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EFFECT OF FIBER SURFACE TREATMENT ON MECHANICAL AND THERMAL PROPERTIES OF POLYLACTIC ACID/KENAF FIBER COMPOSITE

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled: "**Effect of fiber surface treatment on mechanical and thermal properties of polylactic acid/kenaf fiber composite**".I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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LIST OF ABBREVIATIONS

ATKF	Alkali treated kenaf fiber
APS	Amino silane
APTES	3-Aminopropyltriethoxysilane
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
FTIR	Fourier transform infrared spectroscopy
PLA	Polylactic acid
PLA/ATKF20	PLA filled with 20 wt% ATKF
PLA/STKF20	PLA filled with 20 wt% STKF
PLA/UTKF20	PLA filled with 20 wt% UTKF
SEM	Scanning Electron Microscope
STKF	Silane treated kenaf fiber
TGA	Thermogravimetric Analyzer
UTKF	Untreated kenaf fiber

LIST OF SYMBOLS

T_{10}	Temperature when 10 % of weight is lost
T_{cc}	Cold crystallization temperature
T_g	Glass transition temperature
T_m	Melting temperature
T_{max}	Maximum decomposition temperature
T_o	Onset decomposition temperature
W_f	Weight fraction of kenaf fiber
X_c	Degree of crystallinity
ΔH_m	Enthalpy of heat of fusion
ΔH^o_m	Enthalpy of perfect heat of fusion

KESAN PENGUBAHSUAIAN PERMUKAAN GENTIAN ATAS SIFAT-SIFAT MEKANIKAL DAN TERMA POLILAKTIK ASID/ GENTIAN KENAF KOMPOSIT

ABSTRAK

Dalam kajian ini, kesan pengubahsuaian permukaan gentian atas sifat-sifat mekanikal dan terma Polilaktik asid/gentian kenaf komposit yang dihasilkan daripada ekstruder skru tunggal diikuti oleh pengacuan suntikan telah dikaji. Pengubahsuaian alkali telah dilakukan dengan merendam gentian kenaf dalam 5% kepekatan NaOH selama 2 jam manakala modifikasi silana telah dilakukan dengan merendam gentian kenaf dalam 5% kepekatan ejen pengkupel silane yang telah dilarutkan dalam campuran air - etanol (40:60 w/w) selama 3 jam. Pengaruh pengubahsuaian gentian ke atas sifat-sifat kimia dan morfologi gentian kenaf telah dicirikan dengan menggunakan Fourier Transform Infrared Spektroskopi (FTIR) dan mikroskop elektron imbasan (SEM). Didapati modifikasi alkali berkesan dalam menghilangkan bendasing di permukaan gentian dan bahan-bahan bukan selulosa seperti hemiselulosa dan lignin manakala modifikasi silana tidak menunjukkan kesan yang ketara ke atas sifat-sifat ini. Sifat mekanikal PLA/gentian kenaf komposit telah disiasat dengan menggunakan ujian tegangan dan hentaman, manakala sifat terma telah dicirikan dengan menggunakan penganalisa termogravimetrik (TGA) dan kalorimeter pengimbasan pembezaan (DSC). Modifikasi alkali didapati meningkatkan kedua-dua sifat mekanikal dan terma PLA / gentian kenaf komposit berbanding dengan komposit yang gentiannya tidak dimodifikasi atas sebab pembuangan hemiselulosa dan lignin telah mengasarkan permukaan gentian, membawa kepada meningkatkan interaksi lekatan antara gentian and matrik melalui saling kunci mekanikal. Sifat-sifat mekanikal dan terma komposit yang gentian dimodifikasi dengan silane meningkat selanjutnya disebabkan oleh peningkatan dalam interaksi lekatan antara gentian dan matrik oleh ikatan kimia yang lebih kuat berbandingan dengan saling kunci mekanikal.

EFFECT OF FIBER SURFACE TREATMENT ON MECHANICAL AND THERMAL PROPERTIES OF POLYLACTIC ACID/KENAF FIBER COMPOSITE

ABSTRACT

In the present study, the effect of fiber surface treatment on mechanical and thermal properties of Polylactic acid/kenaf fiber composite manufactured by single screw extruder followed by injection moulding were investigated. The alkali treatment was done by treating the kenaf fiber with 5 % NaOH solution for 2 h while silane treatment was done by soaking fiber in 5 wt% of silane coupling agent which was dissolved in a mixture of water – ethanol (40:60 w/w) for 3 h. The influence of fiber treatment on chemical and morphological properties of kenaf fiber was investigated with Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM). It was found that alkali treatment effectively removed surface impurities and non-cellulosic materials such as hemicellulose and lignin while silane treatment did not show a significant effect on these properties. Mechanical properties of PLA/kenaf fiber composite were investigated with tensile and impact test, while the thermal properties measurement was carried out using Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC). The alkali treatment was found to improve both mechanical and thermal properties of PLA/kenaf fiber composite as compared to untreated fiber composite which appears to be due to the removal of hemicellulose and lignin roughen the fiber surface, led to increase in interfacial adhesion via mechanical interlocking. The mechanical and thermal properties of silane treated fiber composite were increased further due to enhanced interfacial adhesion by chemical bonding which is stronger than mechanical interlocking.

Chapter 1

INTRODUCTION

1.1 Research Background

Polymer composite is currently used for a wide range of applications. However, synthetic fibers in the reinforcement of petrochemical-based composite do not undergo biodegradation in landfill or composting environment, resulting in a serious environmental pollution (Zini and Scandola, 2011). As environmental awareness is raising in the community, it led to growing interest in the use of more environmental friendly and sustainable materials. Over the past decades, natural fiber reinforced bio-derived polymer matrix composites, commonly referred as bio-composites have attracted attention as subject of many research studies and commercial product in engineering market (Yousif et al., 2012)

The application of natural fiber reinforced bio-composites are growing in many sectors such as automotive, construction, furniture and packaging fields. In addition to being biodegradable, natural fiber reinforced bio-composites also possess several other advantages such as lightweight, low cost, high specific strength, high modulus, reduced tool wear and safe manufacturing process (Akil et al., 2011). Therefore, they are widely manufactured into interiors of automotive, engine and transmission cover, door panels, seal backs and packages. Some research studies say that adoption of natural fiber bio-composite in automotive parts emit lesser carbon dioxide when poly(lactic acid) (PLA) was used as compared to other petrochemical-base thermoplastics (Chen, 2005).

