

**DEVELOPMENT AND PROPERTIES OF *MIMUSOPS ELENGI* SEED SHELL
POWDER FILLED POLYVINYL ALCOHOL FILMS PRODUCED THROUGH
MEMBRANE CASTING METHOD**

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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**

May 2018

DECLARATION

I hereby declare that this project 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 degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

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ABSTRACT

Petroleum based plastic films have high resistance toward degradation and contribute towards many environmental problems. Besides, many challenges and limitation causes inadequacy of recycling, contributing to generation of tremendous plastic waste by time. In response to the problem associated with the low degradability of plastic waste, it can be conquered with the development of biopolymer by adding natural fibers which makes the plastic films to be biodegradable. In this research, *Mimusops elengi* seed shell powder (MESSP) filled polyvinyl alcohol (PVOH) films were prepared through membrane casting method with various MESSP loading (i.e. 0, 5, 10, 15 and 20 wt %). Instead of using solution casting method, the films were produced through membrane casting method to avoid inconsistency of film thickness. Attenuated total reflectance-Fourier transform infrared spectroscopy analysis revealed that both MESSP and PVOH were hydrophilic in nature and confirmed that there was no chemical interaction formed between MESSP filler and PVOH matrix. This research study is aimed to highlight on the tensile properties, resistance towards water absorption and the biodegradability of the PVOH/MESSP blended film. In addition, the investigation on the surface morphology and surface fracture of the blended films were carried out by using scanning electron microscopy. Based on the result obtained, PVOH/MESSP blended films with higher MESSP loading have lower tensile strength and elongation at break due to the weak intermolecular bonding between the MESSP and the PVOH matrix.

However, elastic modulus was increased gradually contributed by the increasing of MESSP loading that result in stiffer blended films as compared to unfilled PVOH film. Resistance towards water absorption was increased as the MESSP loading was increased. Besides, PVOH/MESSP films showed an improved biodegradation with increasing MESSP loading as investigated through weight loss and SEM morphological observation upon soil burial test over a period of 3, 6 and 9 weeks. SEM morphological observation revealed that PVOH/MESSP films can be easily degraded through microorganism activities as compared to unfilled PVOH films which remain intact over exposure period.

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LIST OF SYMBOLS/ABBREVIATIONS

B_i	Initial weight of the sample before soil burial test, g
B_f	Weight of the sample after soil burial test, g
W_i	Initial weight of the sample, g
W_f	Weight of the sample after swelling test, g
wt %	Weight percent
$Al(OH)_3$	Aluminum hydroxide
Al_2O_3	Aluminum oxide
ASTM	American Society for Testing and Materials
ATR- FTIR	Attenuated total reflectance-Fourier transform infrared spectroscopy
$BaSO_4$	Barium sulphate
$CaCO_3$	Calcium carbonate
CAGR	Compound annual growth rate
CAS	Chemical abstract service
$CaSO_4$	Calcium sulphate
EPA	Environmental Protection Agency
HDPE	High density polyethylene

LDPE	Low density polyethylene
MD	Machine direction
MESSP	<i>Mimusops elengi</i> seed shell powder
Mg (OH) ₂	Magnesium hydroxide
MgO	Magnesium oxide
MMT	Montmorillonite
MSW	Municipal Solid Waste
PAAm	Polyacrylamide
PE	Polyethylene
PEG	Polyethylene glycol
PET	Polyethylene terephthalate
PHA	Polyhydroxyalcanote
PHB	Poly-3-hydroxybutyrate
PHBV	Polyhydroxybutyrate-co-valerate
PLA	Polylactic acid
PP	Polypropylene
PS	Polystyrene
PSA	Particle size analysis
PVAc	Polyvinyl acetate
PVC	Polyvinyl chloride
PVOH	Polyvinyl alcohol

S.P.I	Society of the Plastics Industry
Sb ₂ O ₃	Antimony trioxide
SEM	Scanning Electron Microscopy
SiO ₂	Silicon dioxide
TD	Transverse direction
TPS	Thermoplastic starch
ZnO	Zinc oxide

CHAPTER 1

INTRODUCTION

1.1 Overview

For many years, plastic application has been increasing in worldwide due to its wide utilization in packaging, construction, electrical and electronic applications and automobile appliances. Utilization of petroleum-derived plastics in large quantities have caused many environmental problems due to its non-degradable nature which makes it resistance to microbial degradation. Besides, the reduction in resources from non-renewable petroleum and the environmental awareness have gained more attention particularly in petrochemical and polymer industries. Therefore more development and exploration on the usage and production of polymers from renewable resources have been widely carried out (Ghanbarzadeh and Almasi, 2013).

Biodegradable component which is also known as natural fibers or bio-filler such as starch and fiber extracted from various types of plants was incorporated for the production of biodegradable polymer. Biodegradable polymer is a polymer that can be decomposed easily by the action of microorganism. Meanwhile, natural fiber plays an important part in the improvement of technology through environment safety. Natural cellulose fibers produced from plant can be classified into bast fibers, seed fibers, leaf fibers, grass and reed fibers, core fibers and other kinds of fiber such as wood and roots. There are several advantages of natural fiber over synthetic fibers which have attracted

an increasing amount of attention on fiber reinforced polymer matrix. Cellulose fibers are economic, good relative mechanical properties in tensile modulus and flexural modulus, biodegradable, low weight and has high availability as compared to synthetic fibers. These properties make natural fiber serve as feasible filler which is incorporated into the synthetic plastic matrices as degradable component. Natural fiber is sourced from animals or plants. For instance, starch is incorporated to polyethylene to improve its biodegradation property whereas the addition of cellulose fibers in a polypropylene matrix based materials causes an increment in its tensile modulus (Chauhan and Chauhan, 2013). Nevertheless, other studies of incorporation of natural resources as a component in producing biodegradable polymers were also reported in recent years. Biodegradable plastics produced from the blending of various tropical fruit waste such as rambutan and jackfruit into polyvinyl alcohol were reported by Ooi et al. (2011).

In spite of their advantages, the major challenge of using natural fibers in bio-composite production is the deficient in properties as it permit moisture absorption from the surroundings which causes poor binding between the fiber and polymer. The variety of the chemical structures of both fibers and matrix also causes the coupling problem between natural fiber and polymer. Besides, natural fiber reinforced polymer consist of different chemical functionality whereby the fibers are hydrophilic nature and the polymer is hydrophobic. The difference in chemical functionality generally led to weak adhesion and incompatibility between natural fiber and polymers (Mohammed et al., 2015).

Basically, biodegradable polymers can be classified into three groups. The first group consists of biopolymers produced from natural origins. Second group includes synthetic biodegradable polymers which mainly consist of oil based polymers with a hydrolysable backbone chain whereas the last group is the biodegradable synthetic polymers produced through physical or chemical modification. Polyvinyl alcohol (PVOH) is a ubiquitous synthetic biodegradable polymer to be used as matrix in producing fiber reinforced bio-composites (Tan et al., 2015). Also, it is highly polar due to the presence of the hydroxyl functional group which allows the film production

through the commercial solution casting method (Chauhan and Chauhan, 2013). However, the thickness of the film produced from solution casting varies with the volume mixture prepared that will affect the process ability. Besides, the experimentally used solution casting method will produce polymer films with inconsistent thickness. Thus in this research work membrane casting method was used to produce the polymer film which can controlled the thickness more efficiently in producing films with consistent thickness.

1.2 *Mimusops Elengi*

Mimusops elengi Linn is popularly known as Bakul and it belonging to the Sapotaceae family. In English, it is named as Spanish cherry and bullet wood. It is a type of tree that natively grows in Western Ghat region of the peninsular India (Fern, 2017). As time flies, the tree have distributed and founded in other parts of the country namely Sri Lanka, Thailand, Malaysia, Indonesia, Philippines and New Guinea. Bakul is an evergreen tree and usually growing up to 30 m tall with spreading crown. Different part of this plant such as stem, barks, leaves and fruits and flower are used in various Ayurvedic and act as a tradition medication to cure ailments (Baliga et al., 2011).

The main aim of this research is to introduce new natural filler called *Mimusops elengi* seed shell powder (MESSP) as bio-filler in PVOH to produce a bio-degradable polymer film using membrane casting method. MESSP was produced from the seed shells of the ripe *Mimusops elengi* fruits and used as bio-filler. MESSP filled PVOH films were produced from solution mixing and membrane casting method as various MESSP loading.

1.3 Problem Statement

Applications of petroleum based plastic materials have been widely used in several applications due to its long life properties. According to scientists from University of Georgia at year 2017, 8.3 billion metric tons of plastics were manufactured by human since large-scale production of the synthetic materials began in the early 1950s which end up on landfills or ocean upon disposal. For instance, the most significant application of polymer plastics is used as the materials for food and industrial packaging. However, instead of the advantages, the defeat of these synthetic plastics is that the high chemical stability (high resistance towards degradation) of petroleum polymers. This will lead to environmental pollution caused by synthetic plastics degradation problem as the synthetic plastic polymers take more than 500 years to decompose in landfills. Landfill disposal of plastic waste is not an effective problematic solution due to land scarcity in some countries. A study from UC Santa Barbara had stated that there was almost 8 million metric tons of plastic was accumulated in the world's oceans annually. In addition, the accumulation of the plastic in ocean was estimated to be more than 10 times greater by year 2020 as reported from Ellen MacArthur Foundation (LeBlanc, 2017).

On the other hand, in conjunction with the increasing plastic production and consumption as reported by World watch Institute, the global plastic consumption is continually increased while plastic recycling lacks. The inadequate of recovering and recycling of plastics causes most of the plastic wastes being disposed in landfill or destroyed through open burning (Gourmelon, 2015). US National Library of Medicine National Institutes of Health had reported that majority of plastics used in packaging, agricultural films and disposable consumer items are used for single-use disposable applications only (Hopewell, Dvorak and Kosior, 2009). In 2014, recycling of the plastic wastes generated from U.S. Municipal Solid Waste (MSW) stream was insufficient, as low as 9.5% only reported from Environmental Protection Agency (EPA) (Szaky, 2015). There was 75.5% of plastic waste was sent to landfills and 15% of plastic

waste combusted for energy (LeBlanc, 2017). The main concern on the burning process of plastic waste is that hazardous substances may be released into the environment.

In response to these problems associated with the low biodegradability of plastic waste, it can be conquered with the research and development in the natural fibres, or bio composite material for the production of biopolymer with the degradable character (Chauhan and Chauhan, 2013). However, the drawback of biodegradable plastic is the lower tensile strength of biodegradable plastic as compared to the commercial plastic. The mechanical properties of petroleum-based plastic compost bag and biodegradable plastic compost bag were studied. The research study has proved that the polyethylene (PE) plastic bag was stronger than the polylactic acid (PLA) based biodegradable bag. The tensile strength of the biodegradable bag was lower than polyethylene polymer (Kim and Kim, 2008).

Thus, the study of the incorporation of MESSP as the biofiller in PVOH will be carried out in the research study. Solution casting is the commercial casting method used to produce plastic films. Inconsistency in thickness of films produced through this method will lead to the process difficulty (Stein et al., 1994). So, membrane casting method will be used to obtain consistent film thickness as various desired thickness of film can be adjusted in.

1.4 Objectives

The main goal of the research is to study and characterize the potential of MESSP as filler in producing biodegradable PVOH plastic film. The other objectives in this research are as followed:

- i) To prepare MESSP filled PVOH films with consistent thickness through membrane casting method at different MESSP loading.

- ii) To characterize the chemical functionality and surface morphology of PVOH/MESSP films.
- iii) To study the effect of MESSP loading on the tensile properties, water absorption, morphological properties and biodegradability of PVOH/MESSP films.

CHAPTER 2

LITERATURE REVIEW

2.1 Polymer Films

2.1.1 Introduction

Plastics are formed by joining thousands of smaller monomers through polymerization known as polymer. Main feedstock of polymer comes from the petrochemical resources. Cracking of non-renewable fossil fuels such as crude oil and natural gas create long polymer chains produce plastic. Different forms of polymers are widely used such as films, fibers, elastomers and biopolymers from renewable sources (Tardif, 2013). Figure 2.1 shows domestic plastic production was increased after year 2008 recession due to low U.S natural gas price.

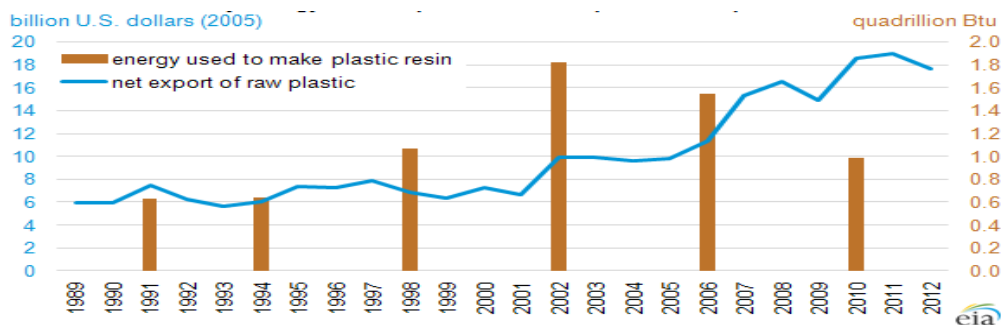


Figure 2.1: Plastic Resin Industry Energy Consumption and Net Export of Raw Plastics (Sendich, 2014)

The ductility of plastic is the unique properties which able to be shaped to any form. Plastics are widely used as the substituent to other material like metal and glass due to their light weight, low cost and desirable properties. Plastic's properties can be altered depend on the different method or processing parameters. It can be stiff and hard or flexible and soft (Stein, 2017). Plastic film can be transparent or coloured, single or multiple layered. Plastic films that are flexible in nature are used as grocery bag whereas the rigid plastics are used as soft drink bottles or containers. Basically, plastic bag composed a wide range category of material either in simple or complex product (Marsh and Bugusu, 2007). Plastic film or packaging film is made from different resins which are categories in Table 2.1.

Table 2.1: Major Types of Plastic by S.P.I Codes (Stein, 2017)

SPI Code	Type of Resin	Example Product
1	Polyethylene terephthalate (PET)	Soft drink bottle, medicine containers
2	High density polyethylene (HDPE)	Milk and water bottles, detergent bottles, toys
3	Polyvinyl chloride (PVC)	Pipe, meat wrap, cooking bottles
4	Low density polyethylene (LDPE)	Wrapping films, grocery bags
5	Polypropylene (PP)	Syrup bottles, yogurt tubs
6	Polystyrene (PS)	Coffee cups

2.1.2 Application

According to a study published by Zion Research with the title, “Plastic Packaging (Rigid Plastic Packaging and Flexible Plastic Packaging) Market for Food & Beverages, Industrial, Household Products, Personal Care, Medical and Other Applications— Global Industry Perspective, Comprehensive Analysis and Forecast, 2014-2020,” reported that the main application segment for plastic film was in the food and beverage packaging market in 2014. As shown in Figure 2.2, global demand for plastic packaging was \$270 billion and forecasted to reach \$375 billion in 2020 where there is a 4.8 % increase of compound annual growth rate (CAGR) between 2014 and 2020. Besides, the forecast on the years to come, the plastic usage in other applications such as membrane, pharmaceutical and medical application also drive the growing demand of plastic applications (Embree, 2016).

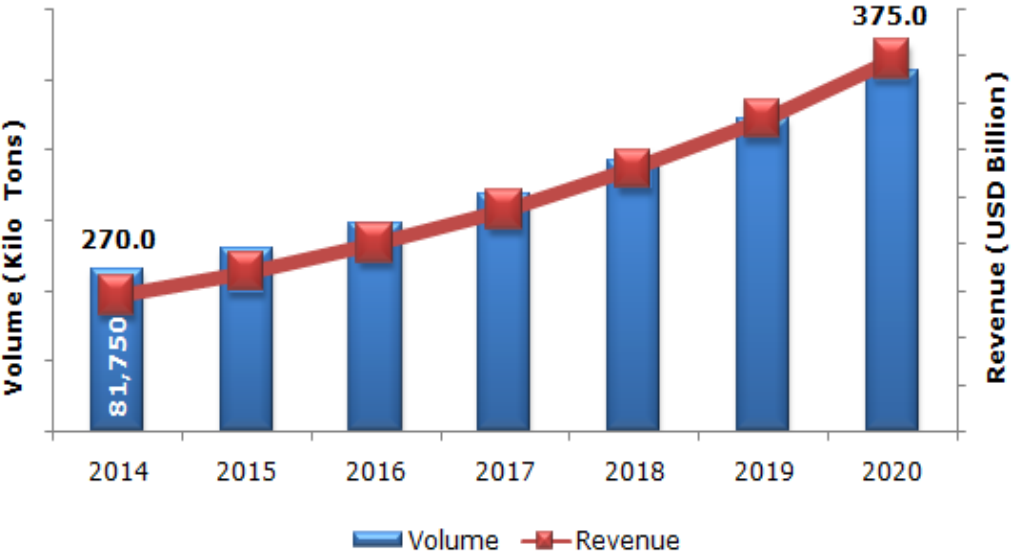


Figure 2.2: Global Plastic Packaging Market from 2014 to 2020 (Kilo Tons) (USD Billion) (Embree, 2016)

Based on Figure 2.3, packaging applications govern 39.6% for the plastics industry which is the largest sector in total plastics demand due to the superior barrier properties of plastic against moisture and air (Marsh and Bugusu, 2007).

