLA has limited applications due to its inherent brittleness, toughness and low elongation at break. One of the option for improvement is through blending with polyoxymethylene (POM). Melt blending of polylactic acid (PLA) and polyoxymethylene (POM) was performed to investigate the effects of POM loadings on mechanical, morphology and thermal properties of PLA/POM blends. The PLA/POM blends was loaded with 1wt%, 3wt% and 5wt% modified nano clay (C-20).The mechanical properties of the blends were assessed by means of universal testing machine while thermal properties were analysed using differential scanning calorimetry (DSC). Scanning electron microscope was used to study the dispersion and particles size of POM in PLA also C-20 in PLA matrix. The results show, the tensile strength, young’s modulus and elongation at break PLA/POM increased with increasing ratio of clay (C-20). It was found out, the incorporation C-20 is expected increased the tensile strength of the PLA/POM blends.

ABSTRAK

Plastik adalah bahan yang penting dalam menghasilkan barang, sebagai contoh bekas elektronik, beg plastik, lampin, barangan runcit peralatan dan bahagian-bahagian automotif. Banyak kajian telah dijalankan dan asid polilaktik (PLA) telah dihasilkan sebagai poliester termoplastik yang boleh diperbaharui daripada asid laktik. Walau bagaimanapun, PLA mempunyai aplikasi yang terhad disebabkan oleh sifat kerapuhan, kekuatan dan pemanjangan pada takat putus. Salah satu pilihan untuk penambahbaikan adalah melalui pengadunan dengan polioximetilena (POM). Pengadunan pencairan asid polilaktik (PLA) and polioximetilena (POM) telah dijalankan untuk menyiasat kesan beban POM pada sifat mekanikal, morfologi dan terma pada adunan PLA/POM. Sifat mekanikal campuran dinilai melalui tengangan, lenturan dan ujian impak, manakala sifat haba dianalisis dengan menggunakan kalorimeter pengimbasan perbezaan (DSC). Mikroskop imbasan elektron telah digunakan untuk mengkaji saiz dan penyebaran zarah POM dalam PLA juga C-20 di PLA matriks. Hasil kajian menunjukkan kekuatan tegangan, modulus muda dan pemanjangan takat putus PLA/POM meningkat dengan penambahan berat C-20. Melalui projek penyelidikan ini, penggabungan C-20 dijangka meningkatkan kekuatan tegangan daripada adunan PLA/POM.

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LIST OF SYMBOLS

T_g	Glass transition temperature
T_c	Crystallization temperature
T_m	Melting temperature
D	Diffusivity ($m^2 s^{-1}$)
C-20	Cloisite-20
t	time (s)
D	diffusivity ($m^2 s^{-1}$)
X	distance of diffusion (m)

LIST OF ABBREAVIATIONS

POM	Polyoxymethylene
PLA	Poly lactic acid
FTIR	Fourier transform infrared spectroscopy
SEM	Scanning electron microscopy
DSC	Differential scanning calorimetry
TGA	Thermogravimetric analysis
TEM	Transmission electron microscope
TS	Tensile strength
ATR	Attenuated total reflectance
UTM	Universal test machine

CHAPTER 1

INTRODUCTION

1.1 Background

Polylactic acid is ecofriendly because it is derived from renewable resources such as from corn starch, wheat or rice . These materials are renewable and ecofriendly make polylactic acid an attractive biopolymer. The next advantages is polylactic acid is a nontoxic and carcinogenic material (biocompatibility). Polylactic acid (PLA) is a well-known bioplastic produced using renewable biomass. Compared to the petroleum based plastics, PLA has received attention in the marketplace due to its biodegradability and renewability. However, PLA has limited applications due to its inherent brittleness, toughness and low elongation at break (Bijarimi et al, 2012). The targets for improvement of PLA is improve lower impact strength and thermal stability. One option for improvement is through blending with polyoxymethylene (POM).

With that, polyoxymethylene (POM) is an important engineering thermoplastic that was derived from formaldehyde synthesis, which has been found an application in the fields of vehicles, electronics applications and precision machinery. POM has good-balance mechanical properties, excellent creep resistance, and excellent thermal stability during molding, low friction coefficient as well as excellent anti-wear properties. This is due to its outstanding and well-balanced properties and because no other products can be substituted for POM in some application fields. POM occupies an important position in industry as well as in society. It shows excellent physical and mechanical properties which are mainly based on its high crystallinity. It is expected that the development of high-value-added materials will result in the requirement to distinguish them from existing POM materials. This broad range of useful properties in addition to its ability to retain properties over a long period under elevated temperatures, mechanical stresses and demanding environmental conditions make it an engineering plastic of choice for many applications (Xiaojie Guo, 2015).

In this research, polymer that will be blended with PLA is POM. The PLA/POM blend shows the extremely high elongation at break of the POM/PLA blends although the tensile strength reduced when POM content increased. Morphology of POM/PLA blend shown an uneven fracture surface but it did not show a phase separation. In other word, POM/PLA blend is a miscible blend, which may be both POM and PLA is a semi-crystalline polymer and there are the similar melting temperature and melt flow rate. With the related characteristics of them, it is easy to manage the viscosity and to obtain optimum dispersion (S. Mathurosemontri, 2014).

1.2 Motivation and problem statement

Plastics only become a problem when it is disposed incorrectly by dumping or burning. Plastics have made the 20 and 21st century much easier for the human race to live a better life. There are no disadvantages to using plastic as for its many purposes, just disadvantages in the way humans dispose of plastics.

This problem increase awareness among people the use of biodegradable and bio-based plastic. Over the past decades, scientist have found a synthetic biodegradable thermoplastic which is polylactic acid. Polylactic acid is obtained from ring opening polymerization of lactide, a dimer of lactic acid which is obtained from fermentation of corn starch (Bijarimi et al, 2012).

Nowadays, there are many usages of polymer for community of people. The demands are increasing over time. It was proven that polylactic acid is better than petroleum base plastic in term of energy consumption and carbon dioxide emission in the life cycle assessment (Bitinis et al, 2011). The main problem in preparation of polymer blends is compatibility between polymers mixtures with different properties. However, polylactic acid is too brittle for use in commercial applications with less than 10% elongation at break. PLA has very low toughness and from this problem, it is not suitable for demanding mechanical performance applications unless this biodegradable material is suitably modified and toughening this material is required (Rasal, Janorkar and Hirt, 2009).

The aim of this research is to thoroughly study the effect of blending polylactic acid (PLA) with polyoxymethylene (POM) for suitable use in durable applications. The blend will be evaluated based on its mechanical, thermal, and morphological properties.

1.3 Objectives

The following are the objectives of this research:

- To prepare polylactic acid (PLA) with polyoxymethylene (POM) blends.
- To characterise the mechanical, thermal and morphological properties of polylactic acid (PLA) with polyoxymethyene (POM) blends.

1.4 Scope of research

The following are the scope of this research:

i) Sample Blending Preparation

In this research project, sample preparation and blending PLA with POM to produce PLA/POM blends by using twin screw extruder.

ii) Testing and Analysis

The mechanical, morphological and thermal properties of PLA and POM toughness will be investigated by using the following test and analysis:

- Physical and mechanical analysis is measure with Tensile Test
- Fourier Transform Infrared (FTIR) – attenuated total reflectance (ATR) Spectroscopy is used to monitor the chemical changes after blending
- Morphological evaluation using Scanning Electron Microscopy (SEM)
- Thermal analysis is measured by Thermogravimetry and Differential Scanning Calorimeter

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

Recently, biodegradable polymers derived from natural resources have gained much interest as they can be an alternative to petroleum based polymeric materials as well as a solution to waste disposal problems. Thus, the development of such materials is a crucial issue in order to reduce the environmental impact of plastic production and waste (Bitinis et al., 2011). Renewable resources can create a platform to substitute petroleum-based polymers through innovative bio-based polymers which can compete with or even surpass existing petroleum-based materials on a cost performance basis with the added advantage of eco-friendliness. There is a growing urgency to develop and commercialize new bio based products and other innovative technologies that can reduce widespread dependence on fossil fuel and the same time would enhance national security, the environment and the economy (Miyagawa et al., 2005).

Biodegradable polymers are polymers that undergo microbial induced chain scission leading to mineralization. Biodegradable polymers may not been produced from bio-source only, but it can be derived from the petroleum source (Ray and Bousmina, 2005) .In addition, blending of two or more types of polymer is a useful technique for the preparation and developing materials with properties superior to those of individual constituents (F. Findik et al,. 2003).

2.2 Polylactic acid (PLA)

Figure 2-1: Polylactic acid

PLA is eco-friendly because PLA is being derived from renewable resources such as from corn, wheat or rice. These sustainability and eco-friendly make PLA an attractive biopolymer (R.M. Rasal et al, 2009). The second advantages are biocompatibility and this is the most attractive aspect of PLA. A biocompatible material should not produce toxic or carcinogenic effects in local tissues. Rahul M. Rasal also stated that the third advantages are processibility compared to other biopolymers such as poly (hydroxyalkanoates) (PHAs), PLA has better thermal processibility. The last advantages of PLA are having an energy saving. Lower energy use makes PLA production potentially advantageous with respect to cost as well (R.M. Rasal et al, 2009). Table 2.1 shows some advantages of PLA.

Table 2.1 : PLA Advantages (Rasal et al., 2009)

PLA Advantages	Explanation	Referances
Eco-friendly	PLA is biodegradable, recyclable, and compostable. Its production also consumes carbon dioxide. These sustainability and eco-friendly characteristics make PLA an attractive biopolymer.	Sawyer, 2003; Drumright et al., 2000; Dorgan et al., 2001
Biocompatibility	the most attractive aspect of PLA, especially with respect to biomedical applications, is its biocompatibility. A biocompatible material should not produce toxic or carcinogenic effects in local tissues. Also, the degradation products should not interfere with tissue healing.	Athanasiou etal., 1996; Tian et al., 1997; Eling et al., 1982; Gupta et al., 2007
Processibility	PLA has better thermal processibility compared to other biopolymers such as poly(hydroxy alkanoates) (PHAs), poly(ethyele glycol) (PEG), etc. It can be processed by injection molding, film extrusion, blow molding, thermoform- ing, fiber spinning, and film forming, with PLA resins for these methods commercialized by NatureWorks LLC.	Auras et al., 2004
Energy savings	PLA requires 25–55% less energy to pr duce than petroleum-based polymers and estimations show that this can be further reduced to less than 10% in the future. Lower energy use makes PLA production potentially advantageous with respect to cost as well.	Vink et al., 2003

It also is well-known that bio-based plastics are prepared using the renewable biomass that offers a sustainable alternative to the petroleum-based plastics such as poly (lactic acid) (PLA) (Bijarimi et al., 2012). But PLA have some limitations to be used in commercial applications. Table 2-2 shows some limitations of PLA.

Table 2-2 : PLA Limitation(R.M. Rasal et al., 2009)

PLA limitatation	Explanation
Poor toughness	PLA is a very brittle material with less than 10% elongation at break
Slow degradation rate	PLA degrades through the hydrolysis of backbone ester groups and the degradation rate depends on the PLA crystallinity, molecular weight,molecular weight distribution, morphology, water diffusion rate into the polymer, and the stereoisomeric content
Hydrophobicity	PLA is relatively hydrophobic, with a static water contact angle of approximately 80%
Lack of reactive side-chain groups	PLA is chemically inert with no reactive side-chain groups making its surface and bulk modifications as a challenging task

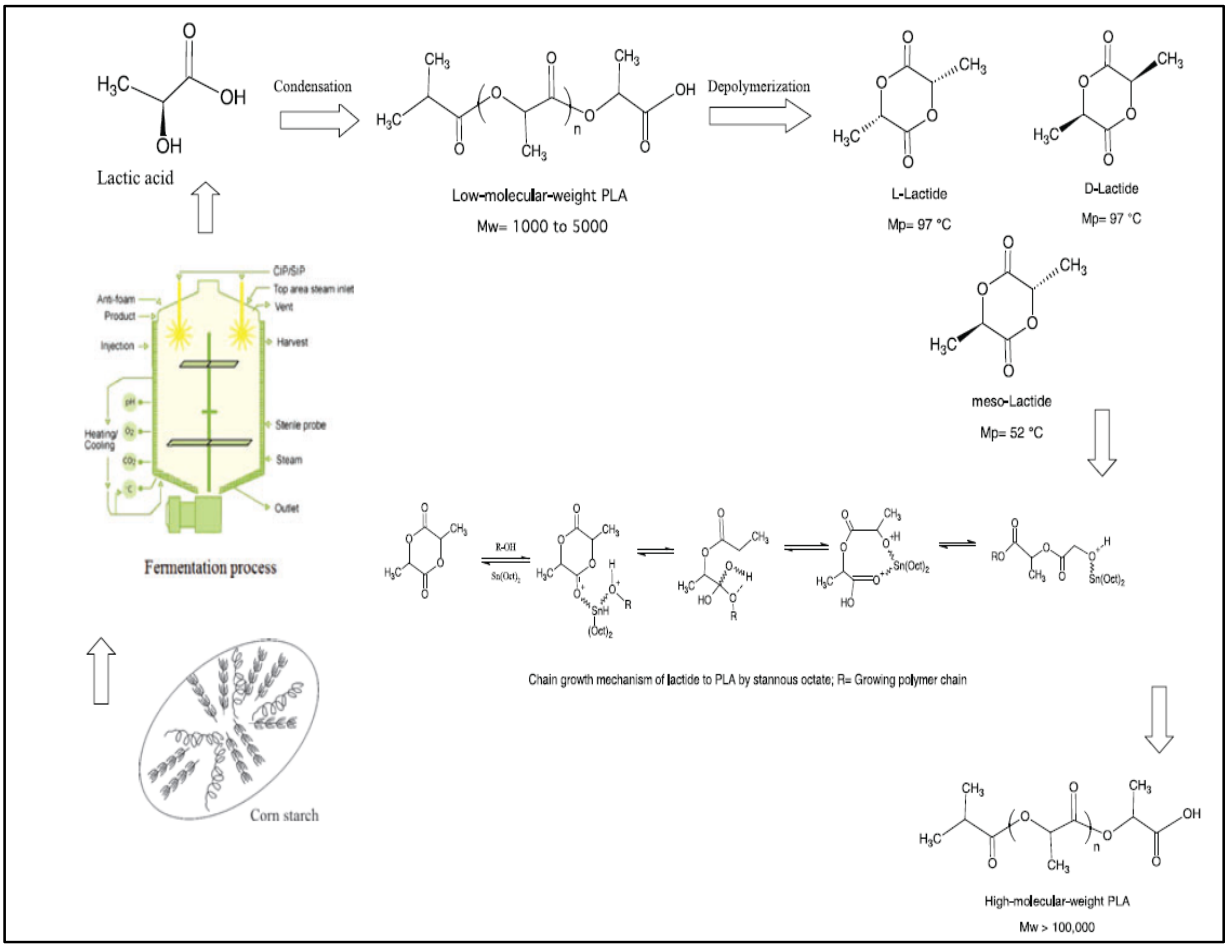


Figure 2-2: Chain growth of polylactic acid

Polymerization of lactic acid to PLA can be achieved by a direct condensation process that involves solvents under high vacuum (Rahul M. Rasal et al,2009). Figure 2-2 shows the example polymerization process of low molecular weight and high molecular weight of polylactic acid. Corn starch undergoes fermentation process producing monomer of polylactic acid, lactic acid.

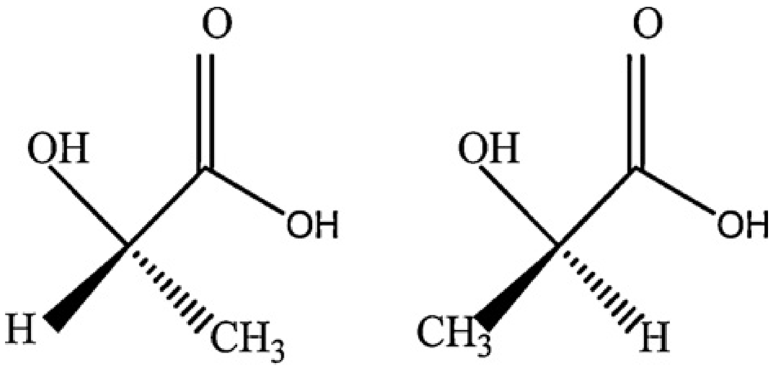
Condensation of the monomer will produce low molecular weight polylactic acid. To produce high molecular weight of polylactic acid, monomer of L-lactide or D-lactide is required. These two monomer can be obtain by depolymerize the low molecular weight of polylactic acid. Long chain of this monomer will produce high molecular weight of polylactic acid (Garlotta, 2001).

Polylactic acid is a thermoplastic, high strength and high modulus polymer. The glass transition temperature and melting temperature is approximately 55℃ and 175℃ respectively. Thus the suitable processing temperature range is between 185℃ to 200℃ since polylactic acid undergoes thermal degradation on temperature above 200℃. Table 2-3 below show the physical properties of polylactic acid.

Table 2-3: Properties of polylactic acid (Prospector, 2013)

Quantity	Temperature	Value	Unit	Test Method
Specific Gravity	22.8 ℃	1.24 to 1.26	$^{g}/_{m^3}$	ISO 1183
Tensile Modulus	22.8 ℃	310 to 5619	MPa	ISO 527-2
Tensile Strength	22.8 ℃	15 to 71	MPa	ISO 527-2
Tensile Elongation	22.8 ℃	1.0 to 12	%	ISO 527-2
Flexural Strength	22.8 ℃	9 to 111	MPa	ISO 178
Notched Izod Impact	22.8 ℃	36 to 67	Pa	ISO 180

Lactic acid exists in two isomeric states, D- and L- enantiomers, which can be controlled during synthesis by modifying strains of lactobacillus. The properties of PLA are what makes it such an attractive polymer for biodegradable and renewable resource applications. It has good process ability, biocompatibility, and biodegradability(Mohanty AK,et al,2005). Lactic acid exists as two optical isomers, l- and d-lactic acid. The l-lactic acid rotates the plane of polarized light clockwise, and d-lactic acid rotates it counterclockwise (Rahul M. Rasal et al,2009).



