PROPERTIES ENHANCEMENT OF PROPIONYLATED KENAF FIBER REINFORCED VINYL ESTER COMPOSITES WITH THE ADDITION OF BIONANOCARBON

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by

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TABLE OF CONTENTS

ACKNOWLEDGEMENT ..... **ii**

TABLE OF CONTENTS ..... **iii**

LIST OF TABLES ..... **viii**

LIST OF FIGURES ..... **xi**

LIST OF SYMBOLS ..... **xvii**

LIST OF ABBREVIATIONS ..... **xx**

ABSTRAK…… ..... **xxii**

ABSTRACT…… ..... **xxiv**

CHAPTER 1 INTRODUCTION **1**

1.1 Research background 1

1.2 Problem statement 5

1.3 Objectives 8

1.4 Thesis layout 9

CHAPTER 2 LITERATURE REVIEW **10**

2.1 Composites 10

2.1.1 Introduction 10

2.1.2 Classification 10

2.2 Polymer biocomposites 11

2.3 Matrix 13

2.3.1 Thermoset 13

2.3.2 Vinyl ester 16

2.4 Reinforcement 19

2.4.1 Biofiber 20

2.4.2 Kenaf fiber 23

2.5 Chemical modification of kenaf fiber 27

2.5.1 Introduction 27

2.5.2 Propionic anhydride modification 29

2.6 Nanomaterial 31

2.6.1 Introduction 31

2.6.2 Nanomaterial as nanofiller 32

2.7 The importance of utilization of the oil palm shell as bionanocarbon precursor for nanobiocomposite applications 33

2.7.1 Structure and properties of oil palm shell 35

2.7.2 Bionanocarbon from oil palm shell as enhancement nanofiller in polymer composites 37

2.8 Methods in the production of polymer composites 38

2.8.1 Introduction 38

2.8.2 Hand lay-up technique for fabrication of polymer composites 41

CHAPTER 3 MATERIALS AND METHOD 43

3.1 Experimental design 43

3.2 Materials 43

3.2.1 Vinyl ester 43

3.2.2 Methyl ethyl ketone peroxide 45

3.2.3 Cobalt naphthenate 45

3.2.4 Oil palm shell as bionanocarbon precursor 45

3.2.5 Nonwoven kenaf fiber mat 46

3.2.6 Propionic anhydride 46

3.3 Fabrication of bionanocarbon 47

3.4 Characterization of bionanocarbon 48

3.4.1 Yield. 48

3.4.2 Textural analysis 48

3.4.3 Morphological analysis 49

3.4.4 Particle size distribution and zeta potential 49

3.4.5 Elemental analysis 49
3.4.6 Chemical structural analysis 50
3.4.7 Thermogravimetric analysis 50
3.5 Propionic anhydride modification of kenaf fiber 51
3.6 Characterization of kenaf fiber 52
3.6.1 Weight percent gain. 52
3.6.2 Morphological analysis 53
3.6.3 Wettability characterization 53
3.6.4 Chemical structural characterization 53
3.6.5 Thermogravimetric analysis. 54
3.7 Effect of kenaf fiber loading in the production of composites 54
3.8 Fabrication of bionanocarbon enhancement in kenaf fiber reinforced vinyl ester composites 55
3.9 Physical characterization of composites 58
3.9.1 Density. 58
3.9.2 Void content 59
3.9.3 Density profile. 59
3.9.4 Water absorption 59
3.9.5 Thickness swelling. 60
3.10 Mechanical characterization of composites 61
3.10.1 Tensile test 61
3.10.2 Flexural test 62
3.10.3 Izod impact test. 63
3.11 Morphological characterization of composites 64
3.12 Chemical structural characterization of composites 64
3.13 Thermal characterization of composites 65
3.14 Chemical resistance characterization of composites 65
3.15 Statistical analysis 66

CHAPTER 4 RESULTS AND DISCUSSION 67

4.1 Properties of bionanocarbon 67

4.1.1 Yield 67

4.1.2 Textural properties 67

4.1.3 Morphological analysis 69

4.1.4 Particle size distribution 71

4.1.5 Zeta potential 72

4.1.6 Elemental analysis 73

4.1.7 Chemical structural analysis 74

4.1.8 Thermogravimetric analysis 75

4.2 Properties of propionylated kenaf fiber 76

4.2.1 Weight percent gain 76

4.2.2 Morphological analysis 78

4.2.3 Wettability analysis 83

4.2.4 Chemical structural properties 85

4.2.5 Thermal properties 87

4.3 Preliminary study on the optimum fiber loading reinforced vinyl ester composites 89

4.3.1 Tensile strength 89

4.3.2 Tensile modulus 91

4.3.3 Flexural strength 92

4.3.4 Flexural modulus 93

4.3.5 Impact strength 94

4.4 Physical characterization of bionanocarbon/kenaf fiber/vinyl ester composites 96

4.4.1 Density 96

4.4.2 Void content 99

4.4.3 Density profile 103

4.4.4 Water absorption 106

4.4.5 Thickness swelling 114

4.5 Mechanical properties of bionanocarbon/kenaf fiber/vinyl ester composites 117

4.5.1 Tensile strength 117

4.5.2 Tensile modulus 122

4.5.3 Elongation at break 126

4.5.4 Flexural strength 131

4.5.5 Flexural modulus 136

4.5.6 Impact strength 141

4.6 Morphological analysis of bionanocarbon/kenaf fiber/vinyl ester composites 146

4.7 Chemical structural analysis of bionanocarbon/kenaf fiber/vinyl ester composites 152

4.8 Thermal properties of bionanocarbon/kenaf fiber/vinyl ester composites 155

4.9 Chemical resistance analysis of bionanocarbon/kenaf fiber/vinyl ester composites 162

4.9.1 Acid resistance 162

4.9.2 Alkali resistane 165

4.9.3 Solvent resistance 167

CHAPTER 5 CONCLUSION AND FUTURE RECOMMENDATIONS 169

5.1 Conclusion 169

5.2 Recommendations for Future Research 171

REFERENCES. 172

LIST OF PUBLICATIONS

LIST OF TABLES

Page

Table 2.1 A comparative study of thermosetting matrices.....15

Table 2.2 The microstructure, mechanical, chemical, thermal, and electrical properties of kenaf fiber.....26

Table 2.3 Proximate, lignocellulosic, and ultimate properties of OPS 36

Table 2.4 Comparison of various manufacturing processes 40

Table 3.1 Typical characteristics of vinyl ester.....43

Table 3.2 Typical characteristics of MEKP 45

Table 3.3 Typical properties of propionic anhydride.....47

Table 3.4 Formulation parameters of propionic anhydride modification onto kenaf fiber 51

Table 3.5 Fabrication formulation of unmodified and propionylated kenaf fibers reinforced vinyl ester composites with different bionanocarbon loadings 55

Table 4.1 Characteristics of the porous texture of bionanocarbon.....69

Table 4.2 Theoretical density and experimental density of unmodified and propionylated kenaf fibers reinforced vinyl ester composites 99

Table 4.3 Void content of unmodified and propionylated kenaf fibers reinforced vinyl ester composites 102

Table 4.4 Water absorption of unmodified and propionylated kenaf fibers reinforced vinyl ester composites 114

Table 4.5 Thickness swelling of unmodified and propionylated kenaf fibers reinforced vinyl ester composites 117

Table 4.6 Tensile strength of unmodified and propionylated kenaf fibers reinforced vinyl ester composites 121

Table 4.7 ANOVA of the effect of modification of fiber and bionanocarbon loading on tensile strength 122

Table 4.8 Tensile modulus of unmodified and propionylated kenaf fibers reinforced vinyl ester composites 125

Table 4.9 ANOVA of the effect of modification of fiber and bionanocarbon loading on tensile modulus 126

Table 4.10 Elongation at break of unmodified and propionylated kenaf fibers reinforced vinyl ester composites 130

Table 4.11 ANOVA of the effect of modification of fiber and bionanocarbon loading on elongation at break 131

Table 4.12 Flexural strength of unmodified and propionylated kenaf fibers reinforced vinyl ester composites 135

Table 4.13 ANOVA of the effect of modification of fiber and bionanocarbon loading on flexural strength 136

Table 4.14 Flexural modulus of unmodified and propionylated kenaf fibers reinforced vinyl ester composites 140

Table 4.15 ANOVA of the effect of modification of fiber and bionanocarbon loading on flexural modulus 141

Table 4.16 Impact strength of unmodified and propionylated kenaf fibers reinforced vinyl ester composites 145

Table 4.17 ANOVA of the effect of modification of fiber and bionanocarbon loading on impact strength 146

Table 4.18 Decomposition temperature and mass loss data of unmodified and propionylated kenaf fibers reinforced vinyl ester composites with different loadings of bionanocarbon 161

Table 4.19 Acid resistance properties of unmodified and propionylated kenaf fibers reinforced vinyl ester composites with different bionanocarbon loadings 163

Table 4.20 Alkali resistance properties of unmodified and propionylated kenaf fibers reinforced vinyl ester composites with different bionanocarbon loadings 165

Table 4.21 Solvent resistance properties of unmodified and propionylated kenaf fibers reinforced vinyl ester composites with different bionanocarbon loadings 167

LIST OF FIGURES

Page

Figure 1.1 Thesis layout 9

Figure 2.1 Chemical structure of vinyl ester monomer 18

Figure 2.2 Classification of natural and man-made fibers 21

Figure 2.3 Digital image of (a) kenaf plant, (b) kenaf bast and kenaf core, and (c) kenaf bast fiber 24

