

**CHARACTERIZATION AND MECHANICAL
PROPERTIES OF KENAF CELLULOSE
NANOCRYSTAL REINFORCED NANOHYBRID
DENTAL COMPOSITE FROM AGRICULTURAL
BIOWASTE**

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UNIVERSITI SAINS MALAYSIA

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DENTAL COMPOSITE FROM AGRICULTURAL
BIOWASTE**

by

SU BING SHENG

**Thesis submitted in fulfilment of the requirements
for the degree of
Master of Science**

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LIST OF SYMBOLS

S_{BET}	BET specific surface area
a	Molecule cross section area
N_{A}	Avogadro Number
n_{m}	Monolayer capacity
σ	Stress
P	Load
l	Length
b	Width
d	Thickness

LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
APS	3-aminopropyltriethoxysilane
ASTM D	American Society for Testing and Materials - Miscellaneous materials
BC	Bacterial Cellulose
BET	Brunauer–Emmett–Teller
Bis-GMA	Bisphenol A-glycidyl methacrylate
CNC	Cellulose nanocrystals
CNF	Cellulose Nanofibrils
CO ₂	Carbon dioxide
CP	Cross-Polarization
CQ	Camphorquinone
DC	Degree of Conversion
DMAEMA	dimethylaminoethyl methacrylate
DTG	Differential thermogram
EMA	Ethylene methyl acrylate
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier-transform infrared spectroscopy
GPa	Giga-Pascal
GPS	3-glycidoxypropyltrimethoxysilane
H ₂ SO ₄	Sulfuric acid
HCl	Hydrochloric Acid
IARC	International Agency for Research on Cancer
ISO	International Organization for Standardization
KSFE	Kumpulan Saintifik F.E. Sdn Bhd
MHz	Megahertz
MPa	Megapascal
γ-MPS	γ -methacryloxypropyltrimethoxysilane
NMR	Nuclear Magnetic Resonance Spectroscopy
PEGDMA	Polyethylene glycol dimethacrylate
PLA	Poly(lactic acid)
PMMA	Polymethyl methacrylate

RI	Refractive index
RSFRT	Random Short Fiber Reinforced type
SD	Standard deviation
SEM	Scanning electron microscope
SPSS	Statistical package for social sciences
TEGDMA	Triethyleneglycol dimethacrylate
TEM	Transmission electron microscope
TGA	Thermogravimetric Analysis
TLRT	Textile laminate reinforced type
TMOS	Tetramethoxyl orthosilicate
TMPS	Trimethoxyphenylsilane
UCFRT	Unidirectional Continuous Fiber Reinforced type
UDMA	Urethane dimethacrylate
UK	United Kingdom
USA	United States of America
USM	Universiti Sains Malaysia
UV	Ultraviolet
VS	Versus
VTMS	Vinyltrimethoxysilane
XPS	X-ray photoelectron spectroscopy

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**PENCIRIAN DAN SIFAT MEKANIKAL KOMPOSIT PERGIGIAN
NANOHIBRID DIPERKUKUH NANOKRISTAL SELULOSA KENAF
DARIPADA SISA PERTANIAN**

ABSTRAK

Inovasi nanoselulosa sebagai pengisi pengukuhan didalam komposit telah menarik minat pelbagai bidang untuk mencipta biobahan baharu. Kajian ini bertujuan untuk mencirikan selulosa nanokristal (CNC) yang diperolehi daripada kenaf sebagai pengisi pengukuhan dalam komposit gigi silika sekam padi. Komposit yang diperkukuh dengan serat kenaf telah dinilai dari segi kekuatan lenturan dan mampatan. Ciri-ciri permukaan retak juga telah dikaji. CNC kenaf telah diperolehi daripada beberapa siri proses kimia, kemudian dirawat dengan γ -methacryloxypropyltrimethoxysilane (γ -MPS). CNC tersebut telah dicirikan dengan menggunakan mikroskop electron penghantaran (TEM), spektroskopi inframerah transformasi Fourier (FTIR) dan analisis termogravimetrik (TGA). Komposit eksperimen telah dihasilkan dengan kandungan serat yang berbeza, iaitu 1wt%, 2wt%, 3wt%, 4wt%, 6wt% CNC kenaf terawat, dan dilabelkan K0, K1, K2, K3, K4, K6. Komposit komersial iaitu Filtek Z350XT (3M ESPE, Amerika Syarikat), Neofil (Kerr Corporation, Amerika Syarikat), dan Ever-X Posterior (GC Corporation, Tokyo, Jepun) digunakan sebagai perbandingan. Tujuh spesimen komposit telah disediakan untuk setiap kumpulan (n=7) dengan menggunakan acuan keluli tahan karat berdimensi 25mm x 2mm x 2mm berbentuk batang dan 6mm x 4mm berbentuk silinder masing-masing untuk penilaian kekuatan lenturan dan mampatan. *Light curing* dikenakan ke atas spesimen menggunakan *Light cure unit* (Elipar Deep Cure L, 3M, USA) selama 40 saat dan seterusnya diuji menggunakan Mesin Ujian Universal Instron (Shimadzu, Japan). Pengimbas electron mikroskop

(SEM) digunakan untuk meneliti sampel pada permukaan yang retak selepas ujian kekuatan lenturan. Diameter CNC di bawah TEM adalah 6.31nm. Keputusan FTIR mencadangkan penyerapan γ -MPS di atas CNC kenaf. Keputusan TGA menunjukkan tiada peningkatan sifat terma. Untuk penilaian kekuatan lenturan dan mampatan, *ANOVA* sehala menunjukkan perbezaan yang signifikan secara statistik ($P < 0.05$) di antara semua kumpulan. Penambahan CNC kenaf (1wt%) ke dalam komposit gigi silika sekam padi nanohibrid telah menunjukkan peningkatan yang sedikit dari segi sifat mekanikal. Analisis SEM menunjukkan serat sebagai penahan keretakan walaupun pelekatan di antara permukaan adalah suboptimum. Keputusan menunjukkan bahawa kandungan 1wt% CNC kenaf adalah optimum bagi tujuan pengukuhan komposit nanohibrid silika sekam padi. Kandungan serat yang berlebihan sebaliknya akan menyebabkan penurunan sifat mekanikal akibat penyebaran serat yang lemah dalam komposit. CNC kenaf adalah bahan pengisi pengukuhan sampingan yang berpotensi untuk ditambahkan dalam kandungan yang rendah dan perlu dikaji dengan lebih di masa hadapan supaya dapat menyerlahkan kelebihan sifatnya dengan sepenuhnya.