L-Lactic acid D-Lactic acid

Figure 2-3: Lactic Acid optical monomers(R.M. Rasal et al..,2009)

2.3 Polyoxymethylene (POM)

Figure 2-4: Polyoxymethylene

Polyoxymethylene is a kind of semi-crystalline thermoplastic polymer which is widely used in high resistant and precision components. This polymer is also known as polyacetal or polyformaldehyde (Osswald & Menges, 1995). Polyoxymethylene or polyacetal became commercially available early 1960. POM has a good potential to replace metal because of its unique properties (Sabel *et al.*, 1996). POM resins are crystalline polymers with a degree of crystallinity ranging from 58 to 77% (Mark *et al*, 1988).

The POM has a good balance in their strength, stiffness and toughness. Besides that, POM performs remarkably well in applications where metals were historically used. The ability to predict the long term strength, toughness, creep, fatigue, chemical resistance, dimensional stability and wear resistance of POM in known environments of temperature, pressure and atmosphere allows engineers the freedom to design parts, which is lower in cost than metals in the final form (Sinker, 1990).

The blending of PLA with other polymers such as polyoxymethylene (POM) is more practical and less expensive and will achieve a more ductile multiphase material, by taking in to account the effect of composition on phase distribution (Pongtanayut et al., 2013). POM is an engineering thermoplastic used in precision parts requiring high stiffness, low friction, and excellent dimensional stability (Babu & Mettilda, 2014).

POM is frequently used in industrial applications due to its excellent mechanical properties such as resistance to variable loads, vibration and overload damping capability, impact load transfer, silent-running and good lubricity (Dziadur, 2003). POM is also commonly used as a construction material such as in fixtures, pump and fan propellers, gears, bearing liners and rings (Dziadur, 2001). Generally, the blending of two different polymers leads to be incompatible blends and will show different phases of blend morphologies, that is, dispersion of one polymer in the matrix of another polymer (Bijarimi et al., 2012). Hence, blending PLA with POM will improve the brittleness of PLA and increase the elongation at break.

2.4 Bio-plastic

Bio-plastics are plastics derived from renewable biomass sources, such as vegetable fats and oils, corn starch, pea starch. A bio-plastic may fall into one or more of several categories.

Renewable sources of polymeric materials offer an answer to maintaining the sustainable development of economically and ecological attractive technology Therefore the main categorization of bio-plastics is as follows: Bio-based polymers, biodegradable polymers, and mixed source polymers. Mixed source polymers have a fundamental constituent which is bio-based, but also has petroleum based components (Mohanty AK et al., 2005).

Table 2-4: Broad classification of biodegradable polymers/biobased polymers (Mohanty AK et al., 2005)

Renewable resource based	Petroleum/fossil fuel based	Mixed resource-based renewable resources + petroleum resources
-Polyhydroxy-alkanoates(PHA) - Polylactides(PLA) - Cellulose esters - Starch plastics	-Aliphatic polyesters -Aliphatics-aromatic polyesters - Poly(ester amide) - Poly(vinyl alcohol)	Condensation polymer of corn-derived 1,3 propane diol & petroleum derived terephtalic acid
		Blendings of : -Two/more biodegradable polymer(example: starch + PLA) -One biodegradable + one fossil fuel-made polymer (example : starch plastic + polyethelene) -Epoxidized soybean oil + petro-based epoxy resin

2.5 Polymer Blending

A two-polymer system may be composed of polymers with extremely high mechanical strength, but together, they are only as strong as the bond between them. Thus, final mechanical properties can be decreased from original. By blending different polymers, it is possible to bring the properties of the individual components to a single material. The phenomenon of blending can be implemented more rapidly and economically (K. Habeeb Rahiman et al, 2004).

Blending is probably the most extensively used methodology to improve PLA mechanical properties. PLA has been blended with different plasticizers and polymers (biodegradable and non-biodegradable) to achieve desired mechanical properties (R.M. Rasal., 2009).

Melt blending of polymers is a much more economic and convenient methodology than synthesizing new polymers to achieve the properties unattainable with existing polymers. Toughening is usually an integral part of blend design, especially for those blends involving rigid polymers. PLA has been blended with various polymers for different purposes (Hongzhi Liu,et al 2011).

2.6 Degradation Mechanism of PLA

The degradation rates of modified samples were slightly faster than the rate of neat PLA. For the day 45 all the samples fragmented and became invisible to the naked eyes. During the degradation test scanning electron microscopic images were done. In Figure 2-5, degradation process can be seen. After 14 days white dots appeared on the sample surfaces, which were contributed to the activity of the microorganisms. The SEM images proved that the degradation of PLA was truly biodegradation; the tiny bacteria can be clearly seen in the images. The small dots became small holes as time went by; the holes together formed bigger holes, and finally the samples fragmented into small, invisible pieces or they totally biodegraded (Halász and Csóka, 2013).

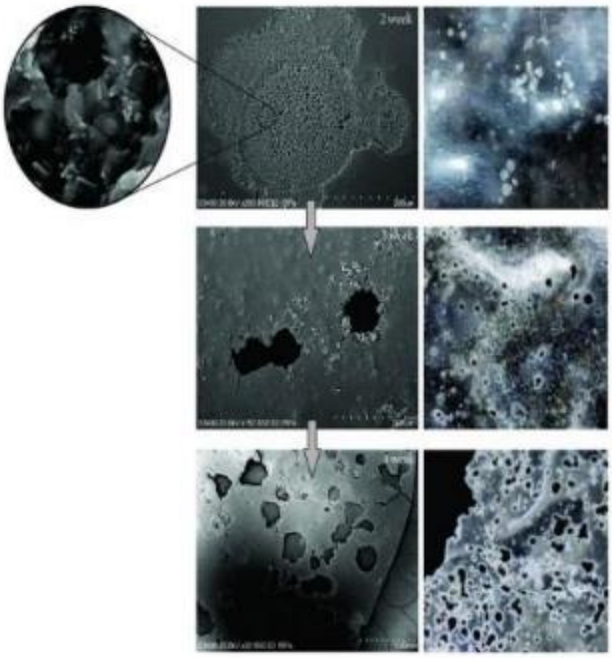


Figure 2-5: SEM and photo images of degradation mechanism of PLA films under composting condition (Sources: Halász and Csóka, 2013)

2.7 Compatibilization in polymer blend

Polymer blending is one of method for produce a new polymeric materials, which combine the excellent properties of more than one existing polymer. Besides that, blends can effects the characteristic and also the specific application. The properties of the blends are strongly depending on the compatibility of the system. However most of the polymer blends are found to be incompatible. These incompatible blends are characterized by a two-phases morphology, narrow interphase, poor physical and chemical interaction across the phase boundaries and poor mechanical properties (George et al., 1995). These problems can be solved by the addition third component into the incompatible polymer blends to enhance the degree of compatibility between the component (Bonner & Hope, 2013). The third component is called compatibilizer. Compatibilizers are macromolecular species exhibiting interfacial activities in heterogeneous polymer blends. Usually the chains of a compatibilizer have a blocky structure, with one constitutive block miscible with one blend component and second block miscible with the other blend component (Koning et al., 1998).

The mechanical properties of the blends will be determined not only by the properties of its component, but also by the phase morphology and the interphase adhesion. The phase morphology and the adhesion are important from the viewpoint of stress transfer (Bonner & Hope, 1993). From theoretical perspective, much can be learned about the nature of the compatibility and the expected properties of the blends by proving its morphology. Figure 2-6(a) shows a miscible polymer blend consists of a single phase. On the molecular level, the polymer A molecules is intermingle with polymer B. In addition, the miscible polymer blend has only one phases, it is much like random copolymer in properties and processing. In order to be miscible, some attraction between the two polymers must present to partially overcome the intramolecular cohesive forces of the individual polymer. Interpolymer attractions are due to the specific interactions between functional groups on polymer A with different functional group on polymers B. However, only few polymer blends are totally miscible (Mark et al., 1988).

Polymer A forms a separates phase from polymer B as shown in figure 2-6(b) is the second possible morphology for polymer blend, immiscible blends. Immiscible blend is more common than one phase miscible blend. Generally, the polymer with lower concentration form a discontinuous or discrete phase, however the polymer with high concentration forms continuous phase. Partially miscible polymers may form completely miscible blends when each polymer is present in small amounts. Figure 2-6(c) shown that polymer A molecules can significantly penetrate into the polymer B phases. The molecular mixing that occurs at the interface of a partially miscible two phases blend can stabilize the domains and improve interfacial adhesion, which explains why these two phase blends usually have good bulk properties (Mark et al., 1988).

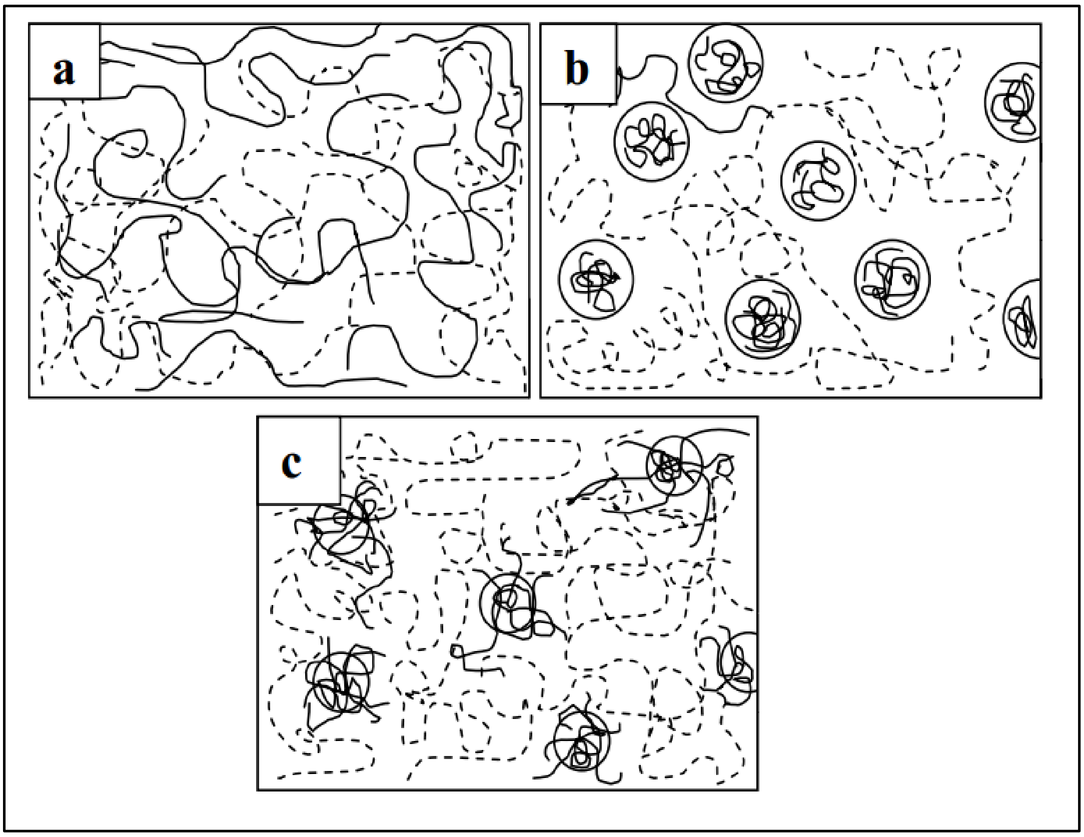


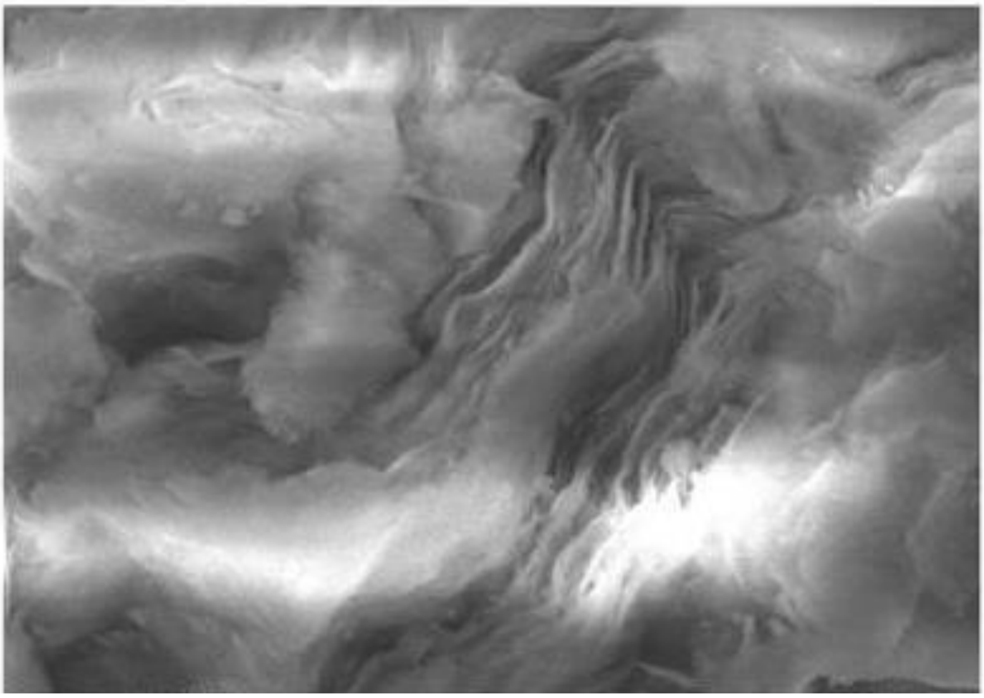
Figure 2-6: Morphology of a blend of polymer A (solid lines) and polymer B (dashed lines): (a) miscible (b) immiscible (c) partially immiscible

2.8 Nano-sized organoclay (Nanoclay)

Organoclay is a chemically modified type of clay that is artificially added chemical compounds known as quaternary amines, which give the clay its useful industrial properties. There are many types of organoclay nanocomposite or montmorillonite (MMT) that commercially used as filler for preparing polymer nanocomposite. One of the primary nanofillers used in polymer nanocomposites production are nanoclays. Cloisite Na+ (Na+ MMT), Cloisite 20A and Cloisite 30B are types of nanoclay. Cloisite Na+, is a type of natural, pure (unmodified) montmorillonite made up of smectite clay minerals which consists of aluminosilicate layers which have been surface-substituted with metal cation, Na+. Cloisite 20A is modified from natural MMT is an organoclay where give the chance to be well intercalated even exfoliated in PBS matrices.

Abundant of investigations has been made to improve the mechanical properties of PLA. These efforts have made use of biodegradable and non-biodegradable fillers and plasticizer or blending of PLA with other polymer. Nanocomposite also called as nanoparticle is an ultrafine particles in the size of nanometer order can be classified into activation of particles surface and increase of surface area.

For activation of particles surface consist of nano-sized atoms or molecules, they affected on the materials characteristic and the properties are varies from those bulk solid of the same materials. To sum up that, as the surface area is increase, the particle size is decrease filler (Meng et. al., 2004).



Figures 2-7: (a) SEM images of modified clay C-20A (Pranav Nawani, 2008)

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials and Method

Materials are needed to run these experiments are PLA and POM. Meanwhile, the equipment being used for this experiment is Twin-screw extruder for blending and film block for moulding.

3.2 Equipment

Equipment’s needed are

1. Instron Universal Testing Machine
2. Fourier Transform Infrared (FTIR)
3. Scanning Electron Microscopy (SEM)
4. Thermogravimetric analysis (TGA)
5. Differential Scanning Calorimeter (DSC)

3.3 Blend Composition

Firstly, PLA is dried at 40^0C and for 24 hours prior to compounding. Sample of different composition of PLA and POM is prepared as follows:

Blending formulation

The blending compositions of polylactic acid polyoxymethylene are varied as shown in table below.

Table 3-1: Composition of polylactic acid and polyoxymethylene

Sample (Composition)	Composition(Weight ratio%)
PLA/POM	100/0
PLA/POM	90/10
PLA/POM/C20-1	90/10/1
PLA/POM/C20-3	90/10/3
PLA/POM/C20-5	90/10/5

Assuming that the weight total for each composition is 500 gram, thus the weight of each component is:

$$\text{mass of polylactic acid} + \text{polyoxymethlyene} = 500\text{g}$$

$$\text{mass of polylactic acid} = \frac{\text{composition \% of PLA}}{100\%} \text{ x } 500\text{g}$$

$$\text{mass of polyoxymethylene} = \frac{\text{composition \% of POM}}{100\%} \text{ x } 500\text{g}$$

Equation 1

3.4 Blending and Moulding

Polymer blend formulation is compounded by adding clay to PLA / POM blends by using twin-screw extruder. The barrel temperature profile adopted during compounding of all blends was 210^{o}C at the feed section, decreasing to 140^{o}C at the die head. The screw rotation speed fixed at the 35 r/min.

After the blending all the materials, then collect from the film block moulding. The test material is allowed to cool and keep under ambient temperature. The sample was in the form of homogenous film measuring 20mm wide × 200mm long with 1mm thickness so that the film can be ready for testing procedures.

