PHYSICAL AND MECHANICAL PROPERTIES EVALUATION OF EXPERIMENTAL NANOHYBRID DENTAL COMPOSITE REINFORCED WITH NANOSIZED ZIRCONIA AND MACROSIZED ALUMINA

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by

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β	beta
α	alpha
*	Asterisk
π	pi constant
X^2	Chi-square

LIST OF ABBREVIATIONS

IPS	Institute Postgraduate Studies
USM	Universiti Sains Malaysia
DMAEMA	Dimethylaminoethyl methacrylate
SSS	Sodium silicate solution
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier transform infrared radiation
EDX	Energy Dispersive X-ray Spectroscopy
NHDC	Nanohybrid dental composite
ASDS	American Society of Dental Surgeons
UDMA	Urethane dimethacrylate
ZrO_2	Zirconium oxide
BIS-GMA	Bisphenol A glycerolate dimethacrylate
BIS-EMA	Bisphenol aethyl methacrylate
TEGDMA	Triethyleneglycoldimethacrylate
CQ	Camphorquinone
DMPT	N,N- dimethyl-4-toluidine
ESR	Electron spin resonance
PBN	Phenyl-tert-butyl nitrone
SiO_2	Silicon oxide
RH	Rice husk
ISO	International Organization for Standardization
RBC	Resin based composite
VHN	Vickers hardness
TP	Translucency parameter
EPR	Electron paramagnetic resonance
NMR	Nuclear magnetic resonance
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
ASTM	American Society for Testing and Materials
DC	Degree of conversion
SDR	Stress decreasing resins

WPC	Wood plastic composite
UV	Ultraviolet radiation
EB	Electron beam
MDL	Multidisciplinary dental laboratory
SD	Standard deviation
USA	United States of America
HCL	Hydrochloric acid
RO	Reverse osmosis
NaOH	Sodium hydroxide
UK	United Kingdom
γ-MPS	γ-methacryloxypropyltrimethoxysilane
US	United States
KBr	Potassium bromide
UTM	Universal testing machine
ATR	Attenuated Total Reflection
SPSS	Statistical Package for the Social Sciences
OH	Hydroxy group
PEGDMA	Poly(ethylene glycol) dimethacrylate
FS	Flexural strength
NH	Amide

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PENILAIAN SIFAT FIZIKAL DAN MEKANIKAL KOMPOSIT PERGIGIAN NANOHIBRID EKSPERIMEN YANG DIPERKUAT DENGAN ZIRKONIA BERNANO DAN ALUMINA BERMAKRO

ABSTRAK

Komposit pergigian nanohibrid eksperimen (NHDC) menggunakan silika yang diekstrak daripada sekam padi telah dibangunkan. Walau bagaimanapun, sifat fizikal NHDC masih lebih rendah berbanding komposit pergigian komersial. Kajian ini bertujuan untuk menambah baik sifat NHDC menggunakan pengisi tetulang zirkonia bersaiz nano dan alumina bersaiz makro, dengan memberi fokus kepada sifat fizikal dan mekanikal NHDC. Serbuk putih nanosilica, yang diperoleh daripada sekam padi, digunakan sebagai pengisi dalam NHDC. Komposit pergigian ini diperkuat dengan zirkonia bersaiz nano (ZrO_2) dan pengisi tetulang alumina bersaiz makro (Al_2O3), yang dibahagikan kepada tiga kumpulan NHDC: diperkuat dengan Zirkonia (3%) & Alumina (2%), diperkuat dengan Zirkonia (2%) & Alumina (3%), dan diperkuat dengan Zirkonia (3%) sahaja. NHDC tanpa tetulang pengisi dan Filtek^{TM} Z250XT masing-masing digunakan sebagai kawalan negatif dan positif. Taburan zarah pengisi di dalam NHDC dinilai menggunakan FESEM. NHDC kemudiannya diuji untuk sifat fizikal dan mekanikal masing-masing. Pengagihan zarah pengisi diagihkan secara homogen, dan permukaan NHDC eksperimen kelihatan licin. Kekerasan Vickers, kekasaran permukaan, kekuatan lentur dan sifat lutsinar yang ditunjukkan NHDC bertetulang zirkonia dan alumina secara statistik lebih tinggi daripada kawalan. Walau bagaimanapun, nilai ini jauh lebih rendah daripada produk komersial Filtek^{TM} Z250XT ($p < 0.05$). Untuk kandungan gel, semua nilai kajian NHDC menunjukkan perbezaan tidak ketara antara tiada pengisi bertetulang (kumpulan kawalan) dan Filtek^{TM}

Komersial Z250XT, ($p > 0.05$). Tetulang Zirkonia & Alumina juga meningkatkan tahap penukaran NHDC eksperimen berbanding dengan produk kawalan dan komersial Filtek^{TM} Z250XT ($p < 0.05$). Kajian ini merumuskan bahawa tetulang zirkonia dan alumina menambah baik sifat NHDC eksperimen dan boleh digunakan sebagai pengisi dalam tetulang komposit pergigian pada masa hadapan.

