# CHARACTERIZATION AND PROPERTIES OF MIMUSOPS ELENGI SEED POWDER (MESP) FILLED POLYPROPYLENE COMPOSITES

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**A project report submitted in partial fulfillment of the**
**requirements for the award of Bachelor of Engineering**
**(Hons.) Petrochemical Engineering**

**Faculty of Engineering and Green Technology**
**Universiti Tunku Abdul Rahman**

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# DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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# APPROVAL FOR SUBMISSION

I certify that this project report entitled **“CHARACTERIZATION AND PROPERTIES OF MIMUSOPS ELENGI SEED POWDER (MESP) FILLED POLYPROPYLENE COMPOSITES”** was prepared by **LEONG WENG LI** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Petrochemical Engineering at Universiti Tunku Abdul Rahman.

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# CHARACTERIZATION AND PROPERTIES OF MIMUSOPS ELENGI SEED POWDER (MESP) FILLED POLYPROPYLENE COMPOSITES

## ABSTRACT

*Mimusops elengi* seed powder (MESP) was introduced as a new bio-filler to reinforce the polypropylene (PP) matrix in this research. Several characterizations and testing have been carried out on both MESP and PP/MESP composites to determine the physical, chemical, thermal, and morphological properties of the particles. The particle size analysis, FTIR-ATR, and SEM were used to characterize the MESP before it was used to reinforce into PP matrix. PP resins and MESP were pre-dried and melt mixed using rheometer Branbender® internal mixer (Plastograph® EC815652, Duisburg, Germany) at different compounding loadings to produce PP/MESP composites. The processability, tensile properties, chemical properties, and morphological properties of PP/MESP were characterized and determined using FTIR-ATR, scanning electron microscopy, processing torque, differential scanning calorimetry, and tensile test. MESP were irregular in shape and were existed as a mixture of aggregates and small agglomerates. Also, MESP has a narrower particle size distribution, smaller mean diameter and high surface area as compared to other particulate fillers. On the other hand, the FTIR-ATR analysis has shown that there was no chemical reaction occurred between PP and MESP as there has no new peaks formation after the PP/MESP composites reinforcement. Nonetheless, the addition of MESP filler up to 10.0 wt % gave slight effect of the processability of PP/MESP composites as shown in the value obtained from processing torque. The loading and stabilization torques decreased gradually as increased of MESP loading. This is because MESP has acted as a plasticizer and has placed itself between the polypropylene chains and disturbed the initial orientation of PP by lowering the viscosity of PP/MESP composites, making it easier to flow, thus, better processability of PP/MESP composites were achieved. However, instead of improved tensile strength, addition of MESP has gradually reduced the tensile strength of PP/MESP composites, increased of E-modulus, as well as reduction of elongation at break of PP/MESP composites. The SEM morphological observation revealed that MESP particles were dispersed well in PP matrix but has a weak interfacial interaction with PP. Agglomeration of MESP can be seen at higher MESP loading of 10.0 wt %. Thus, the weak interfacial interaction between MESP and PP and the formation of agglomerates of MESP is responsible to the reduction of tensile strength and high stiffness of PP/MESP composites as compared to unfilled PP.

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# LIST OF SYMBOLS / ABBREVIATIONS

| | |
|---|---|
| CAS | Chemical Abstract Service |
| $C_3H_6$ | Propylene |
| $C_nH_{2n}$ | Standard Formula for Alkenes |
| DSC | Differential Scanning Calorimetry |
| ER | Epoxy Resin |
| FAME | Fatty Acid Methyl Ester |
| FTIR | Fourier Transform Infrared Spectroscopy |
| FTIR-ATR | Fourier Transform Infrared Spectroscopy – Attenuated Total Reflection |
| GPS | Global Positioning System |
| HDPE | High Density Polyethylene |
| IR | Infrared Spectroscopy |
| KBr | Potassium Bromide |
| LDPE | Low Density Polyethylene |
| MESP | *Mimusops Elengi* Seed Powder |
| MESSP | *Mimusops Elengi* Seed Shell Powder |
| MW | Molecular Weight |
| NFPCs | Natural Fibre Reinforced Polymer Composites |
| PE | Polyethylene |
| PP | Polypropylene |
| PS | Polystyrene |
| PSA | Particle Size Analysis |
| PVC | Polyvinyl Chloride |
| SBR | Styrene Butadiene Rubber |
| SEM | Scanning Electron Microscopy |
| TGA | Thermo |

| | |
|---|---|
| UHMWPE | Ultrahigh Molecular Weight Polyethylene |
| UV | Ultraviolet |

| | |
|---|---|
| $\Delta H_m$ | Melting Enthalpy (J/g) |
| $\Delta H_{100}$ | Melting Heat for 100% Crystalline Polypropylene, 207 J/g |
| $T_c$ | Crystallization Temperature ($^oC$) |
| $T_m$ | Melting Temperature ($^oC$) |
| $W_P$ | Weight Fraction of Polypropylene in Composite |
| $X^m_c$ | Degree of Crystallinity (%) |

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# CHAPTER 1

# INTRODUCTION

## 1.1 Background

Nowadays, natural fibres composites are gaining interest in polymer industrial applications as natural fibres can be produced at a lower cost with improved sustainability, lower density, high tensile strength and stiffness, renewable resources, biodegradable resources, and lower hazardous emissions (Pickering, 2015). For instance, natural fibres are potential to replace the existing synthetic fibres as natural fibres are mostly biodegradable and recyclable as compared to synthetic fibres (Joseph, 2016).

Natural fibres are usually from plants, animals, and geological processes that can be utilized as a composite materials and can make great impacts to the properties of the parent materials (Joseph, 2016). The examples of natural fibres are hemp, kenaf, rice husk, sisal and others, which usually used in reinforcement of polymer matrix nowadays.

Moreover, the high productions of synthetic fibre reinforced non-biodegradable polymer products have led to the large amount of polymer wastes and have increased the dependent on fossil fuels. The issues of polymer wastes have become a major concern for every country as it cannot be burnt and degraded itself (Malkapuram et al., 2009). Nevertheless, open burning the polymer wastes can lead to greenhouse effect in long length run and global warming. Thus, reduction usage of petroleum resources together with the awareness of global environmental issues have led to the alternative developments for new green natural fibres to replace the dependent on fossil fuels resources (Mohanty et al., 2012). Governments have been strongly encouraged industries to develop a new biodegradable polymer composite material from renewable resources to promote green technology as well as act as an alternative way to solve the problems associated with agricultural residues (Sapuan, 2011).

In this research, *mimusops elengi* seed powder (MESP) was introduced as a filler in polypropylene (PP). The polypropylene is one the dominating thermoplastic materials that currently available in the market demand. Other common thermoplastic materials such as polyethylene, polyvinyl chloride, and polyethylene terephthalate are also highly demand in the market (Melvin, 2012).

In the preliminary studies by Ng (2016), a new bio-filler *mimusops elengi* seed shell powder (MESSP) was used as reinforcement of PP matrix. The research has shown that MESSP addition into PP matrix showed significant improvements in physico-mechanical properties. However, the FTIR analysis revealed that no chemical interactions happened between MESSP and PP. Furthermore, the improved properties of MESSP/PP declined when it approached after 5.0 wt% of MESSP loading. Besides, the optimum properties of MESSP in PP matrix could not be achieved and further investigations are required.

Nativity of *mimusops elengi* is India, Myanmar and Sri Lanka but is cultivated across the tropics including Malaysia, Singapore and Australia. The *mimusops elengi* fruits are one of the food sources for birds and squirrels. The flowers can be used as adornments or garlands for women wear and used as a stimulant in India. Besides, the bark, fruits, seeds, and leaves of *mimusops elengi* are mainly used in traditional medication and other treatments in India (Henry, 1988). Furthermore, *mimusops elengi* fruits are edible and often used as cooking oils. However, it is not as well-known as other oils such as sunflower and peanut. Chemical properties of *mimusops elengi* bark contains chemical components such as tannin, wax, starch, and ash whereas the flowers contain volatile oils, and certain amount of fatty oils can be found in seeds of *mimusops elengi* (Gami et al., 2012).

Nowadays, the *mimusops elengi* can be found in the application of pesticides, fertilizer and fatty acid methyl ester (FAME) productions. Thus, researchers are more concentrate on the utilization of *mimusops elengi* fruits and kernels to produce biodiesel mainly used in FAME production (Bora et al., 2014; Dutta and Deka, 2014). Nonetheless, *mimusops elengi* can be considered a good alternative as new source of bio-filler for bio-composite development as *mimusops elengi* trees can be easily found anywhere in roadside and does not require additional plantation areas as compared to other existing bio-fillers (Gami et al., 2012).

Moreover, MESP contains higher fatty acid content as compared to MESSP that it is possible to facilitate the processing of composite by acting as a plasticizer or it can chemically bind to PP due to its hydrophobic fatty acid content. Hence this research is focused on study of MESP as filler in PP composite. Furthermore, the processability and physico-mechanical properties for MESP as filler in polypropylene matrix will be studied.

## 1.2 Problem Statement

According to preliminary studies reported by Ng (2016) a new polypropylene based bio-composite using *mimusops elengi* seed shell powder (MESSP) as a new bio-filler has been successfully introduced. Studies on mechanical properties, morphology properties, and processability of PP/MESSP composites using different MESSP loadings were discussed in the report (Ng, 2016).

The mechanical properties of PP/MESSP composites were enhanced and improved at highest of 5.0 wt % of MESSP loading. Subsequently, the addition of MESSP loadings at above 5.0 wt % has led to the formation of agglomerates and aggregates, which in turn possessed to the reduction of tensile strength of the PP/MESSP composites. Also, it can be seen based on the SEM analysis, the MESSP fillers were hardly dispersed well when more loading of MESSP has added into the PP matrix. It can be also observed that there was a loss of characterization of PP matrix tearing when more MESSP fillers were added and have shown a poor interfacial interaction between PP and MESSP. Moreover, incompatibility of MESSP as a natural filler in PP matrix has occurred due to poor interaction between MESSP and PP. Optimum properties or enhanced properties of MESSP in PP could not be obtained and further investigation has to be carried out.

Thus, finding a new polypropylene based bio-composites is necessary to solve the issue of incompatibility of PP matrix due to the hydrophilic nature of natural filler. The examples of existing natural fillers or fibres in polymer matrix can be divided into non-wood natural fibres and wood fibres. It can be further categorised into five sectors from non-wood natural fibres such as bast, leaves, seeds, fruits, and grass fibres (Tudu, 2009).

In Malaysia, several automotive components have already produced with natural fibre composites based on polypropylene such as flax, hemp or sisal fibres (Sanjay, 2016). Other examples of natural filler such as jute, kenaf, and bamboo can be used to replace glass fibre to enforce or enhance polymeric resins. This is because most of the natural fillers can be produced by low cost, lower energy consumption, non-abrasive nature and environmental friendly. Unfortunately, most of the organic fillers are not compatible as compared to synthetic fibres due to the presence of hydroxyl group causing the organic fillers hydrophilic in nature, which similar to MESSP in the previous studies reported by Ng, 2016.

In this study, MESP was used as a new bio-filler to replace the MESSP in PP matrix in order to enhance or improve the mechanical properties of polypropylene without major changes of the characteristic of neat PP. It is believed that that MESP may have a better enhancement of interfacial interaction in polypropylene as compared to MESSP. As compared to MESSP, MESP includes the kernel of the seed which contains approximately 20 % oil and fatty acids such as stearic acid, behenic acid, oleic acid, linoleic acid, and palmitic acid which can facilitate the processability and contribute towards improving the properties of composite by chemically binding with PP (Dutta and Deka, 2014). Usage of MESP is believed to overcome the incompatibility to PP due to its hydrophobic nature as compared to hydrophilic MESSP.

## 1.3 Research Objectives

i) To prepare and characterise *mimusops elengi* seed powder (MESP) from *mimusops elengi* fruits.

ii) To develop *mimusops elengi* seed powder filled polypropylene composites (PP/MESP composites) through melt mixing using Brabender Internal Mixer at different filler loadings.

iii) To study the processability, physico-mechanical properties, and morphological properties of PP/MESP composites.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Polypropylene (PP)

### 2.1.1 Introduction

Polypropylene is a type of synthetic resins that are produced by the addition polymerization of propylene. Polypropylene is one of the family of polyolefin resins with the formula of $C_3H_6$. It can also be polymerised with ethylene to produce ethylene-propylene copolymer. Polypropylene is a thermoplastic polymer which widely used in applications of household and industrial applications. Applications such as stationery, packaging, textiles, labelling, plastic parts for automotive components and others are commonly can be seen in the market (Johnson, 2016).

There are mainly three major types of marketable polypropylene in the industries nowadays which are homopolymer, random polymer and impact copolymer. Homopolymer and random polymer are often produced in a loop reactor whereas impact copolymer is produced in the fluidized bed reactor. The quality of polypropylene resins can be significantly affected by factors such as additive content, particle size distribution of the resins, filler content and other rheological properties (Lanord, et al., 2015).

Also, polypropylene is the second major plastic production with revenues expected to exceed US$145 billion by year 2019. According to Russian Federation

2011, the annual production of polypropylene in year 2011 was as shown in Table 2.1: Annual production of polypropylene.

Table 2.1: Annual Production of Polypropylene (Russian Federation, 2011).

| **Annual production of polypropylene in year 2011** | **Amount and volume of production of polypropylene in year 2011** |
|---|---|
| World | 52.2 million tonnes |
| Europe | 13.1 million tonnes |
| Russia | 0.64 million tonnes |

According to Markets and Markets Research (Martberg, 2016), Asia Pacific is the largest market for polypropylene followed by Europe and North America. The countries of major consuming markets for polypropylene such as China, India and Japan are the leading emerging economics for polypropylene productions. Based on the data research, it is anticipated that China will grow its propylene capacity at the fastest rate of any country in the world over the next five years. China is expected to make up for almost 70% of the Asian capacity addition and 45% of the global capacity addition in the next five years.

### 2.1.2 Chemical and Physical Properties of PP

Propylene, raw material of polypropylene can be obtained by thermal cracking of naphtha, ethane, propane, and butane. It is often existing in gaseous form and can be categorised into lower olefins which consists of a carbon atoms pairing linked by a double bond (Michieal, 2015). It is also a linear hydrocarbon polymer with the chemical structure of polypropylene molecule $C_nH_{2n}$. In order to form a chain polymer, the double bonding of propylene molecule will break if there is presence of catalyst with the action of polymerization process. This reaction takes place continuously until the structure is formed (Justin, 2016).

Essentially, polypropylene is one of the most versatile polymers available in market, in the form of sheets, profiles and fibre. The significant and remarkable properties of polypropylene are as such, good heat resistance, semi-rigid, translucent, good chemical resistance, tough, and good fatigue resistance. Polypropylene also offers good electrical and chemical resistance even at high temperatures and does not give any stress cracking problems as compared to the other polymers (Michieal, 2015). Although the properties of polypropylene are similar to polyethylene, there are some differences as well. For example, polypropylene has a lower density and higher softening point as polypropylene does not melt below 160 °C when comparing to polyethylene may melt at around 100 °C. The following Table 2.2 and Table 2.3 show the physical properties and chemical properties of polypropylene, respectively (Hindle, 2017).

Table 2.2: Physical Properties of PP (Hindle, 2017).

| **Physical Properties** | **Value** |
|---|---|
| Tensile Strength | $0.95N/mm^2 – 1.30N/mm^2$ |
| Notched Impact Strength | $3.0Kj/m^2 – 30.0Kj/m^2$ |
| Thermal Coefficient of Expansion | $100 \times 10^{-6} – 150 \times 10^{-6}$ |
| Melting Point | 160°C - 170°C |
| Density | $0.905g/cm^3$ |
| Elasticity | Very good |
| Resiliency | Good |
| Colour | White |
| Frictional Resistance | Excellent |
| Thermal Resistance | Medium |
| Symbol of PP Developed by Society of Plastic Industry |  |

Table 2.3: Chemical Properties of PP (Louis, 2016).

| **Chemical Properties of PP** | **Explanation** |
|---|---|
| Acid | PP has excellent acid resistance and does not affect the properties of PP. |

| | |
|---|---|
| Basic | PP has moderate basic resistance. |
| Organic Solvent | PP has enough ability to prevent organic solvent to cause harm on it. |
| Light Resistance | PP loses energy by sunlight. |
| Dyes | Difficulty to dye on PP due to its moisture regain is 0 % except for pigment dyeing. |
| Toxicity | Non-toxic product and alternative of BPA containing products. |
| Electrical Conductivity | Low level of electrical conductivity and highly effective in electronic products. |

Moreover, another significant characteristic of polypropylene is the backbone of the polypropylene chain consists of methyl group that attached alternatively or randomly which can alter the properties based on the isotactic, syndiotactic and atactic structural arrangement (Michieal, 2015). For instance, the degree of crystallinity of polypropylene can be modified by changing the molecular symmetry and it can have a slight stiffening effect of the chain by increasing the crystalline melting point. Figure 2.1 shows the different molecular configurations of polypropylene.

Generally, isotactic polypropylene is the major form of the polymer. As compared to atactic and syndiotactic configurations of PP, isotactic has the greatest degree of crystallinity which it is useful in many kinds of the applications. Furthermore, isotactic PP can be produced at low temperature and pressure using Ziegler Natta catalyst, which similar to the properties of polyethylene but it is stiffer, harder, and softens at higher temperature, approximately 170 °C. Isotactic PP is also slightly more prone to oxidation as compared to polyethylene unless stabilizers and antioxidants are added (Michieal, 2015).

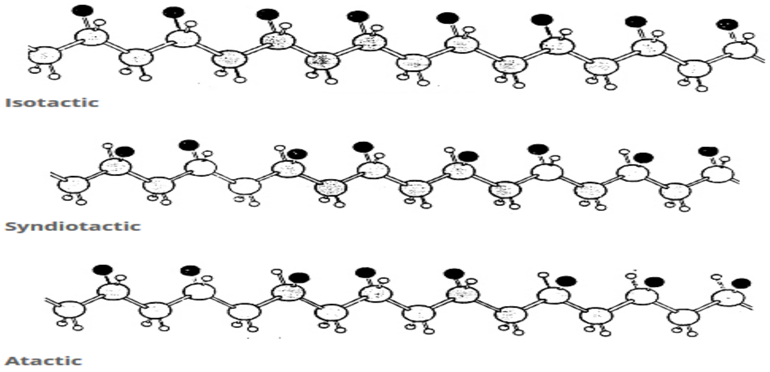

Figure 2.1: Different Molecular Configurations of Polypropylene (Michieal, 2015).

### 2.1.3 Manufacturing and Development Trends

The distinctive properties and ability of polypropylene to adapt to several fabrication techniques and methodologies such as ability to behave like plastic material and as a fibre make it a valuable material for wide ranges of applications in either household or industrial applications. It can be manufactured through variety methods such as injection moulding, extrusion, shaping and foaming, and extrusion blow moulding (Jade, 2017).