Figure 3: A twin screw extruder at FKKSA lab

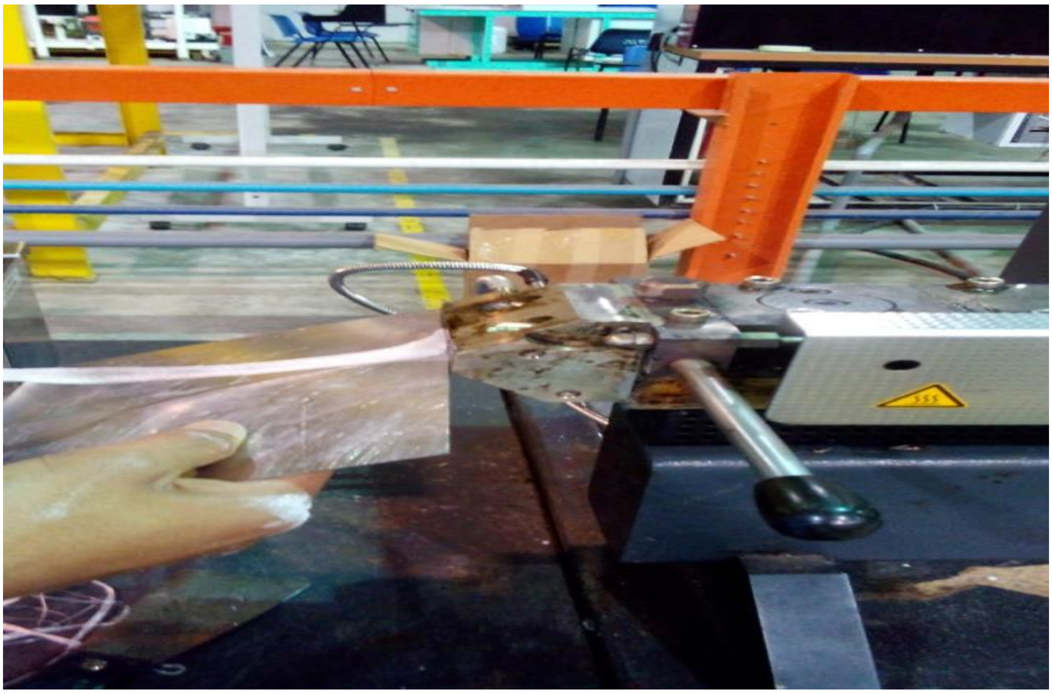
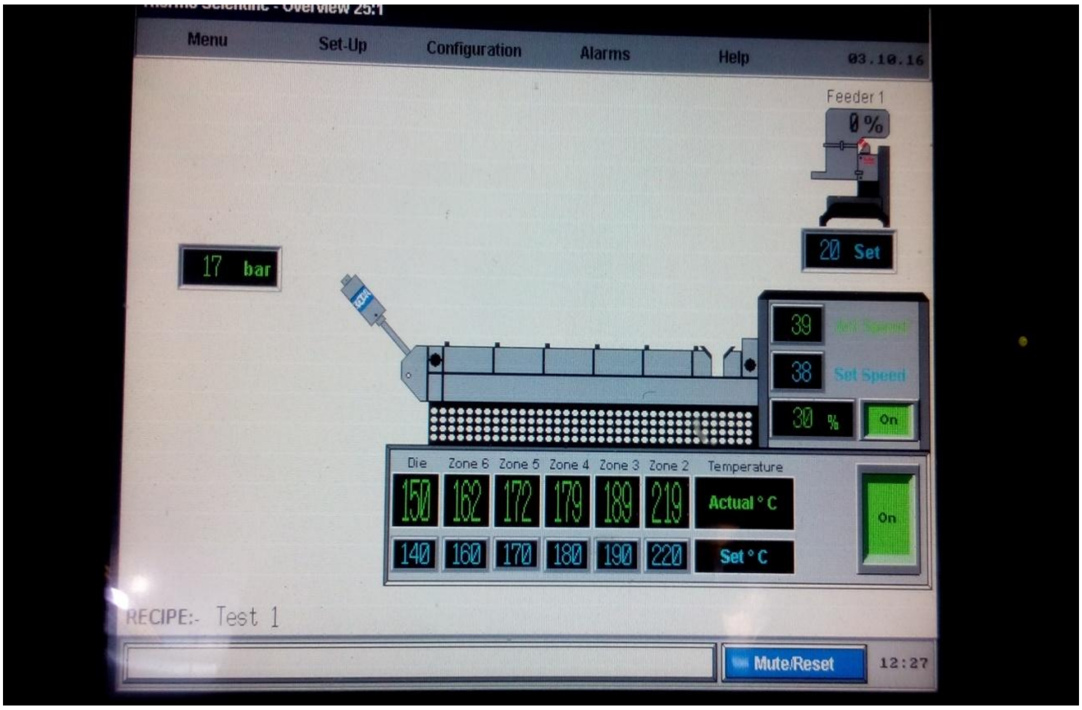


Figure 3-1: The film block moulding



03.10.16

Feeder 1 0 %

20 Set

17 bar

39 Act Speed

38 Set Speed

30 %

Die	Zone 6	Zone 5	Zone 4	Zone 3	Zone 2	Temperature
150	162	172	179	189	219	Actual ° C
140	160	170	180	190	220	Set ° C

RECIPE:- Test 1

12:27

Figure 3-2: Temperature of the twin screw extruder

3.5 Analysis and Characterization

3.5.1 Morphology Analysis using SEM

The scanning electron microscopy (SEM) morphology characterisation provides an insight into the distribution of the POM impact modifiers in a polymer matrix, distribution of components in binary blends, the effect of interfacial addition to the particle size, the crystalline phase and dispersion/ agglomeration of particles as well as particle size (Robeson, 2007). SEM was performed on small pieces of the fractured specimens after the tensile test using a LEO 1450 VP scanning electron microscope. Prior to the microscopic observation, the fractured surfaces were sputter coated with a thin layer of gold (Bijarimi et al., 2013).

3.5.2 Thermal Degradation

Thermogravimetric analysis (TGA) is a technique that measures the mass and the change in mass of the sample during heating as a function, time and/or temperature. Decomposition of mass could be occurred due to chemical reactions or physical changes during heating. The evaluation of thermal stability of PLA and blends was carried out with a Mettler Toledo TGA/SDTA 851e apparatus. Samples (12±0.2 mg) were added to the alumina crucibles. An empty alumina crucible was used as a reference. Samples were heated from ambient temperature, that is, 25–600^{o}C at a scanning rate of 20^{o}C/min under nitrogen. The sample temperature, weight, derivative and its heat flow were recorded (Bijarimi et al., 2012).

3.5.3 Fourier Transform Infrared (FTIR) - attenuated total reflectance (ATR) Spectroscopy

The chemical changes after blending were monitored by FT-IR spectroscopy. Fourier Transform Infrared - attenuated total reflectance (FT-ATR) Spectroscopic studies is will carry out on film samples using a Perkin Elmer FT-IR spectrophotometer in the horizontal ATR mode, using zinc-selenide crystal. The infrared (IR) spectra were recorded using a Spectrum 400 FT-IR and spectrometer with 4 cm^{-1} resolution and 10 scans. All the spectra were recorded in the absorbance mode at the 4000–600 cm^{-1} region (Bijarimi et al., 2012).

3.5.4 Physical and Mechanical Analysis

Tensile test is will carry out according to Instron test machine under ambient conditions with crosshead speed 5 mm/min. Flexural test is done according to Instron testing machine under ambient condition with crosshead speed of 3 mm/min. Five specimens of each formulation will be test and the average value will record for determining stress at peak, elongation at break, Young’s modulus and maximum force load (Bijarimi et,al 2012).

3.5.5 Thermal Analysis

The crystallization behaviour of blend components was demonstrated on compression moulded specimens. Differential scanning calorimetric (DSC) measurements were taken under nitrogen atmosphere on samples of 5–8mg using a Mettler Toledo DSC 822 apparatus. Samples were placed in standard aluminium pans with pierced lids. Samples were heated to 200^{o}C at a scan rate of 10^{o}C/ min. The glass transition, crystallization temperature and melting temperatures were determined. Polymer crystallinity was determined with DSC using the heat associated with melting (fusion) of the polymer. The degree of crystallinity (X_c) was calculated from the following equation:

$$X_c = \frac{\Delta H_m}{\Phi_{PLA}\ (\Delta H_m^o)} \times 100\%$$

where ΔH_m is the measured enthalpy of melting and ΔH_m^o is the melting ethalphy assuming 100% crystalline PLA at 93.0 J/g. The Φ_{PLA} is the weight fraction of PLA in the blend (Fischer et al., 1973).

CHAPTER 4

RESULT AND DISCUSSION

4.1 INTRODUCTION

In this chapter, the result of blending of PLA with POM was discussed. Based on the result, the parameters that involve are physical and mechanical analysis, morphology analysis, thermal analysis, thermal degradation and fourier transform infrared. The result were discussed and the compared with the theoretical data obtained from previous research on the blending of the PLA and POM.

4.2 Result and discussion of mechanical and physical analysis

Table below shown that the data for PLA, POM and clay content on the tensile strength and elongation at break of PLA/POM and clay blends data. The analysis on tensile strength and elongation at break is based on table below. The stress-strain properties of the PLA and PLA/POM blends with different ratios of clay are shown in table below. It is well known that blends show increase and improve the properties such as strength and modulus. Tensile properties are expected to increase if the clay is well dispersed in the polymer matrix. It was found that the tensile strength showed the highest value at 5% of clay loading that is 6.847 N/mm^2 compared another blends. The tensile strength increased as the percentage clay loading increased in the blends. Table 4 shows the values of tensile strength of PLA and POM blends.

Table 4: Tensile strength and elongation at break for different ratio of clay composition

Composition	Tensile strength, N/mm^2	Elongation at break, %	Young's modulus, N/mm^2
Neat PLA	1.568	0.202	18.900
PLA/POM	3.201	1.569	37.380
PLA / POM / C20-1	4.547	2.618	115.685
PLA / POM / C20-3	5.612	3.478	212.951
PLA / POM / C20-5	6.847	4.834	239.186

From Figure 4, the elongation at break increases gradually with the content of clay. The PLA blends containing1%, 3% and 5% clay exhibited higher elongation at break compared to neat PLA. An earlier study reported by Anderson et al the increases of the elongation at break of PLA with addition clay is increased. Besides that, the PLA and POM is semi-crystalline polymer and there are the similar melting point. With the related characteristic, it is easy to manage the mechanical properties of the polymer (Sushalinee Mathurosemontri, 2014).

The effect of clay in PLA/POM blends on elongation at break is given in Table 4. It is evident that the addition of clay increased the elongation at break of 2.618%, 3.478% and 4.834% for 1% of clay, 3% of clay and 5% of clay loading, respectively. This is probably attributed to the alignment of nanoparticle upon applying stress when clay was loaded in the system. As a result the alignment of nanoparticle acts as stress homogenizers allowing slippage and redistribution of stress among polymer chains. This phenomenon was believe to hinder the growing cracks. This suggests that the addition of clay changed the strain response in both unfilled and filled blend systems.

For young’s modulus of all ratio of clay shows an increasing trend for all compositions as shown in table 4. Young’s modulus increased gradually with the concentration of clay. The increasing of young’s modulus due to the hydrogen formed between the functional group of PLA itself. This phenomena may be due to dispersion of clay in the PLA matrix. According to Bitinis et,al, the increasing of young’s modulus also due to the strong affinity of the clay with continues phase. From the figure 4-1 showed the higher of concentration clay, the increasing values of the young’s modulus.

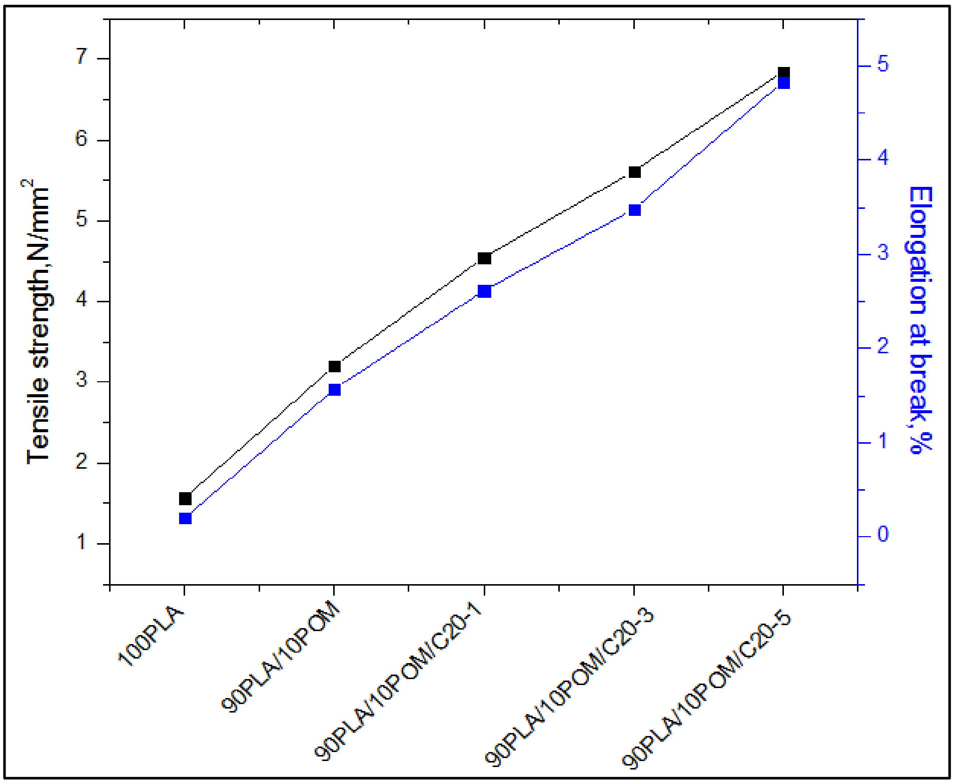


Figure 4: Graph of tensile strength and elongation at break

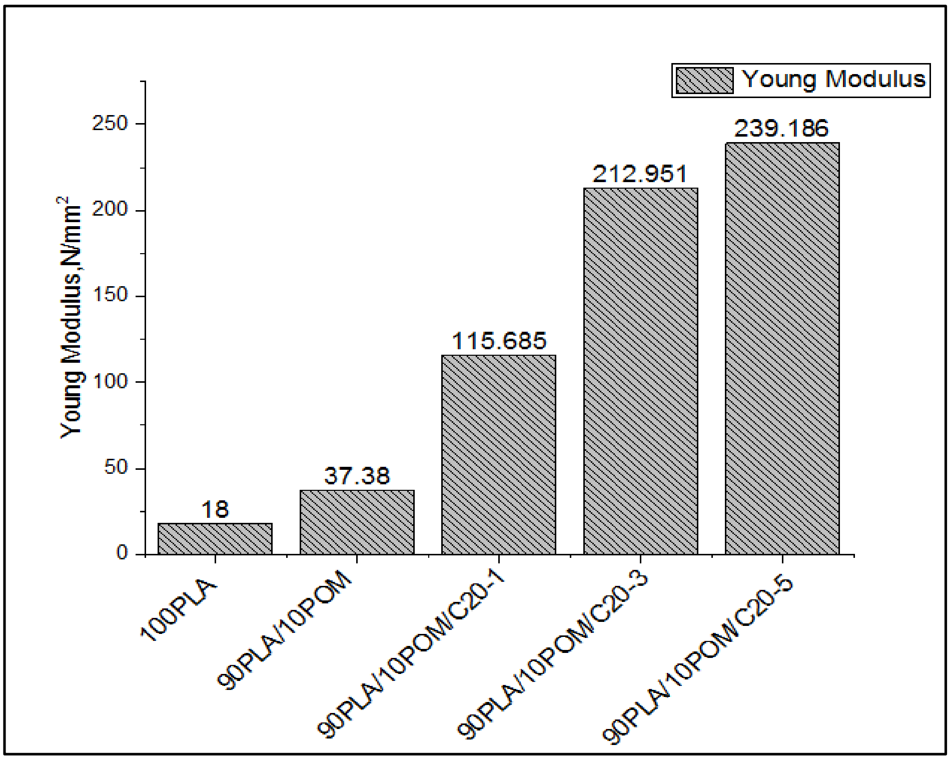


Figure 4-1: Graph of young’s modulus vs concentration

4.3 Result and discussion of FTIR analysis

The FITR analysis indicated that the specific interaction in the blend with compatibilizer. It also was used to detect the miscibility of PLA and POM and the bonding natures in the composite. Fourier Transform Infrared – attenuated total reflectance (FT-ATR) Spectroscopic studies was carry out on film samples using a Perkin Elmer FT-IR spectrophotometer in the horizontal ATR mode, using zinc-selenide crystal. The spectrum will be analyse using spectrum software (Perkin Elmer, Shelton, USA).

Figure 4-2 below shows the FT-IR spectra of PLA, POM, Nano clay and blends are shown in Figure. The IR bands at 2994.27 cm^{-1}, 2994.43 cm^{-1} and 2993.61 cm^{-1} are C-H stretching regions. It also reported that peak 868.50 cm^{-1} and 754 cm^{-1} are related aromatics region. The peak at 1180 cm^{-1} belong to C-O-C stretching of PLA. Then, the carbonyl group C=O stretching at about 1747.52 cm^{-1} as a broad asymmetric while the CH bending appears at 1452 cm^{-1}. It was observed that there were no obviously changes of the carbonyl group of PLA/POM components. There was a small changes and difference between the FT-IR spectra blends with POM. Since there were not too difference, this blend between PLA/POM not miscible (Sahrim Ahmad, 2014).

