POLYMERIZATION SHRINKAGE, DEGREE OF CONVERSION OF ZIRCONIA REINFORCED RICE HUSK NANOHYBRID COMPOSITE AND ITS FRACTURE STRENGTH ON THE ENDODONTICALLY TREATED MAXILLARY INCISORS

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2020

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by

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Thesis submitted in fulfilment of the requirement
For the degree of
Master of Science

NOVEMBER 2020

ACKNOWLEDGEMENT

First and foremost, I would like to extend my warmest gratitude to my God for His blessings and wisdom given to me during the entire Master’s programme.

I would also like to express my sincere appreciation to Dr. Nik Rozainah Nik Abdul Ghani, my main supervisor, for the continued support of my Master's degree and related research, for her patience, motivation and immense knowledge. Her guidance has helped me through the entire research and writing process of this thesis.

Besides, I would like to thank my other co-supervisors: Dr. Noor Huda Ismail, Prof. Dr. Kiran Singbal, and Dr. Noraida Mamat for their insightful feedbacks and encouragement, that inspired me to extend my work from different perspectives.

Special thanks to Universiti Sains Malaysia Fellowship scheme, University Grant Scheme 1001/PPSG/8012215 and Short-Term Grant Scheme 304/PPSG/6316456 for financial support. I am grateful to all the staff at the Multidisciplinary Laboratory (MDL), the Polyclinic C and the Material Testing Lab, the School of Dental Sciences, Universiti Sains Malaysia who have given me access to the laboratory and research facilities.

Furthermore, I would also like to express my deep gratitude to my family and friends for giving me endless support throughout my studies. Finally, I also record my appreciation for one and all of those who have lent their hands directly or indirectly to my Master’s programme.

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LIST OF SYMBOLS

%	Percentage
w/w	Weight by weight
µm	Micrometre
Cm	Centimetre
Nm	Nanometre
Mm	Millimetre
~	Approximate
W/mK	Watt per metre-kelvin
ºC	Degree Celsius
g/cm^3	Gram per cubic centimetre
cm^{-1}	Wavelength
N	Newton
V	Volume
Vol	Volume
G	Gram
Kg	Kilogram
Ml	Millilitre
mW/cm^2	Milliwatt per square centimetre
J/cm^2	Joules per square centimetre

LIST OF ABBREVIATIONS AND ACRONYMS

ANOVA	Analysis of variance
AgO_2	Silver oxide
Bis-EMA	Ethoxylated bisphenol-A-di-methacrylate
Bis-GMA	Bisphenol A-glycidyl methacrylate
BPA	Bisphenol A
CEJ	Cemento-enamel-junction
CQ	Camphorquinone
C=C	Carbon double bonds
DMAEMA	2-(N, N-dimethylamino)-ethyl-methacrylate
DMPT	N, N-dimethyl-p-toluidine
DSC	Differential scanning calorimetry
D_3MA	Decane diol di-methacrylate
EDTA	Ethylenediaminetetraacetic acid
EPR15	Electron paramagnetic resonance
ET	Endodontic treatment
et al.	And others
FTIR	Fourier Transform Infrared
GIC	Glass ionomer cement
HEMA	Hydroxyethyl methacrylate
HSD	Honest significant difference
HQ	Hydroquinone
ISO	International Organization for Standardization
LED	Light-emitting diode
LVDT	Linear vertical displacement transducer
MDL	Multi-disciplinary Laboratory
microCT	Micro computed tomography
MIR	Multiple Internal Reflection
MOD	Mesio-occlusal-distal
MPD	Mesio-palatal-distal

NaOCl	Sodium hypochlorite
NIR	Near-infrared spectroscopy
NiTi	Nickel-titanium
NMR9	Nuclear magnetic resonance
NPG-GMA	N-phenyl glycine glycidyl methacrylate
OCT	Optical coherence tomography
OPPI	p-octyloxy-phenyl-phenyl iodonium hexafluoro-antimonate
PDL	Periodontal ligament
PEG	Polyethylene glycol
PEGDMA	Polyethylene glycol di-methacrylate
PMMA	Polymethyl methacrylate
PPD	1-phenyl-1,2-propanedione
SD	Standard deviation
SPSS	Statistical Package for the Social Sciences
TEG	Triethylene glycol
TEGDMA	Tri-ethylene glycol dimethacrylate
TiO_2	Titanium dioxide
UDMA	Urethane di-methacrylate
USM	Universiti Sains Malaysia
UTMA	Urethane tetra-methacrylate
UV	Ultraviolet
QTH	Quartz tungsten halogen
RMGIC	Resin modified glass ionomer cement
rpm	Round per minute
Y-TZP	Yttria tetragonal zirconia polycrystal
Zr	Zirconia
ZrO_2	Zirconium dioxide
γMPTS	γ-methacryloxypropyl-triethoxysilane
4-EDMAB	Ethyl-4-(dimethylamino) benzoate
π-π	Pi bonds

PENGECUTAN POLIMERISASI, TAHAP PENUKARAN KOMPOSIT ZIRCONIA DIPERKAYAKAN DENGAN SEKAM PADI DAN KEUPAYAANNYA PADA DAYA TAHAN PATAH PADA GIGI SERI LATERAL RAHANG ATAS YANG MENERIMA RAWATAN ENDODONTIK

