DEVELOPMENT AND CHARACTERISATION OF KENAF-NANOHYBRID DENTAL COMPOSITES

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DEVELOPMENT AND CHARACTERISATION OF KENAF-NANOHYBRID DENTAL COMPOSITES

By

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LIST OF SYMBOLS

cm	Centimetre
g	Gram
GPa	Gigapascal
h	Hour
Hz	Hertz
kN	Kilonewton
kV	Kilovolt
min	Minute
mL	Millilitre
mm	Millimetre
mm min^{-1}	millimetre per minute
mm s^{-1}	millimetre per second
MPa	Megapascal
nm	Nanometre
s	second
µm	Micrometre

LIST OF ABBREVIATION

Bis-GMA	Bisphenol A glycidyl Methacrylate
CQ	Camphorquinone
DMAEMA	2-(Dimethylamino)ethyl Methacrylate
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier-Transform Infrared Spectroscopy
H_2SO_4	Sulfuric Acid
HCl	Hydrochloric acid
HOAc	Glacial Acetic Acid
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
LED	Light Emitting Diode
MPS	[3-(Methacryloyloxy)propyl] Trimethoxysilane
$NaClO_2$	Sodium Hypochlorite
NaOH	Sodium Hydroxide
PMMA	Polymethyl Methacrylate
SD	Standard Deviation
SSS	Sodium Silicate Solution
TEGDMA	Triethylene Glycol Dimethacrylate
TEM	Transmission Electron Microscope
TEOS	Tetraethyl Orthosilicate
UDMA	Urethane Dimethacrylate

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PEMBANGUNAN DAN PENCIRIAN KOMPOSIT PERGIGIAN KENAF-NANOHIBRID

ABSTRAK

Kenaf merupakan serat semulajadi yang mempunyai potensi yang besar untuk menggantikan serat sintetik sebagai pengukuhan komposit. Kajian ini dijalankan untuk mengoptimumkan ikatan antara serat kenaf dan komposit nanohibrid pergigian daripada sekam padi serta mengkaji tentang sifat mekanikal komposit. Selulosa nano kristal (SNK) yang diekstrak daripada serat kenaf dirawat dengan *tetraethyl orthosilicate* (TEOS) gel sol dan *γ-Methacryloxypropyltrimethoxysilane* (γ-MPS) dengan nisbah yang berbeza. Analisa spektroskopi inframerah transformasi Fourier (FTIR) dan termogravimetrik (TGA) dijalankan terhadap SNK yang terawat. Enam sampel dari setiap kumpulan specimen yang mempunyai nisbah TEOS gel sol kepada γ-MPS yang berbeza dimasukkan ke dalam nanohibrid komposit dari sekam padi dan diuji dengan kekuatan lenturan dan mampatan. Komposit komersial (Ever-X, Filtek Z350 dan Neofil) digunakan sebagai perbandingan. Data dianalisa secara statistik melalui ANOVA sehala. FTIR menunjukkan bahawa terdapat ikatan antara serat dengan γ-MPS dan TEOS. TGA menunjukkan serat kenaf yang tidak terawat mempunyai suhu penguraian yang paling tinggi berbanding serat yang terawat**.** Komposit dari kumpulan eksperimen yang mengandungi serat terawat menunjukkan kekuatan lenturan yang lebih tinggi sebanyak 31%, manakala kekuatan mampatan meningkat sebanyak 38% berbanding komposit tanpa serat, namun masih rendah berbanding dengan kekuatan komposit komersil. Kekuatan mampatan komposit dari kumpulan eksperimen lebih rendah secara signifikan ($p=0.00$) berbanding dengan kumpulan komposit komersial. Selepas rawatan, terdapat bukti modifikasi permukaan secara kimia pada CNC yang meningkatkan ikatan antara serat dengan matrik resin. Keadaan ini menyumbang kepada peningkatan kekuatan lenturan pada komposit yang diuji walaupun kekuatan ini lebih rendah berbanding komposit komersial.

Kata kunci: Serat Kenaf, Komposit Nanohibrid, Selulosa Nano Kristal, Ikatan

DEVELOPMENT AND CHARACTERISATION OF KENAF-NANOHYBRID DENTAL COMPOSITES

ABSTRACT

Natural fibres such as kenaf fibres have enormous potential in replacing synthetic fibre used for composite reinforcement. This study aimed to optimize the bonding mechanism between kenaf and nanohybrid dental composite from rice husk and investigate mechanical properties of this composite. Kenaf fibres was processed to obtain cellulose nanocrystals (CNC) and silane treated with hybridization of tetraethyl orthosilicate (TEOS) sol gel and γ-Methacryloxypropyltrimethoxysilane (γ-MPS). The treated CNC was investigated through Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Six specimens from each group with different ratio of γ-MPS and TEOS were prepared for compressive and flexural investigation. The experimental composites were compared with commercial nanohybrid composite and fibre reinforced composite (Ever-X posterior, Filtek Z350 and Neofil). Data was statistically analysed using one-way ANOVA test and the fracture surfaces of the samples were subjected to scanning electron microscope (SEM) assessment. FTIR results showed formation of chemical bonds between kenaf CNC with γ-MPS and TEOS sol gel. TGA showed highest decomposition temperature in non-silane treated kenaf fibre compared to silane treated kenaf fibre. Mean flexural and compressive strength between all groups showed statistically significant results (p=0.000). Experimental composite group with fibre reinforced showing higher flexural strength by 31 % while compressive strength increases by 38% compared to non- fibre reinforced composite, however the strength was lower as compared to commercial composites. The compressive strength of all the experimental composites were significantly lower than that of commercial composites. Silane treatment showing evidence of modification and improved bonding between the kenaf fibres and the resin matrix, even though the strength was lower than the commercial composite.

