PREPARATION AND CHARACTERIZATION OF POLYURETHANE COMPOSITES REINFORCED BY KENAF CORE

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by

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AZIZAH BINTI ABU BAKAR

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF EQUATIONS

Page

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
DMA	Dynamical Mechanical Analysis
DTGA	Differential Thermogravimetric Analysis
EDX	Energy Dispersive X-ray
FR	Flame Retardant
FTIR	Fourier Transform Infrared
KC	Kenaf Core
KCP	Kenaf Core – Polyurethane
LOI	Limited Oxygen Index
MDI	Methylene Diphenyl Diisocyanate
NF	Natural Filler
OKC	Tetramethoxyl Orthosilicate Treat Kenaf Core
OKCP	Tetramethoxyl Orthosilicate Treat Kenaf Core – Polyurethane
PCM	Percentage of Crosslinked Material
PKC	Trimethoxy Phenylsilane Treat Kenaf Core
PKCP	Trimethoxy Phenylsilane Treat Kenaf Core – Polyurethane
PU	Polyurethane
SEM	Scanning Electron Microscopy
TDI	Toluene Diisocyanate
TGA	Thermogravimetric Analysis
TKC	Treated Kenaf Core
TKCP	Treated Kenaf Core – Polyurethane

TMOS	Tetramethoxyl Orthosilicate
TMPS	Trimethoxyphenylsilane
UKC	Untreated Kenaf Core
UKCP	Untreated Kenaf Core - Polyurethane
UL-94	Underwriter’s Laboratory 94
VKC	Vinyltrimethoxysilane Treat Kenaf Core
VKCP	Vinyltrimethoxysilane Treat Kenaf Core – Polyurethane
VTMS	Vinyltrimethoxysilane
WPG	Weight Percent Gain

PENYEDIAAN DAN PENCIRIAN KOMPOSIT POLIURETANA YANG DIPERKUAT OLEH TERAS KENAF

ABSTRAK

Dalam kajian ini, kesan rawatan silana ke atas teras kenaf (KC) dan komposit poliuretana (PU) diperkuat KC (KCP) telah dikaji. Komposit ini disediakan dengan menggunakan proses sekaligus yang mana; pertama PU disediakan dari difenilmetana diisosianat (MDI) dan gliserol dengan nisbah NCO/OH yang berbeza. Kemudian komposit KCP disediakan dengan peratusan pengisi KC menggunakan nisbah NCO/OH yang sesuai. Daripada ujikaji sifat mekanik didapati nisbah NCO/OH 1.5 dan beban KC sebanyak 20% adalah sesuai untuk dikaji dalam fasa seterusnya. Dalam fasa seterusnya, KC dirawat dengan menggunakan (1–3 %); vinil-trimetoksi-silana (VTMS), trimetoksi-fenil-silana (TMPS), dan tetra-methosi-orto-silikat (TMOS) menggunakan kaedah hidrolisis dengan etanol/air (80:20 isipadu) yang dijadikan sebagai medium silanisasi untuk KC. Sifat-sifat KC yang tidak dirawat (UKC) anda KC dirawat (TKC) diselidiki melalui analisis morfologi, analisis pemetaan unsur mikroskopi imbasan elektron–X-ray penyebaran tenaga (SEM – EDX), analisis fourier transformasi inframerah (FTIR) dan analisis termogravimetrik (TGA). Daripada keputusan yang diperoleh melalui morfologi permukaan dan analisis pemetaan SEM-EDX terhadap UKC dan TKC, tertunjuk kehadiran elemen silikon pada permukaan TKC. Analisis terma sampel TKC telah menunjukkan meningkatkan kestabilan terma jika dibandingkan UKC. Sifat visko-mekanik komposit KCP yang dihasikan daripada TKC dengan silana (TKCP) diukur melalui analisis DMA. TKCP menunjukkan modulus simpanan dan kehilangan yang tinggi berbanding dengan komposit dengan UKC. Hal ini.kerana ikatan kimia antaramuka antara teras kenaf dan poliuretana dapat dipertingkat yang juga menigkatkan dan kekakuan komposit. Kajian kestabilan terma pada TKCP menunjukkan haba penguraian yang tinggi diperlukan untuk komposit terurai pada suhu yang tinggi. Kestabilan terhadap rintangan api ke atas TKCP juga ditingkatkan.

