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EFFECT OF ALKALI TREATMENT CONDITIONS OPTIMIZATION ON KENAF FIBER POLYMER COMPOSITE CHARACTERIZATION

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EFFECT OF ALKALI TREATMENT CONDITIONS OPTIMIZATION ON KENAF FIBER POLYESTER COMPOSITE CHARACTERIZATION

MOHD YUSSNI BIN HASHIM

A thesis submitted in
fulfillment of the requirement for the award of the
Doctor of Philosophy

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For my beloved mother PATIMAH BINTI SAHDAN,
my father HASHIM BIN MARMAN, my dear wife SITI AISYAH BTE MISRAN,
my mother in law KHATIJAH BTE NORUDIN and my little hero
MUHAMMAD HARITH NAUFAL

“THANK YOU for your endless support”

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In the name of Allah, The Most Gracious and The Most Merciful

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ABSTRACT

This study was conducted to evaluate the alkali treatment conditions optimization impact on kenaf fiber and its short random oriented kenaf fiber reinforced polyester matrix composite mechanical properties characterization. The selected treatment conditions are alkali solution concentration (2% w/v ~ 10% w/v), immersion duration (30 minute ~ 480 minute) and immersion temperature (room temperature ~ 100^{o}C). Two types of experimental design approach were used in this work. It was three factors at three levels full factorial design for evaluating the kenaf fiber mechanical properties characterization and Response Surface Methodology (RSM) for determining the optimum alkali treatment conditions on kenaf polyester composite mechanical properties characterization. As the outcome of this study, the significant main-and-interaction effect of alkali treatment condition for kenaf fiber was determined. Furthermore, the correlation between optimum alkali treatment conditions with enhancement of kenaf fiber polyester matrix mechanical properties was suggested in the form of regression model. Based on the results, several regression models have been constructed according to Analysis of Variance and the regression model. Confirmation tests have been conducted towards selected predicted regression model. The confirmation test results shows good agreement with the proposed regression model. Finally, the outcome with a reliable database for optimum alkali treatment condition setting presented through this dissertation is expected to enhance insight regarding the knowledge of significant parameters in alkali treatment optimization that is extensively used in natural fiber surface treatment.

ABSTRAK

Kajian ini dilakukan untuk menilai kesan pengoptimuman parameter rawatan alkali ke atas ciri-ciri mekanikal gentian kenaf dan juga kompositnya yang diperbuat dari gentian kenaf pendek dan berterabur secara rawak yang dicampur poliester resin. Parameter untuk rawatan alkali adalah kepekatan larutan alkali (2% w/v ~ 10% w/v), tempoh rendaman (30 minit ~ 480 minit) dan suhu rendaman (suhu bilik ~ 100^{o}C). Dua jenis kaedah rekabentuk eksperimen telah digunakan. Ia adalah kaedah rekabentuk faktorial penuh menggunakan tiga faktor di tiga tahap untuk menganalisa sifat mekanikal gentian kenaf dan kaedah Response Surface Methodology (RSM) untuk mengenalpasti sifat mekanikal komposit daripada kenaf dan poliester pada ketetapan rawatan alkali yang optimum. Melalui hasil kajian, faktor utama dan perkaitan diantara faktor semasa rawatan alkali untuk gentian kenaf telah dapat ditentukan. Selain itu, korelasi antara parameter rawatan alkali yang optimum dan mampu meningkatkan sifat mekanikal komposit berasaskan gentian kenaf dan poliester telah diterjemahkan dalam bentuk model regresi. Berdasarkan hasil kajian, beberapa model regresi telah dibina menggunakan analisa variasi dan model regrasi. Ujian pengesahan turut dijalankan terhadap beberapa model regresi terpilih. Keputusan ujian pengesahan mempamerkan kualiti prestasi yang baik dengan model regresi yang dicadangkan. Kesimpulannya, maklumat data berkaitan rawatan alkali pada keadaan optimum yang disampaikan melalui disertasi ini dijangka mampu meningkatkan pemahaman dan memberi pengetahuan berkaitan parameter penting yang terlibat dalam mengoptimumkan proses rawatan alkali yang digunakan secara meluas untuk rawatan permukaan gentian asli.

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LIST OF SYMBOLS AND ABBREVIATIONS

$\widehat{y_1}$	-	Predicted or estimates response
y	-	Measured responses variable
b_1, b_2, b_3	-	Regression coefficients
b_o	-	Intercept
ε	-	Experimental error
α	-	Alpha or Significance level of the test
ANOVA	-	Analysis of variance
ASTM	-	American Society for Testing and Materials
CCD	-	Central Composite Design
D	-	Desirability functions
d	-	Depth of specimen (mm)
d	-	Impactor diameter
DF	-	Degrees of freedom
DIN	-	German Institute for Standardisation
DMA	-	Dynamic Mechanical Analysis
DOE	-	Design of experiments
E_{max}	-	Impact energy (J)
EP	-	Epoxy
FCCCD	-	Face Centered Center Composite Design
GRP	-	Glass reinforced polymer
H_a	-	Alternate or experimental hypothesis
H_o	-	Null hypothesis

IFSS	-	Interfacial shear strength
ISO	-	International Organization for Standardization
KMnO4	-	Potassium Permanganate
L	-	Support span length (mm)
$\boldsymbol{L}$	-	length of fiber
$\boldsymbol{L_o}$	-	Length of elementary unit of the fiber
m	-	Number of responses
$\boldsymbol{m}$	-	Weibull modulus
MAPP	-	Maleic Anhydride Polypropylene
MEKP	-	Methyl Ethyl Ketone Peroxide
MS	-	Mean squares
NaOH	-	Sodium hydroxide
NKTB	-	The National Kenaf and Tobacco Board
-OH	-	Hydroxyl groups
OVAT	-	One variable at a time
p	-	maximum probability
PE	-	Polyethylene
P_f	-	Probability index or estimators
$\boldsymbol{P_f(\sigma)}$	-	Probability of failure
PLA	-	Poly- Lactic Acid
PP	-	Polypropylene
PP	-	Polypropylene
PS	-	Polystyrene
PUR	-	Polyurethanes
PVC	-	Polyvinyl chloride
R	-	Rate of crosshead motion (mm/min)
R^2	-	Coefficient of determination
RSM	-	Response surface methodology
RT	-	Room temperature
S	-	Standard error of a regression

SEM	-	Scanning electron microscope
SS	-	Sum of squares
σ	-	Stress
σ_o	-	Characteristic strength
σ_υ	-	Lowest value of strength
σ_{impact}	-	Impact strength (kJ/m^2)
TAPPI	-	Technical Association of Pulp and Paper Industry
TGA	-	Thermo gravimetric analysis
UP	-	Unsaturated polyesters
UTS	-	Ultimate tensile stress
$\boldsymbol{v}$	-	Volume fraction
$\boldsymbol{V}$	-	Ratio of volume
$\boldsymbol{V_f}$	-	Volume fraction
$\boldsymbol{V_c}$	-	Composite volume
$\boldsymbol{w}$	-	Weight fraction
$\boldsymbol{W}$	-	Ratio of weight
$\boldsymbol{W_f}$	-	Weight fraction
$\boldsymbol{x_1}$	-	Alkali concentration (w/v%)
$\boldsymbol{x_1x_2}$	-	Interaction
$\boldsymbol{x_2}$	-	Immersion time (min)
$\boldsymbol{x_3}$	-	Immersion temperature (^oC)
Z	-	Rate of staining of the outer fiber (mm/mm/min)