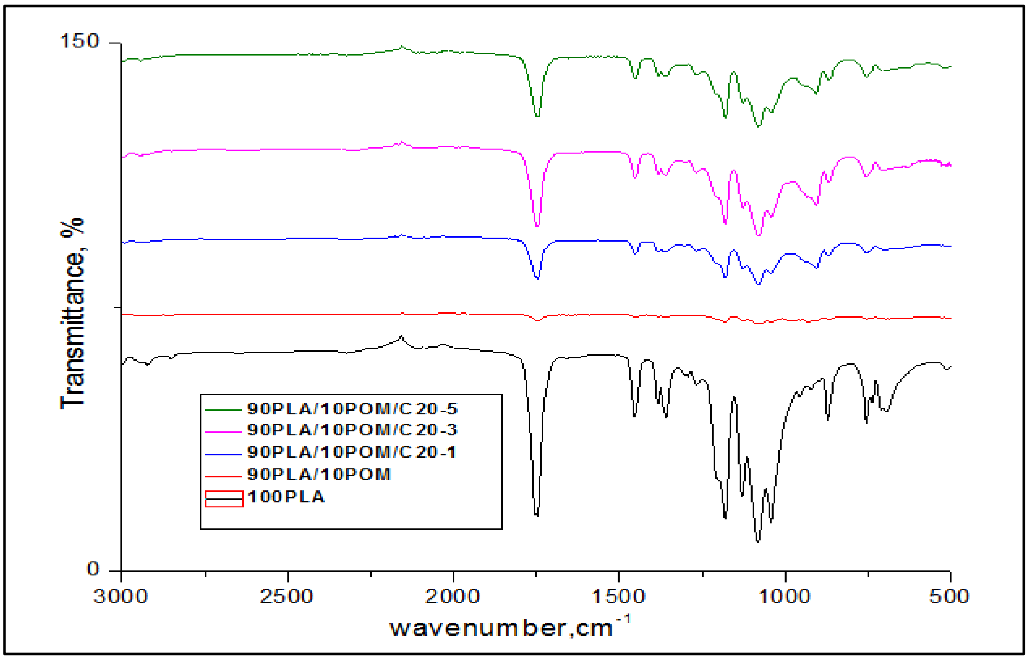


Figure 4-2: Graph of Transmittance vs Wavenumber

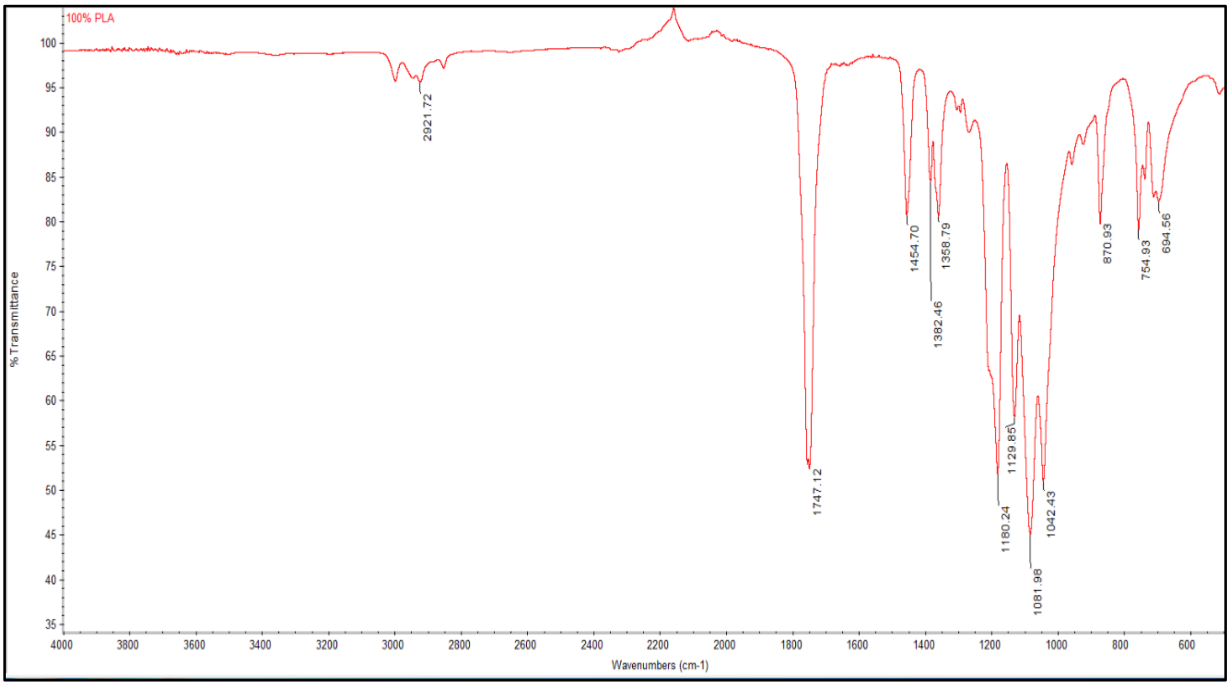


Figure 4-3: 100% PLA

The figure above shows the neat PLA with the highest peak of wavenumber is 2921.72 cm^{-1} and lowest peak range is 1200 cm^{-1} - 1000 cm^{-1}. For medium transmittance positioned in the range of 3200 cm^{-1} - 2600 cm^{-1}.

Table 4-1: The wavenumber and functional group of 100% PLA

Wavenumber, cm^{-1}	Functional Group
2921.72	C-H stretch (alkanes)
1747.12	C=O stretch(ester saturated aliphatic)
1454.70	C-H bend(alkanes)
1180.24	C-O-C

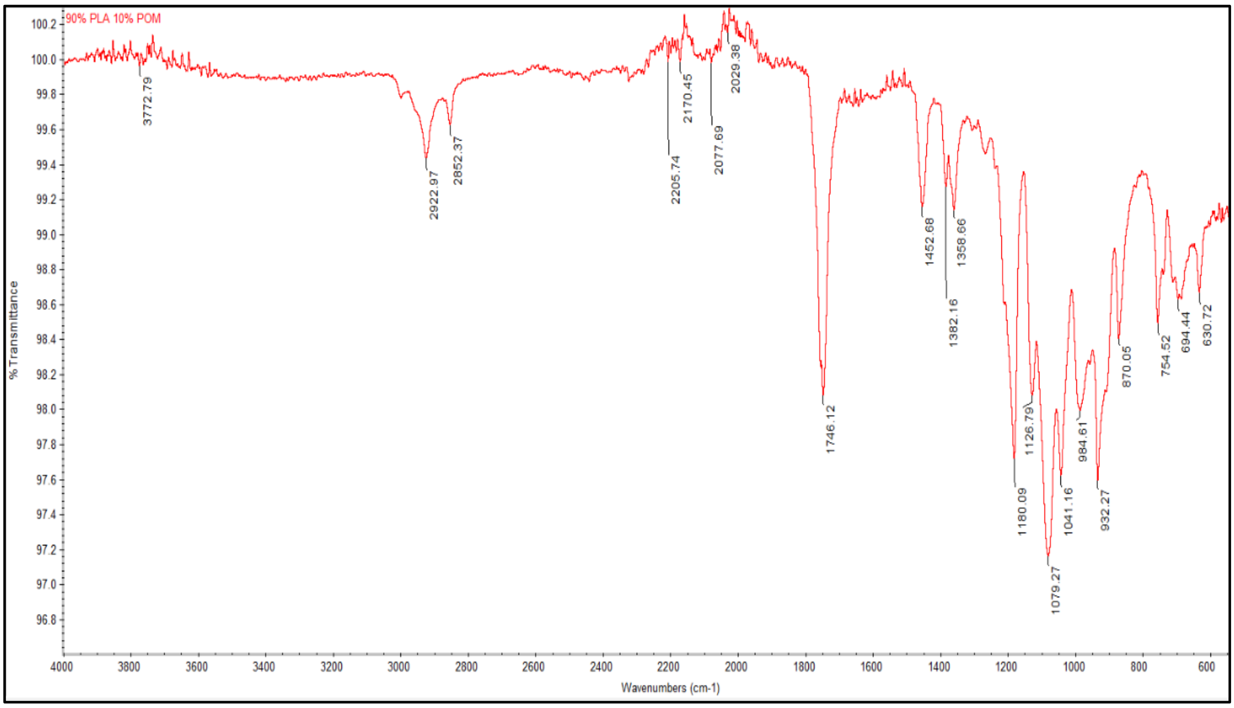


Figure 4-4: 90% PLA 10% POM

The figure above shows the blends of 90% of PLA and 10% of POM with the highest peak of wavenumber is 2170.45 cm^{-1} and lowest peak range is 1200 cm^{-1} - 1000 cm^{-1}. For medium transmittance positioned in the range of 3200 cm^{-1} - 2600 cm^{-1}.

Table 4-2: The wavenumber and functional group of 90% PLA 10% POM

Wavenumber, cm^{-1}	Functional Group
2922.97	C-H stretch (alkanes)
1746.12	C=O stretch(ester saturated aliphatic)
1452.68	C-H bend(alkanes)
1180.09	C-O-C

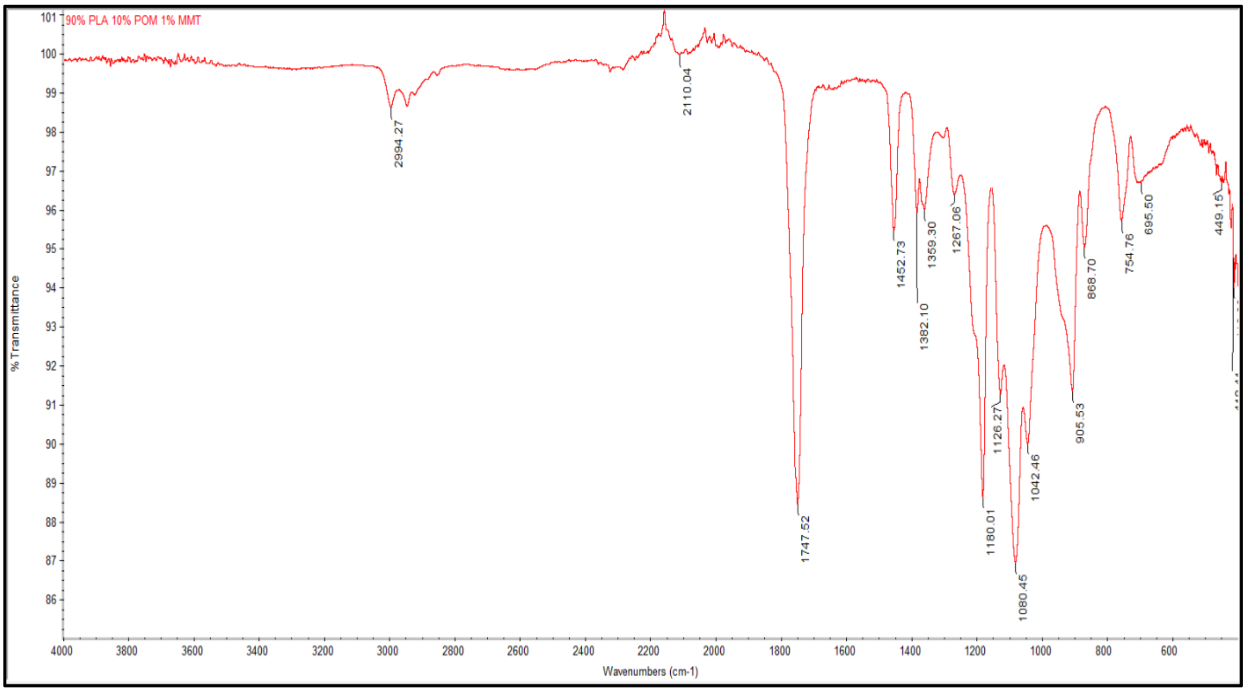


Figure 4-5: 90% PLA 10% POM 1% Clay

The blends of 90% of PLA and 10% of POM and 1% clay shows the highest peak of wavenumber is 2110.04 cm^{-1} and lowest peak range is 1200 cm^{-1} - 1000 cm^{-1} as in figure 4-5. For medium transmittance positioned in the range of 3200 cm^{-1} - 2600 cm^{-1}.

Table 4-3: The wavenumber and functional group of 90% PLA 10% POM 1% clay

Wavenumber, cm^{-1}	Functional Group
2994.27	C-H stretch (alkanes)
1747.52	C=O stretch(ester saturated aliphatic)
1452.73	C-H bend(alkanes)
1180.01	C-O-C

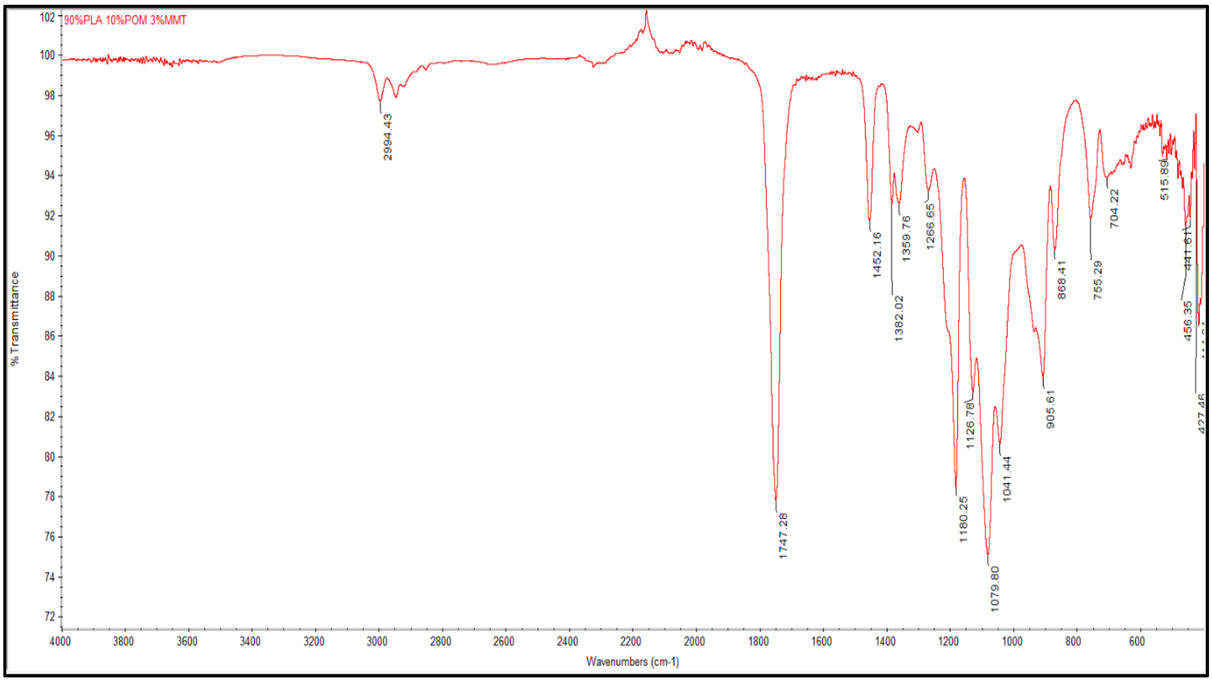


Figure 4-6: 90% PLA 10% POM 3% clay

The figure 4-6 also shows blends of 90% of PLA and 10% of POM and 3% clay and the highest peak of wavenumber is 2994.43 cm^{-1} and lowest peak range is 1200 cm^{-1} - 1000 cm^{-1} as in figure 4-6. For medium transmittance positioned in the range of 3400 cm^{-1} - 2600 cm^{-1}.

Table 4-4: The wavenumber and functional group of 90% PLA 10% 3% clay

Wavenumber, cm^{-1}	Functional Group
2994.43	C-H stretch (alkanes)
1747.28	C=O stretch(ester saturated aliphatic)
1452.16	C-H bend(alkanes)
1180.25	C-O –C stretch (alcohol, ester, ether , carboxylic acid

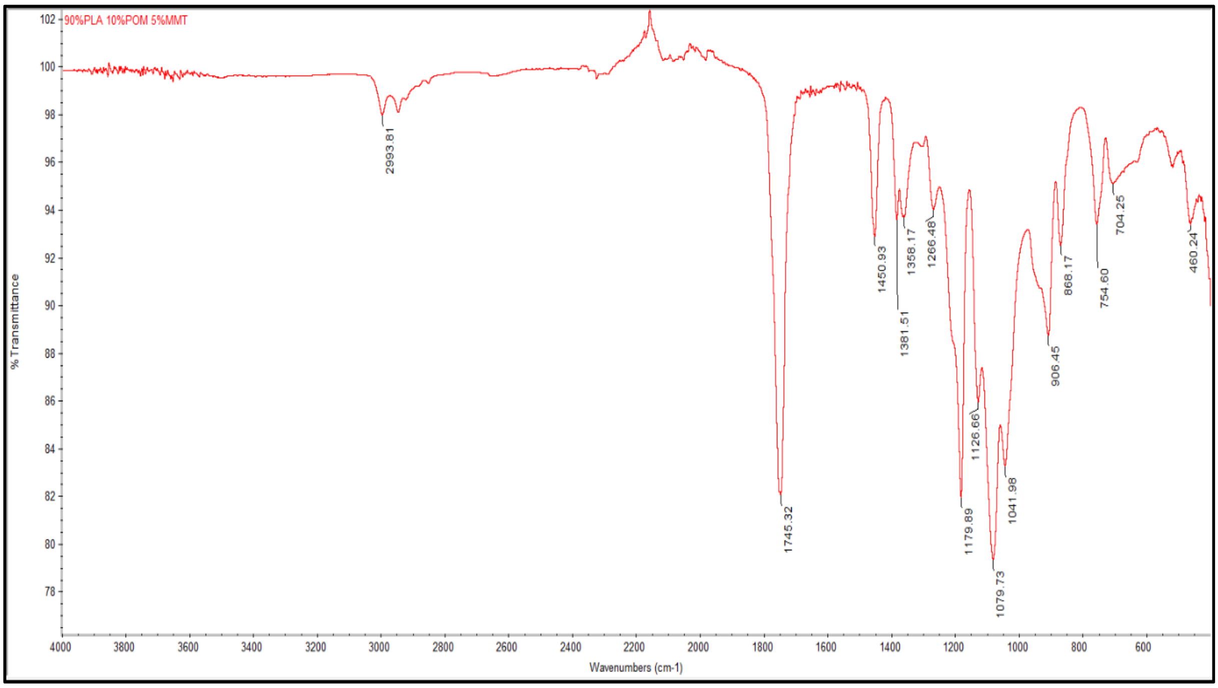


Figure 4-7: 90% PLA 10% POM 5% clay

The blends of 90% of PLA and 10% of POM and 5% clay shows the highest peak of wavenumber is 2110.04 cm^{-1} and lowest peak range is 1200 cm^{-1} - 1000 cm^{-1} as in figure 4-7. For medium transmittance positioned in the range of 3200 cm^{-1} - 2600 cm^{-1}.

Table 4-5: The wavenumber and functional group of 90% PLA 10% POM 5% clay

Wavenumber, cm^{-1}	Functional Group
2993.61	C-H stretch (alkanes)
1745.32	C=O stretch(ester saturated aliphatic)
1450.93	C-H bend(alkanes)
1266.48	C-O-C stretch (alcohol, ester, ether , carboxylic acid

4.4 Result and discussion of Thermogravimetric Analysis (TGA)

Thermogravimetric is a technique that to measure the mass and the change in mass of the sample during heating as a function of time and also temperature. Decomposition of mass could be occurred due to chemical reactions or physical changes during heating. TGA was perfomed to determine the stability of the PLA. Samples were heated from ambient temperature, that is, 25–600°C at a scanning rate of 20°C/min under nitrogen. The table 4-6 below showed the onset, peak and final degradation temperature (Xiaojie Guo, 2012).