PHYSICAL AND MECHANICAL PROPERTIES EVALUATION OF EXPERIMENTAL NANOHYBRID DENTAL COMPOSITE REINFORCED WITH NANOSIZED ZIRCONIA AND MACROSIZED ALUMINA

ABSTRACT

An experimental nanohybrid dental composite (NHDC) using silica extracted from rice husk has been developed. However, the physical properties of NHDC are still inferior as compared to the commercial dental composite. This study aimed to enhance the NHDC properties using nano-sized Zirconia and macro-sized alumina reinforcing fillers, focusing on the physical and mechanical properties of the NHDC. Nanosilica white powder, derived from rice husk, was used as a filler in NHDC. This dental composite was reinforced with nano-sized zirconia (ZrO_2) and macro-sized alumina reinforcing fillers (Al_2O_3), which were divided into three NHDC groups: reinforced with Zirconia (3%) & Alumina (2%), reinforced with Zirconia (2%) & Alumina (3%), and reinforced with Zirconia (3%) only. NHDC with no filler reinforcement and Filtek^{TM} Z250XT were used as a negative and positive control, respectively. The distribution of filler particles inside NHDC was evaluated using FESEM. The NHDCs were then tested for their physical and mechanical properties, respectively. The distribution of filler particles is homogenously distributed, and the surfaces of the experimental NHDCs appeared smooth. The Vickers hardness, surface roughness, flexural strength, and translucency properties showed that zirconia and alumina reinforced NHDC were statistically higher than the control. However, these values are significantly lower than the commercial product Filtek^{TM} Z250XT ($p < 0.05$). For gel content, the values of all experimental NHDC indicate non-significant difference between no reinforced filler (control group) and Commercial Filtek^{TM}

Z250XT, ($p > 0.05$). Zirconia & Alumina reinforcement also improves the degree of conversion of experimental NHDC compared to the control and commercial product Filtek^{TM} Z250XT ($p < 0.05$). This study concludes that zirconia and alumina reinforcement improve the properties of the experimental NHDC and could be used as future filler in dental composite reinforcement.

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Restorative dentists have long been intrigued by the idea of conserving tooth structure while fixing tooth surface defects. This restoration procedure can be carried out using materials that can restore the tooth's lost structure and function while also conserving the natural aesthetic values of the tooth. Dental composites are materials that meet the majority of these characteristics (Patodiya & Hegde, 2012). Dental composites have a long history, dating all the way back to the development of silicate cement as the first material used in direct aesthetics restorative material. In 1945, O’Brien (2002) reported that self-curing unfilled acrylic resins were introduced as a substitute for silicate cement and quickly gained popularity in the 1950s. In the 1960s, resin composites containing hard, inorganic filler particles were developed (O’Brien, 2002). These composites were composed of a soft dimethacrylate polymer and hard, inorganic filler particles. This tooth-coloured restorative material offers superior aesthetics, making it a more attractive alternative to the standard dental amalgam.

Dental composites are classified as macrofills (conventional composites), microfills, hybrids, nanofil and nanohybrid (Miletic, 2018). Nanohybrid and nanofil composites produce a highly filled and polishable composite material that can be used in both posterior and aesthetic concern areas of the oral cavity (Lowe, 2015). Dental composites are made up of resin matrix, inorganic filler particles, and silane coupling agent that acts as a crosslinker between the organic matrix and the filler particles. As a result, the organic matrix and filler content have a considerable impact on the production of dental composites.

Advancement in nanotechnology has led to the production of nanosized silica, SiO_2, which has been widely used as filler in engineering composite (Rahman & Padavettan, 2012). Recently, the manufacture of composite materials from agricultural residues sources such as rice husks has been able to be converted into a commercial stock for the production of silica powder (Surata, Suriadi & Arnis, 2014). Hence, the silica was modified to have a spherical shape with a low specific surface area (Noushad *et al.*, 2016) which is also known as one of best characteristic of filler for better dental composites. The mechanical properties of composite resin are mainly due to its filler content. Filler loading had a significant impact on filler morphology, which in turn affected the mechanical properties of the composite tested. The purpose of this study was to reinforce zirconia and alumina filler with different compositions (3% wt zirconia and 2% wt alumina; 2% wt zirconia and 3% wt alumina; 3% wt zirconia) in order to determine the physical and mechanical properties of nanohybrid dental composite and compare them to the commercial product Z250 XT (3M ESPE).

1.2 Problem Statement & Justification of the study

The inclusion of silica from rice husk as fillers in dental composites would significantly reduce their cost, as the commonly used raw materials in the classic sol-gel method such as tetraethylorthosilicate and high modulus sodium silicate, are relatively expensive (Noushad *et al.*, 2013).

The study focuses on obtaining silica from an inexpensive source without the use of toxic chemicals (Noushad *et al.*, 2016) as a filler in dental composites. The synthesis of nanosilica powder from rice husk is one of the methods utilized in the dental medicine sector to save money while producing NHDC characteristics that are equivalent to commercial composites at a lower cost. An experimental nanohybrid dental composite (NHDC) made from silica extracted from rice husk has been developed. Despite the overall improvement in mechanical properties of the experimental NHDC, it is still inferior to a commercially available dental composite (Ismail *et al*., 2020).

Hence, theoretically in this study, we are attempting to improve the properties of composite by employing two different types of reinforcing fillers, nanosize and macrosize (to obtain a blend homogenous composite) and by employing several difference physical and mechanical tests, which are quite different from the study conducted previously in this experimental of dental composite. In addition, when making dental composites, we also use UDMA as a base monomer in a resin matrix. A novel nanohybrid composite made from rice husk and reinforced with zirconia and alumina is also being produced with the intention of comparing it to the dental composite commercial product Z250XT.

Therefore, the aim of the study to fabricate the NHDC and determine the validity of physical and mechanical properties of nanohybrid composite from rice husk reinforced with zirconia and alumina.