Keywords: Kenaf fibre, Nanohybrid composite, Cellulose nanocrystal, Bonding

CHAPTER 1

INTRODUCTION

1.1 Research Background

Composite resin is widely used in dentistry for various applications for example, in restorative materials dental composite is used for fillings the cavity, veneer and crown, as preventive pit and fissure sealants, cores and buildups, inlays, onlays, crowns, cements, orthodontic devices, endodontic sealers, and root canal posts (Ferracane, 2011). 'Post-amalgam era' within the field of restorative dentistry, dental material advancement has allowed aesthetic tooth- coloured restorations such as dental composite to be used widely (Magne, 2006). Over the years, researchers have worked tirelessly to improve the properties of the dental composite to be more reliable, aesthetic and ensure longevity of the tooth-restoration to function well in the oral environment.

Current composite resin has adequate mechanical properties, however, at a high load bearing area fracture or wear may occur. The key for long term restoration longevity depends on its durability and reliability. The common causes for the clinical replacement of dental composites are secondary caries, followed by fracture (Sarrett, 2005). The polymerization shrinkage led to marginal gap eventually causing secondary caries whilst fracture may be contributed by poor bonding between material that reduce the strength to withstand the load (Beck *et al.,* 2015; Al Sunbul *et al.,* 2016). Over the years research and development of dental composite resin comprised of curing, filler and resin modification to improve its properties (Hambire *et al.,* 2012; Miletic, 2018).

There is a need to develop new composite which is more economical and provide the alternative to replace existing high- cost tooth- coloured materials in the market (Miletic, 2018). In our study, filler modification in terms of size, and properties of bonding is the main focus for parameters manipulation. Filler originating from plant based natural fibre is a promising alternative that needs further exploration.

Nowadays, natural fibre from a plant is commonly used for polymer composites as filler fibres reinforcement to enhance the mechanical properties of the materials (Joshi *et al.*, 2004). Production of the composites using synthetic fibres, such as glass and carbon fibres, pose serious environmental and health risks to the workers. Comparatively speaking, composites made of natural fibres offer a healthier working environment (Jawaid & Abdul Khalil, 2011). Natural fibre composite has gained popularity in recent years due to its many benefits over synthetic fibres, including low density, abundance, lower cost, renewable nature, and biodegradability (Andilolo *et al.*, 2017). The contents of natural fibre are generally composed of cellulose, hemicellulose, and lignin (Eleutério *et al.*, 2017).

Kenaf plant is a dicotyledons plant, belonging to genus *Hibiscus Cannabinus* (family *Malvaceae*). Malaysia is one of the major kenaf fibres supplier in the world which comprised of about nine supplier centres (Ramesh, 2016). Utilizing kenaf fibre as a filler component in a composite could boost its profitability and economic value (Akil *et al.*, 2011). Kenaf can survive and grow more than 3 m in diameter and 25-51 mm in length under a wide range of conditions and provide a long fibre within three months (Ramesh, 2016). The fibrous stalk also only needs less or require no usage of pesticide due to its resistance to insects (Aziz *et al.*, 2005). Kenaf plants have been discovered to be a significant source of fibres for composite materials and other industrial uses. In comparison to other fibres, kenaf bast fibre has higher toughness properties and a higher aspect ratio (Nishino *et al.,* 2003: Bledzki *et al.,* 2015). Saba *et al.,* 2015 also mentioned that kenaf bast fibre exhibits mechanical qualities that make it a good replacement for synthetic glass fibre in polymer composites.

Kenaf fibre was chosen in our study as it is comparatively commercially available, economically cheap and has striking mechanical properties amongst other natural fibre reinforcing material (Saba *et al.,* 2015). In comparison to other fibres, kenaf bast fibre has a higher aspect ratio and tougher consistency. Tensile strength and modulus of a single fibre can reach 450–750 MPa and 66 GPa, respectively (Yamamoto *et al.,* 2007; Akil *et al.,* 2011; Ramesh, 2016). Furthermore, kenaf fibre has a lighter weight as it has low density in comparison to synthetic glass fibre but specific strength and modulus of the fibre are still comparable to the glass fibre (Ali *et al.,* 2014).