Traditionally, PP is known for relatively easy materials to be injection moulded due to its semi-crystalline nature. The low molecular weight of PP has led to lower entanglement between PP chains and increase the volume between the chains, making it easier to flow and has a lower melt viscosity. Moreover, the pseudoplastic nature of PP has significant shear thinning behaviour which can improve the effect and fast filling rates according to Power Law (Creighton, 2017). The common melt temperatures for injection moulding of PP are between 210 °C to 250 °C. It is recommended by Flame Retardant Grades the temperature for injection moulding should not exceeded 220 °C in order to ensure high mould filling rates and good surface finish. In addition, in order to avoid burn marks, optimum venting of the mould is essential (Creighton, 2017).

According to Creative Mechanisms Company INC (Creighton, 2017), the company has used PP in application across a range of industries such as the ability to machine PP to include a prototype living hinge development. Since PP is a very flexible, low melting point and a soft material, it has prevented from being able to properly machine the material because it gums up easily and does not cut clean which requires a high skill level to be cut with precision. However, Creative Mechanisms Company INC has been successfully overcome the problem by using a machine and cut the PP cleanly with outstanding detail such as the thickness of a PP made living hinge as thin as 0.010 inches (Creighton, 2017).

### 2.1.4 Applications of PP

Conventionally, polypropylene can be processed and manufactured into wide ranges of products by several techniques such as extrusion blow moulding, injection moulding, and general purpose extrusion as other thermoplastics. The major breakdown of PP applications can be seen as below Figure 2.2 which include food packaging, rigid packaging, textiles, technical parts and consumer products. Figure 2.2 shows the applications of polypropylene.

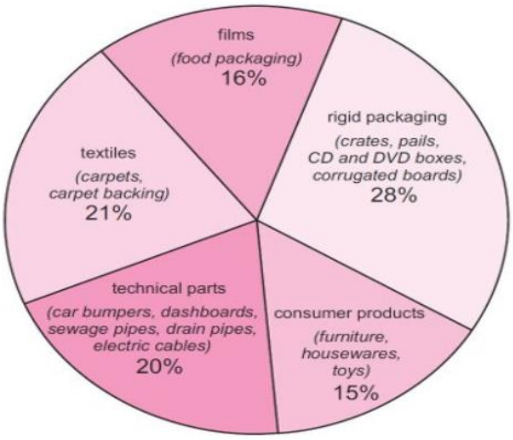

Figure 2.2: Applications of PP (York, 2016).

Commonly, polypropylene serves as raw materials used for film extrusion owing to its excellent puncture resistance, low sealing threshold and affordable price (York, 2016). The film can be categorised into three major sectors such as food and confectioneries, tobacco, and clothing.

Rigid packaging includes crates, pails, CD and DVD, and corrugated boards. Since PP is a thermoplastic, it has the ability of reuse and recycle providing ease to transport to replace the available plastic materials in the market. Besides, PP also acts as an alternative of polystyrene by offering a cheaper material option with similar properties (Hindle, 2017).

In recent years, the usage demand of PP material has been increased dramatically in automotive sector as it used as a nanomaterial solution for automotive interiors (Hindle, 2017). Moreover, products such as bumpers, cladding, and exterior trim also available in markets. This is because the superior properties of PP including high chemical resistance, processability and impact balance make PP stands out than the other polymers available in the industries (Hindle, 2017).

The consumer products include furniture, housewares, toys are also another high demand production in the market available nowadays which consists of 15% out of the 100% application of PP products (Hindle, 2017).

## 2.2 Mimusops Elengi

### 2.2.1 Overview

Mimusops Elengi is a large evergreen tree which grows up to an average height of 12 m to 15 m. The tree is well-known for its shade, fragrant flowers and elegant looks as well as wide application in medical uses. The heartwood is deep red, usually with a darker streaks not sharply demarcated from the paler 5 cm to 7 cm wide (Florence et al, 1991). The seed kernel contains about 22 % of oil. The fatty acid compositions of the refined oil are 64.0 % of oleic acid, 14.5 % of linoleic acid, 11.0 % of palmitic acid, 10.0 % of stearic acid, and 0.5 % of behenic acid. In addition, the main chemical compounds in the *mimusops elengi* flowers are aromatic alcohols and esters derived from the phenyl propanoild metabolism (Dutta & Deka, 2014).

The bark and flowers of *mimusops elengi* are acrid, sweet and cooling sensation. It is believed that the bark can cure biliousness, diseases of the gum and teeth whereas the flowers are used to cure liver complaints, diseases of nose, headache and asthma. Meanwhile, the seeds of *mimusops elengi* is famous for curing nasal congestion and headache. The root is sweet and sour which is good for gonorrhoea, as a gargle, and strengthens the gums (Gami, et al., 2012). Figure 2.3 shows the ripen fruits of *mimusops elengi.*

Figure 2.3: Fruits of *Mimusops Elengi* (Morad, 2011).

The Table 2.4 and Table 2.5 show the general properties of *mimusops elengi* and physiochemical properties of *mimusops elengi* seed oil, respectively.

Table 2.4: General Properties of *Mimusops Elengi* (Dutta & Deka, 2014).

| **General Properties** | **Explanation** |
|---|---|
| Habit | Evergreen Tree. |
| Height | 15.0 m |
| Growth Rate | Medium. |
| Pollinators | Wind. |

| | |
|---|---|
| Self-fertile | No. |
| Cultivation Status | Cultivated, Ornamental, Wild. |
| Colour | Light Green. |
| Heartwood Density | 780 kg/m$^3$ to 1120 kg/m$^3$ at 15 % moisture content. |
| Shrinkage Rate of Heartwood | Moderate to high. |

Table 2.5: Physical Properties of *Mimusops Elengi* Seed Oil (Dutta & Deka, 2014).

| **Parameters** | **Values** |
|---|---|
| Colour | Light Green. |
| Oil Content (%) | 64.0 % of oleic acid, 14.5 % of linoleic acid, 11.0 % of palmitic acid, 10.0 % of stearic acid, and 0.5 % of behenic acid. |
| Density (g/cm$^3$) | 0.8573 |
| Acid Value (mg KOH/g) | 1.107 |
| Iodine Value (gI$_2$/100g) | 90.31 |
| Refractive Index | 1.4571 |
| Moisture Content (%) | 0.112 |

### 2.2.2 Applications of *Mimusops Elengi*

The fruit of *mimusops elengi* can be eaten raw, preserved and pickled with a sweet flavour when ripe. The pulp is starchy with a floury flavour. Besides, the high contents of oil obtained from the seed can be used for cooking directly (Morad, 2011). For the medicinal uses, the bark is used in the treatment of diarrhoea and dysentery. Then, the bark is sometimes mixed with the flowers and used as a gargle to treat gum inflammation and toothache. Furthermore, it is used to treat gonorrhoea, snakebites, fevers, wounds, and eczema. Meanwhile, the leaves can be used to treat headache, toothache, wounds and sore eyes whereas the flowers are used as a remedy against diarrhoea. The pounded seeds are also used to cure constipation (Morad, 2011).

The different parts of *mimusops elengi* is often used in the accessories for women. For instance, the aromatic flowers can retain their fragrance even after being dried and usually used as a perfume for women. The flowers are also used as a filling in pillows, strung in garlands or necklaces for decorations. Sometimes, the seeds are also used for making necklaces (Morad, 2011). In addition, the oil obtained from the leaves, bark, or seeds is used to make paint and FAME productions. Applications of pesticides, fertilizers and others are also can be found using *mimusops elengi* oil (Morad, 2011). Figure 2.4 shows the *mimusops elengi* seeds.

Figure 2.4: *Mimusops Elengi* Seeds.

## 2.3 Natural Fibre Reinforced Polymer Composites (NFPCs)

### 2.3.1 Introduction

Natural fibre is one of the environmental friendly material which consists of a wide range of properties as compared to synthetic fibre. It can be sourced from plants or animals, providing composite materials from different types of renewable or non-renewable sources and the primary constituents can be categorised into cellulose, hemicellulose, pectin and lignin. The cellulose is a semi-crystalline polysaccharide which corresponds to the hydrophilic nature of natural fibres. On the other hand, hemicellulose is a fully amorphous polysaccharide with a lower molecular weight compared to cellulose which it being partially soluble in water and alkaline solutions in spite of its amorphous nature (Westman, et al., 2010). Moreover, pectin is a polysaccharide and is responsible to hold the fibre together whereas lignin is comprised mainly of aromatics and act as an amorphous polymer with little effect on water absorption. The Figure 2.5 shows the structural configurations of cellulose (A), hemicellulose (B), pectin (C), and lignin (D) (Westman, et al., 2010).

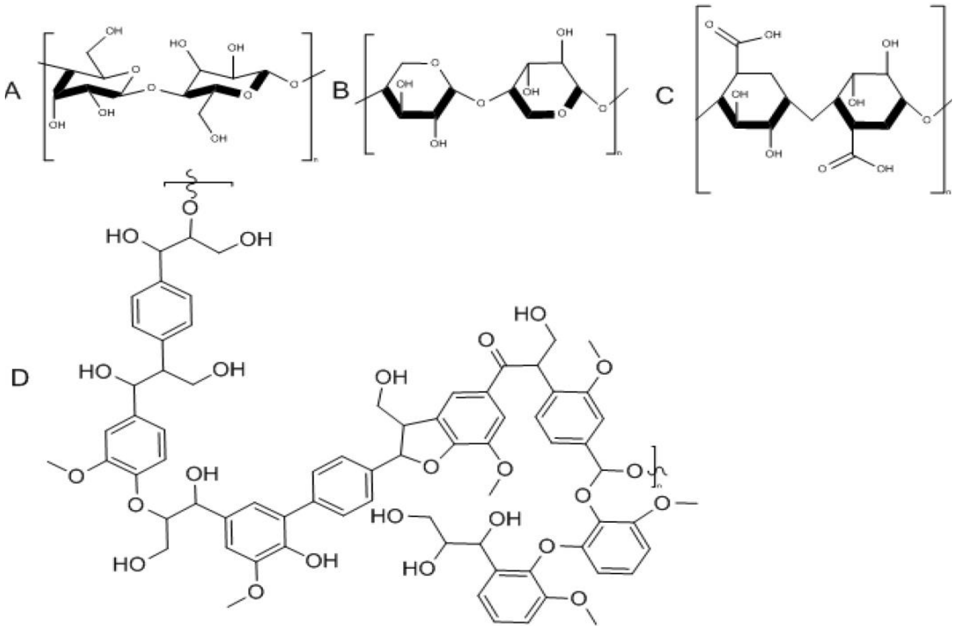

Figure 2.5: Structural Configurations of Cellulose (A), Hemicellulose (B), Pectin (C), and Lignin (D) (Westman, et al., 2010).

Natural fibre polymer composites (NFPCs) are a composite material which a polymer matrix reinforced with natural fibres such as jute, oil palm, sisal, kenaf and other possible natural fibre materials. In addition, reinforcement provides strength and rigidity which help to support structure load whereby the matrix maintains the orientation of the reinforcement (Mohammed, et al., 2015).

The polymers can be classified into thermoplastics and thermosets. The thermoplastic matrix materials consist of one or two dimensional molecular which have the ability to become softer at an increased temperature and reverse properties throughout cooling process. Meanwhile, thermosets is a highly cross-linked polymers which cured using thermal and light irradiation only. As a results, this structure provides thermosets to have good properties such as high flexibility for modifying desired properties (Taj, et al., 2007; Mohammed, et al., 2015).

The examples of thermoplastics that have been fabricated as matrix for composites reinforcement are polypropylene (PP), polyethylene (HDPE/LDPE), polyvinyl chloride (PVC), polystyrene (PS), and recycled thermoplastics. On the other hand, epoxy resins and other resins were also utilized as matrix for thermoset composites reinforcement (Dixit, et al., 2017).

### 2.3.2 Types of Natural Fibres in Plastics

Nowadays, there are variety types of natural fibres have been implemented into the plastic such as flax, hemp, jute, wood, rice husk, wheat, grass, oil palm empty fruit bunch and others which originated from either renewable sources or non-renewable sources. According to a Food and Agricultural Organization survey, natural fibres are commonly lignocellulose in nature (Sanjay, et al., 2016). Figure 2.6 shows the variation types of natural fibre plants that can be used for composites reinforcement.

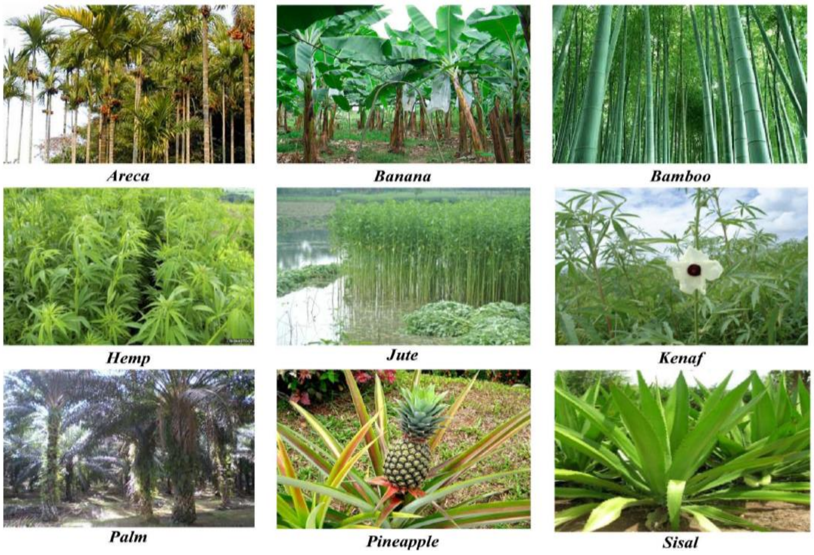

Figure 2.6: Variation Types of Natural Fibre Plants (Sanjay, et al., 2016).

Table 2.6 shows the different types of natural fibres reinforced into different matrix polymers.

Table 2.6: Natural Fibres Reinforced Matrix Polymers (Saheb & Jog, 2000).

| Natural Fibre | Matrix Polymer |
|---|---|
| Wood flour/fibre | PE, PP, PVC, PS, Polyurethane |
| Jute | PP, SBR nitrile rubber, Epoxy, Polyester |
| Sisal | PE, Natural rubber, Polyester epoxy |
| Pineapple | PE, Polyester |
| Hemp | PP, Polyester |
| Kenaf | PE,PP |
| Flax | PP |
| Wheat Straw | PP |
| Bamboo | Epoxy |
| Coir | Natural rubber |
| Oil Palm | Rubber |

### 2.3.3 Chemical Compositions and Properties of Natural Fibres

In fact, the rheological properties and performance of NFPCs can be greatly affected by fibre-matrix interaction, surface adhesion between fibre and polymer, thermal stability of fibres, and aspect ratio of fibres. The hydrophilic nature of natural fibres and the fibre loadings may affect the composite properties. High fibre loading is required to maintain good properties of NFPCs. Meanwhile, the increased in fibre content commonly may improve the tensile properties of the composites. The chemical composition of natural fibres changes depending on the types of natural fibres. For instance, natural fibres contain cellulose, hemicellulose, pectin, and lignin. The overall chemical properties of each fibres are affected by the properties of each constituent (Taj, et al., 2007; Saheb & Jog, 2000).

Basically, most of the plant fibres are composed of cellulose, hemicellulose, pectin, and lignin as well as moisture components. Hemicellulose is corresponding for biodegradation, micro-absorption and thermal degradation of the fibres owing to its unique characteristic. On the other hand, lignin is corresponding for thermal stability and ultraviolet degradation. Typically, natural fibres contain 60 % to 80 % of cellulose, 5 % to 20 % of lignin and approximately 20 % of moisture content (Saba, et al., 2014). The cell wall of the natural fibres will experience pyrolysis with increasing temperature and involves into char formation. The char formation will help to insulate the lignocellulose from further heat degradation. The Table 2.7 shows the chemical composition of the natural fibres (Mohammed, et al., 2015).

Table 2.7: Chemical Composition of Natural Fibres (Mohammed, et al., 2015).

| **Fibre** | **Cellulose (wt %)** | **Hemicellulose (wt %)** | **Pectin (wt %)** | **Lignin (wt %)** | **Moisture Content (wt %)** |
|---|---|---|---|---|---|
| Bamboo | 26 to 43 | 30 | - | 21 to 31 | - |
| Flax | 71 | 18.6 to 20.6 | 2.3 | 2.2 | 8.0 to 12.0 |
| Kenaf | 72 | 20.3 | 3.0 to 5.0 | 9 | - |
| Jute | 61 to 71 | 14 to 20 | 0.2 | 12 to 13 | 12.5 to 13.7 |
| Hemp | 68 | 15 | 0.9 | 10 | 6.2 to 12.0 |
| Sisal | 65 | 12 | 10.0 | 9.9 | 10.0 to 22.0 |
| Oil Palm | 65 | - | - | 29 | - |
| Abaca | 56 to 63 | 20 to 25 | 1.0 | 7 to 9 | 5.0 to 10.0 |

### 2.3.4 Application of NFPCs

The varieties of natural fibres reinforced polymer composites have excellent impacts and performance in automotive applications, packing and construction. The excellent properties of natural fibres reinforced polymer composites such as low density, high tensile strength, low wear on tools, alternatives for new production technologies and materials, relatively high puncture resistance (Sanjay, et al., 2016), resistance to corrosion and fatigue, high stability, no off-gas of toxic compounds, reduce fogging behaviour, and low price production have attracted the market demand in automotive sectors (Mohammed, et al., 2015). Most importantly, natural fibres are biodegradable and renewable sources which give them easy availability. Table 2.8 shows the application of natural fibre composites.

Table 2.8: Natural Fibre Composite Applications (Mohammed, et al., 2015).

| Fibre | Applications |
|---|---|
| Hemp | Construction products, textiles, cordage, geotextiles, paper and packaging, electrical, and furniture. |
| Oil Palm | Building materials such as windows, door frames, structural insulated panel building systems, siding and fencing. |
| Wood | Window frame, panels, door shutters, and railing systems. |
| Flax | Window frame, decking, railing systems, fencing, tennis racket, bicycle frame, and laptop cases. |
| Sisal | Construction materials such as panels, doors, shutting plates, and roofing sheets. |
| Kenaf | Packing material, mobile cases, insulations, clothing-grade clothes, animal bedding, and bags. |
| Coir | Building panels, flush door shutters, roofing sheets, storage tank, and packing materials. |
| Jute | Building panels, roofing sheets, door frames, and packaging. |

### 2.3.5 Comparison between Natural Fibres and Synthetic Fibres

Recently, applications of natural fibre have increasingly gained attention from several manufacturing sectors including structural composites, automobiles, packaging, moulded manufacturing products, and other construction industries (Sanjay, et al., 2016).

According to studies reported by Quazi et al., (2010), degradable phosphate glass fibre and natural silk fibre were used in reinforcement of PP composites. The mechanical properties such as tensile strength, elongation at break, impact testing and bending strength for both PP/phosphate glass fibre and PP/silk fibre composites were studied. As a result, it has been found that silk fibre composites produced higher tensile strength (46 MPa), bending strength (50 MPa), and impact strength (17 kJ/m$^2$) as compared to phosphate glass fibre composites for given value of 39 MPa, 46 MPa, and 8 kJ/m$^2$ respectively (Shubhra, et al., 2010).