Generally, matrix that is used in polymer composite can be categorized into thermoset and thermoplastic. The difference between these is that thermoplastic remains permanently fusible when heated while cured thermoset do not soften upon heating (Akhtar et al., 2016). Common thermoset matrices are polyester resin, epoxy, and phenolic, while polyethylene (PE), polypropylene (PP) and PLA are the common thermoplastic material used in research studies on polymer composite. To obtain an environmentally friendly composite, the biodegradable thermoplastic is more desirable selection for the matrix. PLA, polyhydroxybutyrate (PHB), polyhydroxyalkanoates, cellulose esters, and soy-resin are the examples of fully biodegradable thermoplastic polymer (Doppalapudi et al., 2014). These biodegradable matrices have limited processability, poor commercial availability and high moisture absorption (Nor Azowa et al., 2009). Among these matrices, PLA can be used commercially in its non-reinforced form. PLA has good properties in term of strength, aesthetics and processability in most equipment (Huda et al., 2008). However, the cost of PLA is significantly high and its brittleness limits its potential for practical commercial application.

Besides that, the selection of the type of natural fiber to produce bio-composite is another major issue. Various types of natural fiber can be used in the production of bio-composite. Natural fiber can be classified into two major categories, that are plant fiber and animal fiber (Zini and Scandola, 2011). Plant fibers such as sisal, jute, hemp and kenaf are commonly used in recent research studies because they are biodegradable, low cost, low weight, less damage to processing equipment, good relative mechanical properties in term of strength and stiffness and lastly their renewable and abundant resources (Li et al., 2007). These advantages of natural fiber as compared to synthetic fiber make them a potential substitute to synthetic fiber as reinforcement and filler for polymer composites. Among the wide variety of plant fibers, Kenaf (*hibiscus cannabinus*) is an attractive choice due to its capability to growth rapidly over a wide range of climatic conditions (Asumani et al., 2012).

In a composite, the fibers contribute strength and stiffness to support load while the matrix holds fibers together, protects them from environmental factors and transfer applied load to the fiber via the interface (Pickering et al., 2016). Although addition of natural fibers aims to reinforce the polymer matrix, there are limitations that limit the effect of reinforcement. Therefore, research aims to address the shortcoming of natural fiber reinforced bio-composite would be expected to increase commercial availability of these materials.

1.2 Problem Statement

The mechanical properties of a composite not only depend on properties of its matrix and fiber but also the interfacial bonding between them. Many research studies reported that the mechanical properties of natural fiber reinforced composite highly depended on the interface adhesion between fiber and polymer matrix. A strong interfacial bonding provides composite that shows good strength and stiffness (Huda et al., 2008).

Natural fibers, such as kenaf are polar and hydrophilic material due to the hydroxyl group of celluloses, hemicelluloses, pectin and lignin which composed in most of the natural fibers. On the other hand, polymer materials such as PLA are nonpolar and hydrophobicity in nature. Therefore, there is a significant limitation in term compatibility between both natural fiber and polymer matrix regardless of thermoset or thermoplastic (Taib et al., 2014). This limitation causes undesirable mechanical properties of natural fiber reinforced composite due to difficulties in obtaining an effective fiber-matrix interface adhesion, which further resulting ineffective load transfer between reinforcing fiber and polymer matrix (Pickering et al., 2016).

Large group of recent researchers has focused on modification of natural fiber and polymer matrix to tackle the limitation of compatibility and interfacial adhesion (Yousif et al., 2012). Various treatments have been suggested to improve the compatibility between lignocellulosic fibers and polymer matrices such as alkali treatment, silane treatment, use of maleated coupling agent, acetylation, and benzoylation. Alkali treatment and silane treatment have been widely studied and reported among these methods (Li et al., 2007).

Alkali treatment is normally done by soaking the fibers in an alkaline solution for a period of time. This method causes the removal of wax and oil from fiber surface and fiber cell wall polymer which is hemicellulose and lignin (Li et al., 2007). Many research work state that alkali treatment improves surface roughness and increase the number of cellulose on the fiber surface so that more surface of fiber exposed to chemical bonding with the matrix (Akhtar et al., 2016). Many research works studied using a different concentrations of alkaline solution with a different periods of immersion time for the fiber treatment. According to previous study (Edeerozey et al., 2007), 6 wt% NaOH solution was effective at removal of impurities from the fiber surface. When the concentration of NaOH solution further increased more than 6 wt%, the fiber surface appears to be damaged, defects in fiber had increase thus the fiber strength reduced.

Silane treatment is done by immersing fibers in a diluted silane solution by a mixture of water/alcohol or water/ketone. Silane will break down into silanol and alcohol in the presence of water. This silanol will form a stable covalent bond with the hydroxyl group of celluloses in natural fibers. Thus, the fiber surface area and degree of cross-linking in the interface region increased, which further increase the interfacial bonding between fibers and matrix (Huda et al., 2008). Previous study, Van de Weyenberg et al. (2003) report that flax fiber immersed in 1% solution of 3-aminopropyltrimethoxysilane diluted in a 50/50 mixture of acetone and water for 2 h. The silane treated fiber was used to reinforce epoxy at a volume fraction of 40%. The tensile strength only increased by 4% as compared to untreated fiber, however, the tensile modulus improved by approximately 45%.

Commonly used processing techniques of thermoplastic polymer based composite are extrusion, compression molding, pultrusion, resin transfer molding and injection molding. Among these processing techniques, injection molding is the front-runner in term of productivity in producing polymer composites. At present, polymer composite manufacturers need to fabricate quality product at a low price, which is practically related to production time, volume, and cost of composite systems due to the rapid development of markets (Tanahashi, 2010). Therefore, injection molding has been widely used in various industries to produce thermoplastic polymer based composite for a long time. It is more encouraging to use industrial automatic processing technique than the manual conventional method in research studies to enhance commercial success of polymer composite. However, studies reported on PLA/kenaf fiber composite prepared by injection molding technique is still limited.