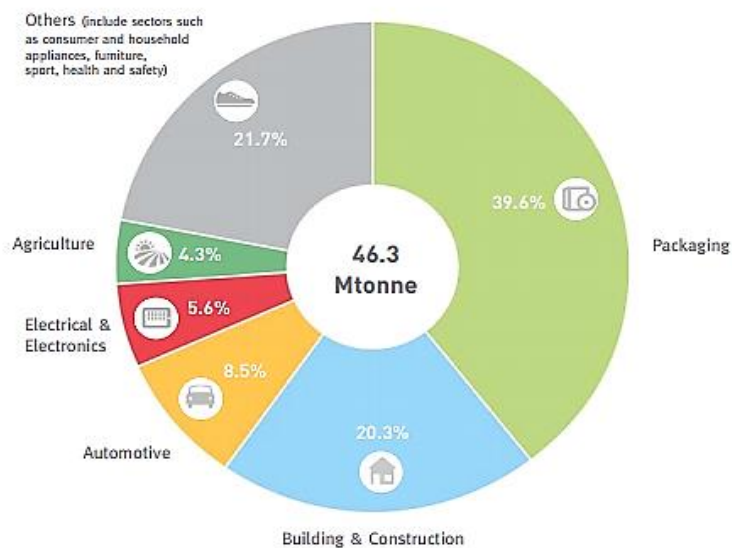


Figure 2.3: European Plastic Demand in 2013 (Christiansen, 2013)

2.1.3 Processing

Ease of the processing actually is one of the factors that contribute to the growth in demand of polymer. Polymers undergo different processes according to their functional uses. For instance, polymers film undergoes continuous blow molding, solution casting and solvent evaporation or membrane casting and solvent evaporation (Stein et al., 1994). The melted polymer undergoes the injection, compression or blow moldings are the most common methods for polymer films. In blown film process, the plastic is extruded through a circular die and expanded to a desire shape of flexible film. Extrusion blow molding is used for the production of the rigid plastic film such as bottles and containers. The molten polymer is transferred to a right angle die before molded in the hollow parison (Stein et al., 1994).

Other than melting process, solution processing is used when the heated polymers do not melt and flow due to their strong interchain bonding. Aggressive solvent such as sulphuric acid is used to dissolve the polymer. Then, this solution is extruded into the film form or casted into films. Solidification of polymer is carried through evaporation process. However, different thicknesses of plastic films are produced with the volume solution prepared lead to the process difficulty (Stein et al., 1994). Thus, membrane casting is designed to minimize movement to obtain smooth and consistent film thickness. Various desired thickness of film can be adjusted in membrane casting.

2.1.4 Disadvantage of Polymer Films

The issues related to the pilling up of plastics in the planet become a critical issues concerned when the generation of plastic is far greater than the amount of plastic being recovered or recycled as shown in Figure 2.4. The disadvantage of polymer film produced from the non-biodegradable petroleum based is difficult to recycle. Collection, identification, sorting and processing on the different kinds of plastics are time consuming and not economical. In order to save cost, disposal on landfill and open burning are considered as the convenient disposal method to manage the plastic waste. Emission of greenhouse gases and the scarcity of landfill are the problems resulted from the increasing petroleum based plastic consumption (Tardif, 2013). According to Miller, there is 1.93% disposal of MSW by weight contributed by 4.83 million tons of plastic film in 2012 as shown in Figure 2.5.

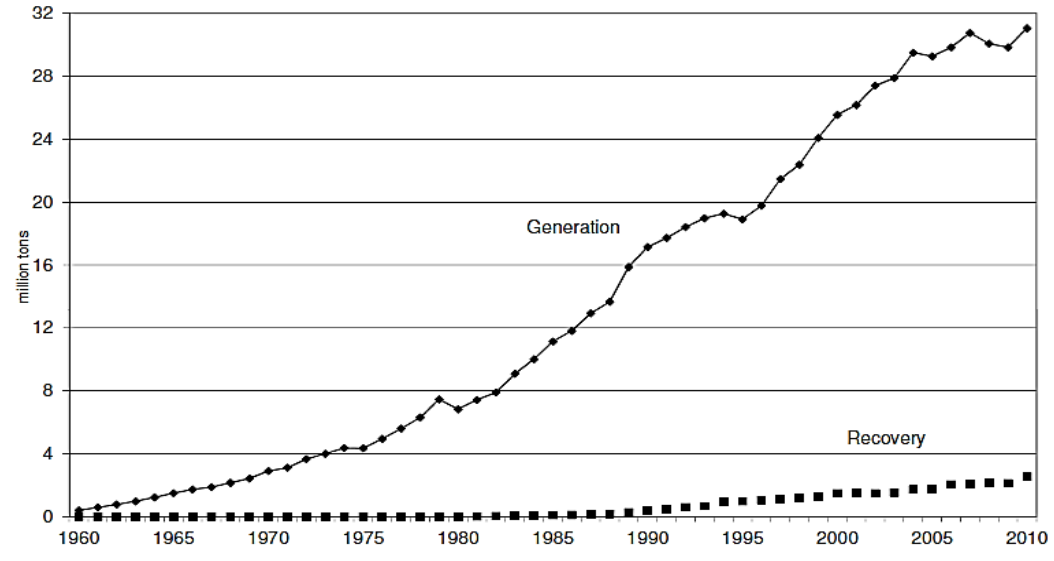


Figure 2.4: Plastic Generation and Recovery from 1960 to 2010 (Tardif, 2013)

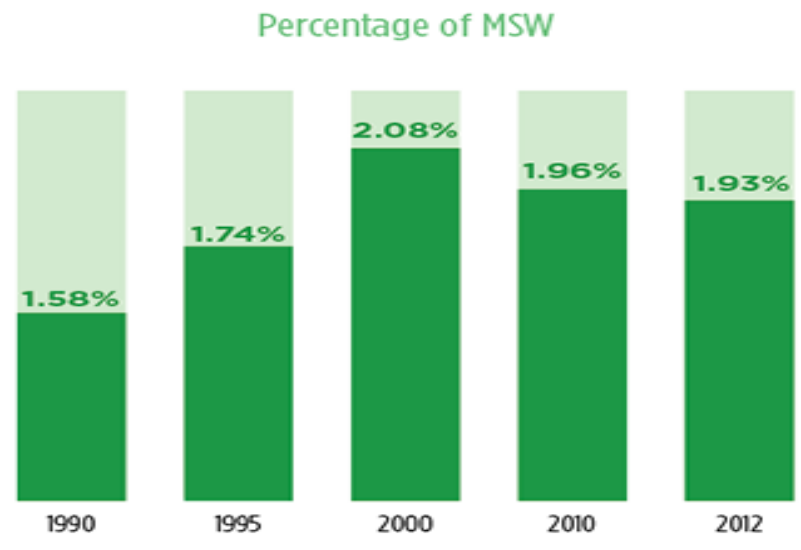


Figure 2.5: Plastic Film Percentage of Municipal Solid Waste (MSW) Generation Chart from 1990 to 2012 (Miller, 2014)

2.2 PVOH

2.2.1 Chemistry

PVOH is a versatile synthetic polymer. Instead of polymerisation reaction which is the commercial process for the production of the polymer from single unit precursor molecules, PVOH also can be made by dissolving polyvinyl acetate (PVAc) in an alkali or an acid in a suitable medium (Azahari et al., 2011). The degree of hydrolysis process will produce different types of PVOH which categorised as partially hydrolysed and fully hydrolysed. The chemical structure of partially hydrolysed and fully hydrolysed PVOH's repeating units is shown in Figure 2.6.

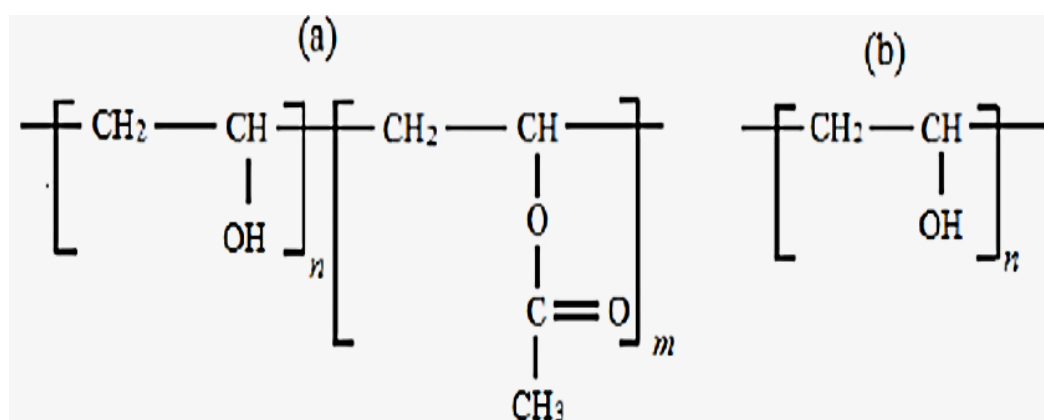


Figure 2.6: Structural Formula for PVOH: (a) Partially Hydrolysed; (b) Fully Hydrolysed (Hassan and Peppas, 2000)

Molecular weights of PVOH produced depend on the hydrolysis condition or the extent of its hydrolysis which is the removal of acetate group on the initial length of the vinyl acetate polymer. Crystalline structure of PVOH contain layer of structure whereby the double layer of molecules are held together by hydroxyl bonds and there is weak van der Waals forces held between the double layers. The amorphous polymer matrix is cause by the folded chain structure of PVOH chains (Hassan and Peppas, 2000).

2.2.2 Properties of PVOH

PVOH is a white or cream colored granular powder. It is a water-soluble synthesised polymer with -OH bonds at the backbone. The chemical and physical properties are strongly depending on the percentage of hydrolysis and the molecular weight. The extent of the hydrolysis and polymerization affect the solubility of PVOH in water. PVOH is less soluble in water with the higher degree of hydrolysis. Molecular weight is one of the parameters that can effect on the crystallinity, adhesion, biodegradability and mechanical properties of the PVOH. The molecular weight of PVOH is in the range of 26,300 to 30,000 with 86.5 degree of hydrolysis. Its glass transition and melting temperature are 85 °C and 240 °C, respectively (Campos et al., 2011). The pH of the 5% solution of polyvinyl alcohol is between 5.0 and 6.5. PVOH itself has the considerable tensile and mechanical strength, higher flexibility and good protective barrier from gas and aroma. For instance, PVOH has the mechanical strength of 1.6 ± 0.1 GPa, elastic modulus of 48 ± 3 GPa, and toughness of $(40 \pm 6 \text{ Jg}^{-1})$ in dry state (Saxena, 2004).

PVOH with higher degree of hydrolysis has higher water resistance, tensile strength and more adhesion to hydrophilic surface as compare to partially hydrolysed PVOH. Fully hydrolysed grade PVOH will swell in room temperature. Over the temperature of 90 °C, PVOH could dissolve in water. Thus, fully hydrolysed grade PVOH should be used when high water resistance and humidity resistance properties are desired (Azom, 2001). PVOH hydrogels is produced from the nearly fully hydrolysed reaction which formed a polymer fluid species. PVOH properties can be altered through crosslinking of the linear polymers as crosslink act as a barrier to diffusion. Furthermore, the physical status of the polymer fluid species is affected by the polymer content. The material's matrix is stiffer and stronger with higher polymer content. On the other hand, soft material is produced with the lower polymer content due to the reason of the fluid can moves freely through the matrix. In addition, PVOH has the unique biocompatible properties to human tissues which can absorb protein molecules. Also, it can take part in the minimal cell adhesion without any toxic effect. Besides, PVOH hydrogels exhibit

swelling properties in water which can retain water within its matrix without dissolving (Gaaz et al., 2015).

2.2.3 Application

PVOH has been the subject of intensive research recently because of their outstanding versatility, processing and physical properties. In textile industry, the application of PVOH include warp sizing, resin finishing and adhesive for screen printing. PVOH can be used as the warp size for spun and filament yarn due to the good properties such as high film strength, high abrasion resistance and its flexibility. PVOH is able to reduce the abrasion on the sizing machine as well as increase the production efficiency. Besides, PVOH is used as modifier for thermosetting resin. Addition of PVOH in resin finishing for textile will improve the resistance of fabric toward wrinkle and shrinkage and reducing the brittleness of resin (Patel and Bhrambhatt, 2008).

In addition, PVOH is also widely used in paper industry as a surface treatment agent. Another usage of PVOH is used as adhesive for paper and the paper board. For instance, production of solid fibreboard and linerboard use PVOH as paper laminating adhesive (Patel and Bhrambhatt, 2008).

Furthermore, the applications PVOH in construction industry are act as a variety of building materials binder. For example, it is used to bind the maturity of asbestos, rock wool and gypsum board. Also, different grades of PVOH are designed for cement additives. Mixing of PVOH with plaster could improve the properties like flexibility, water retention, and plaster viscosity (Scribd, 2002).

PVOH is widely used in the food industries as the binding and coating agent. It is used in the high moisture food which acts as the moisture barrier to preserve the texture, taste and the quality of the food. For instance, PVOH is coated on the food supplement

tablets to protect the active ingredient from moisture and oxygen as well as to sustain the taste and odor. In addition, it facilitates ingestion and swallowing. Different food categories require different level of polyvinyl alcohol coating. Maximum level of PVOH usage is depending on the greatest proportion of the moisture sensitive component and the total surface of the coating area needed. Table 2.2 shows the use levels of polyvinyl alcohol.

Table 2.2: Usage of PVOH Level (Saxena, 2004)

Food categories	Proposed Food-Use	Use Levels for PVOH (%)
Dairy-based desserts	Ice cream and frozen yogurt with inclusions	0.2
Confectionery	Multi-component chocolate Bars	1.5
Cereals and cereal products	Ready to eat breakfast cereals with dried fruits	0.5
Food supplements	Food supplement tablets	1.8
Ready to eat savouries	Nut and fruit mixtures	1.5

Polyvinyl alcohol (PVOH) has been a popular component selected for the preparation of blends and composites with natural, renewable polymers. This is because PVOH possesses salient features with the –OH active groups with the hydrophilic nature exhibit the biocompatibility properties form an excellent composite (Gao et al., 2014). Development of composite material on PVOH is one of the most promising examples to achieves ecological sustainability as they are the most suitable biodegradable matrix polymers. As the substitution for the non-biodegradable polymer film, natural fiber/PVOH blending films were prepared and used as food packaging material and mulching material in agricultural field (Tan et al., 2015). For instance, there are several

researches on the biodegradable polymer film had been carried out such as PVOH blended with tropical fruit waste, PVOH blended with corn starch and polyvinyl alcohol/xylan blending film (Azahari et al. 2011; Gao et al., 2014; Ooi et al., 2011).

Furthermore, the notable application of PVOH as hydrogel membrane is getting significant in biomedical and pharmaceutical area (Kadri et al., 2011). The cross-linked PVOH (hydrogel) prepared by freezing–thawing method is useful in variety application. PVOH hydrogel has 80 to 90% water content, hydrophilic, non-carcinogenic, nontoxic and the biocompatibility characteristic make them excellent candidates for biomaterials. Also, PVOH has the simple chemical structure associated in the ease of processing where the modification can be done by uncomplicated chemical reaction. PVOH gels with these features have been used for contact lenses, drug delivery and the lining for artificial hearts application. With the elastic nature, the usage of the hydrogel for the reconstruction of vocal cords was examined (Davim, 2014). The compatibility of PVOH to the human tissues triggers the attention of PVOH hydrogel as the bio-membrane in artificial kidney application. Also, crosslinked PVOH hydrogel membrane acts as the barrier for the diffusion process and myriad other applications that utilize the semi-permeability of PVOH (Kadri et al., 2011; Hassan and Peppas, 2000). On the other hand, PVOH gels are considered for waste water cleaning application. The usage of PVOH gel particles for the waste water treatment is under research and compared with the use of polyethylene glycol (PEG) and polyacrylamide (PAAm) gels (Hassan and Peppas, 2000).

2.3 Biodegradable Plastic Films

2.3.1 Chemistry and Properties

Biodegradable polymers films can be categorised according to their origin, chemical composition, and synthesis method. Figure 2.7 shows the classification of biodegradable polymers. Synthetic polymers produced from petroleum based resources are polyvinyl

alcohol and others type of aliphatic polyester. On the other hand, biopolymers that are directly extracted from biomass or produced from modified organisms are other sources of natural biodegradable plastic films.