Table 4-6: TGA onset and final degradation temperature data of neat PLA, and others composition

Sample	Temperature(°C)(onset)	Temperature(°C)(peak)	Temperature(°C)(end)
PLA	300.1	362.5	390.6
90PLA/10POM	330.3	368.8	392.8
90PLA/10POM/C20-1	250.2	365.2	420.1
90PLA/10POM/C20-3	252.2	366.3	422.2
90PLA/10POM/C20-5	252.1	372.5	423.4

PLA/POM: poly (lactic acid/polyoxymethylene); C-20: cloisite-20 (modified nanoclay).

The onset temperature is the beginning of weight loss while the final temperature is the end of degradation. It was found that the decomposition of PLA started at 300.1°C and completed at 390.6°C while PLA/POM blends started to decompose at 330.3°C and completed as 392.8°C. Based on the result obtained, for the PLA/POM/C-20 blends the onset of degradation started earlier, slightly faster than that of neat PLA. In general, it was observed that there were little changed in term of onset, peak and end temperatures of blends with 1%, 3% and 5% of C-20 loadings. This behaviour can be attributed by the decreased in molecular weight as a consequences of a melt mixing process and thus the low molecular weight can volatilize easily. Moreover, at the higher concentration of clay, onset, peak and end temperatures were found to be the highest that are 330.3°C, 372.5°C and 423.3°C respectively.

Based on the result obtained, at lower concentration of C-20 that is 1%, the onset degradation temperature shows a slightly lower with 49.9°C as compared to the neat PLA as given in the Table 4-6. This result suggests that the beginning of degradation seems to be more sensitive by the introduction of lower C-20 loadings as illustrated in Figure 4-8.

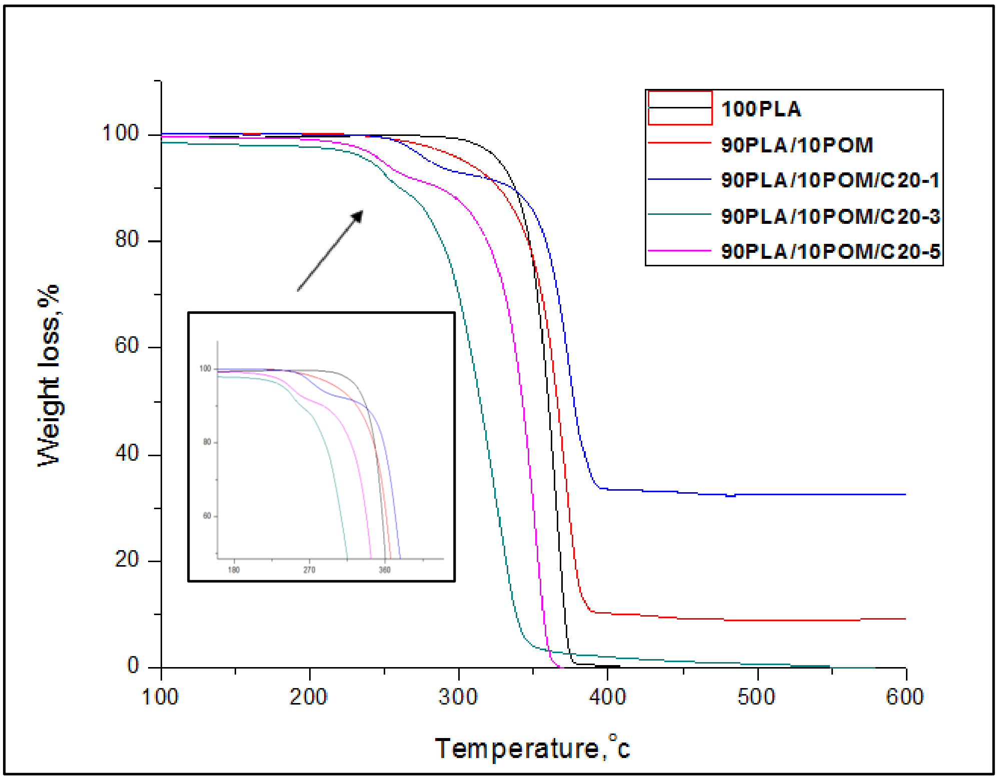


Figure 4-8: Weight loss vs temperature

4.5 Result and Discussion of Differential scanning calorimeter (DSC)

Crystallization behaviour of the blends was studied by differential scanning calorimeter (Mettler Toledo, DSC 822e). The sample sizes were about 5mg. To determine the crystallization and melting temperatures, the sample were heated from -50^{o}C to 200 ^{o}C at 10 ^{o}C/min heating rate (Xiaojie Guo, 2012).

Table 4-7 presents the glass transition temperature (T_g), crystallization temperature (T_c) and melting point (T_m) obtained from the DSC analysis. The T_c peak of PLA did not appear during cooling in PLA and PLA/POM/C-20 blends. It is believed that the main reason for this occurrence was due to a slow crystallization rate of PLA during cooling. It observed by Balakrishan etal, 2010.

Table 4-7: DSC result for PLA, PLA/POM and PLA/POM/Clay

Composition	Glass Transition Temperature(^{o}C),T_g	Crystallization Temperature(^{o}C),T_c		Melting point(^{o}C), T_m
		Heating	Cooling	
Neat PLA	60.43	97.83	Not observed	168.50
90PLA/10POM	59.63	88.06	Not observed	167.87
90PLA/10POM/C20-1	62.59	92.47	Not observed	168.95
90PLA/10POM/C20-3	61.70	89.40	Not observed	168.40
90PLA/10POM/C20-5	55.93	88.83	Not observed	168.19

The glass transition temperature, cold crystallization, melting temperature are given in Table 4-7. The cold crystallization peak of the neat PLA occurred at 97.83^{o}C as shown in figure. It can be seen in table 4-7, the crystallization temperature shifted lower temperature with increasing the clay which are 92.47 ^{o}C for 1% of clay, 89.40 ^{o}C for 3% clay and lastly decreasing to 88.83^{o}C for 5% clay. The lowest crystallization temperature shows the better of crystalline and geometry shape. The drop in T_c indicate that the nanosized of C-20 plates provide large surface thus it is reasonable to consider C-20 particle could act as effective nucleating sites of PLA crystallization as Lee at al., reported that the crystallization temperature decreased by the incorporation of clay as compared to neat PLA. Moreover, the incorporation of clay in the blend leads to different state of melt dispersion, so the crystallization behaviour of PLA could be influenced.

It was observed that the T_g of PLA/POM was lower than that of neat PLA by about 0.8^oC. The glass transition temperature show that slightly shifted to lower temperature as the clay content increased. The T_g decreased from 62.59 ^oC for 1% clay to 61.70^oC for 3% clay. The T_g of the PLA/POM phase for blends with 1% of became the higher which was probably due to presence of large of amount of highly crystallized POM (Xiaojie Guo, 2015). Gamez et al. stated that the reduction of T_g for the PLA nanocomposites could be related to the polymer chain in nanocomposites that have more free volume than in pure PLA.

The melting temperature, T_m shows the temperature inversely proportional to the content of clay which is the T_m decreasing with the increasing the content of clay. It is evident that the addition of clay increased, T_m decreases from 168.95 ^oC for 1% clay to 168.40 ^oC for 3% clay and 168.19 ^oC for 5% clay. The T_m of PLA/POM reduced only 0.63^oC. From the previously research the higher melting temperature, T_m and glass transition temperature, T_g but lowest crystallization temperature, T_c which more good and better materials. This observation is consistent with other studies on PLA and clay which reported that clay filler content did not significantly influence the T_m of PLA.

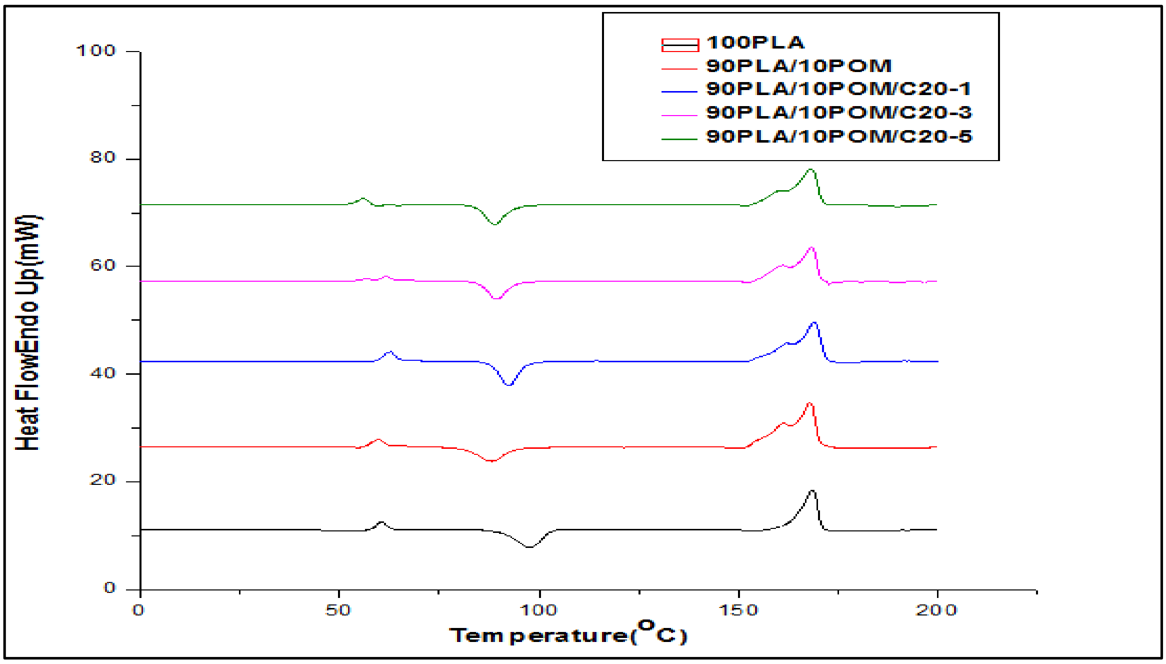
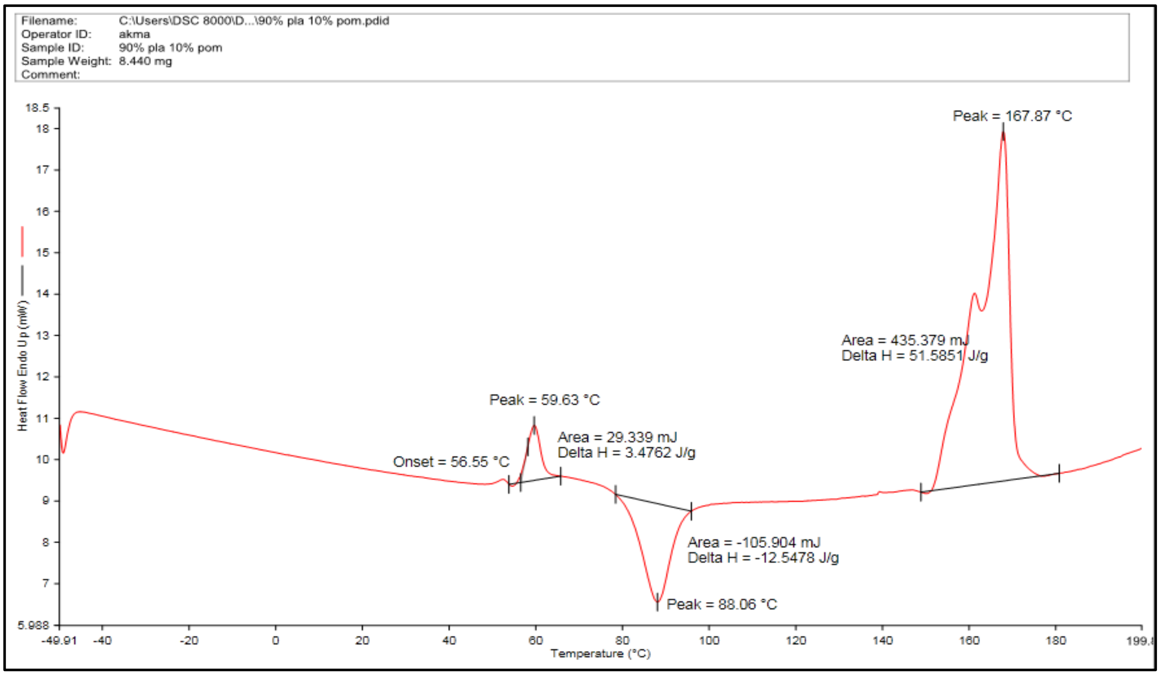


Figure 4-9: Graph of heat flow vs temperature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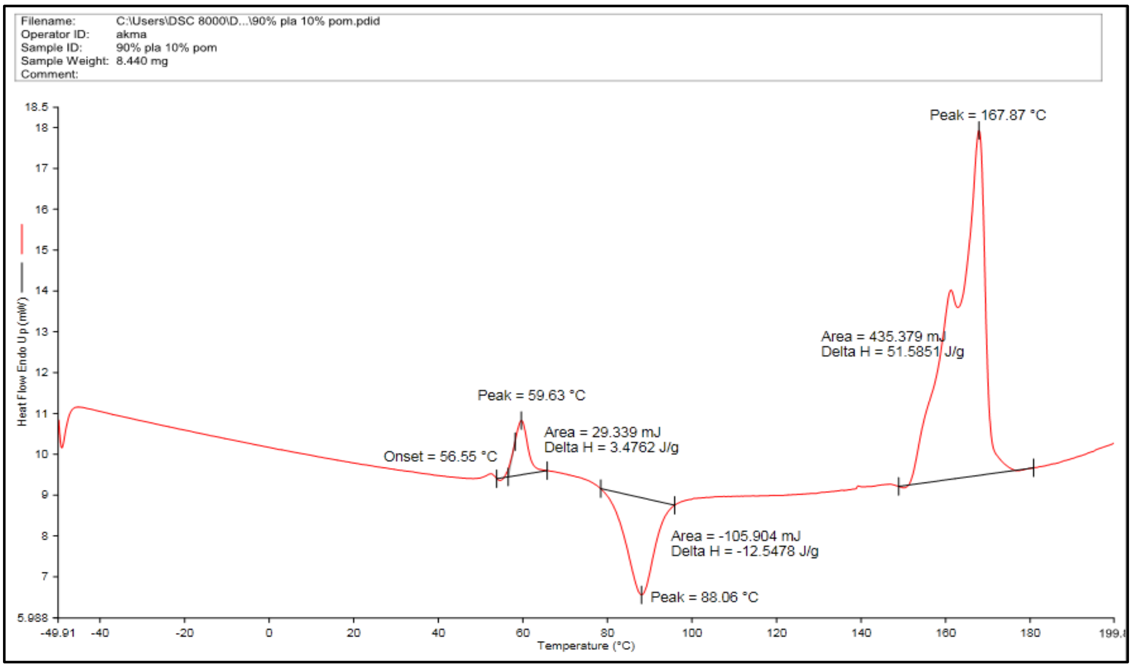
Operator ID: akma
Sample ID: 90% pla 10% pom
Sample Weight: 8.440 mg
Comment:

Figure 5: DCS result for 100% PLA



Filename: C:\Users\DSC 8000\D...\90% pla 10% pom.pdid
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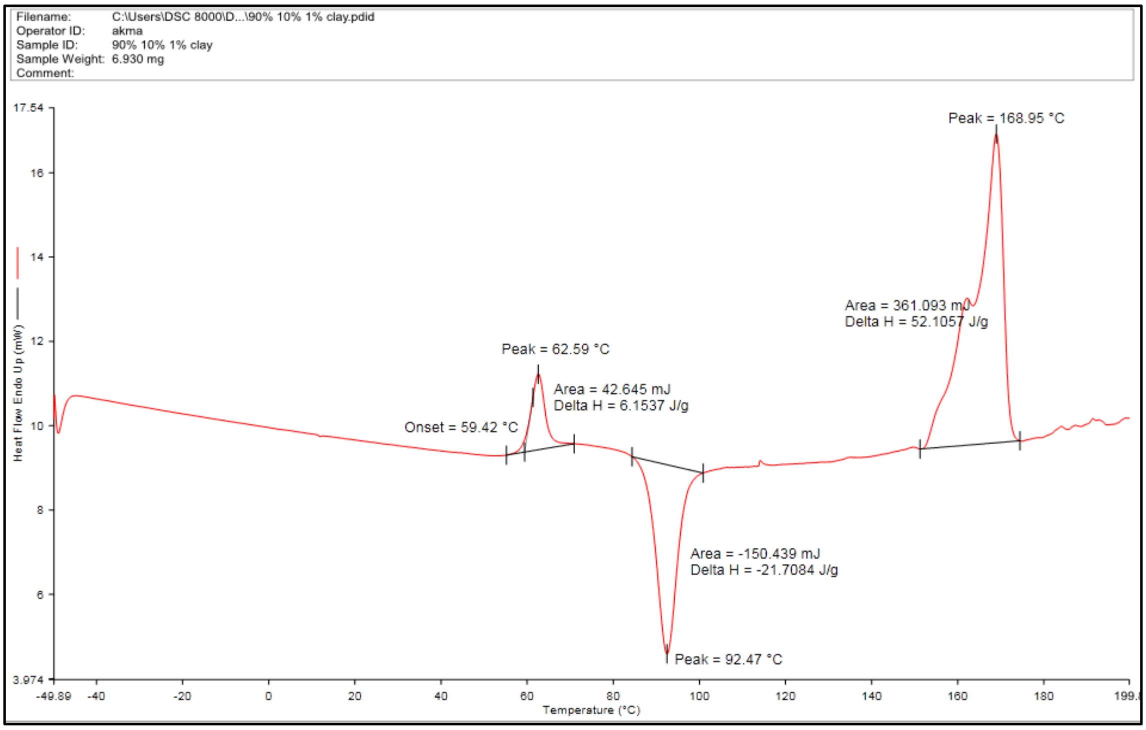
Sample ID: 90% pla 10% pom
Sample Weight: 8.440 mg
Comment:

