INVESTIGATION OF STRUCTURAL, PHYSICAL AND THERMAL PROPERTIES OF BIO-COMPOSITE THIN FILM FROM WASTE BANANA PEEL

by

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DECLARATION

I declare that this thesis entitled "Investigation of Structural, Physical and Thermal Properties of Bio-composite Thin ilm from Waste Banana Peel" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ________________________________

Name : ________________________________

Date : ________________________________

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TABLE OF CONTENTS

TITLE **PAGE**

CHAPTER 1 INTRODUCTION

CHAPTER 2 LITERATURE REVIEW

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CMF	Cellulose Microfibril Fiber
CrI	Crystallinity Index
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermogravimetry
EWE	Epoxy/ Waste banana peel/ Eggshell filler
FTIR	Fourier Transform Infrared
FTIR-ATR	Fourier Transform Infrared- Attenuated Total Reflectance
IR	Infrared
NFPC	Natural fiber polymer composites
PDF	Powder Diffraction File
PLA	Poly (lactic acid)
PP	Polypropylene
SI	Swelling Index
SPS	Sugar Palm Starch
TGA	Thermogravimetric Analysis
XRD	X-ray Diffraction

LIST OF SYMBOLS

θ	Angle (theta)
°C	Temperature (degree Celsius)
%	Percentage
λ	Wavelength
x	Multiply
w/w	Mass per mass

Investigation of Structural, Physical and Thermal Properties of Bio-composite Thin Film from Waste Banana Peel

ABSTRACT

This study summarized the research on the organic filler which eggshell used as reinforcement and banana peel as matrix in the manufacturing of bio-composite thin film. Banana peel fibers exhibit a good renewable material for the substitution of cement based composite. However, the bio-composite properties are limited by the poor adhesion between natural fiber interface and polymer matrix, which could be then improved by chemical modifications on fibers. In this research, banana peels were subjected to silane treatment. Bio-composite thin film manufacturing processes were carried out with blending and hand lay-up technique with various concentrations of eggshell filler which were EWE 0%, EWE 5% and EWE 10%. X-ray diffraction (XRD), Fourier Transformation Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA) and thickness swelling test were conducted on silane treated and untreated banana peel bio-composite samples. In XRD analysis, it was found that EWE 10% samples has the highest crystallinity compared to EWE 0% and EWE 5% and silane treated samples achieved higher crystallinity than untreated samples. For FTIR test, lignin component has been removed in silane treatment with the evidence of the characteristic IR peak changed and new bonds (-Si-O-C-, –Si-O-Si- and -Si-C-) found in silane treated samples. Besides, TGA results showed thermal stability of silane treated samples was highly improved along with the increased of eggshell filler percentage with the proof of decreased in decomposition stage. In thickness swelling test, the samples achieved higher swelling percentage when the percentage of eggshell filler increased. However, the decreases of 5-6% in thickness swelling of treated sample were possibly offset by the enhancement in fiber/ matrix interfacial adhesion. In conclusion, silane treatment can modified fiber's surface and its structure, therefore silane treated samples showed the increased in crystallinity, enhanced in its thermal stability and also reduced in the water absorption. Besides, eggshell fillers helped to increase water absorption and thickness swelling percentage on samples.

Kajian Sifat Struktur , Sifat Fizikal dan Sifat Haba Terhadap Bio-komposit filem nipis yang diperbuat daripada Kulit Pisang

ABSTRAK

Kajian ini membentangkan ringkasan pengetahuan pada pengisi organik- kulit telur digunakan sebagai pengukuhan dalam bio-komposit filem nipis kulit pisang. Serat kulit telur merupakan bahan yang boleh diperbaharui dan boleh dijadikan penggantian komposit berasaskan simen. Walau bagaimanapun, sifat-sifat bio-komposit adalah terhad oleh kelemahan lekatan semula jadi antara serat dengan polimer matriks. Namun, keadaan ini boleh diperbaiki dengan rawatan kimia pada permukaan serat. Kulit pisang akan didedahkan kepada rawatan silana dalam kajian ini. Proses pembuatan bio-komposit filem nipis dijalankan dengan pengadunan dan teknik hand lay-up diikuti dengan mencampurkan pelbagai nisbah (EWE 0%, EWE 5% dan EWE 10%) pengisi kulit telur. X-ray Diffraction (XRD), Spektroskopi Transformasi Fourier Inframerah (FTIR), Analisis Termogravimetri (TGA), dan ujian pengampulan ketebalan dijalankan ke atas sampel bio-komposit yang telah dirawat dan tidak dirawat. Dalam ujian XRD, didapati bahawa EWE 10% mempunyai tahap kehabluran yang paling tinggi berbanding dengan EWE 0% dan EWE 5%. Selain itu, sampel dirawat silana dengan penambahan kulit telur telah mencapai tahap kehabluran yang lebih tinggi berbanding dengan sampel yang tidak dirawat. Bagi ujian FTIR pula, ia telah mendapati bahawa komponen lignin telah dikeluarkan dalam rawatan silane dengan bukti sifat IR peak yang berubah dan ikatan baru (-Si-O-C-, –Si-O-Si- and-Si-C-) dijumpai dalam sample dirawat silana. Keputusan kajian TGA mendapati sampel dirawat silana telah menunjukkan kestabilan sifat haba yang sangat baik serentak dengan peningkatan peratus pengisi kulit telur di dalam sampel tersebut dengan bukti berkurangan pada peringkat penguraian. Bagi ujian pengampulan ketebalan pula, pengampulan ketebalan sampel meningkat serentak dengan peningkatan pengisi kulit telur. Namun, penurunan sebanyak 5-6% pada kajian pengampulan ketebalan dalam sampel dirawat silane berkemungkinan disebabkan peningkatan lekatan antara fasa di antara serat dengan matriks polimer. Kesimpulannya, rawatan silana boleh mengubahsuaikan permukaan serat dan strukturnya, oleh itu sampel dirawat silana menunjukkan peningkatan dalam tahap kehabluran dan kestabilan haba dan ia juga menunjukkan pengurangan dalam penyerapan air. Selain itu, pengisi kulit telur meningkatkan penyerapan air dan peratusan pengampulan ketebalan pada sampel.

CHAPTER 1

INTRODUCTION

1.1 Background of study

According to Nathalie & Silvia (2014), bio-composite materials have gained attractiveness due to both economic and ecological concern in the last decades. The impact of visible pollution has first driven the scientific and industrial communities to look further at biofragmentable and biodegradable material to substitutes for traditional petroleum-based non-biodegradable materials. Before the economic crisis of year 2007, the significantly increasing of fuel price affected the transformation from biodegradable to bio-based material. Eventually, the compliance of the obtained materials with thermo-mechanical enforcement has changed to the partially bio-based materials.

During the last years, that was an interesting issue where the polymer is added with organic filler instead of inorganic filler (Abdel-Salam *et al.*, 2011). This issue had grown the consideration and experimentation among the researchers. Some experiments had carried out and it has been proven that the replacement of organic filler in thermoplastic polymer really gave rise to several benefits. There are typically very low cost of organic filler and it is also biodegradable. These are the two most important advantages that people concerned about because it will contribute to an improved environmental impact. Nevertheless, it can also enhance some of the mechanical and thermomechanical properties in thermoplastic polymer (La Mantia *et al.*, 2005).

In past research, researchers have focused their study on utilisation of waste banana peel as fibre reinforcement in polymer matrix. According to Yuvaraj & Jeyanthi (2015), brake pads are produced using banana peel powder and kenaf powder as fiber or filler material. The result showed the brake pads composite had relatively compressive strength to withstand load application. Even though wear test and morphological test had not been performed to predict its wear resistance in the research, however, banana peel power and kenaf were assumed and candidated as filler material for the mass-scale fabrication of asbestos-free brake pad due to without any harmful effect.

Renewable agricultural waste lignocellulose materials and bio-based polymer matrices will provide an attractive eco-friendly quality as well as to sustain environment to the resulting natural fiber reinforced bio-based composites. The interest in agricultural wastes as a substitute for wood based raw materials has increased tremendously. For instance, water bamboo husk powder is added to poly (lactic acid) (PLA) to produce novel reinforced biodegradable composites. The results showed that char yields were increased since the plant powder was integrated to PLA. Moreover, the mechanical properties were also enhanced besides the 50% - 200% increments of storage modulus of PLA (Avella *et al.*, 2009).

In fact, natural plant fibers have favorable behavior in terms of specific strength and modulus, low density, reduced tool wear, economic viability and enhanced energy recovery. Despite the advantages, applied natural fibers in composite reinforcement results to undesirable properties. This is due to the different interfacial properties between thermoplastic matrix and natural fibers. Nevertheless, treatment of natural fibers is necessary in order to improve the interfacial matrix-fiber bonding and therefore resulting in enhancement of physical and mechanical properties of composites. For instance, chemical treatments of fiber surface have been sometimes successful in enhancing the interfacial bonding. However, the industrial application of chemical surface treatments in fiber surface has limited due to the concerning about environmental pollution, high cost treatment problem and the disposal of chemical products (Oliveira *et al.*, 2012).

1.2 Problem Statement

Studies by the government last year showed the average Malaysian produced 800 g of solid waste a day especially for those who lived in the urban areas produced 1.25 kg of waste daily. This is a major and serious problem due to it is an estimated 30,000 to 33,000 ton of waste production daily by 2020 with less than 5% of the waste is being recycled. Kitchen waste is among of the 5% trash that seldom used to recycle (Ismail, 2014).

Due to the reasons of environmental problem and consumption of non-renewable resource besides the high cost of synthetic fibres, researchers have focused their study on the use of environmentally friendly materials to produce composite in recent year. Thus, there is an increased the number of using natural fibres to produce composite compare with synthetic fibres which is bio-composite. Bio-composite consist of matrix and natural fibres as reinforcement. There is potential replacement of the use of natural fibers to synthetic fibers. Low cost and low density are the advantages of natural fibers which it had been chosen to replace synthetic fibers (Sethy, 2011).

The most commonly used natural fibres in bio-composite are from plant. This includes kenaf, hemp, coir and flax. In this research, food wastes are used to produce bio-composite thin film. The food wastes used are banana peel and eggshell. There is large amount of food waste produced and thrown away in the world. Therefore they are good resources in manufacturing composite by utilization of food waste.

In this study, bio-composite thin film is produced from waste banana peel and eggshell throughout this research. Moreover, silane treatment is applied to modify the surface and structure of fibre. The physical and thermal properties of treated and untreated bio-composite thin film are investigated.

1.3 Significance of study

Bio-composite can be produced by waste banana peel. They can be manufactured at lower cost. This is because the materials used are food wastes. Moreover, utilization of food wastes can reduce environmental problem. There are more options for sources of natural fibres used in bio-composite. Therefore, bio-composite can be more widely used in application.

The important of this research is to reduce the number of waste especially kitchen waste and thus can help to reduce and solve the issues of environmental pollution. The developing of alternative polymer which is the organic based polymer can helps to sustain environment as it is biodegradable and bio-fragmentable. Besides that, the new creation material from bio-based polymer thin film may be helpful and beneficial towards society such as agricultural field. The banana fruit's peel is selected for the experiment as it is waste materials rich of starch.

The aim of this research is to determine the physical and thermal properties of the bio-composite thin film. Their properties according to different percentage of filler reinforced might directly influence its strength and weakness. Besides, surface modification on banana peel fibers may significantly affect its thermal properties and the result of water sorption. As a result, this will help in producing the bio-composite with improved and enhanced its physical and thermal properties, therefore the bio-composite with desired properties can be produced.

1.4 Objectives

1. To produce bio-composite thin film from untreated and silane treated waste banana peel.
2. To determine the structural, physical and thermal properties of untreated and silane treated waste banana peel bio-composite thin film.