Figure 2.4 Chemical structure of propionic anhydride 29

Figure 2.5 OPS as a solid biowaste from the oil palm tree and the bionanocarbon as its derivative material 35

Figure 2.6 Illustration of the hand lay-up manufacturing process 41

Figure 3.1 Experimental design 44

Figure 3.2 Visual images of OPS 46

Figure 3.3 Photograph of bionanocarbon produced from OPS with the impregnation ratio (OPS:KOH) of (a) 1:0.25, (b) 1:0.5, and (c) 1:1 48

Figure 3.4 Digital image of (a) unmodified kenaf fiber and (b) propionylated kenaf fiber 52

Figure 3.5 Schematic diagram of fabrication of bionanocarbon enhancement in unmodified and propionylated kenaf fibers reinforced vinyl ester composites 56

Figure 3.6 Composite products of unmodified and propionylated kenaf fibers reinforced vinyl ester composites with bionanocarbon loading of (a, b) 0%, (c. d) 1%, (e, f) 3%, and (g, h) 5% 57

Figure 3.7 Tensile test of bionanocarbon enhancement in kenaf fiber reinforced vinyl ester composite 61

Figure 3.8 Flexural test of bionanocarbon enhancement in kenaf fiber reinforced vinyl ester composite 62

Figure 3.9 Izod impact test of bionanocarbon enhancement in kenaf fiber reinforced vinyl ester composite 63

Figure 4.1 N_2 adsorption (closed symbols) and desorption (open symbols) isotherm at 77 K of bionanocarbon with different impregnation ratios at 700 °C 68

Figure 4.2 TEM micrograph of bionanocarbon particles 70

Figure 4.3 TEM micrograph of single nanoparticle of bionanocarbon 71

Figure 4.4 Particle size distribution of bionanocarbon 72

Figure 4.5 Zeta potential distribution of bionanocarbon 73

Figure 4.6 Elemental composition of bionanocarbon 74

Figure 4.7 FT-IR spectra of bionanocarbon 75

Figure 4.8 TGA curve of bionanocarbon 76

Figure 4.9 Weight percent gain of propionylated nonwoven kenaf fiber with different reaction temperatures and different retention times 77

Figure 4.10 Schematic reaction of modified kenaf fiber using propionic anhydride 78

Figure 4.11 SEM micrograph of unmodified nonwoven kenaf fiber (a) and propionylated nonwoven kenaf fiber at 80 °C with the retention time of (b) 30 min, (c) 60 min, (d) 120 min, (e) 180 min, and (f) 240 min 80

Figure 4.12 SEM micrograph of unmodified nonwoven kenaf fiber (a) and propionylated nonwoven kenaf fiber at 100 °C with the retention time of (b) 30 min, (c) 60 min, (d) 120 min, (e) 180 min, and (f) 240 min 81

Figure 4.13 SEM micrograph of unmodified nonwoven kenaf fiber (a) and propionylated nonwoven kenaf fiber at 120 °C with the retention time of (b) 30 min, (c) 60 min, (d) 120 min, (e) 180 min, and (f) 240 min 82

Figure 4.14 Contact angle of unmodified and propionylated kenaf fibers with different reaction temperatures and different retention times 84

Figure 4.15 FT-IR spectra of unmodified and propionylated kenaf fibers at 180 min with reaction temperatures of 80 °C, 100 °C, and 120 °C ... 85

Figure 4.16 Possible chemical interaction of modified kenaf fiber using propionic anhydride 86

Figure 4.17 TGA curves of unmodified and propionylated kenaf fibers at 180 min with reaction temperatures of 80 °C, 100 °C, and 120 °C 88

Figure 4.18 DTG curves of unmodified and propionylated kenaf fibers at 180 min with reaction temperatures of 80 °C, 100 °C, and 120 °C 89

Figure 4.19 Tensile strength of kenaf fiber reinforced vinyl ester composites at different fiber loadings 91

Figure 4.20 Tensile modulus of kenaf fiber reinforced vinyl ester composites at different fiber loadings 92

Figure 4.21 Flexural strength of kenaf fiber reinforced vinyl ester composites at different fiber loadings 93

Figure 4.22 Flexural modulus of kenaf fiber reinforced vinyl ester composites at different fiber loadings 94

Figure 4.23 Impact strength of kenaf fiber reinforced vinyl ester composites at different fiber loadings 95

Figure 4.24 Theoretical density and experimental density of unmodified kenaf fiber reinforced vinyl ester composites 97

Figure 4.25 Theoretical density and experimental density of propionylated kenaf fiber reinforced vinyl ester composites 98

Figure 4.26 Void content of unmodified kenaf fiber reinforced vinyl ester composites 100

Figure 4.27 Void content of propionylated kenaf fiber reinforced vinyl ester composites 101

Figure 4.28 Possible interaction mechanism of nonwoven kenaf fiber nanocomposites with and without bionanocarbon 103

Figure 4.29 Density profile analysis of unmodified kenaf fiber reinforced vinyl ester composites 104

Figure 4.30 Density profile analysis of propionylated kenaf fiber reinforced vinyl ester composites 105

Figure 4.31 Water absorption of unmodified kenaf fiber reinforced vinyl ester composites 108

Figure 4.32 SEM images before and after immersion of unmodified kenaf fiber reinforced vinyl ester composites filled bionanocarbon of (a, b) 0%, (c, d) 1%, (e, f) 3% and (g, h) 5% 109

Figure 4.33 Water absorption of propionylated kenaf fiber reinforced vinyl ester composites 111

Figure 4.34 SEM images before and after immersion of propionylated kenaf fiber reinforced vinyl ester composites filled bionanocarbon of (a, b) 0% (c, d) 1%, (e, f) 3% and (g, h) 5% 112

Figure 4.35 Thickness swelling of unmodified kenaf fiber reinforced vinyl ester composites 115

Figure 4.36 Thickness swelling of propionylated kenaf fiber reinforced vinyl ester composites 116

Figure 4.37 Tensile strength of unmodified kenaf fiber reinforced vinyl ester composites 118

Figure 4.38 Tensile strength of propionylated kenaf fiber reinforced vinyl ester composites 120

Figure 4.39 Tensile modulus of unmodified kenaf fiber reinforced vinyl ester composites 123

Figure 4.40 Tensile modulus of propionylated kenaf fiber reinforced vinyl ester composites 124

Figure 4.41 Elongation at break of unmodified kenaf fiber reinforced vinyl ester composites 127

Figure 4.42 Elongation at break of propionylated kenaf fiber reinforced vinyl ester composites 129

Figure 4.43 Flexural strength of unmodified kenaf fiber reinforced vinyl ester composites 132

Figure 4.44 Flexural strength of propionylated kenaf fiber reinforced vinyl ester composites 134

Figure 4.45 Flexural modulus of unmodified kenaf fiber reinforced vinyl ester composites 137

Figure 4.46 Flexural modulus of propionylated kenaf fiber reinforced vinyl ester composites 138

Figure 4.47 Impact strength of unmodified kenaf fiber reinforced vinyl ester composites 142

Figure 4.48 Impact strength of propionylated kenaf fiber reinforced vinyl ester composites 143

Figure 4.49 SEM micrograph tensile fracture surface of unmodified kenaf fiber composites filled bionanocarbon of (a) 0%, (b) 1%, (c) 3%, and (d) 5% 147

Figure 4.50 SEM micrograph tensile fracture surface of propionylated kenaf fiber composites filled bionanocarbon of (a) 0%, (b) 1%, (c) 3%, and (d) 5% 149

Figure 4.51 Possible mechanism of bionanocarbon enhancement in unmodified and propionylated kenaf fibers reinforced vinyl ester composites 152

Figure 4.52 FT-IR spectra of unmodified and propionylated kenaf fibers reinforced vinyl ester composites 153

Figure 4.53 Possible chemical interaction between propionylated kenaf fiber, bionanocarbon, and vinyl ester in the composite network 155

Figure 4.54 TGA curves of unmodified kenaf fiber reinforced vinyl ester composites 157

Figure 4.55 DTG curves of unmodified kenaf fiber reinforced vinyl ester composites 157

Figure 4.56 TGA curves of propionylated kenaf fiber reinforced vinyl ester composites.....158

Figure 4.57 DTG curves of propionylated kenaf fiber reinforced vinyl ester composites.....159

LIST OF SYMBOLS

°	Degree
%	Percentage
±	Plus-minus
+	Addition
–	Subtraction
÷	Division
×	Multiply
<	Less than
>	More than
=	Equal
~	Tilde
λ	Wavelength
ρ	Density
°C	Degree Celcius
°C/min	Degree Celcius per minute
0D	Zero-dimension
1D	One-dimension
2D	Two-dimension
3D	Three-dimension
b	Breadth
C=C	Carboxyl
C≡C	Alkynes
C–H	Methyl
cm	Centimeter

cm^{-1}	Reciprocal centimeter
C–O	Alkoxy
C=O	Carbonyl
cPs	Centipoise
D_p	Average pore diameter
g	gram
g/cm^3	Gram per cubic centimeter
GPa	Gigapascal
h	Hour
HV	Vickers hardness
kg/m^3	Kilogram per cubic meter
kJ/m^2	Kilojoule per square meter
kV	Kilovolt
l	Length
m	Mass
m^2/g	Square meter per gram
mg/°C	Milligram per degree Celcius
min	Minute
mL	Milliliter
mm	millimeter
mm/min	Millimeter per minute
mm/s	Millimeter per second
MPa	Megapascal
mV	Millivolt
nm	Nanometer
O–H	Hydroxyl
rpm	Revolutions per minute