In this work, research efforts to overcome the shortcoming listed above were taken. PLA/kenaf fiber composite was produced using single screw extruder and injection molding. Efforts were made to increase the interfacial strength between matrix and fiber by using alkali treatment and silane treatment. The thermal, morphological and mechanical properties of untreated fiber, treated fiber and PLA/kenaf fiber composite were then evaluated.

1.3 Research Objectives

The objectives of the study are summarized as follow:

1. To study the effect of fiber surface treatment on chemical and morphological properties of kenaf fiber.
2. To investigate the effect of fiber surface treatment on the mechanical and thermal properties of PLA/kenaf fiber composites.

1.4 Scope of study

In this study, the kenaf fiber was modified using alkali treatment and silane treatment. The chemical and morphological properties of untreated and treated fibers were investigated using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope. Next, pure PLA and PLA/kenaf fiber composite were prepared using single screw extruder and injection moulding. The mechanical properties of pure PLA and PLA/kenaf fiber composite were characterized by tensile and impact test. The thermal properties of pure PLA and PLA/kenaf fiber composite were investigated using Thermogravimetric Analyzer and Differential Scanning Calorimetry (DSC).

1.5 Thesis structure

This thesis is divided into 5 chapters.

Chapter 1 gives general information about the study including an introduction, research rationale, research objectives and a structure of the thesis.

Chapter 2 presents general knowledge and relevant literature related to matrices and natural fires. It also includes fiber surface modification method and processing method of the thermoplastic composite.

Chapter 3 provides the information of materials and method of fiber surface modification and composite preparation used in this study. The general description of the characterization methods used also included in this chapter.

Chapter 4 covers the experimental result and discussion of the effect of fiber surface treatment on chemical and morphological properties of fiber and mechanical and thermal properties of the composite.

Chapter 5 draws the conclusion of this study and recommendation for future work.

Chapter 2

LITERATURE REVIEW

2.1 Biodegradable polymer

Synthetic polymers had been used in our life in a wide range of applications in diverse fields such as consumer products, packaging, agriculture, medical appliances, building materials, industry and aerospace materials. However, the good chemical resistance of synthetic polymers make it difficult to undergo physical and biological degradation and this becomes a serious issue when used in areas such as surgery, agriculture and the environment (Luckachan and Pillai, 2011). Therefore, polymeric materials that satisfy the conditions of biodegradability, biocompatibility, and release of low-toxicity degradation products which are known as biodegradable polymers are necessary to be used as an alternative to these existing polymers.

Biodegradable polymers are defined as polymer that undergoes deterioration of its physical and chemical properties and a decrease of its molecular mass by decomposing into carbon dioxide, methane, water and other low molecular weight products under the influence of microorganisms in both aerobic and anaerobic conditions aided by abiotic chemical reactions like photodegradation, oxidation and hydrolysis (Luckachan and Pillai, 2011).

Generally, biodegradable polymers can be divided into two groups, natural and synthetic, based on their origin (as seen in Figure 2.1). Natural origin biodegradable polymers have excellent biocompatibility, but due to their undesirable properties like antigenicity and batch-to-batch variation, they are not gaining interest in fully be investigated. In comparison, synthetic origin biodegradable polymers offer huge advantages over natural polymers by being versatile with a wide spectrum of applications, the capability to tailor made the mechanical properties and altering the rate of degradation according to the requirement (Doppalapudi et al., 2014). However, these biodegradable polymers have poor processability and high moisture absorption problems (Nor Azowa et al., 2009).

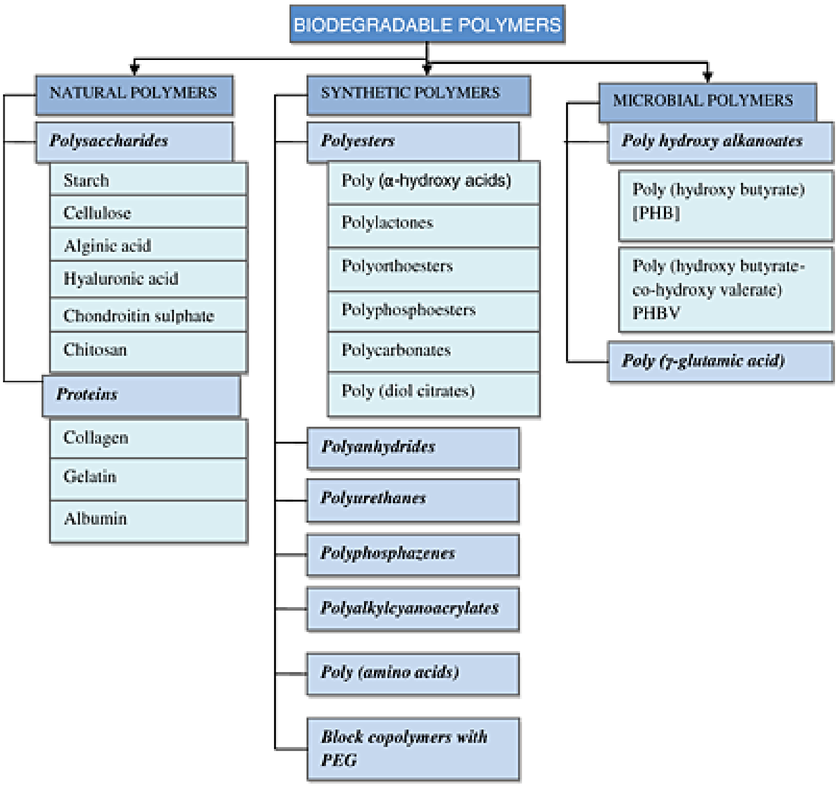


Figure 2.1: Classification of biodegradable polymers (Doppalapudi et al., 2014).

Biodegradable polymers have wide uses of applications, especially in the medical industry. Among the biodegradable synthetic polymers, polyesters are an attractive option in many biomedical applications due to their excellent biocompatibility and tunable degradation properties. The category of poly (α-hydroxy acids) includes poly (glycolic acid) and poly (lactic acid) (Doppalapudi et al., 2014).

