DEVELOPMENT AND CHARACTERIZATION OF FLOWABLE COMPOSITE DERIVED FROM RICE HUSK USING URETHANE DIMETHACRYLATE

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by

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LIST OF SYMBOLS

<	less than
>	greater than
µg	microgram
µL	microliter
µm	micrometer
cm	centimeter
df	degree of freedom
g	gram
GPa	Gigapascal
kN	kiloNewton
kV	kilovolt
L	liter
M	molar
mA	milliampere
mL	milliliter
mm	millimeter
mm^3	millimeter cubic
MPa	Megapascal
nm	nanometer
º	degree
Pa·s	Pascal-second
s^{-1}	per second
α	alpha
γ	gamma
θ	theta

ρ	density
$\sim$	tilde

LIST OF ABBREVIATIONS

ADA	American Dental Association
AFM	Atomic force microscopy
ANOVA	Analysis of variance
ATR	Attenuated total reflectance
BisGMA	Bisphenol A glycidyl methacrylate
BisMEPP	Bisphenol A ethoxylate dimethacrylate
CAS	Chemical Abstracts Service
CQ	Camphorquinone
DMAEMA	2-(dimethylamino)ethyl methacrylate
DMTA	Dynamic Mechanical Thermal Analysis
DSLR	Digital single-lens reflex
ESR	Electron Spin Resonance
FC	Flowable composite
FTIR	Fourier transform infrared
ISO	International Organization for Standardization
JPEG	Joint Photographic Experts Group
LED	Light-emitting diode
MPS	[3-(Methacryloloxyl)propyl]trimethoxysilane
MPS	Methacryloxypropyltrimethoxysilane
NaOH	Sodium hydroxide
SD	Standard deviation
SEM	Scanning electron microscope
SFE	Surface free energy
TEGDMA	Triethylene glycol dimethacrylate
UDMA	Urethane dimethacrylate

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PEMBANGUNAN DAN PENCIRIAN KOMPOSIT BOLEH ALIR DIPEROLEH DARIPADA SEKAM PADI MENGGUNAKAN URETANA DIMETAKRILAT

ABSTRAK

Kajian ini bertujuan untuk membangunkan dan mencirikan komposit boleh alir menggunakan silika yang diperoleh dari sekam padi sebagai pengisi utama, uretana dimetakrilat (UDMA) sebagai monomer asas dan zirkonia sebagai agen radiolegap. Matriks resin menggabungkan UDMA dengan trietilena glikol dimetakrilat (UDMA:TEGDMA) pada nisbah 20:80, 30:70, 50:50, 60:40, 80:20, dan 90:10. Komposit aliran komersial, termasuk Revolution Formula 2, G-aenial Universal Flo, dan Filtek Supreme Flowable Composite, digunakan sebagai perbandingan. Komposit alir baharu ini dikategorikan sebagai aliran tinggi (20:80, 30:70), sederhana (50:50, 60:40), dan aliran rendah (80:20, 90:10) berdasarkan keupayaan aliran. Komposit ini kemudiannya dicirikan dari segi sifat kimia, fizikal dan mekanikal, serta pengecutan pempolimeran. Data kajian dianalisis secara statistik menggunakan ANOVA sehala untuk semua set data, diikuti dengan ujian post hoc Tukey atau Games-Howell untuk tujuan perbandingan, kecuali bagi kedalaman pengerasan, yang dianalisis menggunakan ujian Kruskal Wallis. Sifat kimia, yang dinilai melalui analisis fourier transmisi infra merah (FTIR) dan darjah penukaran, mengesahkan kehadiran silika dan zirkonia di dalam komposit baharu mudah mengalir serta menunjukkan peningkatan dalam darjah penukaran pada nisbah UDMA yang lebih tinggi (55.38 – 68.58%). Sifat fizikal yang dinilai merangkumi radiolegapan, kelikatan, kedalaman pengerasan, kekasaran permukaan, penyerapan air dan keterlarutan, serta kebolehbasahan. Komposit baharu mudah mengalir pada semua nisbah didapati bersifat radiolegap (2.87 – 3.06 mmAl) dan memenuhi piawaian International Organization for

Standardization 4049 (ISO 4049). Seiring dengan peningkatan nisbah UDMA dalam komposit baharu yang boleh mengalir, kelikatan dan kedalaman pengerasan turut meningkat. Kekasaran permukaan yang lebih baik dan penyerapan air yang lebih rendah turut diperhatikan dengan peningkatan nisbah UDMA. Bagi keterlarutan, nilainya tidak dipengaruhi oleh nisbah UDMA. Kebolehbasahan, yang dinilai melalui pengukuran sudut sentuh, menunjukkan peningkatan yang bererti dalam nilai sudut selepas pempolimeran, menandakan peralihan daripada tingkah laku hidrofilik (24.218 – 50.617º) kepada lebih bersifat hidrofobik (85.901 – 88.669º). Sifat mekanikal yang dinilai merangkumi kekerasan Vickers, kekuatan lenturan dan modulusnya, serta kekuatan mampatan dan modulusnya. Kebanyakan sifat ini bertambah baik dengan peningkatan nisbah UDMA, dengan beberapa nilai kekuatan lenturan (79.61 – 102.1 MPa) memenuhi keperluan minimum yang ditetapkan oleh ISO 4049. Pengecutan pempolimeran turut berkurangan dengan peningkatan nisbah UDMA. Secara keseluruhan, nisbah UDMA yang lebih tinggi (80:20, 90:10) menunjukkan sifat kimia, fizikal dan mekanikal, serta pengecutan pempolimeran, yang lebih rendah. Nisbah sederhana (50:50, 60:40) dan rendah (20:80, 30:70) masing-masing memperlihatkan prestasi sederhana dan rendah. Penemuan ini mencadangkan bahawa komposit baharu boleh mengalir yang dibangunkan terutamanya pada nisbah UDMA yang lebih tinggi, berpotensi untuk menjadi alternatif yang berdaya saing kepada komposit aliran komersial yang terdapat di pasaran, menyokong industri berasaskan hijau yang mengurangkan pembaziran dan mempromosikan kelestarian.