PREPARATION AND CHARACTERIZATION OF POLYURETHANE COMPOSITES REINFORCED BY KENAF CORE

ABSTRACT

In this study, the effect of silane treatment on kenaf core (KC) and KC reinforced polyurethane (KCP) composites were discussed. The composite was prepared using one shot process. Firstly, polyurethane (PU) was prepared from methylene diphenyl diisocyanate (MDI) and glycerol using different NCO/OH ratio and KCP composites with different KC loadings were prepared using a suitable NCO/OH ratio. From the mechanical properties measurement, it was found that NCO/OH ratio of 1.5 and KC loadings of 20% were suitable to be studied. In the next phase, KC was treated with different types of silane (1 – 3%); which were vinyltrimethoxysilane (VTMS), trimethoxyphenylsilane (TMPS), and tetramethoxy orthosilicate (TMOS) using hydrolysis method with ethanol/water (80:20 volume) as silanization medium for KC The properties of untreated KC (UKC) and treated KC (TKC) were investigated through filler morphology analysis, Scanning Electron Microscopy – Energy Dispersive X-ray (SEM – EDX) mapping element analysis, Fourier Transform Infrared (FTIR) analysis, and Thermogravimetric Analysis (TGA) analysis. UKC and TKC surface morphology and SEM – EDX mapping analysis showed the presence of Si element on the TKC surface. Thermal analysis revealed that, silane treatment had enhanced the thermal stability. The visco-mechanical properties of kenaf core treated with silane – polyurethane (TKCP) composite were measured by Dynamical Mechanical Analysis (DMA). TKCP exhibited high storage and loss modulus compared to the composite with UKC due to the enhanced interfacial chemical bonding and stiffness of the KCSP composite. Thermal stability study had shown TKCP has higher thermal stability and produced higher amount of char residual. The flame retardancy on TKCP was improved too.

CHAPTER 1

INTRODUCTION

1.1 Background

Nowadays natural filler is the most attractive as potential materials as reinforcement in composite and has been well known a long time ago. With the development of durable materials such as metal, the interest in natural materials decreased. It was not until the early 1900s when natural materials remerged as possible future materials for a lot of advanced applications such automobile, furniture, ordinary applications like consumer goods [1], low-cost housing, civil structure [2], aircraft, and aerospace structures [3].

Natural filler is a valuable material which has served human beings for thousands of years. Today, natural filler is not only used as in its original solid form, but also is used to make a variety of composite material. these materials have been developed in response to the decreasing supply of the high-quality virgin natural filler materials [4]. Although many natural filler composites have been commercialized, much work remains to more fully utilize the lower quality of natural filler materials [5].

In the natural filler industry, traditional natural filler composites are systems in which elements such as fiber, flakes, particles, chips, and strands, are the load carrying component materials, while the polymer resin act as adhesives to bond the filler elements together [6]. Although they are both called composites. Natural filler is a thermal degradable and combustible material. Natural filler like other cellulosic materials, when exposed to fire or any other high-intensity heat source, are subject to thermal decomposition and combustion depending on conditions [4,7].

Kenaf is an herbaceous annual plant originating in Asia and Africa is a member of the Malvaceae family. Kenaf has a single, straight, and unbranched stem consisting of an outer fibrous bark and an inner core (wood). Kenaf grows 1.5 to 3.5 m tall, with stems 1 to 2 cm diameter and leaves 10 to 15 cm long. The flowers are 8 to 15 diameters. Kenaf or Hibiscus Cannabinus L is a fast-growing fibrous plant within 3 to 4 months [8]. Kenaf is green, renewable, and sustainable products which definitely have a market premium in future [9].

Kenaf is an industrial crop with high potential for cultivation in a tropical climate. It is a source of raw material for paper production and fiber-based industries. Considerable research has been conducted to explore its adaptability and utilization in Malaysia since 2000, under the supervision of governmental and private organizations. A number of technologies and expertise among researchers have been developing to enhance kenaf production in Malaysia [10].

Polyurethane products historically have been proven to be one of the most versatile polymers available. The wide range of physical properties from super soft flexible foams, to tough elastomers, and to long-wearing coating has resulted in many application [11]. Polyurethanes are prepared by reacting polyfunctional isocyanates with polyfunctional active hydrogen-containing compounds such as R—SH, R—NH, and R—OH. Thus, an active hydrogen-containing compound is suspected to be able to react with isocyanates to form polyurethane.

1.2 Problem statement and justification

A major drawback of natural filler-polymer composite is their vulnerability to degradation by moisture. The hydrophilic behavior of natural fillers affects the properties of the composites. These limitations of natural filler-polymer composites can be improved through chemical treatment of natural fillers [12]. The main difficulty of natural fillers is their tendency to entangle with each other and form filler agglomerates during processing. The formation of agglomerates prevents uniform filler dispersion in polymer matrix and affects the properties and appearance of the finish products [13]. Natural filler like kenaf core has natural combustibility and vulnerability in a fire. However, the natural filler is excellent resistance to fire penetration due to low thermal conductivity and ability to form super facial char layer and allow natural filler to maintain the physical-mechanical properties. However, protection of natural filler against fire is limited to a retardancy effect, since no chemical can transform natural filler into the non-combustible material but it can reduce or delay the combustion of the material [14]. Nowadays, many organosilane compounds are chosen as an environmental friendly flame retardant to replace the traditional halogenated ones, for served material protection including kenaf core [15].

Being aware of this Sumaila et al. (2006) proposed a natural filler-polyurethane composite system act as the structural material and polyurethane as the continuous matrix phase. their goal was to utilize the low filler content to make high performance natural filler-polymer composites. Through their studies, the interaction between natural fillers and matrix were observed. However, tensile of the composites decreased as the amount of natural filler added to the polyurethane increased. They suggested that there is a need to adjust isocyanate to polyol ratio when natural fiber is added into the system in order to obtain good strength properties of the composites [16].