Theng *et al.,* (2019) found that by adding kenaf fibre to a composite resin at a ratio of 1 wt% and 2 wt% did not increase the flexural or compressive strength of the material. This may be because the kenaf fibres were not sufficiently surface-treated, which led to poor bonding between the fibres and the composite. Therefore, in this study we will conduct further investigation and modification on the bonding between the fibres and composite. A study by Ibrahim *et al*., (2021) found out numerous pulled out fibres as well as voids across the fractured surface of kenaf-reinforced composite resin. Insufficent surface treatment on kenaf fibre may lead to inadequate interfacial bonding between kenaf fibres and matrix based on the result shown by the pulled out kenaf fibres from fracture polypropylene matrix (Zamri *et al.,* 2016;Akhtar *et al.,* 2016; Ibrahim *et al.,* 2021). The effect of incorporation of cellulose kenaf fibre in composite resin on mechanical properties was also assessed with further improvement on the kenaf surface treatment.

1.2 Problem Statement

The mechanical and physical characteristics of the rice husk composite resin were reported to be acceptable however the value was lower than the commercial dental composites (Noushad *et al.,* 2016). Currently, there was no report on the availability and strength properties of kenaf reinforced composite resin derived from rice husk. Theng *et al* (2019) reported the inferior properties of composite resin incorporated with kenaf fibres in comparison to the commercial composite could be due to insufficient surface treatment of kenaf fibres resulted in poor bonding between fibres and composite. Therefore, in this study, the surface treatment of kenaf fibres was done using hybridization of tetraethyl orthosilicate (TEOS) sol gel and *γ-Methacryloxypropyltrimethoxysilane* (γ-MPS) treatment for the bonding optimization between fibres and composite.

1.3 Justification of the study

Kenaf fibre possess striking mechanical properties and has been used to reinforce polymer composite as a replacement of E-glass fibre (Faruk *et al.,* 2012; Saba *et al.,* 2015). The synthetic fibre in composite fields has been used widely due to its excellent performances, however they are non- renewable resources and debatable health issues toward industrial workers (Joshi *et al.,* 2004; Saba *et al.,* 2014). Nowadays, the application of natural fibres as a filler in composite materials are becoming more common in the industrial application. Nevertheless, to this date, there is no natural fibre reinforced composite in dental composite available in market.

Development of dental composite with plant based natural filler currently is still limited. Previous study of fabrication of dental nanohybrid composite with silica derived from rice husk has been studied and has fascinating results (Noushad *et al.*, 2016). From their study, it was reported that the composite had the flexural strength of 107 MPa, flexural modulus of 6.2 GPa and compressive strength of 191 MPa. By incorporating another type of filler which is fibre, our study aimed to investigate the possibility of improving the mechanical strength of the nanohybrid composite.

Incorporating natural fibre which is kenaf fibre as a filler into nanohybrid resin composite derived from rice husk silica aims to improve its mechanical properties as an alternative to commercially available composite and environmentally friendly choice. Benefitting from agricultural biowaste to produce silica derived from rice husk, dental composite reinforced with kenaf fibre is hoped to further enrich the usage of natural fibre toward sustainable resources. Insufficient surface treatment of kenaf fibres resulted in poor bonding between fibres and composite which lead to no mechanical strength improvement of composite with kenaf fibre reinforced (Theng *et al.*, 2021). In a study by Hina Abbas *et.al.*, (2021) (Master thesis) kenaf fibre surface was treated with TEOS sol gel and they found that fibre reinforced composite improved in compressive strength, however, no favourable effect in the flexural strength observed. Based on these two studies, kenaf surface treatment through modification and hybridization of γ-methacryloxypropyltrimethoxysilane (γ-MPS) and tetraethyl orthosilicate (TEOS) sol-gel was performed to optimize the bonding and improve the mechanical properties of this composite. Therefore, in this study, the kenaf surface treatment was performed by hybridizing two silanes, γ -MPS and (TEOS) sol-gel, to further assess the effect of cellulose nanocrystal (CNC) of the kenaf fibre in nanohybrid dental composite from agricultural biowaste on mechanical properties. The findings from this study would provide further knowledge for the development of fibre reinforced dental composite using natural resources for the future use as an alternative composite in restorative dentistry.

1.4 Scope of Study

This research was limited to the surface treatment of the kenaf CNC and fabrication of experimental kenaf fibre reinforced composites that incorporated nanohybrid silica derived from rice husk and kenaf fibre as the filler and dental monomers with the combination of bisphenol A-glycidyl methacrylate (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA). The nanohybrid size of the filler was selected due to it can produce excellent quality of the restoration in term of physical appearances and mechanical strength value and most of the composite nowadays incorporating nanohybrid fillers. The commercially available dental composite chosen were Filtek™ Z350 Universal Restorative Dental Composite (3M ESPE, St. Paul, Minn., USA), Neofil Composite Resin (Kerr, California, USA) and fibre reinforced composite Ever-X Posterior composite (GC corporation, Tokyo, Japan) which their mechanical properties was determined and compared with our experimental composites.

1.5 Research Questions

1. Can modification of surface treatment of kenaf CNC be done via hybridization of tetraethyl orthosilicate (TEOS) sol gel and *γ-Methacryloxypropyltrimethoxysilane* (γ-MPS) treatment? If successful, what is thermal stability of kenaf CNC after the surface treatment?
2. Is there any difference in compressive and flexural strength of the nanohybrid composites reinforced with kenaf fibres in comparison to the commercial nanohybrid composite?
3. Are there any changes in surface morphology and distribution of kenaf fibres incorporated into nanohybrid composite from rice husk silica when analysed at its fractured site?