DEVELOPMENT AND CHARACTERIZATION OF FLOWABLE COMPOSITE DERIVED FROM RICE HUSK USING URETHANE DIMETHACRYLATE

ABSTRACT

The study aimed to develop and characterize flowable composites (FCs) using silica derived from rice husk as the primary filler, urethane dimethacrylate (UDMA) as the base monomer, and zirconia as the radiopacifying agent. The resin matrix combined UDMA with triethylene glycol dimethacrylate (UDMA:TEGDMA) at ratios of 20:80, 30:70, 50:50, 60:40, 80:20, and 90:10. Commercial FCs, including Revolution Formula 2, G-aenial Universal Flo, and Filtek Supreme Flowable Composite, were used for comparison. The newly developed FCs were categorized into high (20:80, 30:70), medium (50:50, 60:40), and low-flow (80:20, 90:10), based on the flowability evaluation. These newly developed FCs were subsequently characterized for their chemical, physical, and mechanical properties, as well as polymerization shrinkage. Data were statistically analyzed using one-way ANOVA, followed by posthoc Tukey or Games-Howell tests for comparison, except for the depth of cure, which was analyzed using the Kruskal-Wallis. The chemical properties, assessed through Fourier transform infrared (FTIR) and degree of conversion analyses, confirmed the presence of silica and zirconia in the newly developed FCs and showed an increase in the degree of conversion with higher UDMA ratios (55.38 – 68.58%). The physical properties evaluated included radiopacity, viscosity, depth of cure, surface roughness, water sorption and solubility, and wettability. The newly developed FCs at all ratios were radiopaque (2.87 – 3.06 mmAl) and passed the International Organization for Standardization 4049 (ISO 4049) requirement. As the UDMA ratio in the newly developed FCs increased, both viscosity and depth of cure increased.

Improved surface roughness and reduced water sorption were also observed with higher UDMA ratios. For solubility, the values were independent of the UDMA ratios. Wettability, assessed through contact angle measurements, revealed a significant increase in contact angle after polymerization, indicating a shift from hydrophilic (24.218 – 50.617º) to more hydrophobic behaviour (85.901 – 88.669º). The mechanical properties evaluated included Vickers hardness, flexural strength and modulus, and compressive strength and modulus. Most properties improved with increasing UDMA ratios, with some flexural strength values (79.61 – 102.1 MPa) meeting the requirement of ISO 4049. Polymerization shrinkage was also reduced as the UDMA ratio increased. Overall, higher UDMA ratios (80:20, 90:10) exhibited superior chemical, physical, and mechanical properties, along with reduced polymerization shrinkage. Moderate (50:50, 60:40) and lower UDMA ratios (20:80, 30:70) demonstrated intermediate and inferior performance, respectively. These findings suggest that the newly developed FCs, particularly at higher UDMA ratios, could serve as viable alternatives to commercially available FCs, supporting a green-based industry that reduces waste and promotes sustainability.

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Dental restorative materials are essential in treating caries, a prevalent condition affecting populations worldwide. The National Oral Health Survey 2020 reported that approximately 17 in 20 adults in Malaysia have experienced caries, with an average of 10 teeth affected per person (Ministry of Health Malaysia, 2020). Commonly used dental restorative materials include amalgam, glass ionomer cements (GICs) and resin composites. Dental amalgam, historically valued for its strength and durability (Moraschini et al., 2015), is being replaced due to environmental, health and aesthetic concerns associated with mercury. Glass ionomer cements, both conventional and resin-modified, are renowned for their biocompatibility and sustained fluoride release (Ge et al., 2024). While GICs and resin composites are both tooth-coloured restorative materials, resin composites demonstrate excellent clinical performance and are widely utilized for restoring both anterior and posterior teeth (Cribari et al., 2023), due to their superior properties such as higher strength and wear resistance (Rodrigues et al., 2015). Among them, flowable composites (FCs) are currently gaining attention due to their lower filler content and enhanced flowability, which improve their versatility in clinical applications (Nadgouda et al., 2023).

Since their introduction to dentistry in 1996, FCs have been widely used in preventive resin restorations, cavity lining, and pit and fissure sealants (Al-Rawas et al., 2022; Vouvoudi, 2022). These composites primarily consist of fillers and monomers, with filler content ranging from 37% to 53% by volume, which is lower than the 50% to 70% filler content found in conventional mini-filled hybrid composites (Baroudi & Rodrigues, 2015). The lower filler content results in a flowable character, reducing the

viscosity. This property allows FCs to be delivered in a syringe (Beun et al., 2008), ensuring a uniform and intimate spread on the tooth structure, as well as smooth, controlled flow during application.

Fillers play an important role in enhancing the strength of dental composites (Liu et al., 2021). In most dental composites, silica is the preferred filler due to its compatibility with resin monomers in terms of refractive index, robust mechanical properties, and good stability (Habib et al., 2016). Both synthetic silica (Rahim et al., 2011; Timpe et al., 2014) and silica derived from agricultural waste, such as rice husk, the outer grain of rice, has exhibited potential as fillers in resin composites (Zulkifli et al., 2013; Noushad et al., 2016; Lin et al., 2021) and flowable composites (Al-Rawas et al., 2021; Yusoff et al., 2019). Besides providing a good source of silica and an abundantly available, cost-effective resource (Noushad et al., 2016; Zulkifli et al., 2013), silica derived from rice husks also aligns with the waste-to-wealth, minimizing environmental pollution and waste management issues. However, its low atomic number (Z) results in radiolucency in dental radiography, posing diagnostic challenges (Bahaa et al., 2022; Ermis et al., 2014), which can be addressed by incorporating radiopacifying agents such as ytterbium trifluoride (Amirouche et al., 2007; Nicholson, 2023), strontium oxide, zirconium oxide, barium oxide, and barium sulphate (Amirouche et al., 2007). Among these, zirconium oxide or zirconia (ZrO_2) is commonly used due to its radiopacity (Alsharif et al., 2013; Hu et al., 2019; Bapat et al., 2022), esthetical appeal, biocompatibility (Aljamhan et al., 2022), bioinertness (Lin et al., 2021), and excellent physical and mechanical properties (Alhavaz et al., 2017; Hu et al., 2019; Li et al., 2020).