Meanwhile, Ismail et al. (2015) found there were some problems in using natural fillers, such as interfacial adhesion and water absorption. These problems must be solved. They suggest a further study is a must, therefore, be conducted to improve the physical and mechanical properties of the kenaf-thermoset composite to the desired level [17].

Other studies have been conducted on using natural fillers reinforced polyurethane composites using different types of natural filler such as flax [18], sisal [19,20], jute [21] , oil palm empty fruit bunch [22–24], kenaf bast [25–27], and kenaf core [28,29].

Nar et al. (2015) studied the production of higher volume in composite production of kenaf core. They found out that naturally porous structure of kenaf-core provides a novel reinforcement particle. In their work, foams of rigid polyurethane with 5, 10, and 15% kenaf core were formed. To date efforts at using it as reinforcement have proven unsuccessful. However, introducing constraint during foaming resulted in reinforcement. The results show that free foaming resulted in poor reinforcement while a constrained expansion on the foam increased the reinforcement potential of the kenaf core [29].

Meanwhile, Batouli et al. (2014) reported that outstanding thermal, mechanical, and environmental properties of kenaf core based polyurethane insulation board in structural insulated panels. The composite foams made of rigid polyurethane (PU) reinforced with 5 - 15% of kenaf core and they found that kenaf core does not replace the PU; instead, it mostly fills the void space, which is initially filled with air and, hence, the kenaf core decreases the porosity of PU composites and increases the density without improving thermal resistance [28].

Kenaf core is environmental friendly materials and it consists of three major hydroxyl-containing components which are known to be cellulose, hemicellulose, and lignin. These components have the potential to react with isocyanates to form kenaf core-urethane materials. It is suspected that the interaction of hydroxyls from kenaf core with isocyanates will result in good mechanical performance of the composite materials due to the good interfacial bonding properties. It is believed that the interaction can be enhanced if kenaf core is treated with silane coupling agent.

Although some knowledge have been obtained through these excellent studies, there is still a large body of information to be studied concerning natural filler and urethane chemistry, especially the knowledge about the interfacial characteristics between natural filler and isocyanates or polyurethane in the natural filler-polyurethane composite system. Therefore, it is necessary to carry out a study on this subject to understand the performance of natural filler-polyurethane-isocyanate composite system.

Chemical treatments on the natural fillers are very important to increase the adhesion between the hydrophilic natural filler and the hydrophobic polymer matrix at the interface. Resistance to moisture absorption of natural filler composites can also be improved by treating these fillers with suitable chemical treatments. At the same time to give a protection on natural filler against fire to reduce and delay the combustion of natural fillers. Many investigations have been carried out by a number of researchers with different methods and chemicals were used especially to treat kenaf core such as alkaline treatment sodium tetraborate decahydrate (borax) [30], benzoyl chloride [31], phosphate [32,33], and silane [15].

Ismail et al. (2010) studied the effect of kenaf core filler loading and silane treatment from FTIR and SEM observations indicate that better adhesion was observed for the composite with chemically treated kenaf core filler. Chemical treatment of kenaf core caused a significant increase in stabilization torque, water resistance and the mechanical properties of HDPE/soya powder/kenaf-core composites. The treatment reaction was carried out in a mixture of water/ethanol (40/60 volume). 3 g of γ-aminopropyltri-thoxysilane was first introduced into 1000 mL of the mixture water/ethanol and was allowed to stand for 1 hour. The pH of the solution was maintained at 4 with the addition of acetic acid. Then, 10 g of kenaf core powder was added into the solutions and the solutions were continuously stirred for 1.5 hours. The filler was filtered and was dried in the air and then in the vacuum oven at 80°C for 24 hours [15].

Thus, this study will focus on several attempts to address these issues. A better interface between filler and polymer matrix can be obtained by chemical treatments on the filler. The introduction of reactive sites in the matrix with a higher chemical affinity toward the fillers can improve filler-matrix interfacial strength. Flammability is one of the very vital parameters, restricting the utility of a composite to a given application area. It is regarded that additions of natural filler to polymer matrix alternate the mechanical as well as flammable properties of the composite which is different from those of the components. Thus, appropriate treatment of the filler is warranted to enhance the above-mentioned properties.

1.3 Objective

Given the gaps in knowledge of kenaf core and its potential as reinforcement material for polyurethane composite has drawn much interest. Extensive literature review reveals the methods for simultaneous improvement of the mechanical, physical and flame retardancy of kenaf core reinforced polyurethane are limited. In this study, several novel coupling agents were investigated for the chemical treatment of kenaf core.

The main objective of this study is to enhance the mechanical and flame retardancy performance of kenaf core reinforced polyurethane composite. In order to achieve the objective, approaches centering on silane treatment of kenaf core and manufacturing process of the composite were implemented. In this study, four aspects of composite performance were (i) investigated the effect of silane treatment of kenaf core, (ii) to develop kenaf core reinforced polyurethane composite and their characterization in terms of mechanical, physical, and thermal properties. The effect of filler concentration and isocyanate index formulation on polyurethane composite properties are defined, (iii) to increase understanding of the viscoelastic properties of the composite, and (iv) to evaluate FR properties of KCP composite prepared from untreated and treated KC.