S_{BET}	BET surface area
t	Thickness
T	Transmittance
T_1	Initial thickness
T_2	Final thickness
T_{max}	Maximum degradation temperature
T_{onset}	Initial degradation temperature
V	Volume
v/v	Volume per volume
V_T	Total pore volume
W	Weight
W_1	Initial weight
W_2	Final weight
w/w	Weight per weight
W_f	Filler weight fraction
W_{fb}	Fiber weight fraction
W_m	Matrix weight fraction
wt. %	Weight percentage

LIST OF ABBREVIATIONS

Al	Aluminum
Al_2O_3	Aluminum oxide
ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
BET	Brunauer-Emmet-Teller
BMC	Bulk molding compound
C	Carbon
C_6H_6	Benzene
$C_6H_{10}O_3$	Propionic anhydride
C_7H_8	Toluene
$CaCO_3$	Calcium carbonate
CCL_4	Carbon tetrachloride
CH_3COOH	Acetic acid
CNTs	Carbon nanotubes
Cu	Copper
DLS	Dynamic light scattering
DTG	Derivative thermogravimetric
EDX	Energy dispersive X-ray
FESEM	Field emission scanning electron microscope
FT-IR	Fourier transform infrared
GNPs	Graphene nanoplates
HCl	Hydrochloric acid
HDPE	High-density polyethylene
HNO_3	Nitric acid

IUPAC	International Union of Pure and Applied Chemistry
KBr	Potassium bromide
KOH	Potassium hydroxide
MWCNT	Multi-wall carbon nanotubes
MEKP	Methyl ethyl ketone peroxide
N_2	Nitrogen
NaOH	Sodium hydroxide
Na_2CO_3	Sodium carbonate
NH_4OH	Ammonium hydroxide
O	Oxygen
OPS	Oil palm shell
PHA	Polyhydroxyalkanoates
PHBV	Polyhydroxybutyrate-co-valerate
Pt	Platinum
RI	Refractive index
RTM	Resin transfer molding
SADT	Self-accelerating decomposition temperature
SMC	Sheet molding compound
SRIM	Structural reaction injection molding
SiC	Silicon carbide
SiO_2	Silicon dioxide
TEM	Transmission electron microscope
TGA	Thermogravimetric analysis
TiO_2	Titanium dioxide
WPG	Weight percent gain

PENAMBAHBAIKAN SIFAT KOMPOSIT VINIL ESTER DIPERKUAT GENTIAN KENAF TERPROPIONILASI DENGAN PENAMBAHAN NANO BIOKARBON

ABSTRAK

Penggunaan biomas dan sisanya telah digunakan secara meluas dalam aplikasi biokomposit. Kajian ini berkaitan dengan penggunaan biokarbon nano daripada tempurung kelapa sawit (OPS) dalam komposit vinil ester yang diperkuat oleh gentian kenaf yang tidak diubah suai dan terpropionilasi. Sebagai bahan peningkatan sifat dalam komposit vinil ester diperkuatkan dengan gentian kenaf, biokarbon nano telah diselidiki untuk aplikasi bahan yang mampan. Pada masa ini, saiz mikro biokarbon sebagai bahan pengisi atau penguat telah dikaji secara meluas. Walau bagaimanapun, antara muka gentian-matriks yang lemah mengakibatkan sifat fizikal, mekanikal, haba, dan rintangan kimia komposit yang rendah. Oleh itu, partikel nano biokarbon dalam kajian ini telah disintesis dan digunakan sebagai bahan berfungsi dan peningkatan sifat dalam bahan komposit vinil ester. Biokarbon nano telah dihasilkan daripada tempurung kelapa sawit, prekursor sisa pertanian menggunakan kaedah pengaktifan satu langkah. Pemuatan pengisi biokarbon nano dipelbagaikan daripada 0, 1, 3, dan 5% sebagai peningkatan sifat zarah nano dalam gentian kenaf bukan anyaman yang tidak diubah suai dan terpropionilasi dalam komposit vinil ester melalui kaedah “hand lay-up”. Sifat kefungsian biokarbon nano diselidiki menggunakan gravimetrik, Brunauer-Emmet-Teller (BET), mikroskop elektron penghantaran (TEM), taburan saiz zarah, potensi zeta, serakan tenaga X-ray (EDX), spektrometer transformasi Fourier-inframerah (FT-IR), dan analisis termogravimetrik (TGA). Luas permukaan tertinggi, jumlah isipadu liang, saiz zarah

purata, dan potensi zeta biokarbon nano ialah 1697 m^2/g, 0.81 cm^3/g, 74.18 nm, dan -34.7 mV. Sebaliknya, kebolehcampuran antara matriks hidrofobik dan gentian semulajadi hidrofilik telah menjadi satu cabaran dalam menghasilkan biokomposit polimer. Penggunaan pengubahsuaian kimia selulosa gentian kenaf digunakan untuk meningkatkan hidrofobisiti, seterusnya meningkatkan keserasian antara gentian kenaf dan ikatan matriks vinil ester. Kesan pengubahsuaian propionik anhidrida gentian kenaf dinilai menggunakan gravimetrik, mikroskop imbasan elektron pancaran medan (FESEM), FT-IR, sudut pendarjahan, dan analisis TGA. Sementara itu, sifat peningkatan komposit ditentukan melalui sifat kefungsian, termasuk sifat fizikal, mekanikal, morfologi, struktur, haba dan rintangan kimia. Hasil kajian yang diperolehi menunjukkan peningkatan biokarbon nano yang sangat baik dalam ikatan gentian-matriks yang dengan ketara meningkatkan sifat-sifat kefungsian biokomposit nano. Pengubahsuaian kimia gentian kenaf dengan penggabungan biokarbon nano dalam matriks menunjukkan peningkatan sifat fungsi yang tinggi. Juga, komposit yang diperolehi mempunyai suhu degradasi yang tinggi yang menandakan sifat kestabilan haba yang baik. Kajian morfologi FESEM mengesahkan penyebaran seragam pengisi nano yang meningkatkan interaksi gentian-matriks. Dalam kajian ini, peningkatan optimum dan keserasian yang lebih baik bagi sifat fungsi komposit telah dicapai pada 3% pemuatan biokarbon nano dalam interaksi gentian-matriks terpropionilasi. Kekuatan tegangan, modulus tegangan, kekuatan lentur, modulus lentur dan kekuatan hentaman tertinggi komposit ialah 82.78 MPa, 3.27 GPa, 103.24 MPa, 7.85 GPa, 6.52 kJ/m^2. Peningkatan ini boleh dikaitkan dengan peningkatan kehomogenan biokarbon nano dan pengubahsuaian permukaan gentian kenaf yang meningkatkan interaksi antara muka bahan penguat dalam rangkaian matriks vinil ester.

PROPERTIES ENHANCEMENT OF PROPIONYLATED KENAF FIBER REINFORCED VINYL ESTER COMPOSITES WITH THE ADDITION OF BIONANOCARBON

ABSTRACT

The use of biomass and its waste has been extensively applied in biocomposite applications. This study deals with the utilization of bionanocarbon from oil palm shell (OPS) in vinyl ester composites reinforced by unmodified and propionylated kenaf fibers. As a properties enhancement material in kenaf fiber reinforced vinyl ester composites, bionanocarbon was evaluated for sustainable material applications. Recently, the micro size of biocarbon as reinforcement materials or filler has been widely investigated. However, the weak interface of fiber-matrix results in poor physical, mechanical, thermal, and chemical resistance properties of the composites. Hence, the nanoparticle of biocarbon in this study was synthesized and used as a functional material and properties enhancement in vinyl ester composite materials. The bionanocarbon materials were produced from an oil palm shell, an agricultural waste precursor using a one-step activation method. The bionanocarbon filler loading was varied from 0, 1, 3, and 5% as nanoparticle properties enhancement in unmodified and propionylated nonwoven kenaf fibers reinforcement in vinyl ester composite via a hand lay-up protocol. The functional characteristics of bionanocarbon were investigated using gravimetric, Brunauer-Emmet-Teller (BET), transmission electron microscope (TEM), particle size distribution, zeta potential, energy dispersive X-ray (EDX), Fourier transform infrared (FT-IR) spectrometer, and thermogravimetric analysis (TGA). The highest surface area, total pore volume, average particle size, and zeta potential of

bionanocarbon were 1697 m^2/g, 0.81 cm^3/g, 74.18 nm, and -34.7 mV, respectively. On the other hand, the miscibility between hydrophobic matrix and hydrophilic biofiber has been a challenge in developing polymer biocomposite materials. The utilization of a chemical modification of cellulosic kenaf fiber is implemented to improve the hydrophobicity, thus increasing the compatibility between the kenaf fiber and vinyl ester matrix bonding. The effect of propionic anhydride modification of kenaf fiber was investigated using gravimetric, field emission scanning electron microscope (FESEM), FT-IR, contact angle, and TGA analyses. Meanwhile, the composite enhancement properties were determined through the functional properties, including physical, mechanical, morphological, structural, thermal, and chemical resistance properties. The obtained results signified excellent bionanocarbon enhancement in fiber-matrix bonding that significantly improved the functional properties of the bionanocomposites. The chemical modification of kenaf fiber with the incorporation of bionanocarbon in the matrix exhibited a high enhancement of the functional properties. Also, the obtained composites possessed high degradation temperature which indicated good thermal stability properties. The FESEM morphology study confirmed the uniform dispersion of the nanofiller enhancing the fiber-matrix interaction. In the present work, the optimum enhancement and better compatibility of the composite functional properties were achieved at 3% bionanocarbon loading in propionylated fiber-matrix interaction. The highest tensile strength, tensile modulus, flexural strength, flexural modulus, and impact strength of composites were 82.78 MPa, 3.27 GPa, 103.24 MPa, 7.85 GPa, 6.52 kJ/m^2, respectively. This enhancement can be attributed to homogeneity bionanocarbon enhancement and surface modification of kenaf fiber that improved interfacial interaction of the reinforcing agents in vinyl ester matrix networks.