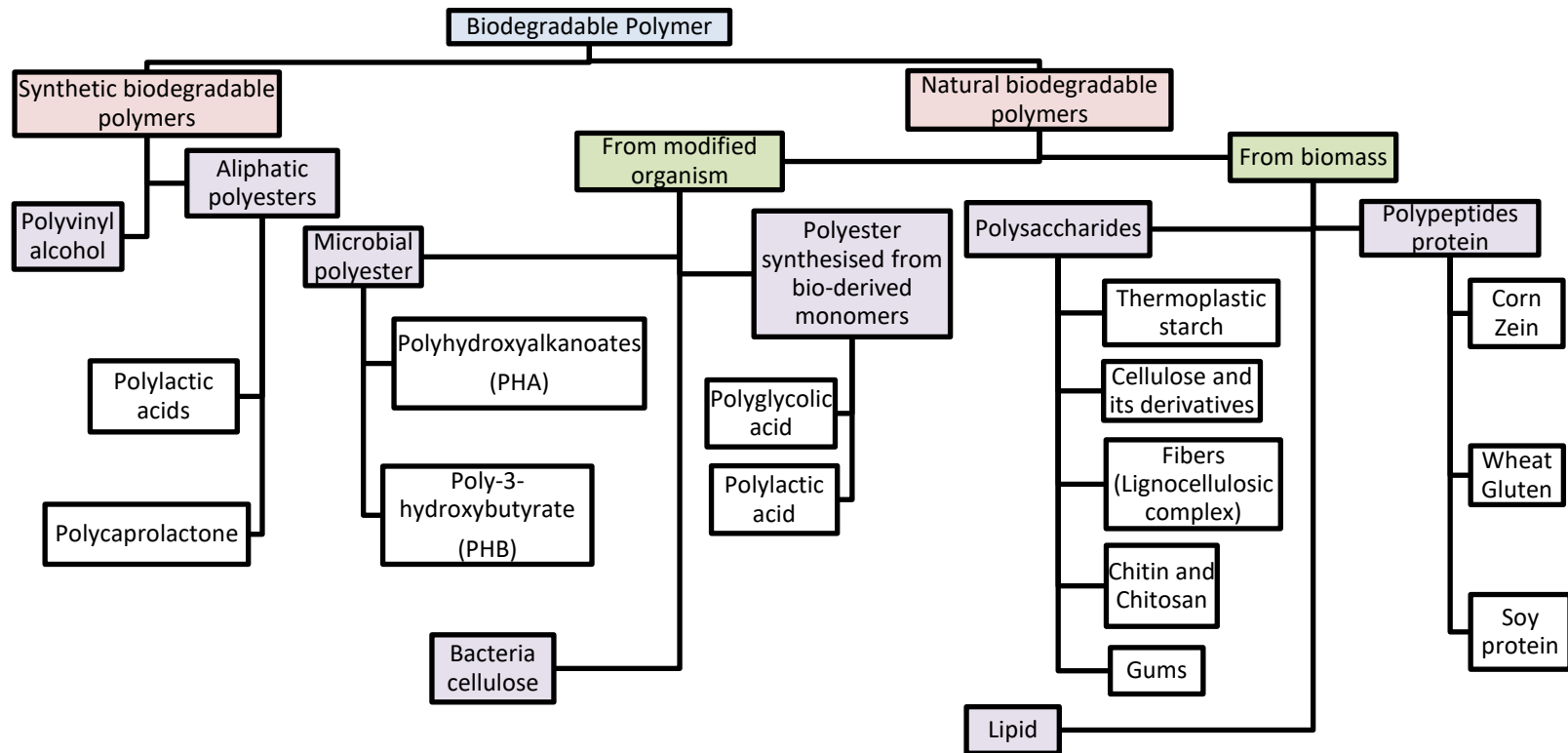


Figure 2.7: Classification of Biopolymer Film Based on Their Origin (Ghanbarzadeh and Almasi, 2013)

Cellulose and starch are the principal polysaccharides of interest. Cellulose is the most abundant natural polymer available worldwide and it is the main constituent of cell wall in lignocellulose plant. Chemical structure of cellulose is shown in Figure 2.8.

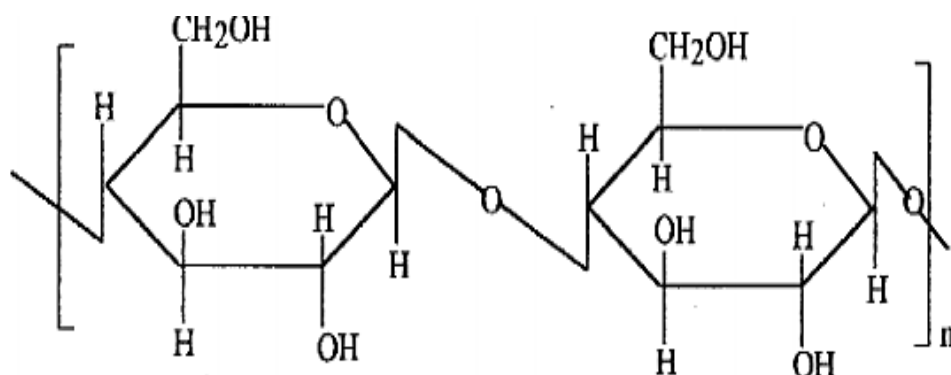


Figure 2.8: Chemical Structure of Cellulose (Ghanbarzadeh and Almasi, 2013)

The principal crops used for its production include potatoes, corn and rice. Starch is produced in the form of granules where composed of amylose and amylopectin polysaccharides. Complex crystalline structure of starch can be completely destroyed which form plasticised starch known as thermoplastic starch (TPS) (Ghanbarzadeh and Almasi, 2013).

Polyhydroxyalkanoates (PHAs) are family of microbial polyester. Figure 2.9 show the chemical structure of PHA. Plastic like properties of PHA that produced from bacteria have attracted attention as a potential replacement for non-degradable petroleum based polyethylene and polypropylene. The most representative member of this family is poly (3-hydroxybutyrate) (PHB) where it is produced the fermentation of sugars by the bacterium *Alcaligenes eutrophus* (Ghanbarzadeh and Almasi, 2013).

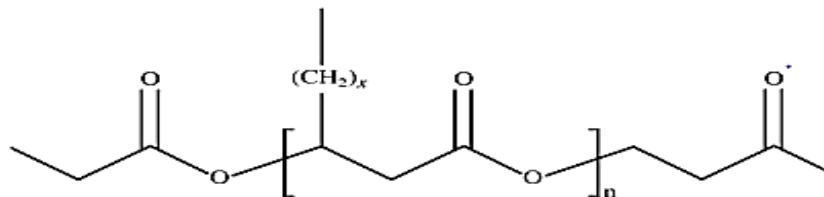


Figure 2.9: Chemical Structure of PHA (Ghanbarzadeh and Almasi, 2013)

Biodegradable polymers are used as raw materials in film production due to the variety of renewable resources in the sustainability of biopolymer. Biodegradability is the main properties of polymer desired nowadays. Biological degradation of the plastic films will release carbon dioxide, water, inorganic compounds and biomass without leaving toxic residues actually contributes to its application on replacing the non-renewable petroleum plastic film. Besides, the good oxygen, odour barrier and not electrostatically charge of the biopolymer are the important properties (Ghanbarzadeh and Almasi, 2013).

2.3.2 Advantages and Disadvantages

Advantages of biopolymer film often associated with its application especially in packaging use. The application of biopolymer film offer an alternative packaging source can help to reduce consumption of natural resources such as crude oil and fossil fuel. Besides, the environmental impact such as greenhouse effect and disposal of non-degradable plastics in landfill can be greatly reduced (Tardif, 2013). Biodegradation of loose-fill packaging materials, garbage bags or food packaging material disposed produce a positive effect on both environmentally and economically. Good oxygen and moisture barrier of bio plastic film used in versatile food products provide physical protection and keep the good quality and safety on the food packed (Malhotra et al., 2015). Research work with the objective to test on suitability of biodegradable

polylactic acid (PLA) packaging film for fruits and vegetables was done. The study proved that PLA is one of the widely used biodegradable polymers for food packaging replacing on the petroleum based plastic bag such as PET and PP in commodities application (Dukalska et al., 2008; Kuruppallil, 2011). In agricultural field, other than mulching films is produced, biopolymer materials also been used to produce containers such as biodegradable plant pots and disposable containers and bags (Kolybaba et al., 2003). However, the main drawbacks as compared to conventional synthetic polymers are the poor mechanical properties of biopolymer. As reported by Kim (2008), polyethylene (PE) compost bag has a higher elongation as it fractures almost at the peak loading with high plastic deformation characteristic as illustrated in Figure 2.10. Figure 2.11 shows the plastic deformation of biodegradable compost bag. The tensile strength of the biodegradable bag is lower than PE plastic bag at 40 in/min.

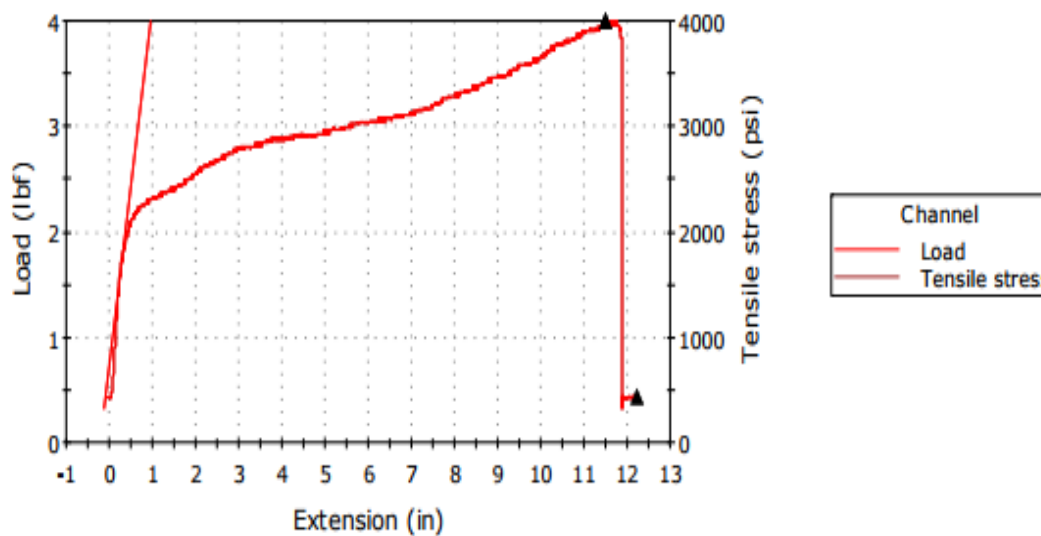


Figure 2.10: Stress-curve of PE Compost Bag at 40 in/min (Kim and Kim, 2008)

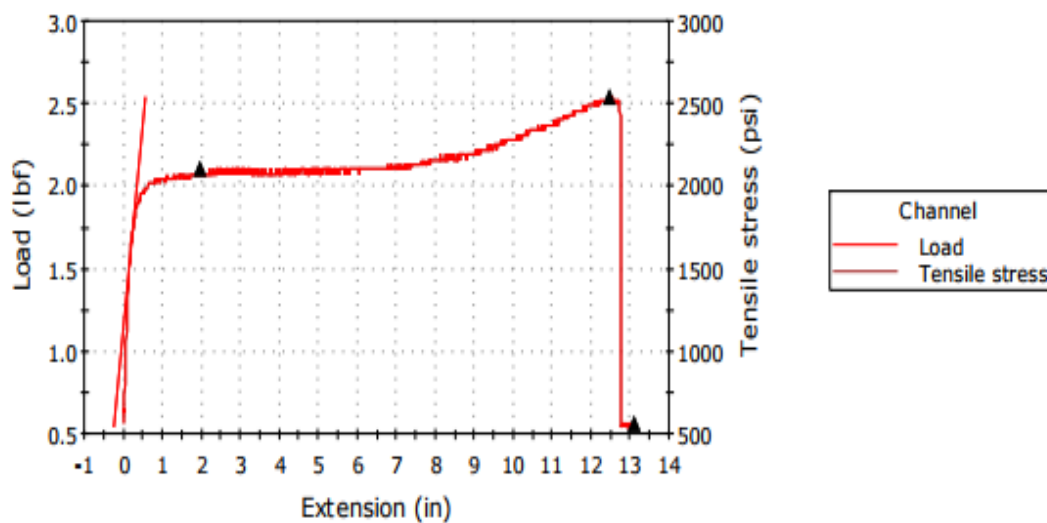


Figure 2.11: Stress-curve of Biodegradable Polymer Compost Bag at 40 in/min (Kim and Kim, 2008)

Figure 2.12 summarised the values of the tensile strength of compost bags at 8 in/min testing speed. For PE compost bag, the mean values of the tensile strength in machine direction (MD) and transverse direction (TD) were 25.95 MPa and 17.42 MPa, respectively. On the other hand, the mean values of the tensile strength in MD and TD for biodegradable compost bags were 15.87 MPa and 10.24 MPa, respectively. Obviously, PE has higher tensile strength values than those of the biodegradable bags.

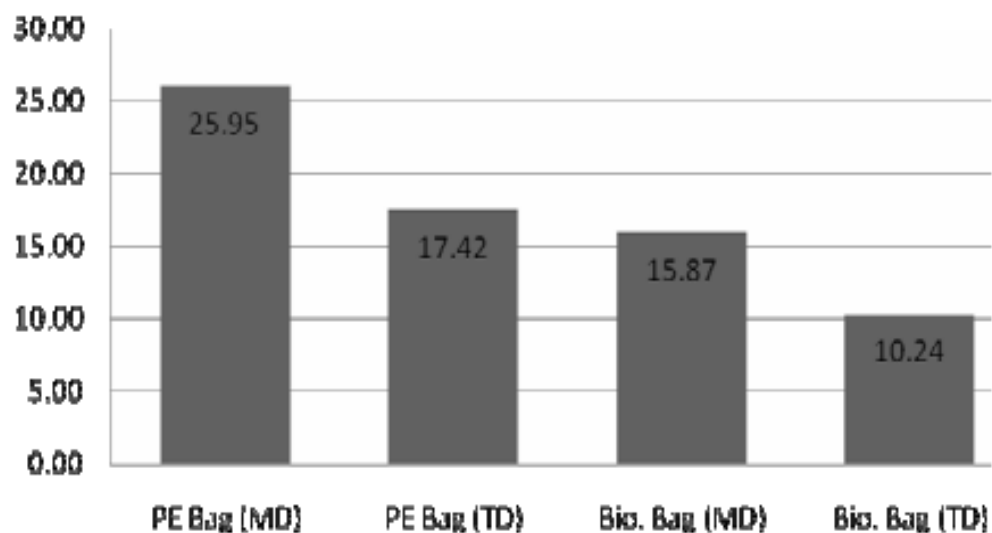


Figure 2.12: Comparison of Mean Values of Tensile Strength (MPa) of Compost Bags in Testing Speed of 8 in/min (Kim and Kim, 2008)

2.3.3 Research Works Done

Due to the concern on the low tensile strength of the pure biopolymer films, researches on the reinforcement of natural fiber to form biopolymer composites have been carried out intensively. For instance, tensile properties of PLA reinforced with kenaf fibres composite was studied by Orchi (2008). In his investigation, there was an enhancement of tensile strength of the composite and shows the positive result on the biodegradability properties (Ochi, 2008).

Besides, the mechanical properties of the biodegradable composite consist of starch reinforced with jute was investigated (Vilaseca et al., 2007). Vilaseca et al. (2007) reported that the tensile strength of the biodegradable polymer composite increased with the increasing of fiber content from 10, 20 and 30 % (w/w). Moreover, injection moulding following the extrusion compounding method was used to produce bamboo fibre in polyhydroxybutyrate-co-valerate (PHBV) which is member of the family of

PHAs. The composite gave positive result where by the tensile modulus of the PHBV composites increased with the increase in fibre loading (Sahari and Sapuan, 2012). In current development, good thermal stability film was discovered by blending chitosan with TPS. This composite is promising for the high output of processed polymer which also potential for applications in packaging (Mendes et al., 2016).

2.4 Filler Material for Plastic Film

2.4.1 Introduction

Fillers are known as additives which are reinforced in polymer. Their major contribution in plastic industry is to improve the physical and chemical properties of polymer. Also, reinforcing filler help to reduce the cost of materials by replacing the most expensive polymer (Mark, 2007). Filler can be categorised according to their origin, function, morphology and composition. Principal filler properties govern on the morphology and properties of plastic products. For example, the geometry, concentration, density, modulus, strength, and surface chemistry of the composites are altered with the reinforcement of filler. Other than that, filler properties will affect the hardness, thermal conductivity and moisture absorption on the composite (Xanthos, 2010). Basically, filler are classified as inorganic and organic substances and further subdivide based on their size, shape and the aspect ratio. Table 2.3 shows the examples of chemical families of fillers reinforced in the plastics (Xanthos, 2010).

Table 2.3: Chemical Families of Fillers for Plastics (Xanthos, 2010)

Chemical family	Examples
Inorganics	
Oxides	Glass (fibers, spheres, hollow spheres, and flakes), Magnesium oxide (MgO), Silicon dioxide (SiO ₂), Antimony trioxide (Sb ₂ O ₃), Aluminum oxide (Al ₂ O ₃), and Zinc oxide (ZnO)
Hydroxides	Aluminum hydroxide (Al(OH) ₃) and Magnesium hydroxide (Mg(OH) ₂)
Salts	Calcium carbonate (CaCO ₃), Barium sulphate (BaSO ₄), Calcium sulphate (CaSO ₄), phosphates, and hydrotalcite
Silicates	Talc, mica, kaolin, wollastonite, montmorillonite, feldspar, and asbestos
Metals	Boron and steel
Organics	
Natural polymers	Cellulose fibers, wood flour and fibers, flax, cotton, sisal, and starch

2.4.2 Natural Fillers/ Fibers

Natural filler, fibers and biological materials are the degradable component and reinforced into the synthetic plastic (Chauhan and Chauhan, 2013). The origin of natural fibers extracted either from plant or animal are illustrated in Figure 2.13. Hairs, wool or silk are the example of animal fibers. Stalk, root, seed, stem, grass, fruit and leaf are the sources where the natural fibers can be extracted from plant (Azwa et al., 2013).

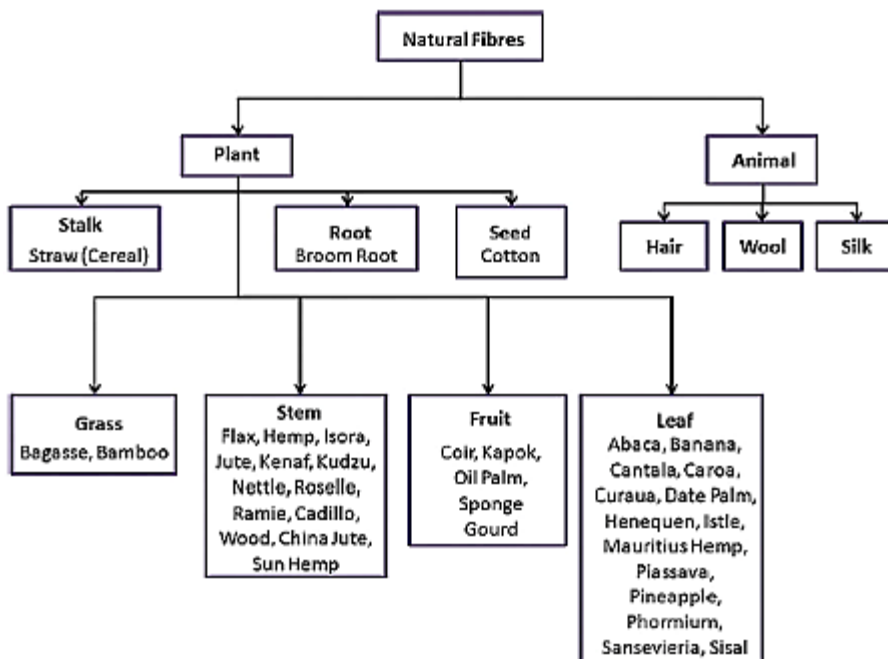


Figure 2.13: Classification of Natural Fibers Based on Their Origins (Azwa et al., 2013)

Natural fibers extracted from plant consist mainly of cellulose fibrils implanted in lignin matrix. Biofibre's complex layered structures which consist of a primary cell wall and three secondary cell walls are illustrated in Figure 2.14. Mechanical properties of fibre are depending on the thick middle layer of the secondary cell walls. This layer is made up from long chain of cellulose molecules (Azwa et al., 2013). The three main components that made up the cell wall are cellulose, hemicelluloses, and lignin. The matrix in the cell wall is amorphous and made up of lignin-hemicelluloses whereas the microfibrils act as fibres in the structure. Lumen is present in natural fibre, making it a hollow structure unlike synthetic fibres. (John and Thomas, 2008) Unlike synthetic fibres, the present of lumen contribute to the hollow structure of biofibre (Liu et al., 2012).