**CHARACTERIZATION AND MECHANICAL PROPERTIES OF
KENAF CELLULOSE NANOCRYSTAL REINFORCED NANOHYBRID
DENTAL COMPOSITE FROM AGRICULTURAL BIOWASTE**

ABSTRACT

The innovation of nanocellulose as reinforcement filler in composites has attracted interest in various fields for development of new biomaterials. This study aims to characterize cellulose nanocrystals (CNC) extracted from kenaf as reinforcement filler in rice husk silica nanohybrid dental composite. The kenaf fiber reinforced composite was evaluated in terms of flexural and compressive strength. Features of fractured flexural samples were also investigated. Kenaf CNC was isolated from a series of chemical processes, then treated with γ -methacryloxypropyltrimethoxysilane (γ -MPS). Properties of CNC was characterized using transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Experimental composite was fabricated with different fiber loading of 1wt%, 2wt%, 3wt%, 4wt%, 6wt% silane-treated kenaf CNC, which are K0, K1, K2, K3, K4, K6 respectively. Commercial composite of Filtek Z350XT(3M ESPE, USA), Neofil (Kerr Corporation, USA), and Ever-X Posterior (GC Corporation, Tokyo, Japan) were used as comparison. Seven composite specimens were prepared for each group (n=7) using stainless steel molds with dimensions 25mm x 2mm x 2mm bars and 6mm x 4mm cylinders for evaluation of flexural and compressive strength respectively. After light curing using a light cure unit (Elipar Deep Cure L, 3M, USA) for 40 seconds, specimens were tested using an Instron Universal Testing Machine (Shimadzu, Japan). SEM was used to examine fractured flexural samples. Average diameter of kenaf CNC under TEM was 6.31nm. FTIR results suggested adsorption of γ -MPS on kenaf CNC. TGA

results did not show significant improvement in thermal properties. For flexural and compressive strength tests, one-way ANOVA showed statistically significant difference ($P < 0.05$) between all groups. The incorporation of kenaf CNC (1wt%) into rice husk silica nanohybrid dental composite has shown slight improvement in mechanical properties. SEM analysis showed fibers as crack stoppers despite suboptimum interfacial adhesion. The results indicate that 1 wt% of kenaf CNC is optimum for reinforcement of rice husk silica nanohybrid dental composite. Excessive fiber content can result in decline in mechanical properties due to poor dispersion of fibers within composite. Kenaf CNC is a viable reinforcement co-filler at low concentrations and may be further studied to fully elicit its profound properties.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Studies have been extensively conducted following the introduction of dental composites in 1960s to enhance physical and mechanical properties (Lloyd and Adamson, 1987; Shenoy, 2008; Abouelleil *et al.*, 2015; Kapoor and Ahmed, 2021). High strength and fracture toughness are one of the key mechanical properties for enhanced longevity of restorative materials (Ilie and Hickel, 2011).

Dental composite has three phases, namely organic phase, interfacial phase, and dispersed phase (Lutz and Phillips, 1983). The key determinant of its mechanical properties is the dispersed phase (Halvorson *et al.*, 2003; Gonçalves *et al.*, 2010; Shah and Stansbury, 2014; Randolph *et al.*, 2016a).

In dentistry, fibers have been utilized as an approach to reinforce dental composites (Suzaki *et al.*, 2020). Incorporation of fibers into dental composite has been shown to increase flexural strength and fracture toughness, which works by stopping crack propagation when stress is transferred from the matrix to the reinforcement fibers (Garoushi *et al.*, 2013a; Lassila *et al.*, 2018). The stress transfer from weaker resin matrix to stronger fine fibers allows improvement in mechanical properties of fiber-reinforced composites (Wang *et al.*, 2016).

Being a renewable source, natural fibers have been gaining major attraction from researchers due to its environment and economic benefits. The benefit of natural fiber includes it releases the carbon dioxide (CO₂) neutrally upon decomposition. Hence, it is biodegradable and poses no threat towards human health upon inhalation of the particles (Tholibon *et al.*, 2019). In comparison to synthetic fibers, natural fibers are

not dermatological irritant and not dubious of causing lung cancer, which is a major concern where miniscule glass fibers may have possible carcinogenic effect on lungs (Jawaid and Abdul Khalil, 2011).

Kenaf, being one of natural plant-based fibers and has been extensively utilized in developing fiber reinforced composite for various applications as they are inexpensive, yet possess specific strength comparable to that of glass fibers (Nishino *et al.*, 2003; Akil *et al.*, 2011; Anuar and Ahmad, 2011).

However, the main limitation of addition of natural fiber as reinforcement of composite is the inadequate fiber-matrix bonding, leading in poor mechanical performance of end product (Akil *et al.*, 2011). Another issue arising from hydrophilic nature of natural fibers is moisture absorption, which causes hygroscopic swelling and leads to voids at composite interfaces, thus reducing dimensional stability and inferior mechanical properties (Akil *et al.*, 2011).

However, chemical modification of fibers may help to rectify issues of natural fibers. Alkaline treatment removes impurities, aids in cellulose depolymerization which exposes short length crystallites, and decreases fiber diameter which increases aspect ratio (Bismarck *et al.*, 2005; Li *et al.*, 2007; Akil *et al.*, 2011; Fiore *et al.*, 2015; Asyraf *et al.*, 2021). Mechanical interlocking is achieved by increasing surface roughness, as well as increasing amount of cellulose exposed, increasing possible reaction sites to allow better interfacial bonding (George *et al.*, 2001; Herrera-Franco and Valadez-González, 2005; Abd Manaf *et al.*, 2007; Bogoeva-Gaceva *et al.*, 2007; Han *et al.*, 2007; Li *et al.*, 2007). Silane treatment improves adhesion of natural fiber to polymer matrix by forming stable covalent bonds with hydroxyl group. Hydrocarbon chain produced by silane improves chemical affinity of the polymer, thereby increasing adhesion. A

firm bonding would allow stress transfer and subsequently enhance tensile strength (George *et al.*, 2001; Bogoeva-Gaceva *et al.*, 2007; Li *et al.*, 2007; Akil *et al.*, 2011).