1.6 Objective

General Objective

To investigate and optimize bonding between kenaf fibre and nanohybrid composite from agriculture biowastes and assess their mechanical properties.

Specific Objective

1. To modify the surface treatment of kenaf CNC via hybridization of tetraethyl orthosilicate (TEOS) sol gel and *γ-Methacryloxypropyltrimethoxysilane* (γ-MPS) treatment.
2. To investigate thermal stability of kenaf CNC after surface treatment using thermogravimetric analysis (TGA).
3. To evaluate the compressive and flexural strength of the nanohybrid composites reinforced with kenaf fibres in comparison to the commercial nanohybrid and fibre reinforced composites.
4. To observe the surface morphology and distribution of kenaf fibres incorporated into nanohybrid composite from rice husk silica at its fractured site.

1.7 Research Hypothesis

1. There is potential for modification on surface treatment of kenaf CNC can be obtained via hybridization of tetraethyl orthosilicate (TEOS) sol gel and *γ-Methacryloxypropyltrimethoxysilane* (γ-MPS) treatment.
2. Thermal stability of kenaf CNC improves after the surface treatment.
3. There is significant difference in the compressive and flexural strength of the nanohybrid composites reinforced with kenaf fibres in comparison to the commercial nanohybrid and fibre reinforced composite.
4. There are changes in surface morphology and distribution of kenaf fibres incorporated into nanohybrid composite from rice husk silica which can be analysed at its fractured site.

CHAPTER 2

LITERATURE REVIEW

2.1 Dental Resin Composite

Over the decades, composite resin as tooth coloured restoration has become high demand as it provides natural teeth aesthetic appearances over the unnatural amalgam restoration appearances in addition to issues concerning mercury content. In term of clinician's experiences, composite resin gives more handling time, easier to contour, and vast shade of colour as compared to amalgam (Sadowsky & Angeles, 2006). The composite is generally a mixture of dental resins monomer and diverse filler material. The properties of the composite are generally affected by the size and volume of the filler particles, the resin composition, the matrix-filler bonding, and the polymerization conditions (Cho *et al.*, 2022; Garoushi *et al.*, 2018). Other composite components include initiator, photo-initiators and accelerators.

2.1.1 Types of Dental Composite

Dental composites are categorized differently according to their particle size of the filler (macro, micro, nano-filled composite), type of filler (quartz, silica, zirconia, fibre), the activation process (light-activated, chemically activated composite) and its implementation (bulk filled, flowable composite). Macro-filled or conventional composites (10 to 100 μm), microfillers (0.01 to 0.1 μm), and more recently nanofillers

(0.005 to 0.01 μm) are three categories for composite resin sizing. (Alsharif *et al.*, 2010; Riva & Rahman, 2019).

Nanohybrid Composite

Nanohybrid composite is a hybrid of composite resin with a combination of macrofilled and microfilled particles sizing between of 15–20 μm and colloidal silica particles (0.01–0.05 μm) (Ferracane, 2011). The combination of two filler types aims to combine the physical properties of macrofilled composite resin with the smooth polishing surface of microfilled composite resin, and as a result, it has good wear resistance and mechanical properties and is suitable for high stress area in tooth restoration (Hamouda & Abd Elkader, 2012; Itanto *et al.*, 2017; Sonwane & Hambire, 2015).

Nanocomposite applications provide new technology and commercial opportunities for a variety of industries because of its advantage of increased aspect ratio, surface area, and fascinating properties plus environmentally friendly (Saba *et al.*, 2014). Extremely fibre size reduction in term of diameter within nanometre range, offer special properties such as simultaneous improvement ins strength, modulus, and toughness which contribute to fibre reinforced composite development and improvement (Vidotti *et al.*, 2015).

Fibre Reinforced Composite

Fibre reinforced composites (FRCs) are a type of composite material composed of a polymer matrix that has been strengthened by the addition of thin, fine fibres, such as E-glass fibres (Khan *et al.,* 2015). The composition of the polymeric matrix includes polymerized monomers which hold the fibres together in the composite structure to enhance the mechanical properties of the dental composite to be utilised as base in restoration of high stress- bearing area in posterior tooth (Zhang & Matinlinna, 2012). Fibre is incorporated in dental material as a strategy to reduce the risk of the composite bulk fracture (Maas *et al.,* 2017). E- glass fibre is commonly used for reinforcement in dental application (Khan *et al.,* 2015). In various industrial products, composite materials are produced using both non-renewable (non-biofibre such as petroleum based) and renewable resources (biofibres such as kenaf fibre, oil palm and various sources with polymer matrices) (Khan *et al.,* 2015).

2.1.2 Common Dental Resin Composite Monomers

Bowen in 1992 introduced the first monomer, dimethacrylate oligolimer, monomer base which is Bisphenol A Glycidyl Methacrylate (Bis-GMA). Composites core structure follows the fundamental triad proposed by Bowen, which consists of an organic phase (monomers blends), an inorganic phase (fillers), and a coupling agent (organosilane) (Yokota *et. al*, 1995). Bis-GMA contains hydroxyl group that makes it a highly viscous due to its polarity resulting in a strong intermolecular attraction. Dilution with triethylene glycol dimethacrylate (TEGDMA) of Bis-GMA aims to enhance the handling qualities. which allow more filler fraction to be loaded into resin, however it can cause an increase in polymerisation shrinkage and water sorption (Alshali *et al.,* 2015).