Cellulose is the most vital structural component in the natural fibers. The repeating units of the polymer consist of three hydroxyl groups which are resistance to hydrolysis and degradable when reacted with other chemical (John and Thomas, 2008). The hemicellulose molecules are low molecular weight polysaccharides. The cellulose–

hemicellulose network is formed where the hemicellulose molecules are hydrogen bonded to cellulose and function as cementing matrix between the cellulose microfibrils. Lignin that is hydrophobic in nature will act as the coupling agent in the amorphous region of the biore fiber and increase the stiffness of the cellulose/hemicellulose composite (Azwa et al., 2013).

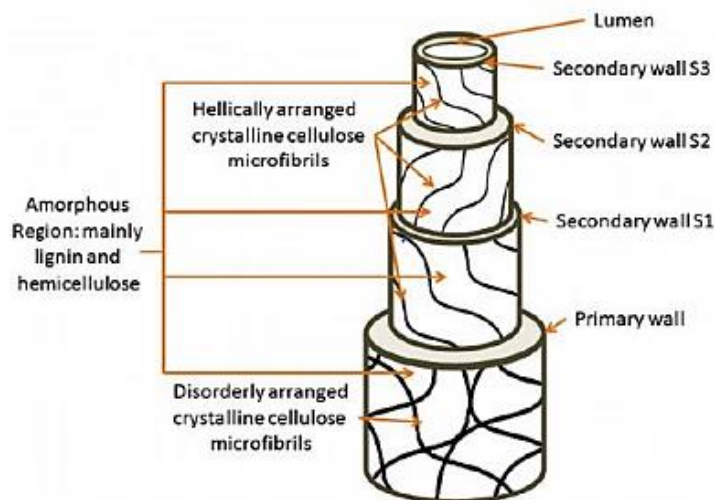


Figure 2.14: Structure of Natural Plant Fiber (John and Thomas, 2008)

2.4.3 Application of Filler

Filler reinforced polymer composites can be classified based on the different intended usage area. Mechanical property modification may be considered as their principal function. For instance, filler that can provide reinforcement is embedded in the polymer and increase its modulus and strength of biocomposites (Xanthos, 2010).

Applications of natural fibers in composite industry are more prevalent as compared to synthetic fibers because of their superior strength comparable to synthetic fibers together with the biodegradable nature (Tan et al., 2015). Mica flakes is inorganic filler reinforced in the polymer. Addition of the mica flakes able to improve the barrier

properties of blow-moulded container and packaging film. For instance, the oxygen permeability of the blown LDPE film embedded with 10% of mica was reduced from 4.16 to 3.03 Barrer (Xanthos, 2010). However, lower weight of the natural fibres than inorganic reinforcements in the composites has the advantage on fuel savings in both transportation and packaging applications (Xanthos,2010).

There are two types of biocomposite. The intended degradability properties of biocomposites for ecological application can be obtained by combining the natural fiber with the polymer matrix from both nonrenewable and renewable resources. Also, another type of composites obtained by combining the degradable polymers with bioactive fillers is widely used for biomedical application. The capability of natural fibre-polymer composites to fully degrade and compatible with the environment drive the potential of natural fiber in plastic film application. Thus, the invention of the polymer reinforced with natural fiber likely to experience continual growth in usage. This is because the harmful effects on the disposable of petroleum based plastic film can be reduced by replacing with the biopolymers. These composites can restrict the carbon dioxide emissions during creation, and undergo biological degradation to organic matter without leaving toxic residue (Nakasaki et al., 2000). For instance, the biodegradability of kenaf as the natural fiber reinforced with PLA was tested for four weeks. Figure 2.15 shows the SEM images of kenaf/PLA composites before (a) and after (b) composting test. The result reported that the composite exhibit the biodegradable properties, provide positive environmental advantages as the composite weight decreased by 38% (Ochi, 2008).

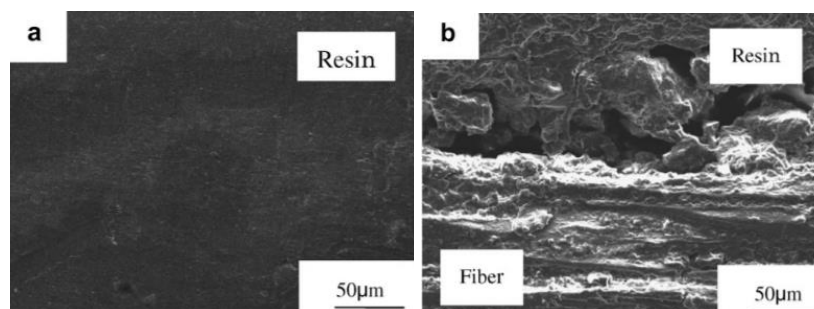


Figure 2.15: SEM Images of Kenaf/PLA Composites (Ochi, 2008)

Usually the processing temperature of polymeric material is above their melting temperature and low thermal conductivity will cause high processing cost and time-consuming problem. Thus, adequate polymeric thermal conductivity is important for processing as well as in electronic packaging and encapsulation area which good heat dissipation are required. Polymer reinforced with organic or inorganic filler is under research to overcome the problem of the intrinsic low thermal conductivity of polymer which is much lower as compared to metal or ceramic material (Mark, 2006). This is because the filler can help to increase the thermal conductivity and create economic advantage by increasing on the moulding cycles for plastic production (Xanthos, 2010).

In the latest technology, the development on the nanocomposites is a new approach to cover up some drawback on the properties of biopolymer in food packaging materials such as inadequate mechanical and barrier properties. There is high increment on the surface area of the fillers at the nano-scale level due to the dramatic filler's size reduction. Large surface area of the nanofiller provides the large interfacial or boundary area on the polymer matrix. Organic nanosized filler used are clay (Montmorillonite, MMT), natural biopolymer (chitosan) or natural antimicrobial agents (e.g. nisin). Metal such as silver and copper; metal oxide such as titanium dioxide and zinc oxide are the examples of inorganic nanofillers (Othman, 2014). Despite improving the mechanical and barrier properties, nanofiller that exhibit antimicrobial properties allow the attachment of the microorganisms on the large surface area of filler. Bacteria could be killed by eliminating oxygen or water vapour to enhance the food safety (Azeredo, 2009; Sorrentino et al., 2007). Researches on cellulose, starch and PLA nanocomposites showed positive results. These nanocomposite possess the desired properties which can be widely used in the food packaging film application (Arora and Padua, 2010).

2.5 *Mimusops Elengi* Linn

2.5.1 Introduction

Mimusops elengi is a ubiquitous evergreen tree grows in India due to its potential in medical application since prehistoric days. It is belonging to the Sapotaceae family and its common vernacular names in various languages are tabulated in Table 2.4.

Table 2.4: Names of *Mimusops elengi* Linn in Different Language (Baliga et al., 2011)

Language	Names
English	Spanish cherry, Medlar and Bullet wood
Sanskrit	Bakula, Bramarananda, Stri-mukhamadhu, Anankantha, Madhuparijara
Hindi	Maulseri, Molchari, Maulsiri, Bakula
Bengali	Bakul
Malayalam	Elengi, Ilanni, Ilenji
Tamil	Alagu, Kesaram, Magilam, Mogadam, Nakum, Magizham Magizhamboo
Malay	Tanjong
Myanmar	Kha-Yay
Thai	Pikul

The height of Bakul tree is around 20-30 m tall. The bark of the tree is thick and tough which is black in colour. The trunk grows upright with the spreading branches. The hard and tough properties of the central wood make them an excellent timber. The heartwood is valuable and used as the construction material for temples in India to build ornate pillars, ceilings, windows and doors. The star-shaped of Bakul tree flowers are in yellowish-white colour with pleasant smell. The ovoid shape of berry is 2.5 cm long. The ripen berry are sweet and edible.



Figure 2.16: Flowers and Ripe Fruits of *Mimusops Elengi* Linn (Baliga et al., 2011)

Being a neglected fruit, the information regard to the composition of the fruit is scarce. However, based on the research done by Nazarudeen (2007), the compositions on Bakul fruits were approximated in the study. There is 79.27% moisture, 1.29 % protein and 2.76% fat in the fruit. From 15.2% of the total sugar, there is 8.9% of reducing sugar and 6.3% of non-reducing sugar. Fiber content in the fruit is around 1.13% and other small amounts of minerals, vitamin C, iron, sodium and potassium. In phytochemistry study, betulinic acid, β -sitosterol, lupeol and ursolic acid are found to be the main chemicals in the bark as shown in Figure 2.17 (Nazarudeen, 2007).

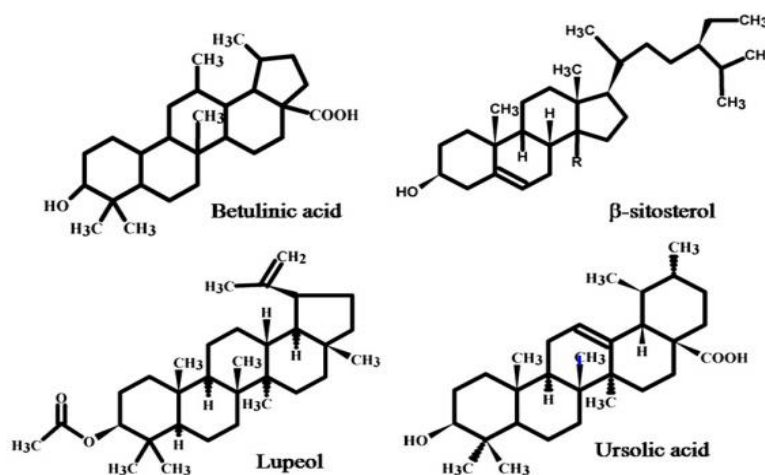


Figure 2.17: Important Phytochemicals Present in Bakul (Baliga et al., 2011)

Hentriacontane, carotene and lupeol are the phytochemical constituents isolated from the leaves, heartwood and roots. Also, volatile oils can be extracted from the flowers (Kadam et al., 2012). The seeds are known to have pentacyclic triterpenes, mimusopgenone and mimugenone, triterpenoid saponins (Gami et al., 2012).

2.5.2 Application

Mimusops elengi is widely used in India for daily application. For instance, the fruit is edible whereas the oil extracted from seed is used for cooking. In previous time, the dried flowers are used as a filling in pillows because the fragrance of the flower can last for long time. Flowers are used to make necklaces for decoration (Fern, 2017). *Mimusops elengi* is well known in India due to its high value as traditional medicinal. In modern study, the researches regard to the application of *Mimusops elengi* in biological and medical have been carried intensively. Tannin, saponin, quercitol, d-mannitol, quercetin, alkaloids and taraxerol are found to be the active components embedded in different parts of *Mimusops elengi* (Baliga et al., 2011).

According to Kadam et al. (2012), the bark, fruit, leaves, seed and flowers extracted from the plant has pharmacological or toxicological effect. (Kadam et al., 2012). Table 2.5 summarises the effect contributed by different parts of *Mimusops elengi* plant.

Table 2.5: Pharmacological/Toxicological Effect of *Mimusops Elengi* Plant (Singh et al., 2014)

Parts used	Effect
Bark	Antimicrobial
	Antiviral
	Antiulcer
	Anti-inflammatory
	Antihyperlipidemic
	Antianxiety
	Diuretic
	Wound healing
	Larvicidal activity
	Anthelmintic
Leaf	Anti-inflammatory
	Antioxidant
	Antihypertensive
	Antidiabetic
Stem	Analgesic
	Antiprotozoal
Fruit	Antioxidant
Seed	Molluscicidal activity

The bark was found to have in vitro antimicrobial effect on the *Staphylococcus aureus*, *Streptococcus mutans*, *Streptococcus salivarius*, *Lactobacillus acidophilus* and *Candida albicans* (Prabha et al., 2010). Other than antimicrobial properties, the bark was examined to have antiulcer activity against serotonin induced

ulcer in albino rats. Antiurolithiatic activity was tested in male albino wistar rats by using the petroleum ether, chloroform, and alcohol extracts of bark. Gargle could be made from the mixture of the decoction of the bark with the flowers and helped to cure gum inflammation and toothache (Hebbar, 2016).

Based on the research done, the leaf extract was evaluated to have in vitro antibacterial activity especially on *Xanthomonas campestris* and *Bacillus anthracis*. Extraction process of volatile oil from the leaf was used to investigate the effect on fungal. Positive result get where the oil showed the anti-fungal activity on *Keratinomyces ajelloi*, *Microsporum gyseum* and *Trichophyton equinum* on the agar plates. The alcoholic extracts like ethyl acetate, ethanol and water extract of *Mimusops elengi* were evaluated in diuretic activity. Hence, the investigation and researches had been carried out are the supporting evidence to prove that *Mimusops elengi* plant is a potential medicinal plant for now and future (Roqaiya el al., 2015).

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Overview of the Work

This chapter discusses the details of the source of raw materials used, experimental steps of *Mimusops Elengi* Seed Shell Powder (MESSP) and polyvinyl alcohol blended with MESSP (MESSP/PVOH) film with the specified parameters. Besides, this chapter also discusses on the procedure for characterization of MESSP and unfilled PVOH film as well as the testing of PVOH/MESSP films.

3.2 Raw Materials

3.2.1 Polyvinyl Alcohol (PVOH)

PVOH was the polymer matrix used in this research study which was supplied by Alfa Aesar Chemical manufacturing company. The chemical abstract service (CAS) registry number is 9002-89-5. The PVOH resin in powder form used is 98-99 % hydrolysed. It has the average molecular weight in the range from 89,000 to 98,000 g mol⁻¹ and a density of 1.269 g/cm. PVOH is soluble in water.

3.2.2 *Mimusops Elengi* Seed Shell Powder (MESSP)

Mimusops elengi seed shell powder (MESSP) was the filler added to the matrix. It was produced from the seeds of ripe fruits of *Mimusops elengi* plants which can be found at Taman Kampar Perdana, Kampar, Perak (Google map coordinate: 4°20'20"N, 101°9'9"E). The fruits were collected and the seeds were gently squeezed out from the ripe *Mimusops elengi* fruits. The seeds were exposed to sunlight for over 4 – 5 hours daily for one week until it changes into brownish color indicating dried seed. Dried seed shells were obtained by breaking the seed and removing the kernel. The dried seed shells were then cleaned by immersing in distilled water with a stirring speed of 300 rpm using a magnetic stirrer at 80 °C for about 2 hours. The ratio of distilled water to seed shell was at least 1:3 by volume. Next, the cleaned seed shells were tossed using a sieve and dried in oven (Memmert, Schwabach, Germany) at 80 °C for 24 hours. The seed shell was grinded and sieved to < 45 µm particle size using a sieve shaker (RX-29-10) to obtain MESSP. Preparation steps of MESSP from *Mimusops elengi* fruit are illustrated in Figure 3.1 (Muniyadi et al., 2018).

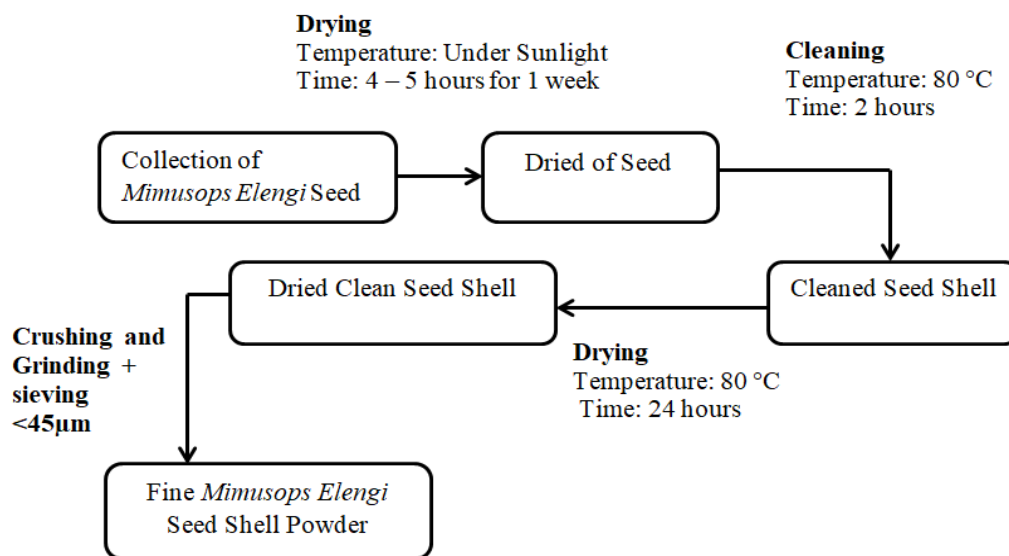


Figure 3.1: Overall Flow of MESSP Preparation

In the past, the characterization on MESSP was reported by Muniyadi et al. (2018), where the result for particle size analysis (PSA) is tabulated in Table 3.1. In the study, MESSP was found to have the particle size range from 0.0375-37.2425 μm . Also, as mentioned in the study conducted by Muniyadi et al. (2018), MESSP particles were small in size with 0.583 μm which has a high specific surface area of 21.9 m^2/g .