The incorporation and uniform dispersion of fillers in restorative materials is facilitated by the presence of monomers. A methacrylate-based monomer system,

typically consisting of basic and diluent monomers, ensures effective filler dispersion and optimal clinical handling (Dickens et al., 2003). Basic monomers, such as bisphenol A glycidyl methacrylate (BisGMA) and urethane dimethacrylate (UDMA), are highly viscous and have higher molecular weight than diluent monomers such as triethylene glycol dimethacrylate (TEGDMA). Compared to methyl methacrylate (MMA), one of the earliest small-sized dental monomers, BisGMA offers advantages such as higher modulus, less volumetric shrinkage, and reduced toxicity due to its lower volatility and diffusivity into tissues (Sideridou et al., 2002). However, its rigid molecular structure and high molecular weight limit the conversion of the double bond, necessitating a greater amount of co-monomers to enhance the degree of conversion and optimize filler loading (Asmussen & Peutzfeldt, 1998). Alternatively, UDMA possess several advantages, including greater structural flexibility, lower toxicity, reduced residual monomer content, lower water sorption (Barszczewska-Rybarek et al., 2020), and a refractive index value closer to that of silica fillers (Fujita et al., 2005). The combination of both basic and diluent monomers in specific ratios is crucial, as it directly influences the flowability and overall performance of dental resin composites (Li et al., 2022).

Previously, BisGMA-based FC has been successfully developed (Yusoff et al., 2019), however, the use of BisGMA exhibits limitations, making it less competitive than commercial FCs. To date, the development of FCs using UDMA as a base monomer at various ratios, in combination with rice husk-derived silica as the primary filler and zirconia as a radiopacifying agent, remains limited. Given that different monomer ratios affect certain mechanical properties, a comprehensive investigation is essential to assess the potential of these newly developed FCs for future clinical applications.

1.2 Problem statement

Dental caries remains a significant public health concern in Malaysia, with high prevalence among both children and adults, affecting their overall health, well-being, and quality of life. From the given number of Malaysian adults experiencing caries and with a number of teeth affected, approximately 6 in 10 adults require dental care due to tooth decay, as per the National Oral Health Survey for Adults 2020 (Ministry of Health Malaysia, 2020). Despite advancements in dental care, access to affordable, high-quality restorative materials is limited due to Malaysia's heavy reliance on imported products, which contributes to the high cost of dental treatments.

At the same time, Malaysia faces environmental pollution and waste management issues due to the abundantly available millions of tonnes of rice husk being discarded each year, with approximately 770000 tons of rice husk produced each year in Malaysia, of which 200 kg of rice husk is produced per tonne of rice (Wan-Mohtar et al., 2023). Improper disposal of rice husk, particularly through open burning that releases greenhouse gases such as carbon dioxide and methane (Alexandri et al., 2020; Wan-Mohtar et al., 2023), and landfilling that alters soil chemistry and leaches contaminants (Bashar et al., 2018), contributes to environmental hazards and increases the carbon footprint. To address these issues, Malaysia aims to reduce 50% of rice husk as waste (Wan-Mohtar et al., 2023), which, with such an alternative, has created the opportunity to address environmental sustainability and transform agricultural waste into wealth. As rice husk is rich in silica, it offers a sustainable source for the production of silica, useful as fillers in the development of restorative materials. The radiolucent property of silica can be aided by the incorporation of a radiopacifying agent, with zirconia offering radiopacity enhancement and excellent physical and mechanical properties, making it an ideal functional filler.

In addition to fillers, the choice of monomers significantly affects the performance of dental restorative materials. Urethane dimethacrylate has shown many advantages compared to Bis-GMA. Previously, a BisGMA-based FC was successfully developed (Yusoff et al., 2019), however, the use of BisGMA presents certain limitations. Its incorporation has been associated with inferior mechanical properties compared to commercial FC, reducing its clinical competitiveness and highlighting the need for alternative monomers such as UDMA. The combination of UDMA as a base monomer and TEGDMA as a diluent monomer, particularly at various ratios, remains underexplored. To date, the investigations on the silica derived from rice husk as a primary filler, and zirconia as a radiopacifying agent, incorporated with UDMA as a base monomer and TEGDMA as a diluent monomer at various ratios, are still limited. As this combination of various ratios of UDMA:TEGDMA affect certain mechanical properties, a comprehensive evaluation of the newly developed FCs is important to further explore their potential as dental restorative materials.

1.3 Justification of the study

Developing a locally sourced, cost-effective dental restorative material is crucial to addressing Malaysia's dependence on imported products and improving access to affordable dental care. Utilizing rice husk as a precursor for silica supports waste management efforts while aligning with Malaysia's target of reducing 50% of rice husk waste by 2025. Given its abundance and high silica content, rice husk presents a sustainable alternative for dental applications. The incorporation of zirconia as a radiopacifying agent further enhances the radiopacity of the FCs, ensuring better diagnostic accuracy in dental radiography. Additionally, the use of UDMA as a base monomer in varying ratios expands its application in restorative dentistry, aiming to

improve the previously BisGMA-based FC, which has some limitations. Despite these benefits, no locally produced FC is currently available, highlighting the need for this development.

By introducing these newly developed FCs, this study aims to provide an affordable alternative to imported materials, making high-quality dental care more accessible to Malaysians. This initiative aligns with Pillar 1 of Vision 2030, which emphasizes the universal availability, accessibility, and affordability of high-quality oral healthcare (Glick et al., 2021). Additionally, reducing the reliance on imports can stimulate local industries, foster a strong business network, and position Malaysia as a leading hub for dental research and innovation. By promoting a sustainable and economically beneficial approach to dental care, this development supports cost-effective solutions that enhance the quality of life and align with Sustainable Development Goal 3 (SDG 3), which advocates for health and well-being for all.

1.4 Objectives

1.4.1 General objective

This study was carried out to develop, prepare and characterize the newly developed FCs incorporating nanohybrid silica derived from rice husk as the main filler and UDMA as the base monomer at various ratios on the chemical, physical and mechanical properties, as well as polymerization shrinkage in comparison to commercially available flowable composites.