CHAPTER 2

LITERATURE REVIEW

2.1 Waste Banana Peels

Banana (*Musa sapientum*) is the herbaceous plant that belongs to the family Musaceae. Bananas are the most important tropical fruits in the world market and it is most eaten fruits in this world. Banana also named as the World Healthiest Fruit. According to the Global Analysis Report 2014, bananas are listed in the top ten crops in Malaysia. Banana production reached 335,974 ton and recorded the best volume growth in 2012 with 9.7% compared to the previous year 2011 (Halal Industry Development Corporation, 2014).

Banana peel (also known as banana skin) is the outer covering of banana fruit. At present, the banana peels are not being used for any other purposes and generally removed and dumped as solid waste at large expense. Therefore, a significant amount of organic waste is generated. There are several utilizes of wasted banana peels such as it is used for water purification, as fertilizer and used in the production of ethanol, cellulose and laccase. However, sometimes wasted banana peel is used as feedstock typically in small farms for pigs, goats, rabbits, cattle and other several species (Emaga *et al.*, 2011).

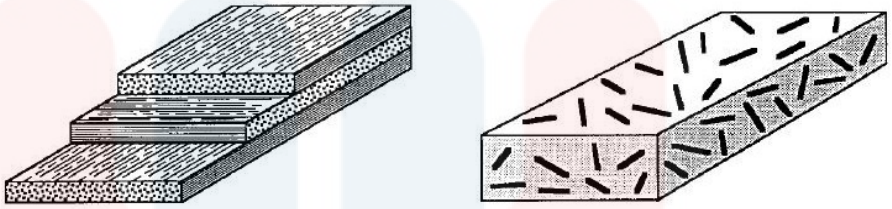
Banana peels are the major by-product and it is a waste material rich in starch. Significant quantities of banana peels equivalent to 40% of total weight of fresh banana are generate as waste product in industries producing banana based products. Banana peels are rich in carbohydrates (56.35%), followed by fiber (15.30%), ash (12.62%), moisture content (7.65%), crude fat (4.34%), and protein (3.74%) (Singanusong *et al.*, 2013). Some studies show that banana peels are good sources of polyphenols, carotenoids and other bio-reactive compounds that possess various beneficial effects on human health. The potential applications for banana peels are depend on its chemical composition (Rodriguez de Sotillo *et al.*, 1994; Wolfe *et al.*, 2003; Larrauri, 1999).

Table 2.1: Biological components present in banana peels.

(Jaishankar *et al.*, 2014; Anhwange *et al.*, 2009)

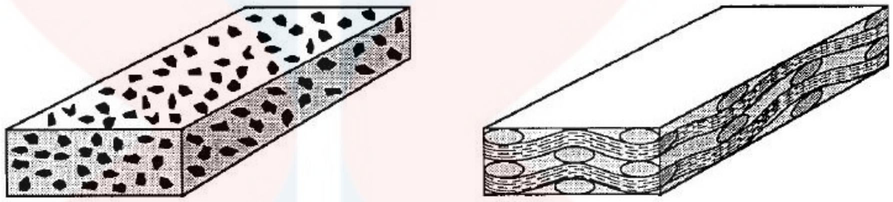
Components	Component Contains (%)
Moisture	6.7
Protein	0.9
Carbohydrate	59.0
Crude Lipids	1.7
Ash	8.5
Organic Matter	91.5
Crude Fibers	31.7
Minerals	Potassium, Manganese, Iron, Sodium, Calcium, Bromine, Rubidium, Strontium, Zirconium, Niobium

2.2 Composite



Continuous Fibers

Discontinuous Fibers, Whiskers



Particles

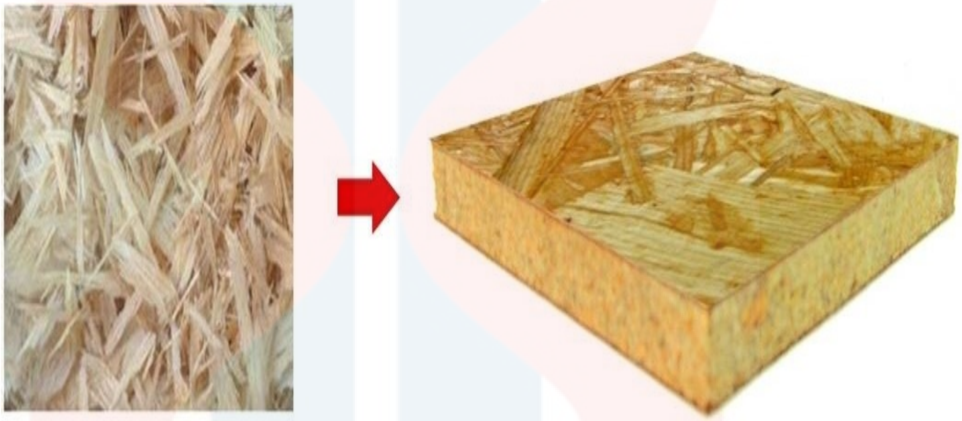
Fabric and Braid

Figure 2.1: Various types of reinforcement forms (Shah, 2011).

Composite can be defined as a solid material which is composed of two or more substances which having different physical characteristics. In other words, composite refers to a combination of several materials that the reinforcing phase is embedded in other materials called matrix phase to form a new material system in order to enhance the material properties (McEvoy & Correll, 2015).

Composite parts have several advantages when compared to the metal parts they are being used to replace. For instance, the production cost might be reduced due to composite may be made by a wide range of methods, low maintenance cost due to the laminate patterns and ply build up in a part can be tailored in order to provide the required mechanical properties in various direction, and excellent corrosion resistance and chemical resistance. However, composite also have its disadvantages such as it is more brittle than wrought metals and therefore easily can be damaged and tends to be brittle (Chung, 2001).

2.3 Bio-composite



Bamboo Flake Bamboo Flakeboard

Figure 2.2: Examples of Bamboo based Bio-composite (Suhaily *et al.*, 2013).

Bio-composites are the combination of natural fibers (bio-fibers) such as wood fibers or non-wood fibers with polymer matrices from both of the renewable and non-renewable resources. Wood fibers divided into hard wood and soft wood while the examples of non-wood fibers are rice straw, pine apple, banana, hemp, oil palm, jute, sisal, flax and sugar cane. The term ‘bio-composites’ generally covers the composite materials where at least one component should be bio-based. For instance, bio-polymers reinforced synthetic fibers such as carbon or glass and bio-fiber reinforced with non-degradable petroleum derived polymers such as polyolefins polyester, epoxy and phenolics (Mitra, 2014).

Bio-composite can be categorized into two main groups for its application which are structural and non-structural. A structural composite refers as one that is required to carry a load in use. For instance in housing industry such as load bearing walls, subflooring, roof systems, framing components, stairs and furniture. Structural wood-based composites for the indoor use purpose and it is typically made with low cost adhesive which is not stable to moisture unlike exterior grade composites that contain a thermosetting resin that is higher in cost but stable to moisture. On the other hand, non-structural composites are not intended to carry a load in use. These can be made from variety of materials such as textiles, thermoplastics and wood particles. Non-structural composites are used for product such as doors, windows, ceiling tiles, furniture, automotive interior parts and others (Rowell, 1997).

Bio-composite becomes popular when market demand for environmental friendly products increased and this situation urge of finding alternative materials to cover up the demand of natural fibers from forest resources. Despite that, bio-composite have a lot of great reputations to offer where nowadays this technology is gradually accepted to be applied commercially. This technology has good mechanical properties, biodegradable good appearance and it is able to reduce environmental pollution (Bourmaud & Baley, 2009).

2.4 Natural Fibers Polymer Composite

Natural fiber polymer composites (NFPC) are a composite material consisting of a polymer embedded with high- strength natural fibers, for instance kenaf, sisal, flax, oil plam, jute, pineapple, ramie and bananas. In the few past years, various investigations and research has been made to prove the worth of natural fibers against synthetic fibers. Many environment problems can be prevented or solved by using bio-fibers (natural fibers) with renewable resources polymer (Drzal *et al.*, 2001).

Natural fibers structure consists of cellulose, lignin, pectin, hemicelluloses and waxy substances and it allows the moisture absorption from the surroundings which will cause weak binding between the fiber and polymer. Moreover, the couplings between polymer and natural fiber are considered a challenge due to the chemical structures of both matrix and fibers are various (Mohammed *et al.*, 2015).

In previous studies, many researchers have examined and studied the suitability, capabilities and competitiveness of natural fibers embedded in polymeric matrices. The researchers emphasized on the effect of the fiber surface modifications as well as manufacturing processes in order to improving the fiber or polymer compatibility (Faruk *et al.*, 2012; Shinoj *et al.*, 2011; Arrakhiz *et al.*, 2013). Mohanty *et al.*(2000) showed that the mechanical properties of the resulted composites, tensile strength, impact strength and bending strength will increased when compares with pure Biopol. The tensile strength of jute Biopol was enhanced by 50%, whereas impact strength and bending strength of the composites were increased by 90% and 30% respectively in the comparison to pure Biopol.

Nowadays, natural fibers have become attractive to those researchers, scientists and engineers as an alternative reinforcement for fiber reinforced polymer composites.

Natural fiber reinforced polymer matrix got considerable attention in numerous applications due to its good properties and superior benefits of natural fiber over synthetic fibers. Besides the advantages of eco-friendly and biodegradability, fiber reinforced polymer are low weight, low cost, high specific strength, non- abrasive, fairly good mechanical properties such as tensile modulus and flexural modulus, improved surface finish of molded parts composite, renewable resources, flexibility during processing, being abundant, and also minimal health hazards (Ku *et al.*, 2011).

2.5 Fillers

Filler refers to dispersed phase of composite resins. Fillers enable increase the strength and characteristics necessary for use as a restorative material. Generally, filler divided into two categories which are organic and inorganic filler. Organic fillers such as eggshell are biodegradable and it came from renewable sources, which gives rise to less concern about their disposal problem. The inorganic such as quarts, glass, silica and colorants and/ or organic resin particles that are designed to strengthen a composite, decrease thermal expansion, minimize polymerization shrinkage and reduce the amount of swelling caused by the water sorption (Margeas, 2012).

There are various functions of fillers which are strengthen the composite, reduce the amount of matrix material, reduction in polymerization shrinkage, increase fracture toughness, increase in abrasion resistance, increase in compressive strength, tensile strength, modulus of elasticity, and also reduction in thermal expansion and contraction.

Silane coating of fillers may increase resistance to hydrolytic degradation (Deepthi, 2013).

2.5.1 Organic filler- Eggshell

Eggshells are litter and kitchen waste that can be collected in a large amount from many places such housing areas, restaurants, hotels, food industries and even from the hatcheries and farm (Pereira *et al.*, 2013).

Eggshell consists of 95% calcium carbonate ($CaCO_3$) as its main component and it is in the form of calcite. In the form of calcium carbonate, calcite is the most stable which forms elongated structures called columns, crystallite or palisade (Nik Yusuf *et al.*, 2016). Besides that, there are remaining 5% of others inorganic material in the eggshell which are calcium phosphate, magnesium carbonate, soluble proteins and insoluble proteins. Calcium carbonate is a compound that brittle white stuff that limestone, chalk, sea shells, coral and pearls are made of (Senese, 2010).

The chicken eggshell is another natural composite with emerging relevance. In America, millions of eggshells produced annually pose a serious challenge to the environment. Some issues of the eggshells are the decomposing organic components causing to the emission of the repugnant smell as well as the creation of enabling environment for invasion by potential diseases causing pathogens. Alternative uses of eggshells as components in structural materials will benefits in mitigating these challenges while providing for other societal needs (Rahman *et al.*, 2014).