Table 3.1: Physical Properties of MESSP (Muniyadi et al., 2018)

Physical properties	Values
Particle Size Distribution (μm)	0.0375 – 37.2425
Mean Diameter (μm)	0.583
Specific Surface Area (m^2/g)	21.9

3.3 Preparation of PVOH/MESSP Films

PVOH/MESSP films were prepared through solution mixing of MESSP in PVOH. 18 g of PVOH was weighed and dissolved in 180 mL deionised water in a 250 mL conical flask. The solution was then heated on a hot plate with magnetic bar at constant stirring speed at 110 $^{\circ}\text{C}$ until PVOH was fully dissolved. Time taken for PVOH to dissolve was around 2 hour and 30 minute. For MESSP filled PVOH solution, the MESSP was added slowly into the conical flask after 30 minute of dissolving the PVOH in deionised water. The solutions was continuously heated and stirred for 2 hours (Ooi et al., 2017). The compounding formulation of PVOH/MESSP films is shown in Table 3.2. The solutions prepared were then casted into thin films using the membrane casting machine and let to dry overnight.

Table 3.2: Compounding Formulation of PVOH/MESSP Films

Film Codes	Composition		MESSP loading (wt %)
	PVOH (g)	MESSP (g)	
PVOH/MESSP 100/0	18	0	0
PVOH/MESSP 95/5	17.1	0.9	5
PVOH/MESSP 90/10	16.2	1.8	10
PVOH/MESSP 85/15	15.3	2.7	15
PVOH/MESSP 80/20	14.4	3.6	20

3.4 Membrane Casting of PVOH/MESSP Films

Approximately about 60 mL of the prepared PVOH/MESSP solution were casted on a glass plate using the membrane film casting method (Autonics corporation LOT NO IJ29) and dried overnight until a constant weight was produced. The casted films were kept in a desiccator prior to any characterization and testing. The flowchart for PVOH/MESSP film casting and testing is shown in Figure 3.2 (Ooi et al., 2017).

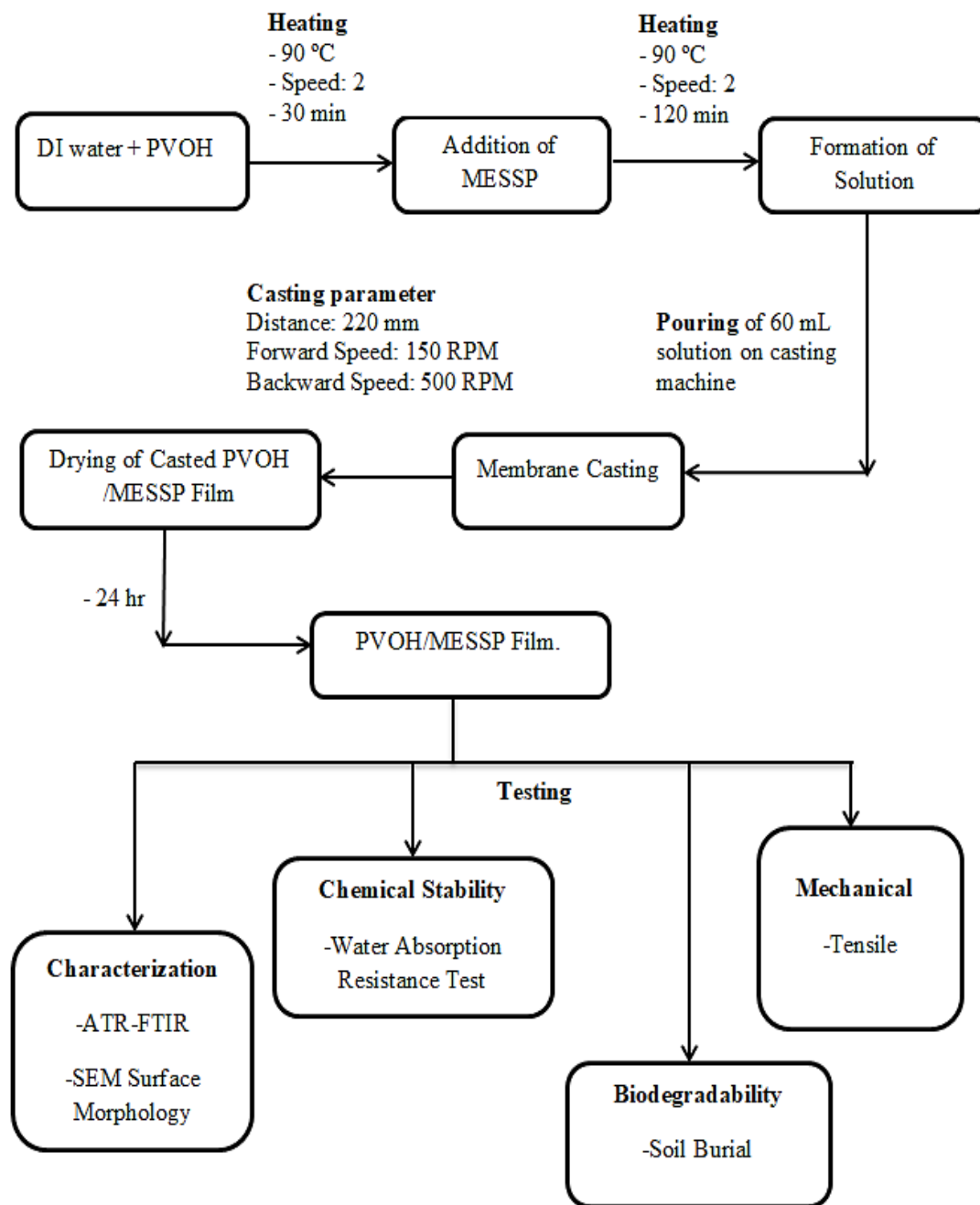


Figure 3.2: Flow Chart of PVOH/MESSP Film Preparation and Testing

3.5 Characterization of PVOH / MESSP Films

Before carried out the characterization and testing of PVOH/MESSP films, consistency in thickness of the films prepared was investigated. This was crucial to achieve uniform properties of the films. For each composition, the thickness of five dumbbell shape specimens that were cut using dumbbell cutter was measured by using the digital thickness gauge (series 542 Flat Anvil type, Mitutoyo America Corporation, Kuala Lumpur, Malaysia). The average values for the thickness of the five repeated specimens were summarised in Table 3.3 for each composition.

Table 3.3: Average Thickness for PVOH/MESSP Films

PVOH/MESSP loading. (wt %)	Average Thickness (mm)	Standard deviation (mm)
100/0	0.04873	0.00245
95/5	0.05340	0.00329
90/10	0.06140	0.00271
85/15	0.06360	0.00111
80/20	0.06653	0.00259

The consistency in thickness of the films was achieved with the overall average thickness of the films is 58.7 μm . The average thickness of the films experienced an increasing trend due to the increasing of the MESSP loading added in the films.

3.5.1 Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR- FTIR)

ATR-FTIR (Perkin Elmer RXI IR spectrophotometer) was used to identify the types of chemical bonds and functional groups in MESSP, PVOH and PVOH/MESSP films. The

analysis was carried out to determine the absorption band with a wavelength from 4000 cm^{-1} to 400 cm^{-1} with three scans at a resolution of 4 cm^{-1} .

3.5.2 Scanning Electron Microscopy (SEM) Analysis

The morphology of MESSP and casted PVOH/MESSP films were studied using SEM (JOEL JSM 6701-F, Jeol, Akishima, Japan). Prior to scanning, the samples were placed on a disc and held in place using a double – sided carbon tape then sputter coated with a thin layer of platinum. The approximate thickness of the layer of the coating was 15 nm with the density of 21.45 g/cm^3 using a sputtering machine (JFC-1600, Jeol, Akishima, Japan) to avoid electrostatic which may cause to the poor resolution of the scanning process. SEM analysis was carried out at an accelerating voltage of 4 kV with a working distance of 10 mm depending on the focus point. The analysis were studied to observe and analyze the shape and surface morphology of MESSP, PVOH as well as the quality of the MESSP coated on the PVOH film. After tensile test, the fracture surfaces of the film was also analysed to study the MESSP dispersion on PVOH, interfacial adhesion between MESSP and PVOH as well as the fracture mode. The surface morphology of PVOH, and MESSP/PVOH films were also investigated after the soil burial test to analyze on the biodegradability properties. The analysis on different stages of films requires different magnification power to achieve a better resolution of the result where the specifications are summarised as Table 3.4.

Table 3.4: Magnification Power Used on Different Stages of Films

Stages of films	Magnification	
	Low	High
MESSP	1000×	-
Film before testing	500×	5000×
After Tensile Test	1500×	5000×
After Biodegradable Test	500×	5000×

3.6 Testing of PVOH/MESSP Films

3.6.1 Tensile Properties

Measurement on the tensile properties of PVOH / MESSP films such as elastic modulus, ultimate tensile strength and elongation at break were carried out according to American Society for Testing and Materials (ASTM D638) under ambient condition. The tensile test was conducted by using a light-weight tensile tester (Tinius Olsen H10KS-0748, Salfords, UK) with a load cell of 450 N at a crosshead speed of 20 mm/min until the specimen fractured. The specimen was subjected to 1200 mm of extension range with a 26 mm of gauge length. Prior to the tensile test, the films were cut into dumbbell shape specimens by using a dumbbell cutter (Leader Technology Scientific (M) Sdn.Bhd., Balakong, Malaysia). Five dumbbell shaped specimens were cut and labeled for each of different MESSP loading films. The average values of the results for the five repeated specimens were determined for each composition (Ooi et al., 2011).

3.6.2 Water Absorption Test

PVOH / MESSP films were cut into dumbbell shaped specimens using a dumbbell cutter (Leader Technology Scientific (M) Sdn.Bhd., Balakong, Malaysia). Water absorption test was carried out according to ASTM D 570-98. The samples were oven-dried for 24 hours at 80 °C. Next, the weights of the samples (W_i) were weighed using an electronic analytical and precision balance (Sartorius M-pact AX224, Sartorius AG, Germany) and recorded. The films were then immersed in the distilled water at room temperature, 25 °C. The samples were then kept in dark place for 72 hours. After 72 hours, the surface of the samples were wiped off using the tissue and weighed again. The weight of the samples after the swelling test (W_f) was recorded. Water absorption resistance of PVOH/MESSP film was analysed from the water absorption percentage of film in distilled water. The lower the water absorption percentage, the lower the swelling percentage and this indicates that the PVOH/MESSP film has higher water resistance. Water absorption percentage was calculated based on equation 3.1 (Ab-Ghani and Ahmad, 2011).

$$\text{Water Absorption Percentage (\%)} = \frac{w_i - w_f}{w_i} \times 100\% \quad (3.1)$$

where

W_i = initial weight of the samples, g

W_f = weight of the sample after swelling test, g

3.6.3 Soil Burial

The soil burial test was conducted to examine the biodegradability of the PVOH/MESSP films. The test was carried out by referring to the steps published by Obasi et al. (2013), with a slight modification. The bottom part of the plastic container was perforated with small hole to avoid water accumulation. The film specimen for each

composition were cut into a dumbbell shape and buried in soil at a depth of 9 cm in the containers. All the samples were placed in an exposed area at the Faculty of Engineering and Green Technology (FEGT), Universiti Tunku Abdul Rahman, Kampar, Perak. To measure the biodegradation of the samples, the initial appearance and weight (B_i) of the samples were recorded before placing into the soil. The samples were taken out from the soil after 3, 6 and 9 weeks and washed with distilled water then were oven-dried at 70 °C for 24 hours to remove the moisture. Next, the final appearance and weights (B_f) of the samples were recorded. The weight loss of the samples was calculated using equation 3.2 (Obasi, et al., 2013).

$$\text{Weight Loss (\%)} = \frac{w_i - w_f}{w_i} \times 100\% \quad (3.2)$$

where

B_i = initial weight of the samples before soil burial test, g

B_f = weight of the sample after soil burial test, g

The weight loss of the samples was used to determine the percentage of degradation of the samples. Furthermore, the morphology of the sample films before and after the soil burial test was examined using SEM.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Overview

This chapter includes the results and analysis on characterization of *Mimusops elengi* seed shell powder (MESSP) and unfilled polyvinyl alcohol (PVOH) as well as the testing on the PVOH/MESSP films. Moreover, all the results such as Attenuated total reflectance—Fourier transform infrared spectroscopy (ATR-FTIR), Scanning electron microscope (SEM), water absorption test, tensile test and biodegradability test of MESSP and PVOH / MESSP films were investigated and discussed.

4.2 Characterization of PVOH/MESSP Films

4.2.1 ATR-FTIR

Figure 4.1 shows the spectra of unfilled PVOH and MESSP where PVOH has the strong and wide absorption band at 3271.71 cm^{-1} which confirm there were plenty of water hydroxyl groups (Ooi et al,2011). Spectrum (a) in Figure 4.1 shows the asymmetric methyl group; C-H stretching bands appeared at the peaks 2940.75 cm^{-1} . Stretching peak appeared at 1415.15 cm^{-1} and 1324 cm^{-1} were corresponds to C-H bending. Besides,

there were asymmetrical flexible vibrations peaks of C-O-C occur at 1142.15 cm^{-1} and 1087.45 cm^{-1} . The main absorption bands that were corresponding to the PVOH component are tabulated in Table 4.1. The incomplete removal of acetate groups during the manufacture of PVOH by the hydrolysis of poly(vinyl acetate) could be the reason for the presence of carbonyl band at 1656.8 cm^{-1} (Ooi et al., 2011). The significant peak value observed was the hydroxyl functional group which confirms the hydrophilic nature of PVOH.

Table 4.1: FTIR Spectroscopy of PVOH (Stuart, 2004)

Spectroscopic Assignments	Wavenumber (cm^{-1})
O-H stretching	3650 – 3200
C-H stretching bands	3000–2800
Asymmetric C-H stretching	2940.85
Methylene scissoring	1415.91
Methylene wagging	1328.44
C-O-C stretching	1142.15 and 1087.45

ATR-FTIR spectrum as illustrated in Figure 4.1 spectrum (b) are similar and consistent with those plant fibers such as kenaf (Bakar et al., 2015), hemp fibers (Troedec et al., 2008), wheat straw, soy hulls (Alemdar and Sain, 2008) and starch (Stuart, 2004). The main absorption bands present in MESSP appeared were 3340.79 cm^{-1} , 1729.51 cm^{-1} , 1632.01 cm^{-1} , 1239.56 cm^{-1} and 1035.76 cm^{-1} . There was a strong and broad stretching band appeared at 3340.79 cm^{-1} which in the range of $3200\text{--}3650\text{ cm}^{-1}$ was correspond to stretching -OH group. This could also confirm the polarity of the MESSP where the assumption of the good compatibility between the MESSP fibers and the PVOH matrix could be made. In addition, there was a peak appeared at 2927.9 cm^{-1} within the range of 3000 cm^{-1} to 2800 cm^{-1} attributed to a weak stretching C-H group. Apart from that, infrared analysis stated that plant comprise up to 80% of their dry weight of carbohydrate which included the main components such as cellulose, pectins

and hemicellulose which also could be found in MESSP (Stuart, 2004). Table 4.2 reports on the major mid-infrared bands of common plant carbohydrates.

Table 4.2: Major Mid-infrared Bands of Common Plant Carbohydrates (Stuart, 2004)

Carbohydrate type	Wavenumber (cm ⁻¹)
Cellulose	1170–1150, 1035
Lignin	1590, 1510
Hemicellulose	1732, 1240
Pectin	1680–1600

The absorption band around 1730 cm⁻¹ to 1740 cm⁻¹ may be attributed to the presence of C=O stretching in the acetyl groups of hemicellulose and the absorption peak was found at 1729.51 cm⁻¹ in MESSP (Alemdar and Sain, 2008). Also, the peak 1632.01 cm⁻¹ appeared was corresponded to the absorbed moisture by the cellulose (Fan et al, 2014). The peak near 1510 cm⁻¹ appeared on MESSP spectrum could be connected with C=C stretching vibration of aromatic skeletal found in lignin (Shi et al., 2012). In addition, the presence of CH₂ symmetric bending of cellulose existed at the peak 1439 cm⁻¹ could be found in the infrared analysis. The peak at 1238.9 cm⁻¹ was attributed to the O-H phenolic in lignin (Muniyadi et al., 2018). The presence of the peak at 1163.6 cm⁻¹ was corresponded to C-O-C asymmetric stretching in cellulose I and cellulose II whereas the peak at 1035.76 cm⁻¹ was attributed to the C-O of alcohol (primary and secondary) stretching vibration of cellulose, lignin and hemicellulose (Shi et al., 2012). On the other hand, in the research of Jeyasundari et al. (2016), the ATR-FTIR spectroscopy of *Mimusops elengi* flower extract has prominent peak at 1050.08 cm⁻¹, 1679.89 cm⁻¹ and 3501.01 cm⁻¹ due to C-N stretching (aliphatic amines), C=O stretching and O-H stretching respectively which were similar to the peaks appeared from the spectrum of MESSP.