Nanocellulose, more specifically cellulose nanocrystals (CNC) are producible via acid hydrolysis of treated fibers. Nanofibers have larger surface area compared to micro fibers, thus allowing better adhesion due to large surface contact between matrix and fiber (Surip *et al.*, 2012). CNCs have high structural strength and stiffness due to high crystalline structure chains as compared to its nano-sized counterparts (Cho and Park, 2011; Dufresne, 2017; Kausar, 2020). It is said to have specific modulus similar to Kevlar (Kim *et al.*, 2015), and has been speculated to enhance mechanical strength when incorporated into polymers (Lu and Hsieh, 2009; Zhou *et al.*, 2011; Azmi *et al.*, 2013; Xiang *et al.*, 2013; Arias *et al.*, 2015; Spinella *et al.*, 2015). Silva *et al.* (2016) reported that CNCs increase mechanical properties of glass-ionomer cement considerably. Abaszadeh *et al.* (2020) found that 2 wt% nanocellulose increased compressive strength of flowable dental composite.

Similarly to cellulose, CNCs are hydrophilic which hampers interfacial compatibility with most hydrophobic polymer matrices (Kim *et al.*, 2015). In order to achieve homogenous dispersion and strong interfacial adhesion, functional groups can be imparted onto nanocellulose via surface modification such as acetylation, etherification, silylation, urethanization, amidation, cationisation, fluorescent labeling, carboxylation and polymer grafting (Lin and Dufresne, 2014; Thomas *et al.*, 2018). Silane surface modification is an easy way to increase the hydrophobicity of a hydrophilic cellulose surface (Thomas *et al.*, 2018).

Rice husk silica nanohybrid composite has inferior mechanical properties relative to commercial composites (Noushad *et al.*, 2016; Yusoff *et al.*, 2019; Al-Rawas

et al., 2021). Based on our knowledge and literature search, commercially available fiber-reinforced dental composite resin still utilizes synthetic fibers. In this study, we have characterized and assessed the mechanical properties of composite incorporated with silane treated kenaf CNCs as previous studies have demonstrated improved mechanical and physical properties of composite with incorporation of fibers. This study will further explore the suitability of using natural fibers in producing fiber reinforced composite resin and broaden its clinical application especially in high stress bearing areas.

We hope our findings will contribute to the production of new fiber reinforced composite derived from natural sources which can offer an alternative fiber reinforced composite resin to the dental practitioners and patients which is low in cost and readily available. At the same time, the development of this product will support our industry's growth, competitiveness, and sustainability.

1.2 Objectives of the Study

1.2.1 General Objective

To characterize γ -MPS treated kenaf CNCs and assess mechanical properties kenaf CNCs nanohybrid rice husk silica composite resin.

1.2.2 Specific Objective

1. To isolate and characterize nanocellulose from kenaf fiber using Transmission Electron Microscope (TEM).
2. To characterize kenaf CNC modified with γ -methacryloxypropyltrimethoxysilane (γ -MPS) using Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA).

3. To compare flexural and compressive strength of kenaf CNC reinforced rice husk nanohybrid composite to commercial nanohybrid and fiber-reinforced composite.
4. To analyze morphology of fractured flexural samples using scanning electron microscope (SEM).

1.3 Research hypothesis

1. There is a potential to isolate and characterize nanocellulose from kenaf fiber under TEM.
2. There is a potential to perform surface treatment of nanocellulose based kenaf fiber using γ -methacryloxypropyltrimethoxysilane (γ -MPS).
3. γ -MPS-treated kenaf CNCs increase the flexural and compressive strength of nanohybrid rice husk silica composite resin in comparison to commercial nanohybrid and fiber reinforced composite resin.
4. There are changes in the morphology of flexural fractured sample using scanning electron microscope (SEM).

1.4 Justification of Study

Nanohybrid silica derived from rice husk has been utilized as filler in dental composite, but showed lower mechanical properties compared to commercial composites (Noushad *et al.*, 2016; Yusoff *et al.*, 2019; Al-Rawas *et al.*, 2021). Fonseca *et al.* (2016) proved that dental composite reinforcement with short glass fiber has shown to improve mechanical properties However, glass fiber has shown to be harmful to human's health if the particle is inhaled (Tholibon *et al.*, 2019) and may have possible carcinogenic effect on lungs (Jawaid and Abdul Khalil, 2011). Akil *et al.* (2011)

mentioned that kenaf fiber is known to have potential as reinforcing fiber in thermoplastic composites and has been used in various industries. In the field of dentistry, Theng *et al.* (2019) has incorporated kenaf fiber into dental composite but the result was not significant due to inadequate bonding between fiber and composite. Johari *et al.* (2021) found that kenaf reinforced polymethyl methacrylate (PMMA) showed higher flexural strength than conventional PMMA. Ibrahim *et al.* (2021) showed lower flexural and compressive strength of kenaf incorporated composite than commercial composite due to poor fiber matrix adhesion.

In previous studies, favorable mechanical properties of kenaf as reinforcement fibers in dental composites were obscured due to limitation of poor fiber-matrix adhesion. Nanocellulose has also been proven to exhibit better reinforcement properties compared to its micro-sized counterpart (Surip *et al.*, 2012; Silva *et al.*, 2016). Therefore, this study aimed to characterize kenaf CNCs and investigate the mechanical properties of silane-treated kenaf CNCs as reinforcement fibers in nanohybrid dental composites derived from rice husk.

CHAPTER 2

LITERATURE REVIEW

2.1 Composite resin

Dental composite has been around since early 1960s and is widely used since then. Amalgams have fracture toughness of 1.4 to 2.4MPa while composite resins range from 0.7 to 1.9 MPa (Soderholm, 2010). Although having lower strength and fracture toughness than amalgam, extensive research has been conducted to enhance its physical and mechanical properties (Lloyd and Adamson, 1987; Shenoy, 2008; Abouelleil *et al.*, 2015; Kapoor and Ahmed, 2021). High strength, and fracture toughness are important mechanical properties for enhanced longevity of restorative materials (Ilie and Hickel, 2011).

In material science, the term “composite” means a physical mixture of any phases (metal-metal, metal ceramic, ceramic-ceramic, ceramic-polymer, polymer-metal, polymer-polymer) (Bayne, 2013).

Resin-based restorative materials are defined as three-dimensional combinations of at least two chemically different materials with a distinct interface (Lutz and Phillips, 1983). Generally, a composite resin includes three phases: (1) organic phase; (2) interfacial phase; and (3) dispersed phase.