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Introduction

"We do not *inherit* the earth from our ancestors, we borrow it from our children" is an ancient Indian proverb that could be a suitable phrase to emphasize the global challenges on environmental issues and energy crisis nowadays. As the world population increase rapidly, intense pressures are placed on earth resources to provide an adequate supply of food and other compulsory needs to support this incredible pace of change. According to the Concise Report on the World Population Situation in 2014, the world population was over 7 billion in late 2011 and expected to reach 9 billion people by 2050. In conjunction with increasing number of world population growth, it gives a significant impact on environmental and energy issues. The global crisis like climate change, oil peak, water resources, sanitary landfill, deforestation and many others challenge closely affected with the human activities either from its needs or from its wastes. The work presented in this thesis is not an attempt to solve the world problems but this is a small effort in contributing to the environmental sustainability aspiration. For that reason, this chapter discussed the overview of the study begins with research background section and followed by problem statement section. Research objectives, research contributions, research scopes, research methodology and research significance are presented in following section. Thesis organization was written at the end of this chapter.

1.2 Research background

"Sustainable Development" is a concept that emerged from The Brundtland Report of 1987, entitled *Our Common Future*, which can be defined, as "*... development that meets the need of the present without compromising the ability of future generations to meet their own needs*" [1]. This sustainability development concept had stimulated environmental awareness in every aspect of life including social, political and economic activity [2]. Typical product development practices in manufacturing industries are predominantly based on traditional cost and profit models focused at achieving high quality of a product at low cost and high profit. Environmental requirements are mainly considered as unavoidable regulation, which generates additional design constraints and increases the cost [3]. However, with raising concern related to environmental issues like diminishing non-renewable resources, stricter regulations related to environment and occupational safety and health, increasing consumer preference for environmentally-friendly products it changes the perception of negativity and confrontation between environmental and profitable business activity with a positive spirit of collaboration and partnership. Indeed, many industries are taking aggressive action on improving efficiency to lower their environmental impact, which also improves business performance [4]. In particular, the manufacturing sector, which lies at the core of industrial economies, must be made sustainable in order to preserve the high standard of living achieved by industrialized societies and to enable developing societies to achieve the same standard of living sustainably [5].

Historically, the use of cellulosic natural fiber can be traced back more than 10,000 years. According to Bledzki [6], seventy years ago, nearly all resources for the production of commodities and many technical products, were materials derived from natural textiles. Textiles, ropes, canvas and also paper, were made of local natural fibers, such as flax and hemp. As early as 1908, the first fiber reinforced plastic composite materials were applied for the fabrication of large quantities of sheets, tubes and pipes for electronic purposes [7]. These composite materials (notably aramid, carbon and glass fiber reinforced plastics) dominate the aerospace, leisure, automotive, construction and sporting industries. Glass fiber are the most widely used to reinforce plastic due to their low cost and fairly good mechanical properties [8]. For that reasons, these man-made fibers was widely used in diverse

industrial field where the application of natural fibers came to a near halt. However, these synthetic fibers have serious drawback such as higher density compared to natural fiber, abrasion to machine, health risk when inhaled, high energy consumption and cannot be recycled and renewed after the end of life time. Consequently, motivated by the effort to achieve sustainable development and the increasing environmental consciousness, the last two decades have seen resurgent interest in utilizing natural fiber as reinforced material in polymer matrix composite. Another factor that prompted the usage of natural fiber in polymer composite is the availability of improved data on the properties and morphologies through modern instruments at different levels. Thus it gives better understanding of their structure and property correlations [9].

Natural fiber claimed to offer environmental advantages such as reduced dependence on non renewable sources, lower pollutant emissions, lower green house gas emissions, enhance energy recovery and end of life biodegradability of component [10]. Furthermore, these natural fiber are usually drawn from relatively abundant plants, therefore low cost. During processing, natural fiber are less abrasive than inorganic mineral counterparts to processing machinery, less dangerous for the production employees in case of inhalation, easy to be incinerated, they lead to final composites with lower specific weight and allow obtaining interesting properties in terms of thermal and acoustic insulation [11]. Because of such tremendous advantageous in the utilization of natural fibers, they are fast emerging as a reinforcing material in composites. Considering the high performance standard of composite materials in terms of durability, maintenance and cost effectiveness, applications of natural fiber reinforced composites as construction material holds the enormous potential and very critical for achieving sustainability [12]. In automotive industries, composites made of renewable materials have been widely used in interior and exterior body parts. Similar components are used as trim parts in dashboards, door panels, parcel shelves, seat cushions, backrests and cabin linings [13]. In Europe, the main application areas of natural fiber reinforced composites for automotive industries are limited almost exclusively to the passenger car range. Nevertheless, in future these composite materials applications could expanse not only be limited to car components, but can also be used in trucks, buses, and trains or in the furniture and design industry [14]. Beside these two applications, natural fiber

reinforced composite also used in packaging, insulation, filters, sorbents, non structural composite, geo-textiles and furniture industries [15] .

Natural fiber reinforced polymer composite offers promising opportunities toward developing environmental friendly products. However, despite the undoubted attraction of using natural fiber as composite reinforcement, there are still several critical issues that need to be addressed before natural fiber can be extensively used for a wide range of applications products. These issues had limited the potential usage of natural fiber composite applications mainly to non structural and lightly loaded materials [16]. Furthermore, recent review presented by Satyanarayana [9] highlight that one of the major hurdles for commercialization of natural or lignocellulosic fiber composite was due to non-recognition of research and development in developing countries, where these fibers are abundantly available.

The shape, size and strength of the natural plant fibers may vary widely depending on cultivation environment, geographical origin, weather during growing season, age of maturity, and retting process used to get the fibers [17]. The retting process which breaks down chemical bonds that hold the fiber together such as water retting, dew retting, enzymatic retting or chemical retting also can contribute to the variation of fiber end product properties [18]. Some key issues that need to emphasize in dealing with natural fiber reinforced composite are:

i. Natural fiber have an irregular cross section with a central void which make the determination of their mechanical properties more complex than for solid circular glass fiber [19].
ii. Variability of physical and mechanical properties of natural fiber, which results in large variation of its composite properties [20].
iii. Natural fiber shows a high moisture absorption characteristic, which initiated dimensional changes thus leading to micro-cracking and poor thermal stability [21].
iv. Lack of sound fiber and matrix compounding process where the fibers not evenly distributed within the matrix [22].
v. Fiber matrix incompatibility due to the hydrophilic natural fibers character and the hydrophobic polymer matrices character [23].
vi. Natural fibers and their composites had a low heat resistance [24].

1.3 Problem statement

In Malaysia, planting, cultivating and harvesting of kenaf plant has become the subject of interest and encouraged by the government so that it will replace the tobacco plant in near future [25]. As reported by The National Kenaf and Tobacco Board (NKTB), an attempt have been made to increase a planting of 10,000 hectares of kenaf throughout Malaysia in 2020 due to the target sales of kenaf is about RM 80 million in year 2020. Currently there are 2,000 cultivated hectares of kenaf planting [26]. Kenaf fiber has become a national agenda for further advancement in various applications such as automotive components, packaging and furniture.