CHAPTER 1

INTRODUCTION

1.1 Research background

Composite, a complex solid material, is produced from a combination of at least two distinct materials with better and improved characteristics, which are unattainable if utilized alone. Polymer composites serve various applications in daily life due to their beneficial properties. These composite products are enticing as they incorporate material characteristics not found in nature. Abdul Khalil et al. (2012a) reported that composites with the incorporation of sustainable natural fibers dominate modern society because the materials have renewable and environmentally friendly properties. Fibers have been widely utilized in many field applications (Weiland et al., 2021), resulting in sustainable fibers having a promising prospect as renewable reinforcement material in composites (Le Phuong et al., 2019).

Natural fibers, or biofibers, have a comparative benefit over synthetic fibers. They have been applied as functional reinforcing fiber in composite due to their recyclable, biodegradable, and non-toxicity (Bari et al., 2021). Also, they have low-density materials with comparative stiffness and high strength (Abdul Khalil et al., 2011a). A paradigm change from synthetic fiber reinforced composite to composite reinforced with biofiber has been implemented in the literature due to their functional properties. Biofibers such as kenaf, hemp, jute, sisal, bamboo, and wood have been studied and reported as reinforcing agents in polymer composite (Sreenivas et al., 2020). Using kenaf fiber as a reinforcing material has been extensively investigated in the literature because of its abundant nature and inherent characteristics, including biodegradability, non-abrasiveness, high aspect ratio, and superior toughness (Wu et al., 2020).

Kenaf fiber, a biofiber, has been widely used for nonwoven fiber mats. As an alternative to synthetic fiber, it has unique and inherent advantageous characteristics, including low-density with relatively good thermal stability and high strength features which correspond to the favorable lignocellulosic biomass for reinforcement material in biocomposites (Sapiai et al., 2020). The utilization of kenaf fiber has gained attention in composite applications because of its renewability, biodegradability, and non-toxicity characteristics. Many studies have been widely devoted to establishing kenaf fiber as a reinforcement agent in composite materials (Yusuff et al., 2020). Moreover, Arun Prakash & Viswanthan, (2019) employed kenaf fiber as a reinforcement agent in preparing composite and reported enhanced thermal stability and mechanical characteristics than unreinforced composite. In another study, Chee et al. (2020) evaluated the physical characteristics of bionanocomposites reinforced with nanofiller and kenaf fiber. The authors found that combining the nanofiller and kenaf fiber improved the dimensional stability and water barrier of composites at 56% and 37%, respectively. The functional properties of the bionanocomposites were affected by interfacial interaction of fiber-nanofiller-matrix in the composite network.

However, the main drawback of biofiber in its application as a reinforcing agent is the intrinsic moisture absorption behavior (Venkatasudhahar et al., 2021). Weak biocomposite functional characteristics induced by a hydrophobic matrix with hydrophilic biofiber remain a challenge. A surface modification of biofiber to enhance the chemistry and structure of cell walls can be obtained, contributing to increasing the functional properties of biocomposites (Birnin-yauri et al., 2017). In one investigation, Cavdar et al. (2014) evaluated the effect of chemical modification using propionic anhydride of aspen wood flour in the composite structure. The

authors found a noticeable increment in the mechanical characteristics of the obtained composites provided by surface modification with the anhydride. The propionylation on wood flour showed a 23% of enhancement in the flexural modulus of the composite compared to the unmodified composite. More recently, Gallardo-Cervantes et al. (2021) used propionic anhydride to modify chemically agave biofiber that increased the compatibility of biocomposites. The flexural strength and water barrier of biocomposites with propionylated fiber increased up to 35% and 170% in comparison with uncompatibilized biocomposites. Hence, using propionic anhydride modification of kenaf fiber is pivotal to increasing the compatibility and hydrophobicity in the interaction of vinyl ester matrix which is able to improve the biocomposites' functional properties.

Bio-based fillers can improve the thermal and mechanical characteristics of the synthesized composite (Mittal et al., 2014). Moreover, El Assami et al. (2020) and Drissi-Habti et al. (2021) recently found new techniques for the utilization of nanocarbon material to increase the final properties of structural composites. Considerable concern has been recently devoted to evolving biomass material with nanoscale for various industrial-scale applications (Mahmoud Zaghloul et al., 2021). No study has been reported in the literature on the incorporated improvement of bionanocarbon and reinforcement of kenaf fiber in vinyl ester composites. The incorporation of bionanocarbon in vinyl ester composites reinforced with kenaf fiber is able to provide superior mechanical and thermal stability to the prepared composites.

The incorporation of bionanofiller is essential in the enhancement of the functional properties of bionanocomposites (Paturel & Dhakal, 2020). Carbon-based composite presents worthwhile functional properties because of its high strength, low

density, and good thermal stability (Jiang et al., 2021). In different investigations, Li et al. (2014) and Abdullah et al. (2021) revealed that the utilization of nanoscale biomass in the increment of bionanocomposite compatibility contributed to the increased many concerns of scientists. In line with the approaches, Swaminathan et al. (2020) found the great potential of carbon-based nanomaterials in the enhancement of the strength and thermal stability of bionanocomposite.

Bionanocarbon was used to improve the compatibility of filler with hydrophobic vinyl ester matrix and enhanced mechanical and thermal stability of kenaf fiber reinforced vinyl ester composites. Since nanosize of biocarbon has a large surface area and negative surface charge, the bionanocarbon was utilized to improve the strength and compatibility of fiber-matrix interaction. The biocarbon nanoparticles provide promising features in the composite application because it has great thermal, low density, and high strength characteristics (Zhu et al., 2019). Currently, Nikolaeva et al. (2020) revealed the use of nanocarbon filler in the fabrication of nanocomposites where the performance of the prepared composite could be considerably enhanced. In a cationic matrix-like vinyl ester, the negative surface charge and nano-scale size of the material result in the enhancing agent being more dispersive (Zhang et al., 2020a). To decrease the overdependence on wood-based plants, many researchers have studied solid biowaste from agro-industrial wastes as raw materials in the fabrication of biocarbon (Brito et al., 2019; Wang et al., 2021a).

On the other hand, a matrix plays a key role since it can be designed for a specific application if a polymer matrix is properly selected. Vinyl ester, a thermoset polymer, is widely utilized for advanced composite applications. Its chemical resistance, dimensional stability, and good stiffness is being more attractive than a

polyester matrix. Also, the vinyl ester has a lower price than epoxy resin. It can simply be handled in the ambient environment and offers better control over the curing process. The matrix also offers similar mechanical properties to the epoxy matrix. Moreover, vinyl ester has been extensively used for liquid-molding formulations because of its high toughness, low exothermal heat, good chemical resistance, low volume shrinkage, low price, and low weight (Jiao et al., 2017). As a consequence, it has been widely used in various industrial-scale applications, including automobile parts, adhesives, surface vehicles, military/aerospace, coatings, structural laminates, and molding compounds, and (Jahandideh et al., 2020).

It is generally known that a neat vinyl ester composite suffers from its brittleness. A potential breakthrough to improve the features and reduce the cost of the matrix is to strengthen it with enhancement and reinforcement agents (Shaker et al., 2019). Hence, one possible approach for strengthening the vinyl ester is to blend it with kenaf fiber and bionanocarbon. Increasing the interfacial bonding of kenaf fiber in the matrix requires a surface modification using propionic anhydride to reduce the hydrophilicity and impurities on the biofiber. Considering the issues mentioned above, it is necessary to study the incorporation of propionylated kenaf fiber and bionanocarbon in vinyl ester which can be a potential choice for reinforcing and cost-reducing the composites.

1.2 Problem statement

Vinyl ester has become a pivotal matrix in industry and research as the use of the matrix has been expanded. The application of vinyl ester as a primary phase presents considerable benefits, allowing the matrix to replace other thermoset matrices. Infrastructure and transportation sectors, for instance, showed a promising matrix in the production of storage tanks, sewer pipes, and ducts (Oladele et al., 2020). However, a neat composite of vinyl ester matrix has relatively poor

mechanical properties and is relatively brittle. It can be reinforced with kenaf fiber and strengthened by bionanocarbon to improve the basic properties. A further enhancement of the properties is still necessary to broaden the application of vinyl ester-based materials.

Owing to its inherent functional properties like effective thermal and tensile characteristics, kenaf fiber is one of the most utilized biofibers for nonwoven products (J. Zhang et al., 2019). It has been utilized as a promising choice material for reinforcing biocomposites as an alternative to non-renewable fibers (Parvej et al., 2019). The inherent renewability, non-toxicity, and biodegradability potentials of kenaf fiber are attracting and gaining interest. Incorporating biofiber as reinforcement material has been an efficient breakthrough for the reinforcing agent in the matrix (Sapiai et al., 2020). However, the challenge of low mechanical strength because of compatibility with a hydrophobic matrix is still limited to be addressed (Pang et al., 2017). In line with these drawbacks, poor interfacial fiber-matrix bonding induced by the hydrophilicity nature and impurities of kenaf fiber hinder the compatibility of composite. Modification of kenaf fiber using propionic anhydride has the potential prospect to solve the challenge. Instead of using direct unmodified kenaf fiber itself, this study also used propionylated kenaf fiber to determine the properties when compared to unmodified fiber.