2.1.1 Organic Phase (Resin Matrix)

Fast chain polymerization and cross-linking of resin is due to C=C double bonds of alkene groups present in methacrylate monomers. Methacrylate monomers polymerization are initiated with light or chemical initiation of free radicals production, subsequently giving rise to cross-linking reaction, resulting in development of physical and mechanical properties like fracture strength, modulus, shrinkage, and dimensional

stability of the composites (Cho *et al.*, 2022). The main monomeric matrix combinations used by manufacturers today are bisphenol A-glycidyl methacrylate (Bis-GMA), urethane dimethacrylate (UDMA) and triethyleneglycol dimethacrylate (TEGDMA), commonly a combination of Bis-GMA/TEGDMA or Bis-GMA/UDMA/TEGDMA (Hervás-García *et al.*, 2006; El-Banna *et al.*, 2019; Riva and Rahman, 2019). Chemical structures of Bis-GMA, TEGDMA and UDMA are shown in Figure 2.1.

Bisphenol A Glycidyl Methacrylate (Bis-GMA) was formulated by Dr Rafael Bowen in the year 1959, which is a dimethacrylate monomer that remains the backbone of dental composites for decades (Bowen, 1963; Bayne *et al.*, 2019). Back then, Valentine (1987) discovered advantage of Bis-GMA over acrylic resin in terms of good mechanical properties, lower water sorption and solubility, able to accommodate higher filler loading, less polymerization shrinkage and good translucency.

Highly viscous Bis-GMA is usually mixed with a monomer of low viscosity such as triethyleneglycol dimethacrylate (TEGDMA) to improve clinical handling properties, and increases mobility of monomers and radicals in the matrix during polymerization, thereby improving the degree of conversion (DC) and cross-link density (Ferracane and Greener, 1984; Dickens *et al.*, 2003; Cho *et al.*, 2022).

With comparison to Bis-GMA, UDMA is less viscous, thus allows higher filler loading without the need of additional diluent monomers (Kerby *et al.*, 2009). However, it is more brittle and has increased polymerization shrinkage compared to Bis-GMA (Kerby *et al.*, 2009; Cho *et al.*, 2022).

Feilzer and Dauvillier (2003) found that a high post-gel shrinkage is a major contributing factor to high shrinkage stress development, and composites with 50wt% TEGDMA displayed highest maximum polymerization rate as the composites have higher pre-gel viscous flow. Gonçalves *et al.* (2011) reported higher BisGMA:TEGDMA ratio would result in lower shrinkage due lower degree of conversion as it is halted by vitrification. The increase in elastic modulus due to increased filler follows the rule of mixtures. The study also found that polymerization stress was strongly influenced by resin matrix, which challenge is to balance low shrinkage and high conversion without sacrificing filler content.

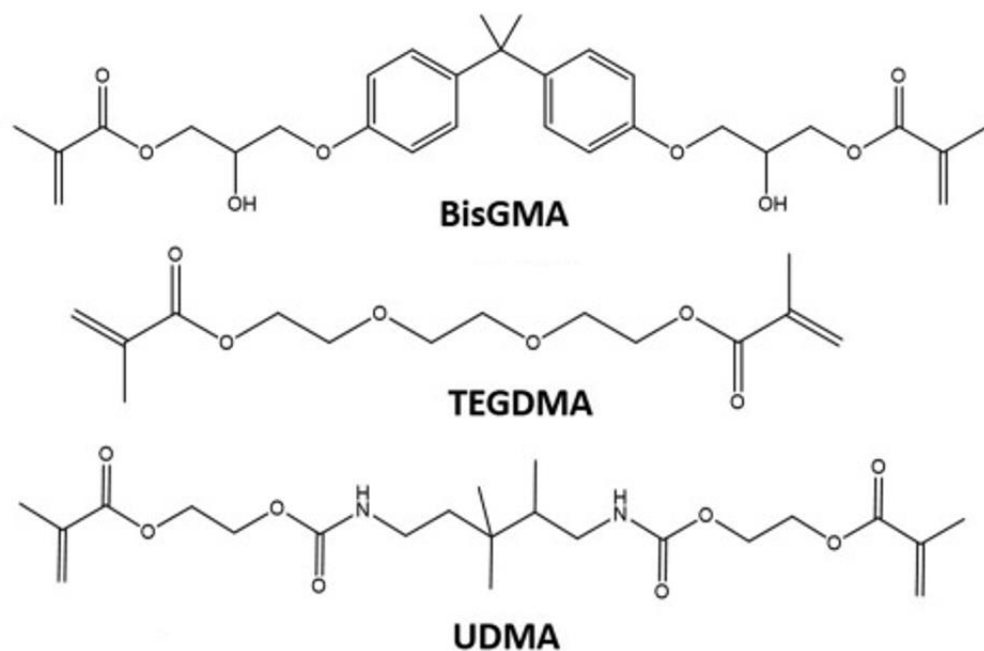


Figure 2.1: Chemical structures of BisGMA, TEGDMA and UDMA

2.1.2 Interfacial Phase (Coupling Agent)

Mechanical properties are also dependent on the interfacial phase where filler-matrix adhesion is crucial for efficient transfer of stress through the organic matrix phase to the reinforcement filler phase. With poor interfacial phase, there will be crack

initiation at the weakest interface and allows further crack propagation along the unstable interface (Cho *et al.*, 2022). Mechanical interlocking and chemical bonding with coupling agents allow strong interfacial bonding between filler and resin matrix (Aminoroaya *et al.*, 2021; Cho *et al.*, 2022). Inorganic filler in methacrylate-based resins commonly undergo surface modification with γ -methacryloxypropyltrimethoxysilane (Riva and Rahman, 2019; Aminoroaya *et al.*, 2021; Cho *et al.*, 2022). Figure 2.2 shows the chemical structure of γ -methacryloxypropyltrimethoxysilane.

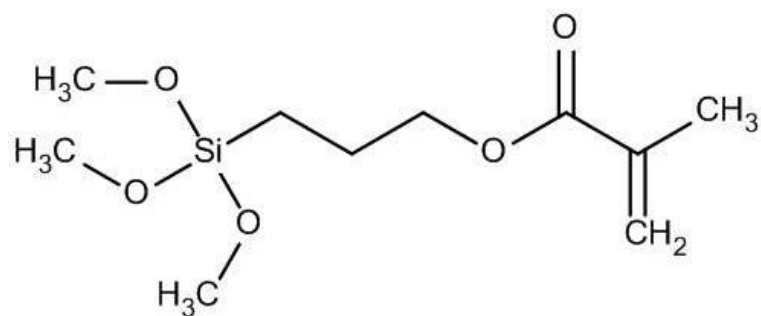


Figure 2.2: Chemical structure of γ -methacryloxypropyltrimethoxysilane

Silanization of filler enhances wettability and dispersion within resin matrix, which improves physical and mechanical properties of composite (Cramer *et al.*, 2010; Tham *et al.*, 2010; Zanchi *et al.*, 2015; El-Banna *et al.*, 2019). It also significantly lowered water uptake of filler particles compared to non-silanized filler particles (Wilson *et al.*, 2005; El-Banna *et al.*, 2019).