One of the major issues in utilizing natural fiber reinforced composite was compatibility between natural fiber and resin matrix surface. Tremendous works had been done to enhance natural fiber-matrix compatibility in order to strengthen composites mechanical properties [9, 11, 20]. One of the methods to improve fiber-matrix interface and reduce moisture absorption capability of natural fiber is fiber treatment process. Mercerization or alkali treatment was a treatment process that widely used due to its low price and low hazard risk [20]. During alkali treatment, there are three major parameters setting involved, which are alkali solution concentration, immersion duration and immersion temperature [6].

However, despite extensive use of alkali treatment process, most of the works are using one variable at a time (OVAT) approach. In this approach, one parameter was set at constant value during determining the others parameter effect on the response. As a result, this leads to the lack of factors or parameters main-and-interaction effect and optimal setting consideration. Furthermore, information regarding parameters combination at optimum alkali treatment conditions level is still scant [27]. Therefore, with kenaf fiber as a selected natural fiber, this research aims to find answers for these following uncertain issues:

i. Does combination of factor levels in alkali treatment have a significant impact on the average kenaf fiber characteristic properties?
ii. Do alkali treatment conditions setting give any significant effects on kenaf fiber polyester composite mechanical properties enhancement?
iii. What are the optimum treatment conditions setting to enhance on kenaf fiber polyester composite mechanical properties?

1.4 Research objectives

The aim of this study is to evaluate the alkali treatment conditions impact on kenaf fiber and short randomly oriented kenaf fiber polyester composite mechanical properties characterization. The specific objectives of this study are listed as follow:

(a) To investigate the effect of alkali treatment conditions on kenaf bast fiber physical properties.

(b) To identify the significant main-and-interaction effect which affect the kenaf bast fiber mechanical properties characteristics.

(c) To evaluate the impact of alkali treatment conditions on short randomly oriented kenaf fiber polyester composite mechanical properties characteristics.

(d) To determine the optimum alkali treatment conditions setting for short randomly oriented kenaf fiber polyester composite mechanical properties enhancement.

(e) To construct a validated regression model based on an optimum alkali treatment conditions setting with multiple responses properties of short randomly oriented kenaf fiber polyester composite.

1.5 Research scopes

This study was divided into two parts, which are fiber properties assessment and composites characterization assessment at different alkali treatment conditions setting. The research has been conducted with the following limits:

(a) Selected natural fiber in this study is kenaf fiber, which was supplied from Kenaf Natural Fiber Industries (Malaysia) Sdn. Bhd. These kenaf fibers were treated with alkali solution at various treatment conditions. Alkali treatment conditions are alkali solution concentration, fiber immersion time and immersion solution temperature. Untreated kenaf fiber was used as a control unit.

(b) Sodium hydroxide (NaOH) in pallet form was supplied from BDH Prolabo. Alkali solution concentration was prepared using weight volume percentage (w/v %) calculation technique.

(c) Polyester resin 2597-I supplied from Wee Tee Tong Chemicals Pte Ltd, Singapore are used as matrix material for interfacial shear strength test and composite fabrication process.

(d) Kenaf bast fiber characteristics that was investigated as a responses in this study are :

   i. Kenaf fiber diameter and cross section area
   ii. Kenaf fiber and polyester matrix interfacial shear strength
   iii. Kenaf fiber tensile strength

(e) Kenaf fiber volume fraction for composite fabrication process was 25% as this percentage shows a highest composite tensile strength from conducted preliminary test. The basic rule of mixture theory and its assumption was applied for fiber volume calculation. The void content calculation in composite was neglected for the simplicity purpose. Composite are fabricate using hand lay-up technique and pressed during curing process.

(f) Short randomly oriented kenaf fiber polyester composite mechanical properties characteristics that was evaluated as responses in this study are:

   i. Tensile strength
   ii. Flexural strength
   iii. Energy absorption

1.6 Research methodology

In order to achieve the objectives of this study, this following methodology were used as a guideline during the course of the study.

(a) Adopting three factors at three levels full factorial experimental design technique for determining the alkali treatment conditions significant impact on kenaf fiber properties.

(b) Adopting Response Surface Methodology (RSM) according to Central Composite Design (CCD) as an appropriate statistical and experimental design for developing the mathematical modeling and optimization of alkali treatment conditions of randomly oriented short kenaf fiber reinforced polyester matrix composite. RSM was selected due to its efficiency in minimizing the total number of experimental run [28].

(c) Conduct alkali treatment process at various conditions setting using dyeing machine (Model: Rapid H-12C) on kenaf bast fiber according to specific experimental design.

(d) Perform mechanical test at fiber level to identify each responses. Single kenaf fiber tensile test was followed ASTM C1557-03. Pull out test between kenaf fiber and polyester matrix was carry out to determine fiber-matrix interfacial shear strength.

(e) Conduct mechanical test at composite level according to ASTM International standards:

   i. Tensile test (ASTM D638-10)
   ii. Flexural test (ASTMD790-10)
   iii. Low velocity drop impact test (ASTM D3763-93)

(f) Carry out the full factorial and response surface methodology analysis, model adequacy checking, model validation and finally proposed the regression model for optimization of alkali treatment conditions setting on short randomly oriented kenaf fiber polyester composite. This regression was required in order to identify relationships among alkali treatment variables and used these relationships to determine optimum alkali treatment conditions predictions that could enhance composite properties.

A schematic diagram of the comprehensive overview of the research work is presented in Figure 1.1, which was followed as a guideline during the course of the study.