The usage of bis-GMA has the advantage of lower polymerization shrinkage, higher young modulus, and lower toxicity to the tissue due to the lower volatility and diffusivity (Furtos *et al.,* 2013; Sideridou *et al.*, 2002). Other types of monomers that are commonly used in dental composite are Urethane dimethacrylate (UDMA), polymethyl methacrylate (PMMA) and Bisphenol A polyethylene glycol diether dimethacrylate (Bis-EMA). Figure 2.1 shows chemical structure of Bis-GMA and TEGDMA.

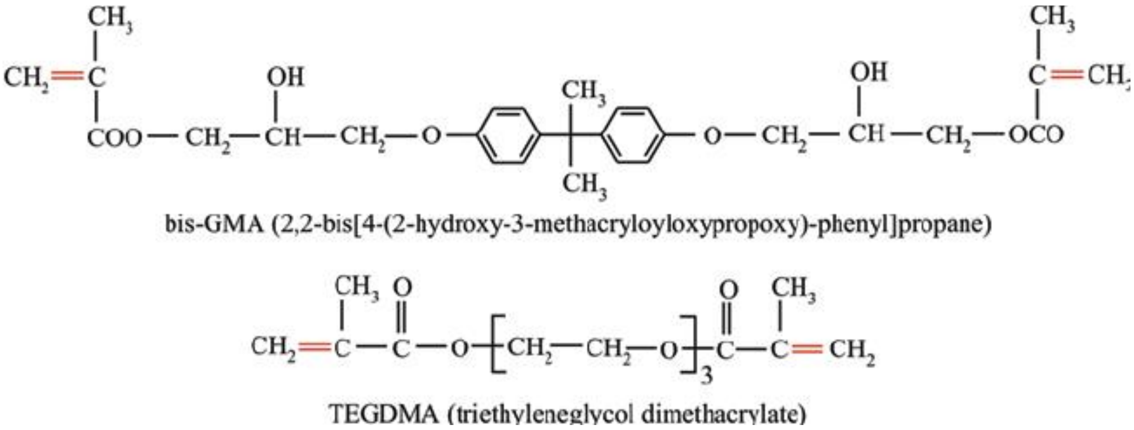
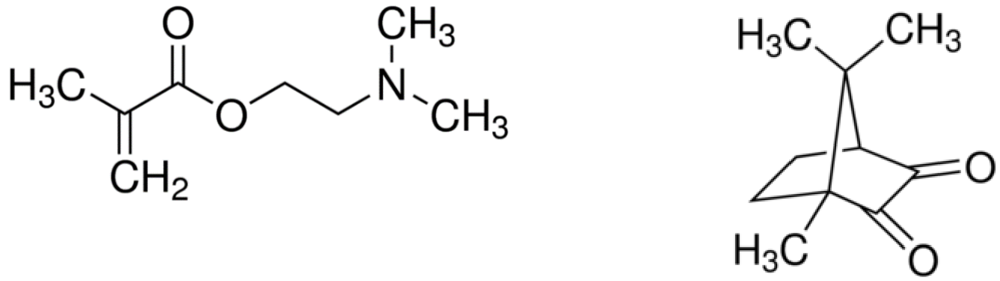


Figure 2.1 Chemical structure Bis-GMA and TEGDMA (Furtos *et al.*, 2013)

2.1.3 Polymerization of Resin Composite

Two types of composite resin activation are light activated and chemically activated. Typically, composites go through a process called vinyl-free radical polymerization, which starts with the release of free radicals from the structure of the methacrylate monomer when external energy, such as thermal, chemical, or radiation energy, is added (Riva and Rahman, 2019). Light activated dental composite commonly used dental photo activator is (1,7,7-trimethylbicyclo[2.2.1] heptane-2,3-dione), Camphorquinone (CQ) which the light absorption varies from 425 to 495 nm

(Rueggeberg, 2017). CQ and Dimethylaminoethyl methacrylate (DMAEMA) which is amine initiator are widely used in dentistry (Rueggeberg, 2017). Radiation limits for dental photopolymerization were set to be between 380 nm and 700 nm, which are only considered to be visible light (Main *et al.*, 1983). Figure 2.2 shows chemical structure of DMAEMA and CQ. Figure 2.3 depicts the light activation of composite resin.