A critical factor in efficiency of silanization process is the silane film thickness (El-Banna *et al.*, 2019). With increased silane thickness, the layers become more disorganized, leading to possibility of weak bond formation (Sideridou and Karabela, 2009; El-Banna *et al.*, 2019). Thus, the quantity of silane used is crucial for achieving the mono-molecular silane layer (Söderholm and Shang, 1993; Sideridou and Karabela, 2009; Zanchi *et al.*, 2015; El-Banna *et al.*, 2019). Zanchi *et al.* (2015) found that 3% γ -

MPS was the optimum concentration for treating barium borosilicate glass fillers with average particle size of 4µm.

Stress transfer at the interfacial phase is expressed as modulus of dental composites which is largely determined by strength of interfacial adhesion and quality of surface modification (Tanimoto *et al.*, 2006; Karabela and Sideridou, 2008; Cho *et al.*, 2020). Spectroscopic and thermogravimetric analyses of filler particles are commonly employed to assess the quality of silane surface modification (Karabela and Sideridou, 2008; Aminoroaya *et al.*, 2021).

Theoretically, Equation 2.1 is used to calculate the minimum weight percent of silane needed for silica silanization (Söderholm and Shang, 1993; Liu *et al.*, 2001; Wilson *et al.*, 2005; Sideridou and Karabela, 2008; Tham *et al.*, 2010):

$$X = (A/\omega)f$$

Equation 2.1: Minimum weight percent of silane

where X = minimum amount of silane (g); A= surface area of filler (m²/g); ω = wetting surface of MPS (2525 m²/g); f=amount of filler (g)

The equation is then modified by Karkanis *et al.* (2022) in terms of % by weight:

$$\text{Organosilane (wt\%)} = \frac{\text{Filler surface area (m}^2\text{/g)}}{\text{Silane surface coveraage (m}^2\text{/g)}} \times 100$$

Equation 2.2: Modified minimum silane percentage by weight

Liu *et al.* (2001) found that after hydrolyzation in 95% ethanol or acetone for 2h at room temperature, MPS is only physically adsorbed onto silica and is removable by simple rinsing. It is only after a drying process at 25°C under vacuum, physically

adsorbed silane forms covalent attachment, and is divided into two types: firm and loose adsorbed silane, where loosely adsorbed silane can either be removed by further washing with methanol. MPS monolayer can be formed at low concentration (1%), while 5% concentration increases MPS adsorption through multilayer formation.

2.1.3 Photo-initiator

Commonly, polymerization of dental composites is initiated by light activation of photo-initiator system, usually with amounts ranging from 0.1% to 1 wt% (Craig, 2006; Van Landuyt *et al.*, 2007). Camphorquinone (CQ) is the most employed photoinitiator, while the common amine co-initiator is dimethylaminoethyl methacrylate (DMAEMA) (Alonso *et al.*, 2014; Riva and Rahman, 2019; Kowalska *et al.*, 2021).

CQ is a type-2 initiator as the polymerization process is initiated by H-abstraction (Randolph *et al.*, 2016b; Kowalska *et al.*, 2021). CQ absorbs visible light in the wavelength range of 360-510nm, with maximum absorbance at 468nm (Kowalska *et al.*, 2021). Although CQ can generate free radicals, incorporation of co-initiators increases efficiency (Kowalska *et al.*, 2021). The amine initiator used together with camphoroquinone is dimethylaminoethyl methacrylate (DMAEMA) (Riva and Rahman, 2019).

Suboptimal concentration of CQ may compromise esthetics, biocompatibility, biomechanical features and high susceptibility of early wear (Kowalska *et al.*, 2021). According to different formulation, the concentration of CQ used in dental composites range between 0.17–1.03wt% of resin (Taira *et al.*, 1988; Alvim *et al.*, 2007; Alonso *et al.*, 2014). This is because light-curing involves degree of conversion, which is affected by light attenuation that varies considerably in different composites, depending on the

opacity, filler size, filler concentration, and pigment shade (Anusavice, 2003). Different monomer systems also affect the optimum concentration of photoinitiator, where Jan *et al.* (2001) found that 0.5% of CQ:DMAEMA in 1:1 proportion is optimal for UDMA/TEGDMA without fillers, while Alonso *et al.* (2014) reported 1.5% CQ/DMAEMA in 1:1 ratio was adequate for their 65% filled BisGMA/TEGDMA composite. Alvim *et al.* (2007) stated that increase in CQ increases degree of conversion and reaches a peak at the ideal level of CQ. On the contrary, poor mechanical properties of composite may be a result of incomplete polymerization due to insufficient concentration of CQ (Musanje *et al.*, 2009).

2.1.4 Dispersed Phase (Filler)

Physical and mechanical properties of composite is largely determined by the disperse phase of composite resins (Ilie and Hickel, 2011; El-Banna *et al.*, 2019). Addition of fillers results in enhancement of strength of resin matrix, reduction in thermal expansion coefficient, polymerization shrinkage and water sorption, as well as improved aesthetic and radiopacity (Labella *et al.*, 1999; Hervás-García *et al.*, 2006; El-Banna *et al.*, 2019). Based on the rule of mixtures, it has always been the main goal to maximize filler loading in composites. (Hervás-García *et al.*, 2006; Bayne *et al.*, 2019)

Fillers of various chemical composition, morphology and dimensions have been utilized (Hervás-García *et al.*, 2006; Aminoroaya *et al.*, 2021; Cho *et al.*, 2022). The main filler is silicon dioxide, while other common fillers include borosilicates and lithium aluminium silicates. To increase radiopacity, heavy metal particles like barium, strontium, zinc, aluminium or zirconium may be used (Hervás-García *et al.*, 2006; Riva and Rahman, 2019).

2.1.4(a) Classifications of fillers

Over the years of composite development, many classifications have been used based on different aspects. The most used classification would be based on filler size, introduced by Lutz and Phillips (1983), where filler particles are mechanically prepared from grinding, with size of 0.1-100 μ m. Chemically, hydrolysis and precipitation produces microfillers with size range of 0.05 - 1 μ m. Hybrid composites contain both macrofillers and microfillers of pyrogenic silica for a better finishing.

Marshall *et al.* (1988) classified composite resins by: 1) amount of filler by weight and volume, with subdivision of unfilled, microfills, hybrids for anterior restorations; macrofills, midifills, hybrids for posterior restoration; 2) filler particle size, which consist of macrofill, midifill minifill, microfill and hybrid; 3) method of filler addition which is subdivided into homogenous and heterogenous.