1.3 Research Objectives

1.3.1 General Objectives

1- To fabricate and evaluate a new experimental nanohybrid dental composite (NHDC) from rice husk reinforced with nano-sized zirconia and macro-sized alumina

1.3.2 Specific Objectives

a. To evaluate the Vickers hardness of nanohybrid dental composites reinforced with nanosized zirconia and macrosized alumina

b. To determine surface roughness of nanohybrid dental composites reinforced with nanosized zirconia and macrosized alumina

c. To investigate the flexural strength of nanohybrid dental composites reinforced with nanosized zirconia and macrosized alumina

d. To characterize the translucency of nanohybrid dental composites reinforced with nanosized zirconia and macrosized alumina

e. To evaluate the gel of content of nanohybrid dental composites reinforced with nanosized zirconia and macrosized alumina

f. To determine the degree of conversion of nanohybrid dental composites reinforced with nanosized zirconia and macrosized alumina

1.4 Research Question

1- Does nanosized zirconia and macrosized alumina improve the Vickers hardness of NHDC?

2- Does nanosized zirconia and macrosized alumina improve the surface roughness of NHDC?

3- Does nanosized zirconia and macrosized alumina improve the flexural strength of NHDC?

4- Does nanosized zirconia and macrosized alumina improve the translucency of NHDC?

5- Does nanosized zirconia and macrosized alumina improve the gel content of NHDC?

6- Does nanosized zirconia and macrosized alumina improve the degree of conversion of NHDC?

1.5 Research Hypothesis

1- Yes, nanosized zirconia and macrosized alumina improve the Vickers hardness of NHDC.

2- Yes, nanosized zirconia and macrosized alumina improve the surface roughness of NHDC.

3- Yes, nanosized zirconia and macrosized alumina improve the flexural strength of NHDC.

4- Yes, nanosized zirconia and macrosized alumina improve the translucency of NHDC.

5- Yes, nanosized zirconia and macrosized alumina improve the gel content of NHDC.

6- Yes, nanosized zirconia and macrosized alumina improve the degree of conversion of NHDC.

CHAPTER 2

LITERATURE REVIEW

2.1 Dental composites restoration

A material that is made up of at least two distinct components that are insoluble in one another is referred to as a "composite material." These insoluble components produce a material that has distinct characteristics, often superior to those of the components alone (Miletic, 2018). Because they look and work like biological tissue, composite restorative materials are one of the many breakthroughs in contemporary biomaterials research. Composite materials now depend for at least half of the posterior direct restoration placements (Pratap & Gupta, 2019). Materials for modern dental composite restorations started in the mid-1960s with the disclosure of Bowen's Bis-GMA (2,2-bis[4-(2-hydroxy-3 methacryloxypropoxy) phenyl]-propane) with inorganic molecule formulations (Chen, 2010). Resin-based dental composites are the most frequently used restorative materials to restore teeth due to their excellent aesthetics and congruity with teeth. The excellent physical, mechanical, optical and tribological properties of resin-based composites make them optimal for producing durable products that can withstand the human oral environment (Pratap & Gupta, 2019).

2.2 Composition of dental composites

The composition of the composite, which consists primarily of an organic resin matrix, reinforced filler particles, a coupling agent between the resin matrix and filler, and an initiator system, has an impact on all of the parameters that influence stress development (Shah & Stansbury, 2014). In addition, the aggregation of two or more dimethacrylate monomers such as bisphenol A-glycidyl methacrylate (Bis-GMA), bisphenol aethyl methacrylate (Bis-EMA), urethane dimethacrylate (UDMA), and triethyleneglycoldimethacrylate (TEGDMA) is commonly found in the organic matrix (Vouvoudi, Baxevani & Sideridou, 2016). For consolidation into the composite resin, a coupling agent is interpreted for interconnecting the inorganic filler and the natural monomer matrix. Erosion of the silane coupling agent between matrix and filler resulted in resin matrix water sorption due to long-term storage in water. Investigations have been carried out on the development of modern composite resins with a growing similarity between the filler molecule and the matrix, along with the silanisation of silica particles (Hwang *et al.*, 2018).

Many techniques relating to the alteration of the chemical composition of the substance were also suggested in the light of the above. For example, novel dental resin-based materials that present the SDR™ chemistry (i.e. stress reduction resin), which has refined the material's organic matrix and filler process (Meereis *et al.*, 2018). The advent of nanotechnology allows nanocomposites to get used to to these practical requirements as quickly as possible. They have improved mechanical properties such as compressive strength, diametral tensile strength, fracture resistance, abrasion resistance, low polymerization reduction, high light transmittance, high gloss retention and strong polishing (Jain & Wadkar, 2015).

2.3 Resin Matrix

Dental composite resin materials are made up of a matrix of resin, an inorganic filler, and a binding agent. Bisphenyl-glycidyl-methacrylate (Bis-GMA), triethylene glycol dimethacrylate (TEGDMA), urethane dimethacrylate (UDMA), and ethoxylated bisphenol adimethacrylate (Bis-EMA) are typical monomers used in resin matrix. The existence and molecular size of the monomer in the resin are important element affecting residual leaching of the monomer. The assumption is that smaller molecules will leach faster than larger molecules. Low molecular weight monomers may be produced in considerably greater amounts than high molecular weight monomers (Cebe *et al.*, 2015). Three main routes of systemic absorption of released chemicals from resin-based restorations have been accepted. The first is by uptake of the released compound in the gastrointestinal tract, the second is by diffusion through the dentinal tubules into the dental pulp, and the third is by absorption of the chemical volatile components of the lungs (Van Landuyt *et al.*, 2011).