On the other hand, research studies reported by Quaiyyum et al., (2011) stated that there were several kinds of synthetic and natural fibres have been studied on their mechanical performance on PP matrix. Figure 2.7 shows the tensile strength of different fibre-reinforced polypropylene composites data reported by Quaiyyum et al., 2011. According to the Figure 2.7, it can be clearly seen that E-glass/PP composites have greater tensile strength as compared to other natural fibres/PP composites. Meanwhile, among the natural fibres, flax fibres have offered the highest reinforcement effect due to the morphology properties of flax fibres as compared to other natural fibres. Besides, according to Quaiyyum et al., 2011, flax fibres have also shown higher fineness as compared to hemp or kenaf fibre which possess a better compatibility into PP matrix during reinforcement. However, since natural fibres are naturally hydrophilic in nature, the natural fibres have a weaker interfacial bonding with PP and poor wettability as compared to synthetic fibres. For instance, some pre-treatment has to be done for natural fibres before it can be used as a filler into polymer matrix (Shubhra, et al., 2010).

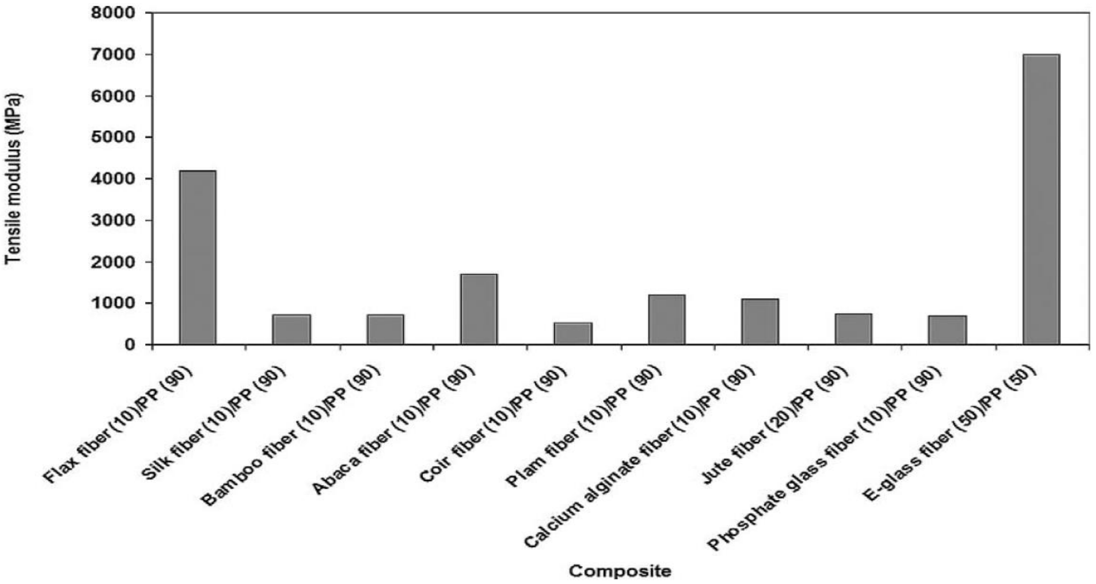

Figure 2.7**:** Tensile Modulus of Different Fibre-Reinforced PP Composites (FRPCs), (Quaiyyum, et al., 2011).

According to studies reported by Dixit, et al., 2017, both synthetic fibres and natural fibres have its own advantages and major drawbacks. For instance, natural fibres offer a better moisture sensitivity, thermal sensitivity and biodegradable ability as compared to synthetic fibres. On the other hand, synthetic fibres offer a better mechanical properties, cheaper in fabrication, and mass production availability. The following aspects such as technical and environmental are being compared between natural fibres and synthetic fibres in Table 2.9 (Dixit, et al., 2017).

Table 2.9: Comparison between Natural and Synthetic Fibres (Dixit, et al., 2017).

| **Aspects** | **Properties** | **Natural Fibres** | **Synthetic Fibres** |
|---|---|---|---|
| Technical | Mechanical Properties | Moderate | High |
| | Moisture Sensitivity | High | Low |
| | Thermal Sensitivity | High | Low |
| | Resource | Infinite | Limited |
| Environmental | Production | Low | High |
| | Recyclability | Good | Moderate |

### 2.3.6 Advantages and Disadvantages of Natural Fibres over Synthetic Fibres.

Table 2.10: Advantages and Disadvantages of Natural Fibres (Tudu & Biswas, 2009).

| Advantages | Disadvantages |
|---|---|
| • It is an eco-friendly material which the production requires lesser energy, and carbon dioxide is used while oxygen is given back to the environment.<br>• It is a renewable resource and biodegradable materials.<br>• Relatively low price.<br>• Relatively low density as compared to synthetic fibre such as glass, carbon and steel fibres. As a results, NFPCs have a higher specific strength and stiffness than glass fibre.<br>• Low cost and high performance of NFPCs contented the economic aspect of the industry.<br>• Disposal of NFPCs are simple as compared to synthetic fibre reinforced polymer.<br>• The abrasive nature of fibre is lower.<br>• Thermal recycling is possible whereas glass fibre causes problem in combustion furnaces.<br>• Good thermal and insulating properties. | • It has a high moisture absorbing properties. As a results, the interfacial bonding between polymer matrix and fibre reduces and causes effect on the mechanical properties.<br>• It has a poor wettability, incompatibility with some polymer matrices.<br>• It cannot be used directly in its natural form. It requires chemical modification by removing the waxy layer of the natural fibres to improve the interfacial adhesion between fibres and polymer matrices. |

## 2.4 Natural Fillers Filled Thermoplastic Composites

### 2.4.1 Processing and Modifications of Thermoplastic Composites

Primarily, extrusion of ingredients at elevated temperature followed by shaping processes such as injection moulding and thermoforming involve in processing of natural fibre thermoplastic composites (Tudu & Biswas, 2009). Generally, fibre-fibre interactions and fibre-matrix interactions are the major factors in determining the properties of such composites. However, the drawback in natural fibre in thermoplastic composites has restricted its applications owing to highly hydrophilic nature of natural fibre causes compatibility problems with the hydrophobic thermoplastics in composites. As a result, the high moisture sensitivity of the natural fibre has led to reduction of mechanical properties due to poor interfacial bonding between resin matrix and fibre (Tudu & Biswas, 2009).

Furthermore, cellulose fibres tend to aggregate and thus the fibres do not disperse well in a hydrophobic polymer matrix causing difficulties in achieving a uniform distribution of fibre in the matrix. Also, the surface characteristics of the reinforcing fibre play an important role in transferring of stress from the matrix to the fibre (Farsi, 2015).

Therefore, the pre-treatment or modification of natural fibres properly in order to improve the mechanical properties of the composites significantly. Several surface chemical modifications of natural fibres have achieved of success in improving fibre strength, fibre-matrix adhesion in natural composites (Farsi, 2015). Chemical treatments such as dewaxing, delignification, bleaching, and chemical grafting are used to modify the surface properties of natural fibres (Farsi, 2015).

Moreover, another chemical modification through graft copolymerization provides a route for changing the physical and mechanical properties of fibres is commonly being used. Chemical grafting involves attaching to the surface of fibre or filler in a suitable polymer with a solubility parameter which acts as an interfacial agent and enhances the bonding between fibre and polymer matrix (Tudu & Biswas, 2009).

## 2.5 Current Developments in PP Composites

### 2.5.1 Natural Fibres/Polypropylene Composites

According to Bataille et al, (2002) and Mohanty, et al., (2002) the study of effect of surface treatment on the properties of PP/cellulose has been carried out. The results proved that additional of coupling agents and maleic anhydride PP have improved the interfacial adhesion and properties of the composites. On the other hand, Sain et al., (2002) reported that poor properties of PP/wood fibre has achieved due to the absence of interface modifiers. However, another example of PP/wood flour composites has successfully increased in tensile and impact strength when rosin was added.

Moreover, an outstanding improvement in the properties was obtained for PP/kenaf fibre composites when PP was used for modifying the fibre-matrix interface according Dalvag et al., (2015).

Based on the studies reported by Shubhra et al., (2010) a higher fineness of fibres can have a better improvement and enhancement of properties of composite materials. The diameter and size of fibres play a significant role on the enhancement tensile strength and ductility (Shubhra, et al., 2010). In the research studied by Shubhra et al., (2010) the natural fibres of flax, hemp, and kenaf were used to reinforce into PP matrix. The final results obtained were shown that PP/flax composites have a higher strength as compared to hemp and kenaf as flax has a better interfacial interaction and adhesion between PP matrix due to its finer and smaller diameter of flax fibre. Table 2.11 shows the comparative studies on PP/natural fibres by few authors.

Table 2.11: Comparative Studies on PP/Natural Fibre Composites.

| Author (Year) | PP/Natural Fibre | Findings | Drawback |
|---|---|---|---|
| Quazi et al. (2013) | PP/Silk | Studies on mechanical properties of | Lower tensile strength than neat PP and PP/Phosphate |

| | | | |
|---|---|---|---|
| | | composites | glass. |
| Furuk et al. (2014) | PP/Wood chips | Studies on mechanical properties of composites | Lower tensile strength than neat PP due to incompatible of filler to matrix. |
| Quaiyyum et al. (2015) | PP/Flax | Studies on mechanical performance | Weak interfacial boding to PP and poor wettability of composite as compared to neat PP. |
| Tiffany Ng (2016) | PP/MESSP | Studies on morphology and mechanical properties | Weaker compatibility and interfacial adhesion between PP and MESSP |

### 2.5.2 Nano-composites

First of all, nano-materials can be categorised into nanotubes, nanoparticles, and nano-layers based on the number of measurements of the dispersed particles. Nanoparticles play an important role as the potential nano-filler materials for improvement of physical and mechanical properties of polymer matrix which they are giving a better properties as compared to traditional composites such as glass fibre reinforced composites. The examples of nano-composites are nano-clays, nano-oxides, carbon nanotubes, and organic nano-fillers (Saba, et al., 2014).

For instance, polymer nano-composites are polymers such as thermoplastics, thermosets or elastomers that have been reinforced with less than 5 wt % of nanoparticles which having high aspect ratio more than 300. In recent decades, it is considered attractive to investors for the reinforcement of polymer materials such as thermoplastics and thermosets with nanoparticles to form nano-composites (Farsi, 2015).

Nowadays, polymer/layered nano-composites can be differentiated into intercalated nano-composites, flocculated nano-composites, and exfoliated nano-composites. The unique characteristics of nano-filler which has a high specific surface area resulting a large interfacial matrix material surface (interphase) as compared to traditional fillers (Saba, et al., 2014). Therefore, the characteristics of nano-filler such as flexibility in surface functionalities, greater surface area to volume ratio as large as 103 times larger than of microfiber, superior stiffness and tensile strength will appear when the dimensions of polymer fibre materials are reduced from micrometres to sub-microns (Farsi, 2015). As a result, nano-composites contribute a better properties improvement as compared to conventional composites. The Table 2.11 below shows the review of technology of nanoparticles reinforcement towards variety of polymer matrices (Saba, et al., 2014).

Table 2.12: Review of Technology of Nanoparticles Reinforcement Polymer Matrix (Saba, et al., 2014).

| **Polymer Matrix** | **Natural Fibre/Nano Filler** |
|---|---|
| Polypropylene (PP) | Nano-clay and nano-carbon fibre |
| Polyethylene (PE) | Carbon nanotube |
| Polystyrene (PS) | Carbon nanotube |
| Ultrahigh MW polyethylene (UHMWPE) | Carbon nanotube |
| Epoxy resin (ER) | Coir-fibre nano-filler |

### 2.5.3 Hybrid Composites

Hybrid composites are two or more reinforcing or filling materials are present in a single polymer matrix. Recently, hybrid composites reinforcement have been incorporated by (i) intermingling of two types of short fibres before adding them into polymer matrix with or without modification, (ii) sandwiching of fibres, and (iii) using non-woven or woven fabrics of both types of reinforcements (Dixit, et al., 2017).

Commonly, hybrid composites are processed with the combinations of synthetic and natural fibres in a single polymer matrix or with combinations of two natural fibres in a single matrix. For instance, factors affecting the hybrid composites properties are length of individual fibres, orientation of fibres, fibre to matrix bonding, and arrangement of both fibres (Zhang, et al., 2005). The Table 2.12 shows the examples of hybrid composites reinforced polymer matrices.

Table 2.13: Hybrid Composites Reinforced Polymer Matrix (Saba, et al., 2014).

| Natural Fibre | Polymer Matrix |
|---|---|
| Bamboo/glass | Vinyl ester |
| Jute/glass | Polypropylene and polyester |
| Coir/glass | Phenolic resin |
| Flax/glass | Polypropylene |
| Kenaf/glass | Natural rubber |
| Cotton/waste silk | Polycarbonate |
| Cellulose/glass | Epoxy resin |

### 2.5.4 Bio-char Reinforced Polypropylene

Bio-char is a renewable, sustainable, easy available, cheap, non-toxic and carbonaceous material which is produced when organic wastes are heated at high temperatures up to 500 °C during pyrolysis process (Das, et al., 2016). The benefits of bio-char as compared to conventional natural fibres are it can produce from wastes, thus increasing landfill capabilities. Besides, a proper pyrolysis conditions can produce a uniform carbon based and porous bio-char structure which will prevent the anisotropy of most lingo-cellulosic fibres as well as exhibiting a high heat stability (Das, et al., 2016).

Technically, bio-char can be produced at low pyrolysis temperature approximately <500 °C. Activation of bio-char leads to creation of great numbers of pores and gaps in bio-char’s structure which can improve the properties in terms of surface area and porosity. The porous nature which in turns improving the adsorptive properties in polymer matrix (Das, et al., 2016).

Recently, according to Das et al. several studies have been carried out where bio-char has been used to produce polymeric bio-composites such as waste pine wood bio-char made at 450 °C to produce manufacture wood/PP bio-composites. The scientists found out that 24 % loading level of bio-char was the most suitable for improving the mechanical properties for the PP matrix. Moreover, DeVallance et al. (2015) also used hardwood bio-char to produce wood/PP bio-composites where they reported several amounts of bio-char were suitable for certain desired properties (Das, et al., 2016).

### 2.5.5 *Mimusops Elengi* Seed Shell Powder (MESSP) Reinforced Polypropylene

According to previous research studies reported by Ng (2016) a new bio-filler *mimusops elengi* seed shell powder (MESSP) has been introduced and used in polypropylene composites. Various characterization testing such as particle size analysis (PSA), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) have been carried out in the research to study the morphology properties and mechanical properties of PP/MESSP composites.

Based on report by Ng (2016) MESSP has a great potential to be used as a new bio-filler in PP composites as it possessed an improvement in tensile strength, E-modulus, and a comparable water absorption percentage of PP/MESSP composites as compared to pure 100 % polypropylene. However, due to the hydrophilic nature of MESSP, it has a weaker compatibility and interfacial adhesion between the PP matrices as compared to other natural fibres/PP composites. The elongation at break was compromised with increased of MESSP loadings (Ng, 2016).

# CHAPTER 3

# MATERIALS AND METHODOLOGY

## 3.1 Introduction

Primarily, Chapter 3 includes the details and specifications of raw materials being used for preparation of MESP/PP, source of materials, and composites preparation methodology with specified parameters. In addition, characterization of MESP as well as composites testing methodology are also explaining in details in Chapter 3.

## 3.2 Raw Materials

### 3.2.1 Polypropylene (PP)

In this study, polypropylene (PP) resins were used to prepare PP/MESP composites. The polypropylene resins were supplied by Lotte Chemical Titan (Pasir Gudang, Johor, Malaysia) under trade name of Titanpro, and available in solid pellets ranging from translucent to white colour. The product grade of the polypropylene homopolymer was Titanpro® PD943, it is used to fabricate plastic articles through extrusion, moulding, injection moulding, coating and rolling, and other conversion processes. The chemical abstract service (CAS) registry number is 9003-7-0 with the density of 0.9 g/cm$^{-3}$ and melt flow rate of 1.1 g/min. The melting point of PP is 160 °C. Before the PP resins were being processed, PP resins were dried in an oven at 100 °C prior to compounding to eliminate any moisture content. Figure 3.1 shows the polypropylene resins used in this research study.

Figure 3.1: Polypropylene Resins.

### 3.2.2 *Mimusops Elengi* Seeds

The *mimusops elengi* ripe fruits were collected from *mimusops elengi* plants around Taman Bandar Barat area located in Kampar, Perak, Malaysia with GPS coordinate of 4.327, 101.135 (N,4°19’38.488”;E,101°8’6.145”). The obtained *mimusops elengi* ripe fruits were further converted into *mimusops elengi* seed powder (MESP) using proper cleaning and grinding process. Figure 3.2 shows the *mimusops elengi* seeds and kernels before being grounded into MESP.

Figure 3.2: *Mimusops Elengi* Seeds and Kernels.

### 3.3 Preparations of *Mimusops Elengi* Seed Powder (MESP)

The obtained *mimusops elengi* fruits were being peeled off and left with the seeds. The seeds were dried under the sunlight for four to five hours for a period of one week. Then, the seeds were washed thoroughly with distilled water by stirring at 300 rpm using a magnetic stirrer about 20 minutes at 80 °C using a beaker. Next, the washed seeds were dried for 24 hours in a vacuum oven (Memmert, Schwabach, Germany) at 80 °C. After 24 hours, the dried seeds were broken into seed shells and kernels using a nutcracker and were dried for another 24 hours in a vacuum oven (Memmert, Schwabach, Germany) at 80 °C to eliminate extra moisture content. Eventually, the dried seeds were ground into powder form using a metal blender (Model RT-08 Grinder Machine, Mill Powder Tech Solutions, Tainan, Taiwan). The grinding process was done in batches of maximum 300 g of *mimusops elengi* seeds and kernels with approximately of 30 s grinding time. The powders were sieved using Sieve Analysis Vibrating Machine (Haver & Boecker Tyler Model: RX-29-10) to obtain an average particle size of below 45 μm. The preparation of MESP procedure from *mimusops elengi* ripe fruits is as shown in Figure 3.3.

Figure 3.3: Flowchart of MESP Preparation.

## 3.4 Preparation of PP/MESP Composites

Polypropylene resins and MESP were pre-dried in a vacuum oven (Memmert, Schwabach, Germany) for 24 hours at 80 °C in order to eliminate extra moisture content. The PP/MESP composites were produced by melt mixing method using a rheometer Brabender® internal mixer (Plastograph® EC815652, Duisburg, Germany) at different compounding loadings such as 0 wt %, 2.5 wt %, 5.0 wt %, 7.5 wt % and 10.0 wt % filler loadings at a weight of 40 g as shown in Table 3.1. The mixing process was carried out at melting temperature of PP at 180 °C for 8 minutes with 60 rpm. The graph of processing torque can be obtained from the Brabender software system and was used to determine the processability of PP. The PP/MESP composites were pressed into composite sheets at 180 °C using a hydraulic hot and cold press machine (GT-7014-A30C, GOTECH Testing Machines Inc., Taichung, Taiwan). Subsequently, the composites were preheated for 10 minutes subsequently followed by 4 minutes of compression, eventually the composites were cooled for 2 minutes. The preparation and testing methodology of PP/MESP composites is as shown in Figure 3.4.