1.4.2 Specific objectives

1. To fabricate the newly developed FCs using silica derived from rice husk with the varying UDMA ratios as the base monomer and zirconia as a radiopacifying agent.
2. To evaluate and compare the flowability of newly developed FCs prepared with UDMA:TEGDMA ratios of 20:80, 30:70, 50:50, 60:40, 80:20, and 90:10 with that of commercial FCs.
3. To assess and compare the chemical properties of the newly developed FCs to commercial FCs on the bonding interaction and degree of conversion.
4. To evaluate and compare the physical properties of the newly developed FCs to commercial FCs on radiopacity, viscosity, depth of cure, surface roughness, water sorption, solubility, and wettability.
5. To evaluate and compare the mechanical properties of the newly developed FCs to commercial FCs on the Vickers hardness, flexural strength, flexural modulus, compressive strength, and compressive modulus.
6. To assess and compare the polymerization shrinkage of the newly developed FCs with that of commercially available FCs.

1.5 Hypothesis

There are no significant differences in the use of UDMA as a base monomer at various ratios in newly developed FCs on flowability, chemical, physical, and mechanical properties, as well as polymerization shrinkage, when compared with commercial FCs.

1.6 Research questions

1. Is there any potential to fabricate newly developed FCs using silica derived from rice husk and zirconia as a radiopacifying agent with varying UDMA:TEGDMA ratios?
2. How do different UDMA:TEGDMA ratios affect the flowability of the newly developed FCs?
3. How do different UDMA:TEGDMA ratios influence the chemical properties of newly developed FCs compared to commercial FCs?
4. How do different UDMA:TEGDMA ratios influence the physical properties of the newly developed FCs compared to commercial FCs?
5. How do different UDMA:TEGDMA ratios influence the mechanical properties of the newly developed FCs compared to commercial FCs?
6. How does the variation in UDMA:TEGDMA ratios affect the polymerization shrinkage of the newly developed FCs compared to commercial FCs?

1.7 Scope of the study

This study was confined to the preparation and characterization of newly developed FCs formulated with nanihybrid silica derived from rice husk as the primary filler and zirconia as the radiopacifying agent, incorporated into a UDMA:TEGDMA resin matrix at varying ratios (20:80, 30:70, 50:50, 60:40, 80:20, and 90:10. The scope covered the fabrication of the FCs, optimization of monomer composition, and in-vitro evaluation of their chemical, physical, mechanical, and polymerization shrinkage properties. The chemical assessments focused on bonding interaction and degree of conversion, while physical analyses included radiopacity, viscosity, depth of cure, surface roughness, water sorption, solubility, and wettability. Mechanical testing

comprised Vickers hardness, flexural strength and modulus, and compressive strength and modulus. Comparative analyses with selected commercial FCs were carried out to establish relative performance. The study is limited to in-vitro investigations, providing baseline evidence for material feasibility, with biocompatibility, long-term aging, and clinical performance identified as areas for future research.

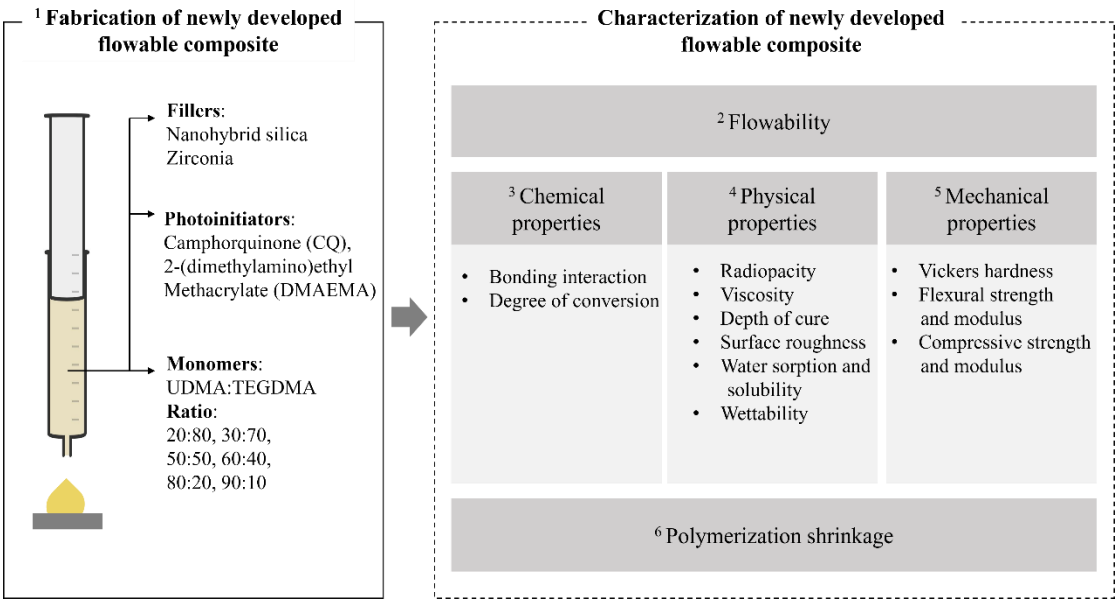

Figure 1: Graphical representation of the study scope

CHAPTER 2

LITERATURE REVIEW

2.1 Dental resin composites

Dental resin composites have become widely used in restorative dentistry, owing to their esthetic appearance and ability to bond adhesively to tooth structures. These properties have made them a preferred alternative to traditional amalgam restorations (Ferracane, 2011). Generally, resin composites are composed of three main components, which are dispersed inorganic filler particles that provide reinforcement and modify properties, an organic polymer matrix that forms the bulk of the material upon polymerization, and a silane coupling agent that promotes adhesion between the organic and inorganic phases. In addition, a photoinitiator system is incorporated to initiate polymerization, typically activated by visible light in direct restorative procedures (Sakaguchi et al., 2018). Over time, resin composite materials have undergone significant advancements, from early macrofilled types to microfilled, hybrid, and more recently, nanohybrid and nanocluster formulations. These developments have aimed to improve physical properties such as strength, wear resistance, surface polish, and aesthetic durability while also addressing challenges such as polymerization shrinkage and associated stress (Ilie & Hickel, 2011). These improvements reflect the continuous effort to enhance the clinical performance of resin composites.