In addition to inorganic fillers, dental composites be expressed by of an organic matrix that is a blend of dimethacrylate monomers and trace amounts of photoinitiators, catalysts, light stabilizers and inhibitors. The main monomers used in composite resins are triethylene glycol dimethacrylate (TEGDMA), bisphenol A glycerol dimethacrylate (BisGMA), and urethane dimethacrylate (UDMA) (Azzopardi *et al.*, 2009). Resins containing 70 mol percent UDMA and 30 mol percent TEGDMA without BisGMA exhibit excellent mechanical stability (Mota *et al.*, 2011).

2.4 Filler

Fillers were utilized in dental composites to improve strength, refractive index, and change the thermal expansion coefficient of the material (Szczesio-Wlodarczyk *et al.*, 2020). Besides, the essential sense for using fillers is to improve the properties of composite materials and lower the price of components (Kiran *et al.*, 2018). As reported in previous study, the filler type, shape and quantity, as well as efficient bonding between the filler and the resin matrix, improve material fulfilment. (Masouras, Silikas & Watts, 2008; M, Somasundaram & R V, 2020).

The chemical bonding between the matrix monomer and the methacrylate groups of the silane coupling agent on the surface of the filler believed to be the main mechanism promote the interaction between the matrix resin and the filler surface in the composite by condensing the hydroxyl groups and silanol functional groups on the surface of the prehydrolyzed silane (Atai, Pahlavan & Moin, 2012).

2.4.1 Filler size and composite properties

Up until the 1990s, the production of fillers accounted for the majority of the work that went into the development of dental composites. The size and structure of fillers varies considerably from over 10 to 50 μm in recent dental composites to the submicron range, extending to 5 nm in some latest nanocomposites (Shah & Stansbury, 2014). According to Szczesio-Wlodarczyk *et al*. 2020, the particle size of the filler varies greatly depending on the formulation, ranging from 0.007 to 70 microns. Composite filling materials were listed in 1985 using the inorganic filler average size, which became the base for future research (Mota *et al.*, 2011). Since the effects of scale, shape, and size distribution of various fillers were thoroughly studied, spherical particles generally exhibited good mechanical properties in multimodal size distributions (Habib *et al.*, 2015).

The use of nano-sized fillers has been demonstrated to decrease surface roughness as the nanoparticles can be uniformly distributed in the polymer matrix (Noushad *et al.*, 2016). Macrofilled composites, microfilled composites, hybrid composites, and, more recently, filler nanocomposites below 100 μm have been used to classify dental composites in the past. Researchers have been able to adjust different shades and opacities of the dental composites to build highly aesthetic restorations because the nanoparticles' incredibly small size offers low visual visibility in non-pigmented dental composites (Rahim *et al.*, 2011).

Besides, the merger of typically small, different size fillers allows for denser packing, thereby raising the possible filler volume fraction of the resin composite (Gajapriya, Somasundaram & Geetha, 2020)(M, Somasundaram & R V, 2020). Therefore, a variety of filler size was suggested to improve the composite resin properties.

2.4.2 Filler shape and properties

It has been demonstrated that spherical form has many benefits, such as allowing an increased filler load in composites (Rastelli *et al.*, 2012). Spherical nanosilica particles have higher glossability and mechanical stress appears to be more evenly distributed than irregularly shaped particles, resulting in superior mechanical properties (Rahim *et al.*, 2011). Spherical shape of filler enables maximum loading and raises the composite fracture strength. The spherical shape of the filler is suitable for geometrically incorporating more inorganic fillers into the resin matrix, especially in mixtures of different sizes (Noushad *et al.*, 2016).

2.4.3 Filler Loading

Filler loading has been recognized as an important aspect in evaluating the composite mechanical properties. However, several classification schemes based on the loading rate and size of fillers are complex, confounding and not clinically relevant (Kim, Ong & Okuno, 2002). The filling of fillers in dental composite resin is highly reliant on 35 to 70 per cent by volume or 50 to 85 per cent composite by weight (Szczesio-Wlodarczyk *et al.*, 2020). The filler plays many significant roles in ultimate restoration, including frame enhancement, radiopacity, and thermal expansion behaviour modification (Bociong *et al.*, 2018). Owing to the increased filler load and decreased resin matrix, nanofilled composites minimized the shrinkage of polymerisation while ensuring aesthetics and strength (Zhou *et al.*, 2019).

Besides, most commercial dental composites use two or more fillers to improve their properties. For example, 3M ESPE's Filtek Silorane uses silanized quartz and yttrium fluoride as fillers. In addition to silica, most commercial dental composites use additional fillers. For example, Filtek Supreme XT is a nanohybrid filler composed of silica nanofillers and zirconia/silicon nanoclusters (Noushad *et al.*, 2016).

2.4.4 Types

In dental composites, inorganic filler was used as the main composition of composites. The filler was added because its properties could provide the filling with rigidity, hardness, and strength (Gajapriya, Somasundaram & Geetha, 2020). Silica, alumina, zirconia, silicate glass, quartz, and ceramics are a few examples of materials frequently used as a reinforcing filler in dental composites (Djustiana *et al.*, 2018; Rangreez & Mobin, 2018; Aminoroaya *et al.*, 2021). Meanwhile, previous study by Szczesio-Wlodarczyk *et al*., 2020 reported that the inorganic phase/filler commonly utilised in dental composites comprises of silica, quartz, borosilicate, lithium aluminium silicate, barium, aluminium, and strontium aluminium or aluminium oxides.