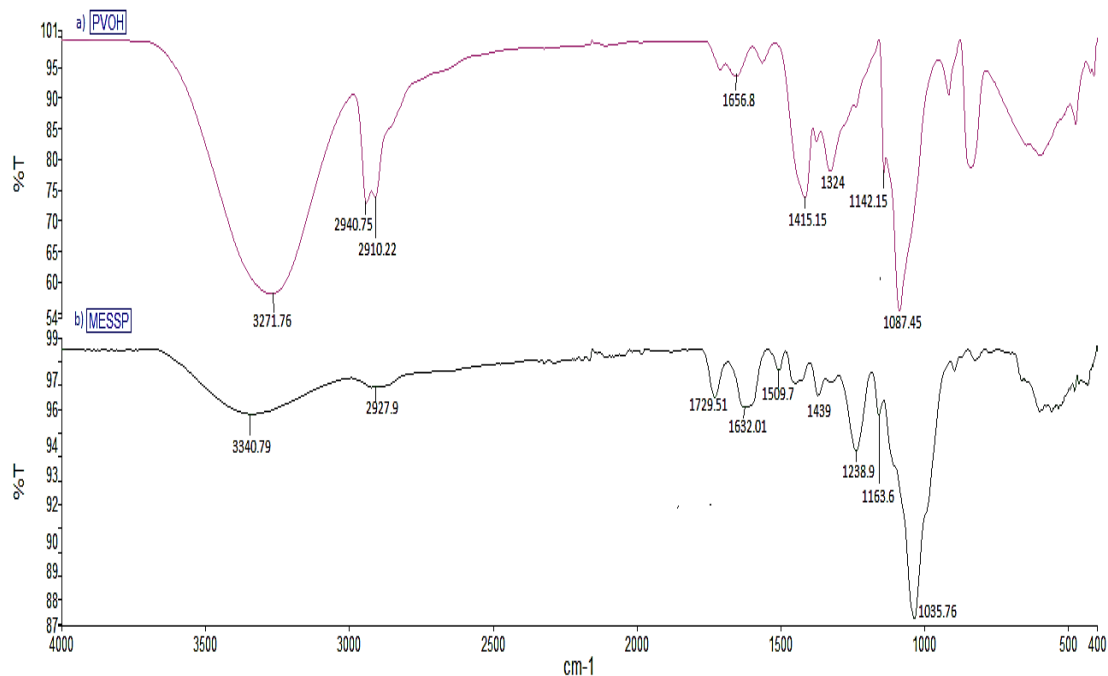


Figure 4.1: ATR- FTIR Spectra of Pure PVOH and MESSP

The spectra blends of PVOH/MESSP were compared with the pure PVOH and the MESSP and showed that the absorption peaks of the PVOH/MESSP films were slightly shifted as shown in Figure 4.2. The vibration peak of the hydroxyl group of pure PVOH and MESSP appeared at 3271.71 cm^{-1} and 3340.79 cm^{-1} , respectively. However, the PVOH/MESSP blend films shows the peak at range from $3271.95\text{-}3272.56 \text{ cm}^{-1}$ which similar to the hydroxyl band of PVOH. This was due to the higher intensity of the O-H group absorption in PVOH as compared to MESSP.

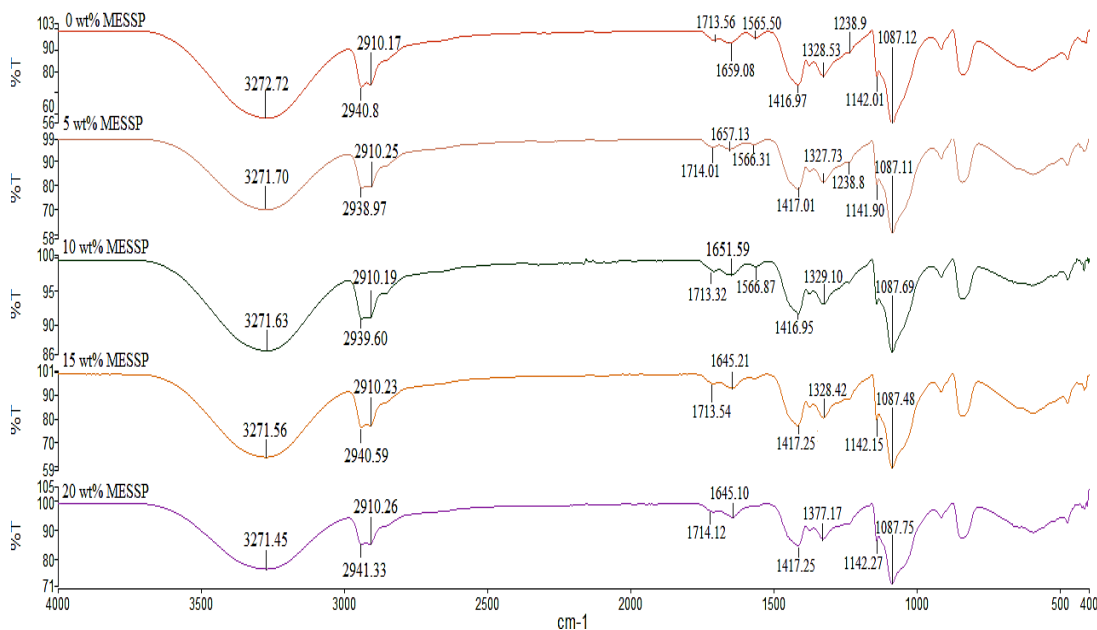


Figure 4.2: ATR-FTIR Spectra of PVOH/MESSP Films at Different wt % MESSP

Figure 4.3 illustrated the spectra of PVOH/MESSP films were overlapping to each other and there was no new peak appeared as compared to the spectra analysed from unfilled PVOH and MESSP. This result showed that there was no new chemical interactions occurring between the functional group of PVOH and MESSP during the solution blending and casting process. The shape and location of the characteristic peaks of the blended film were similar to unfilled PVOH indicated that the interactions among PVOH molecules were dominant as PVOH-PVOH interaction was stronger than those for PVOH-MESSP molecules and MESSP-MESSP molecules (Ooi et al., 2011). For instance, all the peaks found in MESSP spectrum analysis were overlapped in the spectra of PVOH/MESSP blend composites. Thus, this showed that the intermolecular hydrogen bonding between the hydroxyl groups in the PVOH/MESSP was getting weaker as the increasing of the MESSP loading in the films (Ooi et al., 2011).

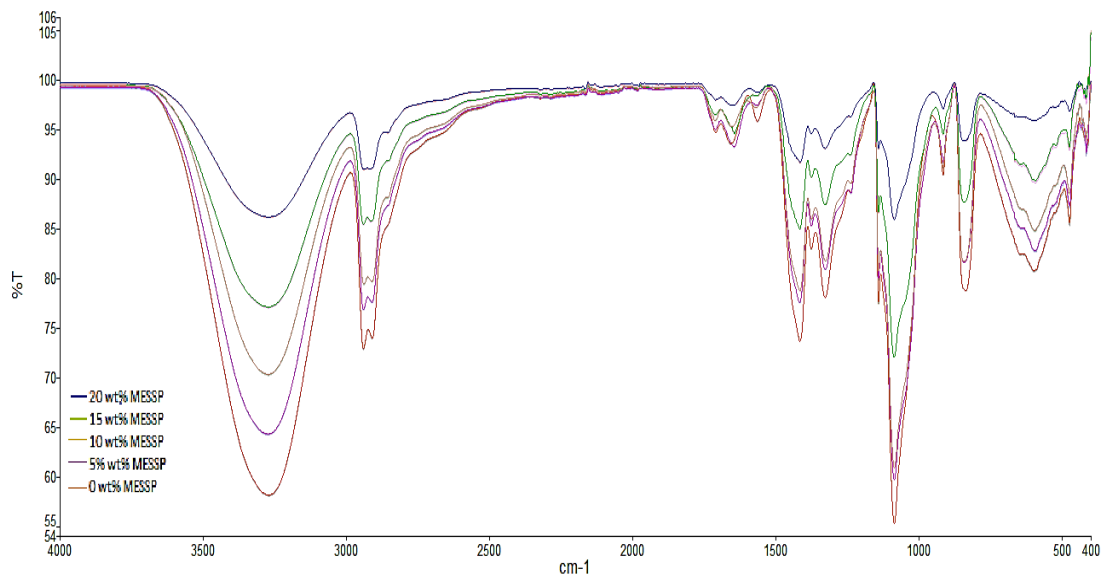


Figure 4.3: Comparison of Overlapping ATR-FTIR Spectra on Different PVOH/MESSP Loading

Figure 4.4 shows the SEM images of the MESSP particles at 1000 \times magnification. Based on Figure 4.4 (a), MESSP particles exhibited in irregular size and shape where they are loosely arranged. The individual particles were flat and smooth as there was no pore or crack appeared on the surface as shown in Figure 4.4 (b). It was expected that there will be good interfacial adhesion between MESSP and PVOH as smooth and flat surface indicating large surface area for any possible physical interaction by interlocking of PVOH chains on the MESSP surface.

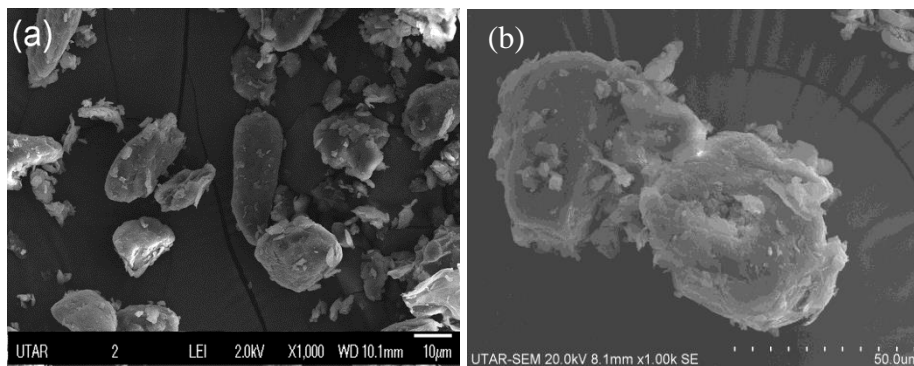


Figure 4.4: SEM Images for MESSP at 1000 \times magnification (Muniyadi et al., 2018)

4.3 Testing of PVOH / MESSP Films

4.3.1 Tensile Test

Mechanical test on the tensile strength, elastic modulus and break elongation of PVOH/MESSP blended films were conducted with different MESSP loading. Determination on stretching of films is important for film's packaging application (Raj, K. and Siddaramaiah, 2004). Particle size, shape and particle distribution are the factors that will affect the mechanical properties of the composite. Other than that, filler loading, filler dispersion and the interfacial adhesion between the matrix and the filler are also the factors that could affect the performance of the blended films (Tan et al., 2015; Thomas et al., 2012).

Figure 4.5 illustrates the tensile strength and the elongation at break for different loading of MESSP incorporated in PVOH where both parameters having the same trends. Obviously, the tensile strength and the elongation at break were decreasing as the MESSP loading increased. The tensile strength was the highest for unfilled PVOH followed by the increasing of the MESSP loadings from 5 to 20 wt %. This was due to the decreasing of the PVOH matrix content as the PVOH exhibited the ductility properties (Ramaraj, 2006). In addition, weak tensile strength and the elongation at break might be due to the weak intermolecular hydrogen bonding between the MESSP filler and PVOH matrix. The supportive evidence was discussed in ATR-FTIR analysis earlier showed that the intensity of the -OH groups in the films was decreasing where this proved that bonding between the PVOH and MESSP was weaker for higher loading of MESSP. Similar result was obtained by Suki et al. (2013) where PVOH/banana front flour blended films have lower tensile strength with higher banana front flour loading.

Despite of the lower tensile strength and elongation at failure of the PVOH/MESSP films as compared to unfilled PVOH, the tensile properties of this type of film was within the range for packaging application. As evidence, the established brand of PLA plastic film such as Biobag L, EcoFilm, EcoWorks 45, Indaco and

Heritage have the tensile strength and elongation at failure at the range from 12.21 MPa to 37.29 MPa and 17.70 % to 1594.5 % respectively. Thus, the performance of PVOH/MESSP on tensile strength and break elongation at the range 26.8 MPa to 46.20 MPa and 41.92 % to 91.07 % were still applicable for the film packaging application (Vanstrom, 2012).

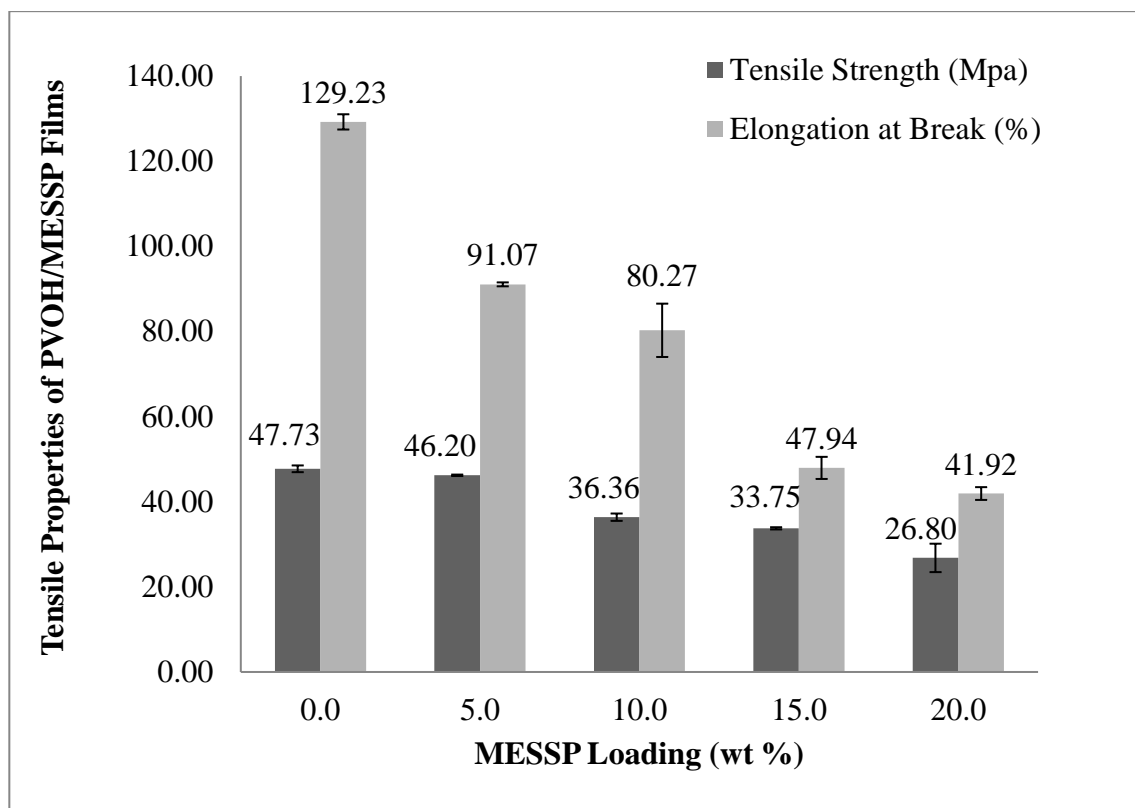


Figure 4.5: Tensile Strength and Elongation at Break of PVOH/MESSP Films

Tensile modulus is the measure of stiffness, in other word, the degree of ductility of the filler reinforced polymer (Siracusa, et al., 2017). Figure 4.6 shows the PVOH/MESSP blended films exhibited higher tensile modulus with increase MESSP loading. Incorporation of fillers in the films will hinder the mobility of the chains when subjected to force which in turn increased the brittleness of the blended films. The films with the higher filler content will become stiffer as a result of higher elastic modulus

(Gao et al., 2014). Table 4.3 summarizes the tensile properties of PVOH / MESSP blended films at different MESSP loading.

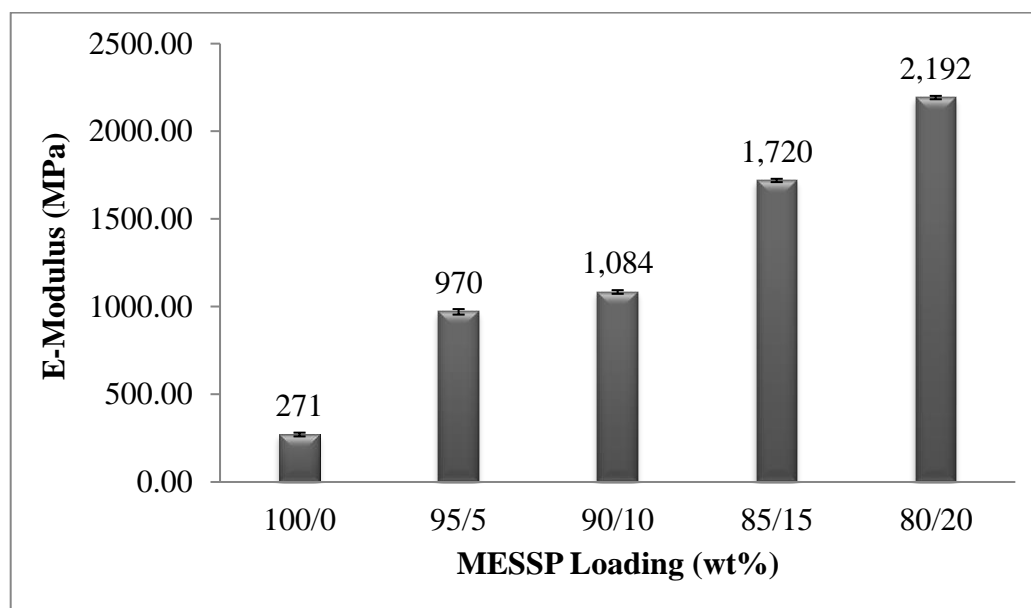


Figure 4.6: Elastic Modulus of PVOH/MESSP Blended Films

Table 4.3: Tensile Properties of PVOH / MESSP Blended Films at Different MESSP Loading

Parameter	Ultimate Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation at Break (%)
0%	47.73	270.63	129.23
MESSP Loading (wt %)			
5%	46.20	970.33	91.07
10%	36.36	1083.67	80.27
15%	33.75	1719.67	47.94
20%	26.80	2192.43	41.92

Surface morphology on tensile fracture shows the dispersion and the filler-matrix interfacial interaction of the blended films which can be used as the evidence to explain on the tensile properties of the composite films. Figure 4.7 shows the SEM images with low magnification power of 1500× of unfilled PVOH, 10 and 20 wt % of MESSP loading in PVOH matrix. Figure 4.7 (a) illustrates that the unfilled PVOH have the roughest surface as compared to others blended films. Rough surface was more ductile contributed to the good matrix tearing as the mobility of the chains was the highest. Thus, the high deformability allowed more elongation as the elongation at break observed for the unfilled PVOH could up to 129 % before breakage. Moreover, adhesion of large particles size of filler to the PVOH was observed in Figure 4.7 (b). This shows there was lower surface area available for adhesion lead to the poor adhesion of MESSP to the PVOH. Hence, to have better filler –matrix interaction, smaller particles size of the fillers was preferred (Thomas et al., 2012). Filler aggregation was shown in Figure 4.7 (c) with 20 wt % MESSP loading films. Aggregation of filler will cause the poor dispersion and non-uniform distribution of MESSP in the PVOH matrix (Kalambettu et al., 2014). MESSP fillers that were coarsely dispersed a consequence of the poor filler-matrix interaction. This will reduce the performance of the blended film on the tensile strength and break elongation parameters (Muniyadi et al., 2018). In addition, the aggregation of the MESSP caused the blended films to become more brittle as the tensile modulus was higher for the higher loading of MESSP blended films. The crazing effect would be incurred by the aggregation phenomena where the adhesion of the MESSP with the PVOH matrix phase was destroyed (Ramaraj, 2006).