2.5.2 Inorganic Filler- Calcium carbonate powder ($CaCO_3$)

Inorganic fillers are usually added to the resin in order to reduce cost and alter the final composite properties especially in rigidity although they are also adversely influence its process ability. The addition of calcium carbonate will increase the gel time and viscosity of the resin and consequently decrease the permeability of the reinforcement. In a studied of polypropylene (PP) filled with mineral filler, it prove that mineral filer can help to improve properties of polypropylene due to they are packaged with the favorable characteristics such as good thermal stability, high strength and also corrosion resistance (Leong *et al.*, 2004).

2.6 Plasticizer

Plasticizer is the fundamental additives for the film-forming polymers. It will reduce the inter-molecular forces which increase the molecular spacing and mobility of biopolymer chains. The addition of plasticizing agent is a necessary to overcome brittleness of the film and to improve its flexibility. According to Brandenburg *et al.* (1993), films that made without plasticizer are extremely brittle and shattered upon handling. Polymer-polymer interactions in biopolymer films will replaced by the polymer-plastics hydrogen bonds that are believed developed by polar groups (-OH) along plasticizer chains. Glycerol is most commonly used as plasticizing agent due to its small size and high porosity (Chinabhark, 2007).

Glycerol is the mostly used plasticizer in the thermoplastics production due to its biodegradability, availability, and affinity with starch. The glycerol content will influences the thermoplastic properties. Low contents of glycerol would lead to an anti-plasticizing effect. If the amount of plasticizer is insufficient to provide extra free volume, the interactions between plasticizer and polymer hinder the mobility of chain segments and the resulting film will be brittle. However, a high content of glycerol will causing the segregation of glycerol-rich phase (Pilla, 2011).

The main role of plasticizers is to enhance the flexibility and processibility of starch by reducing the strong intermolecular interactions between starch molecules (Muñoz & García-Manrique, 2015; Aguirre *et al.*, 2013). As the mobility of polymeric chains increases the flexibility, extensibility and ductility of plasticized films will enhance. On the other hand, the addition of plasticizers will decrease film mechanical resistance.

Besides that, the type and concentration of plasticizer employed has significant effect on the physical, mechanical, thermal and barrier properties of films (Aguirre *et al.*, 2013; Razavi *et al.*, 2015; Smits *et al.*, 2003). Recently, Sahari *et al.* (2013) investigated that the effect of glycerol content (15, 20, 30 and 40% w/w) on the physical and thermo-mechanical properties of Sugar Palm Starch (SPS). They concluded that 30% w/w glycerol plasticized SPS exhibited a better mechanical properties.

2.7 Fiber Treatment Methods

Some researchers have shown that natural plant fiber can be modified to improve its properties. One of the ways is apply treatment on the fiber. There are various types of fiber surface modification such as mercerization, latex coating, gamma radiation treatment, silane treatment, isocyanate treatment, acetylation and peroxide treatment (Sawpan *et al.*, 2011).

Those methods were tried to reduce the hydrophilicity and thus decreasing the sorption characteristics of fiber. Different treatments will cause the changes in physical and chemical modification of fibers such as the water sorption behavior. The effect of sorption on the mechanical treated and untreated was also studied and investigated. As a result of study, it was found that the decreasing in its mechanical properties of fibers upon sorption and regains on desorption (Mohammed *et al.*, 2015).

Mercerization process is known as pre-treated process which is applied on the fiber surface as a pre-treatment. The crystal structures of cellulose are changed during mercerization process. Normally, the fibers were pre-treated by sodium hydroxide (NaOH) with the aimed of activate OH groups of cellulose and lignin in fibers. Later on, different chemicals such as silane coupling agent can be applied on fiber surface to enhance its interfacial properties (Wang *et al.*, 2007).

The mechanism of silane coupling reactions is related with the effect of two reactive surface groups but those reactions are not similar according to the substrate in contact. The strength of the interface in polymer matrix is enhanced by the alkyl groups (R') in silane agent. This is due to alkyl groups (R') enhance the compatibility with organic compound and the hydrophobic properties of fiber surface. Moreover, alkoxy groups (OR) enable silane to bind on OH groups surface after the hydrolysis process (Arsène *et al.*, 2013).

When silane undergoes hydrolysis and condensation, alkoxy groups (OR) in silane is able to form bonds with hydroxyl groups (OH) and hence reached the bond formation stage. The formation of silanol by hydrolysable alkoxyl groups in the presence of moisture condition. This phenomenon allows silanes adhesive on the OH groups of fibre substrates. Later, silanol reacts with hydroxyl groups of fibers and thus form polysiloxane network on surface by self-condensation reaction (Sreekala *et al.*, 2000).

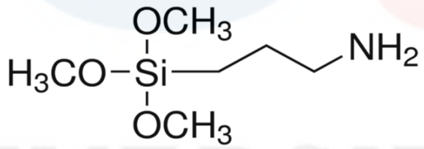


Figure 2.3: Structure of silane coupling agents ((3-aminopropyl) trimethoxysilane) (Shin-Etsu Chemical Ltd., 2015)

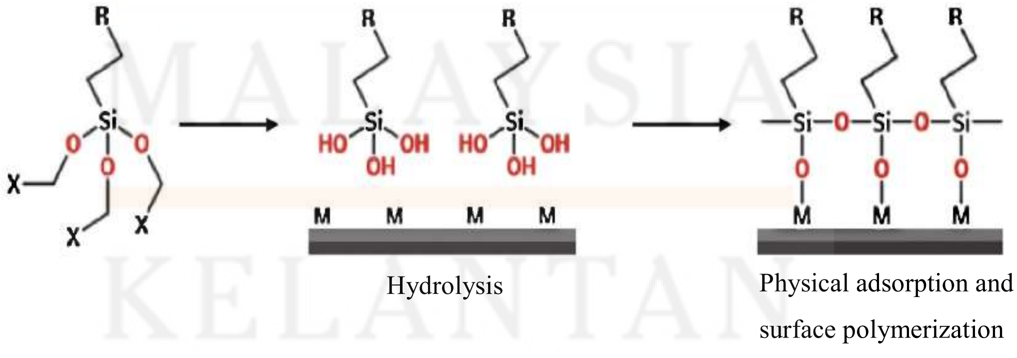


Figure 2.4: Hydrolysis reaction of (3-aminopropyl) trimethoxysilane agent (Dumée *et al.*, 2014)

2.8 Characterization of Bio-composite Thin Film

2.8.1 Phase Identification

Identification of crystalline substance and crystalline phases in a specimen is achieved by comparing the specimen diffraction spectrum with spectra of known crystalline substances. The X-ray diffraction data from a known substance are recorded as powder diffraction file (PDF) (Connolly, 2007). Crystallinity index can be calculated by the use of XRD counts with the help of empirical Segal equation (Sawpan *et al.*, 2011)

X-ray diffractometer (XRD) was used to examine the crystal structure of nanocomposite films. In the report Cellulose Microfibril from Banana Peels as Nanoreinforcing Fillers for Zein Films by Phiriyawirut (2012), XRD patterns in that experiment were obtained by Bruker axx D8DISCOVER with the source of CuKα. The result obtained from the research was the crystalline peak of zein film reinforced cellulose microfibril fiber (CMF) became broader and shape-like cellulose crystalline peak when the CMF content increased.

2.8.2 Chemical Composition and Functional Group

Infrared spectroscopy is among of the essential and crucial characterization technique to determine the structure of matter at the molecular scale. Moreover, Infrared (IR) spectroscopy can analyze chemical composition, functional group and bonding arrangement of constituents in a copolymer, homopolymer, polymer composite and polymeric materials (Baker *et al.*, 2014).

The investigation of the properties and development of bio-composite film is a difficult progress due to classical microbiology does not offer non-destructive methods other than microscopically observations. FTIR-ATR spectroscopy is powerful equipment used for the testing of thin film molecular organization. However, the substrate properties must be considered for the analysis of FTIR-ATR spectra. (Laroche, 2013)

2.8.3 Thermal Behavior

Thermal behavior of bio-composite thin film can be observed through the Thermogravimetric Analyzer (TGA) and Derivative Thermogravimetry (DTG). TGA was conducted to measure the thermal weight loss of samples on a SDT Q600 V8.0 Build 95 instrument at a heating rate of 100 °C per minute in nitrogen atmosphere. The weight losses at different stages were analysed and observed (Johar & Ahmad, 2012).

Acccording to Kabir *et al.* (2013), TGA was used to examine the thermal property of the alkalized fiber samples where the result exhibited alkalized fiber samples had higher decomposition temperatures compared to untreated fibers. Besides, TGA thermographs in this past research also showed the alkalized fibers had less weight loss than untreated fibers. Those results had indicated alkali treatments had removed some portions of hemicelluloses and lignin constituents from the fibers samples.

Differential Scanning Calorimetry (DSC) was used to investigate thermal behavior of film samples in the studied by Phiriyawirut (2012). In that research, the melting temperature (T_m) and glass transition temperature (T_g) of film samples were investigated due to the onset temperature of endothermic melting peak and inflection point of specific heat increment had been observed respectively.

2.8.4 Water Absorption and Thickness Swelling Measurement

Water absorption test is used to determine the water absorption behaviour of a material. Applying treatment on fiber reduced the water absorption because of physical and chemical changes occurred to the fibres on modifications (George *et al.*, 2001). There is relationship between water absorption behaviour of a material and its physical and mechanical properties. Tensile properties of composites decreased after water absorption compared to dry samples (Yahaya *et al.*, 2015). On the other hand, swelling of fibers that is caused by water absorption has positive effects on mechanical properties of the material (Muñoz & García-Manrique, 2015).

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Materials that used in this research were waste banana peels, eggshells, glycerol, epoxy, (3-aminopropyl) trimethoxysilane and acetone. Whereas, the apparatus and equipments that used were spatula, beaker, thermometer, knife, roller, silkscreen, small bowl, mould compressor, oven, blender, electronic scale digital weight balance, digital calipers, forceps and hot plate magnetic stirrer.

3.2 Methods

3.2.1 Preparation of Banana Peels

Figure 3.1: Sliced dried banana peels into small portion.

Waste banana peels were collected from UMK Jeli cafeteria. The stems of waste banana peels were trimming off. The waste banana peels were dried in the oven for an hour at 80 °C to remove water content. Later, the dried banana peels were sliced by scissors into smaller portion and this showed in Figure 3.1.

3.2.2 Preparation of Eggshell Filler

Figure 3.2: The sieved eggshell powder.

Eggshells were collected from UMK Jeli cafeteria. The eggshells were washed with water to remove the dirt and membranes. Later, the cleaned eggshells were dried in the oven for an hour. Then, dried eggshells were blended by using blender. A sieve was used to filter the eggshell powder to obtain constant size of particles which was 75 µm.

3.2.3 Silane Treatment on Banana Peels

Figure 3.3: (3-aminopropyl) trimethoxysilane solution

The banana peels were pretreated by immersing in 1% (3-aminopropyl) trimethoxysilane dissolved in a water acetone mixture for 2 hours later followed by 30 mins of air drying for hydrolysing the coupling agent.

3.2.4 Production of Bio-composite Thin Film

Banana peels was boiled in water for 20 mins to make it soft. The volume of water (ml) and weight of banana peels (g) were in the ratio of 4:1. After 20 mins, banana peels were blended with glycerol and eggshell powder for 10 mins. The amount of glycerol were used is 15% w/w of the dried banana peels. Then, the blended mixture was boiled for 15 mins at 70°C.

Meanwhile, the mesh surface of the silkscreen was moistened with water. The boiled blended mixture was spread over the mesh using spatula. A roller was used to ensure the film surface to be more flat. Then, the mixture on silkscreen was placed in the oven at 80 °C for 3 hours for drying. Lastly, the dried bio-composite thin film was taken from the silkscreen. The thickness of the thin film was in the range of 0.10 mm to 0.15 mm.