DMAEMA (2-(Dimethylamino) ethylmethacrylate)   CQ (Camphorquinone)

Figure 2.2 Chemical structure of DMAEMA and CQ (Lee *et al.*, 2015)

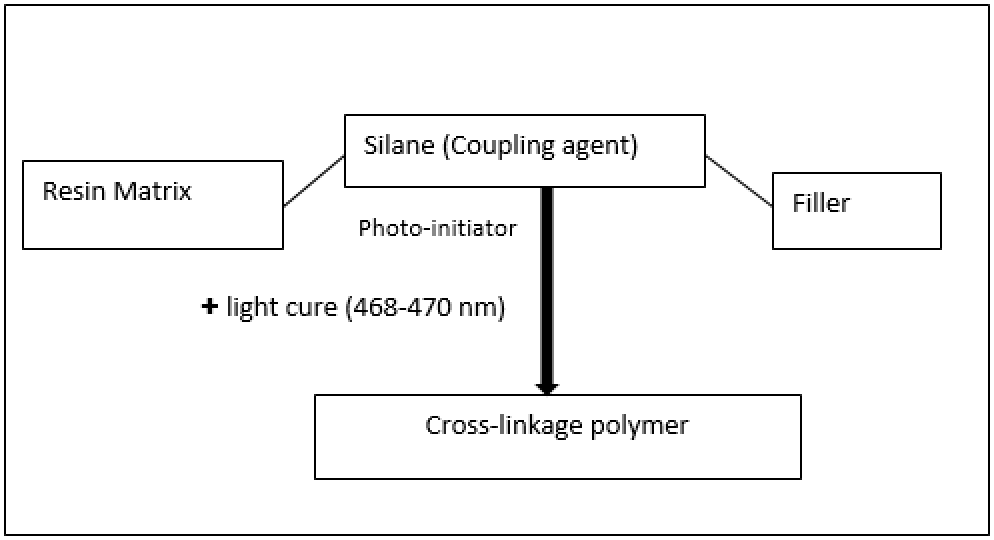


Figure 2.3 Light activation of composite resin

Adapted from (Riva & Rahman, 2019)

2.1.4 Filler

Filler materials act as reinforcement which provide strength, colour, translucency, and opacity of the composite resin (Fonseca *et al.,* 2016; Habib *et al.,* 2016). The type, loading, size, shape, or geometry of the filler, as well as its porosity, have a significant impact on the physical and mechanical properties of the resin composite (Habib *et al.*, 2016). To improve the performance of the resin composite, extensive research had been done to produce a variety of fillers with different properties (Ilie & Hickel, 2009; Karkanis *et al.*, 2022; Shokoohi *et al.*, 2008). There are inorganic and organic type of filler particles. Inorganic fillers, which are composed of finely divided silicate or glass particles and possibly added with radio-opacifying agent like barium oxide, serve to improve the mechanical properties and provide a blended material with overall properties that is suitable for clinical tooth repair. (Wei and Tang, 1994). Silica, silicate glass, alumina and zirconia are among the filler example of fillers used for fabrication of resin (Klapdohr & Moszner, 2005). The primary filler used in most dental composites is silica. Dental composites' properties were improved by using silica particles, which come in a variety of sizes, shapes, and compositions. Many commercial dental composites use silica as fillers such as Filtek Z350, Filtek Z100, and many more (Curtis *et al.*, 2009). Silica is typically synthesized using chemicals as precursors, such as sodium silicate, silicon tetrachloride, and tetraethyl orthosilicate (TEOS). These chemicals can produce high purity silica with predetermined morphologies and reproducible sizes (Rahman & Padavettan, 2012). A good alternative to extracting silica from natural resources is rice husk, which has a high percentage of silica (Athinarayanan *et al.*, 2015). Furthermore, rice husk is widely accessible in nations that grow rice, making it a cheap source of silica. The morphology of spherical nanohybrid silica obtained from rice husk makes it perfect for use as fillers in dental composites (Noushad *et al.*, 2016).

E-glass Fibre as Reinforcement

Synthetic fibre such as glass fibre incorporation in composite has been used in industries and application in dentistry (Zhang & Matinlinna, 2012). Short glass fibre composite has good performances in dental materials such as composites reinforcement, used in prosthesis infrastructure, onlay restorations and endodontic posts (Fonseca *et al.*, 2016). Composition of E-glass fibre consists about 54.5 wt% silica (SiO_2), 14.5 wt% aluminium dioxide (Al_2O_3), 17 wt% Calcium oxide (CaO), 4.5 wt% magnesium oxide (MgO), 8.5 wt% boron trioxide B_2O_3 and 0.5wt% of sodium oxide (Na_2O) (Mallick, 2007). The short glass fibre composite's inorganic fillers are intended to lessen polymerization shrinkage, enhance the material's mechanical characteristics as well as increase viscosity and make it easier to handle (Bijelic *et al.,* 2013).

Heijenrath & Peijs (1996) concerned the disadvantages of glass fibre regarding recycling issues (thermal) and causing processing equipment abrasive wear. Additionally, the processing and assembly of fibre-reinforced parts can result in skin irritations apart from they are non-renewable resources (Joshi *et al.,* 2004; Saba *et al.,* 2014). Several studies have been conducted to compare the environmental impact of natural fibre composites with that of glass fibre reinforced composites throughout their entire life cycle (Schmidt & Beyer, 1998; Wötzel *et al.,* 1999; Corbière-Nicollier *et al.,* 2001). The amount of non-renewable energy needed to produce renewed glass fibre is 5–10 times greater than that needed to produce natural fibre, which causes glass fibre production to emit significantly more pollutants than natural fibre production (Joshi *et al.,* 2004). In their opinion, they concluded natural fibre composites are generally more affordable, lighter, and more environmentally friendly than glass fibre composites.