2.1.1 Poly (lactic acid) (PLA)

Poly (lactic acid) (PLA) is an aliphatic polyester synthetic based on lactic acid ($C_3H_6O_3$) and produced from the fermentation process of agricultural resources, such as corn (Avinc and Khoddami, 2009). In the past decade, advances in the fermentation of corn dextrose have dramatically reduced the cost to make the lactic acid monomer, which allows to the mass PLA production. Figure 2.2 shows the chemical structure of PLA.

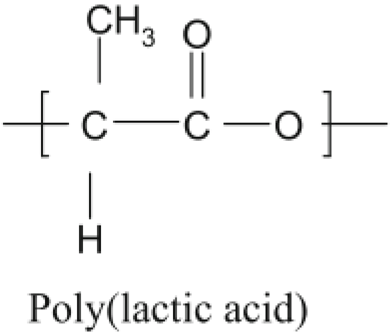


Figure 2.2: Structure of PLA.

PLA is derived in two stages, where the first stage is the fermentation of dextrose into lactic acid, then followed by either condensation polymerization or ring-opening polymerization of lactic acid (Lim et al., 2008). Generally, natural fermentation will yield a mixture of optically active stereoisomers of lactic acid in the approximate proportions 99.5% levo- (L-) form and 0.5% dextro- (D-) form (D) (Avinc and Khoddami, 2009). Figure 2.3 shows chemical structure of stereoisomers of lactic acid.

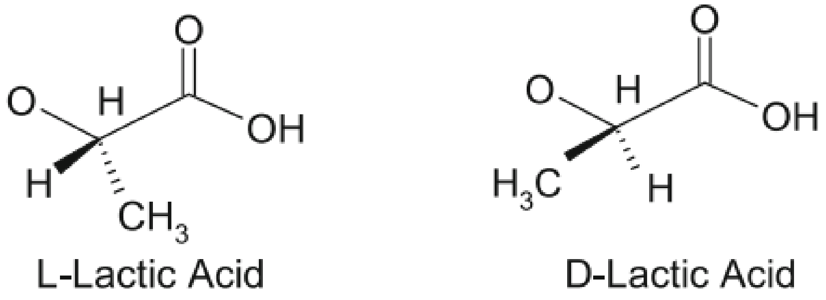


Figure 2.3: Two stereoisomers of lactic acid (Avinc and Khoddami, 2009).

Figure 2.4 shows the polymerization route to PLA. Polycondensation of lactic acid is the conventional process of producing PLA. The process is carried out under high temperature and vacuum condition. The water produced by the condensation reaction is extracted away using suitable solvent. The product obtained from polycondensation tends to have low to intermediate molecular weight (Mw 10,000-20,000) due to difficulties of removing water and impurities (Avinc and Khoddami, 2009). On the other hand, ring-opening polymerization of a cyclic dimer of lactic acid can results in a higher molecular weight polymer since water is removed under mild conditions (Mehta et al., 2005).

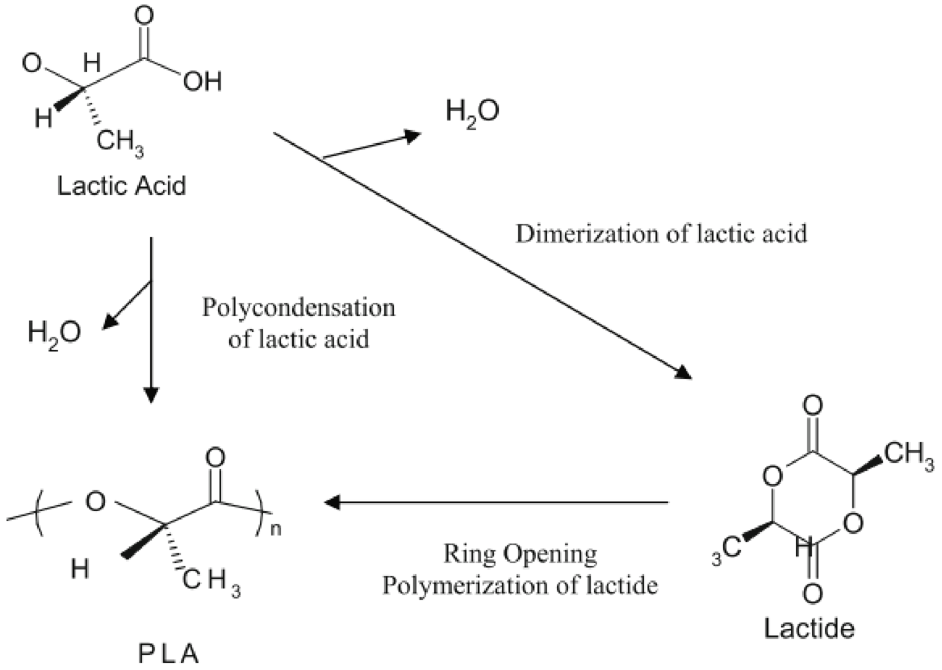


Figure 2.4: Polymerization route to PLA (Avinc and Khoddami, 2009).

PLA is rigid, colorless, glossy and its properties largely depend on the component isomers and molecular weight (Madhavan et al., 2010). PLA becoming one of the most promising biodegradable polymers due to its mechanical properties, thermoplastic processability and both biocompatible and biodegradable (Gupta et al., 2007). PLA also exhibits glass transition temperature (T_g) and melting point (T_m) just like other thermoplastic polymers. PLA has rather low T_g in the range of 55-65 ^{o}C although it is a relatively stiff polymer at room temperature; whereas, the T_m of PLA is between 160-180 ^{o}C (Perepelkin, 2002). Besides that, the molecular weight PLA polymer will start to decrease upon heating above 190 ^{o}C, which indicating the thermal degradation of PLA begin (Lim et al., 2008).

2.2 Natural fiber

Generally, natural fibers can be categorized into two categories based on their origin that are plants and animals. The major component of plant fibers is cellulose, whereas animal fibers mainly consist of protein. Plant fibers are more suitable to be used in composites because of they are generally stronger than animal fibers (Zini and Scandola, 2011). Plant fibers also have greater availability because it can be grown in many countries and can be harvested after a short period. Figure 2.5 shows the classification of natural fibers.