1.4 Scope of study

The overall goal of this study is to fabricate and characterize composite from natural filler utilizing from kenaf core (KC) and polyurethane (PU). The aim of the study is to reduce the fire risk of composite reinforced with natural filler by using constructional concepts of flame retardancy. Furthermore, the mechanism leading to enhanced material properties should be examined.

This study would emphasize the mechanical properties of treated and untreated KCP composite. In order to achieve these objectives, the work would be divided into various scopes. In first step, basic principles of KC and PU were investigated to obtain fundamental knowledge to build on the development of polyurethane-kenaf core (KCP) composite. In a second step, to determine the effect of filler loading on KCP composites from 0 to 30% by weight would be employed. In the third step, three different type of silane additives were treated the KC to increase interaction and flame retardant properties. The comparison between untreated and treated composite would be done to study the change in trend in mechanical and flame retardant behavior of composite.

The mechanical properties of the composite were characterized by tensile and flexural tests. Meanwhile, physical properties analyses were carried out by water absorption and thickness swelling tests. The structural and microstructure of the composite were characterized by Fourier-transform infrared spectroscopy (FTIR), a degree of curing determination, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). Thermal properties of composites were analyzed using dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) studies. Whilst, flame retardancy (FR) of composites were tested using limited oxygen index (LOI), Underwriters Laboratories 94 (UL94) and Methenamine pill test.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Recently, environmental awareness throughout the world has impacted material design and engineering. The interest in the utilization of natural material can handle ecological issues such as environmental protection, recyclability, and renewability. Synthetic materials such as aramid, glass, and carbon are getting utilized extensively in polymer-based composites due to their strength and stiffness properties [34,35]. However, synthetic materials give averse to environmental and ecological impact alters the attention to natural or renewable materials usually natural materials. Besides that, synthetic materials have extreme disadvantages in term of recyclability, their processing cost, recyclability, biodegradability, machine abrasion, energy consumption, health risks, and many others [36,37]. However, the introduction of natural materials as reinforcing material in the polymer matrix give great attention recently especially with its advantages [38–40].

Natural fillers such empty fruit bunch (EFB), jute, sisal, kenaf, coconut, rice husk, and many others, are well known as appropriate potential reinforcements materials for engineering composite resources. The use of those fillers are that they might easily to be processed, light in weight, non-toxic, and have a high specific modulus [41,42]. These properties can open up a large area to applying natural fillers into composite field and will encounter the used of synthetic fillers in this matter.

However, natural fillers also own certain drawbacks in properties itself. Natural fillers consist of structural components such as cellulose, hemicellulose, lignin, waxy, and pectin materials, which can allow moisture absorption from the surroundings will results in dimensional instability and reduced bonding with the hydrophobic polymer matrix materials mainly, the tendency to form aggregate during processing, and poor resistance to moisture significantly ease the ability of natural fillers to be used as reinforcement in polymer [43–45].

As a result, a suitable chemical treatment on the surface is required. Those chemical treatments are primarily based on the usage of reagent functional groups which might be able to be reacting with the filler systems hence converting their behavior. The treatment is to reduce the tendency of moisture absorption of the fillers and facilitate better compatibility with the polymer matrix [46–48]. Many sorts of research have been targeted on the improvement of compatibility of filler and the polymer matrix [15,49,50].

2.2 Composite from lignocellulosic/natural filler

Usually, natural materials were derived from plants, animals, and mineral resources. They can be characterized accordingly followed to their own origin itself as depicted in Figure 2.1. The advantages of using natural fillers comprised of sustain the environment of the parts being built in the automotive industries. In the building industry, the utilization of natural fillers is most cost-effective. As well as in the aerospace industry, utilization Natural fillers are light in weight on a par with lightweight and tough materials commonly used in these industries [51,52].