Biocarbon has been suggested as an appropriate material for thermal enhancement and mechanical strength for polymers because of thermal stability, less energy requirement for its production, and availability. Since it has been mainly produced through thermal conversion from wood-based plants, biocarbon production has a severe environmental impact on forest reserves (Alam et al., 2021). Recently, contemporary researchers widely studied the biocarbon produced from biomass

wastes and suggested decreasing the overdependence on wood-based plants and petroleum products for its fabrication (Kim et al., 2019; Sajjadi et al., 2018). Lignocellulosic materials such as oil palm shell (Rashidi & Yusup, 2021), coconut shell (Umerah et al., 2020), sugarcane bagasse (Liu & Tang, 2020), and coffee grounds (Chiu & Lin, 2019) have been utilized for the production of biocarbon. Several methods have been investigated in the fabrication of biocarbon from biomass wastes or biomass (Oginni et al., 2019b). Energy-efficient and economically viable available methods are proposed using the one-step activation technique (Oginni et al., 2019a). Since OPS is one of the most generated solid biowastes from the agricultural sector in the tropical region, the OPS was used for biocarbon fabrication (Abdullah et al., 2021; Nuryawan et al., 2020). Therefore, the use of OPS as a precursor in the production the biocarbon is a potentially sustainable approach to reducing solid biowaste and promoting its valorization.

Bionanocarbon was employed in this study to improve the compatibility of the hydrophobic polymer matrix with the nanofiller and kenaf fiber. Its nanosize and large surface area were applied to increase the compatibility and strength of fiber-matrix interaction. It has great thermal, strength, and low density properties that can provide promising properties in composite applications (Zhu et al., 2019). Thus, bionanocarbon was used in this study. Its nanosize allows great dispersion, high specific surface area, and adequate distribution.

This study focused on the fabrication and characterization of vinyl ester bionanocomposites reinforced by propionic anhydride-modified kenaf fiber and the enhancement characteristics by adding bionanocarbon. The obtained composites were characterized to evaluate the functional properties, such as the physical, mechanical, morphological, structural, thermal, and chemical resistance

characteristics to determine the effect of the propionic anhydride modification of kenaf fiber and bionanocarbon in bionanocomposites structure. The incorporation of bionanocarbon and propionylated kenaf fiber in vinyl ester composite has not been reported in the literature. This study highlights the feasibility of using propionylated kenaf fiber as a reinforcing agent, novel bionanocarbon as enhancement nanomaterial, and versatile vinyl ester as the matrix to improve the functional properties and observe the potential application in water and chemical storage tanks.

1.3 Objectives

This research aims to investigate the potential of the bionanocarbon and propionic anhydride modification of kenaf fiber to be used in good-performance vinyl ester bionanocomposites. The specific objectives of this present research work are:

1. To characterize the properties of bionanocarbon generated from oil palm shell using ball mill method.
2. To study the effect of propionic anhydride modification on the kenaf fiber (weight percent gain, morphological, wettability, structural, and thermal properties).
3. To study the effect of bionanocarbon with different loadings on the physical, mechanical, morphological, structural, thermal, and chemical resistance properties of bionanocomposites.
4. To evaluate the effect of unmodified and propionylated kenaf fibers reinforced composites filled with the bionanocarbon on the physical, mechanical, morphological, structural, thermal, and chemical resistant properties of bionanocomposites.

1.4 Thesis layout

This entire thesis has been organized into five corresponding chapters as depicted in Figure 1.1.

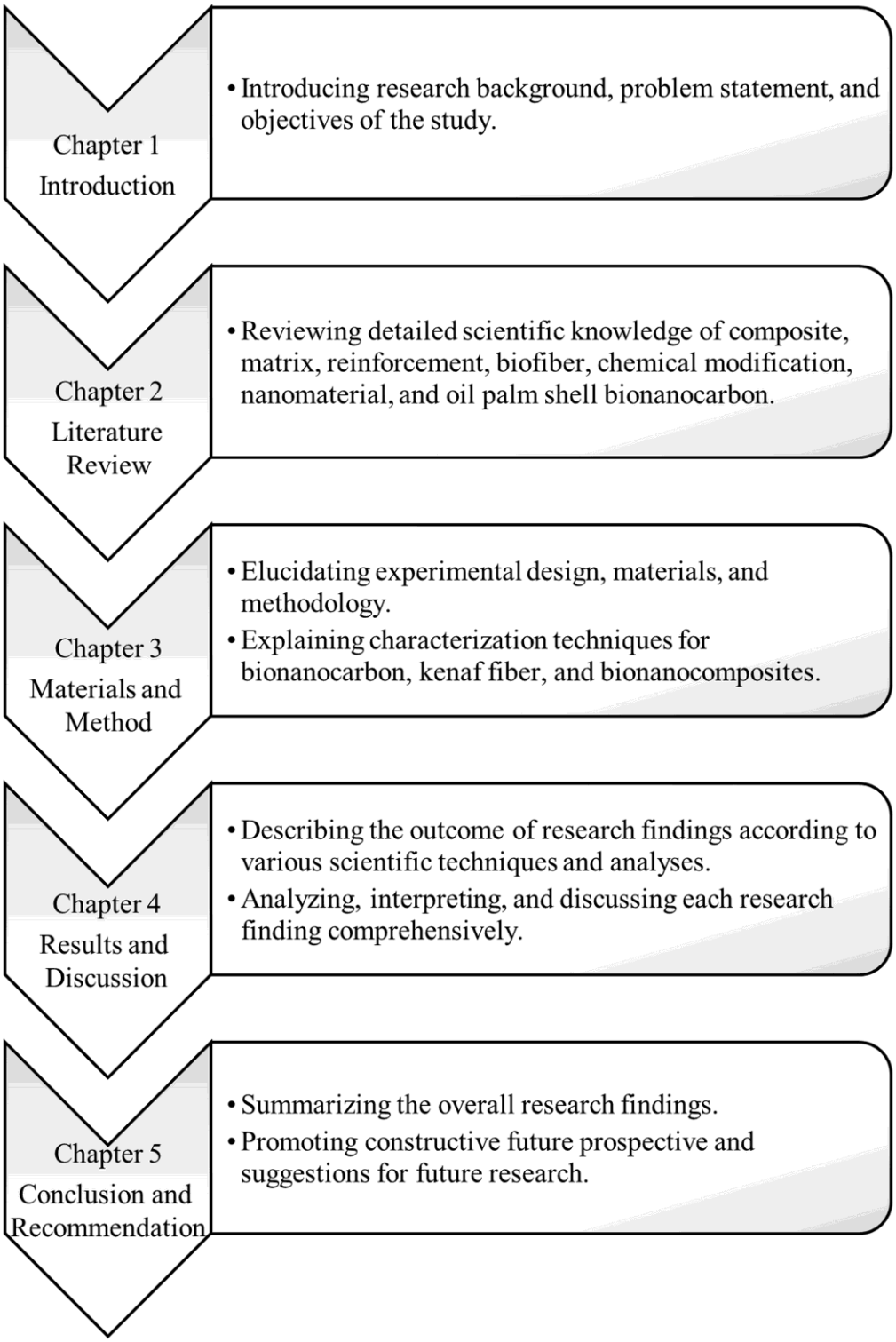

Figure 1.1 Thesis layout.

CHAPTER 2

LITERATURE REVIEW

2.1 Composites

2.1.1 Introduction

Composites are engineered materials produced from at least two combinations of nano- or micro- or macro components differing in physical and chemical composition. The combination of two or more constituent materials aims to enhance the composite products' functional properties. Essentially, the constituents are insoluble or merge with each other and hence, normally result in an interface between one another. A matrix, a primary phase of composites, is generally less hard, more ductile, share load, and embodies the secondary phase. A reinforcement material, the secondary phase of composites, is a discontinuous phase, higher strength, and is embedded in the primary phase (Stelzer et al., 2022).

The matrix in a composite system is able to hold the orientation and position of the reinforcement materials. Meanwhile, the reinforcing materials contribute to rigidity, strength, and assist the structural loading. Composite constituents can retain their characteristics, including physical and chemical. However, the mixture yields a competitive composite product. The introduction of diverse materials produces a new material with multiple structural and ultimate properties that differ from the individual components. The strengthening scenarios of the composite fabrication depend fundamentally on the type, amount, geometry, and arrangement of reinforcing material in the polymer matrix (Balla et al., 2019).

2.1.2 Classification

Composite materials have two classification systems. The first system is defined according to the material of the matrix namely ceramic, metal, and polymer.

Ceramic matrix composites are formed by a ceramic matrix, while metal matrix composites are composed of a metallic matrix such as iron, magnesium, copper, aluminum, and cobalt. Polymer matrix composites, on the other hand, are comprised of a matrix from thermoset (vinyl ester, unsaturated polyester, epoxy, and phenol-formaldehyde) or thermoplastic (Polyethylene, polypropylene, polylactic acid, polystyrene, and polyvinyl alcohol) (Zhang et al., 2020a).