ABSTRAK

Kajian ini bertujuan untuk mengkaji pengecutan polimerisasi, tahap penukaran dan daya tahan patah gigi seri lateral rahang atas yang diberi rawatan endodontik menggunakan komposit nanohybrid campuran sekam padi dan diperkuatkan oleh zirkonia berbanding menggunakkan komposit mikrohybrid dan nanofilled yang dipasarkan. 180 sampel digunakan untuk ujian pengecutan polimerisasi dan tahap penukaran di mana mereka dibahagikan kepada Kumpulan 1 - komposit nanofilled (Filtek-Z350-XT), Kumpulan 2 - komposit mikrohybrid (Zmack-Comp) dan Kumpulan 3 - komposit nanohybrid eksperimen (Zr -Hiybrid). Ujian pengecutan polimerisasi dilakukan dengan kaedah apungan dan optikal. Untuk kaedah daya apung, sampel ditimbang di udara dan air untuk mengira nilai penyusutan, manakala, untuk kaedah optik, gambar sampel sebelum dan selepas penyembuhan cahaya ditangkap menggunakan mikroskop untuk mengira nilai penyusutan. Tahap penukaran diuji dengan spektrometer FTIR. Untuk ujian daya tahan patah, lapan puluh gigi kekal seri lateral rahang atas dipilih dan dibahagikan kepada: Kumpulan 1 - ET + Filtek-Z350-XT, Kumpulan 2 - ET + Zmack-Comp, Kumpulan 3 - ET + Zr-Hybrid dan Kumpulan 4 - Gigi tidak dirawat (kawalan). Rongga MPD standard disiapkan, dan rawatan endodontik dilakukan dengan menggunakan teknik Korona-kebawah hingga ukuran 30. Obturasi diselesaikan menggunakan teknik satu kon gutta-percha dan bahan bancuhan tampalan AH Plus. Akses rongga diisi dengan resin komposit masing-masing. Seterusnya, gigi disimpan di dalam inkubator selama 24 jam dan dibahagikan kepada subkumpulan yang berumur dan yang tidak berumur. Gigi subkumpulan berumur mengalami 2500 kitaran termal. Selepas itu, semua gigi diuji di bawah Mesin Uji Universal sehingga patah. Mereka kemudian dilihat di bawah mikroskop untuk menentukan corak dan jenis patah. Data dianalisis menggunakan ANOVA Sehala untuk pengecutan polimerisasi, tahap penukaran dan daya tahan patah. Corak dan jenis patah dianalisis menggunakan ujian ‘Chi-square’. Zr-Hybrid menunjukkan nilai penyusutan yang setanding ($p>0.05$) dengan Filtek-Z350-XT, tetapi pengecutan yang lebih rendah ($p<0.05$) daripada Zmack-Comp. Zr-Hybrid menunjukkan tahap penukaran yang lebih tinggi ($p<0.05$) daripada Filtek-Z350-XT dan nilai penukaran yang setanding dengan Zmack-Comp. Tambahan pula, ET + Zr-Hybrid menunjukkan daya tahan patah tertinggi dalam subkumpulan yang berumur dan yang tidak berumur. Daya tahan patah menurun dengan ketara bagi ET + Filtek-Z350-XT dan ET + Zmack-Comp ($p<0.05$) apabila kitaran termal meningkat, tetapi tiada perbezaan yang ketara bagi ET + Zr-Hybrid dan kawalan Kumpulan 4. Selain itu, ET + Zr-Hybrid dan kawalan Kumpulan 4 menunjukkan corak patah yang lebih baik. Kesimpulannya, Zr-Hybrid menunjukkan nilai pengecutan dan penukaran yang bagus. Gigi yang dirawat endodontik dan diisi dengan Zr-Hybrid menunjukkan kekuatan daya tahan patah yang unggul dan corak patah yang baik.

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ABSTRACT

The present study aimed to compare the polymerization shrinkage, degree of conversion and fracture strength of endodontically treated maxillary lateral incisors restored using novel zirconia reinforced rice husk nanohybrid composite with commercialized microhybrid and nanofilled composites. 180 samples were used for polymerization shrinkage and degree of conversion tests, divided into Group 1 – nanofilled composite (Filtek-Z350-XT), Group 2 – microhybrid composite (Zmack-Comp) and Group 3 – experimental nanohybrid composite (Zr-Hybrid). The test for polymerization shrinkage was performed using buoyancy and optical methods. For the buoyancy method, samples were weighed in air and water to calculate the shrinkage value, while for the optical method, images of samples before and after light-curing were captured using a microscope to calculate the shrinkage value. The conversion degree was tested using the FTIR spectrometer. Eighty mature permanent lateral maxillary incisors were selected for the fracture strength test and divided into: Group 1 – ET + Filtek-Z350-XT, Group 2 – ET + Zmack-Comp, Group 3 – ET + Zr-Hybrid and Group 4 – Intact teeth (control). Standardised MPD cavity was prepared, and endodontic treatment was performed using crown-down technique up to size 30. Obturation was completed using single cone technique with gutta-percha and AH Plus sealer. Cavity access was restored with respective composite resins. Next, the teeth were stored in the incubator for 24 hours and subdivided into aged and non-aged subgroups. Teeth in aged subgroups underwent 2,500 thermal cycles. Subsequently, all teeth were tested under the Universal Testing Machine until fractures occurred. They were then examined under a microscope to determine the fracture pattern and type of fracture. Data were analysed using One-way ANOVA for polymerization shrinkage, conversion degree and fracture strength. The fracture pattern and fracture type were analysed using the Chi-square test. Zr-Hybrid showed comparable shrinkage ($p>0.05$) to Filtek-Z350-XT, but lower shrinkage ($p<0.05$) than Zmack-Comp. Zr-Hybrid showed a higher conversion degree ($p<0.05$) than Filtek-Z350-XT and a comparable conversion value with Zmack-Comp. Besides, ET + Zr-Hybrid demonstrated the highest fracture strength in both aged and unaged subgroups. The fracture strength decreased significantly in ET + Filtek-Z350-XT and ET + Zmack-Comp ($p<0.05$) as the thermocycles increased but no significant differences were noted in ET + Zr-Hybrid and control Group 4. Moreover, ET + Zr-Hybrid and control Group 4 showed more favourable fracture pattern. In conclusion, Zr-Hybrid exhibited excellent shrinkage and conversion values. Endodontically treated teeth restored with Zr-Hybrid demonstrated superior fracture strength and favourable fracture pattern.