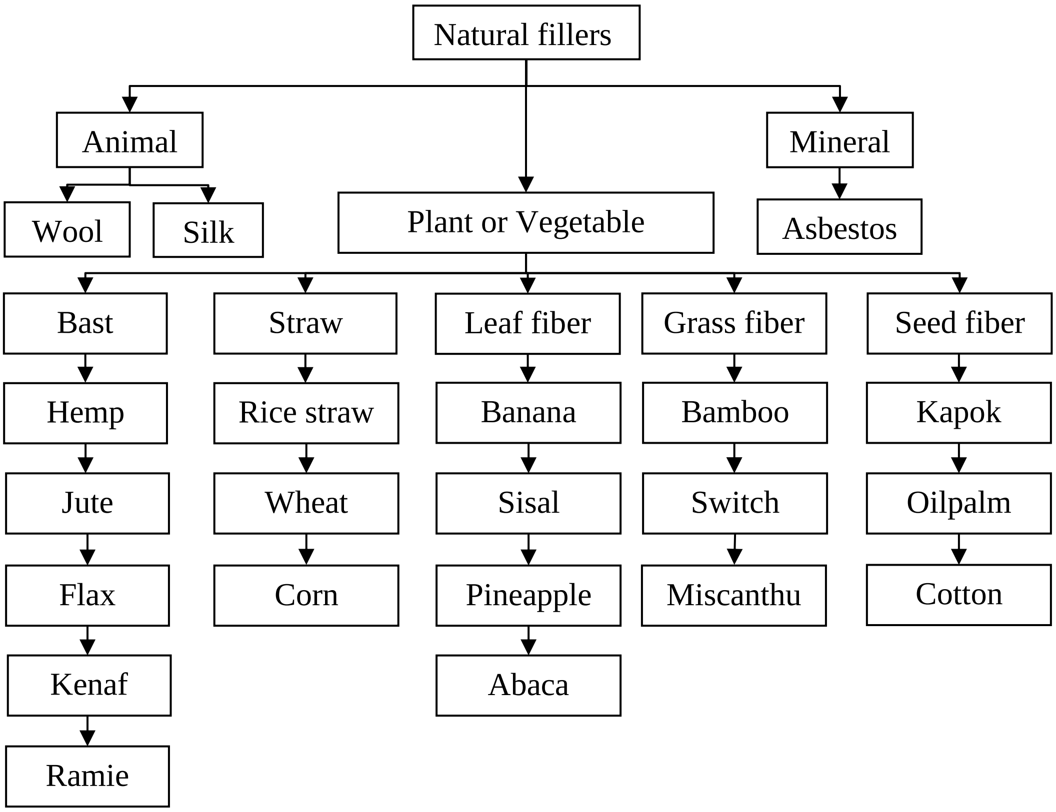


Figure 2.1 Classification of natural materials [51]

Advanced composites are high-performance materials that benefit from the high stiffness of fibrous materials embedded in the polymeric matrix; filler reinforced polymer composites and composite foam are examples. Filler reinforced composites are used in a wide range of applications such as aerospace [53], automobile [54], electronic [55], structural [56], industrial [57], and marine [58] industry[57,59–61]. As environmental are most concerns nowadays, it becomes a crucial point in the industries and 'green' products attract most environmentally-conscious consumers. Hence, composites reinforced with natural fillers are used to replacing those composite with synthetic fillers. The application area and market for natural filler reinforced composites are expected to grow at a steady pace for the future decade [37,50,62,63].

Plant-based totally natural fillers are lignocellulosic in nature and composed of cellulose, hemicellulose, lignin, pectin, and waxy constituents. The structural elements of fillers are presented in Table 2.1. The contents of structural elements are numerous in accordance to distinct natural filler.

Table 2.1 Structural constituents of plant filler

Name	Cellulose (%)	Lignin (%)	Hemi-cellulose (%)	Pectin (%)	Wax (%)	Micro-fibril/spiral angle (^{o})	Moisture content (%)	Ref.
Jute	41-53	21-26	14-20	0.2	0.5	8.0	12.6	[64]
Flax	71	2.2	19-21	2.3	1.7	10.0	10.0	[36]
Hemp	70-74	4-6	18-22	0.9	0.8	6.2	10.8	[64]
Ramie	69-76	0.6-0.7	13-17	1.9	9.3	7.5	8.0	[36] [64] [65]
Sisal	67-78	8-11	10-14	10.0	2.0	20.0	11.0	[36] [64]
PALF	70.82	5-12	–	–	–	14.0	11.8	[64]
Cotton	82.7	0.7-1.6	56	–	0.6	–	33-34	[36] [64]
Kenaf	31-40	15-21	22	3-5	–	–	–	[64] [65]
Banana	63-64	5	10	–	–	–	10-12	[65]
Abaca	56-63	12-13	–	1	–	–	5-10	[65]

Natural filler in polymer composites serves as reinforcing agents to achieve the desired characteristics of composites and thus are widely used in several industries [66]. Natural fillers have high stiffness, low in cost and most abundant materials available to be used in processing a composite product. However, natural filler reinforced composites have some limitations such as follows; can reduced ductility, low resistance under impact and in moist conditions, brittle, a most vulnerability in fire, and high in density compared with those of pure thermoplastics. In order to solve the above-mentioned problems, composite foams were developed [67].

It was demonstrated that composite foams have enhanced fatigue life [68], impact strength, toughness, and most importantly, reduced in density [69]. Natural fillers are added to composite foams as reinforcing fillers. The advantages of using the natural fillers are low cost, renewable sources, and small environmental burden. In addition, the density of the fillers is less than glass fibers and the fillers have better adhesive property between fillers and polymer matrix [35,70,71].

2.3 Kenaf

2.3.1 Origin of kenaf

Kenaf or hibiscus cannabinus is lignocellulosic material, which extracted from kenaf plants. Kenaf is annual plants and can grow more than 3 m high within 3 month with a stem diameter of 25 mm to 51 mm [8,72,73]. Kenaf has been used as raw materials as cordage crop to produce twine, rope, and sackcloth and food for many years [74].