Table 3.1: Compounding Formulation of PP/MESP and PP/MESSP Composites.

| **Materials** | **Composition (wt %)** | | | | |
|---|---|---|---|---|---|
| PP | 100.0 | 97.5 | 95.0 | 92.5 | 90.0 |
| MESP | 0.0 | 2.5 | 5.0 | 7.5 | 10.0 |

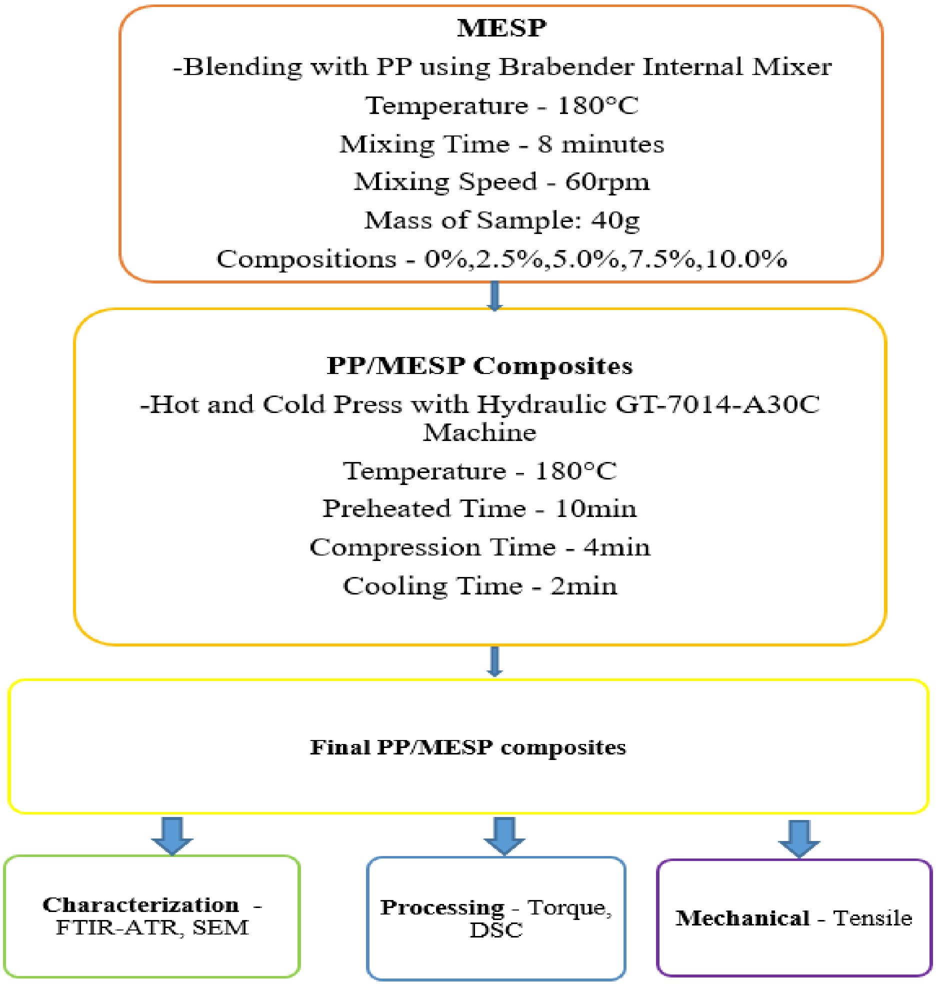

Figure 3.4: Flowchart of Preparation and Testing of PP/MESP Composites.

## 3.5 Characterization of MESP and PP/MESP Composites

Several characterizations were carried out on MESP and PP/MESP composites to determine the physical, chemical, thermal and morphological properties of the particles. The MESP and PP/MESP composites were pre-dried in a cooled vacuum oven (Memmert, Schwabach, Germany) for 24 hours at 80 °C prior to each characterization.

### 3.5.1 Fourier Transform Infrared Spectroscopy – Attenuated Total Reflection

The Fourier transform infrared spectroscopy – attenuated total reflection (FTIR-ATR) analysis (Model:108157, Spectrum Two DTGS, Perkin Elmer Inc., Liantrisant, UK) was carried out to determine the chemical functionality of MESP and PP/MESP composites in order to have a better understanding of possible interaction either in chemical or physical interaction formation between PP and MESP. The analysis was conducted to determine the absorption band in spectrum ranged from 4000 cm$^{-1}$ to 400 cm$^{-1}$, with 16 scans at resolution of 4.0 cm$^{-1}$, interval of 1.0 cm$^{-1}$ and recorded in Transmittance (%T).

### 3.5.2 Particle Size Analysis (PSA)

A digital refractometer (300034, Sper Scientific Ltd., Scottsdale, AZ, USA) was used to determine the refractive index of MESP prior to particle size analysis (PSA). The refractive index for MESP was 1.3334 and distilled water was used as a dispersant with the refractive index of 1.3327. Particle size analysis was conducted using a Malvern Mastersizer particle size analyzer (Model: Hydro 2000 MU, Malvern Instrument Ltd, Malvern, UK) to determine the mean diameter, particle size distribution and specific surface area of MESP.

### 3.5.3 Scanning Electron Microscopy (SEM)

A scanning electron microscope (JSM 6701-F, Jeol, Akishima, Japan) was used to study and analyze the morphology of MESP and PP/MESP composites. The SEM was conducted at an accelerating rate of 4.0 kV with 300x magnification and 10,000x magnification at a working distance of 10.2 mm for MESP. Meanwhile, for PP/MESP composites, SEM was conducted at an accelerating rate of 4.0 kV with 500x magnification at a working distance of 9.7 mm. A sputtering machine (JFC-1600, Joel, Akishima, Japan) was used to sputter coated with a thin layer of platinum with the thickness of 15 nm and density of 21.45 g/cm$^3$ on the surface of MESP in order to prevent electron charging upon scanning and poor resolution results during the analysis.

### 3.6 Testing of PP/MESP Composites

The processability of PP/MESP composites were determined and evaluated via obtained values of processing torque such as loading torque and stabilization torque during melt mixing process in an internal mixer. Meanwhile, the thermal characteristics of PP/MESP composites such as melting temperature, crystallization temperature, and degree of crystallinity were obtained through differential scanning calorimetry (DSC); and values such as E-modulus, ultimate tensile strength (UTS), and elongation at break of PP/MESP composites were obtained from tensile testing.

#### 3.6.1 Processing Torque

The melt mixing process was carried out using a rheometer Brabender® internal mixer (Plastograph® EC815652, Duisburg, Germany) with a processing temperature of 180 °C, mixing time of 8 minutes and mixing speed of 60 rpm. The processing torque such as loading torque and stabilization torque against the mixing time were obtained and recorded upon melt mixing of PP resin and MESP composites. Torque values were recorded for 3 runs of composite mixing for each composition.

#### 3.6.2 Differential Scanning Calorimetry (DSC)

Thermal characteristics of the PP/MESP composites such as melting temperature ($T_m$), crystallization temperature ($T_c$) and degree of crystallinity ($X^m{}_c$) were all determined through DSC (Model: DSC823e, Mettler-Toledo International Inc., Schwarzenbach, Switzerland). The PP/MESP composite samples were weighted at almost 5mg to 8mg and hermetically sealed into an aluminum crucible. Subsequently, the aluminum crucible was placed into the tube furnace, and the melting and crystallization behavior of PP/MESP composites were evaluated by heating the specimens from 25 °C to 300 °C at heating rate of 10 $^{o}$C/min under nitrogen flow of 10 mL/min and followed by an immediate cooling back to 25 $^{o}$C. The degree of crystallinity was calculated by using Equation 3.1.

$$X_c^m = \frac{\Delta H_m}{W_p \; x \; \Delta H_{100}} \times 100\% \qquad \text{(Equation 3.1)}$$

Where $X^m{}_c$ is the degree of crystallinity in percentage, $\Delta H_m$ is the enthalpy of melting of the sample (J/g), $\Delta H_{100}$ is the enthalpy of melting for 100 % crystalline polypropylene which is 207 J/g and $W_P$ is the weight fraction of PP in the composite.

### 3.6.3 Tensile Test

According to ASTM D638, the tensile test was performed by using a Light Weight Tensile Tester (Tinius Olsen, Model: H10KS-0748). A dumbbell presser and cutter (Leader Technology Scientific (M) Sdn. Bhd., Balakong, Malaysia) was used to cut the composite sheet into a dumbbell shape specimens. Five specimens were prepared for each composition and the thickness of each specimen (average thickness around 1 mm) was measured using a digital thickness gauge (Model: Series 542 Flat Anvil Type, Mitutoyo America Corporation, Kuala Lumpur, Malaysia). Test was performed under ambient condition to measure the elastic modulus, ultimate tensile strength, and elongation at break of PP and MESP composites. Meanwhile, the specimens were conducted at room temperature and subjected to a force of 450 N load cells at 1200 mm of extension range percentage; with gauge length of 26 mm and crosshead speed of 50 mm/min. The width of the specimens were fixed to 3 mm.The average values of tensile strength, E-Modulus and elongation at break for each composition were obtained from the stress-strain curve.

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 Introduction

In this chapter, the results on characterization and testing conducted on MESP and PP/MESP composites were discussed. The results such as particle size analysis (PSA) of MESP, scanning electron microscopy (SEM) of MESP and PP/MESP composites, Fourier transform infrared spectroscopy-Attenuated Total Reflection (FTIR-ATR) of MESP and PP/MESP composites, processing torque of PP/MESP composites, differential scanning calorimetry (DSC) and tensile properties of PP/MESP composites were interpreted and discussed based on the previous research carried out by other researchers in similar field.

## 4.2 Characterization of MESP

### 4.2.1 Particle Size Analysis (PSA)

Particle size analysis (PSA) was used to determine the particle size distribution of MESP, the mean diameter and specific surface area of MESP. Particle size analysis is significant in determining the chemical and physical properties of the MESP. For example, the surface area of MESP can affect the rate of chemical reaction and the interfacial interaction to the polymer matrix (Mangrove Alison, 2012). When the surface area of the MESP is large, the rate of chemical reaction will be fast and thus stronger interfacial adhesion between filler and polymer matrix can be formed.

MESP was crushed and sieved to be below 45 µm prior to the characterization and composite preparation. Thus, the physical barriers to dissolution of PP/MESP composites were weakened, and a more efficient processing can be achieved (Wu, et al., 2018). Fine MESP particles can also prevent the possibility of aggregation and agglomeration at higher filler loadings which can affect the final properties of PP/MESP composites. Similar finding was reported by Wu et al., 2018, stating on the specific area of particles increases as particle size decreases, resulting a better processability of PP/filler reinforcement during processing.

Figure 4.1 shows the particle size distribution of MESP. The particle size of MESP ranges between 0.04 µm to 28.3 µm as depicted in the differential frequency plot based on volume fraction of MESP particles versus particle size. As can be seen from Figure 4.1, MESP present in two narrow distributions which lies between 0.04 µm to 0.3 µm, and the second particle size distribution lies between 0.5 µm to 28.3 µm. Based on the volume fraction of the particles, there are finer MESP solids in the mass as the intensity of the first distribution is more than the second distribution.

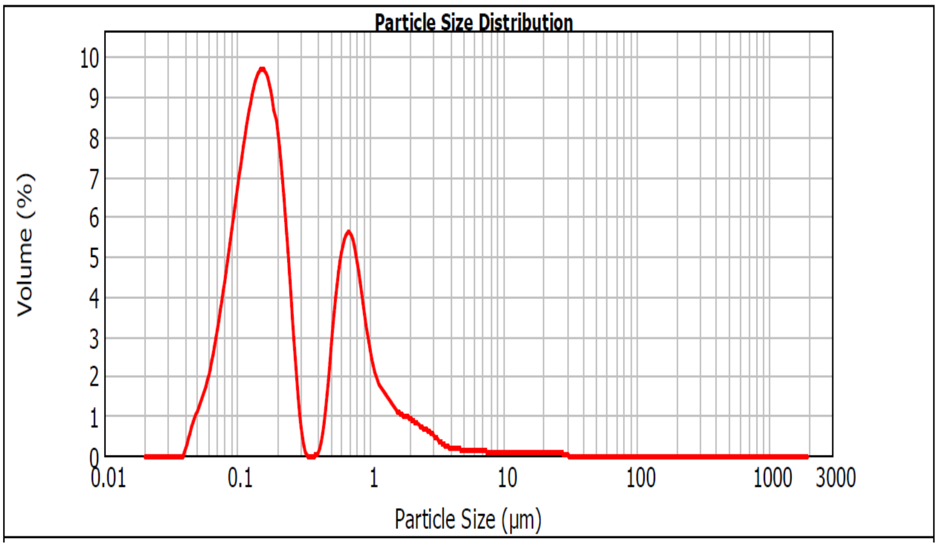

Figure 4.1: The Particle Size Distribution of MESP.

Besides that, the physical properties of MESP was compared to other types of ME fruit based filler used in polymer composite production such as *Mimusops elengi* seed shell powder (MESSP) as reported by Muniyadi et al. (2018), and other commercial fillers used widely in polymer industries such as carbon black, silica, calcium carbonate. Table 4.1 shows the comparison of the fillers which includes the particle size distribution, mean diameter and specific surface area of each of the particulate fillers as analyzed through similar method (Ng, 2016).

Table 4.1: Physical Properties of MESP, MESSP, Carbon Black, Silica and Calcium Carbonate (Muniyadi et al., 2018; Ng, 2016).

| **Particulate Fillers** | **Physical Properties** | | |
|---|---|---|---|
| | **Particle Size Distribution (µm)** | **Mean Diameter (µm)** | **Specific Surface Area ($m^2/g$)** |
| MESP | 0.04 – 28.3 | 0.2 | 36.1 |
| MESSP | 0.04 – 37.2 | 0.6 | 21.9 |
| Carbon Black | 0.2 – 58.7 | 4.6 | 1.3 |
| Silica | 7.9 – 63.9 | 20.0 | 1.1 |
| Calcium Carbonate | 1.2 – 37.8 | 8.5 | 0.9 |

By comparing MESP to other particulate fillers, it can be seen from Table 4.1 that MESP has a narrower particle size distribution which ranges from 0.04 μm to 28.3 μm as compared to other fillers mentioned. In this case, a narrower particle size distribution indicates MESP has more uniform particle size than of broader distribution. Narrow particle size distribution as shown in Figure 4.1 also represents more uniform particle size distribution (Parkin, 2005). Based on the research by Parkin, (2005), a narrow particle size distribution usually gives a very high surface area, better for catalytic activity as filler capable of reinforce the polymer and disperse in a good order.

As shown in Table 4.1, the specific surface area of MESP is the highest which is 36.1 $m^2/g$ as compared to MESSP, carbon black, silica and calcium carbonate which the specific area are 21.9 $m^2/g$, 1.3 $m^2/g$, 1.1 $m^2/g$, and 0.9 $m^2/g$ respectively. Specific surface area is the total surface area exposed of finely divided filler interacts with polymer matrix (Lu, 2013). In general, the porosity, mode of packing, particle size (grain size) and shape of the particle can affect the specific surface area of the particulate filler. Since the specific surface area of MESP is the highest, it means that MESP has smallest particle size and has a higher porosity or surface voids as compared to other particulate fillers. Consequently, higher surface voids can promote a better compatibility between the MESP filler into polypropylene matrix, contributing a more uniform PP/MESP composites as higher surface voids have more contact surface area available (Wu, et al., 2018). Similar research studies have been reported by Wu et al., 2018, the higher surface voids increases the physical interfacial interaction between the PP and filler, promoting a better compatibility in matrix during processing.

Furthermore, mean diameter as shown in Table 4.1 is an average of particle size. According to the results obtained, MESP has the smallest mean diameter which is 0.2 μm as compared to MESSP, carbon black, silica, and calcium carbonate which are 0.6 μm, 4.6 μm, 20.0 μm, and 8.5 μm respectively. Smaller mean diameter indicates MESP is well dispersed, homogenous and has lower tendency to agglomerate and accumulate between PP polymers (Lu, 2013). As a result, the particle size analysis shows that MESP has a very high potential to reinforce PP composites as MESP has a uniform particle size distribution, small particle diameter and can disperse well in PP matrix.

### 4.2.2 Fourier Transform Infrared Spectroscopy - Attenuated Total Reflection

The infrared spectroscopy (IR spectroscopy) is usually used to determine organic and inorganic compounds in a material qualitatively. The IR spectroscopy collects absorption information and analyses the sample in the form of spectrum (Bennet, 2007). The formation of spectrum able to verify the chemical bonds in the sampling materials with different frequency region of the wavelength (Elmer, 2016). FTIR is also used to determine the presence of chemical functional groups in organic compounds. Attenuated total reflection (ATR) is one of the sampling methods to measure FTIR spectra without the need of sample preparation by grinding the solids into powder form with matrix material such as potassium bromide (KBr) to form transparent pallet using hydraulic press (Nylese, et al., 2012).

In this research work, the chemical functional groups of MESP were determined by FTIR-ATR. Figure 4.2 illustrates the FTIR-ATR spectra of MESP and Table 4.2 tabulates the FTIR spectroscopy of MESP (Deka et al., 2014). Based on Figure 4.2, MESP showed a broad and strong O-H stretching band corresponding to the O-H groups in carboxylic acids at 3334.71 cm$^{-1}$. The peak observed indicate the strong intramolecular hydrogen bond in MESP. This is true as MESP consists of linoleic acid, stearic acid, oleic acid, and palmitic acid which are categorized as saturated and unsaturated carboxylic acids having strong intramolecular hydrogen bonding as reported by Deka et al., (2014) and Premaratne et al., (2013).

Furthermore, a medium and sharp C-H stretching band in methyl group was found in MESP at frequency of 2923.24 cm$^{-1}$ and 2853.59 cm$^{-1}$. Based on studies reported by Zein et al., (2016), the methyl group can be found in the MESP as consists of stearic acid which the molecular structure is made up of carboxyl group at one end and methyl group at the other end. Besides, an absorption of strong and well defined C=O stretching band peak was observed at frequency of 1743.90 cm$^{-1}$ due to carbonyl group (Bodirlau and Teaca, 2009), acetyl groups of hemicellulose (Alemdar and Sain, 2008) and esters in the carboxylic groups of MESP (Alemdar and Sain, 2008).

Moreover, absorption peak at frequency of 1614.89 cm$^{-1}$ indicates the medium C=C stretching band due to the conjugated alkenes in unsaturated fatty acid of MESP such as oleic acid (Fan, et al., 2012). It may also correspond to the absorbed moisture by the cellulose in MESP (Troedec, et al., 2008). Meanwhile, the peak at frequency of 1614.89 cm$^{-1}$ and 1454.96 cm$^{-1}$ may also corresponds to aromatics C=C stretching band that can be found in lignin of MESP. The peak at 1454.96 cm$^{-1}$ can also indicate the O-H bend of carboxylic acid groups in MESP (Alemdar and Sain, 2008).