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Composite is a material composed of two distinct stages, typically involving a combination of components with different structures and properties (Radzi *et al.*, 2020). According to the Glossary of Prosthodontics terms, composite resin is defined as a highly cross-linked polymeric material reinforced by a dispersion of amorphous silica, glass, crystalline, or organic resin filler particles and/or short fibres bonded to the matrix by coupling agent ("The Glossary of Prosthodontic Terms: Ninth Edition," 2017). Dental composite resins are tooth-coloured materials that were introduced in the late 1950s and are commonly used in dentistry as restorative materials (Minguez *et al.*, 2003). Composite resins can be used as liners, pits and fissures sealants, inlays, onlays, veneers, core build-up, endodontic posts and also endodontic sealers (Ferracane, 2011).

They have many advantages over amalgam, such as improved aesthetic properties, capable of bonding to the tooth surface with the use of the adhesive system and allowing for better conservation and protection of the remaining tooth structure (Cramer *et al.*, 2011; Lin *et al.*, 2018; Pradeep *et al.*, 2013). Besides, composite resins are advocated to replace amalgam because they are mercury-free, less toxic, non-thermal conductive, and provide better colour matching with the tooth than amalgam (Bayne *et al.*, 2019).

The use of composite resin has increased drastically in modern preventive and restorative dentistry due to the aesthetic demands of patients. Composite resins can be classified into several types based on their filler particle sizes such as macrofilled, microfilled, hybrid and nanofilled, which will be further discussed in heading 2.3. Heliomolar® /Heliomolar® HB (Ivoclar Vivadent, Liechtenstein), Filtek™ Z350 (3M ESPE, St. Paul, US), Zmack Comp (Zhermack, Badia Polesine, Italy), Gradia™ Direct (GC America Inc., US), Brilliant EverGlow (Coltene, Altstätten, Switzerland) and Renamel® Universal Microhybrid (Cosmedent, Chicago, US) are some examples of the composite resins that are currently available in the market.

Despite continuous advances in composite resin, it still suffers from polymerization shrinkage of between 1% and 6% (Braga *et al.*, 2005; Ferracane, 2005; Kleverlaan and Feilzer, 2005). Polymerization shrinkage of composite resin occurs primarily due to the conversion of monomers into polymer chains, in which the van der Waals forces are replaced by covalent bonds, bringing the particles closer together (Kaisarly and Gezawi, 2016). This leads to the polymerization stress on the interfaces, causing gap formation at the dentine-bond interface, increasing the risk of recurrent caries and consequently, restoration failures (Al Sunbul *et al.*, 2016).

Several methods have been described to reduce polymerization shrinkage such as using incremental placement of composite resin into the prepared tooth cavity, soft start light-curing technique, placing stress absorbing liners, use of composite resin with higher filler content or alteration of the resin matrixes in composite material (Al Sunbul *et al.*, 2016; Kaisarly and Gezawi, 2016).

The degree of conversion also has a major impact on the success of composite resin restorations. During polymerization, the physical and mechanical properties of composite resins are directly affected by the conversion point (Moraes *et al.*, 2008a). The degree of conversion is determined by the proportion of the remaining aliphatic carbon-carbon, C=C double bonds in a polymerized sample to the total number of C=C bonds in the non-polymerized sample. Ideally, composite resin should have converted all its monomer to polymer. A lower degree of conversion will result in a reduction in the binding of polymer network, leading to a decrease in polymerization shrinkage (Anusavice *et al.*, 2012).

Endodontic treatment is indicated for the preservation of teeth that have been implicated in pulpal infection mainly due to extensive caries and decay (Liang, 2010). During the treatment procedure, a large amount of tooth structure will be lost and consequently weaken the whole tooth structure. Therefore, the teeth require a resilient permanent restoration to protect them from fractures and provide adequate coronal seal to prevent recurrent infection (Lin *et al.*, 2018).

Inevitably, endodontically treated anterior teeth need more attention because they are subjected to a higher degree of shear force than posterior teeth due to their anatomical location and inclination in the dental arch (Naumann *et al.*, 2012). Moreover, anterior teeth are much more likely to be subjected to horizontal loads as compared to posterior teeth, and this is a critical factor because horizontal load can result in a higher stress concentration within the tooth dentine, contributing to a higher probability of tooth fracture (Wandscher *et al.*, 2016).

For many years, full crown coverage offered predictable and reliable results for endodontically treated teeth, in particular incisors (Valdivia *et al.*, 2018; von Stein-Lausnitz *et al.*, 2018). This approach is undoubtedly invasive and will result in the removal of a large amounts of sound tooth structure. Composite resin has been chosen as one of the direct permanent restorations for endodontically treated teeth because it has been shown to exhibit excellent performance in terms of fracture resistance (Lin *et al.*, 2018; Mannocci *et al.*, 2002). Furthermore, with the current concept of adhesive technology in dentistry, clinical approach has moved towards achieving the goal of conserving the remaining tooth structure and reducing the necessary amount of intervention (Anusavice *et al.*, 2012; Chen, 2010).