Most resin composites are formulated with a putty-like consistency, making them suitable for a wide range of restorative procedures. However, increasing clinical demands have highlighted the need for materials that offer improved handling and adaptability, especially in deep cavity preparations where access is limited (Al-Rawas et al., 2022). These challenges prompted the development of a more flowable alternative

capable of easily adapting to complex cavity configurations, leading to the introduction of flowable composites in late 1996.

2.2 Flowable composites

Flowable composites are tooth-coloured restorative materials distinguished by their low viscosity, which allows easy placement and adaptation in areas with limited access. Introduced in late 1996, FCs are formulated with a reduced filler load and a higher proportion of monomers, which provide their characteristic flowability, enabling the material to spread uniformly and adapt closely to prepared tooth surfaces (Baroudi & Rodrigues, 2015). The improved flowability permits injection through small-gauge dispensers (Beun et al., 2008), simplifying the placement process and broadening clinical applications.

Due to their excellent wettability, FCs can penetrate surface irregularities and adapt well to internal cavity walls, even in small or inaccessible areas. Their ability to be applied in minimal thickness also helps reduce or eliminate air voids or entrapment. Moreover, their high flexibility makes them less prone to displacement in stress-concentration zones (Garcia et al., 2006). Additional advantages include radiopacity and availability in various shades to match tooth colour. However, FCs are associated with certain limitations, such as higher polymerization shrinkage (Baroudi et al., 2007), and comparatively weaker mechanical strength (Baroudi et al., 2008) and wear resistance (Rajabi et al., 2024) than the conventional resin composites.

The overall performance of FCs is governed by various interrelated factors, such as filler loading, monomer composition, viscosity, and the incorporation of other chemical constituents. Fundamental properties, including polymerization shrinkage, physical and mechanical properties, resistance to wear, and colour stability, are crucial

in defining the long-term success of these materials. Among the surface properties, particularly surface roughness, surface energy, surface hardness, and wettability, play a critical role, as they directly influence the interaction of materials with the oral environment. These characteristics impact plaque accumulation, wear progression, discoloration, and the adhesion of the dental restorative materials to the dental substrates (Lagan et al., 2023).

2.3 Compositions of flowable composites

2.3.1 Fillers

Flowable composites consist of fundamental components of fillers, monomers and photoinitiators similar to other dental resin composites. A wide range of inorganic fillers has been employed in dental composites, including quartz, silica, alkaline oxides and glasses, as well as various metal oxides. Alkaline glasses, such as barium borosilicates and strontium silicate, possess higher refractive indices than silica, which contributes to translucency in composite materials (Habib et al., 2016). While other metal oxides have also been studied for use as fillers (Thorat et al., 2012; Yoshida et al., 2001), some of them, such as zinc oxide and titania, are not widely used in commercial applications (Habib et al., 2016).

Silica or silicon dioxide (SiO_2) remains one of the most widely used fillers in dental restorative materials due to its compatibility with the refractive index (n = 1.53) (Oivanen et al., 2021) of common resin matrices, good stability, favourable mechanical performance, and ease of production (Habib et al., 2016). Both synthetic silica, either synthetically made or produced through industrial processes, and bio-based silica, which is extracted from agricultural sources like rice husk, have shown excellent potential as fillers in resin composites as well as flowable composites (Kim et al., 2007;

Rahim et al., 2011; Timpe et al., 2014; Yusoff et al., 2019; Al-Rawas et al., 2021). Most commercially available dental restorative materials use synthetic silica-based fillers through industrial processes (Habib et al., 2016). Common methods for synthesizing silica nanoparticles include the sol-gel process, reverse microemulsion, and flame synthesis. Among these, the sol-gel process is widely employed due to its capacity to precisely control particle size, distribution, and morphology by adjusting reaction parameters. Silica particles extracted from natural resources often contain metallic impurities, making them less suitable for advanced scientific and industrial applications (Rahman & Padavettan, 2012). Therefore, attention is directed towards synthetic silica, such as pyrogenic silica, precipitated silica, silica gels, and colloidal silica, as it is highly pure and typically produced in amorphous powder forms, in contrast to natural mineral silica types like quartz, tridymite, cristobalite, which exist in crystalline structures (Rahman & Padavettan, 2012; Nzereogu et al., 2023). The application of synthetic silica as a filler in dental restorative materials has been extensively reported, showing encouraging performance results (Kim et al., 2007; Rahim et al., 2011; Timpe et al., 2014). However, synthetic silica production often involves complex procedures, high energy consumption, and the use of hazardous chemicals, which raises concerns regarding environmental sustainability and cost-effectiveness, particularly for large-scale or long-term applications (Errington et al., 2022).

Although silica derived from natural sources, particularly rice husk, may contain metallic impurities and is generally considered unsuitable for highly advanced scientific and industrial applications (Rahman & Padavettan, 2012), it presents several advantages over synthetic silica, particularly within the context of sustainable development and the waste-to-wealth initiative. Rice husk is abundantly available as a byproduct of rice milling and contains a significant amount of silica (Nzereogu et al., 2023). The

extraction of silica from agricultural byproducts is a simple method, low in cost, and environmentally safe (Mor et al., 2017). The incineration of rice husk is not encouraged, as this process produces ashes and toxic gases, causing air pollution (Arjmandi et al., 2015). Therefore, the alternative to transform this waste into wealth has been done (Hossain et al., 2018; Noushad et al., 2014). In recent years, silica extracted from rice husk has garnered attention in dental restorative materials, with several studies demonstrating its potential as a cost-effective filler alternative in both resin and flowable composites (Zulkifli et al., 2013; Noushad et al., 2016; Yusoff et al., 2019), offering not only environmental benefits but also reducing overall production costs.

In addition to rice husk, several other natural materials have been investigated for potential use in dental restorative materials, primarily as secondary or functional fillers rather than the main reinforcing component. Sugarcane bagasse, corn stalk, corncob, rice straw, wheat straw, coconut husk, and bamboo leaf contain silica and have been studied for extraction (Morales-Paredes et al., 2023; Sapawe et al., 2018; September et al., 2023; Seroka et al., 2022), but their application as the primary filler in dental composites is limited. While other natural fillers such as calcium-rich biowastes (egg shell powder, hydroxyapatite) (Allam & El-Geleel, 2018; Babalola & Wilson, 2024) or plant fibers (palm oil, woods) (Abolore et al., 2024; Babu et al., 2024; Magalhães et al., 2023) have potential functional roles in dental materials, rice husk remains the most practical and widely studied main silica filler due to its high silica content, abundance as an agricultural byproduct, and well-established application in resin and flowable composites (Al-Rawas et al., 2021; Noushad et al., 2016; Yusoff et al., 2019). Investigations on using silica from other agricultural wastes as the primary filler in dental composites are still limited, reinforcing the central role of rice husk in this application. Having established rice husk as the primary natural silica filler, it is

important to consider how these fillers are classified and incorporated into resin composites based on particle size.