Willems *et al.* (1992) classified the fillers based on morphological and mechanical characteristics as shown in Table 2.1.

Table 2.1: Classification of composite resin filler based on Williams et al.(1992), modified from Hervás-García et al. (2006)

Composite	Filler
Densified	
- Midway-filled	< 60 vol%
Fine	Mean Particle Size > 3 μ m
Ultrafine	Mean Particle Size < 3 μ m
- Compact-filled (>60 vol%)	>60 vol%
Fine	Mean Particle Size > 3 μ m
Ultrafine	Mean Particle Size < 3 μ m
Microfine	Mean Particle Size = 0.04 μ m
- Homogenous	
- Heterogenous	Splintered, Agglomerated, Sintered, Spherical pre-polymerized filler
Miscellaneous	Hybrid of densified and microfine
Traditional	Equivalent to macrofilled composites
Fiber-reinforced	Glass-ceramic fibers (max length of 300 μ m)

Bayne *et al.* (1994) classification is based on filler particle size with megafill (0.5-2mm); macrofill (10-100 μ m); midifill (1-10 μ m); minifill (0.1-1 μ m); microfill (0.01-0.1 μ m).

Due to evolving diversity of composite consistency, Lee *et al.* (2007) classified composites based on viscosity, with categories such as flowable, medium viscosity, and packable composites.

2.1.5 Nanocomposite

Nanootechnology has revolutionized the development of fillers and has been the forefront of composite advancement (Craig, 2006). By definition, materials having at least one linear dimension in the range from approximately 1 nm to 100 nm are called nanomaterials (Ferracane, 2011; Mariano *et al.*, 2014).

Nanomers are non-agglomerated particles of size within 20-75 nm, whereas agglomerates of nano-sized particles are called nanoclusters (El-Banna *et al.*, 2019). While having similar mechanical strength of microhybrid composites, nanofilled composites have high polishability of a microfilled composites (Craig, 2006). The ability to maintain a long-term polished surface is attributed to the similar shear rates of nanoclusters and resin matrix during wear process (Craig, 2006; Ferracane, 2011; El-Banna *et al.*, 2019). Because nanofillers are smaller than wavelength of light, they provide high translucency, which allows a wide range of shades and opacities for highly esthetic restorations (Craig, 2006).

Nanomers have high specific surface area, if used alone, it substantially increases the viscosity of composite resin and reduces mobility of radicals during polymerization, resulting in lower DC, which limits high fraction loading of nanofillers (Cho *et al.*, 2022). Thus, nanomers are lightly sintered to produce nanoclusters, their

size varying from 100 nm to submicron level, with the average size of 0.6 μ m (Craig, 2006). Alternatively, nanofillers are mixed with microfillers (0.1-5 μ m), resulting in a nanohybrid dental composites (Cho *et al.*, 2022). With the mixture of nanomers with nanoclusters or microfillers, interstitial spacing between fillers are decreased, allowing higher filler volume fraction, improved physical properties, and high polishability (El-Banna *et al.*, 2019). Nanoparticles as co-filler in composites can occupy spaces between the large particles, thus enables higher filler loading and reduces polymerization shrinkage (Wilson *et al.*, 2005).

Noushad *et al.* (2016) has successfully prepared nanohybrid silica particles from rice husk to be utilized as filler in dental composite. Although the nanohybrid composite has inferior mechanical properties compared to commercial composite resins, but it is noted that rice husk silica was the sole filler. Yusoff *et al.* (2019) and Al-Rawas *et al.* (2021) also fabricated flowable composites with nanohybrid silica derived from rice husk and have exceeded the requirement for compressive strength. Rice husk derived nanohybrid silica composite resin has potential for improvement and further development (Al-Rawas *et al.*, 2021). That said, co-filler can be added to improve its mechanical properties to be comparable to current commercial dental composites. Ismail *et al.* (2020) utilized zirconia as reinforcement of risk husk nanohybrid dental composite, but the improvement of compressive strength plateaued after 3% zirconia reinforcement. An in-vitro study by Lin *et al.* (2020) showed that restoration of endodontically treated maxillary lateral incisors with zirconia reinforced risk husk nanohybrid composite exhibited higher fracture strength than commercially available nanofilled and microhybrid composite resin. Lin *et al.* (2020) also found no significant difference between aged and unaged zirconia reinforced rice husk nanohybrid

composite, indicating great wear resistance and thermal stability of the rice husk and zirconia nanofillers.

2.1.6 Fiber Reinforced Composite

Commercially, various composites have been reinforced using fibers, which the concept later was adopted into dentistry (El-Banna *et al.*, 2019; Suzaki *et al.*, 2020). It was found that incorporating various high strength, high modulus fiber was distinctively effective in reinforcing dental composite (Xu and Xu, 2014).

Different from isotropic properties of particulate fillers, fibers with high aspect ratio provide isotropic and anisotropic properties depending on the fiber orientation (van Heumen *et al.*, 2008; Vallittu, 2015).

Short fiber reinforced composite shares similarities with dentin at the microstructure level, where dentin can be described as hydroxyapatite matrix with embedded collagen fibers (Garoushi *et al.*, 2007; Garoushi *et al.*, 2012; Garoushi *et al.*, 2013b; Bijelic-Donova *et al.*, 2016; Lassila *et al.*, 2018). Fiber reinforcement of composite has shown improved mechanical properties in terms of fracture toughness, strength, polymerization shrinkage, fatigue resistance compared to particulate filler composite (Garoushi *et al.*, 2007; Garoushi *et al.*, 2015; Bijelic-Donova *et al.*, 2016).

In fiber-reinforced plastic, Suzaki *et al.* (2020) described three patterns of fiber forms: i) Random Short Fiber Reinforced type (RSFRT) – randomly arranged short fibers within matrix resin; ii) Unidirectional Continuous Fiber Reinforced type (UCFRT) – unidirectionally arranged continuous fibers within matrix resin; iii) Textile laminate reinforced type (TLRT) – tailoring fiber bundles into mesh fabrics.

Most commonly used fibers in dental composites are E-glass fibers due to their high strength (El-Banna *et al.*, 2019). E-glass have a tensile strength of 3.4 GPa and a tensile modulus of 72 GPa (Chen *et al.*, 2005).