Owing to the advancement of nanotechnology in adhesive dentistry, nanocomposites were introduced which continuously reduced the size of the filler particles incorporated into the resin matrix of composites, resulting in nanohybrid and nanofilled materials with improved physical and mechanical properties (Chen, 2010; Hegde *et al.*, 2011; Watanabe *et al.*, 2008).

Eco-friendly biocomposite has started to gain popularity among researchers in which natural products were incorporated into composite resins. A group of researchers from Universiti Sains Malaysia have released a new nanohybrid composite resin prototype that uses silica obtained from rice husk as a filler (Noushad *et al.*, 2016). The benefits of using natural resources in dental composites are ascribed to lower cost, lower toxicity, higher sustainability, lighter weight and more environmentally friendly (Noushad *et al.*, 2016). In view of a more innovative approach, the present study added 10% w/w of zirconia nanopowder to this rice husk nanohybrid composite resin to reinforce the material.

Zirconia is nowadays widely used as an alternative to alumina in the field of restorative dentistry, including the construction of crowns, bridges, and implants owing to its optimum properties such as: excellent wear resistance, biocompatibility, superior toughness, strength, and high fatigue resistance (Bona *et al.*, 2015). Furthermore, the 5-year survival rate of zirconia-ceramic implant-supported fixed partial dentures was reported to be as high as 93% (Sailer *et al.*, 2018). The present zirconia reinforced rice husk nanohybrid composite can, therefore, be expected to exhibit a high fracture toughness on endodontically treated teeth to provide long-term success.

1.2 Problem statement and justification of this study

The manufacturer of advanced dental materials with reduced polymerization shrinkage and improved degree of conversion or depth of cure together with better physical and mechanical strengths are of the prime interest in dentistry and material science. Among these dental materials, composite resins have been widely used due to their excellent properties (Pratap *et al.*, 2019).

With the advancement of dentistry, research has led to the production of new types of nanofilled and nanohybrid composite resins. While nanofilled composite resins consist of nano-sized particles in their compositions, nanohybrids take the approach by adding nanometric and conventional fillers together (Chen, 2010). The combination of nanometric and conventional microfillers in nanohybrid composite is somehow identical to those microhybrid composites, thus giving mechanical properties that are almost similar (Mitra *et al.*, 2003). Therefore, one can speculate that nanohybrid composite resin may still suffer from the loss of large particles, as does microhybrid, and it is questionable whether new nanohybrid composites are an innovative material to be more superior than nanofilled composite resin (Moraes *et al.*, 2008b).

There are still many disputes over the selection of the most suitable dental composites for endodontic treatment in anterior teeth. Although amalgam is sometimes used to restore the lingual pits of anterior teeth (Gladwin and Bagby, 2018), the placement of this material on anterior teeth has reduced in popularity among clinicians due to the grey-metallic amalgam colour, as opposed to composite resins that resemble the colour of natural teeth (Hervas-Garcia *et al.*, 2006).

Although the previous study proclaimed that rice husk nanohybrid composite showed acceptable flexural strength, hardness value and flexural modulus (Noushad *et al.*, 2016), the data on polymerization shrinkage and the degree of conversion of this new material are very limited in the literature. Composite resins with a high filler-matrix ratio are known to reduce the polymerization shrinkage, but this leads to a gradual decrease in the conversion rate because filler particles act as an obstacle to polymer chain propagation (Pratap *et al.*, 2019). The achievement of maximum degree of conversion and minimum polymerization shrinkage of dental composite resins has always been a challenge for the researchers. Moreover, no *in-vitro* study has been conducted to evaluate the fracture strength and fracture pattern of endodontically treated teeth restored with this new rice husk nanohybrid composite material.

The present research is, therefore, being conducted as part of a larger project to assess the polymerization shrinkage, degree of conversion and fracture strength of endodontically treated teeth restored with a novel zirconia reinforced rice husk nanohybrid composite compared to other commercially available composite resins. The results of this study will provide a new insight and better understanding of this new zirconia reinforced nanohybrid composite using rice husk silica filler in clinical applications.

It can be anticipated that this novel nanohybrid composite is able to demonstrate better physical properties compared to commercially available composite resin due to the reinforcement of zirconia (Guo *et al.*, 2012), thus increasing the resistance of endodontically treated teeth to fracture. As a result, the long-term success of endodontic treatment is expected. Moreover, the development of this locally produced novel nanohybrid composite is more environmentally friendly as it is composed of biomass waste, rather than adding more chemical components and eventually reducing the material’s cost.

1.3 Research objectives

1.3.1 General objective

To evaluate the polymerization shrinkage, degree of conversion of zirconia reinforced rice husk nanohybrid composite and its fracture strength on endodontically treated maxillary lateral incisors.

1.3.2 Specific objectives

1. To compare the polymerization shrinkage of zirconia reinforced rice husk nanohybrid composite to commercialized nanofilled and microhybrid composites using buoyancy and optical methods.

2. To compare the degree of conversion of zirconia reinforced rice husk nanohybrid composite to commercialized nanofilled and microhybrid composites using Fourier transform infrared (FTIR) spectroscopy.

3. To compare the fracture strength of endodontically treated maxillary lateral incisors restored with zirconia reinforced rice husk nanohybrid composite and commercialized nanofilled and microhybrid composites before and after artificial ageing.

4. To compare the fracture pattern of endodontically treated maxillary lateral incisors restored with zirconia reinforced rice husk nanohybrid composite and commercialized nanofilled and microhybrid composites

1.4 Research questions

1. Does zirconia reinforced rice husk nanohybrid composite show lower shrinkage value compared to nanofilled and microhybrid composites?

2. Does zirconia reinforced rice husk nanohybrid composite show higher degree of conversion compared to nanofilled and microhybrid composites?