Figure 3.4: The boiled blended mixture was spread over the silk screen in the mould.

3.2.5 Hand Lay-up and Compression Moulding Methods

The banana peel based epoxy composite was fabricated using hand lay-up process. The bio-composite thin film was immersed into the epoxy for 10 mins and later it was taken out for drying. Roller was used on the thin film to remove excess epoxy and any trapped air. Then, the thin film was placed in the mould and compressed by mould compressor. Finally, thin film was left in the room temperature for 24 hours.

The methods were repeated with different ratio of banana peels and eggshells. The bio-composite thin film were categorized into EWE 0%, EWE 5% and EWE 10% where EWE refers to epoxy/ waste banana peel/ eggshell filler.

The percentage and ratio of banana peels and eggshells were used in this study are shown in Table 3.1. Besides, the procedures were also repeated using silane treated banana peels.

Table 3.1: Percentage of banana peels and egg shells used.

Banana peels (%)	Egg shells (%)
100	0
95	5
90	10

3.3 Testing Methods of Structural ,Physical and Thermal Properties

Figure 3.5: Sample of banana peel bio-composite thin film reinforced eggshell filler.

The bio-composite thin films produced were tested for their structural and thermal properties. Bio-composite thin films were cut to obtain the desired dimension of specimen. The specimen size was 24 × 10 mm^2.

3.3.1 X-ray Diffraction (XRD)

The crystalline structures of thin film samples were determined by X-Ray Diffraction (XRD) technique. XRD analysis was carried out by using Bruker D8 Advanced Powder XRD with CuK-α radiation (λ=1.5404 nm) and X-ray diffractometer was operated at a voltage of 40 kV with a current density of 30 mA. XRD data were collected within the range of scattering angles (2θ) of 10° to 40° at room temperature.

The crytsallinity index (CrI) was calculated as below:

$$\text{CrI}\ (\%) = \frac{I_{200} - I_{\text{Cr-non}}}{I_{200}} \times 100 \qquad \text{(Equation 1)}$$

where I_{200} = maximum peak intensity of the crystalline region

$I_{\text{Cr-non}}$ = amorphous region.

3.3.2 Fourier Transform Infra-red (FT-IR)

For FTIR analysis, the specimen was tested by Shimatzu 8400 s FT-IR spectrometer, at a resolution of 4 cm^{-1} (40 scans) and the information on the blend, composite composition and polymer- polymer interaction are determined in data as a result.

3.3.3 Thermogravimetric Analysis (TGA)

The TG/DTG curves were measured on Seiko Thermal Analyzer EXSTAR 6000 TG/DTA 6300. Approximately 10.20 mg of samples were placed on an aluminium pan for testing. This testing was carried out from 30 to 900 °C in dynamic nitrogen atmosphere with the flow rate of 10 ml/ min and heating rate of 10 °C/ min.

3.3.4 Water Absorption and Thickness Swelling Analysis

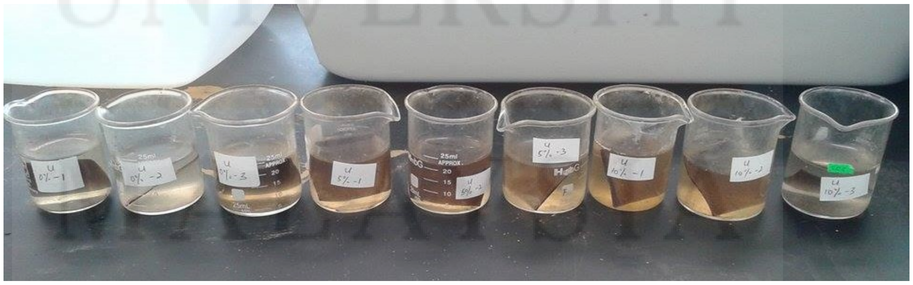


Figure 3.6 (a): Water absorption of untreated samples.

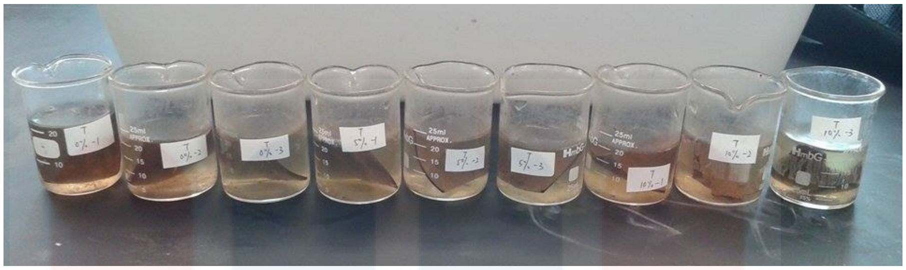


Figure 3.6 (b): Water absorption of treated samples.

Figure 3.6 (a) and (b) shows the water absorption and thickness swelling test of treated and untreated samples. The water absorption test was carried out in accordance with ASTM D570-98 (2010). The samples for each ratio were cut into dimensions of 24 × 10 mm^2. The thin film samples were dried in an oven at 80 °C before the measurement was carried out. Moreover, the weight and thickness of specimens was taken before immersion into the distilled water. The samples were taken out every hour and all the surface moisture was dried with dry and clean tissue paper. Water uptake was measured at 120 hours intervals until weight stabilization was obtained. The water absorption will be then calculated by the weight difference while Swelling Index (SI) is calculated by using the formula:

$$SI = \frac{W_f - W_i}{W_i} \times 100\ \% \qquad \text{(Equation 2)}$$

where SI = Water Absorption of specimen after N hours of water soaking (%)

W_f = Final weight of specimen after N hours of water soaking (g)

W_i= Initial weight of specimen before N hours of water soaking (g)

3.4 Research Flow Chart

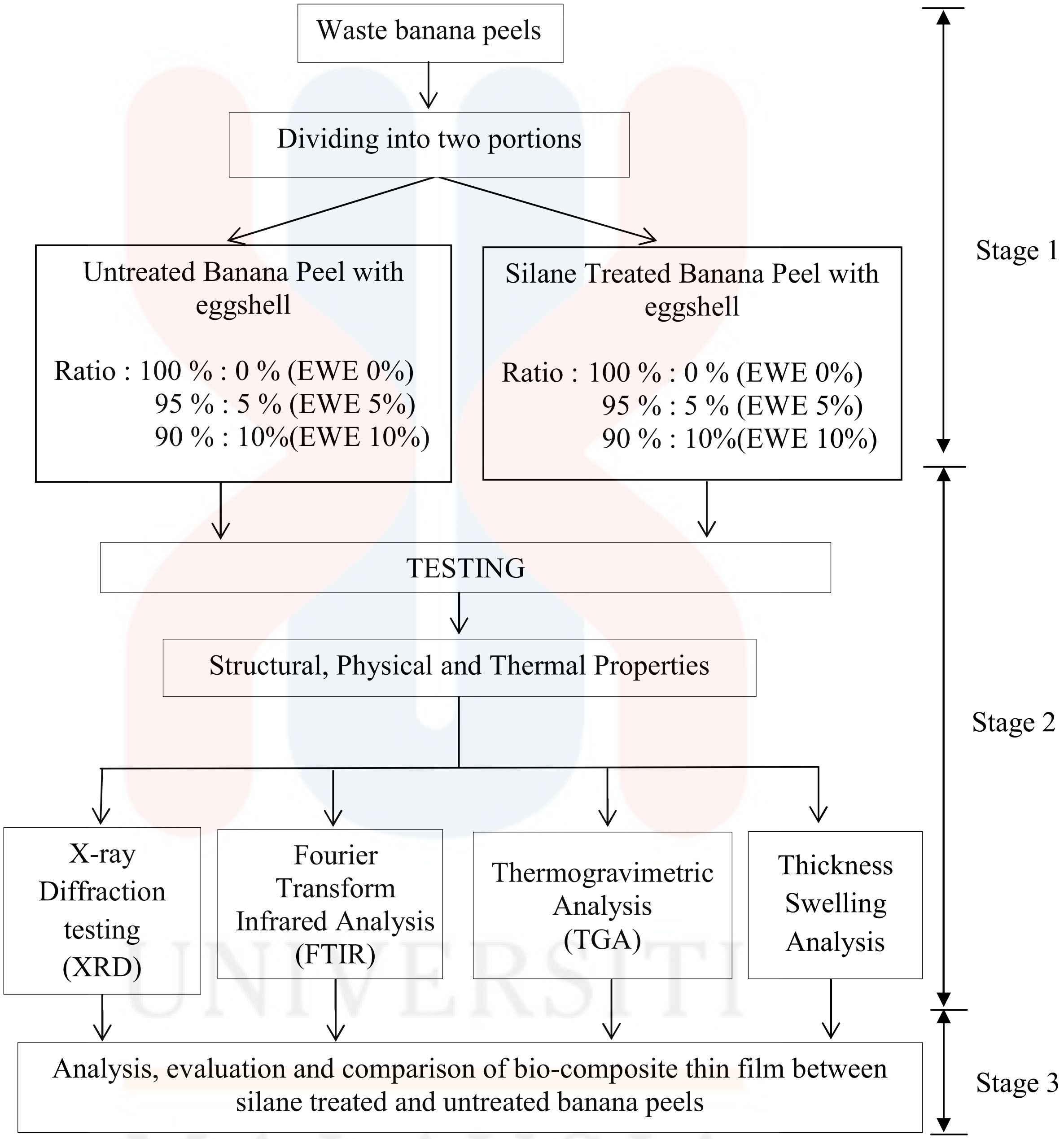


Figure 3.7: Research Flow Chart

Stage 1: Materials preparation

Stage 2: Testing of bio-composite thin film on structural, physical and thermal properties.

Stage 3: Analysis, evaluation and comparison of obtained data.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Crystallinities Analysis by XRD

In order to study the crystallinities phases of the samples, X-ray diffraction (XRD) analysis was conducted with the aim of comparing XRD patterns of silane treated and untreated bio-composite thin film. The crystallinity index (CrI) of samples was calculated by using Equation 1 as reported by Segal *et al.* (1959). Figure 4.1 (a) and (b) show XRD diffractograms of untreated and treated samples while Table 4.1 shows the comparisons of crystallinity index of untreated and treated samples.

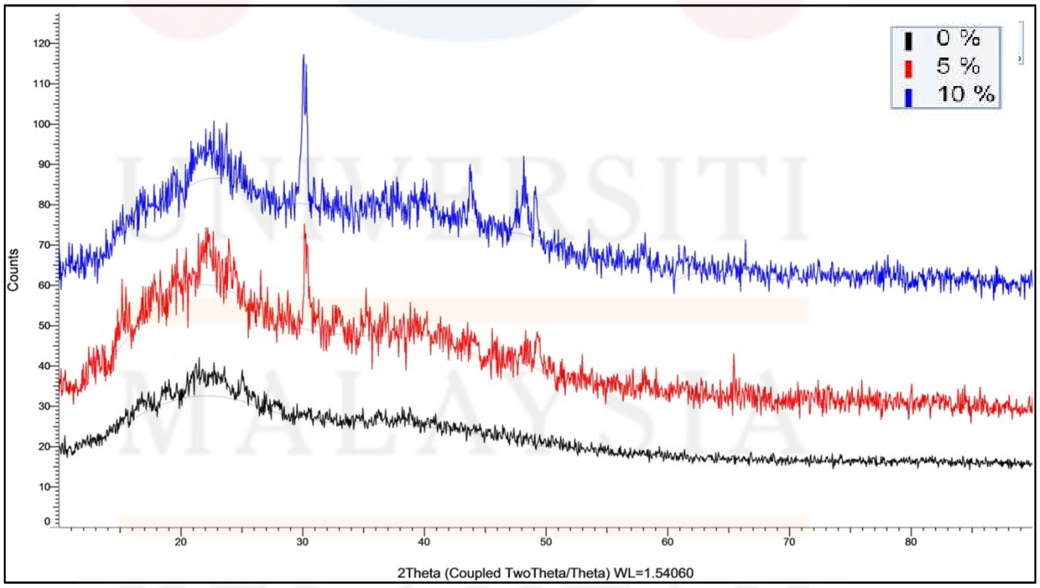


Figure 4.1 (a): XRD patterns of untreated samples.