Parameters such as aspect ratio, critical fiber length, fiber loading and fiber orientation largely influences mechanical properties of fiber reinforced composites (Bijelic-Donova *et al.*, 2016). Aspect ratio is the fiber length to fiber diameter ratio (l/d). It determines flexural modulus, tensile strength, and reinforcing efficiency of the composite (Vallittu, 2015). Critical length (L_c) is a measure of the minimum perfectly aligned fiber dimension required for maximum stress transfer within the cured resin (Petersen, 2005). Studies have concluded that critical fiber length may be as much as 50 times the diameter of the fiber (Petersen, 2005; Vallittu, 2015). When length is greater than L_c , tensile stress acting upon fiber will cause fiber fracture instead of fiber pull-out (Chawla, 2012). However, Mohd Ghazali *et al.* (2015) stated that entanglement of fibers may occur during mixing, causing poor fiber dispersion thereby reducing reinforcement efficiency.

There has been reported health issues regarding synthetic fibers such as irritation to the respiratory system, eyes, and skin (Office and Safety, 1990; World Health Organization, 2002). Carcinogenicity of inhaled glass fiber has been speculated due to increased lung cancer incidence among workers at a glass wool manufacturer in Ontario, Canada. (Bertazzi *et al.*, 1986; Shannon *et al.*, 2005; Jawaid and Abdul Khalil, 2011) In fact, the International Agency for Research on Cancer (IARC) had noted E-glass being possibly carcinogenic to humans (World Health Organization, 2002; Baan and Grosse, 2004).

With environmental and health concerns associated with synthetic fiber as well as uncertain fluctuations of oil prices have led to intensive research on suitability of natural fibers as reinforcement (Jayaraman, 2003). Being a renewable source, natural fibers have been gaining major attraction from researchers due to its environment and economic benefits. Natural fiber composites are advantageous in terms of formability, renewable, abundance, cost effectiveness, thermal insulation, and safer towards health (Davoodi *et al.*, 2010; Saba *et al.*, 2015). At the end of its life cycle, natural fiber releases carbon dioxide (CO₂) neutrally, thus is biodegradable and pose no hazard towards human health upon inhalation (Tholibon *et al.*, 2019). Currently, natural fiber composites compares favorably with glass fiber composites in regards to cost and stiffness, while having impact strength and tensile strength near those of glass fiber composites (Mohd Ghazali *et al.*, 2015).

2.2 Natural Fibers

Biomass has gain attention due to the increasing need for sustainable development. With the diminution of fossil resources, it has become a key objective for industrial production of novel materials from renewable biomass to meet economic development and population growth (Zhu *et al.*, 2016; Shen *et al.*, 2020).

There has been a growing interest in application of natural fibers in composite due to advantages of higher specific strength and comparable specific modulus compared to glass fibers, while being cheaper and widely available (Akil *et al.*, 2011). Other than kenaf, common natural bast fibers includes hemp, jute, flax, and sisal (Bismarck *et al.*, 2005; André, 2006; Rowell, 2008; Akil *et al.*, 2011). Lignocellulosic fibers are high stffness and specific strength, cheaper, lightweight, eco-friendly, safer

towards health, which serves as a potential substitute to the synthetic fibers (Kumar *et al.*, 2008; Athijayamani *et al.*, 2010; Saba *et al.*, 2015).

Natural fibers are composites constituting lignin and hemicellulose matrix holding together hollow cellulose fibrils (Jayaraman, 2003). Cellulose is a natural polysaccharide, with β -(1,4)-glycosidic linkages between D-glucopyranose rings (Winandy and Rowell, 1984). The linear orientation and high degree of polymerization of cellulose which is the main contributor of strength in wood fibers (Winandy and Rowell, 1984). Tensile strength and modulus are influenced by fiber properties such as cellulose content, degree of polymerization and microfibrillar angle (Jayaraman, 2003; Bismarck *et al.*, 2005; Ogunbode *et al.*, 2015; Djafari Petroudy, 2017). The strong hydrophilic nature of natural fibers are mainly due to hydroxyl groups in cellulose molecules (Jayaraman, 2003).

Made up of highly branched polysaccharides, hemicellulose acts as a matrix for cellulose and increases packing density of the cell wall (Winandy and Rowell, 1984; Mohamed *et al.*, 1995). It contributes to the moisture absorption, biodegradation, and thermal degradation of the fibers (Rouison *et al.*, 2004). Lignin is made up of aliphatic and aromatic hydrocarbon polymers positioned around fibers, which binds fibers together and acts as a stiffening agent for the cellulose molecules within the fiber cell wall (Winandy and Rowell, 1984; Bismarck *et al.*, 2005; Akil *et al.*, 2011). It is thermally stable, but responsible for the ultraviolet (UV) degradation of the fibers (Rouison *et al.*, 2004).

Ogunbode *et al.* (2015) reported that the variation in structure and properties of natural fibers are multifactorial, which includes source, age, position, quality of harvest, body of plant which fiber is extracted, extraction techniques, environmental conditions,

experimental conditions such as strain rate, gauge length, fiber diameter, and test temperature.

2.3 Kenaf Plant

Kenaf plant is a plant from *Hibiscus cannabinus* species, where it is grouped under genus Hibiscus and is under Malvaceae family, originating Africa and Asia. They can grow rapidly, reaching up 2.4 to 6m high in 5 months under wide-ranging weather conditions (Bismarck *et al.*, 2005; Akil *et al.*, 2011). Furthermore, it is valuable in combating global warming as it absorbs significant amount of carbon dioxide(1 ton kenaf absorbs 1.5 tons of atmospheric CO₂), proving its significance in terms of environmental friendliness (Bismarck *et al.*, 2005). Among other bast fibers, the low density of kenaf fiber contributes to its high specific mechanical properties (Rohit and Dixit, 2016; Peças *et al.*, 2018). Relative to other natural fibers, kenaf fibers showed superior reinforcement effect in various polymeric composites under different flexural loading conditions (Saba *et al.*, 2015).

Kenaf fibers consist of 45 to 57% cellulose, 21.5% hemicellulose, 8 to 13 wt% of lignin and 3 to 5 wt.% of pectin (Bismarck *et al.*, 2005). Kenaf fibers have density of 1.2g/m³, length of 1.4-11mm, with a diameter of 12-36μm, with tensile strength of 295-930MPa (Rowell, 2008). A single fiber of kenaf can have a tensile strength and modulus as high as 11.9 GPa and 60 GPa, respectively (Karnani *et al.*, 1997). Chemical structure of cellulose in kenaf fiber is shown in Figure 2.3.