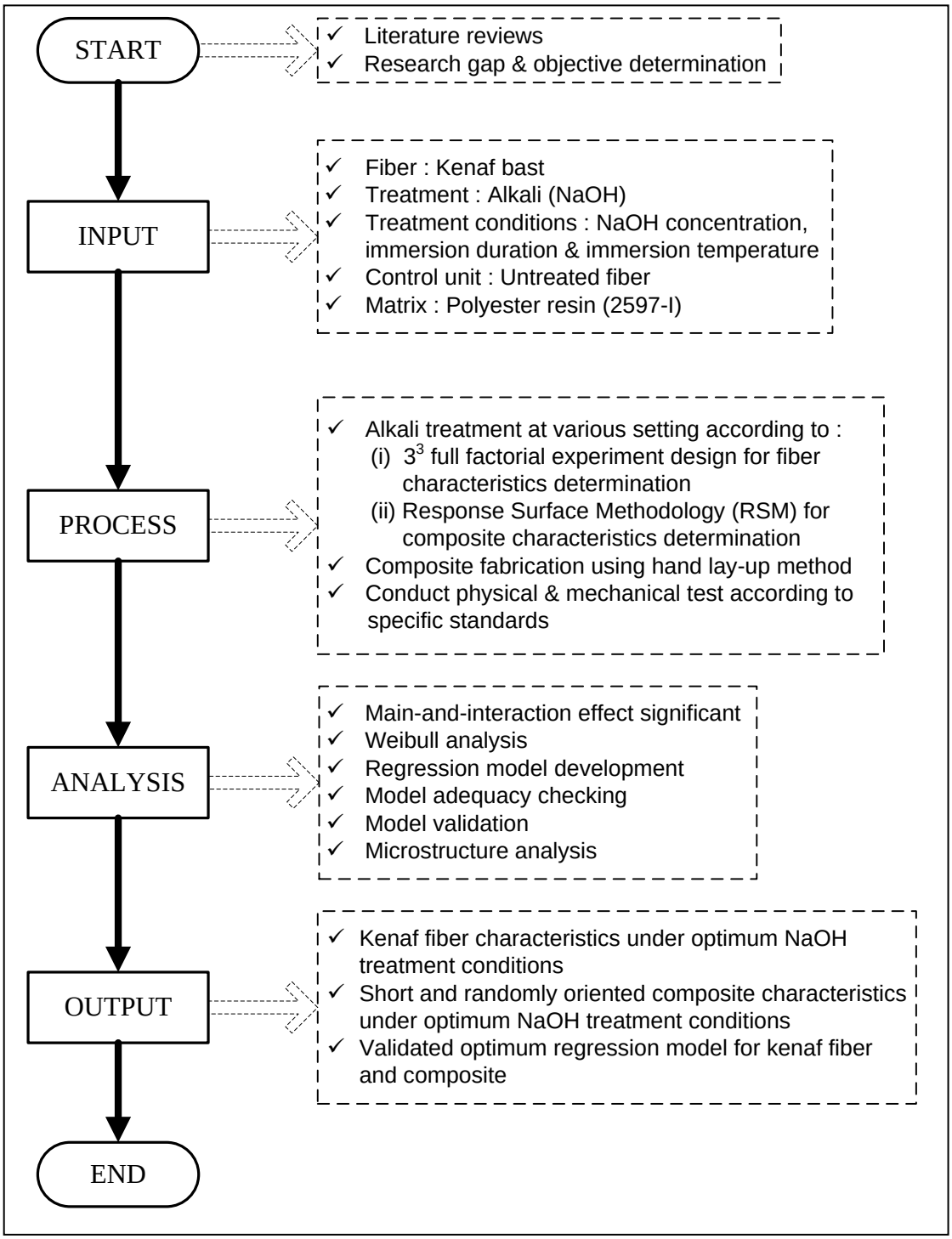

Figure 1.1: A schematic diagram of the comprehensive overview methodology of the research work

1.7 Research significance

From previous research works, it was found that alkali treatment is one of the widely used fiber surface treatment technique in natural fiber reinforced matrix composite applications. As a result, this work has opened up the scope of using alkali treatment at optimum conditions setting for kenaf fiber surface treatment process. Specifically, the significance of this study could be listed as follows:

(a) Enhance insight regarding the knowledge of determining the significant parameters in alkali treatment process for natural fiber surface treatment. Thus, it contributes to the potential time and cost saving of searching the optimum setting conditions during alkali treatment process within specific range.

(b) Comprehensible alkali treatment conditions correlations with the help of full factorial and response surface methodology method is likely to benefit the researcher and industries, as it would help them in selecting optimum value of the treatment process. In consequence, it potentially generates additional knowledge for randomly oriented short kenaf fiber reinforced polyester matrix composite development.

(c) Clearly recognize random oriented short kenaf fiber reinforced polyester matrix composite performance characteristic particularly in tensile strength, flexure strength, and energy absorption behaviour at low velocity impact. This responses characteristic was translated in the form of regression model. Consequently, this could potentially use as support knowledge for natural fiber reinforced polymer matrix composites development which is an optional material for replacing synthetic fiber composite for low cost and light weight materials such as packaging materials, house hold furniture, insulation panel, building & construction materials, automotive interior components and others.

1.8 Thesis organization

Chapter 1 presents brief introduction and motivation of the study. It covers the research introduction, research background discussing the trends, opportunities and challenges in natural fiber reinforced polymer composite materials. Then description of problem statement, research objectives, research contributions, research scopes, research methodology and followed by research significance.

Chapter 2 discussed an overview of the relevant research works conducted by other researcher in this similar area. The discussion covers trending in natural fiber, kenaf fiber, alkali treatment process, fiber characterization, natural fiber reinforced polymer matrix composite, composite characterization and treatment optimization.

Chapter 3 present the experimental matrix design for determining kenaf fiber and kenaf fiber polyester matrix composite properties at different alkali treatment setting. The technique used to investigate and model the relationship between variables was discussed in this chapter. This chapter also includes the explanation of multiple responses optimization, simultaneous optimization technique, a rule of mixture and Weibull analysis description.

Chapter 4 covers the experimental set up and working procedure selected in this work. It started with raw material description, alkali treatment process flow and kenaf fiber properties evaluation process. Then it continued with the discussion of composite fabrication work, calculation of fiber volume fraction, specimen preparation and composite mechanical test explanation according to the specific selected standard.

Chapter 5 covers the experimental work results and discussions. It contains five sections, which explain the research finding. These sections were fiber physical properties analysis, fiber mechanical properties analysis, composite properties analysis, model development and adequacy check and multi responses optimization.

In Chapter 6, the conclusions of this study, research contributions and recommendation of future work are presented.

CHAPTER 2

LITERATURE REVIEW

2.1 Trending in natural fiber

As previously discussed at problem background section, motivated by the effort to achieve sustainable development and the increasing of environmental consciousness, there are increasing interest in utilizing natural fiber as reinforced material in polymer matrix composite. The growing importance of these natural fiber reinforced composites is evident from the increasing number of research publications during the last decade as shown in Figure 2.1[29] . These references was taken from publications found in Science Direct website database by entering the keywords natural fiber, synthetic fiber, reinforcement and short fiber composite as topics in all document types. Recently, there were several publication reviewing on natural fiber applications [13, 20], surface treatment [30], bio degradable [31] and bio composite [32] issues. These publications trends shows that natural fiber had a potential expending market, which could offer significant opportunities for improved materials from renewable resources with enhanced support for global sustainability.