The characteristic peak at frequency of 1238.78 cm$^{-1}$ corresponds to medium C-H bending band of cellulose and hemicellulose in MESP (Bodirlau and Teaca, 2009), or a medium ketone C-C stretch of carboxylic group in MESP (Premaratne, et al., 2013). Besides, the peak at 1238.78 cm$^{-1}$ and 1034.16 cm$^{-1}$ also indicate the C-O stretching of aryl groups in lignin, primary and secondary alcohols, or aliphatic ethers (Troedec et al., 2008; Nacos et al., 2006).

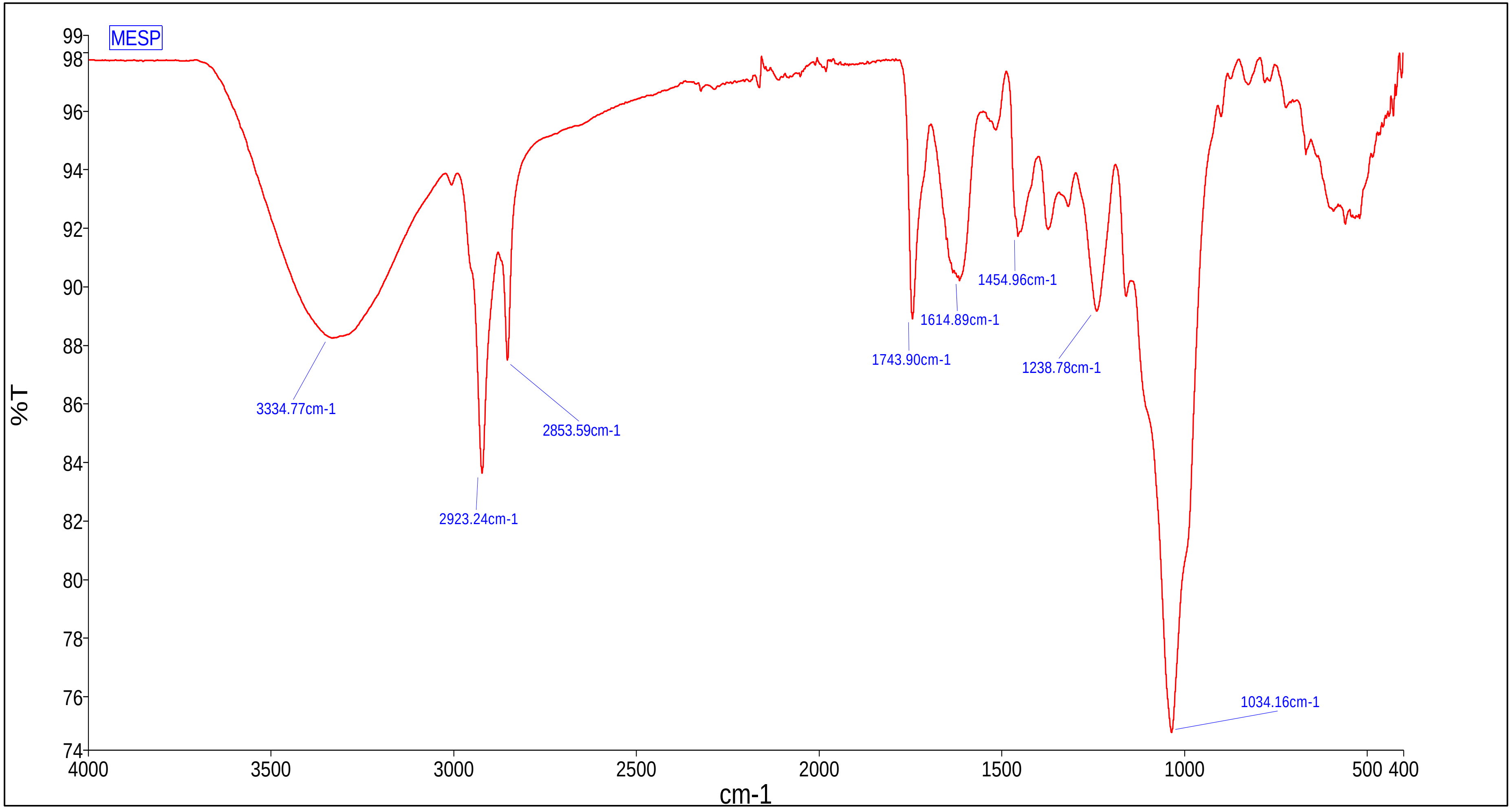

Figure 4.2: FTIR-ATR Spectra of MESP.

Table 4.2: FTIR-ATR Spectroscopy of MESP (Deka, et al., 2014).

| **Characteristics Absorption (cm$^{-1}$)** | **Spectroscopic Assignments** |
|---|---|
| 3400 – 2400 | O-H Stretch |
| 2950 – 2800 ; 1360 – 1230 | C-H Stretch |
| 1750 – 1735 | C=O Stretch |
| 1640 – 1610 | C=C Stretch (conjugated) |
| 1650 – 1430 | Aromatics C=C Stretch |
| 1440 – 1400 | O-H Bend |
| 1320 – 1210 ; 1260 – 1000 | Carboxylic Acids C-O Stretch |
| 1300 – 1100 | Ketones C-C Stretch |

### 4.2.3 Microstructure of MESP

Scanning electron microscopy (SEM) was used to determine the external morphological structure of MESP particles. According to Figure 4.3, it shows the micrograph of MESP surface at 300x magnification and 10,000x magnifications. It can be seen from Figure 4.3 (a), that MESP particles are irregular in shape and exist as a mixture of aggregates and small agglomerates. The formation of agglomerates may be due to the accumulation of small MESP particles as mentioned in particle size analysis (Nichols, et al., 2001).

During the mechanical sieving process, high surface area of MESP particles results in high electrostatic charges and thus, the MESP particles tend to stick together, forming loose agglomerate structure. However, the aggregation of MESP can be easily dispersed in PP matrix due to weak interaction between the particles, which can be separated easily and distributed well during composite preparation. Meanwhile, the agglomerates of MESP are a loose arrangement of aggregates or a mixture of aggregates and agglomerates as shown in Figure 4.3. The agglomerates are more difficult to disperse well as compared to the aggregates and it may result in agglomeration of MESP in composite at higher filler loading. Similar findings on the distribution of natural fillers on matrix surfaces have been reported by Bajpai et al.,

2012. According to report by Bajpai et al., 2012, the increase of rice husk filler loading results in agglomeration of rice husk particles in PP matrix surface. The agglomerate structure formed hindered the physical interfacial adhesion between PP and rice husk, resulting in more voids on tensile fractured surface due to filler pull out. Moreover, the mixture of aggregation and agglomeration of MESP particles can be related to the high filler-filler interaction between the MESP particles.

Besides that, Figure 4.3(b), high surface cracks and voids can be observed on the surface of MESP particles. The cracks formation contributes to high surface area of MESP and suggests the possibility of physical interaction between MESP and polypropylene. According to study by Ng (2016), physical interaction between fillers and polymer matrix can be formed due to interlocking of polymer matrix on the filler surface, which could induce a stronger interfacial adhesion between the polymer and natural filler.

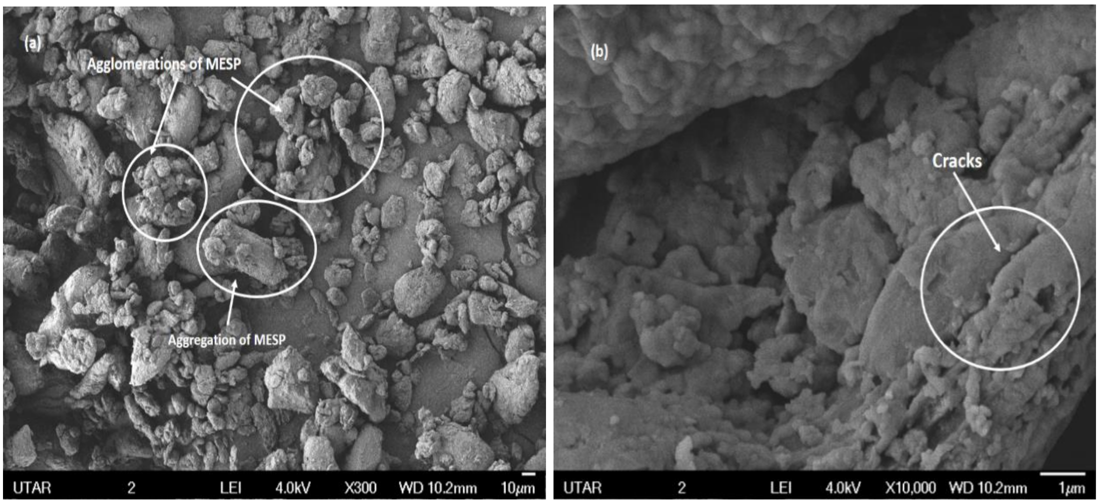

Figure 4.3: Micrograph of MESP particles surface at (a) 300x Magnification (b) 10,000x Magnification

## 4.3 Characterization and Testing of PP/MESP Composites

### 4.3.1 Fourier Transform Infrared Spectroscopy- Attenuated Total Reflection

Generally, polypropylene products are often being manufactured due to their special chemical properties such as resistance to organic and inorganic solvent and hydrophobic properties. Also, the physical properties of polypropylene such as light in weight, mechanical strength and thermal insulating characteristics, making polypropylene highly demanded in the market (Lanord, et al., 2015). Moreover, research on polypropylene/natural fibres composites are increasing by year in order to lower down the production cost of polypropylene with enhanced of product properties. However, most of the research did not credit towards the properties enhancement of PP due to the weak molecular interactions between the filler and polypropylene (Urbaniak-Domagala, 2012). Also, it has to make sure that there is no chemical reaction occurs between the polymer and natural fibre during reinforcement to avoid unwanted product properties (Gurunvenket et al., 2014).

Thus, FTIR-ATR analysis was carried out to determine the possibility of chemical reaction between PP and MESP. Based on Figure 4.3, it shows the FTIR-ATR spectra of PP/MESP composites at different MESP loading. Meanwhile, Table 4.3 and Table 4.4 shows the corresponding functional group of unfilled PP and PP/MESP composites according to the spectrum wavelengths obtained from the FTIR-ATR analysis respectively. As can be seen from Figure 4.4, the unfilled PP and PP/MESP composites, containing different MESP loading shows almost similar peaks in FTIR-ATR spectra. Since polypropylene is made up of propylene monomers, it falls under the alkane family (Lanord, et al., 2015). Hence, the wavelength of 2839 $cm^{-1}$, 2866 $cm^{-1}$, 2917 $cm^{-1}$ and 2950 $cm^{-1}$ indicate strong and sharp alkyl C-H stretching, $CH_2$ and $CH_3$ stretching (Urbaniak-Domagala, 2012).

Furthermore, the peaks at around 1455 $cm^{-1}$ and 1375 $cm^{-1}$ as shown in both unfilled PP and PP/MESP composites at different loading possessed medium intensity of C-H bending in polypropylene molecular structure. Other peaks at wavelength of 1167 $cm^{-1}$, 997 $cm^{-1}$, 972 $cm^{-1}$ and 840 $cm^{-1}$ indicates the $CH_3$ wagging vibrations, symmetrical $CH_2$, a weak C-H bending, $CH_3$ rocking vibrations, a weak C-C stretching, as well as $CH_3$ stretching respectively, that can be found in polypropylene. The results obtained were found similar to the research of FTIR-ATR analysis on polypropylene surface by Urbaniak-Domagala, 2012.

Meanwhile, wavelength at 1729 $cm^{-1}$ and 1720.6 $cm^{-1}$ appeared in unfilled PP, 5.0 wt % MESP loaded PP and 7.5 wt % MESP loaded PP respectively, correspond to the presence of carbonyl group oxidation due to moisture absorption of PP and PP/MESP composites during the processing. This might also occurred due to the pre-drying process of PP and PP/MESP composites were not carried out properly and there were still remaining air moisture on the surface before FTIR-ATR was being tested. According to Barbes et al., 2013, the similar absorption band in between 1700 $cm^{-1}$ to 1750 $cm^{-1}$were also detected in the research on polypropylene FTIR analysis, indicating the presence of carbonyl group in various products of oxidation.

FTIR analysis also confirms that there were no peaks disappeared or new peaks formed when PP and MESP was compounded together as can be seen from Figure 4.4. This confirms that there is no chemical reaction occurred between the PP and MESP. As such, it can be said that the properties enhancement of PP in terms of mechanical, thermal or chemical properties can be credited towards the physical interactions between PP and MESP, as MESP acts as a filler interlocking and entrapping the PP chains on the surface of MESP cracks or voids.

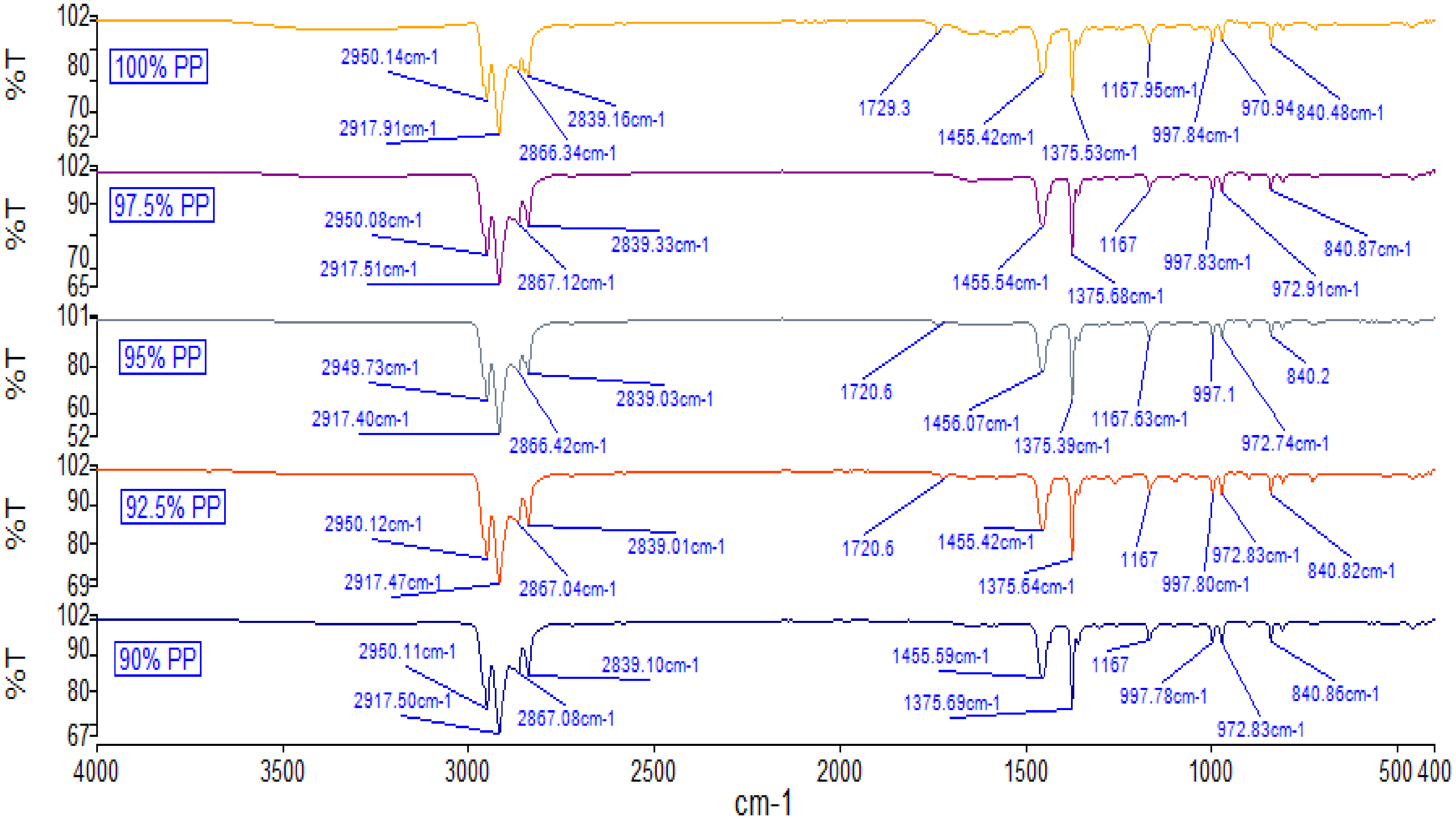

Figure 4.4: FTIR-ATR Spectra of PP/MESP Composites at Different MESP Loadings.

Table 4.3: FTIR-ATR Spectroscopy of Neat PP (Urbaniak-Domagala, 2012).

| **Characteristics Absorption ($cm^{-1}$)** | **Spectroscopic Assignments** |
|---|---|
| 2950 – 2800 | Akyl C-H Stretch |
| 1735 – 1720 | O-H Bend |
| 1465 – 1450 | C-H Bend |
| 1375 | C-H Bend |
| 1170 – 1165 | $CH_3$ Wagging Vibration, Symmetrical $CH_2$, C-H Bend |
| 997 | $CH_3$ Rocking Vibration, C-C Stretch |
| 975 – 970 ; 840 – 800 | $CH_2$ Rocking Vibration, $CH_3$ Stretch, C-H Bend |

Table 4.4: FTIR-ATR Spectroscopy of PP/MESP Composites (Urbaniak-Domagala, 2012).

| **Characteristics Absorption ($cm^{-1}$)** | **Spectroscopic Assignments** |
|---|---|
| 2950 – 2800 | Akyl C-H Stretch |
| 1465 – 1450 | C-H Bend |
| 1375 | C-H Bend |
| 1170 – 1165 | $CH_3$ Wagging Vibration, Symmetrical $CH_2$, C-H Bend |
| 997 | $CH_3$ Rocking Vibration, C-C Stretch |
| 975 – 970 ; 840 – 800 | $CH_2$ Rocking Vibration, $CH_3$ Stretch |

### 4.3.2 Processing Torque of PP/MESP Composites

Brabender Internal Mixer was used to determine and analyse the rheological properties of neat PP and PP/MESP composites at various MESP loading. The loading torque and stabilization torque for unfilled PP and PP/MESP composites at different loading can be obtained via melt mixing of PP pellets and MESP powders at different MESP loading during the processing. The rheological properties of polymer can be affected by polymer structure, processing condition (such as mixing temperature, mixing time and rotor rotational speed), machine design and compounding ingredients (Chun & Husseinsyah, 2014). In addition, it is significant to carry out the melt mixing processing analysis in order to study the rheological properties of PP/MESP composites such as the viscosity, processability, and stiffness of the reinforced polymer matrix (Yang, et al., 2005).

Initially during the melt mixing process, the mixing temperature was set to 180 °C as polypropylene can melt at this temperature. The heat supplied from the Brabender internal mixer was absorbed by the polypropylene and was mixed with the added MESP fillers at different loading. The initial mixing torque indicates the resistant of flow of polymer, meaning that the more viscous the polymer is, the more difficult for the polymer to flow, thus higher loading torque will be obtained as high shear stress need to apply for polymer to flow (Huang, et al., 2009).