The clearer SEM images were analysed by using the higher magnification of 5000× as shown in Figure 4.8. The formation of aggregations will form the flaws in the film (Espert et al., 2004). When the flaws become bigger in size, the flaws propagate into voids and lead to the poor interfacial interaction as shown in Figure 4.8 (b) (Abdul Khalil et al., 2009). In addition, SEM micrograph also shows the filler leached out or pull-out predicted that the low adhesion between the MESSP and PVOH upon force was applied as can be seen from Figure 4.8 (c) (Asim et al., 2015).

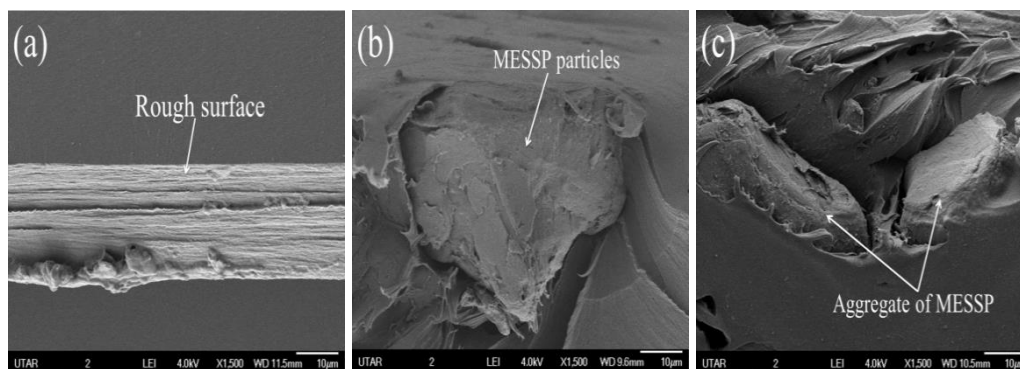


Figure 4.7: Comparison of Surface Fracture of PVOH/MESSP at Low Magnification Power (1500 \times); (a) Unfilled PVOH (b) PVOH/MESSP 90/10 wt % (c) PVOH/MESSP 80/20 wt %

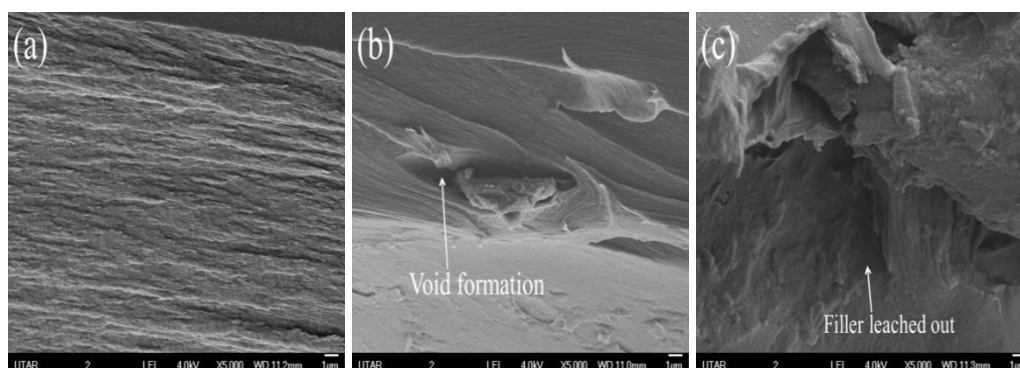


Figure 4.8: Comparison of Surface Fracture of PVOH/MESSP at High Magnification Power (5000 \times); (a) Unfilled PVOH (b) PVOH/MESSP 90/10 wt % (c) PVOH/MESSP 80/20 wt %

4.3.2 Water Absorption

Water absorption test was conducted on different compositions of PVOH/MESSP films to investigate on the water affinity of each blended films. PVOH is water soluble and hydrophilic in nature (Kadajji and Betageri, 2011). Moreover, MESSP also showed hydrophilic properties as they poses the $-OH$ hydroxyl group in the structure as

discussed on the result analysed from ATR-FTIR. Thus, the presence of the hydroxyl group in both PVOH and MESSP will contribute to the moisture absorption on the blended PVOH/MESSP films.

Based on Figure 4.9, the water absorption percentage decreased gradually with the addition of loading of MESSP from 0 % to 20 wt %. By comparison, pure PVOH films experienced the highest water absorption as compared to the others PVOH/MESSP blends films. For instance, the reduction of water absorption percentage of 80/20, PVOH/MESSP blended films was 42 % as compared to pure PVOH films. As a comparison to the unfilled PVOH, all the other blended films showed the decrease in water absorption level. The unfilled PVOH swelled more in the water and has the highest water absorption rate may be due to the highest in intensity of hydroxyl group analysed from the comparison of overlapping ATR-FTIR spectra on different PVOH/MESSP loading. The higher intensity suggested that the unfilled PVOH was more polar and has higher water affinity as the water molecules were attached to –OH groups in PVOH polymer chains by hydrogen bonds lead to the swelling process (Baschek et al., 1999; Thakur and Singha, 2010; Das and Biswas, 2016).

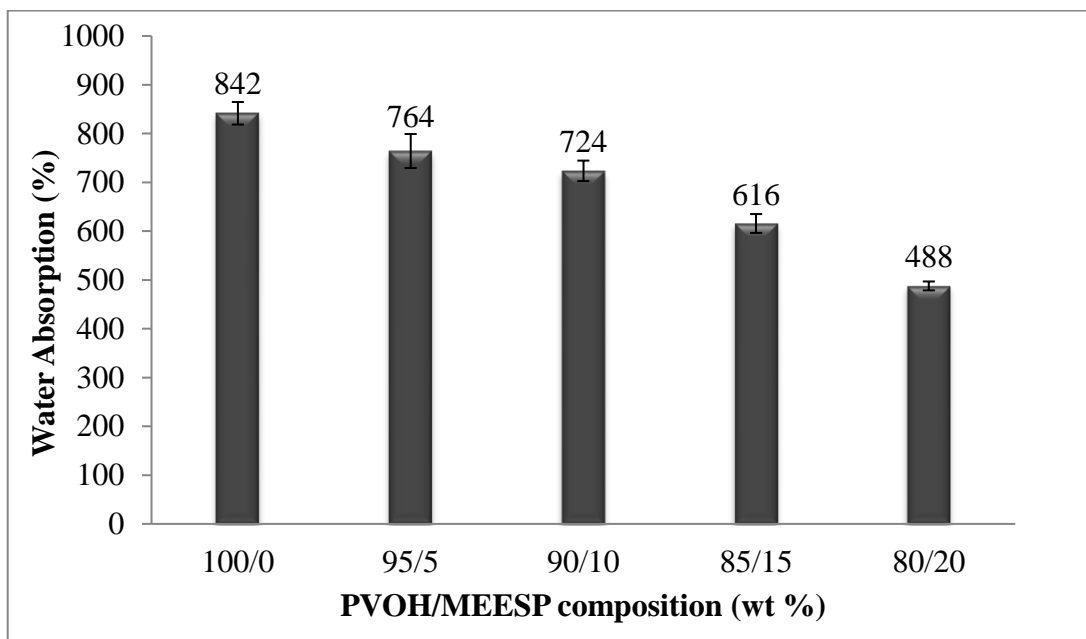


Figure 4.9: Water Absorption Percentage of PVOH/MESSP Films

The reduction of water uptake by the PVOH/MESSP blended films associated with the increasing of MESSP loading from 5 % to 20 wt %. As reported by Yee et al. (2011), natural fibers have less capability to absorb water as compared to PVOH. As the MESSP content was increased in the PVOH/MESSP composite, it corresponds to the decrease of the PVOH content. The MESSP shows lower intensity of hydroxyl group as compared to pure PVOH which would cause the reduction of the hydrophilic nature to PVOH/MESSP composites.

An alternative inference could be that there was a good fibre/matrix interaction interfacial adhesion between the MESSP and PVOH. The MESSP fibers dispersed and adhered well with the PVOH where MESSP act as a binder to hold the PVOH matrix together reduce the water uptake. Also, the fibers get well covered by the PVOH matrix with strong adhesion reduce the polar bonding of the water molecules lead to the lower moisture uptake (Sharma, N., 2104). In the related water absorption behavior study as reported by the presence of pineapple leaf fibers in the composite could reduce the PVOH's dissolution in water. In addition, PVOH/MESSP composites have the similar water absorption behavior to that PVOH/OPA showed the consistency of the result (Muniyadi et al, 2018).

In contrast, the water absorption behavior studied by Tiffany (2016) showed the water uptake was increased with the increasing of the loading of the MESSP fiber in polypropylene matrix. This was because the fiber did not adhere well to the hydrophobic polypropylene matrix lead to the formation of voids, increased the water uptake. Also, jute fibre which was hydrophilic in nature was less compatible with hydrophobic matrix polymers such as polyethylene and polypropylene will have more water absorption at higher filler loading blended films (Karmaker and Shneider, 1996).

4.3.3 Soil Burial Degradation

In this research study, the compost soil provided the realistic environment where biodegradation could be occurred with the present of microorganism, outdoors's humidity, pH and temperature were less controlled. The results for the evaluation of the biodegradation of the samples were collected consecutive for every three weeks. Percentage of the weight loss and the physical appearance were used to evaluate the extent of biodegradability of the unfilled PVOH and PVOH/MESSP films.

From the study, unfilled PVOH showed the highest resistance toward the degradation. However, there were 15.02 %, 14.84 % and 13.71 % weight losses from week 3 to week 9 due to its susceptibility for degradation in water where the films degrade caused by water or moisture content in the soil (Kalambettu et al., 2014). However, the weight loss's trend of PVOH declined could be explained by the hydrophilic nature of its features that causes the swelling of PVOH (Krzeminski and Molisak-tolwinska, 1991). Figure 4.10 shows that there was a slightly rise in the weight loss from 13.84% to 16.14% in Week 3 as the MESSP's loading was increased from 5 to 20 wt %. The observed pattern showed in week 6 and week 9 may also demonstrate the PVOH/MESSP blends with higher MESSP loading were associated with the higher degradation rate as the percentage of the weight loss was higher.

Among all the blended films, PVOH/MESSP 80/20 films showed the highest degradation rate. This can be explained from the presence of highest amount of MESSP as the natural fiber in the PVOH matrix contain the nutrient for the growth of the microorganism such as potassium, sodium, magnesium, calcium and iron (Mendez-Sanchez et.al., 2004). An alternative inference could be that the fibres served as capillaries that enable the migration of moisture and microorganism as degradation by microbial attack is the main mode of degradation of the natural composites in soil (Kalambettu et al., 2014). Incorporation of MESSP in the composites supplied the nutrient where it facilitated the microorganism growth by breaking down the fibers.

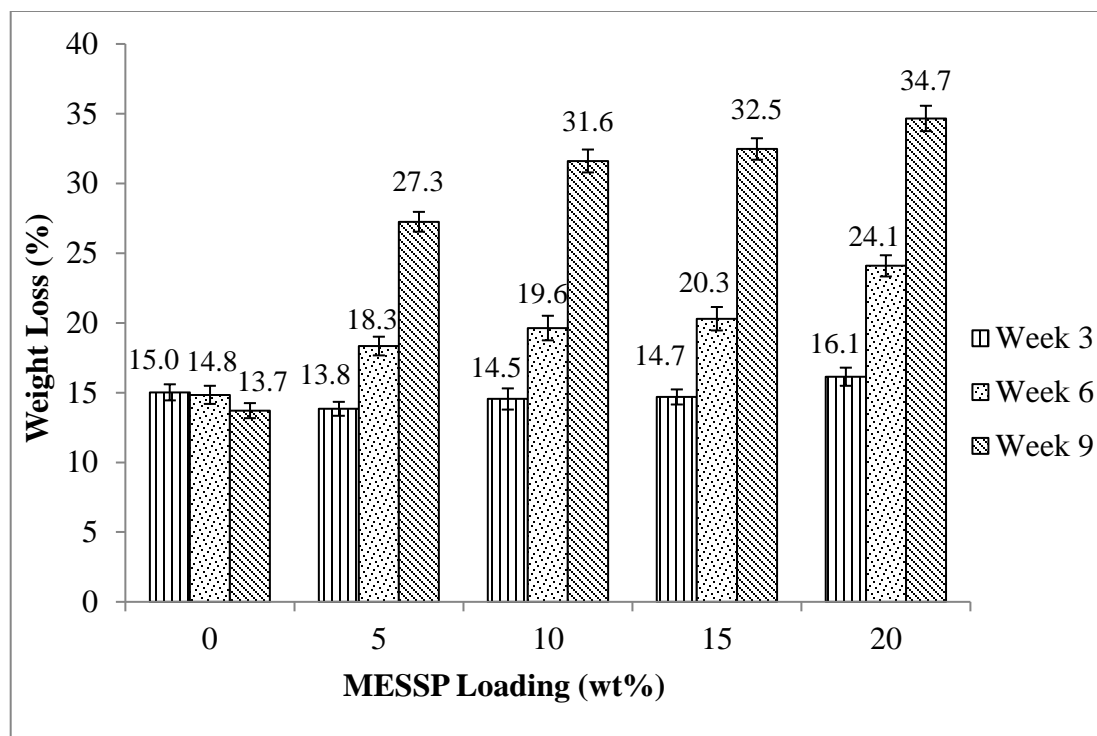


Figure 4.10: Percentage Weight Loss of PVOH/MESSP Film with Respect to Increasing of MESSP Loading

Result illustrated in Figure 4.11 shows the higher weight loss of the PVOH/MESSP films was experienced with prolonged exposure of the films in the soil. For instance, the degradation rate was the highest in Week 9 for different loading of the MESSP as compared to Week 3 and Week 6. This was due to the higher microbial development and the microbial degradation over cellulose and hemicellulose which increased the damages to the films. In short, the longer the prolonged time and the higher loading of MESSP films exhibited higher degradation rate as evident by the associated increase in the molecular weights loss.

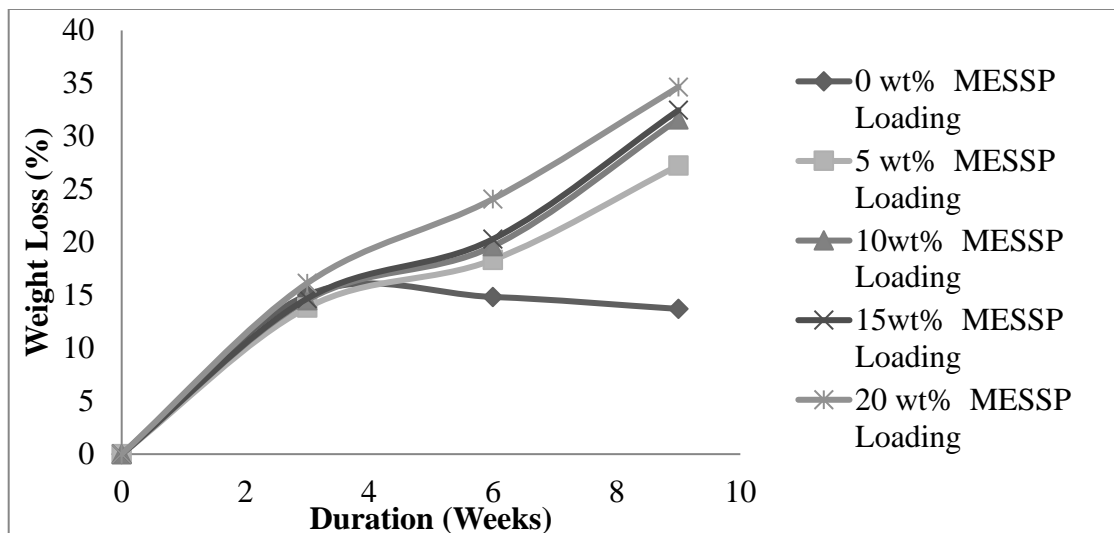


Figure 4.11: Weight Loss Percentage versus Duration from Week 3 to Week 9

Investigation on the surface morphologies of pure PVOH were illustrated in Figure 4.12. Figure 4.12 (a) and 4.12 (b) shows the PVOH thin film at the magnification power of 500 \times and 5000 \times respectively. There were large smooth and fine surface areas that contribute to the transparency of PVOH film (Chan et al., 2009). Meanwhile, Figure 4.13 displayed the SEM micrograph scanned on the PVOH films after the soil burial test. The films started to wrinkle due to the swelling process. Generation of fold and wrinkles were increased on the PVOH films as the period of the PVOH films exposed to the moisture and water in the soil increased lead to the higher degree of swelling and the water absorption (Kadajji and Betageri, 2011). In addition, there was no growth of microorganism or crack formation could be found on the surface of the unfilled PVOH. Thus, Figure 4.13 (a-c) confirming that there were no biodegradation activities takes place on unfilled PVOH film.