Figure 5-1: DSC result for 90% PLA 10% POM



Filename: C:\Users\DSC 8000\D...\90% 10% 1% clay.pdid
Operator ID: akma
Sample ID: 90% 10% 1% clay
Sample Weight: 6.930 mg
Comment:

Figure 5-2: DSC result for 90% PLA 10% POM 1% Clay

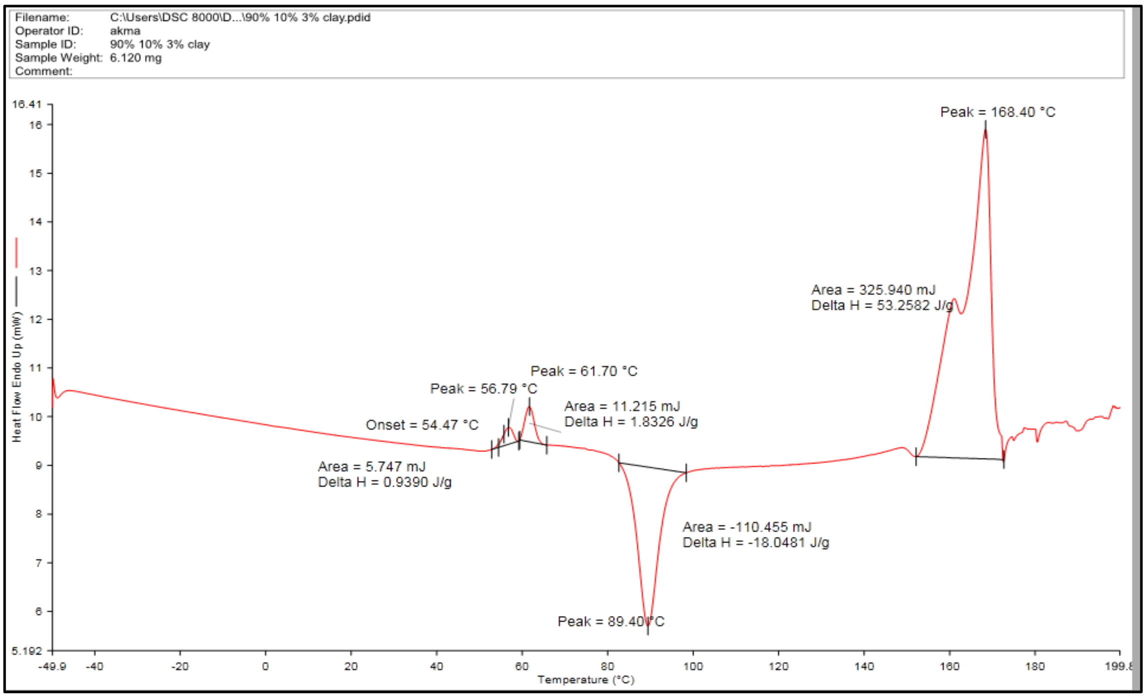


Figure 5-3: DSC result for 90% PLA 10% POM 3% Clay 3%

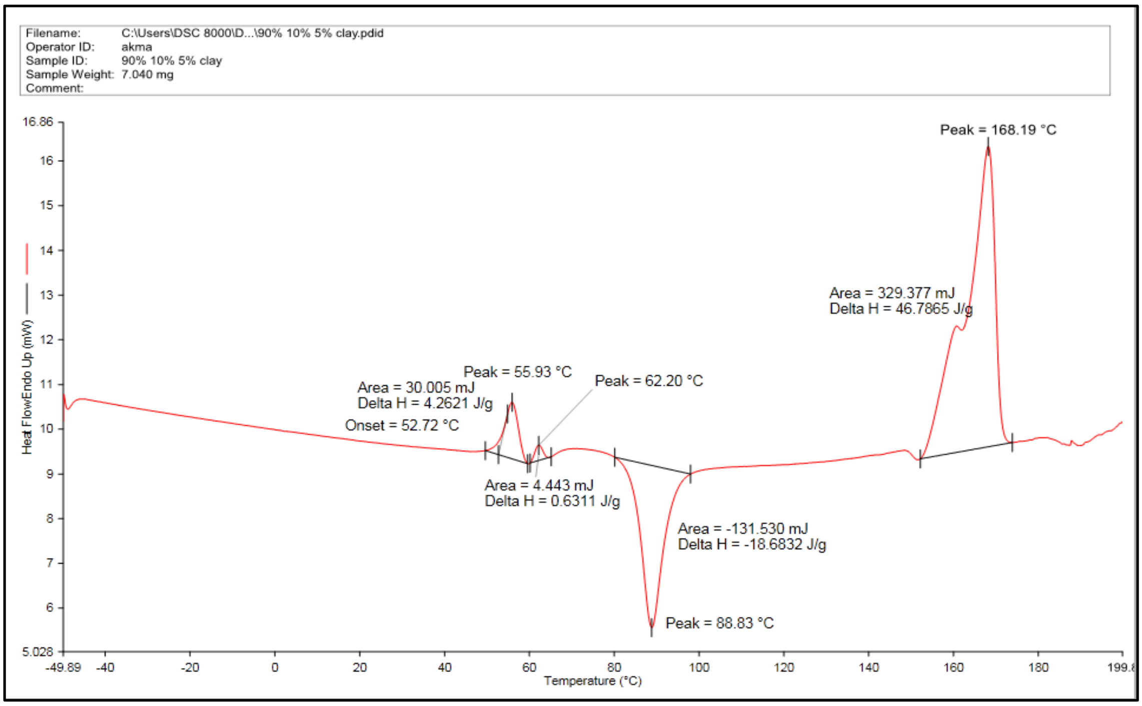


Figure 5-4: DSC result for 90% PLA 10% POM 5% Clay

4.6 Result and Discussion of Morphology analysis-Scanning Electron Microscopy (SEM)

The scanning electron microscopy (SEM) morphology characterisation provides an insight into the distribution of the POM impact modifiers in a polymer matrix, distribution of components in binary blends, the effect of interfacial addition to the particle size, the crystalline phase and dispersion/ agglomeration of particles as well as particle size (Robeson, 2007). SEM was used to investigate the particle size and the dispersion of POM and clay dispersed phase in PLA/POM/clay blend systems. The images were taken on specimens fracture surfaces broken. The figure below shows the fractured surface of neat PLA and PLA/POM and also PLA/POM/clay.

By comparing the result obtained from stress-strain analysis, properties like Young's modulus, tensile strength and elongation at break can be obtained. The result shows that the stress-strain properties increased with increasing of clay loading in the blends. From the experiment, the tensile fracture surface have been taken to study the morphological characterization of the blends. The fracture surfaces exhibit both dispersed POM particles and holes, where POM have been pulled out and are on the other fracture cross sectional area. It can be observed that the PLA/POM blends behave for an immiscible polymer blend, large dispersed phase particles, distinct particles interfaces, and indicating poor interfacial adhesion, were obtained.

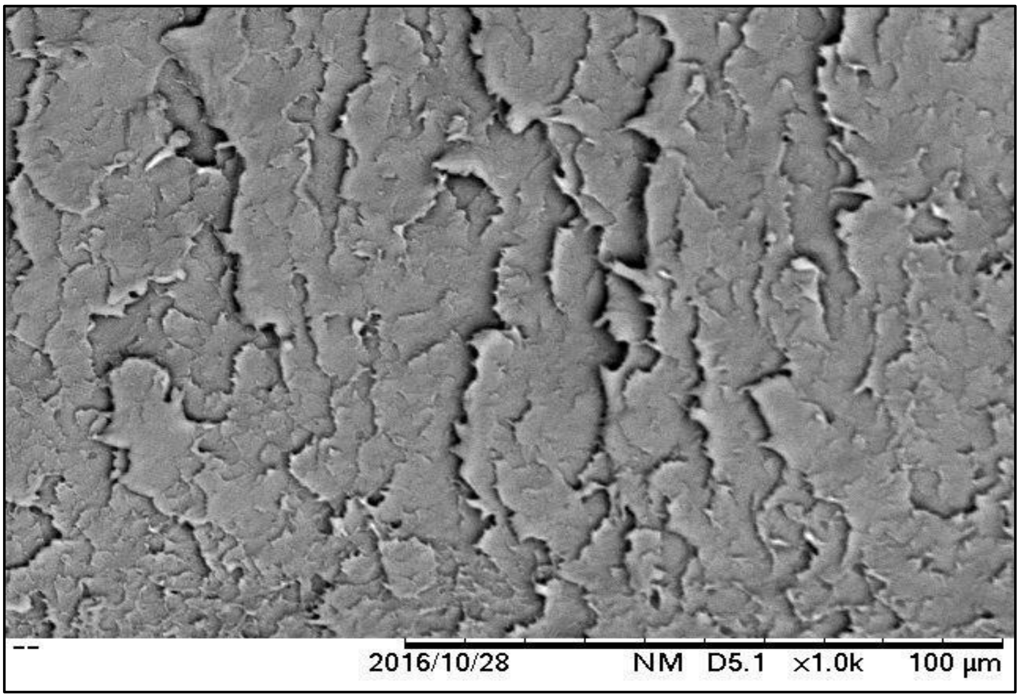


Figure 5-5: SEM images of fractured surface of 100% PLA

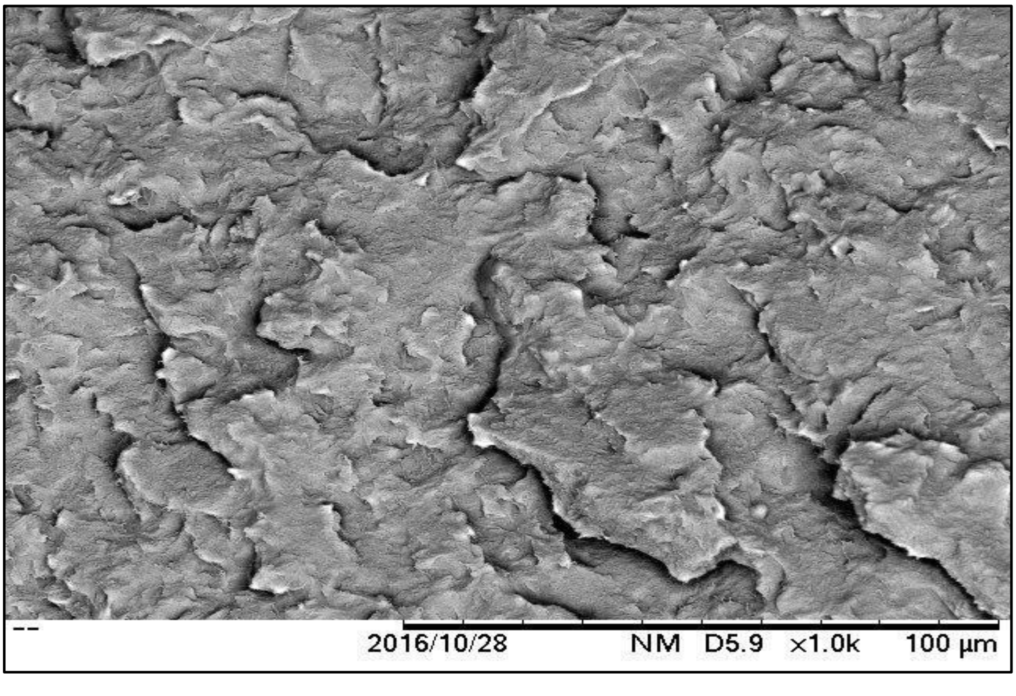


Figure 5-6: SEM images of fractured surface of 90% PLA 10% POM

Phase morphology plays important role to determining the thermal properties and mechanical behaviour of polymer blends. Figure 5-1, shows the phase-separated morphology of PLA/POM blends indicating that PLA is immiscible with POM. The dark phase represents the POM phase while the bright phase does the PLA phase.

Because POM is easy to crystallize and shows high crystallinity up to 80% these dark layers was assumedly composed of POM crystal mainly (Xiajie Gua, 2015).

Figure 5-7 shows the SEM micrograph taken from the tensile fractured specimen at x1000 magnification for PLA/POM with different concentration C-20 blends. It can be seen that Figure 5-7 (a) illustrates the micrographs of the 90PLA/10POM/C20-1 that have rough and uneven structure. Figure 5-7 (b) illustrates even structure of tensile fracture at composition of 90PLA/10POM/C20-3. A uniform dispersion of the PLA particles could be happened due to a good interaction between PLA and POM in the presence of 1% of clay. In figure 5-7(c), there were more small voids appeared compared to Figure 5-7 (a) and (b) micrographs due to increase of percentage of clay loadings. Hence, the presence of clay increased the interaction between phases, thus improving the compatibility and enhancing the tensile strength of the blends.