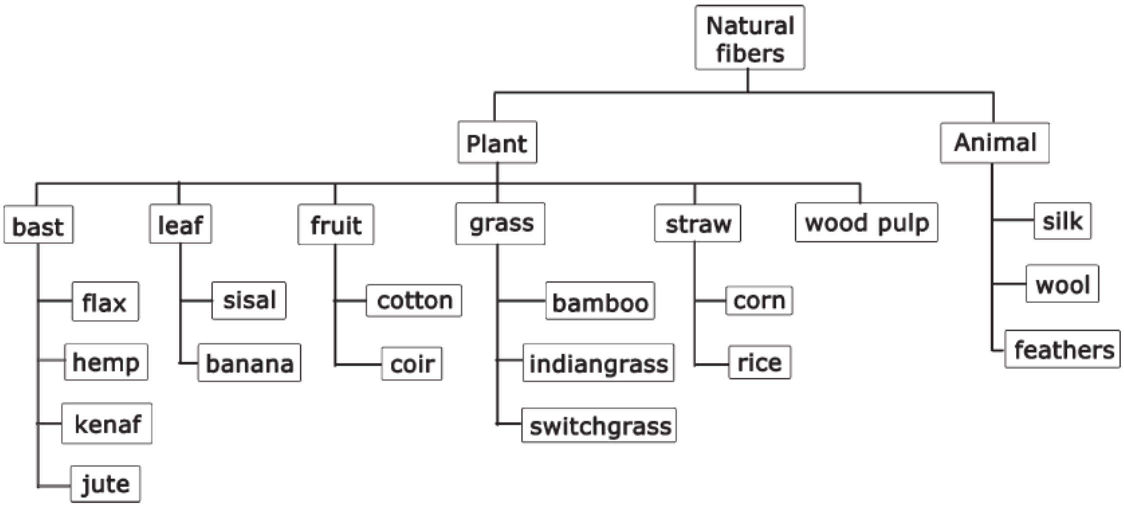


Figure 2.5: Classification of natural fibers (Zini and Scandola, 2011).

The chemical components of plant fibers are similar although their chemical compositions are varied between different plant species. Generally, plant fiber is made up of three major chemical constituents: cellulose, hemicellulose, and lignin (Pérez et al., 2002). The dry materials made up of a total of 80-90% from these chemical major constituents, while the other minor constituents include pectin, waxes and water-soluble components. The major constituents of plant fiber are briefly described in the following sections.

Natural fibers offer several advantages such as low density, high specific strength and stiffness, low cost, renewable and abundant resources and non-abrasive to composite processing equipment make it an alternative for synthetic fibers (Li et al., 2007). However, there is some limitation of natural fiber as compared to synthetic fiber. Natural fibers have lower strength and higher moisture absorption as compared to synthetic fibers. They also have limited processing temperature and high variability of fiber properties (Akhtar et al., 2016).

2.2.1 Microstructure of natural fiber

Figure 2.6 shows a schematic microstructure of a natural fiber. The fiber cell wall consists of primary and secondary layers of cellulose microfibrils. The primary cell wall is where the fiber structure develops and deposits during its growth while the secondary cell wall consists of three layers and each layer has a long chain of helical cellulose microfibrils (John and Anandjiwala, 2008).

According to Kabir et al. (2012) the cellulose content increased from primary to secondary layers while lignin content decreased in this sequence. The hemicellulose content is similar in each layer. Hemicellulose is hydrogen bonded with cellulose fibrils and form cementing material the fiber structure. On the other hand, lignin and pectin are coupled with the cellulose-hemicellulose network and act as adhesive to hold the molecule together. This adhesive and the secondary thick layer (S_2) determine the strength and stiffness properties of the fiber (Pickering et al., 2016). Generally, fiber with higher cellulose content has better strength properties.

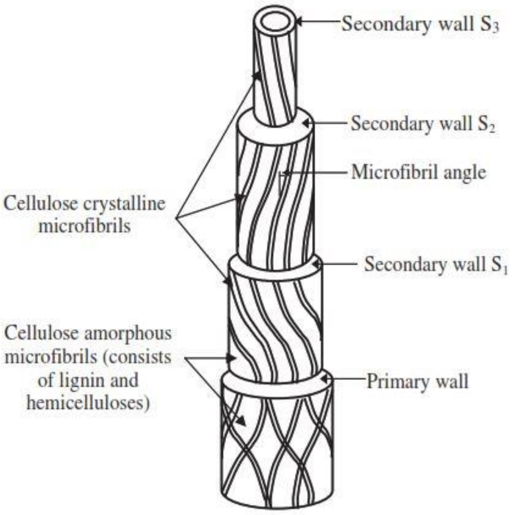


Figure 2.6: Microstructure of natural fiber (Kabir et al., 2012).

2.2.2 Cellulose

Cellulose is the natural homopolymer (polysaccharides) that makes up the main structural component of plant fibers (Akil et al., 2011). The cellulose molecule is in form of long and linear chains (called elemental fibrils) which composed of D-glucose subunits linked by ß-1, 4-glycosidic bonds via hydrogen bonds and Van der Waals forces (Pérez et al., 2002). The chemical structure of cellulose is illustrated in Figure 2.7. Cellulose can appear in two forms namely: crystalline and amorphous. The crystalline cellulose is less hydrophilic due to the closely packed inter-chain bonds that limits numbers of hydroxyl groups available for hydrogen bonding with water molecules. On the other hand, amorphous cellulose is more hydrophilic because it formed lesser inter-chain hydrogen bonds, exposing more hydroxyl groups (OH) to bond with water molecules (Pickering et al., 2016). Cellulose provides strength, stiffness and structural stability of the fibers (Kabir et al., 2012).

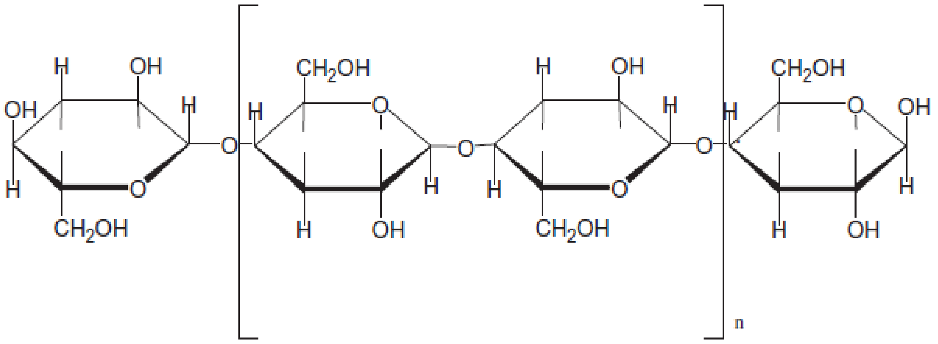


Figure 2.7: Chemical structure of cellulose (Akil et al., 2011).