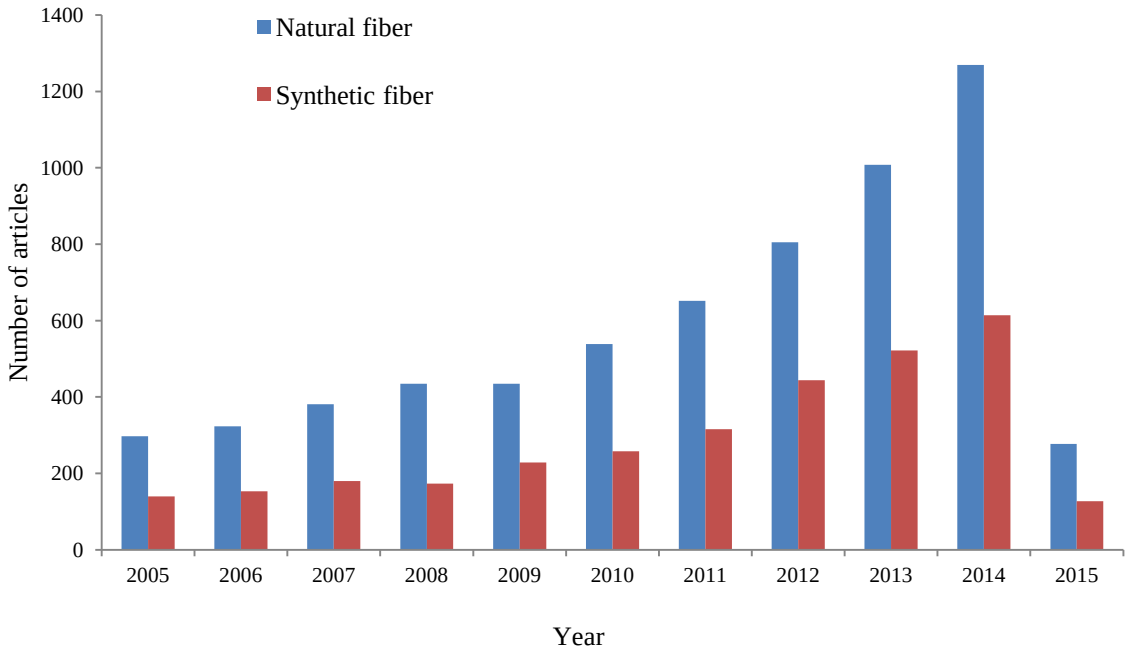

Figure 2.1: Number of synthetic and natural fiber reinforced polymer composite articles. Source: http://www.sciencedirect.com [29]
(Keywords used: Natural fiber, synthetic fiber, reinforcement, short fiber composite)

2.1.1 Classification of natural fiber

In general, natural fiber can be classified based on their origins coming from plants, animal or mineral [33]. For this study, the focused was on plant fiber. For plant fiber, it can be broadly categorized as either wood or non-wood fiber. Both have been extensively used in composites applications [33]. In wood fiber, a fiber is a single cell. Its properties are largely dependent upon types of cell and its location in a tree. This fiber type's mechanical property was significantly different dependent on the plant fiber species [17-18]. On the other hand, non-wood fibers are generally collections of individual cells and can be classified according to the location in the plant they are to be found [16]. It can be differentiate as a grass fiber, straw fiber, seed fiber, fruit fiber, bast fiber and leaf fiber. According to literature, non-wood plant fibers are the most popular of the natural fibers types that were used as reinforcement in fiber reinforced composites [34]. Figure 2.2 show the classification of natural fiber according to the types of it sources [35].

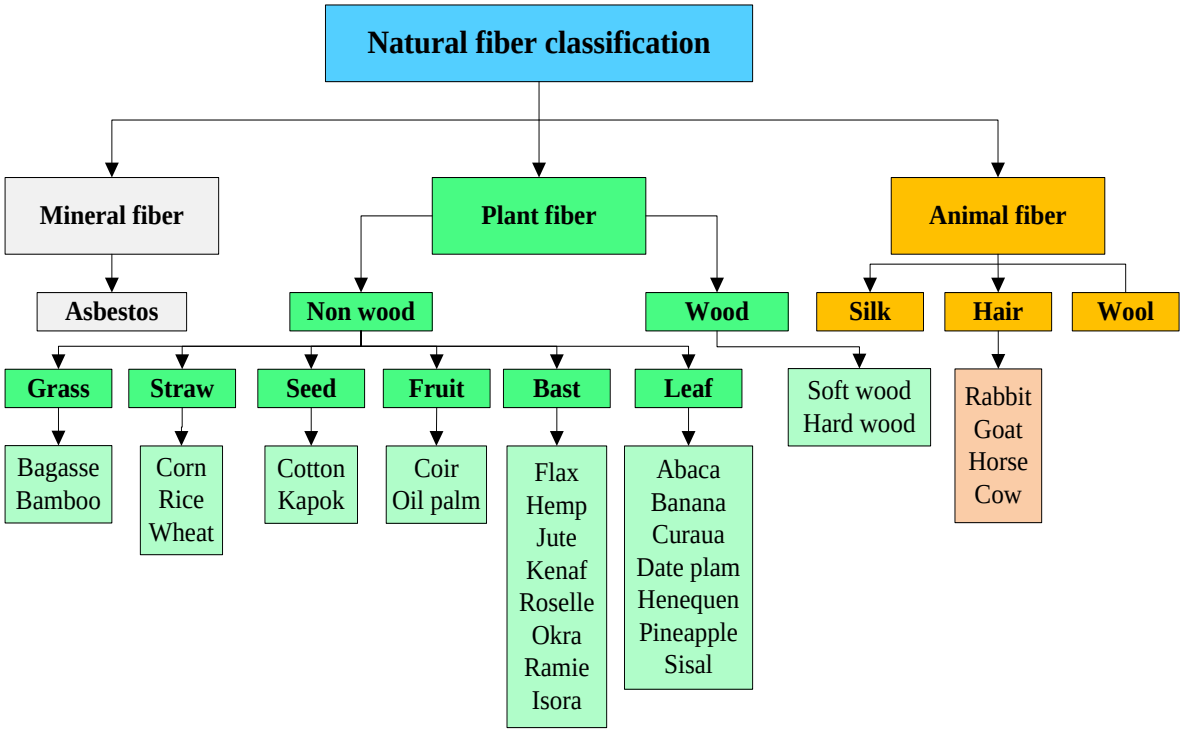

Figure 2.2: Natural fiber classification [35]

2.1.2 Composition of natural fiber

The main chemical composition of plant fiber consist of cellulose, hemi-cellulose, lignin, pectin, wax, with minor amounts of protein, extractives and inorganic [36]. The basic components with regard to the physical properties of the fiber are cellulose, hemicellulose and lignin [6, 37]. The cellulose polymer is composed entirely of carbon, hydrogen and oxygen. It is a strong, strictly linear polymer with no branching, stable and has good resistance to hydrolysis [6, 38]. The molecular structure of cellulose is responsible for its supramolecular structure, which in turn it determine many of fiber chemical and physical properties [6]. On the other hand, hemicellulose is not a form of cellulose. It comprised lower molecular weight polysaccharides that function as a cementing matrix between cellulose micro fibrils, forming the main structural component of the fiber cell. Hemicellulose is hydrophilic and can be easily hydrolyzed by dilute acids and bases [39]. The third essential composition in plant natural fiber is a lignin. Lignin is a complex hydrocarbon polymer that gives rigidity to plant and assists on the transportation of water. It is hydrophobic, resists acid hydrolysis and most microorganisms attacks, soluble in hot alkali, readily oxidized, and easily condensable with phenol [33].

Cellulose in plant fibers consist of helically wound cellulose micro fibrils, bound together by an amorphous lignin matrix, acting like a cementing material. The lignin content of plant fibers influences its structure, properties and morphology [40]. The cross section and schematic representation of plant fiber at different scales from the stem to the ultrastructure is shown in Figure 2.3. Plant fiber can be considered as composites of hollow cellulose fibrils held together by a lignin and hemicellulose matrix. Each fiber has a complex, layered structure consisting of a thin primary cell wall and three secondary cell walls [16]. The thick middle layer of secondary cell walls determines the mechanical properties of the fiber. The middle layer consists of a series of helically wound cellular micro fibrils formed from long chain cellulose molecules. The angle between the fiber axis and the microfibrils is called the microfibrillar angle. The characteristic value of microfibrillar angle varies from one fiber to another [41]. Table 2.1 summarized the range of the average chemical constituents for a wide variety of common plant fiber [32] where Figure 2.4 is the transformation of Table 2.1 in graphical form using the maximum range value.