Furthermore, the reinforcing material structure is the second system of composite materials. These reinforcement materials are classified as fiber reinforced composites, particulate reinforced composites, and laminar composites. Fibrous composites compose of two types according to the fiber length or form, which are continuous fibers (long fibers) and discontinuous fibers (short fibers or chopped fibers). A dispersed phase in particle forms such as carbon, metallic, ceramic, or other particles of different shapes and sizes can be classified as particulate composites. Laminar composites are consisted of several layers with dissimilar orientations of fiber or known as multilayer (angle-ply) composites which are formed by at least two divergent bonded fibers (Ahmad et al., 2019a).

2.2 Polymer biocomposites

Since sustainable materials from renewable bioresources have many benefits compared to synthetic materials, scientists have been devoted to developing approaches to find an alternative to replace petroleum-derived materials. Innovation and technology in the biocomposite fields toward the substitution and reduction of fossil-based polymers remain a challenge in recent decades (Rutitis et al., 2022). Consequently, the use of bioresources as a reinforcement or enhancement material in bio-based polymer composites has gained the attention of scholars in the research fields.

Biocomposite is a composite containing one of the good phase matrices (polymer) or reinforcing material origins from renewable bioresources. Seaweed, starch, and vegetable oils show promising advantages to replace the non-renewable polymer matrix as reported in the literature (Wang et al., 2021b). On the other hand, reinforcing material can be obtained from biofiber such as kenaf fiber, by-products, bio-solid waste, timber or non-timber, and derivatives from plants. Biocomposites have been extensively applied in many industrial applications. This is highly influenced by a substantial interfacial polymer matrix-reinforcing material interaction. As a result, biocomposite products have been utilized in many applications, i.e. automobile parts, military weapons, sporting goods, car aircraft, and surface vehicles.

Recently, polymer biocomposites reinforced or enhanced with natural resources have become an interesting topic and are widely studied in polymer science areas. The resulting products offer non-corrosive, low cost, low density, environmentally friendly, high strength, and relative non-toxicity (Kamaruddin et al., 2022). In comparison with the origin of bioresources such as fruit, bast, root, leaf, seed, grass, and stalk, the bast fiber is the most widely utilized in the application of biocomposite materials (Lee et al., 2020). This attributes to the wide availability, low density, high strength and modulus, and ease in the surface modification

Many researchers have reported on the incorporation of bioresources in composite fabrication and they have revealed futuristic methods to alleviate the commercialization (Lee et al., 2021; Wibowo et al., 2022). Also, experimental results of the previous studies showed that bioresource and its derivative as reinforcement materials in the production of biocomposite provided good functional properties, indicating a prospective candidate to replace or reduce the conventional polymer composites (Chang et al., 2021; Fitzgerald et al., 2021; Gupta et al., 2022).

2.3 Matrix

Matrix serves as a cementing material that is employed as a binder and holds the orientation and position of reinforcement material in its place. It can be easily determined as a material where a composite reinforcement system is embedded. The matrix also plays as supportive material protecting the composites from an attack by external agents. Since it is easily phase and more ductile, the matrix contributes to holding the distributed phase and assists in load and stress transfer within the network of composites. In addition, the matrix renders resistance to the surface of the reinforcing system from mechanical abrasion, crack propagation, and damage tolerance caused by plastic flow at the crack points (Chowdhury et al., 2018).

Generally, a matrix can be classified into two types which are thermoset and thermoplastic. The matrices have various types with divergent characteristic behaviors which produce a wide range of composite properties. Hence, the selection of the matrix material is according to the application's final products. For instance, if elevated thermal resistance together with chemical resistance is required for a composite product then a thermoset matrix is preferred over a thermoplastic matrix. Whereas, if composite product recyclability together with high damage tolerance is required then a thermoplastic matrix is a better choice than a thermoset matrix (Dorigato, 2021).

2.3.1 Thermoset

Thermoset-based composites usually present a higher strength than thermoplastic-based composites. Thermoset materials are stiff, not stretched, and hard to crosslink. They are not softened or not moldable when it is heated. A thermoset matrix is usually liquid in its initial form. This liquid matrix is converted to a hard rigid solid by adding the hardener or curing agent that allows chemical cross-linking

via a curing process involving the application of heat. The major feature of the thermoset is the irreversibility of the solidification mechanism generated by the chemical reaction. This means that once a thermoset matrix is cured, a strong bound three-dimensional structure is created in the matrix, and therefore, the thermoset cannot be reprocessed, reshaped, and melted by the heating process (Yang et al., 2019a). As a consequence, before the thermoset matrix starts to cure, the process of impregnation, shaping, and solidification should be completed in composite manufacturing.

At room temperature, a thermoset matrix is brittle and has weak fracture toughness. Because of its three-dimensional cross-linked structure, it possesses good thermal resistance, dimensional stability, chemical resistance, and creep characteristics (Xu et al., 2020). Common types of thermosetting matrices utilized in the production of composite materials are vinyl ester, unsaturated polyester, and epoxy. A comparative study of the curing characteristic and advantages and disadvantages of these thermosetting matrices are summarized in Table 2.1. Thermoset-based composites are of increased attention because of their advantages such as thermal stability, chemical resistance, mechanical strength, lightweight, low cost, environmental stability, and faster manufacturing (Li et al., 2020; Yuan et al., 2019). They have been used in the substitution of metals and alloys in many industrial scales, including medical, robotics, marine, energy, engineering, and aerospace (Tang et al., 2017; Wang et al., 2020).

Table 2.1 A comparative study of thermosetting matrices (Nabinejad et al., 2017).

Comparison parameter	Vinyl ester	Unsaturated polyester	Epoxy
Curing system	Curing catalyst using methyl ethyl ketone peroxide (MEKP) and cobalt naphthenate as an accelerator in the room environment	Curing catalyst using methyl ethyl ketone peroxide (MEKP) and cobalt naphthenate as an accelerator in the room environment	Curing catalyst using amine hardeners, i.e. triethylene tetramine and diethylene triamine
Advantages	Excellent environmental and chemical resistance, high water resistance, superior mechanical and thermal properties compared to polyester	Easy to utilize, the cheapest cost matrix	High water resistance, good mechanical and thermal characteristics, low polymerization shrinkage, long working times available
Disadvantages	High cure shrinkage, high styrene content, and post-cure generally needed to enhance the properties	Very high styrene emission, high cure shrinkage, moderate mechanical performance, limited range of working time	More expensive than a vinyl ester, high corrosive handling, very high critical mixing, high temperature required for the curing process, higher processing cost and production, and more difficult the manufacture

In thermoset-based composites, a matrix also plays an essential role since it can properly be shaped and designed for certain applications of polymer products. An adequate interfacial adhesion between the matrix and reinforcement agents is necessary in order to obtain the reinforcing impacts in the composite network. The fabrication of composite can be performed using vinyl ester which is a matrix with good mechanical strength and high environmental and chemical resistances. Recently, this thermoset matrix has been reported as a matrix with good potential for the development of high-value-added composite materials (Yadav et al., 2018).

2.3.2 Vinyl ester

Vinyl ester, a thermosetting polymer, has been commercially utilized in polymer composite industries for more than six decades (Rodriguez-Mella et al., 2014). This matrix has been extensively acknowledged as a matrix highly resistant to a wide range of general environmental chemistry. The applications of vinyl ester-based composites such as solvent storage tanks, ducts, sewer pipes, swimming pools, cleaners, and scrubbers are substantial candidates for infrastructure and transportation. Also, its wide range of applications includes coatings, molding compounds, structural laminate, adhesives, military, and parts of reinforcement for bridges, vehicles, aerospace, and automobiles (Muneer Ahmed et al., 2021).

As a matrix, vinyl ester provides many fascinating attributes, i.e. low viscosity, low price, cure at room temperature, and equivalent properties to other thermosetting matrices (Abral et al., 2020). Its low molecular weight and low viscosity allow great wettability for the reinforcing materials in the composite fabrication. In spite of its drawback in the post-cure process to enhance the properties, this polymer presents good mechanical and thermal features such as epoxy, and in composite production, the curing process is easier and quicker in comparison with unsaturated polyester matrix (Moujdin et al., 2022). Moreover, it has higher chemical and water resistance, and hydrolytic stability, and is cheaper compared to polyester, and this matrix offers easier control and reaction over the curing mechanism compared with the epoxy matrix (Pączkowski et al., 2022).

Due to its high performance in chemical resistance and mechanical strength, the thermoset matrix has been widely applied in many industrial applications. Stalin et al. (2020) reported that vinyl ester is high in tensile strength and modulus, while Jaswal et al. (2021) reported that its crosslinking network corresponds to great

resistance to degradation, acids, alkalis, solvents, and water. It is also important to consider that this matrix has substantial properties of the polymer such as thermal stability, durability, and toughness.

Neat vinyl ester matrix is relatively brittle, approaches to increase the functional properties and reduce the cost of production are reinforcing with fiber and strengthening or enhancing by filler. To enhance the performance of structural composite including cast into shape, reinforcing the matrix with a biofiber, and enhancing it with nanofiller are required (Andrew & Dhakal, 2022).