3. Do endodontically treated maxillary lateral incisors restored with zirconia reinforced rice husk nanohybrid composite show higher fracture strength compared to those restored with nanofilled and microhybrid composites even after artificial ageing?

4. Do endodontically treated maxillary lateral incisors restored with zirconia reinforced rice husk nanohybrid composite show more favourable fracture pattern compared to those restored with nanofilled and microhybrid composites?

1.5 Research null hypotheses

1. There is no significant difference between zirconia reinforced rice husk nanohybrid composite and other types of composite resin in terms of polymerization shrinkage.

2. There is no significant difference in the degree of conversion between zirconia reinforced rice husk nanohybrid composite and other types of composite resin.

3. There is no significant difference in fracture strength between endodontically treated maxillary lateral incisors restored with zirconia reinforced rice husk nanohybrid composite and those restored with other types of composite resin.

4. There is no significant difference in fracture pattern between endodontically treated maxillary lateral incisors restored with zirconia reinforced rice husk nanohybrid composite and those restored with other types of composite resin.

CHAPTER 2

LITERATURE REVIEW

2.1 History of composite resin in dentistry

A direct semi-aesthetic filling material, silicate cement, was introduced in 1908 to replace amalgam due to the concern for elemental mercury and the potential for mercury toxicity by amalgam when used as a dental restorative material (Schulein, 2005). It was recommended that silicate cement be used for small restorations in anterior teeth of patients at high caries risk due to its ability to release fluoride (Anusavice *et al.*, 2012).

Unfortunately, the long-term efficacy of silicate cement was found to be reasonably low due to its high solubility in the oral cavity (Schulein, 2005). As a result, self-cure polymethyl methacrylate (PMMA) with quartz particles was introduced in the 1950s to address the limitations of silicate cement and provide a better strengthening effect, but issues of high shrinkage and poor abrasion resistance of PMMA have raised concern among clinicians (Bayne *et al.*, 2019).

Later in the early 1970s, Bowen introduced resin consisting of bisphenol A-glycidyl methacrylate, also known as 2,2 bis [4-2(2-hydroxy-3-methacryloyloxypropoxy)-phenyl] propane (Bis-GMA) and inorganic particles as an alternative to silicates and unfilled resins. This composite resin formulation exhibited superior mechanical properties to silicates and unfilled resins (Chen, 2010; Minguez *et al.*, 2003). However, this type of resin required longer mixing times compared to silicate cements. The mixing process and the bond strength of the material to the tooth structure were therefore considered to be major problems (Hervas-Garcia *et al.*, 2006). Plus, acrylic resins were not indicated for restoring posterior teeth due to their low mechanical strength, high coefficient of thermal expansion and high polymerization shrinkage resulting in microleakage and discolouration of the restoration (Anusavice *et al.*, 2012).

In the late 1970s, acrylic resin was replaced by composite resins that appeared to improve the physical properties and solve the mixing problem by using electromagnetic radiation (Anusavice *et al.*, 2012). The filler particles of the first invented composite resin were too large and only four types of colour shades were available with a poor polish ability (Hervas-Garcia *et al.*, 2006). Additionally, poor colour stability, poor marginal adaptation due to high polymerization shrinkage and poor tooth surface adhesion have also been reported (Bayne *et al.*, 1994). Hence, due to all these negative results and findings, an intensive research study was conducted to mitigate the disadvantages of traditional composite resins.

Ultimately in 1978, microfilled composite resins were used by providing a smooth surface restoration with improved shrinkage and stain resistance (Minguez *et al.*, 2003). Nevertheless, the high surface area of the particles in microfilled composite resins limited the filler concentration which contributed to poor mechanical properties (Bayne *et al.*, 2019). Following the discovery of microfilled composites, research has been focused on the design of new hybrid composites, which were introduced in the 1980s, and then nanofilled composites in the early 2000s. The new composite resins offer greater strength and excellent polish ability as compared to microfilled composite resins (Minguez *et al.*, 2003).

The advancement in composite resin fabrication made it one of the options for permanent restoration in restoring a tooth. The choice for this material not only because of its excellent strength, but mainly because most patients prefer material that mimics natural teeth appearance. Composite resin also comes with several advantages, such as being able to bond to the tooth structure, thus allowing a more conservative approach. Besides, the ease of application, repairability and lack of mercury content compared to amalgam have made composite resins extensively used in dental restorative procedures (Bayne *et al.*, 1994; Minguez *et al.*, 2003).

2.1.1 Remarkable events in the evolution of composite resin

Other notable events in the evolution of composite resin include the advent of light-curing composite resin and the bonding system (Bowen and Marjenhoff, 1992). In the late 1990s, quartz tungsten halogen (QTH) was regarded as the gold standard for clinical use due to its satisfactory performance (Lee *et al.*, 2018). They are available in continuous, rampcure or step-cure modes. However, only about 5% of the total light produced by QTH is suitable for the curing of composite resin and most of the light energy is converted into heat (Lindberg *et al.*, 2004). Hence, QTH was gradually replaced by light-emitting diode (LED) because LEDs have a longer lifespan, lesser heat generated, and are capable of producing a narrower and more precise light spectrum compared to QTH (Anusavice *et al.*, 2012; Mills *et al.*, 1999).

The bonding of composite material to teeth involves the application of an acid to demineralize the enamel surfaces (Swift *et al.*, 1995). In 1955, Buonocore suggested the use of 85% phosphoric acid solution which was found to improve the adhesion of acrylic resin to enamel (Buonocore, 1955). Acid etching technique allows the formation of micro-mechanical retention between the etched enamel surfaces and the resin monomer via the penetration of monomers into the interprismatic spaces (Anusavice *et al.*, 2012). Enamel acid etching treatment will also change the enamel surfaces by removing the smear layer, increasing the permeability and micro porosity for a better adaptation of composite resin to the tooth structure (Swift *et al.*, 1995).