Kenaf is a promising of raw materials for various applications such as pulp, paper, and cardboard, panels, mass uses as an absorbent agent [75], natural fuels [50], cellulose product [76], animal fodder and feed [77], seeds [78], and biomass [79]. Kenaf is made up of 40% cellulose, 21.6% lignin and pectin, and other constituents such as ash and silica. However, the amount of these constituents may differ depending on several factors including the climatic and soil conditions, the age of the plant and the stage of the growing season [80]. The chemical composition of kenaf in comparison with other natural filler is shown in Table 2.2, where the mechanical properties of kenaf in comparison with other natural filler are shown in Table 2.3.

Table 2.2 Chemical composition of kenaf in comparison with other natural fillers

Type of filler		Cellulose (%)	Lignin (%)	Ash (%)	Silica (%)	Ref.
Kenaf	Bast	31-39	15-19	22-23	5	[81]
	Core	31-34	15-21	–	-	
Jute	Bast	45-53	21-26	18-21	0.5-2	[82]
	Core	41	24	22	0.8	
Wood	Coniferous	40-45	26-34	7-14	–	[42]
	Deciduous	38-49	23-30	19-26	–	

Table 2.3 Properties of natural fillers with conventional fillers

Name	Density (g/cm^3)	Tensile strength (MPa)	Young's modulus (GPa)	Specific strength (GPa/g/cm^3)	Specific modulus (GPa/g/cm^3)	Elongation at break (%)	Ref.
Jute	1.3-1.4	393-773	13-26.5	0.3-0.5	10-18.3	1.16-1.5	[54]
Kenaf	1.5	450.24	43.36	319.4	28.9	3.1	[83]
Flax	1.5	345-1100	27.6	0.2-0.7	18.4	2.7-3.2	[84]
Hemp	1.1	690	30-60	0.6	26.3-52.6	1.6	[54]
Sisal	1.5	468-640	9.4-22.0	0.3-0.4	6.4-15.2	3-7	[85]
E-glass	2.5	2000-3500	70	0.8-1.4	28	2.5	[54]
Aramid	1.4	3000-3150	63-67	2.1-2.2	45.47.8	3.3-3.7	[54]

The processing technique to extract kenaf plant has significantly improved. For example, the separation process of an inner woody core material (which constitutes the 60% of the plant,) from the outer bark (which constitutes the remaining 40%) has significantly improved in such a way that different types of processing either the entire plant or its constituents [74,86].

Kenaf bast is like a conventional textile obtained in bundles and can be cut into a specific length. These fibers are coarse and brittle in nature and are made soft and flexible by adding alkali in water emulsions. The density of the bast fiber is 1.293 + 0.006 g/cm^3 [87]. They were traditionally used in making Cordage yarns, Canvas, Sacking, Carpet backing, padding lignocellulosic composites, door and instrument panels [8]. More recently they are being used as a noise insulation material and fiber mat in automobiles [80]. The kenaf bast also offers a very good alternative for making specialty paper and has excellent properties in terms of papermaking [88].

Kenaf core, on the other hand, is a hardwood like material and very porous. The density of the core is 0.09 – 0.11 g/cm^3 and the length of refined fillers is 0.6mm [89]. Kenaf core is mainly used in absorbent application like additive for, potting mixes [90], animal bedding [77] and some wood-based composite [91,92]. Kenaf could have undeniable advantages in the field, but also in organic farms because it could be used as geotextile, used on soil for mulching, erosion control, or soil filters. Kenaf would be promising as biodegradable and competitive material [93,94]

2.3.2 Utilization of kenaf as reinforcing material

The composite industry is actively considering the use of lignocellulosic material such as kenaf, jute, flax, hemp, and coir; as substitutes for synthetic materials. Suddell (2008) reported that about 20 kg of lignocellulosic filler could be used for the parts that do not require high bearing load in each of the 53 million vehicles produced each year [95]. Different automotive manufacturers already make use of lignocellulosic material considering the environmental and economic advantages of natural filler over synthetic filler in conjunction with the public awareness towards green products, it is evident that kenaf has a potential prospective in the composite industry [45,95,96].

2.3.3 Previous work of kenaf core as reinforcing material

Other studies have been conducted on using kenaf core as reinforcing polymer composites. Rizwan (2007) studied the comparison of mechanical properties and microstructure between kenaf core and kenaf bast reinforced polyester composites. They randomly oriented core and bast filler between 5 to 40% filler loading. From mechanical testing shows that higher strength provides from kenaf bast. However, kenaf core is found lead in high absorbent rate due their geometry structural after being water absorption test. SEM analysis for surface topography found that the clean surface of bast and non-uniform in term of filler shape and size of core fiber [97].

Ishak et al. (2010) studied was to compare the mechanical properties of short kenaf bast and core filler reinforced unsaturated polyester composites with varying filler weight loading (0 to 40%). Overall results showed that the composites reinforced with kenaf bast had higher mechanical properties than kenaf core filler composites with optimum filler content for achieving highest tensile strength for both bast and core composites was 20%. It was also observed that the elongation at break for both composites decreased as the filler content increased [98].