The thermoset matrix is formed by a vinyl ester prepolymer monomer and styrene. Terminal reactive sites on double bonds from acrylic acids are contained in the vinyl monomer as exhibited in Figure 2.1. Styrene monomer in the vinyl ester matrix is a reactive diluent, which governs the viscosity, enhances the wetting characteristic of the matrix, and lowers the cost of production (Liu et al., 2019). Hence, as a reactive monomer, styrene is necessary to introduce into the vinyl ester matrix due to its intrinsic high viscosity behavior. The addition of reactive diluents is carried out after the formation of random dispersion of carbon-carbon double bonds and ester group at the end of polymer bonds caused by the co-polymerization during the reaction of crosslinking (Ashfaq et al., 2020). There are other monomers such as methyl methacrylate, triethylene glycol dimethacrylate, epoxy acrylic compounds, and methyl styrene. Styrene monomer, however, is commonly employed in industrial-scale applications with concentration ranging from 31% to 47% (Rajaee et al., 2019).

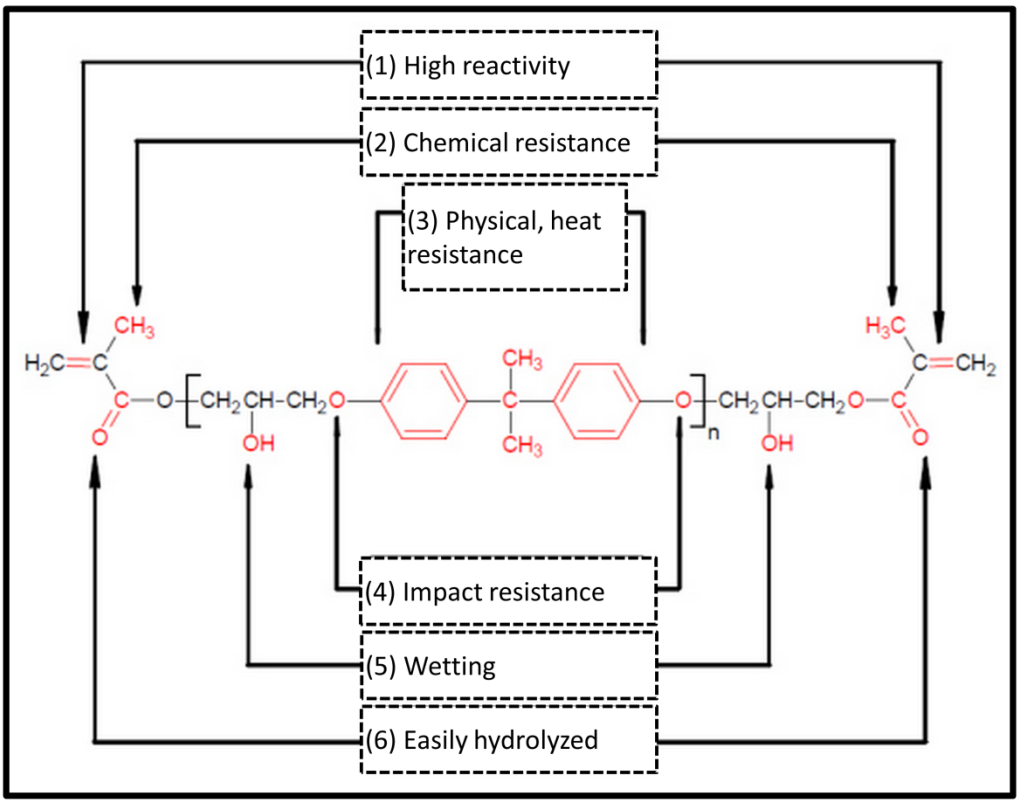

Figure 2.1 Chemical structure of vinyl ester monomer. Adapted from Nabinejad et al. (2017).

In the curing process, the thermoset matrix can be cured either in ambient conditions or at elevated temperatures, yet the rate is affected by the amount of catalyst, accelerator, and temperature. Besides, the viscosity of vinyl ester also influences the degree of curing. It is important to consider that excellent wettability should be obtained while the time consumed during the infiltration process is less than the vinyl ester's gelation time (Rodríguez-Uicab et al., 2021). The molecular weight of the matrix's backbone, amount and type of co-reactant, and source of the termination network affect the functional properties of the matrix. Also, an increase in molecular weight results in higher resiliency and toughness and decreases the resistance of solvent and heat (Ramakrishnan et al., 2022).

Nowadays, vinyl ester has become an important matrix in industry, and research using vinyl ester has been expanded. This is due to its attractive

characteristics such as room temperature curing, low viscosity, low price, and comparable characteristics to other thermosetting matrices. The application and establishment of the matrix concern the new structural properties in an exertion to improve the physical, mechanical, and thermal behaviors. Recently, a review study by Johnson et al. (2018) investigated composite materials which used vinyl ester as a primary phase. The authors reported that important advantages of using the matrix allow it as an effective replacement for other thermoset matrices especially polyester and epoxy, in which application can the vinyl ester employed as an element of the matrix for producing composite products. Moreover, by replacing epoxy and polyester matrices, the matrix provides parametric benefits related to the mechanical, physical, and thermal characteristics of the resultant composites.

More recently, Nagaraj et al. (2020), in their study of vinyl ester composites reinforced with date seed (a solid biowaste) were fabricated via a conventional compression molding procedure. The experiment showed significant enhancement in the functional properties of the resultant polymer composites. They revealed that the obtained vinyl ester composites provide potential and promising material for many industrial-scale applications, in particular home appliances (a table fan blade), furniture (a workbench), and automotive applications (four-wheeler self-motor guard and two-wheeler engine guard).

2.4 Reinforcement

Reinforcement generally contributes to the stiffness, rigidity, and strength of polymer composites. This reinforcement can enhance the functional properties of the matrix, majorly in the reduction of the composite cost, reducing degradation over a usage period, the service life of the end product, and easing the processing. It is also responsible for composite resistance in terms of corrosion and heat. To achieve a strong composite, the reinforcing material should have stiffer and greater strength than

the matrix as the reinforcement system improves the brittleness and decreases the ductility of the composites (Graupner et al., 2020). The type of reinforcement in the composite can vary including fiber, whisker, flake, particle, filler, or a combination of them. The reinforcing materials can be either from organic or inorganic resources. Sathishkumar et al. (2020) reported that these resources are classified into lignocellulosic materials and non-cellulose materials (mineral or animal). Biofiber from lignocellulosic, however, is widely employed for making composite materials.

2.4.1 Biofiber

The utilization of biofibers as reinforcement materials to replace non-renewable or synthetic fiber for making composites has gained the attention of scientists, technologists, and engineers. Sustainability issues, combined with thermal, mechanical, and physical properties of the reinforcing material interlock characteristics of biofiber-based composites, trigger wide research on biofibers used as reinforcing agents.

A biofiber can act as a potential reinforcing agent since it has beneficial properties such as non-hazardous, low cost, light in weight, high specific characteristics, eco-friendly, abundantly available, non-abrasive and renewable resources, biodegradable, good mechanical properties, and less damage (Mohit et al., 2022). These advantageous features lead to the use of biofibers in combination with many polymeric matrices. Currently, the emphasis of modern societies focuses on the use of bioresources, viz. biofibers which have sustainable features and contribute to a healthy environment.

Syduzzaman et al. (2020) reported that there are two main groups of fibers, namely biofibers (natural fibers) and man-made fibers. Biofibers are classified as wood fibers and non-wood fibers. They are lignocellulosic materials that can be

obtained from plants, minerals, and animals. All these lignocellulosic fibers are stiff and strong as they compose of long cells with thick cell walls relatively. The constituents originate from the biosphere, and they can be recycled and biodegradable. As reinforcement fibers, biofibers have many different types of fibers. Meanwhile, man-made fibers are commonly utilized in aircraft industries. Man-made fibers are classified into synthetic fiber and artificial fiber. Figure 2.2 illustrates the classification of biofibers and man-made fibers.