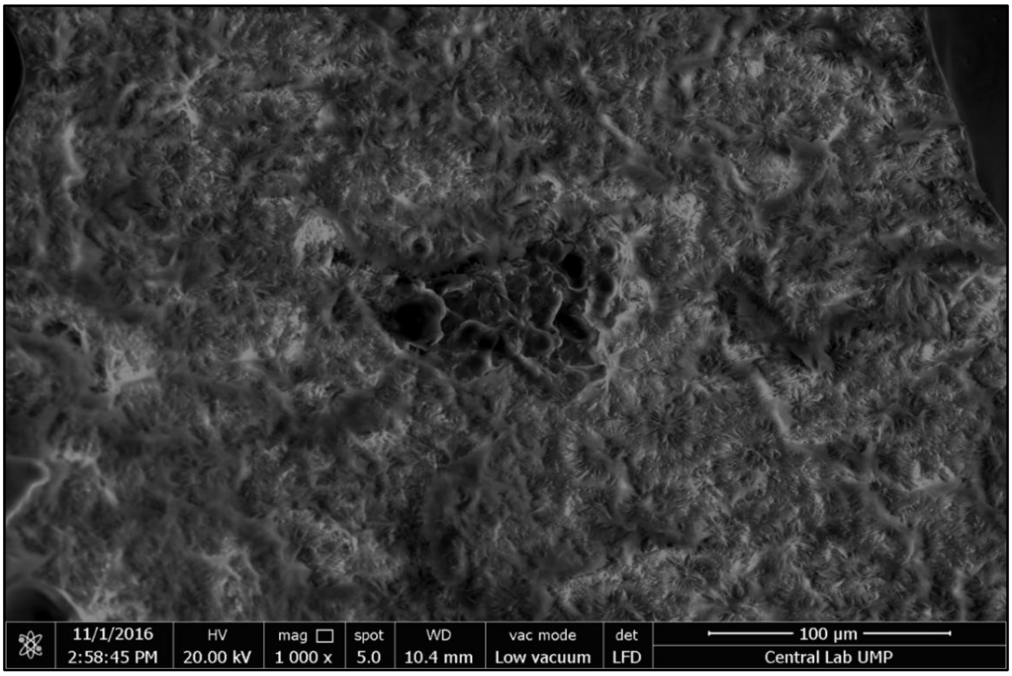


Figure 5-7(a): SEM images of 90PLA/10POM/C20-1

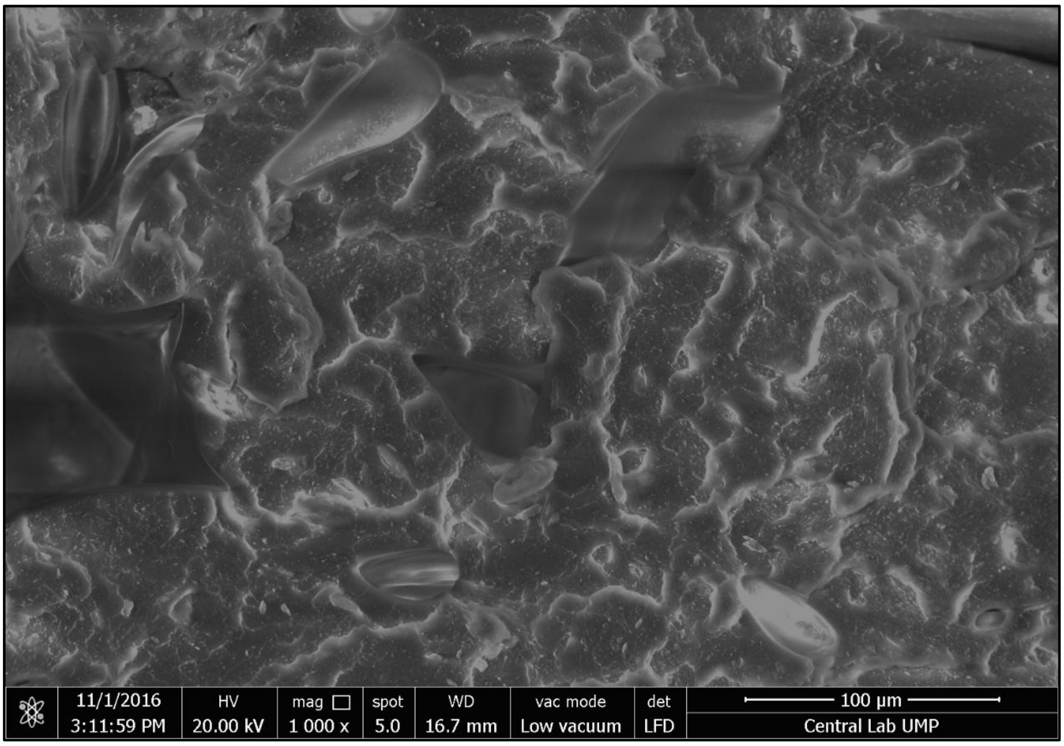


Figure 5-7(b): SEM images of 90PLA/10POM/C20-3

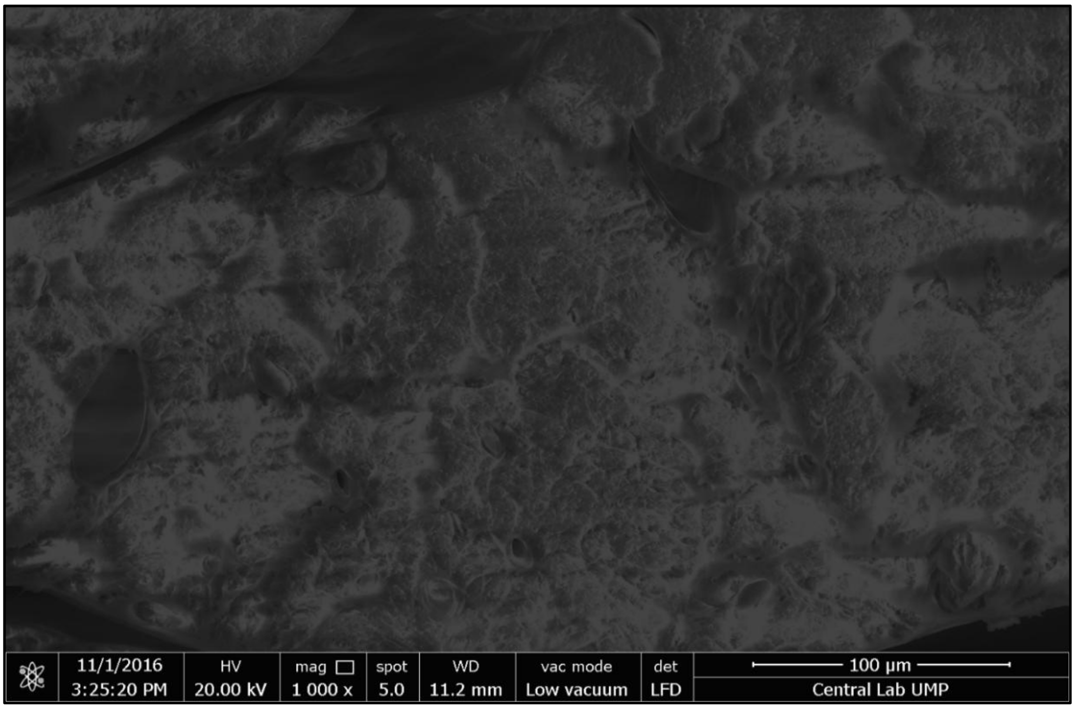


Figure 5-7(c): SEM images of 90PLA/10POM/C20-5

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The effect on the morphology, mechanical and thermal properties of PLA/POM and C-20 blends have been investigated. From the mechanical properties, the young's modulus increased with the addition C-20 in the PLA/POM blends. The young's modulus of PLA/POM also increased significantly as compared to blends with 1% of C-20, from 37.380 N/mm^2 to 115.68 N/mm^2. The elongation at break and tensile strength also increased directly proportional with increasing loading of clay. Thermal analysis through DSC showed that the T_c of PLA dropped in PLA/POM blends indicating the nucleating effect of POM. SEM revealed a two-phase morphology, where the POM (as droplets) is well dispersed in PLA matrix. POM toughened PLA has a great potential for structural applications due to balanced properties in terms of stiffness and toughness.

5.2 Recommendation

There are some suggestions and recommendation for improving the quality of the research**.** Preparation of the sample is the most important things to get better result for the analysis. Before blending the sample in the extruder, conduct the pre-blending two times to make sure homogenous mixed. Lastly, personal protective equipment are important such goggle and mask when handling with fine powder and also hot surface.

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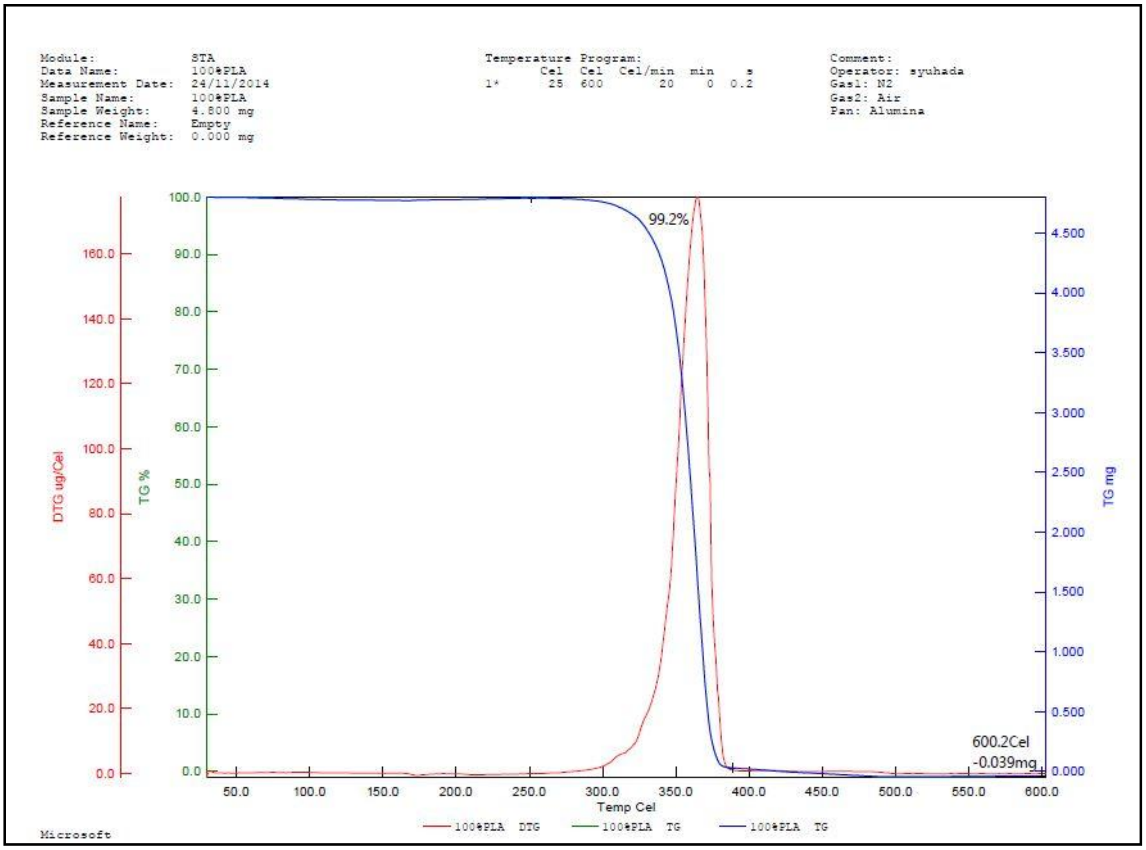
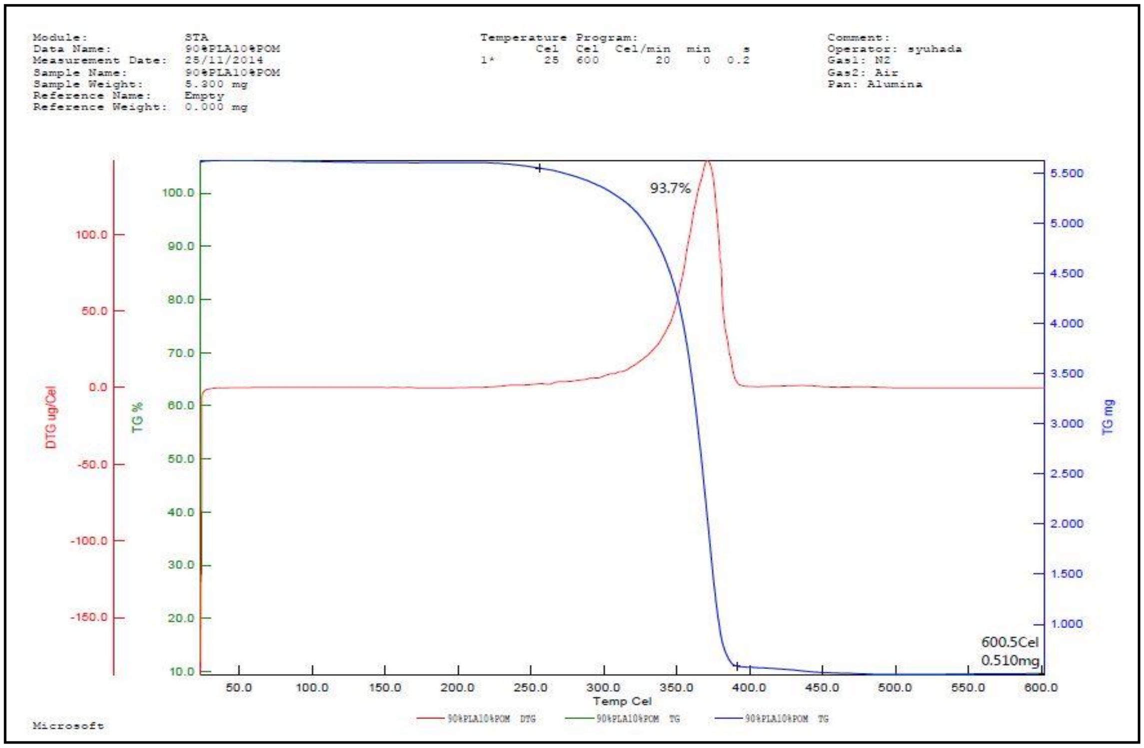
APPENDIX

APPENDIX A: TGA RESULTS



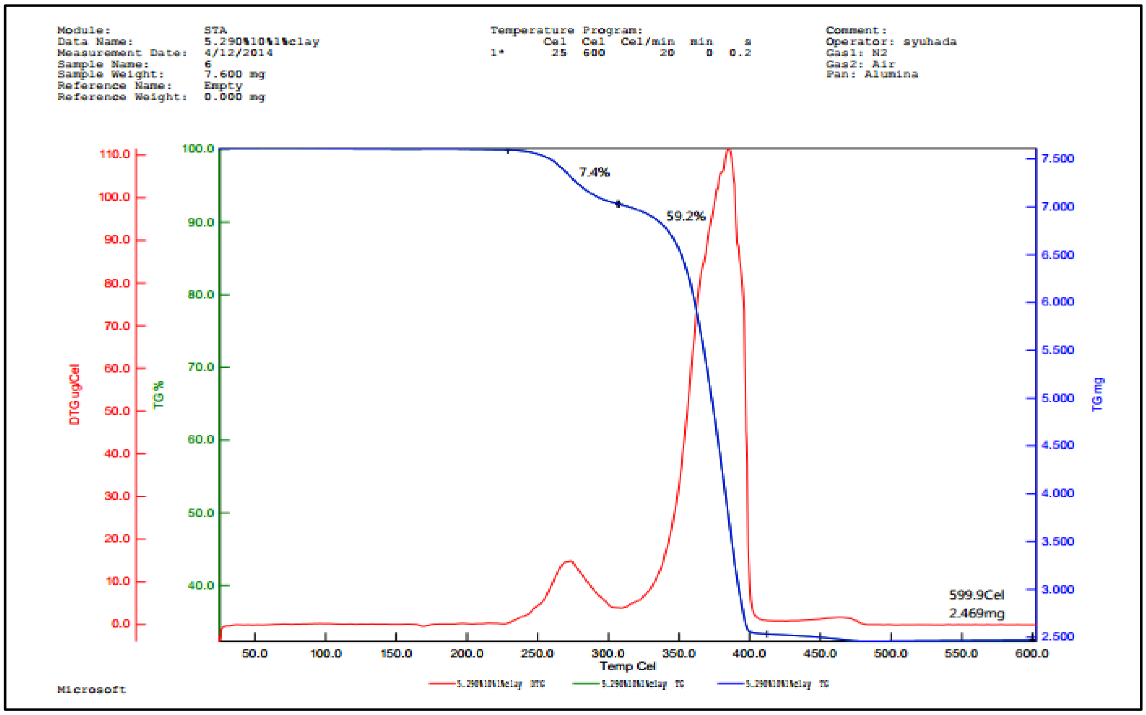
```
Module:             STA                   Temperature Program:                         Comment:
Data Name:          100%PLA                      Cel  Cel  Cel/min  min    s           Operator: syuhada
Measurement Date:   24/11/2014            1*      25  600       20    0  0.2           Gas1: N2
Sample Name:        100%PLA                                                            Gas2: Air
Sample Weight:      4.800 mg                                                           Pan: Alumina
Reference Name:     Empty
Reference Weight:   0.000 mg
```

Figure A-1: TGA result for 100% PLA



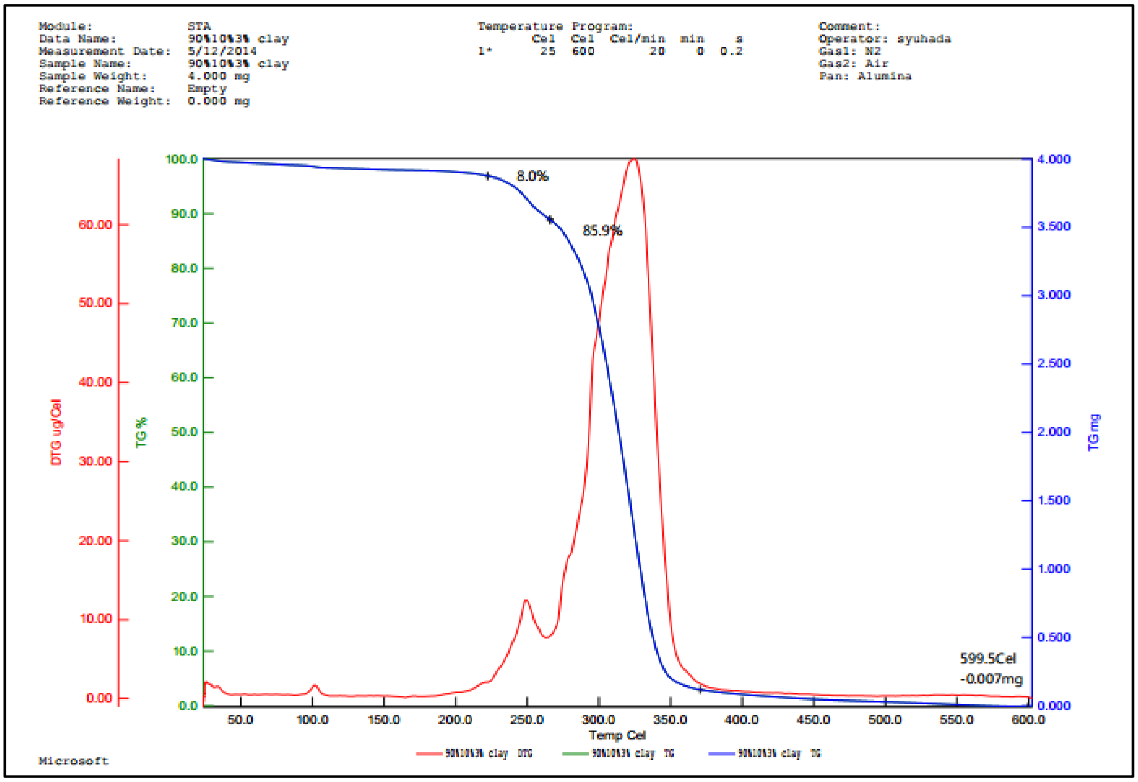
```
Module:              STA                          Temperature Program:                          Comment:
Data Name:           90%PLA10%POM                        Cel  Cel  Cel/min  min    s            Operator: syuhada
Measurement Date:    25/11/2014                   1*      25  600       20    0  0.2            Gas1: N2
Sample Name:         90%PLA10%POM                                                               Gas2: Air
Sample Weight:       5.300 mg                                                                   Pan: Alumina
Reference Name:      Empty
Reference Weight:    0.000 mg
```

Figure A-2: TGA result for 90% PLA 10% POM



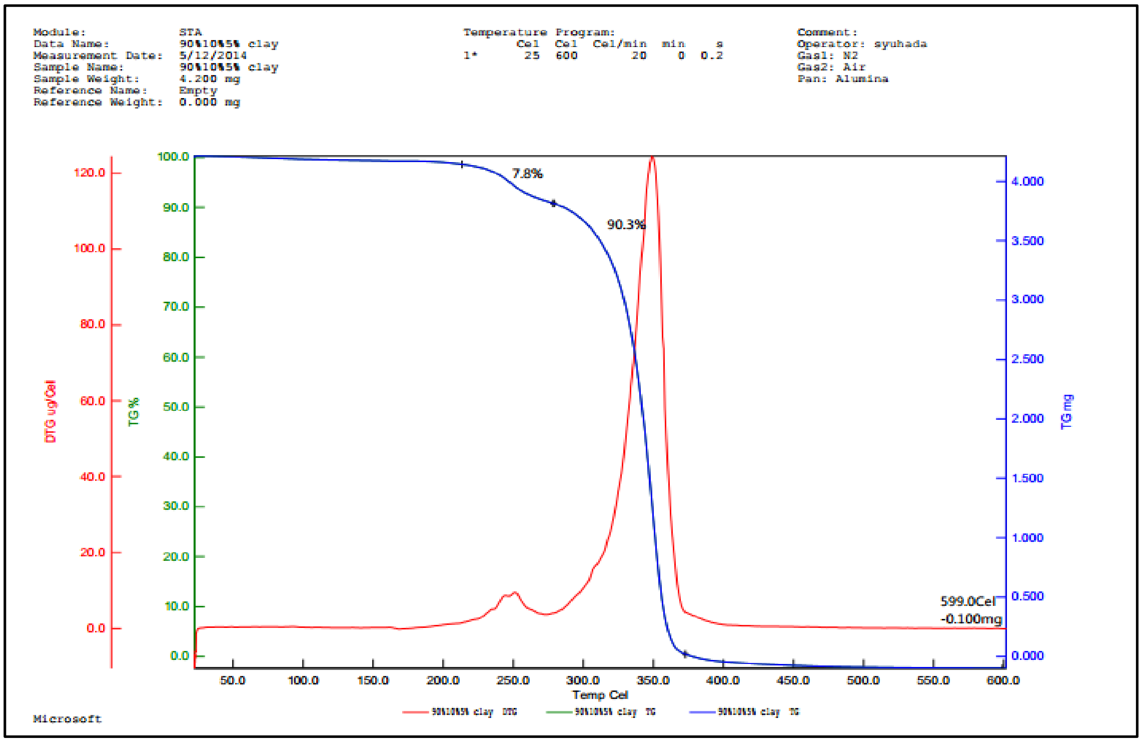
```
Module:              STA                          Temperature Program:                          Comment:
Data Name:           5.290%10%1%clay                     Cel  Cel  Cel/min  min    s            Operator: syuhada
Measurement Date:    4/12/2014                    1*      25  600       20    0  0.2            Gas1: N2
Sample Name:         6                                                                          Gas2: Air
Sample Weight:       7.600 mg                                                                   Pan: Alumina
Reference Name:      Empty
Reference Weight:    0.000 mg
```