2.2 Biowaste from Agriculture

Agricultural sector is one of the major economic sectors in Malaysia contributing 7.4% of gross domestic product (GDP) in the year 2020 (Department of Statistics Malaysia). A fifth of the 500 million tonnes of rice produced annually worldwide, which is the primary food in Asian communities, is made of rice product biowaste, and some agricultural waste is disposed in landfills (Agamuthu *et al.,* 2009; Mahmud *et al.,* 2010). As natural fibres have advantages in term of environmentally friendly, low cost and light weight, the natural fibre becoming importance in polymer industries. Agricultural biowaste is also useful to be alternative resources for natural fibre. Natural sheath around growing rice grains, rice husk is one of the natural fibres obtained from agro-industrial waste. The extraction of silica from the rice husk had undergone active research over the years and developed into dental composite (Noushad *et al.,* 2013; Arjmandi *et al.,* 2015; Yusoff *et al.,* 2019).

2.3 Natural Fibre Reinforced Composite Application

Environmental concerns lead researchers to explore the possibility of incorporating natural fibre into composite applications as filler reinforcements developing natural fiber–reinforced composites (NFRCs) (Li *et al.,* 2020). Plant natural fibres are widely studied and accepted in industries compared to natural fibre originated from animal based or mineral based (Peças *et al.,* 2018). Sisal, flax, hemp and kenaf are among common source of fibre extracted as polymer reinforcement composite (Fahim & Chand, 2008; Cho *et al.,* 2009; Gumrah Dumanli, 2016).

Today, natural fibre reinforced composite application mostly used in automotive industries (Bledzki *et al.,* 2010; Hu *et al.,* 2015). The European automotive composite markets, wood and cotton are the highest share follow with 8% kenaf, 7% jute, 5% hemp (Huda *et al.,* 2008; Peças *et al.,* 2018). Natural bast fibre (eg: fibre such as flax, hemp, kenaf) combined with polypropylene and polyster use as component build up for rear deck trays, door panels cover and many interior components that significantly reduced weight and cost of the production (Witayakran *et al.,* 2017). The light weighting automotive from provide significant energy saving and reduction of greenhouse gas emissions (Joshi *et al.*, 2004; Li *et al.*, 2020).

Incorporation of natural fibre in composite (biocomposite) also has huge potential in load bearing related application such as in construction field, natural fibre reinforced composite materials are also widely used in the food packaging, oil, and chemical industries (Faruk *et al.*, 2012; Balla *et al.*, 2019). Application in other sectors, hemp jute kenaf fibres used for shipping containers component, cases for musical instruments (Ngo, 2018; Peças *et al.*, 2018).

2.3.1 Kenaf Fibre as Co-Filler and Reinforcement

Kenaf is grown commercially in all over the world and regarded as an industrial crop in Malaysia. Kenaf fibre has been used commercially as reinforcement in Polymer Matrix Composite (PMCs) (Ku *et al.*, 2011). Natural fibre has a wide range of industrial uses, including in building materials, sports equipment, and industries other than packaging and papermaking. Incorporation of fibres in dental composites first introduced as fibre reinforced composites (FRCs) in 1960s to reinforce polymethyl-metacrylate (Smith, 1962). There are many applications for kenaf fibre itself as a reinforcing filler for composites, including automotive components and construction. However, to this date, there is limited research of kenaf fibre application in dental composites. Kenaf composite's mechanical strength and thermal characteristics are superior to those of other natural fibre polymer composites, giving it the potential to become a high-performance material that could possibly replace E-glass fibre as a reinforcement filler (Nishino *et al.*, 2003; Paridah *et al.*, 2011; Faruk *et al.*, 2012).

Figure 2.4 Kenaf plantation in Perlis, Malaysia

2.4 Mechanical Properties

Performance of materials is presented in terms of mechanical characteristics as they will determine the ability of material; especially when the materials undergone extreme and critical condition. Tensile properties, thermal properties, compressive properties, impact properties, and wear behaviour are among the mechanical characteristics (Wei and Tang, 1994).

The strength recorded during the compressive and flexural tests are the maximum stress that the sample can withstand before being permanently or plastically crushed or fractured. These tests were used to investigate the ability of the dental composite material to withstand masticatory stress (Ilie & Hickel, 2009). The mechanical strength, stiffness, and toughness of dental composites are typically correlated with the filler content; these characteristics increase with higher filler loading. Dental composite is stronger than glass ionomer cement but has similar flexural strength, fracture toughness, and tensile strength to porcelain and amalgam (Ferracane, 2011). Common flexural strength values of flowable and packable dental composites range from 67- 181 MPa and 76- 132 MPa, respectively (Cho *et al.,* 2022).

Cellulosic natural fibre (ie. flax, hemp, jute, kenaf) offers good mechanical properties comparable to synthetic fibre as an alternative for composite reinforcement materials (Hajlane *et al.,* 2018). Tensile strength of the natural fibres range of 100 to 1000 MPa may be generally lower than synthetic fibres (2000-3500 MPa) however certain natural fibre has comparable or higher specific moduli than the glass fibre (Li *et al.,* 2020). Peças *et al.,* (2018) summarized the findings on the properties of natural fibre, where flax has better tensile strength compared to glass fibre in addition to having high strength and stiffness with low density. Hemp and jute fibre has good insulation properties excellent mechanical strength and young’s modulus while kenaf fibre has high specific mechanical properties with low density (Rohit *et al.,* 2016).