In addition, Indonesia offers an abundance of natural materials that can be used as fillers in dental composites. Some of these are kaolin, feldspar, and zircon sand (Djustiana *et al.*, 2018). According to the previous study, short glass fibres were utilized as fillers to fortify dental composite resins creating restricted changes in composite mechanical properties (Xu, 1999). Furthermore, the brittleness and low toughness of glass properties, limiting the strength of glass fillers in composites (Gajapriya, Somasundaram & Geetha, 2020).

In a recent study, zirconia and alumina were used as reinforcing fillers in a dental composites resin.

2.4.4(a) Zirconia (ZrO_2)

Zirconia, which is also known as zirconium dioxide, is a white crystalline oxide of zirconium. It is widely used in dentistry due to its excellent optical, biocompatibility, and physical and mechanical strength (Sim *et al.*, 2020). Furthermore, a recent trend in dental zirconia technology is the development of full-contour zirconia, primarily to improve mechanical qualities as a monolithic restoration and to eliminate veneering ceramic chipping, which is currently believed to have a predominance (Inokoshi *et al.*, 2016).

In this study, zirconia nanoparticles were chosen as a filler in dental composite. Alqahtani claims that well dispersed nanopowders in polymers are essential for obtaining improved mechanical properties since nanopowders have a high surface energy and a tendency to clump together. Standard techniques are unable to break up these agglomerates (Alqahtani, 2020). In terms of aesthetics, the benefit of zirconia is its clear and white tooth-like color (Gahlert *et al.*, 2009), which as a base for a tooth substitution, shows up indeed more common (Gautam *et al.*, 2016).

2.4.4(b) Alumina (Al_2O_3)

Thorat et al., chose alumina in their previous study to search for stronger composites for latter uses. Although this material has been studied as a filler in bone cements, its application as a tooth restorative composite is relatively recent (Thorat, Diaspro & Salerno, 2013). Alumina great chemical propoerties had been utilized in composites for decades as a reinforcement and additionally as material for excessive temperature application. Moreover, the study of Barkoula *et al.* shows that an alumina-filled dental composite had a higher hardness value than an unfilled alumina composite (Barkoula *et al.*, 2008), which improves the mechanical properties of the composite.

2.5 Other additives (Photoinitiator, CQ)

The photoinitiator absorbs light and is directed into an excited state that interacts with a photoreductant (electron or proton donor molecule) to activate radical addition resin monomer polymerization (Singh, Rajkumar & Gupta, 2017). The most frequently utilized photoinitiator in dental resin formulations is camphorquinone (CQ), a blue light photoinitiator. Di-2,3-diketo-1,7,7-trimethylnorcamphane, or CQ, has an absorption peak around 469 nm and a molecular weight of 166 (Chen, Ferracane & Prahl, 2006).

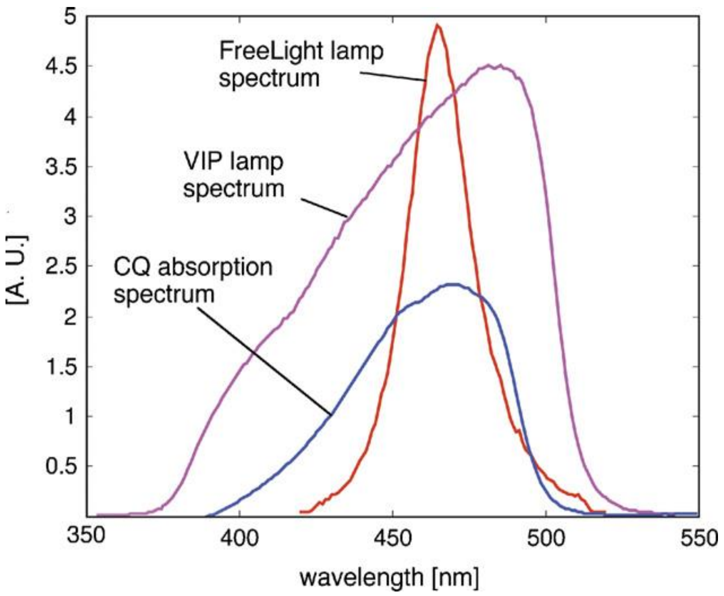

Figure 2.1 Comparison of the spectra 3M FreeLight LED light curing unit between VIP lamp and CQ absorption

This figure was taken from (Chen, Ferracane & Prahl, 2006)

CQ = Camphorquinone

Camphorquinone is vivid canary yellow in colour, and only a fraction of the material is currently used in dental device photocelling. The resulting restorations therefore appear to have a yellowish colour (Rueggeberg *et al.*, 2017). The photoinitiator concentration in the material, the number of photons the material is exposed to, and the photon energy (wavelength) controlled by the curing light, all affect the amount of photoinitiator activated (Santini, Gallegos & Felix, 2013).

2.6 Co-initiator, dimethylaminoethyl methacrylate (DMAEMA)

The Norrish type II photoinitiator system, which is made from the photoinitiator camphorquinone (CQ) and a co-initiator amine like dimethylaminoethyl methacrylate (DMAEMA), is the most frequently utilized photoinitiator system in resin cements. Assuming that the energy of a photon at 468 nm is insufficient to operate directly. In order to initiate polymerization of the materials, the co-initiator (DMAEMA) contributes hydrogen to the carbon-based radical initiator. Tertiary amines tend to react with an acid group, such as phosphoric acid, forming undesired quaternary ammonium salts, or deleterious interactions that lead to discoloration within the system depending on the form and concentration of the amine (Lima *et al.*, 2019). Although numerous amines have been proposed as accelerators, the number of compounds that can be used in dental applications has been severely constrained by biocompatibility and aesthetic requirements. The reduction agent DMAEMA polymerizes to harmless polymer, which prompts better biocompatibility. The most prevalent photoinitiator system used in today's photoactivated dental materials is the CQ/DMAEMA system (Schroeder & Vallo, 2007).