In the late 1960s, Bowen and Rodriguez hypothesized that N-phenyl glycine glycidyl methacrylate (NPG-GMA) could form a chemical bond with the dentinal wall leading to the manufacturer of NPG-GMA dentin bonding agents (Bowen and Rodriguez, 1962). This is the first-generation dentine adhesives. However, the bond strength to dentinal walls is still low due to the presence of hydrophobic structure in this adhesive system

(Fusayama *et al.*, 1979). New generation adhesive systems containing nanoscale particles with improved mechanical properties and penetration of the resin monomer were then subsequently introduced over the years (Hanabusa *et al.*, 2012).

2.2 Compositions of composite resin

Composite resins are a combination of inorganic filler particles widely dispersed within the organic resin matrix. They also contain initiators and activators that allow light-activated polymerization of the organic resin matrix to form a complex cross-linked polymer network (Chen, 2010). The basic constituents of composite resin are illustrated in Figure 2.1.

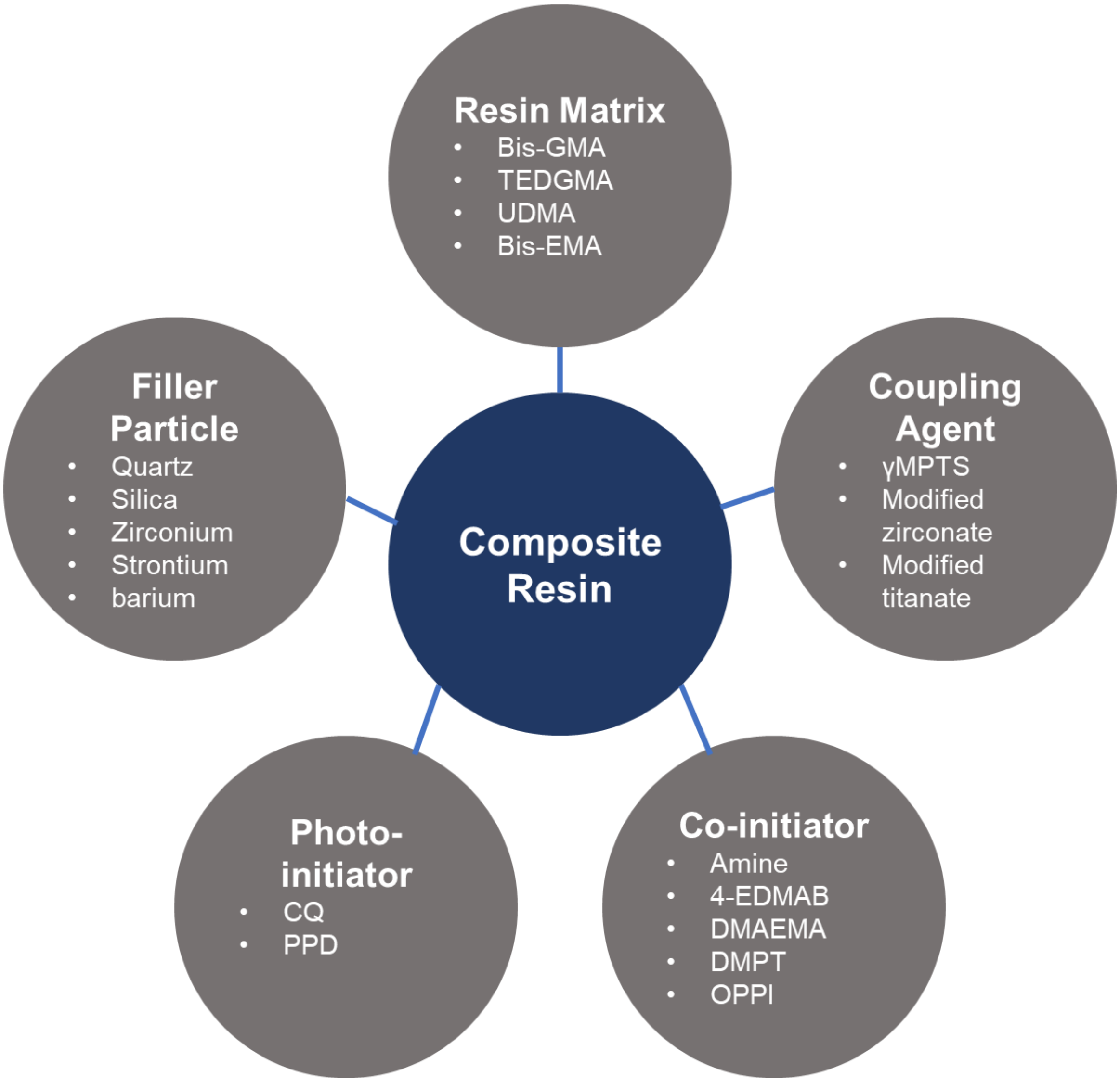

Figure 2.1: Components of composite resin used in dentistry

2.2.1 Resin matrix

Resin matrix can be the backbone of the composite resin network. Composite resin matrix typically consists of organic monomers which are mixed with few additional components such as filler particles, co-initiators, photo-initiators, inhibitors, and ultraviolet (UV) light stabilizers that vary from one composite manufacturer to another (Anusavice *et al.*, 2012; Radzi *et al.*, 2020). The interfacial phase of composite resin consists of either a bipolar coupling agent that binds the organic resin matrix and inorganic fillers together or a copolymeric bond that forms between the organic resin matrix and partial organic fillers (Hervas-Garcia *et al.*, 2006; Pratap *et al.*, 2019).