The fillers in resin composites, including those derived from synthetic or agricultural sources such as rice husk silica, are named according to their particle size, including macrofill, microfill, hybrid, microhybrid, nanofill, and nanohybrid. Early macrofill composites, the first generation of resin composites, incorporated large filler particles ranging from 10 to 50 μm. Although these materials offered good wear resistance, they were difficult to polish and lacked aesthetic appeal (Zhou et al., 2019). This limitation led to the development of microfill composites, which introduced much smaller fillers to improve polishability and surface smoothness. However, the increase in specific surface area due to these fine particles limited the achievable filler loading, thus compromising mechanical performance (Amaya-Pajares et al., 2022; Beun et al., 2007).

To address this, hybrid formulations were introduced, specifically midifill and microhybrid composites, which aimed to combine the mechanical durability of macrofill composites with the improved polishability of microfill types (Ferracane, 2011). Microhybrid composites typically feature filler particles in the range of 0.4 to 1.5 μm, while nanohybrid composites incorporate a higher proportion of nanofillers, often sized between 20 and 75 nm. The inclusion of nanoscale fillers significantly enhances the mechanical properties due to their high surface area, which improves the filler-matrix interaction, leading to increased strength and stiffness (Torno & Soares, 2023). More recently, nanofill composites have emerged, consisting solely of nanoparticles as small as 5 nm. When these are blended with larger fillers, the resulting materials are termed nanohybrids, reflecting the continued evolution of resin

composites toward optimized aesthetic, mechanical, and handling characteristics (Francois et al., 2025).

Filler particles are typically characterized using techniques such as particle size analyzers, dynamic light scattering (DLS), and microscopy, such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Particle size analyzers, often based on laser diffraction, provide rapid, automated measurements of particle size distribution with high accuracy and repeatability (Konstanty & Tyrala, 2024). In contrast, DLS measures particle size in a suspension or emulsion, making it suitable for dispersed nanoparticles but less applicable to solid fillers (Rodriguez-Loya et al., 2024). Microscopy, which allows direct characterization of individual particles, is now generally considered a reliable method for determining particle size (Nijhu et al., 2024). Scanning and transmission electron microscopy (SEM and TEM) are particularly recommended for particle size analysis because they enable high-resolution imaging at the nanoscale and can effectively measure the dimensions of constituent particles even within agglomerates and aggregates (Wouters et al., 2025). While highly effective, SEM also has limitations, such as the need for careful sample preparation and potential charging of non-conductive samples (Fischer et al., 2024). Despite these limitations, SEM remains a preferred technique for the characterization of filler particles in resin composites (Perdigão et al., 2025; Yusoff et al., 2019).

2.3.2 Monomers

Resin monomers serve as the dispersing medium for fillers in resin composites. The resin matrix primarily consists of methacrylate-based monomers, which play a key role in determining the handling properties, mechanical strength, polymerization shrinkage, and biocompatibility of the composites (Wang et al., 2021). Bisphenol A glycidyl methacrylate (BisGMA), triethylene glycol dimethacrylate (TEGDMA), and

urethane dimethacrylate (UDMA) are the most commonly used monomers in most dental composites.

Bisphenol A glycidyl methacrylate (BisGMA) is the fundamental monomer in the formulation of dental resin composites since its introduction by Bowen in 1962. Its molecular structure features rigid aromatic rings derived from bisphenol A, contributing to the high stiffness and mechanical strength of the polymerized network. Structurally, BisGMA also features two pendant hydroxyl groups to a bisphenol A backbone, allowing for extensive hydrogen bonding. This structural rigidity, combined with high molecular weight (512 g/mol), results in low shrinkage during polymerization compared to lower molecular weight monomers such as TEGDMA (286 g/mol) and UDMA (470 g/mol) (Braga et al., 2005). The concentration of reactive double bonds in BisGMA is approximately 3.99 mol/kg, which is lower than that of UDMA (4.25 mol/kg) and TEGDMA (6.99 mol/kg), reflecting its reduced reactivity (Barszczewska-Rybarek, 2009).

Despite its favorable mechanical performance and reduced shrinkage, BisGMA is characterized by extremely high viscosity, which is 1369 Pa·s (Dickens et al., 2003). This viscosity is mainly attributed to its bulky structure and the presence of hydrogen-bonding hydroxyl groups, which significantly hinder mobility. As a result, BisGMA cannot be used as a sole monomer and typically requires the incorporation of low-viscosity diluent monomers to facilitate proper handling and manipulation suitable for clinical use (Sideridou et al., 2002). Moreover, concerns have been raised regarding the potential release of bisphenol A from BisGMA-containing materials, albeit at very low levels, highlighting the need for safer and more biocompatible alternatives (Fleisch et al., 2010).

To improve the handling of BisGMA-based resins, which are inherently difficult to manipulate due to their high viscosity, triethylene glycol dimethacrylate (TEGDMA) is commonly incorporated as a diluent monomer. TEGDMA is a low viscosity, low molecular weight monomer (286 g/mol) that facilitates better mixing with inorganic fillers and improves the ease of placement during clinical application. Its flexible aliphatic chain structure promotes greater chain mobility, thereby contributing to a higher degree of monomer conversion during polymerization (Gajewski et al., 2012).

Despite its benefits, TEGDMA also presents certain drawbacks. Due to its relatively small molecular size, TEGDMA has a high concentration of reactive double bonds per unit mass, which leads to greater polymerization shrinkage upon curing (Sideridou et al., 2002; Barszczewska-Rybarek, 2009). In addition, the presence of ether linkages in TEGDMA increases its hydrophilicity, making the polymer matrix more prone to water sorption and solubility over time (Sideridou et al., 2003). These phenomena can weaken the structural integrity of the material and lead to the leaching of unreacted monomers, which may have cytotoxic implications in the oral environment (Sideridou & Achilias, 2005). Therefore, while TEGDMA is essential for improving the flow and workability of BisGMA-based systems, it also introduces challenges related to shrinkage and durability (Sideridou et al., 2002).