In the photoinitiation process, the co-initiator (amine compound) plays a crucial role. The kinds of co-initiator and its relationship to the photosensitizer affect the quality of the polymerization (Ge *et al.*, 2016). A photoinitiation system comprised of CQ and DMAEMA (0.5 wt percent each, compared to the total composite weight) was used and the photocuring reaction was carried out under visible light irradiation (Burujeny *et al.*, 2017). The following facts were used to classify the lower production of primary radicals in the CQ/DMAEMA system. First, tertiary aromatic amines with a substituent donor of paraelectron are more effective donors of electrons than tertiary aliphatic amines with an electron-withdrawing substituent, and therefore, the excited QC makes DMAEMA less inducible than N,N- dimethyl-4-toluidine (DMPT). Second, Teshima et al. reported that DMAEMA is more possible to be mixed with oxygen than aromatic amines because the electron spin resonance (ESR) technique identified fewer phenyl-tert-butyl nitrone (PBN) – DMAEMA radicals, indicating that they interact with dissolved oxygen instead (Schroeder, Cook & Vallo, 2008).

2.7 Types of dental composites

Several types of composites have been identified as being commonly used in dental restoratives. They are macrofills, hybrid, microfilled and nanofilled composites.

2.7.1 Macrofills

Macrofill was the first composite. These composites were made with large, spherical, or irregularly shaped particles that had an average filler diameter of 20-30 meters. The resulting composite was opaque and had limited wear resistance (Sakaguchi & Powers, 2012). The resins that make up macro type composites are a type of composite resin with inorganic filler that accounts for 70 to 80 per cent of the weight of the material and consists of particles bigger than 1 to 5 metres in diameter.

Due to its huge particle size, this material cannot be polished in a manner to microfilled. The advantage is that the material's hardness and wear resistance have significantly improved (Murariu *et al.*, 2020). The conventional or macrofilled composites, on the other hand, had filler particle sizes ranging from roughly 10 to 50 metres, which made them mechanically robust but difficult to polish and maintain a good colour match (Zhou *et al.*, 2019).

Macrofilled dental composite systems contain large, irregular, or spherical-shaped filler particles with excellent strength and low wear resistance (diameter 20 to 30 metre), but they are difficult to polish. According to the particle size classification of dental composites, their aesthetics are also compromised (Zafar *et al.*, 2017).

2.7.2 Hybrid

Hybrid composites consist of glasses of various compositions and sizes, including fumed silica sizes of 0.04 µm and diameter of particle sizes less than 2 µm. The filler content of these composites is 75-80 weight percent. This blend of fillers provides similar physical properties to conventional ones (Garg & Garg, 2015). The hybrid composites combine two types of fillers: fine particles with an average size of 2 to 4 m and 5 to 15% microfine particles with an average size of 0.04 to 0.2 m, typically silica (Sakaguchi & Powers, 2012). Particle sizes in hybrid composites range from 0.02–0.04 micrometers to 1–3 micrometers. Hybrid composites do not keep a high polish for very long due to the tendency for large particles to pop out from the surfaces of the teeth. However, hybrid composites are wear-resistant and simple to work with. They include particles smaller than a submicron, which are more challenging to remove than larger particles. Composites use only microscopic filler particles, whereas hybrid composites fill more densely (Chaughule, 2018).

Hybrid composites, which were a true combination of macrofilled and microfilled composites, were first made available in the early 1980s. They had amorphous silica microfiller particles (0.04 m) and macrofiller quartz, glass, or Ba/Sr/Al/Zr-silicate particles (1 to 50 m) (Miletic, 2018). Small filler particles in hybrid composites reduce interparticle distances, improving wear resistance and mechanical properties in general, while maintaining microfilled composites' good polishability and aesthetic properties.

2.7.3 Microfilled

Micron-sized filler particles are used in microfilled composites, whereas macro-sized filler particles are used in microhybrids (Maia *et al.*, 2018). The inclusion of submicron inorganic filler particles with an average size of 0.04 m in microfilled resin composites contributes to the material's increased viscosity. Consolidating more filler particles thusly decreases polymerisation shrinkage and works on surface completion. Consequently, it permits high polishability for maximum aesthetic appeal (Heasman, 2003).

Microfill composites are suggested for low-stress Class III and V restorations where high polish and aesthetic are essential (Sakaguchi & Powers, 2012). The superior aesthetic required for anterior restorations were made possible by microfilled composites' superior polishability and color stability in comparison to macrofilled composites (Miletic, 2018)**.** The flexural and compressive modulus of micro and flowable composites are approximately 50% lower than the values for general purpose hybrids and packable composites, reflecting the percent low volume of fillers present in microfilled and flowable composites (Sakaguchi, Ferracane & Powers, 2019).

Microfilled composites containing smaller filler particles allowed for better gloss retention while improving aesthetics, but at the cost of reduced strength.