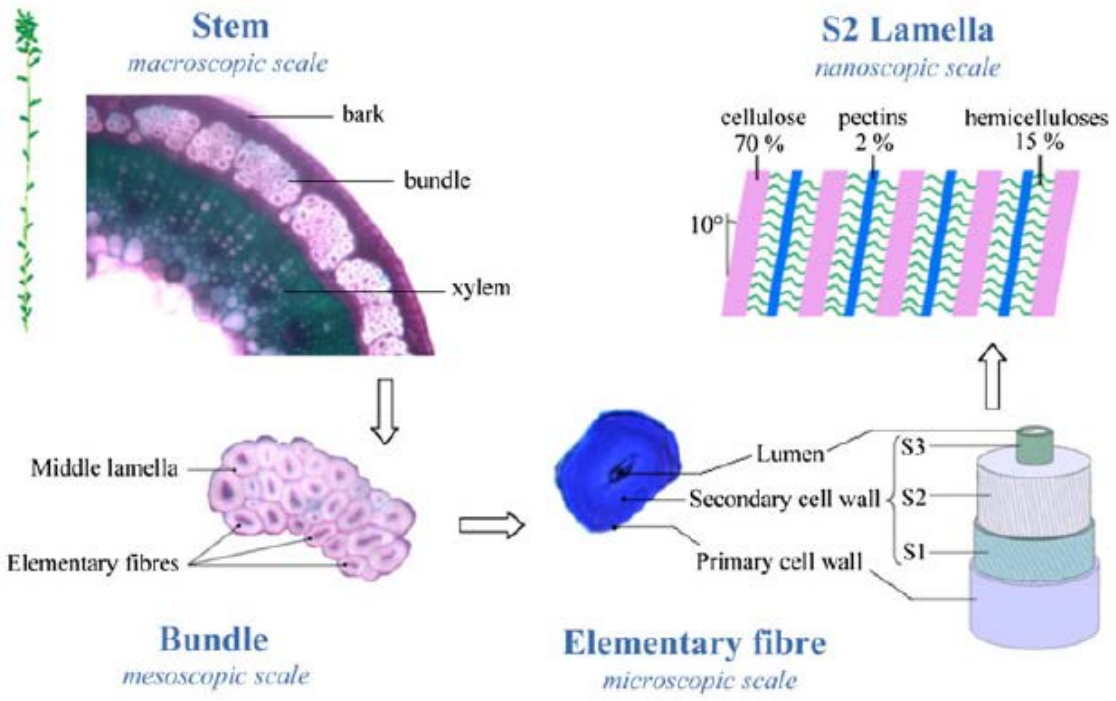

Figure 2.3: The cross section and schematic representation of flax fiber at different scales from the stem to the ultrastructure illustrated by Hughes [16]

Table 2.1: Chemical composition of common natural fibers [32]

Types of natural fiber	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Waxes (wt%)
Bagasse	55.2	16.8	25.3	-
Bamboo	26-43	30	21-31	-
Flax	71	18.6-20.6	2.2	1.5
Kenaf	72	20.3	9	-
Jute	61-71	14-20	12-13	0.5
Hemp	68	15	10	0.8
Ramie	68.6-76.2	13-16	0.6-0.7	0.3
Abaca	56-63	20-25	7-9	3
Sisal	65	12	9.9	2
Coir	32-43	0.15-0.25	40-45	-
Oil palm	65	-	29	-
Pineapple	81	-	12.7	-
Curaua	73.6	9.9	7.5	-
Wheat straw	38-45	15-31	12-20	-
Rice husk	35-45	19-25	20	14-17
Rice straw	41-57	33	8-19	8-38

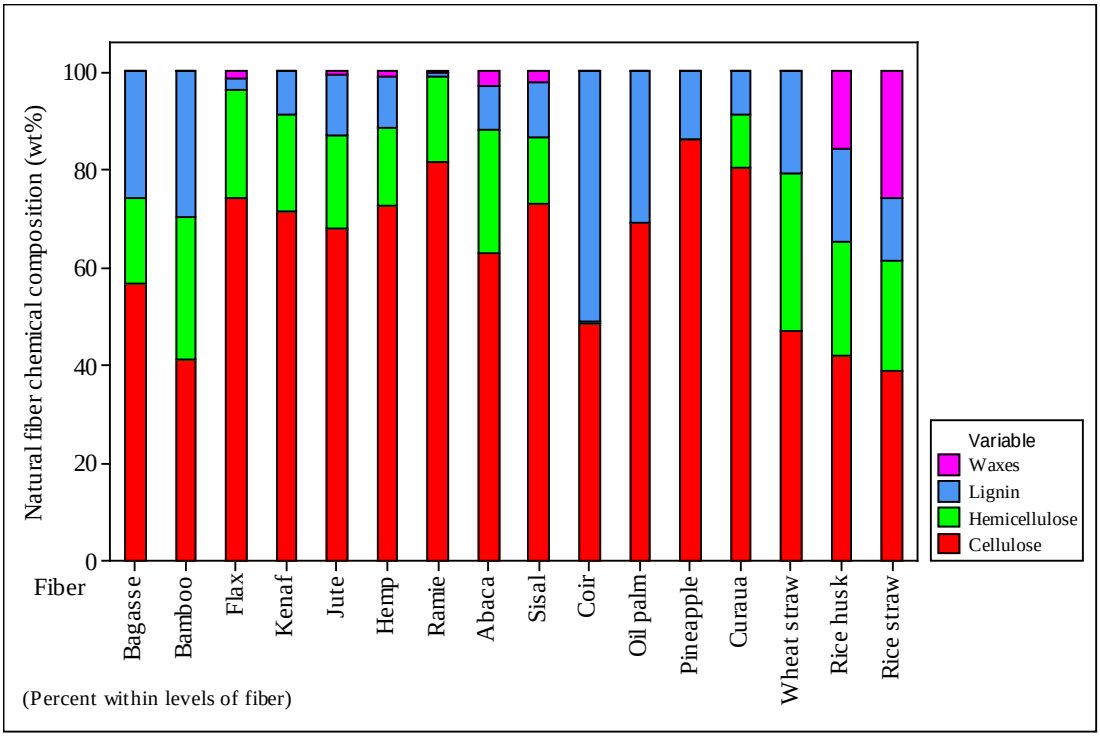

Figure 2.4: Bar chart of chemical composition for common natural fiber

2.1.3 Opportunities and challenges of natural fiber applications

The growing interest in utilization of plant fiber as environment friendly reinforcement material in polymer composite industry is mainly due to their renewable origin, low-cost and abundantly available, relative high specific strength and modulus, light weight, low density, less abrasiveness, desirable fiber aspect ratio, minimal health hazards and also good thermal, electrical and acoustic insulating character. These advantageous make plant fiber as potential replacement for synthetic fiber in composite industries [42-44]. A renaissance in the use of natural fibers as reinforcements in technical applications is taking place mainly in the automobile [13, 45], packaging [46], insulation [47] and construction industries [48].