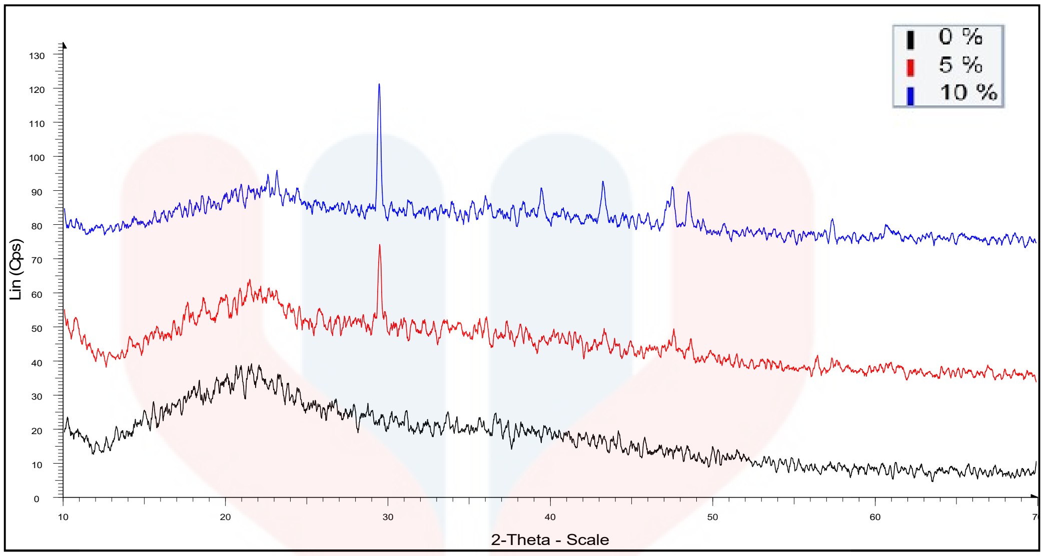


Figure 4.1 (b): XRD patterns of treated samples.

Table 4.1: Comparisons of crystallinity index of untreated and treated samples.

Samples	**Crystallinity Index (%)**	
	Untreated	Treated
EWE 0%	16.9	20.2
EWE 5%	17.1	21.7
EWE 10%	17.8	23.2

The patterns exhibited an intense peak at around 2θ = 30 ° (I_{200}) for both treated and untreated samples. This peak represents the crystallinity region in samples. On the other hand, the amorphous region of the samples is shown by the valley between the peaks which shown in $I_{Cr\text{-}non}$ at around 2θ = 28 °. After the silane treatment of bio-composite thin film, it can be observed that the peak at 2θ position around 30 ° became narrower and more intense compare to untreated samples. This situation indicating a higher degree of crystallinity in treated samples (Razak *et al.*, 2014).

Based on the Table 4.1, calculation of the crystallinity index showed that treated samples have higher value compared to untreated samples. For example, treated EWE 10% (23.2%) has higher degree of crystallinity than untreated EWE 10% (17.8%). Based on the studied by Jonoobi *et al.*, (2010), lignin and hemicelluloses in fibers had been removed during the fiber treatment process and therefore resulting increased in crystallinity index.

Based on Figure 4.1 (a) and (b), both untreated and silane treated samples showed that the shape of 2θ XRD patterns were almost same despite the percentage of reinforced eggshell was different. The crystallization degree of silane treated specimens became lower than untreated specimens due to the reason of banana peel surface had modified by silane coupling agent. The crystal cell structure of cellulose of modified banana peel structure was distinguishable with unmodified banana peel (Miao & Zhang, 2011). This situation showed that with the modification of silane treatment on banana peel, the crystallization degree of treated bio-composite samples increased compared to untreated samples.

For the aspect of intra-comparing of untreated EWE 0%, EWE 5% and EWE 10%, it is found that EWE 10% is more crystallinity (17.8%) and contains higher concentration of calcite, $CaCO_3$ (00-003-0569) (Nik Yusuf *et al.*, 2016) and compared to others. This phenomenon occurred in same situation in intra-comparing of silane treated EWE 0%, EWE 5% and EWE 10% where treated EWE 10% is the most crystallinity (23.2%) and it contains the highest concentration of calcite among them. All specimens of banana peels reinforced eggshell thin film are more considered as amorphous structure due to banana peels functioned as a matrix in the fabrication of bio-composite thin film.

Nevertheless, it is clearly shows that the sharp peaks at 2θ = 42 ° which represent $CaCO_3$ are only appeared on the both graphs of treated and untreated EWE 5% and EWE 10% but not in EWE 0% because of the addition of eggshell as reinforced in the thin film. However, calcite has been reported that it may not significantly influence the crystallinity of the polymer matrix (Leong *et al.*, 2004). Besides, eggshell has not been modified in this research, thus untreated $CaCO_3$ particles did not caused any effect on the crystallinity of the samples (Zuiderduin *et al.*, 2002).

4.2 Functional Group Identification by FTIR

The content of untreated and silane treated banana peel bio-composite thin film is characterized using Shimatzu 8400 s FT-IR spectrometer. The aim of this characterization is to confirm existence of banana peel bio-composite thin film content based on the wave numbers in the range of 4000-600 cm^{-1} on the FTIR spectra as shown in Figure 4.2 (a), (b) and (c). Apart from that, FTIR characterization able to identify functional group and measure transmittance of banana peel bio-composite thin film of each sample (Sutikno *et al.*, 2014). Figure 4.2 (a), (b) and (c) shows the comparisons of FTIR spectrum between silane treated and untreated EWE 0%, EWE 5% and EWE 10%. Comparison of OH stretch absorbance unit is shown in Table 4.2 while wavelength of peaks used for FTIR analysis and its corresponding functional groups is shown in Table 4.3.

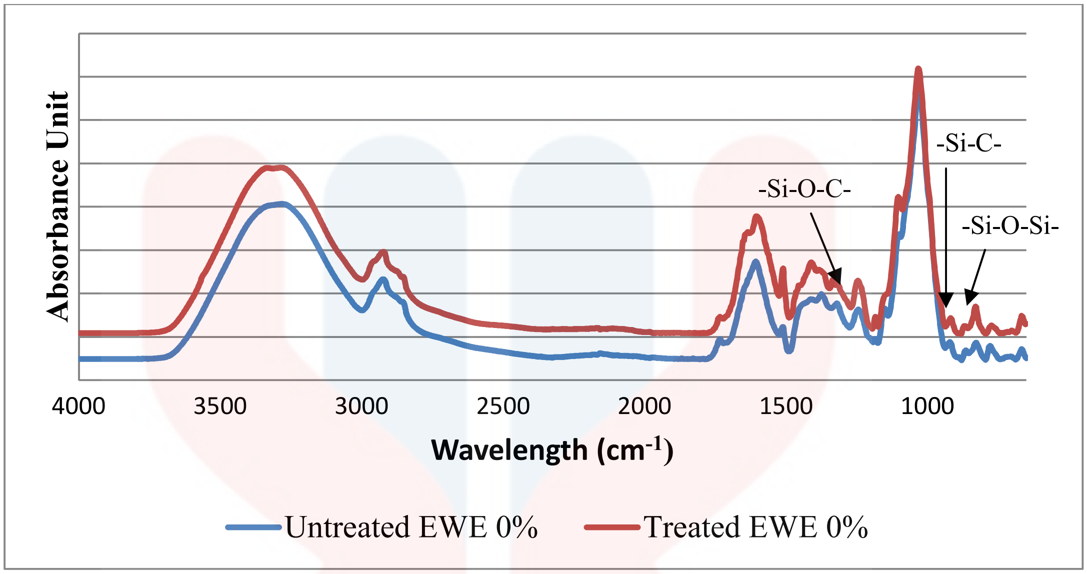


Figure 4.2 (a): Comparison of FTIR spectra between untreated EWE 0% and treated EWE 0%.

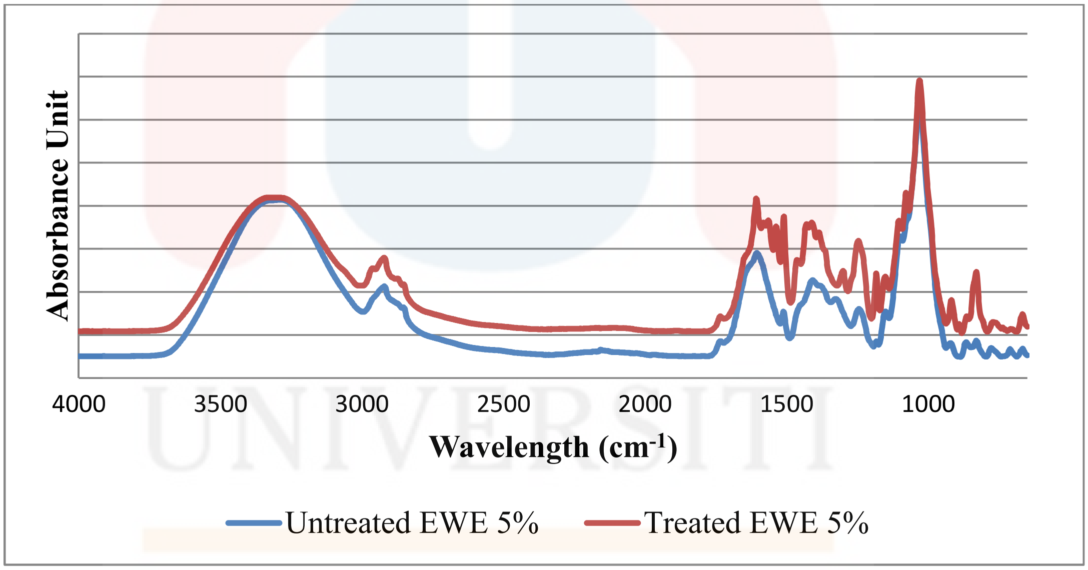


Figure 4.2 (b): Comparison of FTIR spectra between untreated EWE 5% and treated EWE 5%.