2.2.3 Hemicellulose

Hemicellulose has a heterogeneous and branches with short lateral chains. It consists of a group of polysaccharides polymer made up by a combination of 5 and 6 carbon ring sugars (Kabir et al., 2012). Hemicellulose is present in the primary cell walls with the function of filling the cavities between the microfibrils in cellulose and linkage between cellulose and lignin (Choi and Lee, 2012). Pérez et al. (2002) reported that hemicellulose is more easily hydrolyzed by dilute acids or bases than cellulose. This is because of its amorphous structure resulting the hydroxyl groups are more accessible to water. Figure 2.8 shows the chemical structure of hemicelluloses.

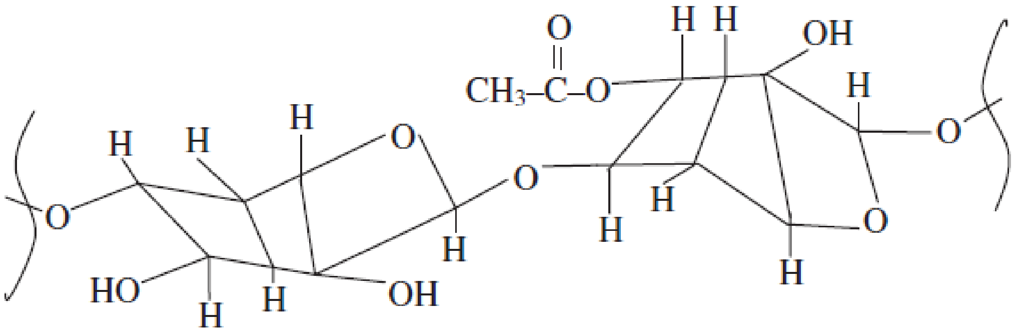


Figure 2.8: Chemical structure of hemicelluloses (Kabir et al., 2012).

2.2.4 Lignin

Lignin is a complex and high molecular weight polymer (as shown in Figure 2.9) making it insoluble in most solvents and cannot be broken down easily to monomeric units as it is held together by many hydrogen bonds and strong chemical bond (Pérez et al., 2002). Natural fibers gain great strength and rigidity from lignin that provides structural support and resistance against microbial attack (Choi and Lee, 2012). Besides that, lignin also contributes to dark color part of natural fibers. Breakdown of bonding in lignin can result in the fiber in that part of will become lighter in color (Kabir et al., 2012).

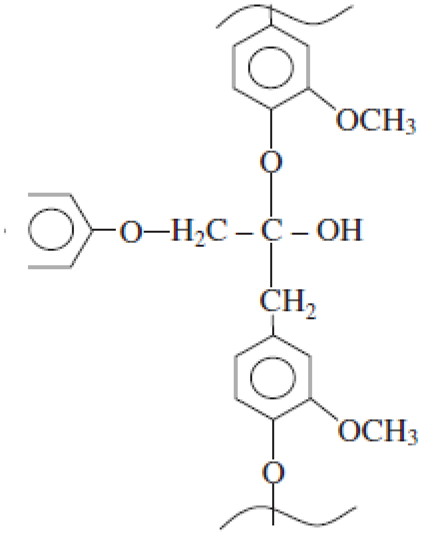


Figure 2.9: Chemical structure of lignin (Kabir et al., 2012).

2.2.5 Kenaf fiber

Kenaf (Hibiscus cannabinus L) is a herbaceous annual plant that grows at a wide range of weather conditions. It is capable of growing to a height of more than 3 m within 3 months even under moderate ambient conditions (Lee et al., 2014). Kenaf is an attractive choice among a wide variety of plant fibers due to its capability to growth rapidly (Asumani et al., 2012). Kenaf has been actively cultivated in recent years due to two main reasons. Firstly, kenaf able absorbs the phosphorus and nitrogen that are present in the soil. The phosphorus and nitrogen promote an increase of crop height, cumulative weed weight, stem diameter, and fiber yield. Secondly, kenaf has higher photosynthesis rate than other conventional trees, that is kenaf converts carbon dioxide to oxygen at a significantly higher rate (Kuchinda et al., 2001).

Meanwhile, kenaf is a potential reinforcing fiber in thermoplastic composites, due to its high aspect ratio and superior specific strength and modulus compare to other fibers. A study reported that a single fiber of kenaf can have a tensile strength and modulus as high as 11.9 GPa and 60 GPa, respectively (Akil et al., 2011). However, there is limitation encountered when adding natural fibers, including kenaf fiber into a polymer matrix, which is the poor interfacial adhesion between the two components that resulting poor properties in the natural fiber composite (Taib et al., 2014). This is because the surface of the kenaf fiber has polar hydroxyl groups that incompatible with a relative nonpolar matrix. Thus, there is difficulty in forming a well-bonded interphase between matrix and fiber (Huda et al., 2008). Furthermore, there is also agglomeration issue when using kenaf fiber as a filler in a polymer matrix due to the tendency of fibers to form hydrogen bonds with each other resulting insufficient dispersion (Corrales et al., 2007).

2.3 Fiber surface modification

In polymer matrix composites, fiber surface modification can be done to improve compatibility and interfacial bonding between fiber and matrix. Li et al. (2007) presented a review article on the various types of chemical treatments had been used such as alkali treatment, silane treatment, acetylation, and benzoylation. These chemical treatments increase the wettability and interfacial bonding of lignocellulosic fibers and polymer matrix by removing impurities and non-cellulosic components to expose more hydroxyl groups on fiber surface for bonding with the matrix and addition of the chemical group to improve wettability for chemical reactions (Dong et al., 2014). Generally, fibers are treated prior to composite processing. Among the various methods presented, alkaline and silane treatments have been widely reported (Asumani et al., 2012).