Most commercialised dental composites use Bis-GMA monomer as their organic matrix and make up approximately 20% by volume of the composite resin composition (Chen, 2010; Hervas-Garcia *et al.*, 2006). Bis-GMA monomer, first developed by Bowen in 1962 to replace acrylic resin, was found to have improved physical properties of composites (Bayne *et al.*, 2019). Furthermore, Bis-GMA monomer also allowed better application of the composite material since it does not require any mixing process of the base-paste, unlike acrylic resin (Hervas-Garcia *et al.*, 2006).

Bis-GMA, a colourless, solid organic compound with a melting temperature slightly above room temperature can be easily produced by reacting the o-alkylation of Bisphenol A (BPA) with epichlorohydrin (Pratap *et al.*, 2019). Bis-GMA has a stiff bisphenol central core and two pendant hydroxyl groups that can form strong hydrogen bond and are responsible for its high viscosity and low mobility (Floyd and Dickens, 2006; Pratap *et al.*, 2019). Hydroxyl groups in Bis-GMA help to increase its water sorption capacity, whereas the central phenyl core exhibits strong hydrogen π-π bonding, which is a type of non-covalent bonding (Pratap *et al.*, 2019). The chemical structure of Bis-GMA is illustrated in Figure 2.2.

The benefits of Bis-GMA in dental composites include higher modulus of elasticity, lower shrinkage, faster hardening and lower toxicity to the human body because Bis-GMA has lower tissue volatility and diffusivity (Peutzfeldt, 1997; Pratap *et al.*, 2019; Sideridou *et al.*, 2002). The high molecular weight of Bis-GMA allows it to demonstrate lower polymerization shrinkage with superior physical and mechanical strengths compared to other monomer forms (Peutzfeldt, 1997). The polymerization shrinkage of Bis-GMA was found to be as low as 0.9% with an average value of 1.5% (Anusavice *et al.*, 2012). Besides, it also displayed an excellent refractive index, which improved the optical properties of composite resin (Pratap *et al.*, 2019).

Nevertheless, Bis-GMA's high viscosity demonstrated several problems such as difficulty in handling the material and lower conversion of the resin monomer (Peutzfeldt, 1997). To minimize the viscosity of Bis-GMA, more diluent and versatile dimethacrylate monomers with lower molecular weight, such as tri-ethylene glycol di-methacrylate (TEGDMA), or urethane dimethacrylate (UDMA), should be added to achieve a viscosity level that is suitable for incorporating inorganic fillers (Kumar *et al.*, 2015; Peutzfeldt, 1997). The lower the viscosity of the resin matrix, the more fillers can be incorporated into the composite mixture.

There are several other resin monomers which are used in current commercial composite products such as TEGDMA, UDMA, ethoxylated bisphenol-A-di-methacrylate (Bis-EMA), hydroxyethyl methacrylate (HEMA), decane diol di-methacrylate (D_3MA), polyethylene glycol di-methacrylate (PEGDMA) and urethane tetra-methacrylate (UTMA) (Ferracane and Greener, 1986; Floyd and Dickens, 2006; Karmaker *et al.*, 1997; Pratap *et al.*, 2019).

TEGDMA (Figure 2.3) is formed when methacrylic acid reacts with triethylene glycol (TEG) and creates a bond between methacrylate groups and each end of the TEG (Pratap *et al.*, 2019). TEG is a reaction product resulting from the high-temperature oxidation of ethylene in the presence of silver oxide (AgO_2) catalyst which forms ethylene oxide (Pratap *et al.*, 2019). The low viscosity of TEGDMA is probably attributed to the weak bonding interaction between each TEGDMA chain and its flexible backbone structure (Goncalves *et al.*, 2009).

As described above, TEGDMA has low molecular weight and is therefore, highly flexible in order to compensate the rigidity of Bis-GMA and forms composite resins with a higher degree of conversion (Asmussen and Peutzfeldt, 2001b). During polymerization, Bis-

GMA and TEGDMA will form a strong acrylic bond with the filler particles to exhibit a three-dimensional network that produces good mechanical and chemical properties (Ferracane, 2011; Peutzfeldt, 1997; Pratap *et al.*, 2019).

Although TEGDMA has two functional methacrylate groups, like Bis-GMA, there is a linear chain between the two methacrylate groups, giving TEGDMA a relatively lower viscosity compared to Bis-GMA. Hence, due to its lower viscosity, TEGDMA has shown to improve the handling of composite resins and allowed more fillers to be incorporated into the composite mixture (Kumar *et al.*, 2015).

With a greater amount of filler loading, it can be speculated that the physical and mechanical properties of composite resins such as the strength, coefficient of thermal expansion and stiffness can be greatly improved (Amirouche-Korichi *et al.*, 2009; Lin-Gibson *et al.*, 2009; Rastelli *et al.*, 2012). However, the drawbacks of adding TEGDMA to resin matrix include higher water sorption, lower colour stability and greater polymerization shrinkage with an increased risk of marginal restoration leakage (Pratap *et al.*, 2019; Sideridou *et al.*, 2003).

Urethane dimethacrylate, UDMA (Figure 2.4), was first introduced by Foster and Walter in 1974 through the synthesis of hydroxyalkyl methacrylate and diisocyanates (Polydorou *et al.*, 2009). The most commonly used monomer of this type of resin is the reaction product of 2-hydroxyethyl methacrylate and 2, 4, 4-trimethyl-hexamethylenediisocyanate (Peutzfeldt, 1997). Unlike Bis-GMA, UDMA has no phenol ring in its monomer chain. This allows UDMA to show higher flexibility, greater mobility, lower viscosity and weaker intermolecular bonds that lead to an increased in physical strength and degree of conversion (Floyd and Dickens, 2006; Polydorou *et al.*, 2009).