In response to the limitations of BisGMA- and TEGDMA-based formulations, urethane dimethacrylate (UDMA) has gained attention as a more versatile base monomer in resin dental restorative materials. Structurally, UDMA contains flexible urethane linkages (-NH-CO-O) which allow for strong hydrogen bonding, improving its adhesion to tooth structure and contributing to improved durability (Moszner & Salz, 2001; Stansbury, 2012). UDMA also has significantly lower viscosity than BisGMA (28 Pa·s) (Dickens et al., 2003), making it easier to handle and more suitable for FCs

where low viscosity is essential. Unlike BisGMA, UDMA does not require large amounts of diluent monomers like TEGDMA, which are known to increase polymerization shrinkage (Braga et al., 2005).

In addition, UDMA exhibits lower water sorption and solubility than BisGMA, suggesting better hydrolytic stability and potentially improved long-term performance in clinical settings (Gonçalves et al., 2010). Optically, UDMA has a refractive index (n) of 1.483, which is closer to that of silica fillers (n = 1.4858) than BisGMA (n = 1.540), potentially improving light transmission and enhancing the esthetic integration of the resin composites (Fujita et al., 2005). The chemical structures of Bis-GMA, UDMA, and TEGDMA are shown in Figure 2.1, and their basic properties are summarized in Table 2.1.

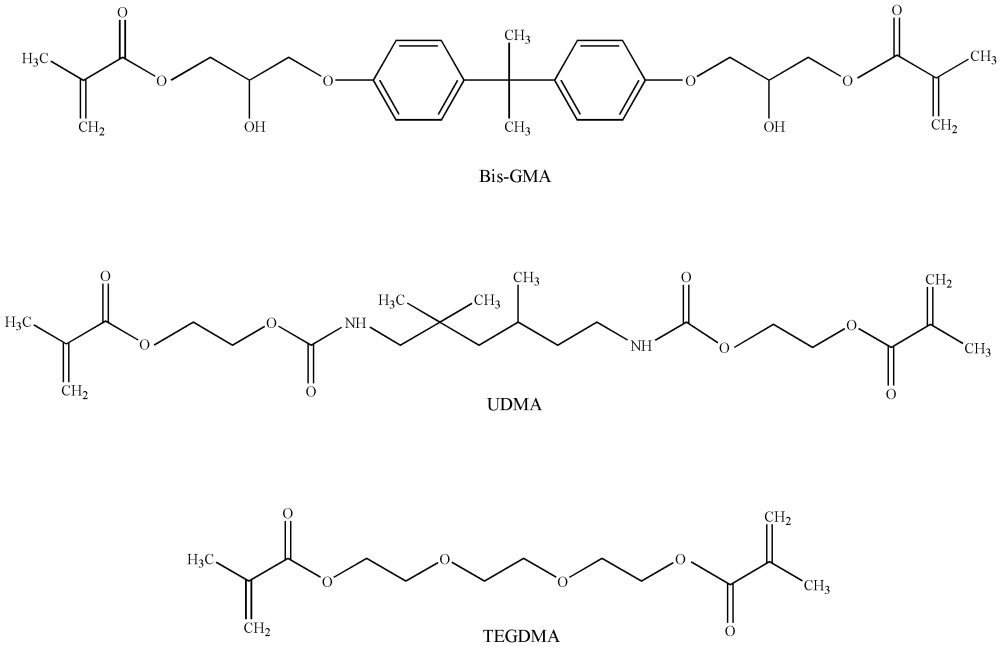

Figure 2.1 The chemical structure of BisGMA, UDMA, and TEGDMA

Table 2.1 Basic properties of BisGMA, UDMA, and TEGDMA

Properties	BisGMA	UDMA	TEGDMA	References
Molecular weight (g/mol)	512	470	286	-
Density (g/cm^3)	1.151	1.110	1.072	Moszner & Salz, (2001)
Viscosity (Pa·s)	1369	28	0.05	Dickens et al. (2003)
Refractive index	1.540	1.483	1.460	Fujita et al. (2005)
Concentration of double bonds (mol/kg)	3.99	4.25	6.99	Barszczewska-Rybarek (2009)

Achieving optimal flowability and viscosity in FCs remains a challenge, as variations in monomer types and their ratios can significantly influence the chemical, physical, and mechanical properties, as well as polymerization shrinkage. A study by Yusoff et al. (2019) investigated BisGMA:TEGDMA monomer blends incorporating silica derived from rice husk as the reinforcing filler. The study explored a limited range of monomer ratios, specifically 40:60, 45:55, and 50:50, and reported that certain properties were inferior to those of commercial counterparts. Given the advantages of UDMA mentioned, examining a wider range of UDMA:TEGDMA ratios could provide valuable insights into optimizing FC formulations. Despite the promising potential of UDMA-based systems, current literature lacks comprehensive evaluations across a broader compositional range, such as from 20:80 to 90:10. Addressing this gap is essential for advancing the development of next-generation FCs with improved performance characteristics. Broader compositional studies may help identify optimal formulations that balance flowability, strength, and shrinkage, leading to materials that are more suitable for clinical applications.

2.3.3 Silane coupling agents

One of the primary challenges in the fabrication of dental composites is achieving homogeneous dispersion and effective interaction between the inorganic fillers and the organic resin matrix (Sideridou & Karabela, 2009). This issue is typically addressed through the surface modification of silica particles using silane coupling agents (Rahman & Padavettan, 2012). These agents are organic silicon-based compounds possessing bifunctional groups capable of forming covalent bonds with both the filler surface and the resin matrix, thereby enhancing interfacial adhesion and compatibility. To strengthen the bond between the filler and the polymeric phase, silane derivatives are covalently attached to the surface of silica particles (Habib et al., 2016). A wide range of silane coupling agents has been employed in dental composites, with common examples being γ-methacryloxypropyl trimethoxysilane (γ-MPS) and vinyltrimethoxysilane (Habib et al., 2016). The silanization of silica fillers, such as γ-MPS, has been reported to significantly enhance mechanical properties (Aydinoğlu & Yoruç, 2017). The chemical structure of γ-MPS is shown in Figure 2.2.