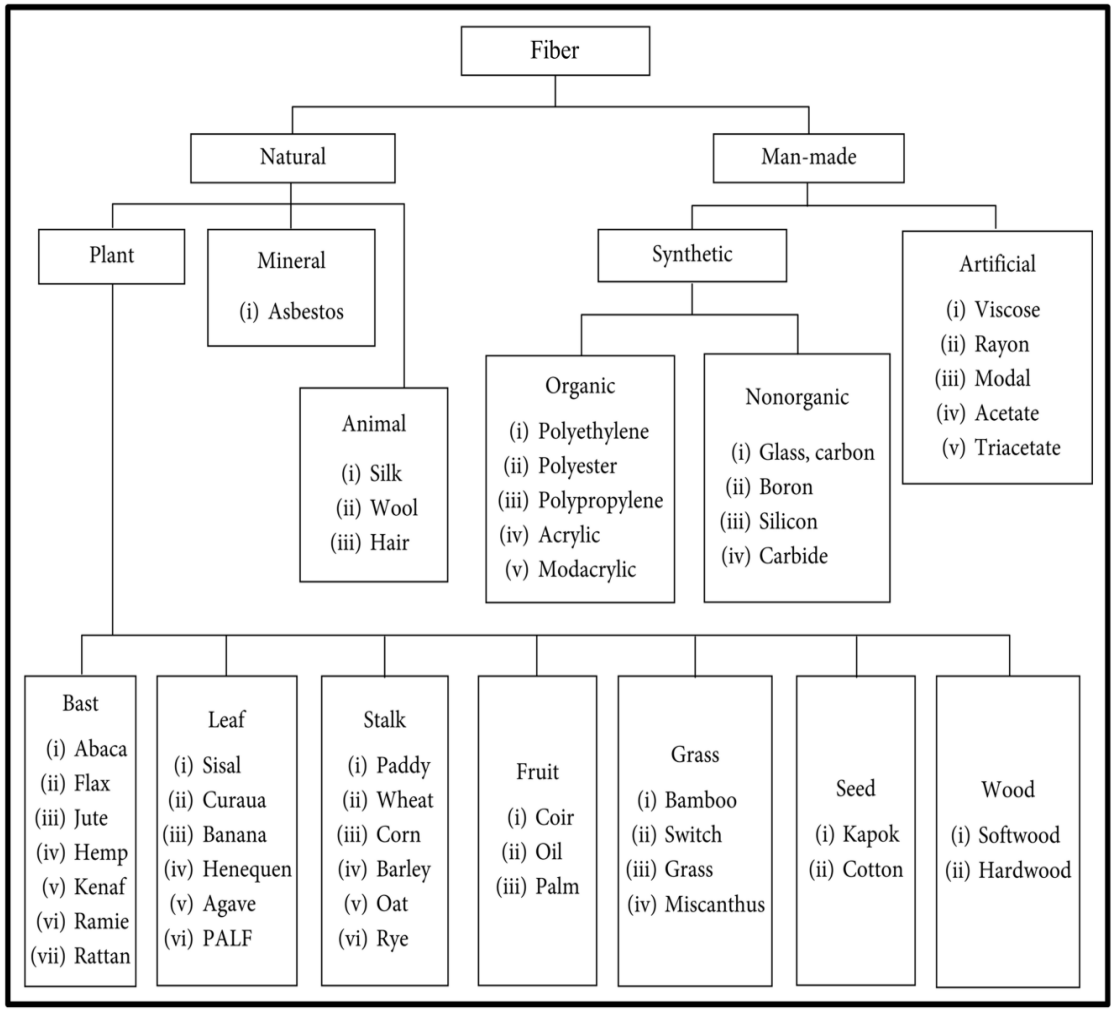

Figure 2.2 Classification of natural and man-made fibers. Adapted from R. Ahmad et al. (2019).

In another study, Mulenga et al. (2021) reported that biofibers such as kenaf, coir, jute, hemp, banana, ramie, and sisal as reinforcing materials in fabricating composite have been extensively used for composite production. Long agricultural biofibers, i.e. kenaf, hemp, flax, and jute are employed as reinforcing agents for making thermoplastic and thermoset composite materials to replace the use of synthetic fiber. Biofiber composites are easily able to recycle as they are eco-friendly and abundant in the biosphere.

It is also important to consider that the reinforcing biofiber can be carried out in many forms including nonwoven strand mat and woven roving mat. In this current era, technology and manufacturing have been implemented in an extensive range of applications of biofibers and synthetic fibers. With increasing awareness of sustainability issues, nevertheless, it has been devoted to optimizing the utilization of bioresources for making composite materials. The utilization of bioresources in manufacturing will also contribute to reducing global warming and climate change due to the decrement in the consumption of petroleum-derived materials.

In addition, the type of biofiber highly influences the difference in the chemical composition of biofibers. The biofibers' cell wall polymers consist of main lignocellulosic constituents such as cellulose, lignin, hemicellulose, and extractive which can impact the overall properties of the biofibers. Lignin is thermally stable but it corresponds to ultraviolet decomposition, while hemicellulose is attributed to thermal decomposition, biodegradation, and moisture absorption since it indicates the lowest resistance. To increase the cellulose content, the biofibers are usually modified which can provide a noticeable impact on the biofibers performance (Aravindh et al., 2022).

2.4.2 Kenaf fiber

Kenaf (*Hibiscus cannabinus L.*) is a type of warm-season annual biofiber crop usually growing in tropical and temperate areas. In Malaysia, there are some varieties of kenaf. The type of kenaf may differ depending on the adaptability to the divergent environmental atmosphere, leaf shape, flower, seed color, and stem color. One of the kenaf species planted extensively in Malaysia is kenaf sp. V36 since it is appropriate to grow in the country's climate and suitable for commercial-scale production (Abdul Khalil et al., 2010). The stalk of this lignocellulosic fiber can grow up to 5 to 6 m with a diameter range of 2.5 to 3.5 cm within 5 months, leading to a regular supply with high availability for market potential, particularly in fiber-based industries (Saba et al., 2015).

Figure 2.3(a) displays the kenaf plant which is mainly cultivated for its fiber. A kenaf stalk is formed by an inner woody core and outer fibrous bark surrounding the core. The bast fiber is similar to the fiber of softwood, while the core fiber is comparable to the fiber of hardwood as presented in Figure 2.3(b). The percentage of bast fiber and core fiber in a kenaf stalk is approximately 25% to 40% and 60% to 75% of the total dry weight, accordingly (Anuar et al., 2018).

In addition, the average length of bast fiber and core fiber is about 2.6 mm and 0.6 mm, respectively. Since the high tensile and flexural strengths, kenaf bast fiber is commonly produced from the outer fibrous bark (Figure 2.3(c)). These superior properties of bast fiber lead to an excellent choice to develop an extensive range of woven and nonwoven, molded, and extruded materials.

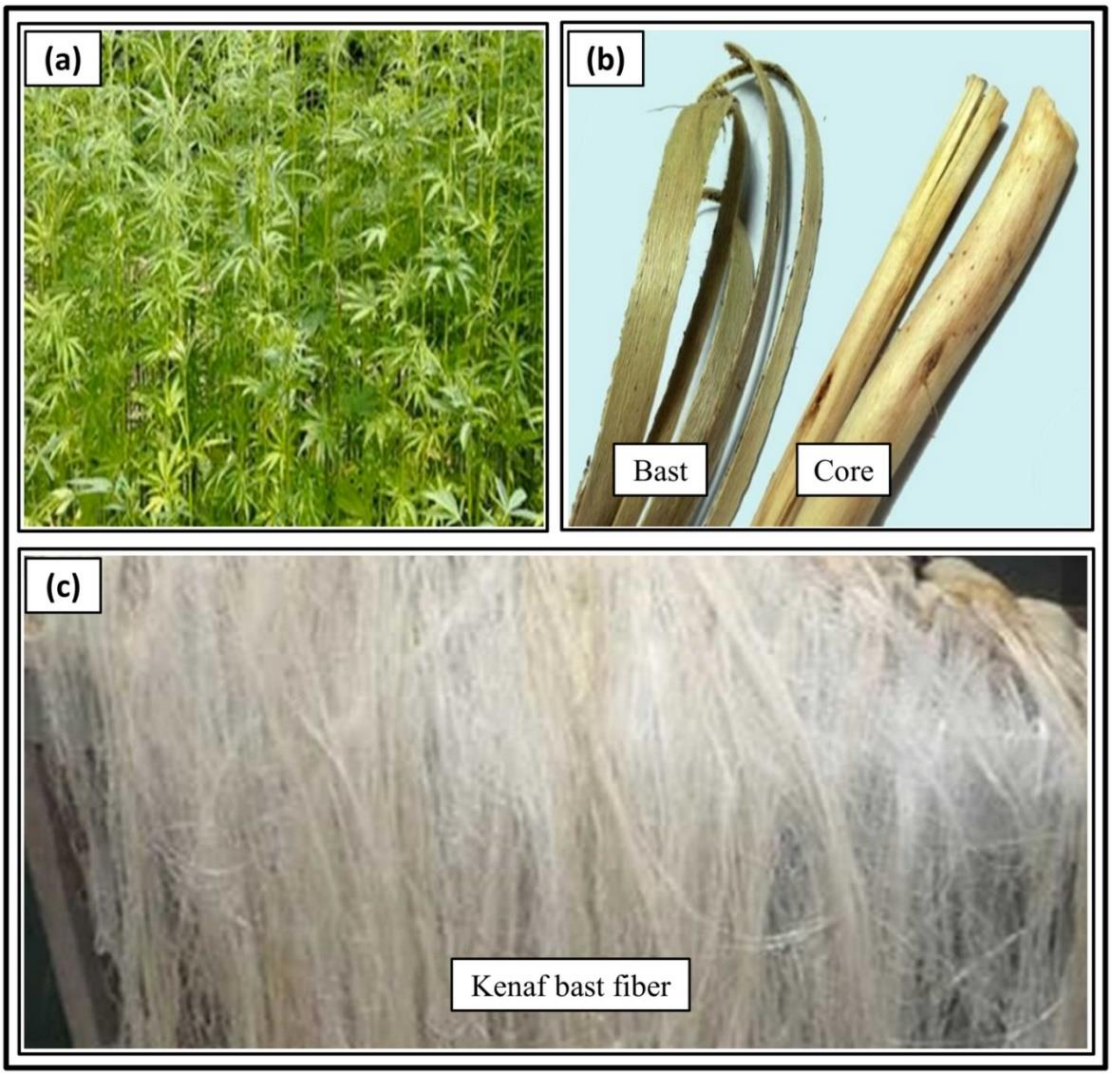

Figure 2.3 Digital image of (a) kenaf plant, (b) kenaf bast and kenaf core, and (c) kenaf bast fiber. Adapted from Uppal et al. (2022).

Since kenaf fiber has intrinsic functional properties which include effective thermal and tensile characteristics, it is widely utilized in the composite fields for nonwoven products (Ismail et al., 2021). The properties of kenaf fiber are listed in Table 2.2. As an alternative to synthetic fibers, biofiber recently has been used as a potential choice for reinforcing material in composites (Malik et al., 2021). Moreover, the inherent potentials of kenaf fiber such as renewability, biodegradability, and non-toxicity are attracting and gaining concern from many researchers.