Besides, UDMA may be used either alone or in combination with TEGDMA and Bis-GMA (Peutzfeldt, 1997). A study was conducted by Khatri *et. al*. showed that UDMA exhibited higher viscosity than TEGDMA and Bis-EMA, but lower than Bis-GMA, due to amino groups in UDMA that form weaker hydrogen bonding as compared to hydroxyl groups in Bis-GMA (Floyd and Dickens, 2006; Khatri *et al.*, 2003). UDMA was also reported to demonstrate a higher polymerization rate and conversion value than Bis-GMA, but a lower degree of conversion when mixed with Bis-EMA (Alshali *et al.*, 2013; Stansbury and Dickens, 2001b).

Another monomer that can also be added into composite resin is Bis-EMA (Figure 2.5). Bis-EMA is an analogue of Bis-GMA in which the pendant hydroxyl group in Bis-GMA is replaced by an epoxy group (Peutzfeldt, 1997; Pratap *et al.*, 2019). Similar to Bis-GMA and TEGDMA, Bis-EMA consists of large homologous dimethacrylate molecules of ethoxylated BPA (Durner *et al.*, 2015).

Due to the absence of pendant hydroxyl groups in Bis-EMA that can form hydrogen bonding, the viscosity of Bis-EMA was found to be lower than Bis-GMA (Goncalves *et* *al.*, 2009). The advantages of adding Bis-EMA into composite material are its low water sorption, low viscosity and low polymerization shrinkage (Pratap *et al.*, 2019; Sideridou *et al.*, 2004). Despite its low viscosity, Bis-EMA still has a low conversion value (Sideridou *et al.*, 2002).

As more research were conducted on the resin matrix of composite resin, new resin technologies have been introduced such as modified UDMA resin with DX511 dimethacrylate structure to reduce polymerization shrinkage due to its high molecular weight compared to Bis-GMA and conventional UDMA (Ferracane, 2011). Dimer acid monomers (DADMA) with relatively high molecular weight have also been shown to exhibit higher degree of conversion with lower polymerization shrinkage than Bis-GMA (Lu *et al.*, 2010). Procrylat, 2-2-bis-4-(3-hydroxy-propoxy-phenyl) propane dimethacrylate has been marketed and was found to have a lower viscosity than Bis-GMA (Radzi *et al.*, 2020). Nevertheless, Bis-GMA still constitutes the vast majority of the resin matrix available commercially for composite restoration.

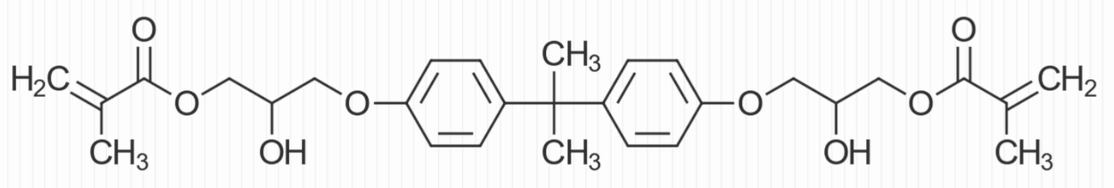

Figure 2.2: Chemical structure of Bis-GMA

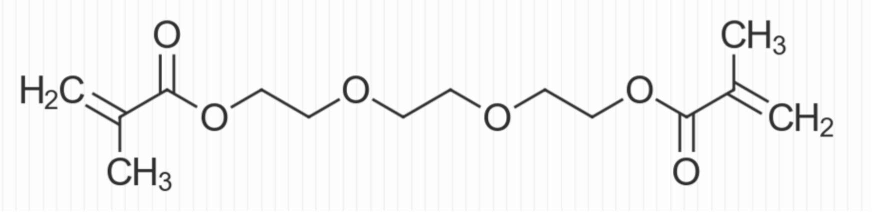

Figure 2.3: Chemical structure of TEGDMA

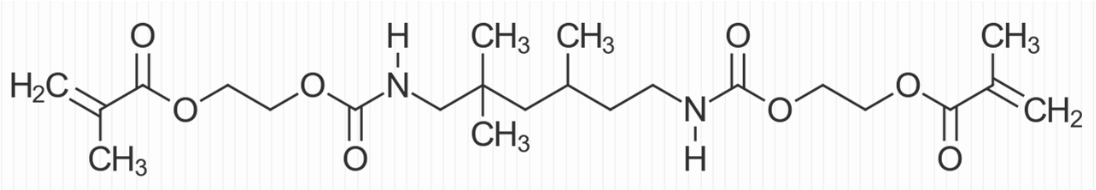

Figure 2.4: Chemical structure of UDMA

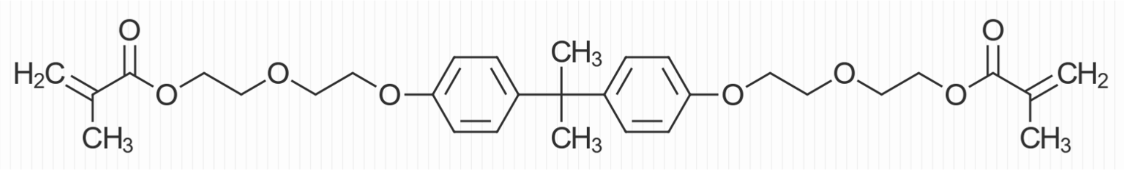

Figure 2.5: Chemical structure of Bis-EMA