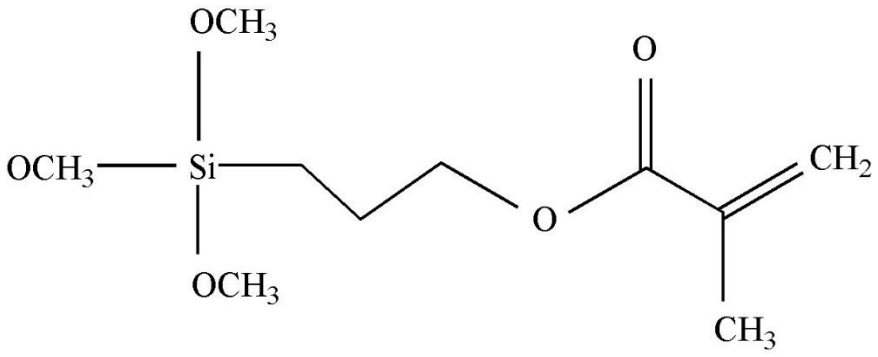

Figure 2.2 Chemical structure of γ-MPS

2.3.4 Photoinitiators

Polymerization refers to the chemical process in which monomer molecules undergo a reaction to form long-chain polymers. This process occurs in three phases, which are initiation, propagation, and termination. The formation and growth of

polymer chains are driven by the generation of free radicals, which act as highly reactive species that initiate and sustain the chain reaction (Garcia et al., 2006). As the FCs in this study utilize a light-activated curing mechanism, the further explanation focuses on polymerization initiated by light curing systems.

The polymerization of resin-based composites is critically dependent on effective photoinitiation, which is typically achieved through the use of camphorquinone (CQ) in combination with a co-initiator such as 2-(dimethylamino)ethyl methacrylate (DMAEMA), photoinitiator systems (Ilie & Hickel, 2008). Camphorquinone, a yellow-coloured compound, serves as the primary photosensitizer due to its broad spectrum ranging from 360 to 510 nm, with a maximum peak around 468 – 470 nm (Ikemura & Endo, 2010; Pérez-Mondragón et al., 2020). This spectral range closely aligns with the output wavelength of most LED light-curing units, particularly used in dental applications (Price et al., 2020). However, CQ alone is insufficient for efficient free radical applications. It requires a co-initiator, typically a tertiary amine such as DMAEMA, to begin the polymerization process (Stansbury, 2000).

When exposed to blue light, CQ absorbs the energy and transitions to an excited state. In this excited state, CQ undergoes an electron transfer reaction with a co-initiator, DMAEMA, forming a temporary excited complex. During this interaction, a hydrogen atom is transferred from the amine to the excited CQ, resulting in the formation of two radicals, which are a CQ-derived ketyl radical and an amine-derived α-aminoalkyl radical. α-aminoalkyl radical is highly reactive and initiates polymerization by attacking the carbon-carbon double bond (C=C) of methacrylate monomers, such as UDMA or TEGDMA. This step marks the initiation of chain propagation, where the reactive center sequentially adds monomer units, leading to the rapid growth of polymer chains

and the eventual formation of a cross-linked network (Jakubiak et al., 2007; Pratap et al., 2019; Rueggeberg et al., 2017). The polymerization process continues until termination occurs, however, complete conversion of all monomer units into polymer is rarely achieved. The extent to which monomers are polymerized is expressed as the degree of conversion (Anusavice et al., 2013), a key parameter that significantly influences the mechanical integrity and biological behavior of the polymerized composite. Insufficient degree of conversion can lead to compromised physical and mechanical properties and increased release of residual monomers, potentially affecting the biocompatibility of materials (Kowalska et al., 2021).

2.4 Optimization of flowable composites formulation

A number of studies have been conducted using locally produced silica from rice husk, showing its potential as filler in dental restorative materials (Table 2.2). Earlier investigations emphasized the influence of filler loading and monomer selection in determining the intended application of resin composites. Noushad et al. (2016) incorporated 40 – 50 wt% silica, while Lin et al. (2020) used a higher filler loading of 75 wt% (65 wt% silica and 10 wt% zirconia), with both studies developing resin composites. Both studies use BisGMA as the base monomer at a single ratio with relatively low content compared to fillers, resulting in a filler-dominant system that provides insights into the formulation of resin composites.

In contrast, Yusoff et al. (2019) and Al-Rawas et al. (2021) formulated flowable composites with 50 wt% silica, with BisGMA serving as the base monomer. Their formulations were limited to 2 – 3 BisGMA:TEGDMA ratios due to the high viscosity of BisGMA, as additional ratios would compromise flowability. For other dental applications, rice husk silica has been utilized in adhesive cements (Ismail et al., 2023)

and pits and fissure sealants (Yassin et al., 2023), where the monomer content exceeded the filler content, resulting in very low viscosity in these materials. Across these studies, additional fillers were incorporated at 10 wt%, such as zirconia (Lin et al., 2020) and nanohydroxyapatite (Yassin et al., 2023). This suggests that 10 wt% may represent an optimal loading for incorporation into restorative materials. The photoinitiator content was generally maintained at 1 wt%, ensuring effective polymerization.

Drawing from this evidence, the present study adopted a 50:50 filler-to-monomer ratio, following Yusoff et al. (2019), with 40 wt% silica and 10 wt% zirconia as additional fillers in line with Lin et al. (2020). However, there is a lack of studies incorporating UDMA:TEGDMA combinations, with the exception of Yassin et al. (2023), who focused on pit and fissure sealant applications. To address this gap, the present study systematically evaluated a broader range of UDMA:TEGDMA ratios (20:80, 30:70, 50:50, 60:40, 80:20, 90:10), while maintaining 0.5 wt% CQ and 0.5 wt% DMAEMA as photoinitiators. These ratios were optimized through preliminary screening to ensure that the experimental composites remained flowable, thereby providing a justified approach for the formulation of the newly developed FCs in this study.