Additionally, conventional microfills containing only silica fillers are not radiopaque. The surface area of the filler is large. Composites are therefore the least loaded and the most viscous. Lower filler concentrations reduce the strength of the final composite compared to macrofill. It is not suitable for use in high stress environments. Two examples of microfills currently on the market are different versions of Ivoclar's Heliomolar, Cosmedent's Vivadent and Renamel (Chaughule, 2018).

2.7.4 Nanofilled

Around the year 2000, nanotechnology enabled the development of nanofilled and nanohybrid dental composites. Nano-filled composites consist of non-aggregated silica and/or zirconia particles (5 to 20 nm) and agglomerated nanoclusters (mean size = 0.6 to 10 μm with respect to non-aggregated particles) (Miletic, 2018). Nanofilled composites are made up of silicon-zirconium particles with sizes ranging from 0.005 to 0.01 metre. The tiny particle size allows for a high level of filling of the organic matrix—roughly 80 per cent. Nanofilled composites have greater mechanical and physical qualities than microhybrid composites, including enhanced polishability with a gloss equivalent to enamel, improved wear resistance, and clarity (Dikova *et al.*, 2021). Besides, the use of nanofillers by the fabrication of nanohybrid composites from microhybrid composites has significantly increased the filler content of the material. As a result, a substantial improvement in their physical characteristics (Vouvoudi & Sideridou, 2013).

2.8 Rice husk

Rice husk (RH) is a by-product of rice processing that accounts for roughly 20 percent of bulk grain weight. RH is composed mostly of organic chemicals such as cellulose, lignin, (Sarangi, Bhattacharyya & Behera, 2009) and others, with the remaining 20 to 30 percent composed of mineralogical components such as silica, alkalis, and trace elements (Hossain, Mathur & Roy, 2018). Meanwhile, previous study defined rice husk as an outgrowth of the rice milling process that accounts for 20 percent of the paddy produced (Chun & Lee, 2020) and is also known as one of the largest residues, accounting for 20 to 33 percent of the paddy rice by weight (Quispe, Navia & Kahhat, 2019). The hard surface, low bulk density, and high amorphous silica content of rice husk are among its common characteristics (the highest among Gramineae plants) (Vieira *et al.*, 2020).

2.8.1 General

In general, the main contents of rice husks are organic substances such as hemicellulose, cellulose, and lignin, which account for 75 to 95 per cent of the total, with the remaining 17 to 20 per cent ash content. Ash is primarily composed of greater than 90 per cent silica and other metallic impurities (Bakar, Yahya & Gan, 2016). The husk has the highest silica (SiO_2) content in rice, which ranges from 8.7 to 12.1 per cent, an average of close to 10.6 per cent. However, the SiO_2 content of rice husk (RH) is similar to that of most other biosphere entities in a hydrated amorphous form (Shen, 2017). Rice husk has a relatively high inorganic compound content, comprising around 20 per cent of the husk's dry weight. Silica accounts for 94 per cent of the total, while the remaining 6 per cent are K_2O, CaO, MgO, Al_2O_3 and P_2O_5 (Carmona *et al.*, 2013).

2.8.2 Rice husk and Its Application

There are various applications of rice husk in general. Rice husk are used as fertilizer and substrate, brewing beer, industrial fuel, preparation of activated carbon, as pet food fibre, making bricks, toothpaste, pillow stuffing, tire additive and also for production of xylitol, furfural, ethanol and acetic acid (Kenechi, Linus & Kayode, 2016). Furthermore, previous research has revealed that many rice-producing nations, including Thailand, Malaysia, and Sri Lanka, use leftover rice husk to generate electricity (Nsaif & Saeed, 2013).

Rice husk is generally a hull used to protect seeds and grains. Composed of hard materials, water-insoluble and abrasive, with a high proportion of cellulose-silica structure (Suhot *et al.*, 2021). Meanwhile, In India, rice husk is typically used in small power plants, as biomass to fuel and co-fuel power plants, soil aeration, and as animals bedding material. Some industries are now manufacturing rice husk composites for making furniture and wood plastic composite (WPC) decking (Moulick, 2015). In addition, rice husk has been reported to be used to make construction boards using the steam explosive hydrolysis technique, which assesses the efficient breakdown of organic raw materials (Satbaev *et al.*, 2021).

2.8.3 Uses in dental composites

A huge quantity of nano silica powder with regulated form, size, and porosity is needed in the face of large industrial applications. The powder of nanosilica is typically prepared using methods of vapour-phase reaction, sol-gel, and thermo-decomposition. Nanosilica powder is synthesized using chemicals as the raw material in most of the above processes. In chemical techniques, the material's scale, shape, and purity are easily controlled but the initial reagents are expensive. Low costs and large quantities of an early precursor are required in industrial applications (Yuvakkumar *et al.*, 2014).

2.9 Physical and mechanical properties test of dental composites

There were several types of physical and mechanical properties of dental composites. This study used flexural strength, Vickers hardness, and degree of conversion to determine the mechanical properties, while surface roughness, translucency, and gel of content to determine the physical properties of dental composites.

2.9.1 Characterisation of dental composite

In this study, we used FESEM as a characterisation method of nanohybrid dental composite (NHDC).