However, there still several drawbacks that limit the potential of plant fiber to be used as alternative to synthetic fibers. Firstly, the inherently polar and hydrophilic nature of plant fiber and the non-polar characteristics of a most polymer matrix results in compounding difficulties leading to non-uniform dispersion of fibers within the matrix, which weaken the properties of the resultant composite. This is a major disadvantage of natural fiber reinforced composites [11, 30]. Secondly, the processing temperature of composites is restricted to 200^{o}C as plant fibers undergo degradation at higher temperatures; this restricts the choice of matrix material [49]. Another serious drawback is the hydrophilicity of plant fiber results in high moisture absorption and leading to swell and presence of voids at the interface, which results in poor mechanical properties and reduces dimensional stability of composites [50]. Furthermore, fiber dispersion also is a big challenge in dealing with natural fiber. Poor fiber dispersion results in a loose bundle, embracing an effectively lower aspect ratio with less reinforcing potential than a single fiber. In addition, the bundle itself may be low in strength due to poor adhesion. Both the above factors reduce the overall strength of the composite [51]. Finally, the shape, size, and strength of the natural plant fibers may vary widely depending on cultivation environment, region of origin, and other characteristics [37]. In turn, these features of the plant fiber are likely to influence the mechanical properties of the composites [17]. The advantages and disadvantages of natural fiber that highlighted by number or researchers is presented in Table 2.2.

Table 2.2: The advantages and disadvantages of natural fiber as reinforce material for polymer matrix composite

Advantages	Disadvantages	References
Abundantly available Biodegradable	Fiber degrade over time at temperatures of ~200^{o}C or higher which limit the choice of matrix for the composite	[16, 52]
Non abrasive Non toxic	High moisture absorption	[10, 15, 53]
Environmentally friendly	Low processing temperature (< 170^{o}C)	[9-10]
High specific stiffness and strength	Poor fiber matrix interface compatibility	[52, 54]
Low cost Low energy consumption Low thermal conductivity	Poor wettability Poor dimensional stability	[6, 8, 55]
Low density Lightweight	Selection of cost effective and suitable fibers type for particular applications	[9, 16]
Lower pollutant and green house gas emission	Tendency to entangle and form fiber agglomerates due to fiber interaction	[10]
Renewable	Widely dispersed resources and variable properties	[9, 16, 36-37]

2.1.4 Treatment of natural fiber

From the discussion in previous section, some of natural fiber disadvantages and limitations when used as reinforcement for composite were clearly identify. One of the major drawbacks that were highlighted by number of researcher was a poor compatibility between the fiber and the matrix, which weakens interface area between natural fibers and matrices [32, 41, 54, 56-58]. The large amount of hydroxyl group in cellulose gives natural fiber hydrophilic properties when used to reinforce hydrophobic matrices. Thus, it results to a very poor interface and poor resistance to moisture absorption [30]. This incompatibility issue will cause problem in composite processing and material properties in comparison to the original polymer properties. Therefore, to overcome this drawback, the fiber surface modification method was used to enhance and improve the interface of fiber and polymer matrix. This modification process relies on physical and chemical techniques, mainly focused on grafting chemical groups capable of improving the interfacial interaction between fiber and matrix [11].

Physical treatments change structural and surface properties of the fiber and thereby influence the mechanical bonding with polymers matrix. These methods include stretching, calendaring, thermotreatment and the production of hybrid yarns for the modification of natural fibers [6]. Physical treatments do not extensively change the chemical composition of the fibers. Therefore the interface is generally enhanced via an increased mechanical bonding between the fiber and the matrix. Two types of physical treatment that generally used were corona treatment and plasma treatment. Corona treatment is one of the most interesting techniques for surface oxidation activation. This process changes the surface energy of the cellulose fibers. Corona discharge treatment on cellulose fiber and hydrophobic matrix was found to be effective for the improvement of the compatibilization between hydrophilic fibers and a hydrophobic matrix. Plasma treatment is another physical treatment method which has two sorts of effect on fiber surfaces. First is physically etching using an inert gas such as argon to modify the fiber surface. Secondly is chemical graft, inducing some polar radicals, such as oxygen and nitrogen to functionalize the surface of the fibers [59].

Instead of physical treatment, there was another treatment called chemical treatment for natural fiber. According to Gaceva *et al.* [60], chemical modification can be defined as a chemical reaction between some reactive constituents of the natural fiber and chemical reagent, with or without a catalyst to form a covalent bond between them. Other review studied related to chemical treatment of natural fiber conducted by Li *et al.* [30], highlight a list of chemical treatment methods used by researcher and it working mechanism. Table 2.3 present some of the common treatments used in natural fiber like mercerization or alkali treatment, silane treatment, acetylation treatment, benzoylation treatment, acrylation and acrylonitrile grafting, maleated coupling agent, permanganate treatment, peroxide treatment, isocyanate treatment, stearic acid treatment and sodium chlorite treatment [11]. The mechanical and outdoor performance of coupling agent treatment with explanation regarding interaction mechanism between natural fiber and polymer matrix was clearly discussed by Xie [61]. Among these chemical treatments, alkali treatment was known as commonly used treatment for natural fiber and obtained a good fiber matrix adhesion, thermal and mechanical properties of composites [62-64]. For that reason, alkali treatment was selected as a chemical treatment in this work. Further

discussions regarding alkali treatment effect on natural fiber and it composite was presented at Section 2.4.

Table 2.3 : Commonly used natural fiber treatment [11]

Treatment	General descriptions
Alkali	Immersed fiber in alkali solution, washing and drying in ventilated oven.
Acetylation	Immersed fiber in glacial acetic acid, then in a mixture of acetic anhydride and few drops of concentrated sulphuric acid and then filtrated, washed and dried in ventilated oven.
Stearic acid	Acid is added to an ethyl alcohol solution, up to 10% of the total weight of the fibers to be treated. The obtained solution is added on the fibers, which are then dried in oven.
Benzylation	Immersed fiber in alkali and then stirred with benzoyl chloride, filtrated, washed and dried. Then the fiber is immersed in ethanol, rinsed and dried in oven.
Peroxide treatment	Immersed fiber in a solution of dicumyl (or benzoyl) peroxide in acetone, then decanted and dried.
Permanganate	Immersed fiber in a potassium permanganate (KMnO4) in acetone, then decanted and dried.
Silane	Immersed fiber in a 3:2 alcohol–water solution, containing a silane-based adhesion promoter, rinsed in water and oven dried.
Isocyanate	The treatment is typically performed with isocyanate compounds at intermediate temperatures for approximately 1 hour.

2.2 Kenaf fiber

There has been a wide variety of literature available on plant natural fiber. Among these natural fibers, kenaf fiber is known as one of the faster growing annual growth plant that harvested for its bast fibers. These fibers have excellent specific properties and have potential to be outstanding reinforcing fillers in polymer composite application [65]. According to Khalil *et al.* [66], Kenaf or it scientific name *Hibiscus Cannabinus L.*; family *Malvaceae* is a traditional, third world crop after wood and bamboo that was poised to be introduced as a new annually renewable resources of industrial purpose in developed economies. Additionally, an interest has grown in

using kenaf as an alternative raw material for pulp because it has the excellent advantages of being renewable, inexpensive, and easily grown even under severe conditions such as low water supply and little fertilizer [66]. From reviewed work regarding kenaf fiber conducted by Aji *et. al* [67], they highlight two main reasons why kenaf cultivation gaining a high interest in recent years. Firstly, it because kenaf fiber has the ability to absorbs nitrogen and phosphorous included in the soil. The second one is the ability to accumulate carbon dioxide at a significantly high rate. Moreover, kenaf fiber like most other natural fibers, demonstrates lightweight, low density, low combustibility, non-toxicity, high specific mechanical properties, and is easily recycled [68]. Furthermore, kenaf plant has a high growth rate, rising to heights of 4 - 6 meter in about 4 to 5 months [39].