Meanwhile, Batouli et al. (2014) reported that outstanding thermal, mechanical, and environmental properties of kenaf core based polyurethane insulation board in structural insulated panels. They have succeeded to create environmentally friendly building material from kenaf core based polyurethane. The rigid polyurethane reinforced with 5 - 15% of kenaf core. In current practice of making the composites, kenaf core does not replace the polyurethane; instead, it mostly fills the void space, which is initially filled with air and, hence, the kenaf core decreases the porosity of polyurethane composites and increases the density. The flexural results show that the more the kenaf loading, the less porous the composites [28].

Nar et al. (2015) studied the production of higher volume in composite production of kenaf core. They found out that naturally porous structure of kenaf core provides a novel reinforcement particle. In their studied, foams of rigid polyurethane with 5 to 15% filler loading. Up till now, efforts at using it as reinforcement have proven unsuccessful. However, kenaf core introducing constraint during foaming resulted in reinforcement. The results show that free foaming resulted in poor reinforcement while a constrained expansion on the foam increased the reinforcement potential of the kenaf core [29].

Ismail et al. (2010) studied high density polyethylene/soya powder reinforced kenaf core composite with different kenaf loading. The effect of kenaf core filler loading and silane treatment from FTIR and SEM observations indicate that better adhesion was observed for the composite with chemically treated kenaf core filler. Chemical treatment of kenaf core caused a significant increase in stabilization torque, water resistance and the mechanical properties of HDPE/soya powder/kenaf-core composites [99]

2.3.4 Interfacial filler – matrix studies

The interface is a boundary region where filler and matrix phases come in contact with zero thickness [100]. An interface between any two phases can be defined as a surface which is common to both filler and matrix and the immediate region about this surface [101]. Theories of mechanisms at the interface were summarized by Plueddemann (2016), mainly as: chemical bonding theory; surface wettability theory; mechanical interlocking mechanism; deformation layer theories; and restrained layer theory [101]. A filler composite material usually consists one or more filamentary phases embedded in a continuous matrix phase [102]. In the filler reinforced polymer composites, two distinct phases, i.e., filler and matrix, and interphase and interface can be recognized.

The chemical bonding theory is chemical bonding through covalent bonds, which can be formed by the reaction of the functional groups of one phase with the ones of the other phase or through coupling agents [103]. Wettability refers to the intimate contact possible at the molecular level, which defines the liquid phase will wet a solid phase by involve physical adsorption. Theoretically, complete wetting of would provide adhesive strength by physical adsorption that would exceed the cohesive strength of resin and it is measured by the contact angle. A low contact angle indicates good wettability [104]. The deformable layer theory was based on the different finishes on the fillers have the power to deactivate, destroy or absorb certain constituents out of the uncured liquid resin to form a plastic layer at the interface, which can provide a mechanism for local relief of residual stresses formed by the different thermal expansion coefficients of the filler and matrix [104]. Theories of mechanisms at the interface described are the general cases involved in the filler-resin composite systems.

2.3.5 Problems in natural filler reinforced polymer composites

The properties of the composites are controlled by the properties of the filler and the quality of interfacial bonding between filler and matrix. The factors of reduction of the composites properties were caused by the hydrophilicity of filler, poor filler compatibility into matrix, and inconsistent filler structure of the filler [105].

Natural filler consists of cellulose which are cover with hemicellulose and lignin. In cellulose crystalline region are present of strong linked hydroxyl group, which inaccessible and difficult to other chemicals penetrating the crystalline region as shown in Figure 2.2. However, in amorphous region the hydroxyl groups are loosely linked with the filler structure are free to react with other chemicals especially water molecules from the atmosphere [106–108].

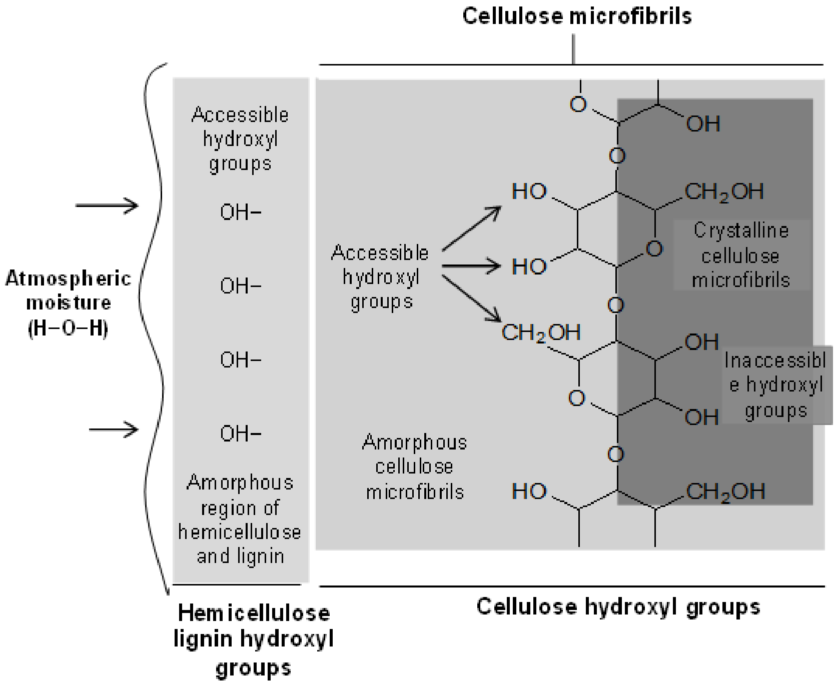


Figure 2.2 Schematic presentation of the orientation of the fiber constituents that absorb moisture [106]