2.9.2 Surface roughness of rice husk nanohybrid composites

In a related analysis on nanohybrid, nanofilled, and microhybrid, Abdurazaq and Al-Khafaji have concluded that all demonstrate a relationship between surface roughness, with consistent results for surface roughness values (Mohammed Magdy *et al.*, 2017). The roughness of surface composite resins depends on various intrinsic and extrinsic variables. Intrinsic factors consist of material, form of filler, shape, size and filler particle distribution, degree of polymerisation, resin matrix composition, and filler matrix bond durability. Extrinsic factors contribute to the finishing and polishing process. They include the versatility of the polishing tool, the hardness of the abrasive particles, the geometrical form of the polishing tool and its application method (Nasoohi, Hoorizad & Tabatabaei, 2017).

Profilometer roughness values, in general, allow for quantitative measurement of surface irregularities. The parameter Ra is used in the current analysis to measure surface roughness. While Ra is considered a weak surface texture indicator, it is the most commonly reported value for evaluating surface topography in dental materials (Kakaboura *et al.*, 2007). The surface roughness of resin composites is related to the composition and porosity of the material, as well as the methods and techniques used for polishing. In addition, surface roughness of composites has been identified as a clinically relevant variable with wear resistance, plaque accumulation, gingivitis, material staining (particularly for Class V restorations), and surface gloss (Senawongse & Pongprueksa, 2007a). Regardless of the cavity class and place, appropriate finishing and polishing of tooth-coloured restorations, which improve aesthetics and restoration durability, are essential steps in restorative dentistry (Erdemir *et al.*, 2013).

2.9.3 Flexural strength of rice husk nanohybrid composites

The maximum stress a material can withstand before failing is its flexural strength when subjected to a bending load. The required flexural strength is determined by the clinical applications. For restorations that are subjected to forces from chewing solids, a high flexural strength is required (Ghavami-lahiji *et al.*, 2018). A three-point bending test for flexural strength is used is to determine the sample's ability to withstand the bending forces (Raorane *et al.*, 2019). The ISO 4049/2000 (Standard, 2000) specification for polymer-based materials recommends the in vitro three-point bending flexural test, which is widely used for comparison purposes (S M Chung *et al.*, 2004).

In some studies, flexural strength and flexural modulus have been identified as clinical wear indicators for composites. Additionally, composite fillings are subjected to flexural stress, particularly in cavities for restoration classes I, II, and IV that bear stress. The flexural test is likewise a strategy that relates well to tensile failure. The ISO 4049 standard for composite restorative materials only specifies flexural strength, which must be at least 80 MPa for occlusal tooth surface restorations and 50 MPa for all other types (Stencel *et al.*, 2018). However, the large bar specimens (25 x 2 x 2 mm) required by ISO 4049 are difficult to prepare without error, especially in compile packaging. As the exit window of all clinical light-cure units is smaller than 25 mm, requiring multiple overlapping exposures. As a result, this leads to an inhomogeneous sample because punctate areas that are exposed to twice as much curing time cannot be avoided (Yap & Teoh, 2003; Calabrese *et al.*, 2015). Material fracture caused by external forces is a common cause of composite resin failure. A flexural strength test is used to determine the material's fracture resistance for this reason (Li *et al.*, 2019).

2.9.4 Hardness of rice husk nanohybrid composites

Hardness is a quantitative measure of resistance to deformation and is determined by dividing the maximum load by the expected contact area. The ratio of applied load to the total contact area determines Vickers hardness. As a result, the Vickers test was chosen for its maximum accuracy (Ehrmann, Medioni & Brulat-bouchard, 2019). Researchers have not reached an agreement on a standard Vickers hardness value. However, resin-based composite (RBC) requires a hardness value of greater than 50 Vickers hardness (VHN) (Hanif & Ghani, 2020).

2.9.5 Translucency of rice husk nanohybrid composites

The colour difference for a homogeneous thickness of a material on a white or black backdrop is referred to as the translucency parameter (TP). Numerous researchers have examined the TP values of dental porcelain and resin composites using the TP technique, which is an excellent way to assess translucency (Park, 2013). The translucency parameter (TP) was created to characterise the masking power of transparent materials and was initially used to evaluate optimal white and black backings (Hyun *et al.*, 2017). Following the main colour, translucency has been considered an essential feature, and it is also one of the most crucial elements in verifying the aesthetic performance of dental restorations (Y.-K. Lee, 2015).

The contrast ratio or translucency parameter has been used in numerous studies to assess the transparency of particular resin composites, recognising that it is a crucial feature equal in importance to the composite's shade (Ryan, Tam & McComb, 2010). The structure of resin composites, which consists of a very transparent basic resin, tiny filler particles, and additional additives, makes them appear translucent from a distance. Small filler particles in the material cause white incident light to be multiplied and scattered before exiting and carrying material-specific optical and color information to the detector (Park, 2013).

Translucency is one of the most important factors in matching the appearance of natural teeth, and it has been highlighted as a crucial element in managing aesthetics and material selection (Carrabba *et al.*, 2017). The translucency of dental tissues and materials is an essential characteristic. As a result, in addition to more widely used metrics like brightness (L*), a* and b* (CIELAB coordinates), hue angle (h), and chroma (C*), for improving optical qualities (Salas *et al.*, 2018).

The inorganic filler is the major component of composite resins and has a considerable impact on translucency. Many researchers have investigated the consequence of filler type, particle size, and content on the dental composites' translucency (Azzopardi *et al.*, 2009). Colour and translucency of aesthetic and restorative materials are thought to be affected by filler particles, opacifiers, the composition of the resin matrix, flowability, light curing, and resin polymerization. According to a previous study, the greater the difference in refractive index between the filler and matrix, the more opaque the resin. This phenomenon is caused by multiple refractions and reflections that exist at the contact of the filler and the matrix (Darabi *et al.*, 2014).