In Malaysia, kenaf was introduced in the early 1970s and was highlighted in the late 1990s as an alternative and cheaper source of material for producing panel product like fiberboard and particleboard [66]. Recently, kenaf fiber has become a national agenda for further advancement in various applications such as automotive components, packaging and furniture [25]. As reported by The National Kenaf and Tobacco Board (NKTB), an attempt have been made to increase a planting of 10,000 hectares of kenaf throughout Malaysia in 2020 due to the target sales of kenaf is about RM 80 million in year 2020. Currently there are 2,000 cultivated hectares of kenaf planting [26]. Recent review by Saba [69] also highlight that kenaf reinforced polymer composites which are moulded into lightweight panels can be used as an alternative material for construction and building application. Due to these particular reasons, kenaf fiber was selected as a reinforced material in this study.

2.2.1 Chemical composition of kenaf fiber

The study of cell wall structure, lignin distribution and chemical composition of kenaf fiber cultivated in Malaysia was conducted by Khalil *et. al* [66]. The fiber composition was analyzed according to Technical Association of Pulp and Paper Industry (TAPPI) standards. They found that cell wall structure of kenaf core and kenaf bast fiber consists of secondary wall layers and middle lamella. In general, they found that kenaf core fibers were higher in holo-cellulose (α-cellulose + hemicellulose) and lignin, while kenaf bast fibers were higher in α-cellulose,

extractive and ash content. Table 2.4 present the chemical composition of kenaf fiber reported by several researchers. As presented in Table 2.4, even thought for a similar type of kenaf fibers, the chemical composition value was different especially for the cellulose content. This different could be due to the growth conditions, maturity, processing and measuring methods [17, 37]. Table 2.4 also indicated that the dominant chemical contents in kenaf fiber was cellulose about 31 ~ 86.8 %, followed by hemicellulose about 10.5 ~ 26.2 % and lignin about 5.9 ~ 20.1 %. However, the cellulose content in kenaf fiber found to be lower if compared to other bast types fiber like flax, hemp, jute and ramie fiber [70]. This cellulose content determines generally the mechanical properties of the cellulose based natural fibers [6].

Table 2.4: Chemical composition of kenaf fiber collected from previous literatures

Cellulose (wt%)	α-cellulose (wt%)	Hemi-cellulose (wt%)	Lignin (wt%)	Pectin (wt%)	Ash (wt%)	Extractives (wt%)	Moisture content (wt%)	Year / References
31-39	-	-	15 - 19	-	22 - 23		-	1997 [71]
31-39	-	21.5	15 - 19	-	-		-	2001 [72]
45 - 57	-	21.5	8 - 13	3-5	-		-	2005 [70]
53 - 57	-	15 - 19	5.9 - 9.3	-	4.7	3.2	-	2007 [60]
76	-	10.5	9	-	5.2		9	2008 [73]
-	56.4	26.2	13.4	-	2.2		-	2009 [67]
86.8	55	-	14.7	-	5.4	5.5	-	2010 [66]
44.4	-	-	20.1	-	4.6		-	2015 [74]

*Decimal point used is exactly as stated in original references

2.2.2 Physical properties of kenaf fiber

The physical property of kenaf fiber reported by several researchers was presented in Table 2.5. In Table 2.5 under density column, the density that reported by Khalil *et al.* [66] was 0.21 ~ 0.29 g/cm^3 which is the lowest value reported. This was a kenaf core and stem density value. Other studied reported that kenaf fiber density was at the range of 1.2 ~ 1.5 g/cm^3. This was a density range of most natural plant fiber as stated by Mwaikambo [75]. On the other hand, for kenaf fiber bundle diameter, the variation was quite large. As can be seen in second column, the diameter range was 11.7 ~ 140 µm. This variation could be came from different kenaf fiber background, measurement technique and apparatus used [76].

Table 2.5: Physical properties of kenaf fiber collected from previous literatures

Density (g/cm^3)	Diameter (µm)	Cross sectional area (µm^2)	Specific gravity (kg/m^3)	Year / References
1.5	15 - 30	-	-	1999 [77]
1.4 – 1.5	-	-	-	2001 [75]
1.19 3 – 1.222	-	-	-	2004 [62]
-	-	3850 - 4762	-	2005 [78]
-	140	-	749	2005 [79]
	18 - 24			2007 [60]
	106	-	970	2008 [80]
1.2 - 1.36	-	-	-	2009 [81]
-	12.17 – 47.85	-	-	2009 [67]
-	11.7 – 12.3	-	-	2009 [82]
-	21.9 ± 4.6	-	-	2010 [83]
0.21 - 0 .29	62 - 83	-	-	2010 [66]
1.4	-	-	-	2012 [20]
-	-	5010 - 7045		2013 [84]
1.193 – 1.206	55.0 – 73.3	-	-	2014 [85]
1.2	55 - 60	-	-	2015 [74]

*Decimal point used is exactly as stated in original references

2.2.3 Mechanical properties of kenaf fiber

The mechanical property of kenaf fiber reported by several researchers was presented in Table 2.6. Generally, the reported fiber mechanical property was tensile strength, tensile modulus and elongation. From literature, it shows four types of testing standard used by researcher while others were not clearly stated. From the results, it shows that although the same standards were used, the fiber tensile strength could be different. These different can be explained by the type of fiber treatment performed on the fiber, load cell used during tensile test and the number of samples test conducted. For example, Xue [86] used 10 N load cell, while Mahjoub *et al.* [85] used 25N load cell during performing the tensile test which give different strength value.

Table 2.6: Mechanical properties of kenaf fiber collected from previous literatures

Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)	Test method / standard	Year / References
233- 420	-	-	-	2005 [78]
223	14.494	-	-	2005 [79]
215.4 - 243.7	-	-	-	2007 [87]
117.9	2.434	-	ASTM D3822-01	2008 [73]
223	14.5	1.5	ASTM D3822-01	2009 [76]
146.4 - 223.0	12.7 - 17.2	1.12 - 1.46	ASTM C1557-03	2009 [86]
623.6	10.99	5.7	DIN EN ISO 139	2009 [88]
223	15	5.7	DIN EN ISO 139	2010 [89]
930	53	1.6	-	2011 [34]
393 - 773	26.5	1.5 - 1.8	-	2011 [90]
223 - 930	14.5 - 53	1.5 - 2.7	-	2012 [20]
155 - 320	2.01 - 30.8	1.28 - 6.14	-	2013 [84]
580.0 – 924.29	40.7	1.25 - 2.55	ASTM C1557-03	2014 [85]
350 - 600	40	2.5 - 3.5	-	2014 [77]
118.3	2.416	8.31	-	2015 [91]
280.56 - 501.56	23.56 - 40.32	-	ASTM 3379-75:1989	2015 [74]

*Decimal point used is exactly as stated in original references