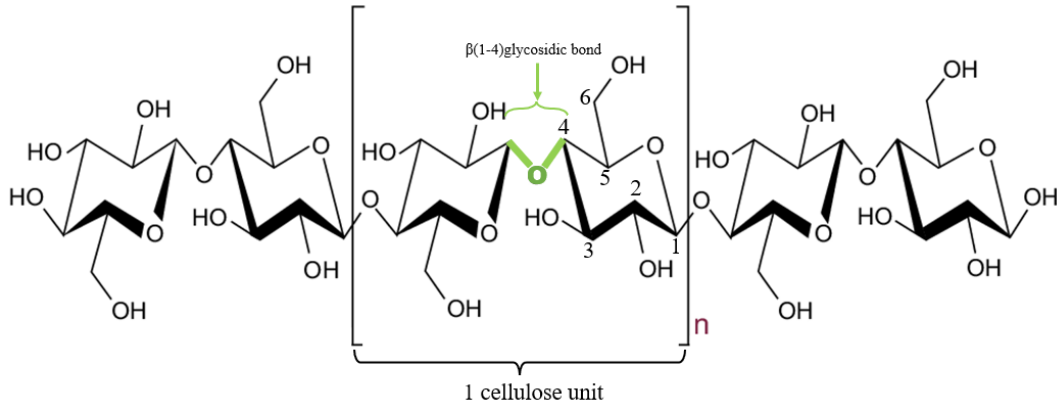


Figure 2.3: Chemical structure of cellulose linked by $\beta(1-4)$ glycosidic bond

The high aspect ratio and superior toughness of kenaf enables vast potential as a reinforcement fiber in thermoplastic composites (Karnani *et al.*, 1997; Bismarck *et al.*, 2005; André, 2006). Kenaf has high specific strength comparable to glass fibers but cheaper, thus is utilized in various fields, including automotive, construction, furniture, sports and other mass production industries (Nishino *et al.*, 2003; Bismarck *et al.*, 2005; Akil *et al.*, 2011; Anuar and Ahmad, 2011). A comparative study by André (2006) proved kenaf fiber as a worthy reinforcing fiber with great mechanical properties that provide a high performance eco-friendly polymer composite. It is two to three times cheaper but with comparable specific stiffness to the glass fibers (André, 2006; Ogunbode *et al.*, 2015).

2.3.1 Problems with Incorporating Natural Fibers

Major concerns of incorporating natural fibers includes its adhesion issue and hydrophilic properties of natural fibers (Akil *et al.*, 2011). The hydroxyl group within the fiber makes them polar and forms hydrogen bonds with water molecules, and incompatible with hydrophobic resin matrix (André, 2006; Akil *et al.*, 2011). Stress cannot be transferred to the fiber due to inadequate interfacial adhesion that leads to poor dispersion of fibers within the matrix, which also creates voids at interphase

between fiber and matrix that acts as microcracks, greatly weakening the composite (Célineo *et al.*, 2014; Mohd Ghazali *et al.*, 2015; Huang *et al.*, 2021). The hydrophilic nature of fibers also results in high water resorption, which this hygroscopic nature would cause significant swelling, causing voids between fiber and matrix (Arjmandi *et al.*, 2021). Moisture absorption also deteriorates mechanical properties of the fiber (Alvarez *et al.*, 2004; Baiardo *et al.*, 2004; Akil *et al.*, 2011).

However, chemical treatment can chemically modify fiber surface can enhance interfacial adhesion by reducing affinity to water absorption, and increasing surface roughness (Tserki *et al.*, 2005; Abd Manaf *et al.*, 2007; Vilay *et al.*, 2008; Saba *et al.*, 2015). Eyley and Thielemans (2014) strongly recommended soxhlet extraction with ethanol prior to surface modification reaction to remove impurities.

According to Mohd Ghazali *et al.* (2015), mechanical properties of fiber reinforced composites are influenced by the following factors: (1) fiber selection; (2) matrix selection; (3) interface strength; (4) fiber dispersion; (5) fiber orientation; (6) manufacturing; (7) porosity.

2.4 Chemical Treatment

2.4.1 Bleaching

Cellulose are the main contributors to the tensile strength fibers, while hemicellulose molecules are only present as amorphous infill (Saha *et al.*, 2010). Removal of hemicellulose and lignin has been found to increase tensile strength (Saha *et al.*, 2010). Lignin negatively affects fiber-matrix interphase (Granda *et al.*, 2016). Delgado-Aguilar *et al.* (2018) reported fiber-matrix interphase improved as amount of lignin was reduced, resulting in 46% increase in tensile strength of jute/PLA composites

after 90 minute sodium hypochlorite treatment. Husnil *et al.* (2019) found that although harsh bleaching conditions removed more lignin and hemicellulose, some parts of cellulose suffered degradation with lower degree of polymerization.

2.4.2 Alkali Treatment

Alkali treatment (also known as mercerization) is simple, inexpensive, thus a widely employed chemical treatment for natural fibers, especially kenaf (Akil *et al.*, 2011; Ismojo *et al.*, 2019). It disrupts hydrogen bonding in fiber network, which increases surface roughness (Asyraf *et al.*, 2021). Moreover, it exposes underlying hydroxyl groups of cellulose by removing the external coating of fiber consisting hemicellulose, lignin, wax, and oils (Bismarck *et al.*, 2005; Li *et al.*, 2007; Fiore *et al.*, 2015; Asyraf *et al.*, 2021). Depolymerization of cellulose via alkali treatment causes fibrillation of fiber bundles into small fibers, while exposing short length crystallites (Akil *et al.*, 2011). Increased surface roughness and surface area allows mechanical interlocking with matrix, and provides more hydroxyl groups for interfacial bonding (Bismarck *et al.*, 2005; Li *et al.*, 2007; Islam *et al.*, 2010; Akil *et al.*, 2011).

Modest treatments increases cellulose crystallinity by removing obstructing materials, whereas at harsh treatments converts crystalline cellulose to amorphous material (Islam *et al.*, 2010). It was found that 5% alkali solution showed better tensile properties of fiber as compared to 10% and 15% (Cao *et al.*, 2007; Mahjoub *et al.*, 2014). Longer immersion time of 144 hours have detrimental effect on fiber surface and mechanical properties (Fiore *et al.*, 2015). It was found that 6% sodium hydroxide (NaOH) concentration was optimum for better mechanical properties of fiber (Abd Manaf *et al.*, 2007; Asumani *et al.*, 2012; Meon *et al.*, 2012). Nor Azowa *et al.* (2009) tested 2%, 4%, 6% and 8% NaOH treatment at room temperature for 3 hours, reported that 4% NaOH concentration yields better tensile strength. However, Ismojo *et al.*