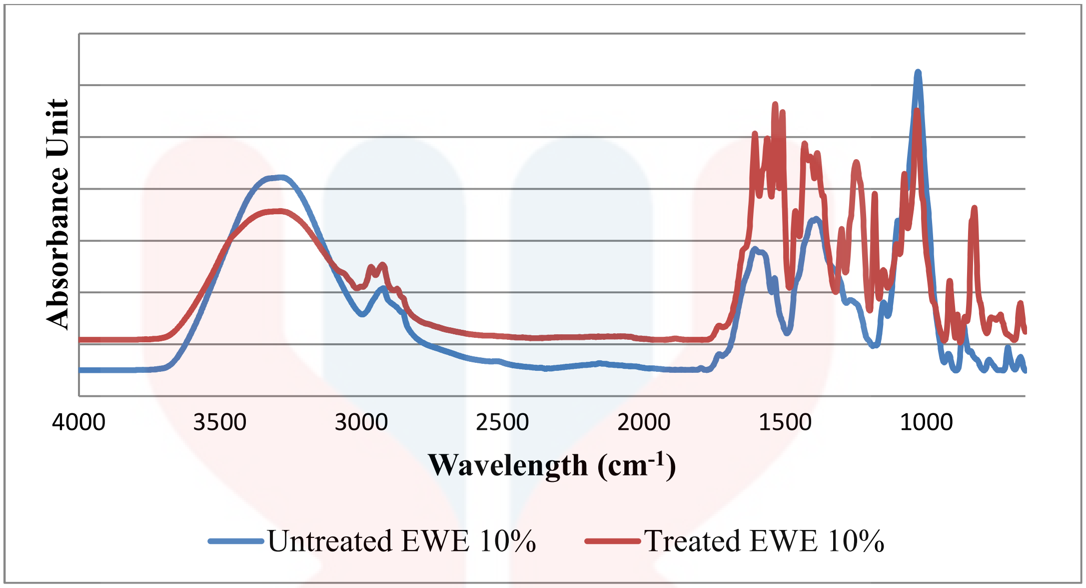


Figure 4.2 (c): Comparison of FTIR spectra between untreated EWE 10% and treated EWE 10%

From the FTIR spectra above, it can be seen that many peaks existed representing many functional groups present in the samples. The first observation dealt with the IR spectra shows the strong absorption band at 3282 cm^{-1} which was assigned to hydroxyl group O-H and amine N-H symmetrical stretching vibrations. This is possibly due to the main component of the bio-composite thin film made up of water. Water has similar properties with alcohols where water molecules contain hydroxyl groups that can form hydrogen bonds with other water molecules besides with alcohol molecules. With the similar properties, alcohol can form hydrogen bonds with other alcohol molecules as well as with water molecules. Another reason for the appearing of hydroxyl group due to the glycerol used in the experiment has three hydroxyl functional groups that are responsible for its solubility in water (Leroy, 2016; Stewart, 2016).

The second observation dealt with the absorption band at 2922 cm^{-1} was due to symmetric hydrocarbon C-H stretching absorption band of CH, CH_2, and CH_3. The C-H stretching mode represented the aliphatic nature of the banana peels (Kamsonlian *et al.*, 2011). The absorbance at 1730 cm^{-1} attributed to carbonyl C=O stretching vibration. This phenomenon represents the linkage of ester group in hemicelluloses or carboxylic acid in lignin (Sawpan *et al.*, 2011). A sharp peak at 1606 cm^{-1} was assigned to the characteristics of C=C in aromatic rings due to the stretching of aromatic ring of lignin (De Rosa *et al.*, 2011).

The peak at 1511 cm^{-1} was corresponding to CH_2 bending in lignin while peak at 1374 cm^{-1} was due to O-H in-plane bending. While the shift at 1029 cm^{-1} was assigned to C-O carboxyl band which it is indicating the stretching of acetyl in lignin (Kamsonlian *et al.*, 2011). Some similar peaks are obtained and observed in the previous studied by Lai *et al.* (2008) and Khormaei *et al.* (2007). Lastly, the small sharp peaks at 900 cm^{-1} was observed and assigned to β-glycosidic linkage between sugar units in cellulose and hemicelluloses (Sawpan *et al.*, 2011).

According to Table 4.2, for treated samples, the absorbance unit of hydroxyl absorption peaks in EWE 0% was higher than of untreated EWE 0% due to the efficiency of silane agent (Sawpan et al., 2011). With the addition of eggshell filler in composite, the absorbance value of treated samples is getting lower than untreated samples at the same constituent and even the absorbance index of treated EWE 10% is ultimately lower than untreated EWE 10%. This situation might due to the addition of filler in composite where the fillers will absorb the considerable amounts of hydroxyl that appeared after silane treatment applied on fibers (De Rosa *et al.*, 2011).

A well-defined peak at 1200 cm^{-1} was assigned to –Si-C-Si- bond and this showed the reaction between cellulose of banana peels and hydrolyzed silane. The characteristic band at 778 cm^{-1} was attributed to –Si-C- symmetrical stretching while band at 710 cm^{-1} was corresponded to –Si-O-Si- symmetric stretching. Moreover, treated samples have showed the slightly weak absorption peak of carbonyl group at 1730 cm^{-1}. Next, the phenomenon of decreased in the band splitting of C-H bond stretching vibrations range of methyl and methylene groups indicated the removal of lignin- like structure (De Rosa *et al.*, 2011).

Table 4.2: Comparisons of OH absorbance unit of untreated and treated samples.

Samples	**Absorbance unit of OH stretch**	
	Untreated	Treated
EWE 0%	0.17	0.20
EWE 5%	0.18	0.16
EWE 10%	0.19	0.13

Table 4.3: Wavelength of peaks used for FTIR analysis and its corresponding functional groups (Gunawan *et al.*, 2010; Kabir *et al.*, 2013; Miao & Zhang, 2011; Sawpan *et al.*, 2011; Grill, 2009)

Characteristics Absorption(s) (cm^{-1})	**Functional Groups**
3550-3200	O-H stretch
2950-2850	C-H stretch
1750-1735	C=O stretching of carboxylic acid or ester (lignin)
1700-1500	C=C stretching of aromatic ring (lignin)
1470-1350	CH_2 symmetrical bending (lignin)
1430-1330	-OH bending
1250-970	C-O stretching of acetyl (lignin)
1000-970	β-glycosidic linkage
1260-1000	-Si-O-C- stretching
800-780	-Si-C- symmetric stretching
720-700	-Si-O-Si- symmetric stretching

4.3 Thermogravimetric Analysis (TGA-DTA)

Thermogravimetric analyses (TGA) were carried out with the aim of determining the thermal stability and the influence of silane treatment on the bio-composite samples thermal properties (Pereira *et al.*, 2013). The onset degradation temperature (T_d) of untreated and treated bio-composite thin film samples for weight loss changed with temperature are tabulated in Table 4.4 (a), (b) whereas TG/DTA curves are shown in Figure 4.3 (a), (b) and Figure 4.4 (a), (b) respectively.

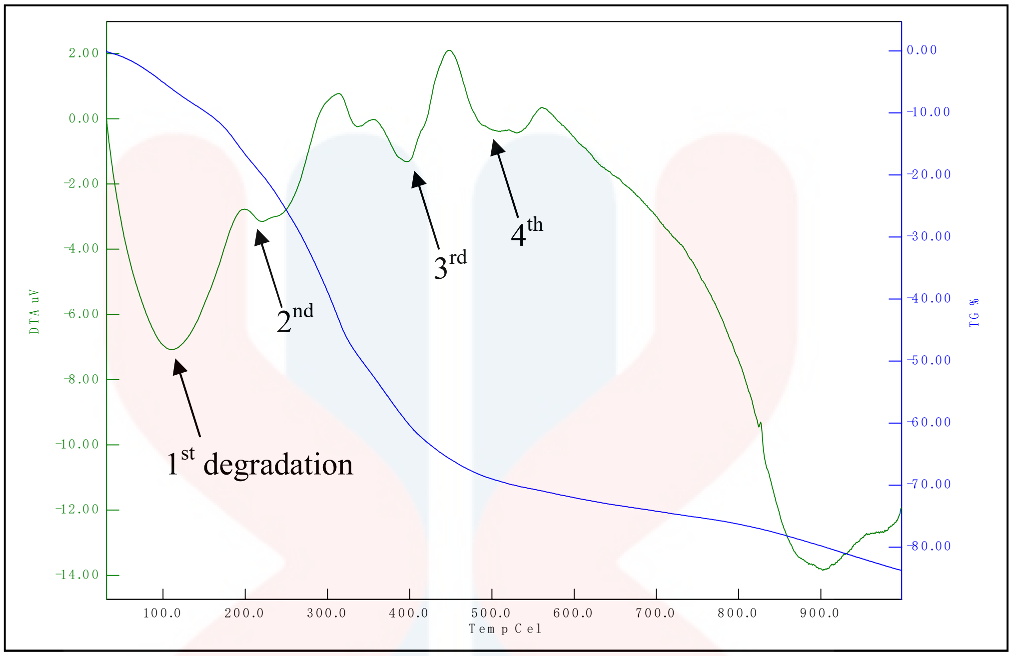


Figure 4.3 (a): TG/DTA curves of untreated EWE 0%.

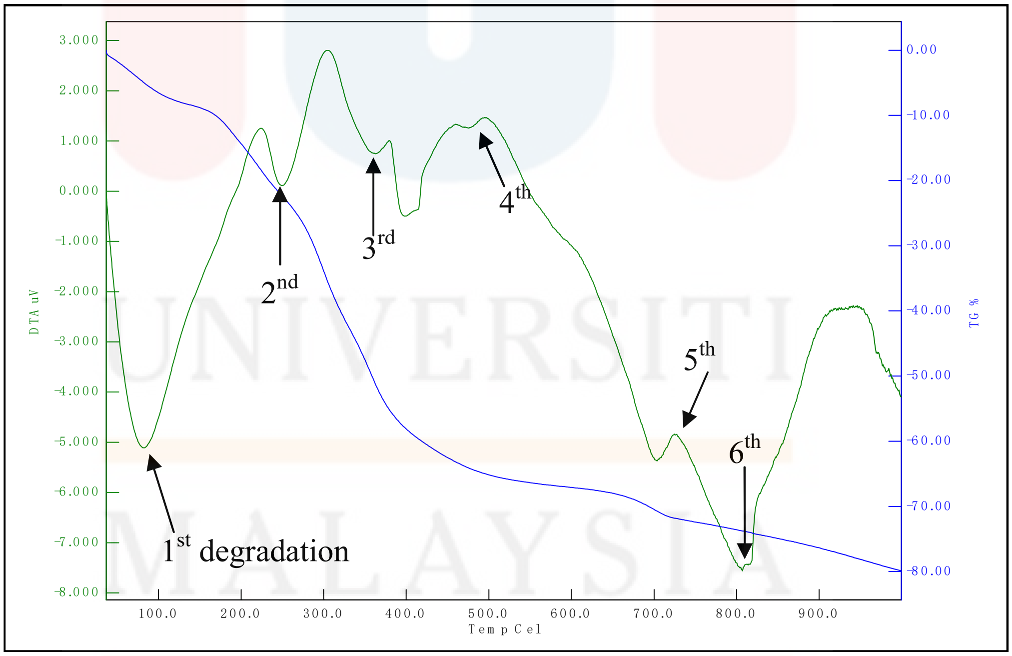


Figure 4.3 (b): TG/DTA curves of untreated EWE 10%.

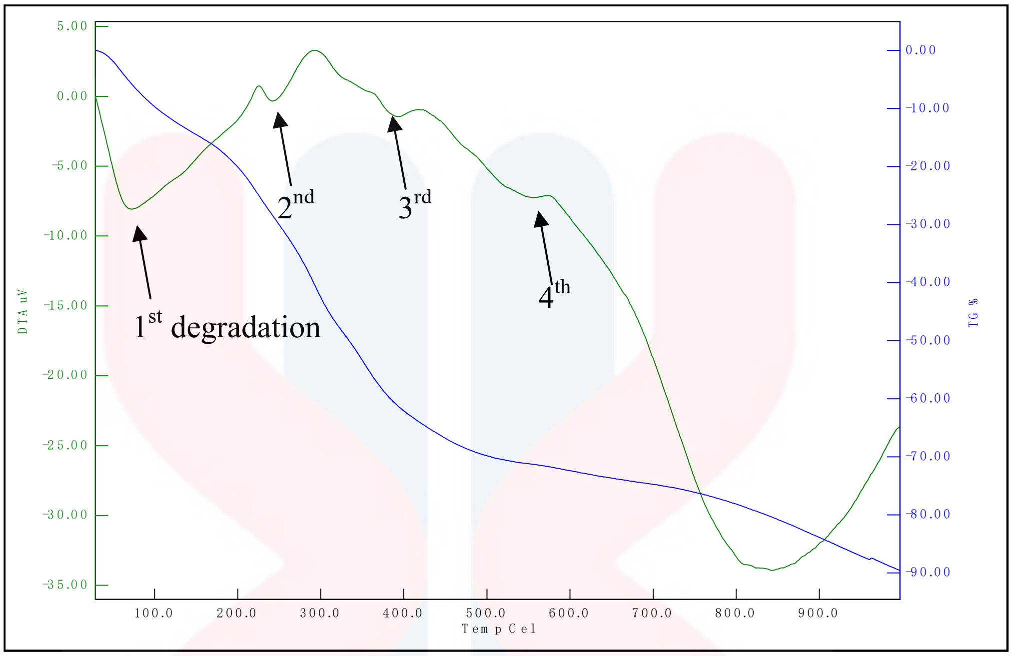


Figure 4.4 (a): TG/DTA curves of treated EWE 0%.