Figure 4.5 shows that the loading torque of PP/MESP composites at different MESP loading. For unfilled PP, it can be observed that the initial mixing torque increases rapidly when PP was charged into the mixing chamber. The high shearing force and high shear stress produced by the rotor was the key factor of the instant increase of loading torque of unfilled PP before the PP started to melt (Yang, et al., 2005). Thus, the amount of PP and MESP fillers plays a crucial factor which affects the loading torque when the PP/MESP composites were being charged into the mixing chamber (Huang, et al., 2009).

According to Figure 4.5, the loading torque decreased gradually with increased of MESP loading. The loading torque decreased from 53.4 Nm to 47.5 Nm when the MESP loading increased from 0 wt % to 10.0 wt %. The decreased of loading torque may be due to the decreased of amount of PP was fed into the mixing chamber. As a result, the lesser amount of PP contributes lower entanglement chain with increases of free volume between the polypropylene chains, hence, lesser shear rate is applied to the polymer as the viscosity of the polymer decreases, and a lower loading torque is obtained. This is also reported by Albooyeh et al., 2015, on the significant effect of PP amount on the viscosity of PP which results in different loading torques.

Commonly, increase of synthetic filler loading will increase the loading torques of polymer melt. This is due to the entrapment and interlocking of polymer chains on the surface of filler. The entrapment of polymer hinders the polymer flow and a higher shear stress is required to dismantle the polymer chain. In addition, the increase of synthetic filler also causes agglomeration and obstruction to the flow of molten polymer, making the polymer more viscous and difficult to flow.

However, most of the natural fibers including MESP are hydrophilic in nature. According to Yeng et al., 2015, the hydrophilic nature of MESP allows MESP act as a plasticizer. A plasticizer is usually a substance added into the polymer matrix in order to promote plasticity and flexibility as well as reduce brittleness of polymer (Koester, 2015). According to Yeng et al., 2015, when MESP is added into the polymer matrix, the low molecular weight of plasticizer places itself between the polypropylene chains. The MESP breaks the initial bonding between the polypropylene chains and forming a new interaction with the polypropylene. The volume of chains will increase and disturb the initial orientation of polypropylene. As a result, a lower shear can be applied to detangle the polypropylene chains with a lower loading torque obtained.

The plasticizing effect of MESP might mainly due to the presence of kernel which contains approximately 20 % of oil content and fatty acid compositions such as oleic acid, linoleic acid, palmitic acid, stearic acid, and behenic acid (Deka, et al., 2014). The presence of kernel might facilitate the processing by lubricating the polypropylene chain movement. This can be supported by research of Ng, (2016), which PP/MESSP composites were used in this research. Based on the results obtained, the loading torque has been increased as more MESSP filler was added into the PP composites due to MESSP did not contain any kernel to provide plasticizing effect to the PP chains, and resulting in higher shear-stress effect (Ng, 2016).

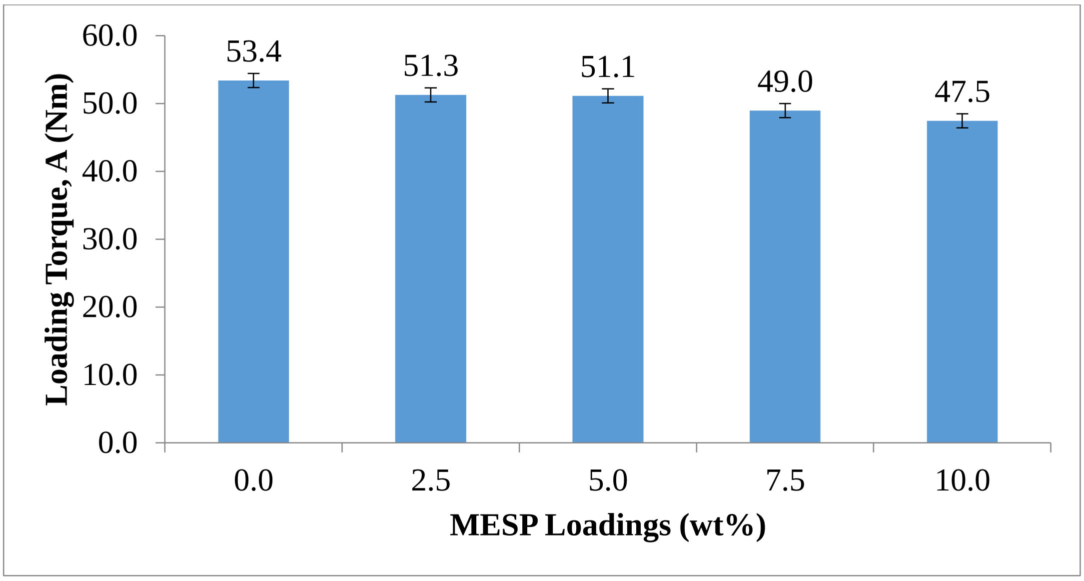

Figure 4.5: Loading Torque of PP/MESP Composites at Different MESP Loadings.

Figure 4.6 shows the stabilization torque of PP/MESP composites at different MESP loadings. The stabilization torque is the torque value obtained at the end of processing time when the polymer achieved homogeneous mixing. According to Figure 4.6, it can be seen that the stabilization torque of PP/MESP decreases gradually from 10.6 Nm to 10.2 Nm. The decreased of stabilization torque indicating PP/MESP composites have a greater processability with lower viscosity upon MESP loadings increment. Moreover, the lower stabilization torque also indicates low stiffness of the compound as well as a good distribution and dispersion of filler in the polypropylene matrix. This can be explained according to Power’s Law. According to Power law, a higher shearing action is required when the viscosity of polymer is high (Yeng, et al., 2015). Since the MESP filler acts as a plasticizer, lower shearing action is required to apply onto the polypropylene matrix as the polypropylene can be dismantled easily when the MESP loading increased. As a result, the polypropylene can flow easier when more MESP is added into the polypropylene matrix and the viscosity of the polypropylene decreases, thus lower stabilization torque can be obtained (Albooyeh, et al., 2015).

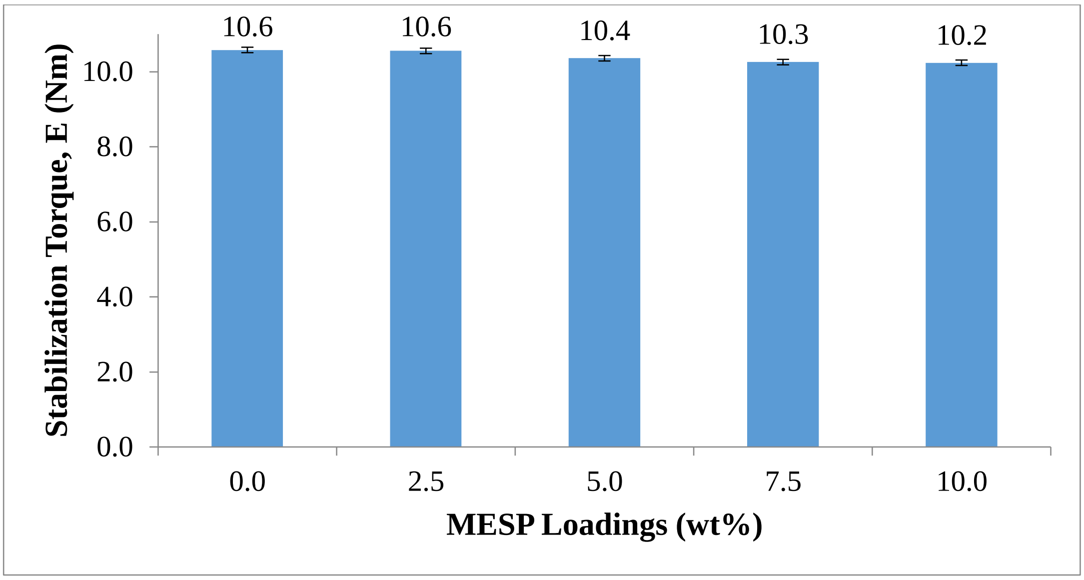

Figure 4.6: Stabilization Torque of PP/MESP Composites at Different MESP Loadings.

### 4.3.3 Differential Scanning Calorimetry (DSC)

Table 4.5 illustrates the thermal characteristics of PP/MESP composites at variation of MESP loading. The DSC results obtained indicates the thermal analysis of unfilled PP and PP/MESP composites by giving the value of melting temperature, crystallization temperature, melting enthalpy, and degree of crystallinity of the PP composites at different MESP loading. Table 4.5 shows that the melting temperature of PP/MESP composites decreases from 171.1 $^{o}$C to 162.8 $^{o}$C whereas the crystallization temperature of PP/MESP composites increases gradually from 120.4 $^{o}$C and stabilize at the temperature of 125.9 $^{o}$C when the MESP loadings increases from 0 wt % to 10.0 wt %. The melting enthalpy of PP/MESP composites decreases from 81.1 J/g to 62.0 J/g when the MESP loading increased from 0 wt % to 10.0 wt %. Similar to the trend of degree of crystallinity, it decreased from 39.2 % to 33.3 % with the increase of MESP loadings, and it can be noticed that there was a slight increment of degree of crystallinity when 5.0 wt % of MESP was added into the PP matrix.

According to Rosa et al., 2008, the increased or decreased of crystallization temperature, $T_c$ can be due to the nucleation effect of natural fillers. Another research studied by Othman et al., 2006, stated that the surface chemistry of natural fillers can greatly affect the nucleation, resulting either increased or decreased crystallization rate and crystallization temperature. Based on the explanation reported by Ferreira et al., 2008, the addition of natural fillers into PP composites can result in two conditions. Firstly, if the fillers acts as a good nucleating agent and promotes a heterogeneous surface to the polymer melt, it improves the crystallinity of PP, making the crystallization process to be more thermodynamically favourable. Secondly, if the filler is not a good nucleating agent, it increases the viscosity of PP composites due to the formation of aggregates or agglomerates, hindering the mobility of PP chains, thus resulting in lower degree of crystallinity and inhibits the rate of crystallization. Thus, lower melting temperature and lower melting enthalpy will be obtained.

Based on the results obtained for PP/MESP composites as shown in Table 4.5, PP/MESP composites have a lower melting temperature, melting enthalpy and lower degree of crystallinity as compared to unfilled PP. This is due to formation of agglomerates and aggregates of MESP on the polymer matrices as well as poorly dispersed in the polymer matrices. Aggregation of MESP hinders the mobility of PP chains due to the stiffening in the PP network, eventually decreases the rate of crystallization. This can confirmed from the SEM morphology observation which shows the formation of MESP agglomerates at higher MESP loading in PP. Similar observation was reported by Othman et al., (2016) on the reduction of melting temperature, melting enthalpy, and rate of crystallization when the amount of bentonite filler was increased in PP matrix. This is due to the incompatibility of bentonite filler into PP matrices and the disturbance of crystalline formation induced by the bentonite during the cooling process.

Table 4.5: Thermal Characteristics of PP/MESP Composites at Different MESP Loadings.

| **Parameters** | **MESP Loadings (wt %)** | | | | |
|---|---|---|---|---|---|
| | **0 %** | **2.5 %** | **5.0 %** | **7.5 %** | **10.0 %** |
| Melting Heat for 100% Crystalline Polypropylene, $\Delta H_{100}$ (J/g) | 207.0 | | | | |
| Melting Temperature, $T_m$ ($^oC$) | 171.1 | 164.5 | 164.0 | 163.7 | 162.8 |
| Crystallization Temperature, $T_c$ ($^oC$) | 120.4 | 125.6 | 125.7 | 125.9 | 125.9 |
| Melting Enthalpy, $\Delta H_m$ (J/g) | 81.2 | 69.2 | 67.9 | 64.4 | 62.0 |
| Degree of Crystallinity, $X^m_c$ (%) | 39.2 | 34.3 | 34.6 | 33.6 | 33.3 |

### 4.3.4 Tensile Properties of PP/MESP Composites

The tensile properties such as tensile strength, E-modulus, and elongation at break of PP/MESP composites were obtained from tensile testing. Tensile strength is known as the ultimate tensile strength, indicating the maximum stress that a polymer can withstand while being pulled or stretched before the polymer breaks (Herz, 2012). Figure 4.7 shows the variation in tensile strength of PP/MESP composites. It can be observed that the tensile strength decreased from 28.2 MPa to 25.4 MPa with the increase of MESP loadings from 0 wt % to 10.0 wt% respectively. According to research reported by Kim et al., (2008), the tensile strength depends on the filler-matrix interaction, filler dispersion on matrix surface, formation of agglomeration or aggregation in the fracture surface, the ratio of filler/matrix, as well as the particle size of fillers. Thus, according to the SEM morphological analysis, it reveals that addition of higher loading of MESP forming more agglomerates or aggregates on PP matrix, weakening the interfacial interaction and adhesion between PP and MESP composites, eventually forming voids and air gaps due to pull out of agglomerates or aggregates from matrix surface. As a result, reduction of tensile strength due to addition of higher MESP loadings was obtained as shown in Figure 4.7.

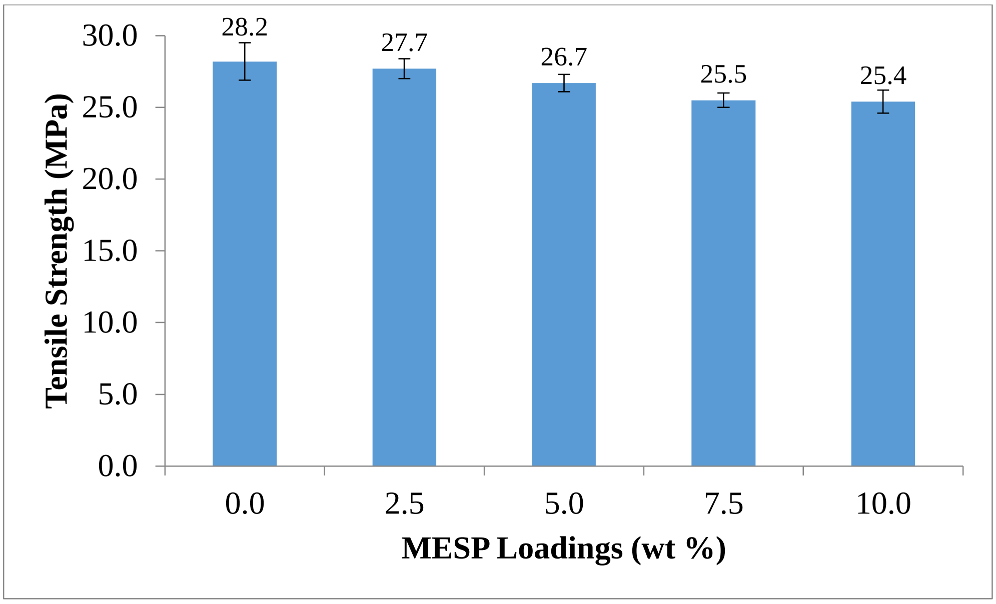

Figure 4.7: Variation in Tensile Strength of PP/MESP Composites.

Moreover, Figure 4.8 illustrates the variation in E-modulus of PP/MESP composites. The E-modulus increases from 1131 MPa to 1155 MPa as the MESP loadings increases from 0 wt % to 10.0 wt % gradually. The E-modulus is also known as elastic modulus that defines the mechanical deformation of polymers and stiffness of the polymer structure according to Hook's Law. According to studies reported by Othman et al., (2006), the filler modulus, filler loading, and filler aspect ratio are the dominant factors that affecting the E-modulus. Furthermore, high aspect ratio of MESP/PP composites and higher filler loadings can cause the composite becoming stiffer, leading the increment on E-modulus as shown in Figure 4.8. This can be explained by the physical bonding between PP and MESP, which MESP acts as filler that interlocks the PP on the surface of MESP. As a result, the interlocking between PP and MESP tends to restrict the flow ability and mobility of the PP chains, as well as reducing the free volume between the PP/MESP composites, thus making the composites structure more rigid and high stiffness. Similar findings have been proved by Ng, (2016), the stiffness of PP/MESSP composites were improved after addition of more MESSP loadings. Then, a good interfacial adhesion between PP and MESSP improved after the mobility of PP chain has been reduced, increasing the E-modulus of PP/MESSP composites eventually.

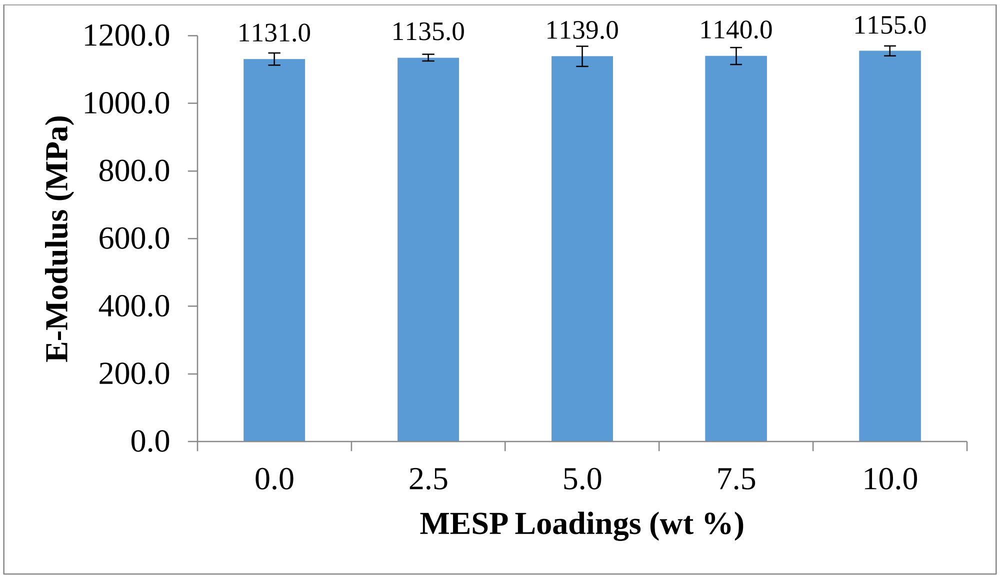

Figure 4.8: Variation in E-modulus of PP/MESP Composites.

On the other hand, Figure 4.9 represents the variation in elongation at break of PP/MESP composites. Different from E-modulus, the elongation at break of PP/MESP composites decreases from 207.6 % to 159.7 % when the MESP loading increased from 0 wt % to 10.0 wt %. The elongation at break is the fracture strain and strongly dependent on the stiffness of polymer composites. According to Othman et al., (2006), a highly rigid particle into PP matrix will decrease the elongation at break. This is because the addition of filler will cause an immediate transition of deformation characteristic of polymer matrices, changes the polymer composites from ductile to brittle behaviour (Othman et al., 2006). Besides, the increased of MESP loadings also reduced the mobility of PP chains and the free volume between PP chains, inhibiting the flow ability of PP chains and deformability of the composites becoming more difficult. Similar findings have shown in report of Ng, (2016), the increased of MESSP filler loadings has been greatly reduced the elongation at break from 191% to 128 % due to the increased rigidity of the composite.