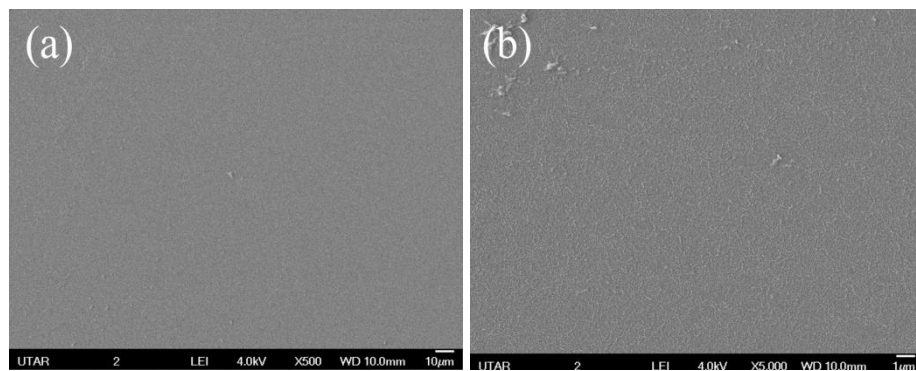


Figure 4.12: SEM Images of Unfilled PVOH Film before Soil Burial Test at Different Magnification; (a) 500× and (b) 5000×

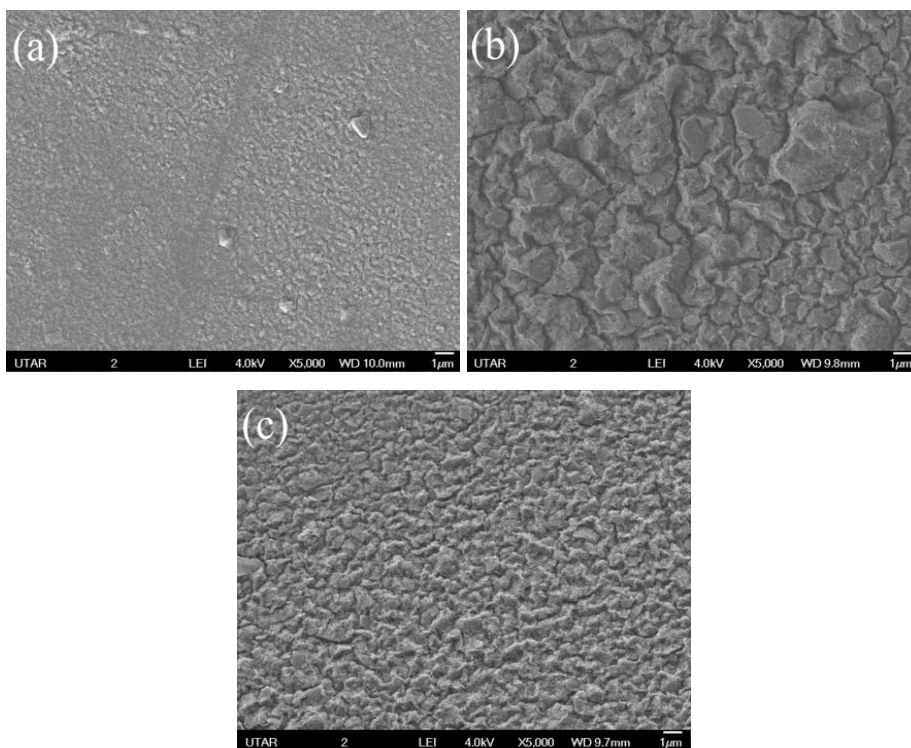


Figure 4.13: Comparison of Surface Morphology of Unfilled PVOH after Soil Burial Test at 5000× Magnification; (a) Week 3, (b) Week 6 (c) Week 9

Figure 4.14 represent the SEM images of PVOH containing 10 wt % MESSP loading. Figure 4.14 (a) shows the MESSP were fully covered by the matrix PVOH. The

assumption of the good interaction and good adhesion between MESSP and PVOH matrix can be confirmed through this observation. Based on Figure 4.14 (b), it can be seen that the MESSP particles were partially appeared on the surface of the matrix which was damaged through the microbial activity. In week 9, the MESSP started to leach out from the matrix as shown in Figure 4.14 (c), suggesting that fibers were consumed by microorganisms as a source of carbon and energy (Gu et al., 1996). The surface morphology of the composites was rougher at the end of week 9. The studies above stated that the rate of degradation was the highest for the 20 wt % loading of MESSP as this could be further proven in the SEM images. The observed patterns shown in Figure 4.15 may demonstrate that the films containing 20 wt % MESSP started to degrade as there were crack propagation formed on the surface of the composites. In addition, Figure 4.16 also shows the ability of bacteria to attach and grow on the surface of the PVOH/MESSP films. The microorganism will degrade the cellulose or lignocellulose found in the MESSP particles and eventually decomposes the film. Thus, MESSP incorporated PVOH film were etched by the microorganisms where damages and the degradation happen (Ali et al., 2016).

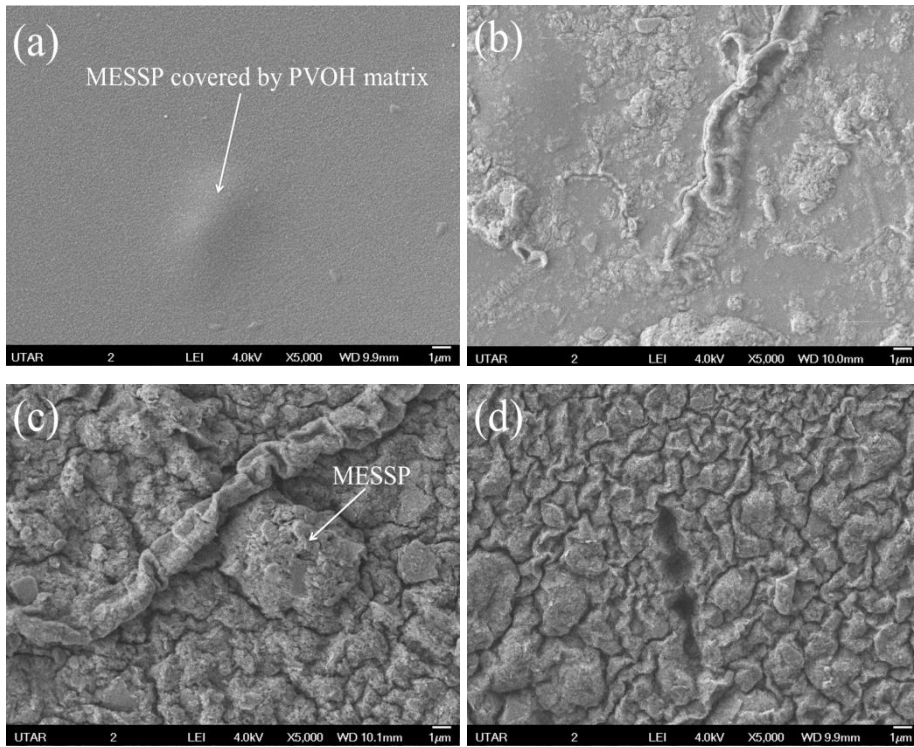


Figure 4.14: Comparison of Surface Morphology of PVOH/MESSP 90/10 wt % at 5000 \times Magnification; (a) Before Soil Burial Test and after Soil Burial Test; (b) Week 3, (c) Week 6 (d) Week 9

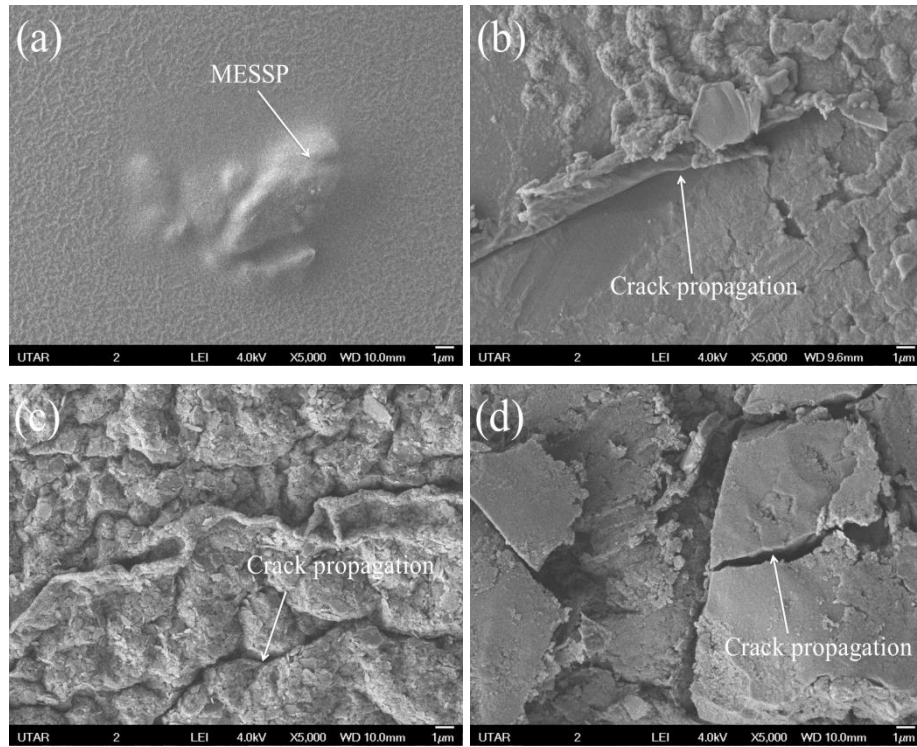


Figure 4.15: Comparison of Surface Morphology of PVOH/MESSP 80/20 wt % at 5000× Magnification; (a) Before Soil Burial Test and After Soil Burial Test; (b) Week 3, (c) Week 6 (d) Week 9

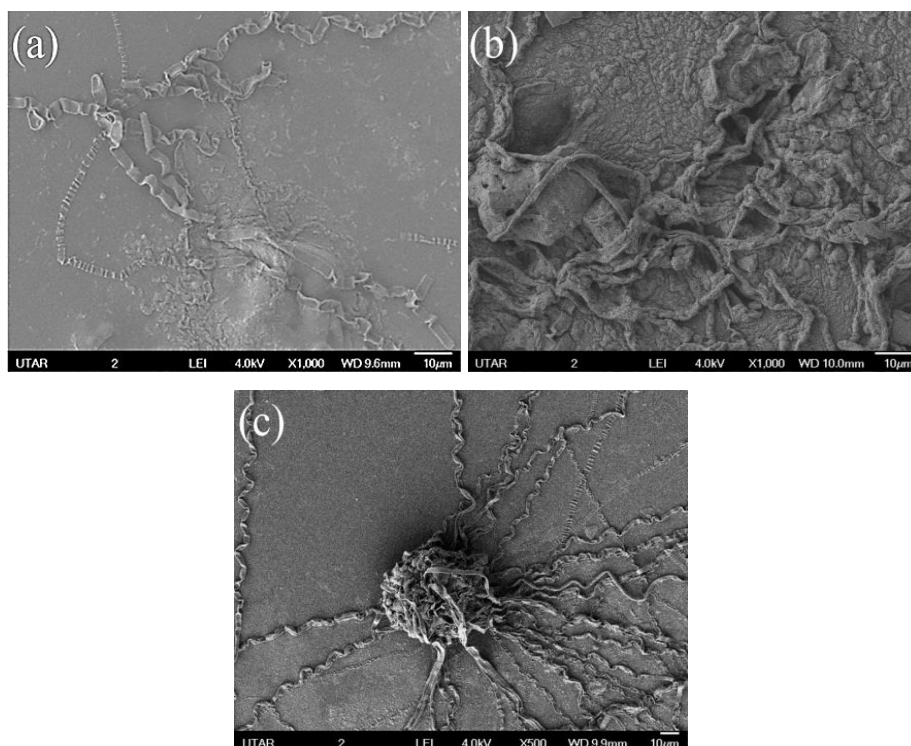


Figure 4.16: Attachment of Bacteria on the Surface of the PVOH/MESSP Film; (a) Week 3, (b) Week 6, (c) Week 9

Other than that, the physical appearances of the films after 9 weeks of soil burial were examined to investigate the extent of biodegradation on the films. In Figure 4.17, the degree of shrinkage was higher for the higher loading of the MESSP. Moreover, the degradation of the composite was more prominent in Figure 4.17 (d) as the crack propagation illustrated in the SEM image caused the film started to break into smaller pieces indicating biodegraded films.

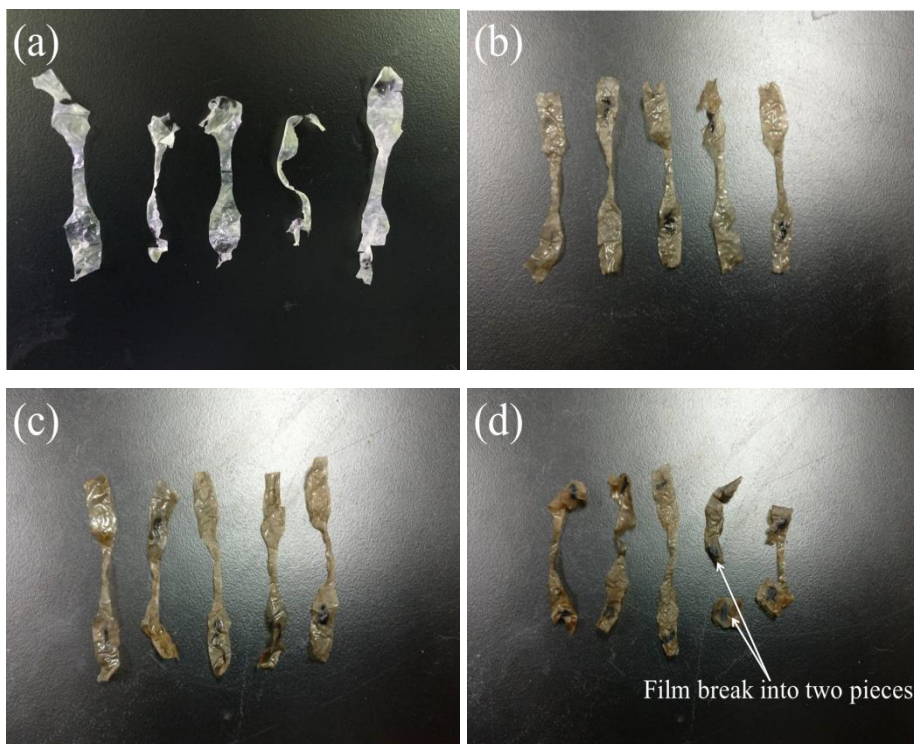


Figure 4.17: Physical Appearance of the Composite Films on Week 9; (a) Pure PVOH, (b) PVOH/MESSP 95/5 wt % (c) PVOH/MESSP 90/10 wt % (d) PVOH/MESSP 80/20 wt %

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

MESSP filled PVOH films with an average thickness of 58.13 μm were successfully produced through membrane casting at 0, 5, 10, 15 and 20 wt % of MESSP loading. MESSP and PVOH are compatible with each other as the ATR-FTIR analysis showed both are hydrophilic in nature. The surface morphology of the PVOH was found to be smooth and fine where it gives the transparency properties. Moreover, MESSP particles have irregular shape and they were loosely arranged. The surface of the particles was flat and smooth where there was no pore and crack appeared.

Incorporation of the MESSP in the PVOH gave the negative effect on the tensile strength and elongation at break. The increasing loading of MESSP from 5-20 wt % blended films have lower tensile strength (46.20-26.80 MPa) and elongation at break (91.07-41.92 %) as compared to the unfilled PVOH (47.73 MPa and 129.23 %). Meanwhile the tensile modulus was increased (970.33 MPa-2192.43 MPa) with the increasing of the MESSP content from 5-20 wt % as compared to pure PVOH (270.63 MPa). However it was found the tensile properties of PVOH/MESSP films is comparable to the typical tensile properties of commercially used plastic films. In the surface fracture analysis, aggregation of MESSP was observed at the higher loading of MESSP where voids were formed lead to poor filler/matrix interaction.

Resistance towards water absorption was increased with increasing MESSP loading as the water absorption capacity was reduced from 842 % to 488 %. Soil burial degradation test revealed that the addition of the MESSP in the PVOH matrix increased the degradation rate of the films as proved by the increasing of the weight loss of the films. The blended film deteriorated more at higher loading of MESSP with a longer period of the exposure time. As the evidenced observed from SEM images and physical appearance, cracks were formed on the surface at the same times the films was started to break into pieces.

5.2 Recommendations

Few recommendations are made to improve the properties of the MESSP/PVOH blended film, especially in the tensile properties and adhesion property.

- i. Smaller particles sizes of MESSP are preferred to be incorporated into the PVOH matrix. This could provide more total surface area available for the adhesion interaction between filler-matrix interactions.
- ii. Production of higher thickness films was suggested because the higher thickness films can produce more ductile films. This might give better tensile strength result.
- iii. Surface modification on the MESSP such as alkaline treatment or by using coupling agent such as silane could be done to enhance the mechanical properties. As reported by Threepopnatkul et al. (2009), mechanical properties were enhanced with the reinforcement of the modified pineapple leaf fibers by using alkaline treatment. Moreover, chemical surface modification on the jute fabrics reinforced in the polyester amide composites could further improve the mechanical properties by enhancing the fibre–matrix interaction.

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