Figure A-3: TGA result for 90% PLA 10% POM 1% Clay



```
Module:             STA                          Temperature Program:                      Comment:
Data Name:          90%10%3% clay                      Cel   Cel   Cel/min   min    s      Operator: syuhada
Measurement Date:   5/12/2014                    1*      25   600        20     0   0.2    Gas1: N2
Sample Name:        90%10%3% clay                                                          Gas2: Air
Sample Weight:      4.000 mg                                                               Pan: Alumina
Reference Name:     Empty
Reference Weight:   0.000 mg
```

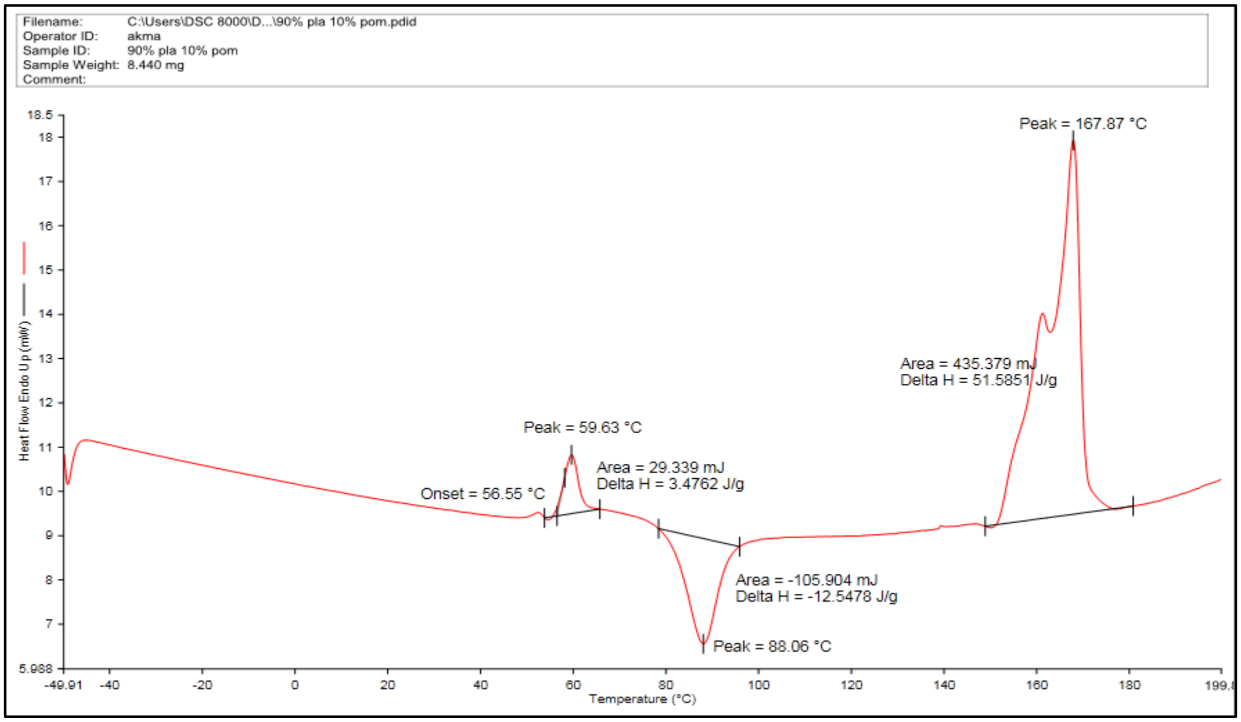
Figure A-4: TGA result for 90% PLA 10% POM 3% Clay



```
Module:             STA                          Temperature Program:                      Comment:
Data Name:          90%10%5% clay                      Cel   Cel   Cel/min   min    s      Operator: syuhada
Measurement Date:   5/12/2014                    1*      25   600        20     0   0.2    Gas1: N2
Sample Name:        90%10%5% clay                                                          Gas2: Air
Sample Weight:      4.200 mg                                                               Pan: Alumina
Reference Name:     Empty
Reference Weight:   0.000 mg
```

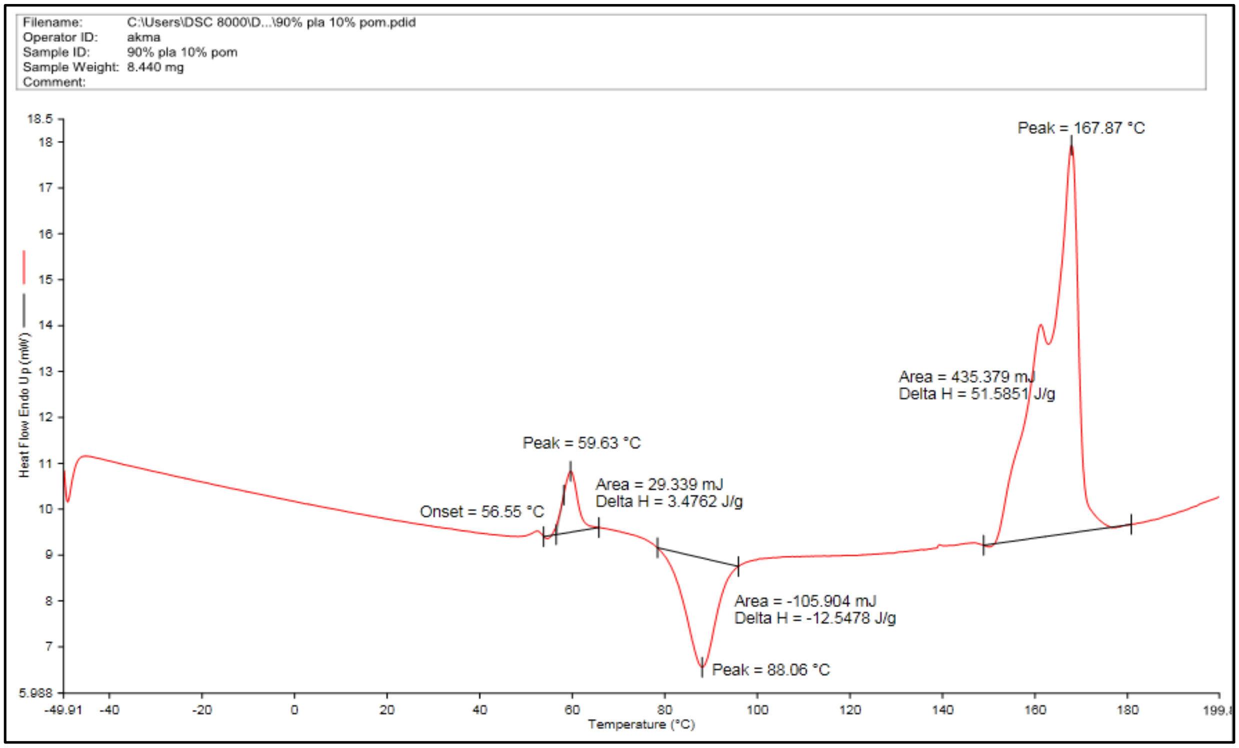
Figure A-5: TGA result for 90% PLA 10% POM 5% Clay

APPENDIX B: DSC RESULTS



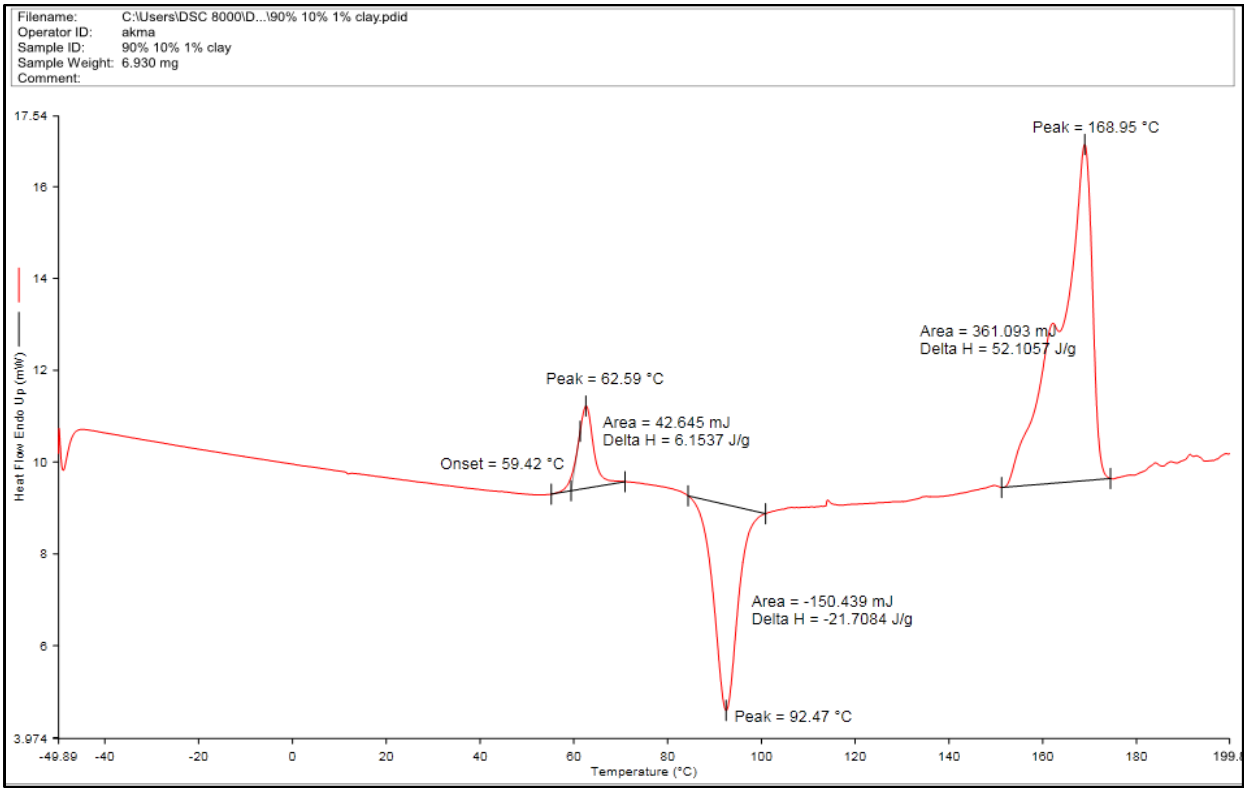
Filename: C:\Users\DSC 8000\D...\90% pla 10% pom.pdid
Operator ID: akma
Sample ID: 90% pla 10% pom
Sample Weight: 8.440 mg
Comment:

Figure B-1: DCS result for 100% PLA



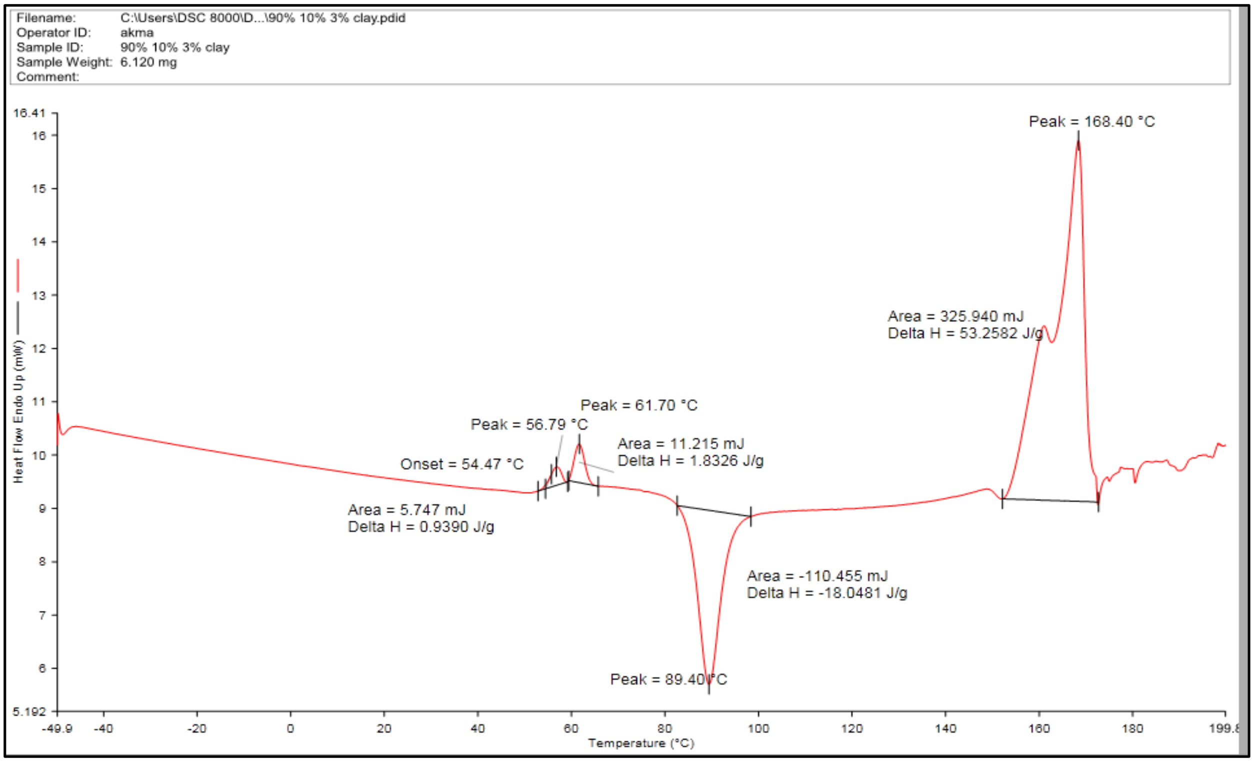
Filename: C:\Users\DSC 8000\D...\90% pla 10% pom.pdid
Operator ID: akma
Sample ID: 90% pla 10% pom
Sample Weight: 8.440 mg
Comment:

Figure B-2: DCS result for 90% PLA 10% POM



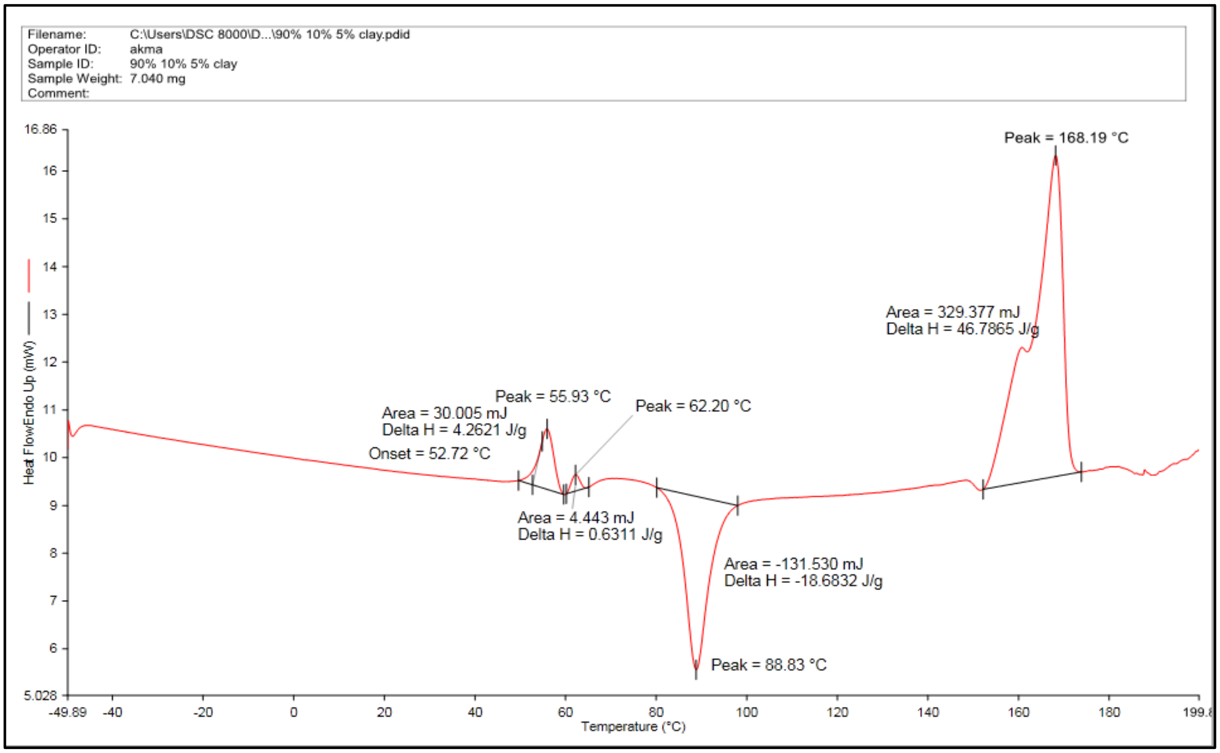
Filename: C:\Users\DSC 8000\D...\90% 10% 1% clay.pdid
Operator ID: akma
Sample ID: 90% 10% 1% clay
Sample Weight: 6.930 mg
Comment:

Figure B-3: DSC result for 90% PLA 10% POM 1% Clay



Filename: C:\Users\DSC 8000\D...\90% 10% 3% clay.pdid
Operator ID: akma
Sample ID: 90% 10% 3% clay
Sample Weight: 6.120 mg
Comment:

Figure B-4: DSC result for 90% PLA 10% POM 3% Clay



Filename: C:\Users\DSC 8000\D...\90% 10% 5% clay.pdid
Operator ID: akma
Sample ID: 90% 10% 5% clay
Sample Weight: 7.040 mg
Comment:

Figure B-5: DSC result for 90% PLA 10% POM 5% Clay