Besides, the obtained elongation at break of PP/MESP composites were slightly higher than PP/MESSP composites by referring to the research of Muniyadi et al., 2018, the reduction of elongation at break of PP/MESP composites were 207.6 %, 188.3 %, 178.1 %, 170.9 %, and 159.7 % respectively from 0 wt % to 10.0

wt % of MESP. Meanwhile, the elongation at break values based on the PP/MESSP composites were 191 %, 182 %, 172 %, 163 %, and 128 % respectively from 0 wt % to 10.0 wt % of MESSP (Muniyadi, et al., 2018). This was mainly due to the plasticizing effect of MESP which MESP interlocked the polypropylene on the surface of MESP, inhibiting the flow of PP chains, causing it had a lower deformability of composites and more stiffening effect as compared to PP/MESSP, resulting a slightly higher value of elongation at break of PP/MESP composites as compared to PP/MESSP (Ng, 2016).

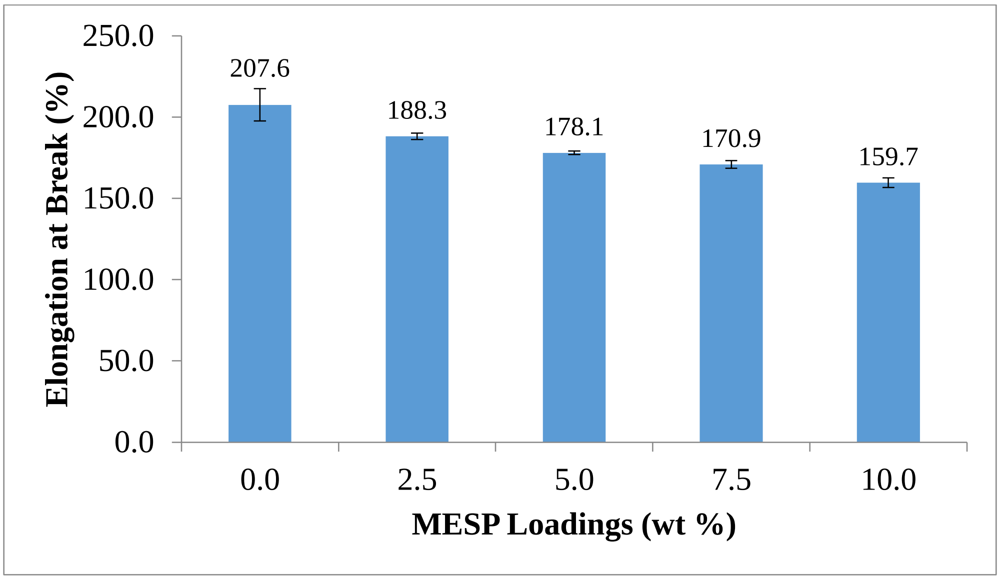

Figure 4.9: Variation in Elongation at Break of PP/MESP Composites.

### 4.3.5 Scanning Electron Microscopy (SEM)

Figure 4.10 represents the SEM micrographs of the tensile fractured surface of PP/MESP composites at various MESP loading at 500x magnification. There are mainly three major observation can be analysed by SEM, which are the surface roughness and matrix tearing, filler dispersion and filler-matrix interaction of PP/MESP composites (Bajpai, et al., 2012). Figure 4.10 (a) depicts the surface of unfilled PP which shows the roughest surface with fibrous structure with highest matrix tearing as compared to the other fractured surface of PP/MESP composites (Figure 4.10 (b) – (e)). The rough surface of unfilled PP reveals that unfilled PP is ductile and has the highest elongation at break and highest tensile strength as compared to the other PP/MESP composites. Similar findings were also reported by Ng, 2016, on the rough surface of unfilled PP indicates that PP can withstand a higher elongation at break before fracturing.

However, it can be observed that there was a reduction of surface roughness of PP composite based on Figure 4.10 (b) to Figure 4.10 (e) when more and more MESP fillers were added into the PP matrix. Besides, the matrix tearing of PP/MESP composites become less significant with addition of MESP particles loading. This represents that the PP/MESP composites becoming stiffer with increased of MESP filler loading, making the fracture surface of PP/MESP composites to become smoother and more brittle. When the fracture surfaces of PP/MESP composites are smooth, it can be said that the PP/MESP composites are highly elastic, increasing of E-modulus and decreasing of elongation at break in the tensile results. Since the PP/MESP composites are becoming smoother and stiffer, it has a reduction of tensile strength as compared to unfilled PP. Similar finding have been reported by Othman et al., (2016), on the reduction of tensile strength, increased of E-modulus and reduction of elongation at break with increasing filler loading in PP matrix from 10.0 wt % to 50.0 wt %.

Meanwhile, the distribution of MESP particles can be observed from Figure 4.10 (b) to Figure 4.10 (e). According to Figure 4.10 (b), MESP particles can disperse well in the matrix at low MESP loading. This indicates the MESP particles might improve the interfacial adhesion between PP and MESP particles causing efficient stress transfer from PP to MESP. However, there is also voids and air gap between the MESP particles that can be seen from Figure 4.10 (b). The formation of voids and air gap may be due to the pulled out of agglomerates or aggregates of MESP during stress application. Thus, it represents a poor interaction between PP and MESP particles. It is also believed that the formation of voids and air gap causing the slight reduction of tensile strength obtained in the tensile results as compared to unfilled PP.

Moreover, the numbers of voids and air gaps between the MESP particles were increased significantly when addition of MESP particles into the PP matrix as shown in Figure 4.10 (c) to Figure 4.10 (e). Although the MESP particles are still embedded in the PP matrix as it can be seen in Figure 4.10 (d) and Figure 4.10 (e), the MESP particles tend to agglomerate and eventually reduce the tensile strength of the composites, as the mentioned in the tensile results. The formation of agglomerations may be pulled out at higher loadings due to its weak interfacial interaction and weak interfacial adhesion between the PP and MESP. As results, more voids and pores were formed as it can be seen from the Figure 4.10 (b) to Figure 4.10 (e). According to Ng, (2016), agglomerate particles tend to act as stress concentration point and contributing an uneven stress distribution from the matrix to the filler which will lower the tensile strength and mechanical properties of polymer composites.

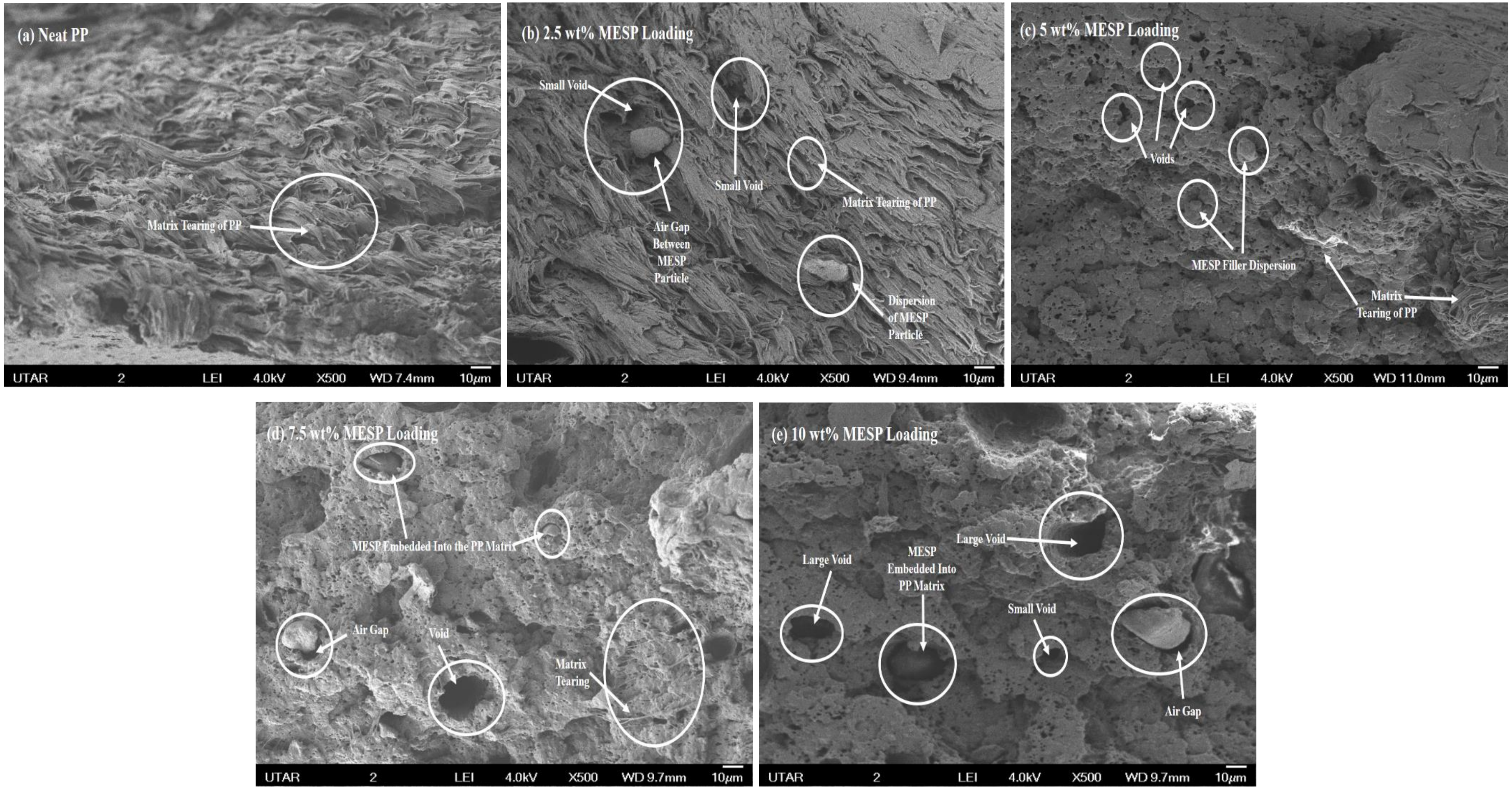

Figure 4.10: Comparison of Tensile Fractured Surface Morphology of PP/MESP Composites; (a) Neat PP, (b) PP/MESP -2.5 %, (c) PP/MESP -5.0 %, (d) PP/MESP -7.5 %, (e) PP/MESP -10.0 % at 500x Magnification.

# CHAPTER 5

# CONCLUSION AND RECOMMENDATIONS

## 5.1 Conclusion

According to the particle size analysis, MESP has a narrower particle size distribution which ranging from 0.0430 μm to 28.2515 μm together with a small mean diameter of 0.18 μm and highest surface area of 36.1 $m^2/g$ as compared to other particulate fillers such as carbon black, MESSP, silica, and calcium carbonate. MESP particles were irregular in shape and existed as a mixture of aggregates and small agglomerates. The narrow particle size distribution of MESP indicating it has a more uniform particle size than of broader distribution. This allowed the MESP has a better catalytic activity as filler reinforcement into the PP matrix and it has been further reviewed using scanning electron microscopy (SEM) to study the morphological properties observation of PP/MESP composites.

FTIR analysis revealed that MESP consists mostly of carboxylic acid, methyl group as well as C-H cellulose and hemicellulose functional groups which was similar to the previous studies by other researchers. On the other hand, the FTIR-ATR analysis has shown that there was no chemical reaction occurred between PP and MESP as there has no new peaks formation after the PP/MESP composites reinforcement.

Moreover, the addition of MESP filler up to 10.0 wt % gave slight effect of the processability of PP/MESP composites as shown in the value obtained from processing torque. The loading and stabilization torques decreased gradually as increased of MESP loading. This is because MESP has acted as a plasticizer and has placed itself between the polypropylene chains and disturbed the initial orientation of PP by lowering the viscosity of PP/MESP composites, making it easier to flow, thus, better processability of PP/MESP composites were achieved.

However, instead of improved of tensile strength, addition of MESP has gradually reduced the tensile strength of PP/MESP composites, increased of E-modulus, as well as reduction of elongation at break of PP/MESP composites. Also, the SEM morphological observation revealed that MESP particles were dispersed well in PP matrix but has a weak interfacial interaction with PP. Agglomeration of MESP can be seen at higher MESP loading of 10.0 wt %. Thus, the weak interfacial interaction between MESP and PP and the formation of agglomerates of MESP is responsible to the reduction of tensile strength and high stiffness of PP/MESP composites as compared to unfilled PP.

Through this research, it can be suggested that PP/MESP composites can be applied in fabricating the products that requires medium tensile strength, medium processing torques as well as medium temperature processing condition as similar to unfilled PP such as rigid packaging, interior parts of automotive, car dashboards, door panels, and furniture.

## 5.2 Recommendations

In order to improve outcome of this study research, several recommendations are made as such:

a) Variation of MESP loadings were used to reinforce into the PP matrix to study and obtain the optimum loadings of MESP in order to produce the optimum properties of PP/MESP composites.
b) Modifications or surface pre-treatment can be implied such as addition of UV stabilizers and surface treatment through alkalization to ease the processability of PP/MESP composites.

c) For instance, chemical treatments such as dewaxing, delignification, bleaching, acetylation, and chemical grafting can also be used to modify the surface properties of MESP filler and enhance the interfacial adhesion between PP and MESP.

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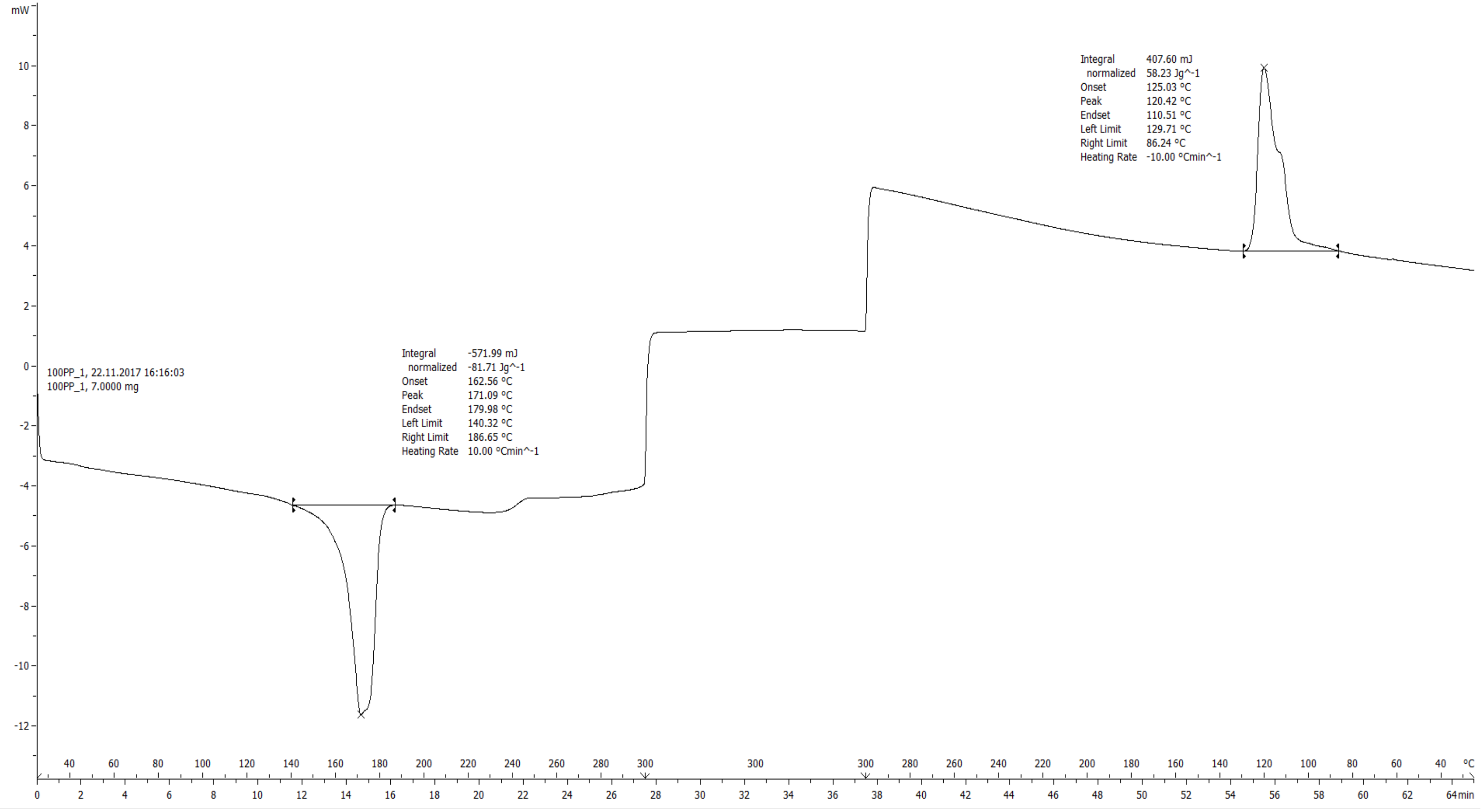
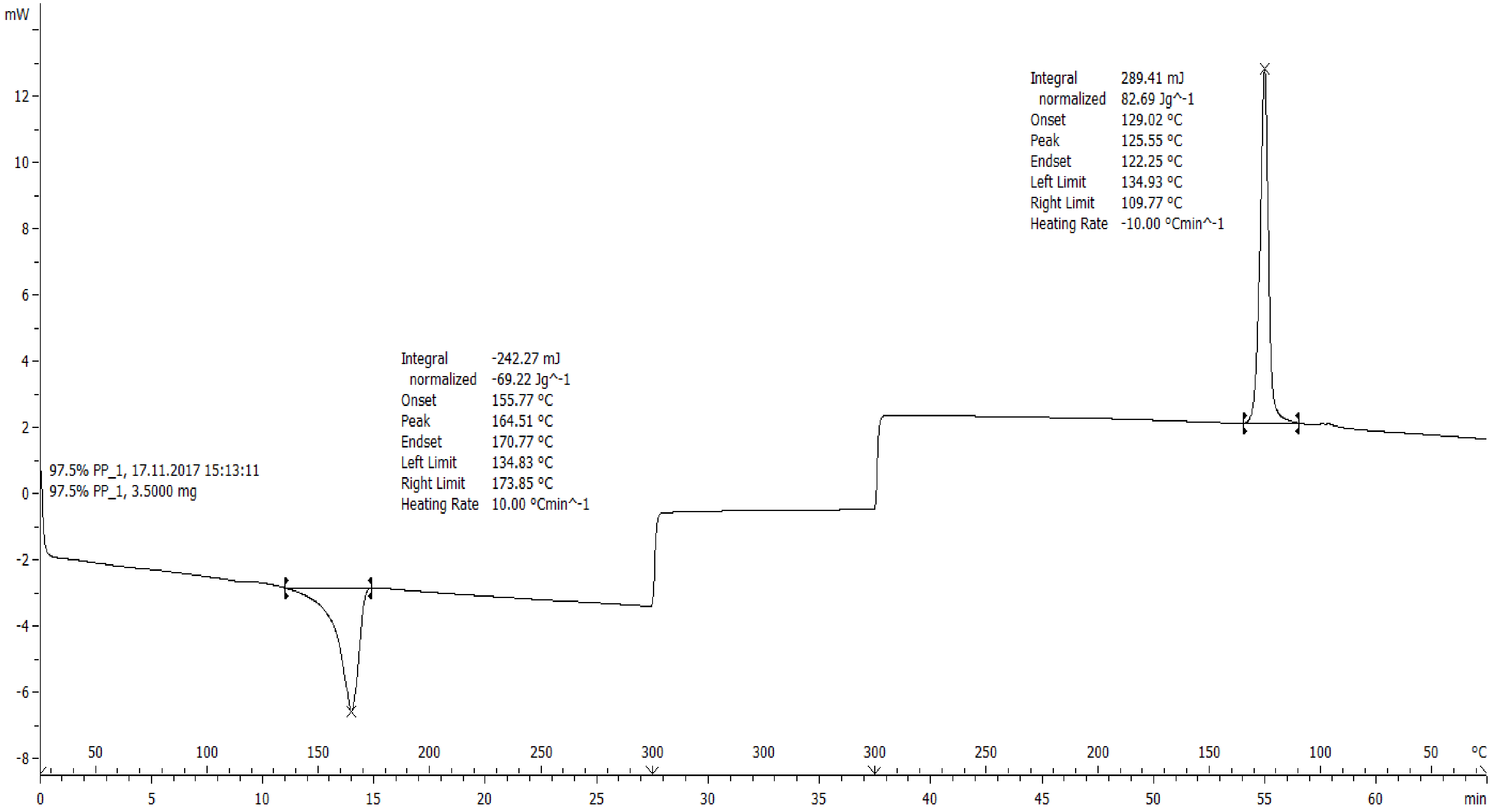
# APPENDICES