2.3.1 Alkali treatment

Alkali treatment is one of the most commonly used chemical treatments to improve interfacial bonding in natural fiber composites. It involves soaking the fibers in an alkaline solution for a period of time. Sodium hydroxide (NaOH) and sodium sulphite (Na_2SO_3) or combinations of both solutions are common alkaline solution that has been used extensively in alkali treatment (Meon et al., 2012).

Alkali treatment causes the removal of non-cellulosic material such as hemicellulose, lignin, pectin, fat, wax, and water soluble substances which result in fiber separation, exposing more cellulose at the fiber surface to potential chemical bonding with the matrix material (Li et al., 2007). Removal of non-cellulosic material could increase the fiber crystallinity due to better alignment of microfibrils which results in higher fiber tensile strength and failure strain (Kabir et al., 2012). Besides that, alkali treatment also improves fiber surface roughness, leading to an increased number of possible reaction sites for bonding and better mechanical interlocking with the matrix (Asumani et al., 2012). Therefore, this method results increased in interfacial strength, tensile strength and Young’s modulus of composites.

Many research works studied alkali treatment on natural fiber using a different concentrations of an alkaline solution with a different periods of immersion time. According to Edeerozey et al. (2007), 6 weight percentage (wt%) of sodium hydroxide (NaOH) solution was effective at removal of impurities from the fiber surface. However, when the concentration of NaOH solution further increases more than 6 wt%, the fiber surface appears to be damaged, defects in fiber had increase thus the fiber strength reduced. A similar trend was obtained by Meon et al. (2012). A later study conducted by Taib et al. (2014) on alkali treatment time reported that optimum improvement in the flexural properties of unsaturated polyester/kenaf fiber mat composite was observed when the kenaf fiber mat was alkali treated for 3 h. Prolonged treatment time gives a negative effect on flexural properties due to excessive extraction of the cementing materials that eventually decrease the fiber stiffness.

Akhtar et al. (2016) found that kenaf fibers treated with 6 wt% NaOH (relative to fiber weight) at room temperature for 24 h improved the tensile strength and modulus of 40 wt% kenaf/PP composite by approximately 18% and 110%, respectively as compared to untreated fiber. This is corresponded to alkali treatment improves surface roughness, interfacial adhesion, and strong bonding between the fibers and the PP matrix. Meanwhile, Yousif et al. (2012) who studied similar fiber treatment condition but using epoxy resin matrix reported that the flexural strength of the epoxy composite achieved an increment of 36% when treated kenaf fibers were used as reinforcement compared to the untreated fibers, which showed only 20%. The alkali treatment highly enhanced the interfacial adhesion by splitting the kenaf fiber bundles into fine fibers which allowed the epoxy resin to penetrate the fiber bundles leading to high interlocking between the fibers and the matrix. Another study conducted by Choi and Lee (2012) reported that the alkali treatment not only increases the strength, stiffness and impact strength, but also the thermal stability of the composites.

2.3.2 Silane treatment

Silane is a molecule having different functional groups at either end which is used as a coupling agent to modify fiber surfaces. The composition of silane at one end interact with hydrophilic groups of celluloses via siloxane bridge, whereas the organic end interacts with the hydrophobic groups of the matrix (Kabir et al., 2012). Silane treatment usually is done by immersing the fibers in a weak solution of a silane diluted in a water/alcohol or water/ketone mixture. In the presence of water, silane undergoes hydrolysis and form both silanol and alcohol (Asumani et al., 2012).

Generally, silane coupling agents have a generic structure of $R_{(4-n)}$–Si–(R'X)$_{n,}$ (n = 1,2), where R is alkoxy, X represents an organofunctionality, and R' is an alkyl bridge connecting the silicon atom and the organofunctionality (Xie et al., 2010). The alkoxy group hydrolyze in water to form silanol which interacts with hydroxyl group of natural fiber; whereas the organofunctionality of the silane coupling agent interacts with the polymer matrices depending on the reactivity or compatibility towards the polymer; while the nonreactive alkyl bridge may increase the compatibility with non-polar matrix due to similar polarities; however, the reactive organofunctionality may covalently bond with as well as being physically compatible with the polymer matrices. (Xie et al., 2010). The most commonly reported silanes used in natural composites are amino (APS), methacryl (MPS), glycidoxy (GPS) and alkyl (HDS) silane (Pickering et al., 2016). Amino silane (APS) is preferred when using polylactide as a matrix because it has the amino group that can react toward the terminal hydroxyl groups on the polylactide backbone (Huda et al., 2008). 3-Aminopropyltriethoxysilane (APTES) is the example of amino silane. It has amino, propyl and ethoxy group as the organofunctionality, alkyl bridge and alkoxy of silane coupling agent, respectively.

The ethoxy groups of APTES hydrolyze in water producing reactive silanols and ethanol. The reactive silanols then react and forming hydrogen bonds with the hydroxyl (OH) groups of the cellulose on the fiber surface in natural fibers as shown in Figure 2.10 (Asumani et al., 2012). The free silanols could react with each other by a stable –Si–O–Si– bond thus forming a rigid polysiloxane structures (Xie et al., 2010). The hydrogen bond between silanols and hydroxyl groups of fibers convert into covalent –Si-O-C- bonds by liberating water whereas the residual silanols will further condense with each other (Xie et al., 2010).When the silane treated fiber is combined with the PLA matrix, another functional group on the silane molecule, which is the aminopropyl group would react with the hydroxyl group of the PLA matrix as shown in Figure 2.11 (Goriparthi et al., 2012). Penjumras et al. (2016) reported that carboxyl groups on the PLA structure form hydrogen bonding with aminopropyl groups of amino silanes. Use of silane have been found to increase the hydrophobicity of natural fibers, fiber surface area, and degree of cross-linking in the interface region thus increase the covalent bonding form between silane and matrix resulting increase in the strength of natural fiber composite (Pickering et al., 2016).