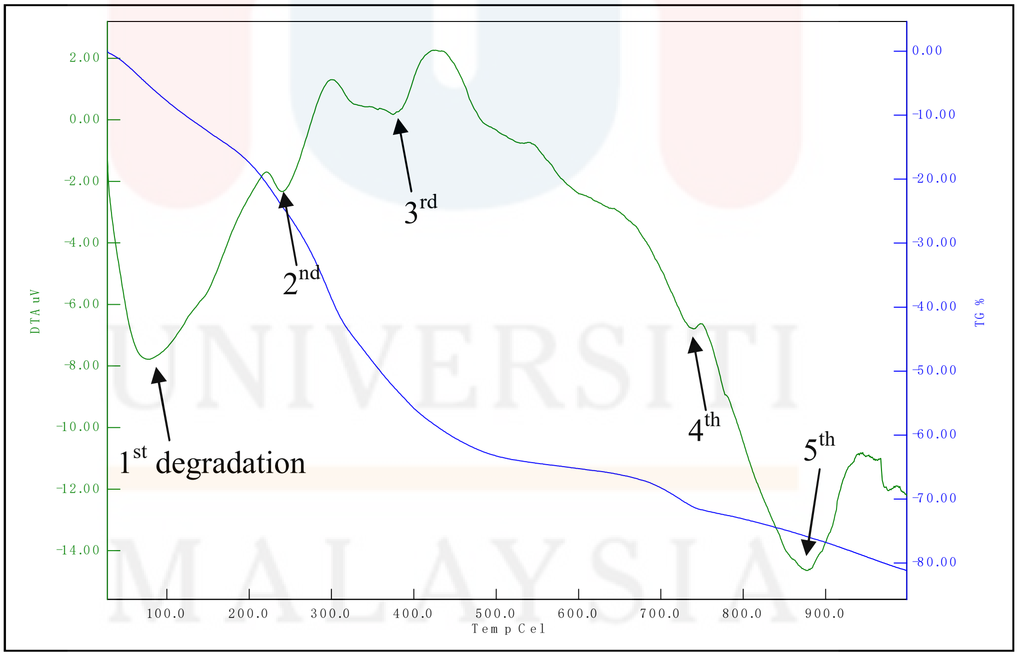


Figure 4.4 (b): TG/DTA curves of treated EWE 10%.

Table 4.4 (a): Thermal degradation data and residual weight of untreated samples

	Sample	ΔT (°C)	T_{peak} (°C)	T_d (°C)	Mass loss (%)	Residue at 900°C (%)
Untreated	EWE 0%	0 - 200 200 - 320 320 - 450 450 – 900	110 220 390 500	205	17.0 26.5 23.5 13.0	20.0
	EWE 5%	0 - 200 200 - 320 320 - 410 410 - 465 465 – 900	90 225 370 500 720	210	21.0 29.0 12.0 4.5 12.5	21.0
	EWE 10%	0 - 200 200 - 320 320 - 390 390 - 510 510 - 715 715 – 900	75 250 360 505 700 820	235	15.0 22.5 19.5 8.5 5.5 5.0	24.0

Table 4.4 (b): Thermal degradation data and residual weight of treated samples

	Sample	ΔT (°C)	T_{peak} (°C)	T_d (°C)	Mass loss (%)	Residue at 900°C (%)
Silane Treated	EWE 0%	0 - 235 235 - 300 300 - 425 425 - 900	80 245 385 560	240	27.0 16.0 22.0 18.0	17.0
	EWE 5%	0 - 220 220 - 310 310 - 485 485 - 900	90 240 375 630	225	26.0 23.0 22.0 9.0	20.0
	EWE 10%	0 - 230 230 - 315 315 - 425 425 - 750 750 – 900	85 240 370 740 880	235	22.0 19.0 18.5 13.0 4.5	23.0

It can be seen that data in Table 4.4 (a), untreated EWE 0%, consists four decomposition steps unlike EWE 5% and EWE 10% which there are five and six steps of degradation, respectively. In the first step of degradation, it shows that 110 °C, 90 °C and 75 °C are on the first degradation peak for untreated EWE 0%, EWE 5% and EWE 10% respectively. This observation shows that a weight loss related to desorption of water of the polysaccharide structure. According to Guimaraes *et al.* (2009), the total elimination of water in fibers was quite difficult since fibers have their hydrophilic nature even though the fibers were dried before the experiment. The hydrophilic nature will then reduce the interfacial bonding between fibers and increase its moisture absorption after it is imparted by hydroxyl groups of cellulose in those fibers (Pai & Jagtap, 2015).

For second phase, untreated EWE 0%, EWE 5%, and EWE 10% show at 220 °C, 225 °C and 250 °C respectively. This second phase of degradation related to the decomposition of the hemicellulose content which present in fibers. It has been reported that the decomposition of hemicelluloses is within the temperature range of 180 °C and 350 °C (Liu & Yu, 2006). Hemicellulose will degrade faster than other chemical components in fibers such as cellulose and lignin. This is due to hemicellulose consists of acetyl groups which may responsible to lower its thermal stability. Thus, hemicelluloses will undergo cellular breakdown as the temperature increasing.

In the previous stage, small amount of amorphous cellulose has been degraded, thus the third stage involved the degradation of crystalline cellulose. In fact, cellulose is more thermally stable than hemicelluloses due to its crystalline nature where it is bonded to form microfibrils structure by hydrogen bonding (Gajiwala & Zan, 2000). Therefore, when the temperature is greater than 300 °C, the samples showed major weight loss (37% to 50%) because of the decomposition of cellulose and lignin. According to Zhang *et al.*, (2009), crystalline cellulose decomposed at the critical temperature of 320°C and in this experiment, untreated EWE 0% (390 °C), EWE 5% (370 °C) and EWE 10% (360 °C) had achieved that temperature range.

The decomposition of lignin was in a slow motion and it occurred under the temperature range up to 850 °C. This is because lignin is composed of heavy cross-linked molecules besides polysaccharides thus making it hard to decompose when undergoes thermal decomposition. Thus, lignin is considered as the most difficult component in decomposition compared to the organic components due to its slow decomposition (Sevilla & Fuertes, 2011). In the previous studied by Bignotti *et al.* (2002), banana fibers showed its maximum decomposition at 502 °C. In this fourth stage, all untreated samples EWE 0% (500 °C), EWE 5% (500 °C) and EWE 10% (505 °C) showed the stage of lignin decomposition. This situation showed the evidence of breaking protolignin bonds in fibers (Sevilla & Fuertes, 2011).

Untreated EWE 0% completed its decomposition at the fourth stage unlike EWE 5% and EWE 10% still have not finished their decomposition due to factor of eggshell filler added into these two ratios of samples. A dry eggshell is approximately 94% of calcium carbonate ($CaCO_3$) by mass (Lechtanski *et al.*, 2000). The addition of $CaCO_3$ in the composite causing the crystalline regions of composite decreased due to bonding energy between polymer chain are reduced by $CaCO_3$ and finally resulting in decreasing its melting point. Hence, the higher the amount of $CaCO_3$ added to the composite, the composite melting point getting lower (Gunawan *et al.*, 2010). The greater the amounts of eggshell in the composite, the stages of decomposition will have increased. For instance, untreated EWE 10% has more decomposition stages than untreated EWE 5%.

Generally, the numbers of decomposition peaks for both treated and untreated EWE 0% are less than EWE 5% and EWE 10%. This is due to the thermal stability of specimen affected by percentage of banana peel fibers. The higher the percentage of banana peel fibers in the sample, the greater the thermal stability, therefore less thermal changes will have occurred in the testing (Ma *et al.*, 2005). This situation is due to fiber contains vacant structure that will lead to low thermal conductivity (Lee *et al.*, 2010). For the aspect of residual weight of samples, untreated EWE 0% left only 20% of samples weight and it considered as the least amount of residue compared to untreated EWE 5% (21%) and EWE 10% (24%). This phenomenon is due to the eggshell filler in EWE 5% and EWE 10% causing the incomplete decomposition of $CaCO_3$ thus resulting ashes and $CaCO_3$ remaining at the end of TGA testing.

According to the silane treated samples result presented in Table 4.4 (b), the results obtained are similar with the results of untreated specimens which included the process of removable of water soluble components at the first stage, decomposition of hemicelluloses at second, decomposition of crystalline hemicelluloses and lignin at third stage and fourth stage respectively. From Table 4.4 (b), it can be observed that silane treated EWE 0% exhibited hemicelluloses peak at around 240 °C which is similar to untreated EWE 0%.

This situation showed silane treatment was incapable of eliminating hemicelluloses from the fibers. In fact, silane molecules formed couplings with lignin and hemicelluloses constituent of fibers instead of eliminating them from the fibers. The silane coupling agent acted as a protective covering layer on fiber surface to protect the fiber from thermal decomposition at higher temperatures and thus, the breakdown of fiber's molecular structure was prevented. Therefore, overall thermal stability of treated samples was enhanced at higher temperature indicating greater thermal stability of silane treated samples (Kabir *et al.*, 2008).

4.4 Water Absorption and Thickness Swelling Characteristics

Figure 4.5 (a) and (b) show the thickness swelling behavior of the silane treated and untreated samples at different relative ratios of eggshell reinforcement. A comparison of thickness swelling percentage has been concluded and tabulated in Table 4.5. Thickness swelling of specimens was calculated from thickness measurements at three different points before and after the specimens soaked into the distilled water for the duration of 120 hours.

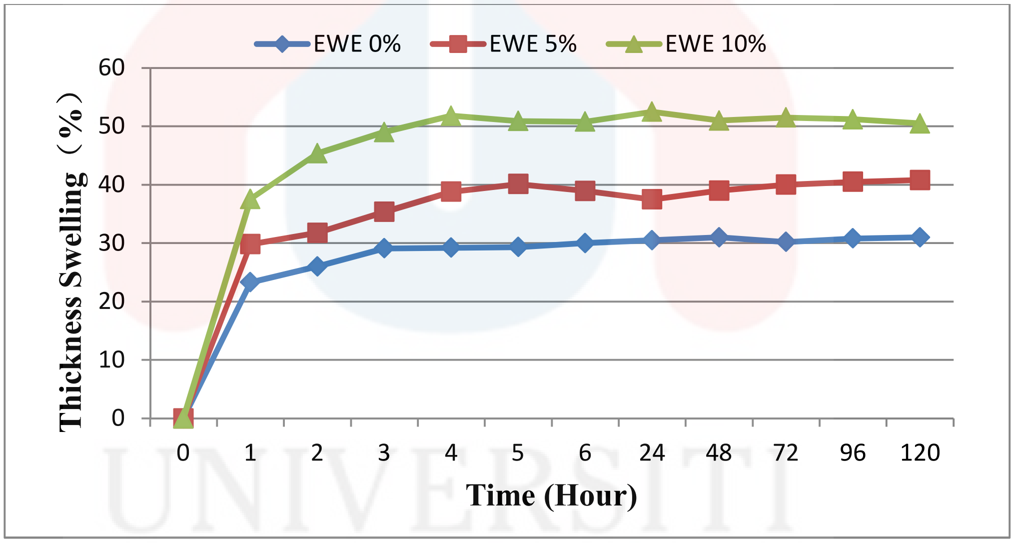


Figure 4.5 (a): Thickness swelling of untreated samples.