The hydrophilic fillers are incompatible with most hydrophobic thermoset and thermoplastic matrices. As a result, incomplete filler wetting into the matrix takes place and weak bonding exists at their interfaces. In addition, the hydrophilic filler causes filler swelling within the matrix and generates extra stresses on the surrounding matrix. Weak interface bonding and the induced swelling stress results in propagation of debonding, cracks and severe deterioration mechanical properties of the composite.

Incorporation natural filler into matrix is often associated with poor compatibility. Cellulose surface from natural filler is covered by hemicellulose and lignin. Both act as weak boundary layer between cellulose and the matrix. due to the weak boundary layer at the filler-matrix interface, the stress distribution capability throughout composite are is decreased [109]. A weak boundary layer can be removed and coverings through different chemical treatments of the filler.

Inconsistency of natural filler physical dimensions are not uniform throughout its length because natural filler comes from different parts of plant has various length and width. The fiber aspect ratio (length/diameter) is one of critical parameter for determine composite properties. It is define as the minimum ratio in which the maximum filler stress can be achieved for given load [110]

2.3.6 Chemical treatment on natural filler reinforced composite

To optimize the properties of the composites, several treatments can be used to enhance the reinforcing material specially to create better filler-matrix interfacial properties. The reinforcing materials can be treated by chemical and physical methods [111]. Reinforcement filler can be treated with a suitable chemical to increase compatibility between filler and polymer matrix. Usually, chemical treatment on the fillers will clean the surface and increased the surface roughness of the filler, which would delay the moisture absorption.

There are various types of chemical treatments on natural fillers that lead to enhanced compatibility at the interface of filler-matrix. Different chemical treatments on the filler lead to certain effect on the properties of composite. Chemical treatment on filler surface consists of alkaline treatment by sodium hydroxide (NaOH) [112], isocyanate treatment [113], benzoyl treatment [31], and silane treatment [107].

2.3.6(a) Silanes

In principle, silanes are compounds of silicon and hydrogen, of the formula $\mathrm{Si_nH_{2n+2}}$ analogues of alkanes. Silane tend to be less stable than their carbon analogues because Si–Si bond has slightly lower strength than C–C bond [114].

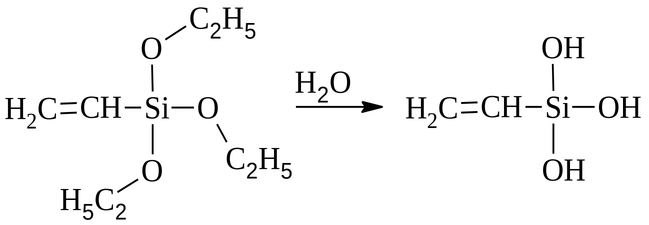
In practice, terminology has been extended and it includes also compounds in which any or all of the hydrogen have been replaced. A silane that contains at least one carbon-silicon bond structure is known as an organosilane. Carbon-silicon (CH_3–Si–) bond is very stable. Very non-polar and give rise to low surface energy and hydrophobic effects as a consequences of silicon’s more electropositive nature when compared to carbon [115].

The silicon hydride (–Si–H) structure is very reactive. It reacts with water to yield reactive silanol (–Si–OH) species and additionally will add across carbon-carbon double bonds to form new carbon-silicon-based materials. The methoxy group on the carbon compound gives a stable methyl ether, while its attachment to silicon gives a very reactive and hydrolyzable methoxsilyl structure [116].

2.3.6(b) Silane chemical treatment on natural filler

Monomeric silicon chemicals are also known as silanes, typically used as a coupling agent. Silane consist at least one silicon-carbon bond $(\mathrm{Si}-\mathrm{CH_3})$ also known as organosilane. Silane treatment on reinforcing filler will form a chemical link siloxane bridge between the surfaces of filler and matrix [117].

Silanes go through numerous stages during the treatment process, such as hydrolysis, condensation, and bond formation at the final stages. In the hydrolysis process, silane will form silanol as explained in Equation 2.1 [118].



Equation 2.1

Through the condensation process, one end of silanol reacts with the OH groups, which consist in cellulose, hemicellulose and lignin as shown in Figure 2.3 and the other end reacts (bond formation) with the matrix (Si − matrix) functional group. This co-reactivity provides molecular continuity across the interface of the composite. It also provides the hydrocarbon chain that restrains the filler swelling into the matrix [46,119]. As a result, filler-matrix adhesion improves and stabilizes the composite properties [120].