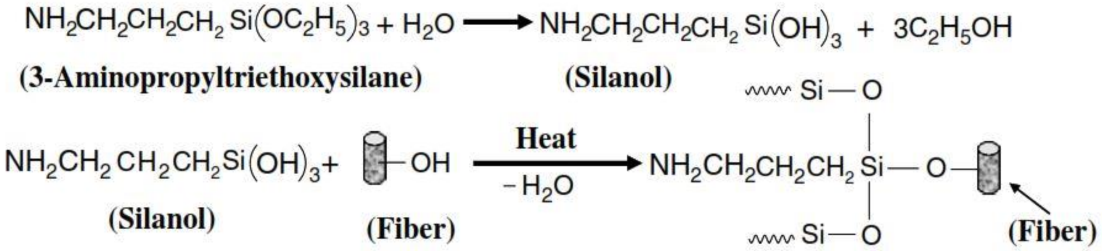
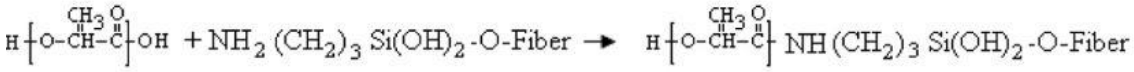


Figure 2.10: Hydrolysis of APTES in water and the hypothetical reaction of silanol and fiber (Huda et al., 2008).



$$H\left[O-\overset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}\right]OH + NH_2(CH_2)_3Si(OH)_2\text{-O-Fiber} \rightarrow H\left[O-\overset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}\right]NH(CH_2)_3Si(OH)_2\text{-O-Fiber}$$

Figure 2.11: Chemical reaction between silane treated fiber and PLA (Goriparthi et al., 2012).

Previous study Van de Weyenberg et al. (2003) reported that flax fiber immersed in 1% solution of 3-aminopropyltrimethoxysilane diluted in a 50/50 mixture of acetone and water for 2 h. The silane treated fiber was used to reinforce epoxy at a volume fraction of 40%. The tensile strength only increased by 4% as compared to untreated fiber, however, the tensile modulus improved by approximately 45%. A later study conducted by Huda et al. (2008) using kenaf fiber treated with a 5 wt% APTES (relative to fiber weight) that dissolved in a mixture of water-ethanol (40:60 w/w) and were stir continuously for 1 h. The kenaf fiber was immersed in the solution for 3 h. The results of the study showed that silane coupling agent significantly improves the mechanical properties of PLA/kenaf composites caused by improved interfacial interaction, resulting in high flexural stiffness.

2.4 Thermoplastic composite processing

Generally, processing methods used in natural fiber composites are similar to those used in the production of the synthetic fiber composite. The quality of composite, the cost of production and production speed are the main factors that determine the suitability of the processing method. The commonly used methods used for the production of natural fiber thermoplastic matrix composites are extrusion, injection moulding and compression moulding.

2.4.1 Extrusion

Extrusion is a process where a solid matrix (pellets or powder) is melted and mixed with the fiber and either by a single or two rotating screws, then compressed and forced out into shape at a steady rate through a die (Lim et al., 2008). Figure 2.12 shows a schematic representation of the major components of an extruder. It typically consists of three sections that are feed section, transition section, and metering section. Generally, the screw speed and temperature are two critical factors that affecting the quality of composite produced. Low screw speed can result in poor mixing and wetting between the matrix and the fibers whereas high screw speed can lead to air entrapment, excessive melt temperatures, and fiber breakage. On the other hand, if the temperature is too low, it can lead to incomplete melting of the matrix; if the temperatures are very high, degradation of fiber could occur, which limits the use of thermoplastic matrices with low melting points (Tanahashi, 2010). Extrusion can be used alone for production or as a pre-cursor to injection moulding.

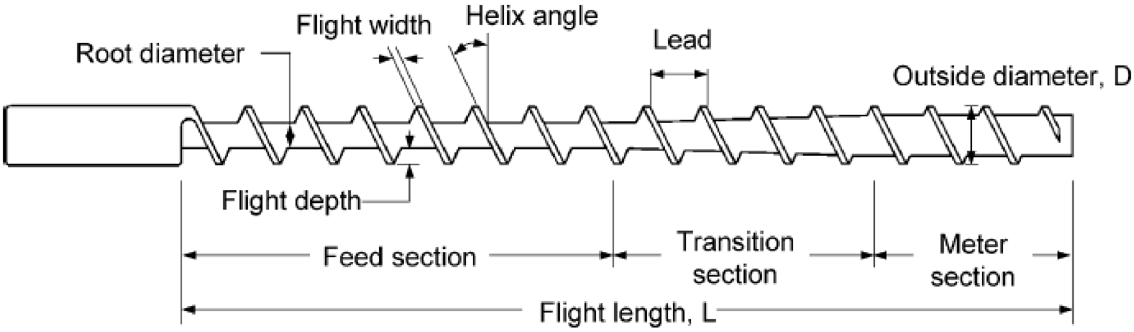


Figure 2.12: Typical geometries of a single-screw extruder (Lim et al., 2008).

2.4.2 Injection Moulding

Injection moulding has been widely used in the automotive and construction industries especially for a product that is complex in shape and requires high dimensional precision. Injection moulding is a process where short fibers and solid matrix (pellets or powder) are supplied via a hopper into a heated barrel with a plunger. The heated barrel melts the polymer into a viscous liquid and injected it by the plunger through a nozzle and forced into a tightly clamped mold cavity where the composite is allowed to cool and solidify (Lim et al., 2008). Injection moulding offers the ability to use a wide range of materials, low labor cost, minimal scrap losses, and less finishing process after molding. It also offers fast and economical processing with minimum defects such as warpage and shrinkage (Akhtar et al., 2016). During injection moulding, lower flow velocity along the wall caused by friction could produce more aligned fiber orientation while higher flow velocity at the center leads to more randomly and transversely aligned fiber (Avinc and Khoddami, 2009).

2.5 Conclusion of literature review

Base on the previous studies, alkaline and silane treatment are very common method used to modify the fiber surface. However, most of the studies using compression moulding to prepare their composite samples. There are limited researches prepared the composite samples using extrusion and injection moulding. It is more encouraging to use industrial automatic processing method than manual conventional method in research study in order to enhance commercial success of biocomposite. Therefore, in this project, kenaf fiber is modify by alkali and silane treatment. Next, the treated fiber mix with PLA using single screw extrusion and lastly produce composite sample using injection moulding.