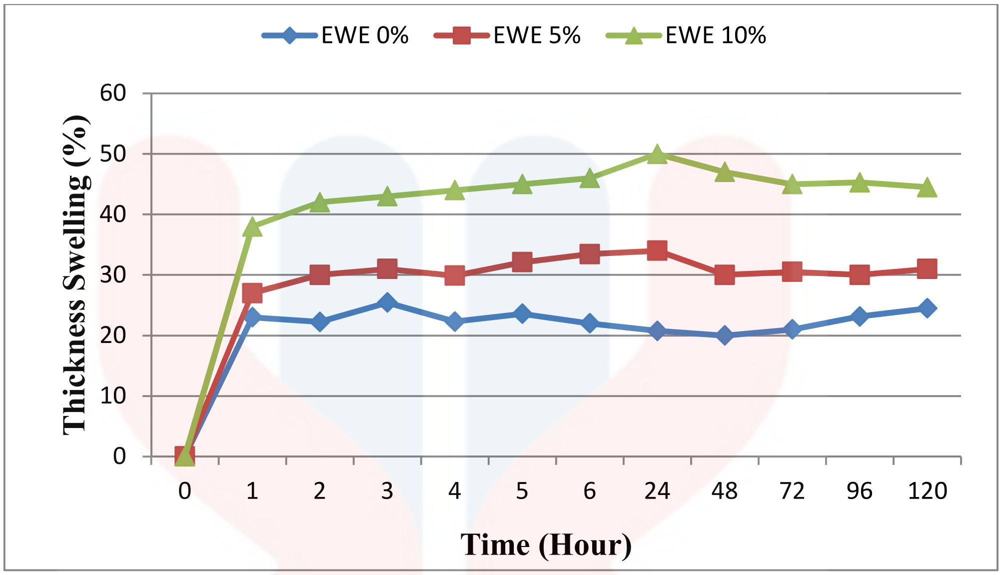


Figure 4.5 (b): Thickness swelling of treated samples.

Table 4.5: Thickness swelling percentage of treated and untreated samples.

Samples	Thickness Swelling (%)	
	Untreated	Treated
EWE 0%	8	2
EWE 5%	10	4
EWE 10%	12	7

At the initial stage of absorption process, both figures show the thickness swelling increased linearly, later, the increasing rates has slowed down and it finally reached to water uptake at equilibrium. In Table 4.5, untreated EWE 0%, EWE 5% and EWE 10% have increased their thickness swelling by 8%, 10% and 12% respectively whereas treated EWE 0%, EWE 5% and EWE 10% have increased by 2%, 4% and 7% respectively. Among three ratios, EWE 10% has the highest moisture absorption, followed by EWE 5% and EWE 0%. This is due to the addition of eggshell in EWE 10% and EWE 5% composite (Santos *et al.*, 2002).

As reported by Abdel-Salam *et al.* (2011), water absorption of the composite increases as the amount of filler ($CaCO_3$) added increases. This situation may be attributed to the fact of $CaCO_3$ contains hydrophilic sites and thus it is expected to increase in moisture absorption in composite (Oksman & Clemons, 1998). This reason was supported by Kord (2011) where the water absorption capacity in HDPE-CC composite had increased as the amount of $CaCO_3$ increased. This situation can be explained by the research of Santos *et al.* (2002) where addition of filler in composite can significantly increase its water uptake due to the presence of filler particle and porosity aggregates in the microstructure of composite, even though the adsorption of water on the filler surface has not been removed.

For the comparison of silane treated and untreated samples in same composition of eggshell filler, it shows that thickness swelling in treated samples is lower than that of untreated samples. For instance, untreated EWE 10% has 12% of thickness swelling and the value drops to 7% after silane treatment due to lesser water absorption in treated samples. According to Arsène *et al.* (2013), silane in aqueous media are reactive molecules which will then form into dimers or oligomers by the condensation of silanol. Hence, silanes are commonly exhibits greater repellent effect and it is used as commercial water repellents. Additionally, silane treatment can decrease the hydrophilicity of fibre by decreasing the hydroxyl groups in the fibers (Wang *et al.*, 2007).

Nevertheless, Arsène *et al.* (2013) also reported that silane grafted onto the fiber surface to form a polysiloxane molecules network. Banana fibers are swelled due to the morphology of fibers had modified and the fibers porosity and its dimensions have increased at the same time. Thus water absorption decreases with the addition of silane content in treatment solution. In a conclusion, silane treatment can decrease water absorption of fibers and it may lead to low moisture absorption properties of the bio-composite samples.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this research, bio-composite thin film was successfully produced by waste banana peel reinforced with eggshell filler and laminated with epoxy resin. Besides, some portions of banana peels were treated with silane coupling agent in order to determine the effect of silane treatment on the fiber properties. The objectives were achieved with the evidence of the physical and thermal properties of bio-composite thin film samples were observed and analyzed.

For physical properties, Fourier Transformation Infrared (FTIR), X-ray diffraction (XRD), and thickness swelling test were carried out. FTIR analysis indicated the presence of new -Si-O-C- bond, –Si-O-Si- bond and-Si-C- bond in silane treated samples compared to untreated samples. These new bonds formed as the evidenced of the reaction between hydrolysed silane agent and banana peel fibers. The intensity of OH absorption peaks in treated samples was higher than untreated samples, however, the intensity of treated samples were getting decreased along with the increased of percentage of eggshell filler in the composite. This phenomenon due to some considerable amounts of hydroxyl was absorbed by eggshell after silane treatment.

For XRD result, treated samples had high crystallinity index than of untreated samples and the crystallinities index increased along with the eggshell percentage. Thus, treated EWE 10% had the highest crystallinity among the samples due to lignin and hemicelluloses in fibers had been removed during silane treatment process and it contained the highest percentage of eggshell filler. On the other hand, silane treatment results in decrease in water absorption and thickness swelling by the composite. Without eggshell filler, further reduction is observed. Silane treatment of banana peel fiber results in greater hydrophobicity and less water absorption by the composite samples.

Last but not least, for thermal properties, thermogravimetric analysis (TGA) was carried out to determine the weight lost of silane treated samples was lower than untreated samples. Addition of silane coupling agent and eggshell filler caused melting point of bio-composite samples increased and hence enhanced its thermal stability. This is due to silane treatment forms a covering layer on fiber surface and fills the spaces among the microfibrils.

5.2 Recommendations

In my opinion, further research can be done in this experiment by using different chemical treatments on fibers such as alkali treatment, acetylation and maleic anhydride treatment. Different chemical treatments used on fibers may result different properties due to their different constituents. Hence, the best chemical treatment can be observed and selected through the comparison. Besides, different chemical treatment used may influence the sample's physical and thermal behavior. Moreover, other testing can be carried out for further investigation such as mechanical testing. Mechanical testing for instance, tensile test, tear resistance test and flexural test can provide us the information about sample's toughness, strength and ductility.

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APPENDICES

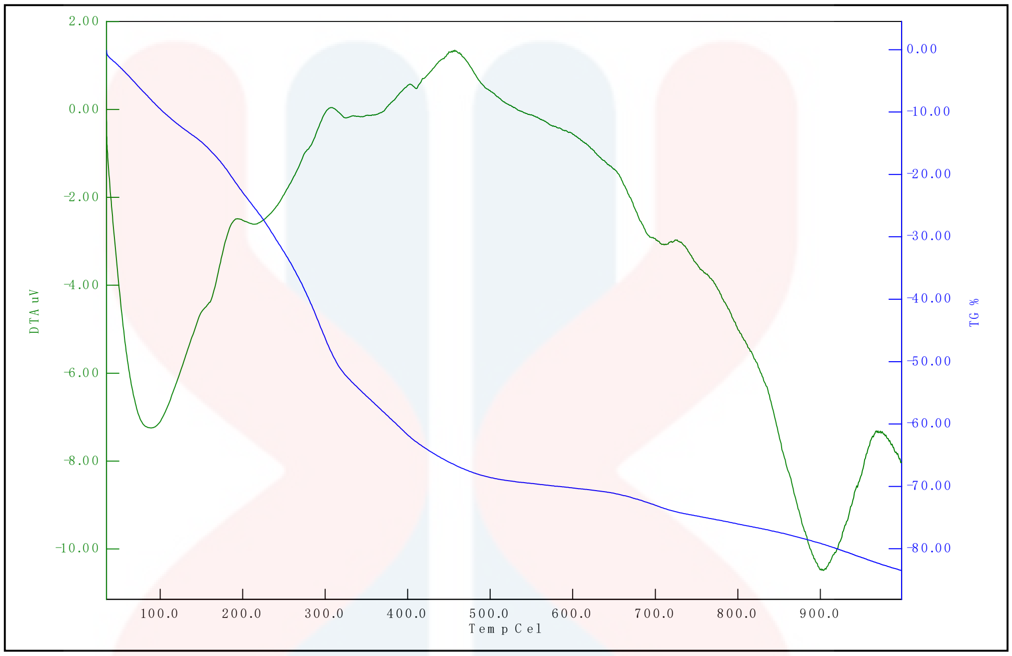

Figure 1: TG/DTA curves of untreated EWE 5%.

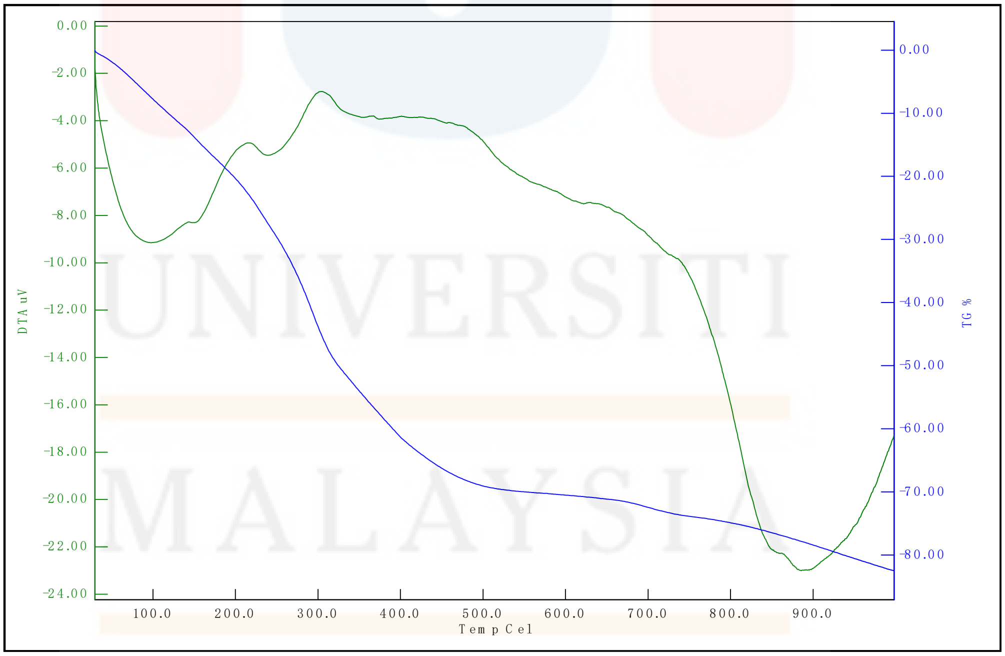

Figure 2: TG/DTA curves of treated EWE 5%.