## APPENDIX A: Differential Scanning Calorimetry

(a) Neat PP


mW
10
8
6
4
2
0
-2
-4
-6
-8
-10
-12
100PP_1, 22.11.2017 16:16:03
100PP_1, 7.0000 mg
Integral -571.99 mJ
normalized -81.71 Jg^-1
Onset 162.56 °C
Peak 171.09 °C
Endset 179.98 °C
Left Limit 140.32 °C
Right Limit 186.65 °C
Heating Rate 10.00 °Cmin^-1
Integral 407.60 mJ
normalized 58.23 Jg^-1
Onset 125.03 °C
Peak 120.42 °C
Endset 110.51 °C
Left Limit 129.71 °C
Right Limit 86.24 °C
Heating Rate -10.00 °Cmin^-1
40 60 80 100 120 140 160 180 200 220 240 260 280 300 300 300 280 260 240 220 200 180 160 140 120 100 80 60 40 °C
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60 62 64 min

(b) PP/MESP Composites at 2.5 wt % Loading

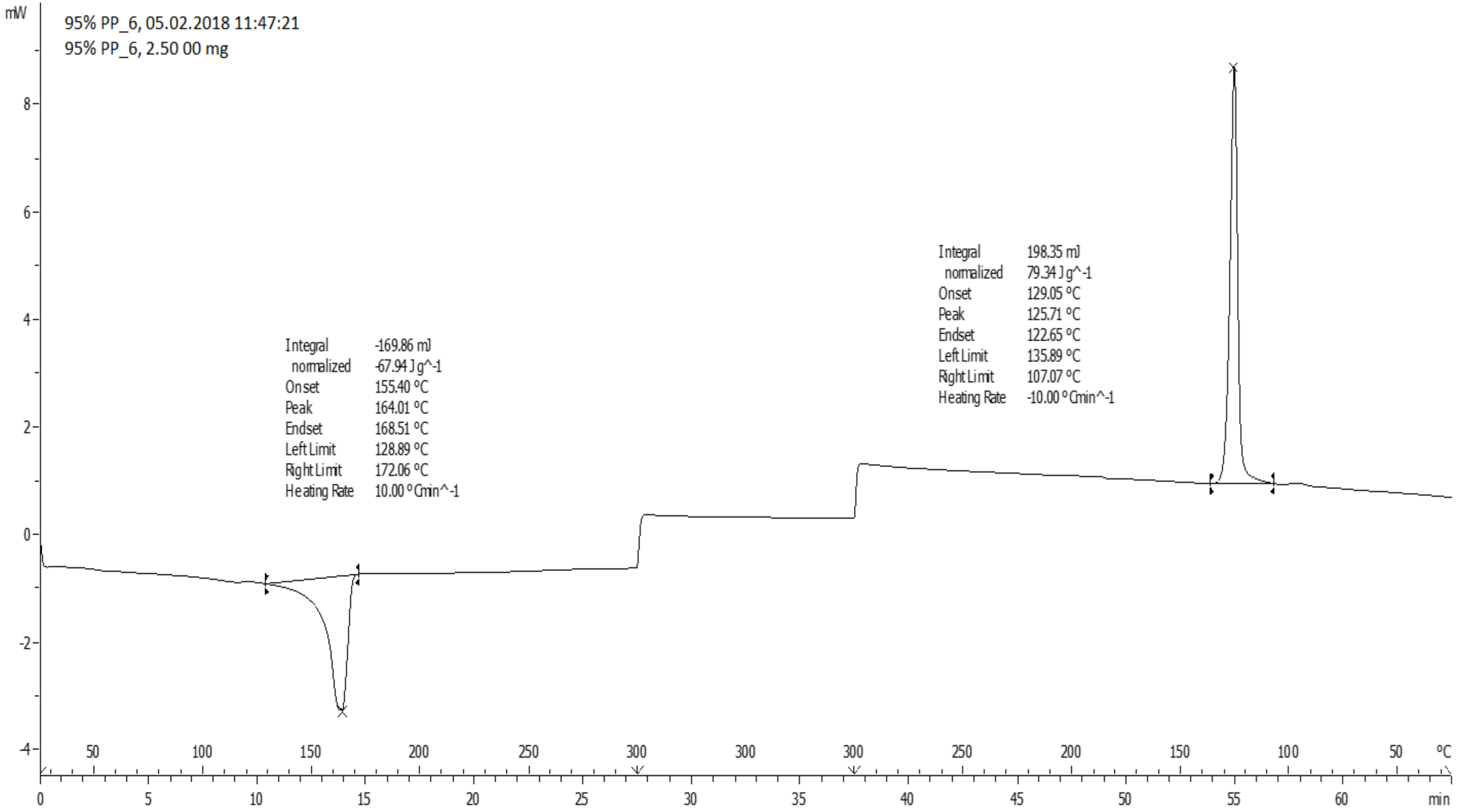


97.5% PP_1, 17.11.2017 15:13:11
97.5% PP_1, 3.5000 mg

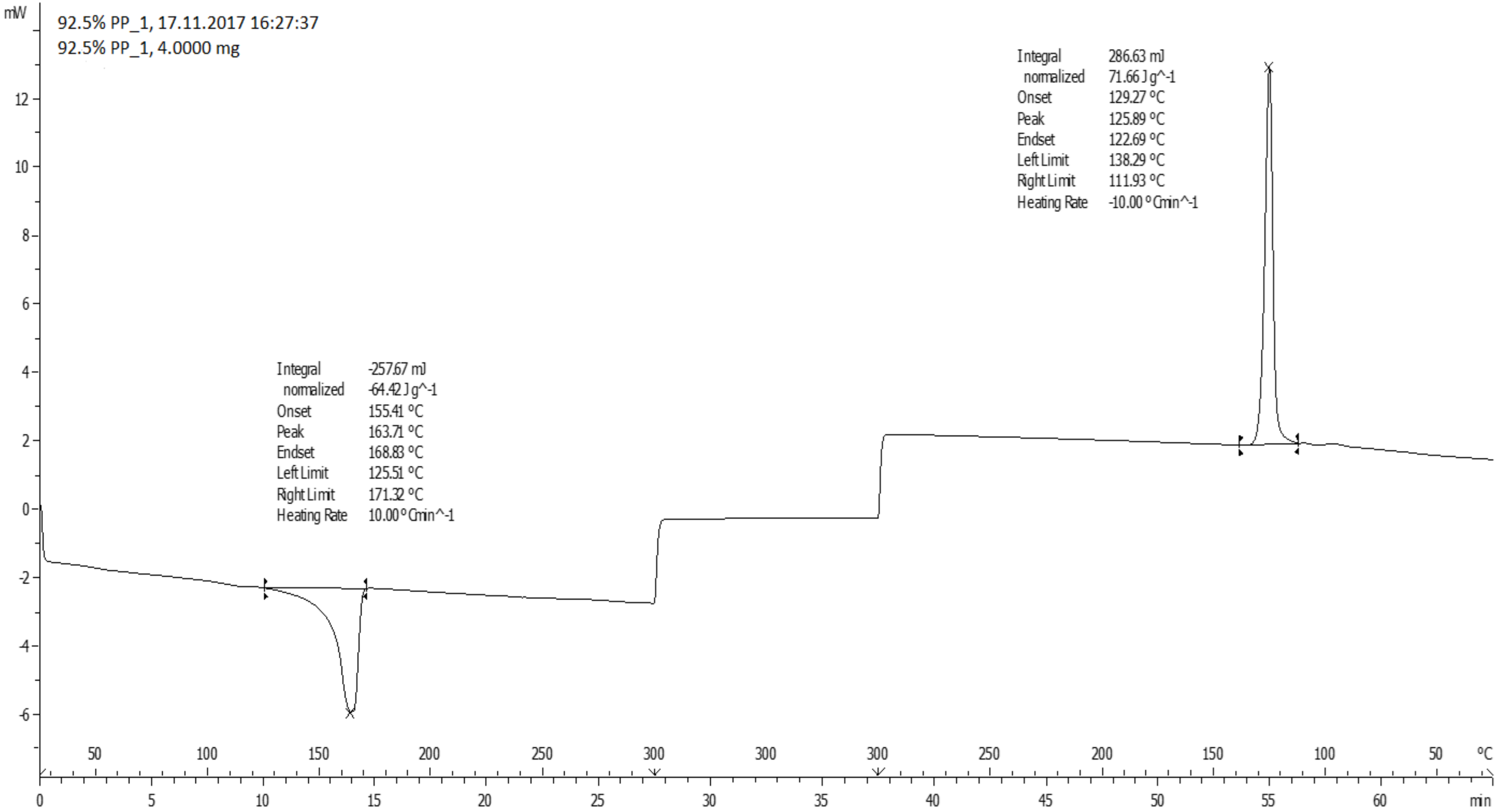
| | |
|---|---|
| Integral | -242.27 mJ |
| normalized | -69.22 Jg^-1 |
| Onset | 155.77 °C |
| Peak | 164.51 °C |
| Endset | 170.77 °C |
| Left Limit | 134.83 °C |
| Right Limit | 173.85 °C |
| Heating Rate | 10.00 °Cmin^-1 |

| | |
|---|---|
| Integral | 289.41 mJ |
| normalized | 82.69 Jg^-1 |
| Onset | 129.02 °C |
| Peak | 125.55 °C |
| Endset | 122.25 °C |
| Left Limit | 134.93 °C |
| Right Limit | 109.77 °C |
| Heating Rate | -10.00 °Cmin^-1 |

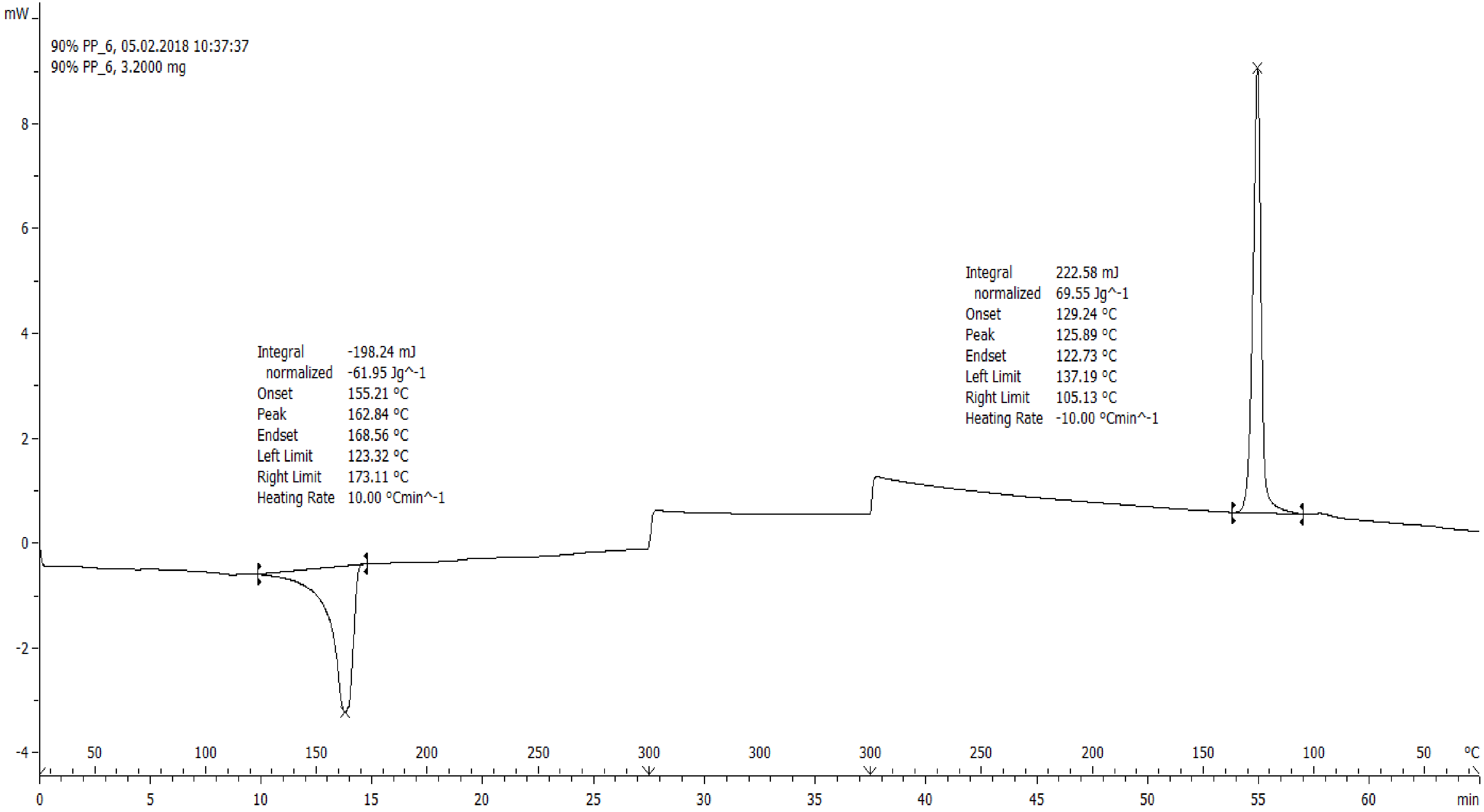
(c) PP/MESP Composites at 5.0 wt % Loading



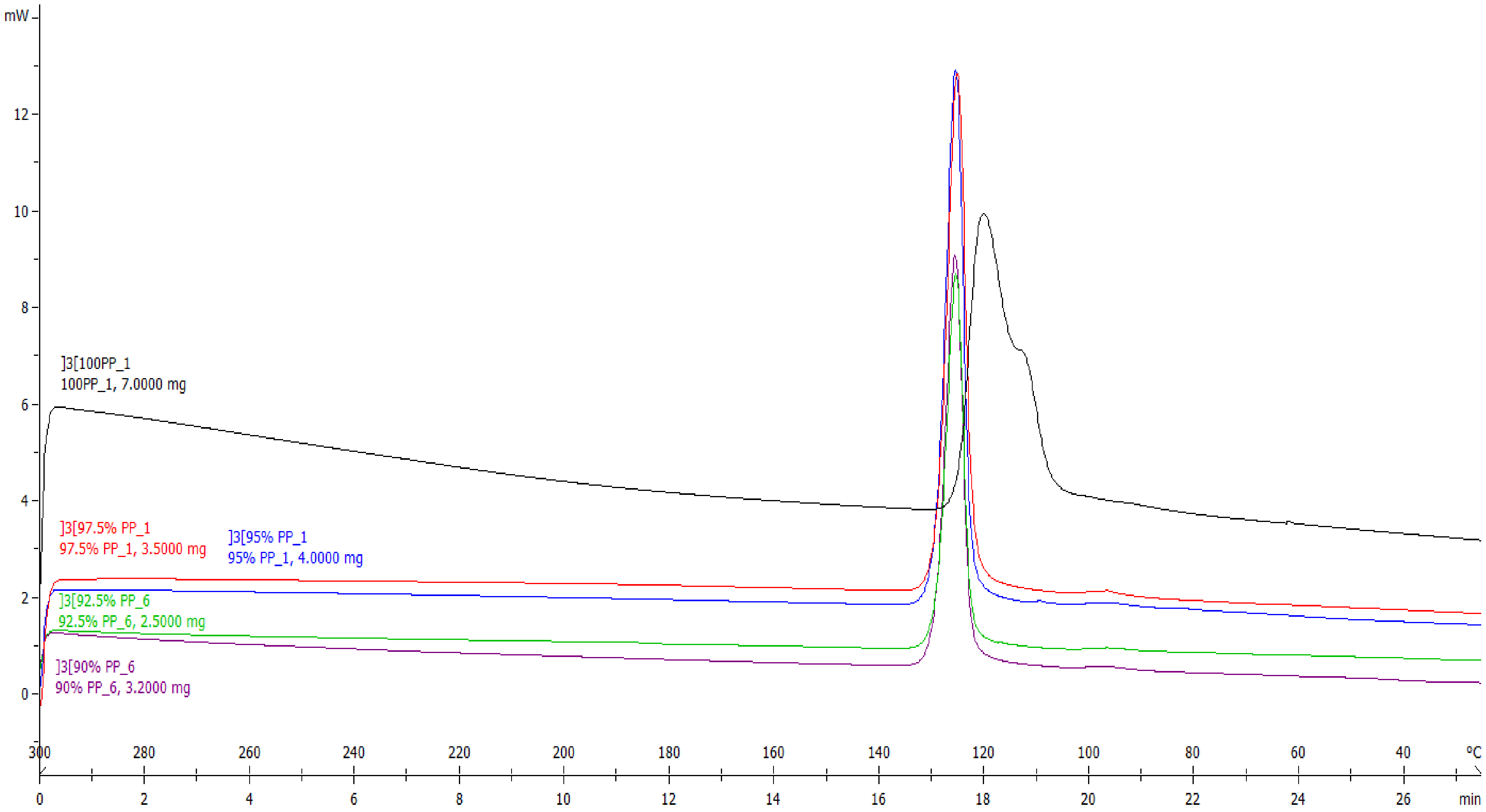
(d) PP/MESP Composites at 7.5 wt % Loading



(e) PP/MESP Composites at 10.0 wt % Loading



(f) Crystallization Curve of PP/MESP Composites at Different Loadings



(g) Melting Curve of PP/MESP Composites at Different Loadings