2.4.1 Mechanical Properties of Kenaf Fibre as Filler Reinforcement

Application of kenaf fibre as reinforcement together with standard softwood improved the flexural strength of polypropolyle (PP) biocomposite by factor 2.45 which surpass jute fibre (Bledzki *et al.,* 2015). Incorporation of treated kenaf fibre in unidirectional long kenaf fibre- reinforced epoxy (KRFE) showed improvement in flexural strength by 36%, while 20% improvement in untreated kenaf fibre (Yousif *et al.*, 2012). According to Ochi (2008), the tensile and flexural strength of kenaf PLA (polylactic acid) composites increased linearly with fibre content up to 50%, demonstrating that kenaf fibre exhibits higher strength when reinforcing the PLA than other natural fibres. In comparison to composites made solely of matrix resin, kenaf reinforcement has higher Young's modulus and tensile strength. This property was proved when sheet of kenaf reinforce composite was stretched using tensile tester. The main deformation mechanism for the sheet was considered as the angular change of the kenaf fibre to the stretching direction was due to matrix resin impregnated into the interfibrillar regions (Akil *et al.,* 2011).

2.5 Overcoming Drawback of Natural Fibre

Despite all the benefits of kenaf fibres, one drawback is that cellulose's hydrophilic properties interfere with the interphase bonding between the fibre and the hydrophobic polymer used as the matrix (Mahjoub *et al.*, 2014). Natural fibre hydrophilicity is due to present of linear chain of glucan polymer 1,4-β- bonded anhydroglucose units containing alcoholic hydroxyl groups (Mohanty *et al.,* 2001). Hydrogen bonds of the kenaf fibre surface prevent the filler surface from being wetted which lead to lack of dispersion when fibre filler incorporated into polymer matrix due to hydrogen agglomeration (Hassan & Ismail, 2015). If the fibres were exposed to the environment or met aqueous media, water absorption would also result in the long-term failure of an organic matrix (Ghani *et al.,* 2012). According to Dhakal *et al.,* (2007), moisture can infiltrate composites by diffusing water molecules into the micro-gaps between polymer chains, traveling through capillary action into gaps and flaws between the fibre-matrix interface, and moving through micro-cracks in the matrix. Esterification method through acetylation was done to introduce plasticization to cellulosic fibres which enhances the composite's interface, dimensional stability, and fibre dispersion in a polymer matrix (Akil *et al.,* 2011).

2.5.1 Surface Treatment of Kenaf fibre with Alkali (Mercerization)

Numbers of efforts have been done to modify the properties of natural fibre using various chemical treatments such as alkali treatment (mercerization), silane treatment, and acetylation (Razak *et al.,* 2014). The presence of these two amorphous structures, namely lignin and hemicellulose prevent the fibre from being reoriented for uniform load transfer, it has been discovered that removing lignin and hemicellulose from the fibre structure is one of the ways to increase the tensile strength of the fibre significantly (Delgado-Aguilar *et al.,* 2018). Yuli *et al.,* (2020) found that the fibre with the maximum tensile strength was the one that was exposed to a 1% v/w sodium hypochlorite ($NaClO_2$) solution at 25°C for one hour. This bleaching procedure reduced some of the fibre's amorphous parts while removing contaminants from the surface. Nonetheless, the cellulose chain in kenaf fibre was degraded by subsequent increases in $NaClO_2$ concentration, mixing temperature, and time, which reduced the fibre's mechanical strength.

Ochi (2008) reported that poor bonding between kenaf fibre and resin matrix, and presence of void in the matrix possibly due to insufficient resin. Surface modification of kenaf using alkaline treatment (mercerization) aims to remove lignin, hemicellulose, wax and oil that covering the fibre surface. Fibres were soaked in sodium hydroxide (NaOH) solution in a period of time to increase surface roughness eventually improve mechanical interlocking (Mahjoub *et al.,* 2014). In addition, this surface treatment process increases the amount of exposed cellulose on the fibre for additional reaction sites that will have a long-lasting impact on the strength and stiffness of the fibre (Mahjoub *et al.,* 2014).

According to Edeerozey *et al.,* (2007), inadequate adhesion between the fibres and the matrix and the matrix's high moisture absorption may cause dimensional changes in the fibres, leading to micro-cracks in the composite and degradation of mechanical properties. The study found that treating kenaf fibres with 6% sodium hydroxide (NaOH) resulted in the highest tensile strength, while 3% NaOH was ineffective in removing impurities from the fibre surface. The cleanest fibre surface was observed after treatment with 9% NaOH, but excessive concentration of NaOH solution could harm the fibres and weaken their tensile strength. Miao & Hamad, (2013) in their review emphasized the need to dry the fibres before processing to remove moisture, which can weaken adhesion between fibre and polymer and create voids in the composite during processing.