SYNTHESIS AND MECHANICAL PROPERTIES OF A MODIFIED LOW-SHRINKAGE DIACRYLATED POLYETHYLENE GLYCOL COMPOSITE RESIN

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by

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LIST OF SYMBOLS

3D	Three dimensions
°C	Degrees Celsius
ΔQ	Heat Flow
cm^{-1}	Per Centimeter
F	Force
G	Gram
kN	KiloNewton
kV	Kilovolt
mg	Milligram
mL	Millilitre
mm	Millimetre
MPa	MegaPascal
M_w	Molecular weight
nm	Nanometre
Pa.s	Pascal Seconds
ppm	Parts Per Million
T_g	Glass Transition Temperature
T_m	Melting Temperature
wt %	Weight Percent

LIST OF ABBREVIATIONS

AFCT	Addition-Fragmentation Chain Transfer
ASEE	Ethyl-2-(tosylmethyl)acrylate
ASTM	American Standard Testing Method
ATR	Attenuated Total Reflectance
$BaSO_4$	Barium sulphate
Bis-GMA	Bisphenol-A glycidyl methacrylate
BPA	Bisphenol A
CaP	Calcium Phosphate
$CDCl_3$	Chloroform
CQ	Camphorquinone
DAPEG	Diacrylated Polyethylene Glycol (also known as PEGDA)
DC	Depth of Cure
DCM	Dichloromethane
DMAEMA	2-(Dimethylamino) Ethyl Methacrylate
DMAHDM	Dimethylaminohexadecyl Methacrylate
DMPA	2,2-dimethoxy-2-phenylacetophenone
DoC	Degree of Conversion
DPI-PF6	Diphenyliodonium Hexafluorophoshate
DSC	Differential Scanning Calorimetry
EDB	Ethyl-4-(dimethylamino) Benzoate
EDMAB	Ethyl4-(N,N-dimethylamino) Benzoate
E-POSS	Epoxycyclohexyl Polyhedral Oligomeric Silsesquioxane
EtOH	Ethanol
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
HCL	Hydrochloric Acid
ISO	International Organization for Standardisation
KBr	Potassium Bromide
ME-POSS	Methacrylethyl Polyhedral Oligomeric Silsesquioxane
$MgSO_4$	Magnesium Sulphate
MMT	Montmorillonite

NACP	Nanoparticles of Amorphous Calcium Phosphate
$NaHCO_3$	Sodium Hydrogen Carbonate
NH_4OH	Ammonium Solution
NMR	Nuclear Magnetic Resonance
PEG	Polyethylene Glycol
POSS	Polyhedral Oligomeric Silsesquioxane
PPD	Phenylpropanedione
RBCs	Resin Based Composites
SiO_2	Silicon Dioxide
TEA	Triethylamine
TEGDMA	Triethylene Glycol Dimethacrylate
TEOS	Tetraethyl Orthosilicate
TGA	Thermogravimetric Analysis
UDMA	Urethane Dimethacrylate
UV	Ultraviolet
ZrO_2	Zirconium Dioxide

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SINTESIS DAN SIFAT MEKANIKAL RESIN KOMPOSIT DIAKRILAT POLIETILENA GLIKOL BERPENGECUTAN RENDAH YANG DIUBAHSUAI

ABSTRAK

Kajian ini menyelidik sintesis, pencirian, dan potensi aplikasi komposit pergigian berasaskan diakrilat polietilina glikol (DAPEG) (juga dikenali sebagai PEGDA – polietilena glikol diakrilat) berpengecutan rendah, berfokus kepada kesan berat molekul dan pembebanan pengisi silika terhadap sifat mekanikal, termal, dan dimensi. Silika disintesiskan melalui proses sol-gel daripada tetraetil orthosilikat, disahkan oleh Fourier Transform Inframerah. Monomer DAPEG disintesiskan daripada polietilena glikol dan akriloil klorida, disahkan oleh FTIR dan Resonans Magnetik Nuklear, menunjukkan pengaruh berat molekul terhadap kestabilan termal. DAPEG 400 berberat molekul rendah, berketumpatan dan berkelikatan rendah, menambahbaikan kelakuan pematangan. Tambahan pula, DAPEG 400 menunjukkan kedalaman pematangan, darjah penukaran yang tinggi, kandungan gel yang baik, dan mudah diurus dibandingkan dengan monomer DAPEG yang berberat molekul lagi tinggi. DAPEG 4000 yang berberat molekul lagi tinggi pula mempamerkan penghabluran dan kestabilan terma yang lebih baik. Komposit berasaskan DAPEG 400 dengan pembebanan pengisi silika optimum meningkatkan sifat mekanikal, iaitu kekuatan lenturan dan mampatan, masing-masing sehingga 10.27 MPa dan 41.42 MPa, rintangan air dan kestabilan dimensi, dengan pengecutan pempolimeran yang lebih rendah. Dalam kajian ini, komposit berasaskan DAPEG 400 dengan pembebanan silika 60 % menunjukkan pengecutan pempolimeran paling rendah 1.58 %, lebih rendah daripada resin komposit pergigian lain yang terdapat dalam pasaran.

SYNTHESIS AND MECHANICAL PROPERTIES OF A MODIFIED LOW-SHRINKAGE DIACRYLATED POLYETHYLENE GLYCOL COMPOSITE RESIN

ABSTRACT

This study investigates the synthesis, characterisation, and application potential of low-shrinkage diacrylated polyethylene glycol (DAPEG)-based (also known as PEGDA – polyethylene glycol diacrylate) dental composites, focusing on the effects of molecular weight and silica filler loading on mechanical, thermal, and dimensional properties. Silica was synthesised via the sol-gel process from tetraethyl orthosilicate (TEOS) was confirmed with Fourier Transform Infrared. DAPEG monomers were synthesised from polyethylene glycol and acryloyl chloride, verified by FTIR and nuclear magnetic resonance, revealing a clear influence of molecular weight on thermal stability. DAPEG 400 with lower molecular weight shows a lower density and viscosity, hence improving the curing behaviour. In addition, DAPEG 400 demonstrated good depth of cure, high degree of conversion, gel content, and also ease of handling compared to higher molecular weight DAPEGs. Higher molecular weight DAPEG 4000 exhibited enhanced crystallinity and thermal stability. DAPEG 400 composites with optimal silica filler loading significantly increased mechanical properties (flexural and compressive strength) up to 10.27 MPa and 41.42 MPa, water resistance, and dimensional stability, plus lower polymerisation shrinkage. In this work, DAPEG 400 composite with 60 % silica loading demonstrated the lowest polymerisation shrinkage of 1.58 %, much lower than other dental composite resins available in the market.

CHAPTER 1

INTRODUCTION

1.1 General instructions

Dental composite resins are tooth-coloured restorative materials used in dentistry for various purposes. They mainly comprise a polymer matrix, typically a resin-based material, and an inorganic filler component, such as silica or ceramic particles (Haque et al., 2019). These dental composite resin materials are designed to mimic the appearance and properties of natural teeth, making them popular for aesthetic dental procedures (Bhattacharya & Seong, 2019). Dental composite resin operates through a process known as polymerisation, where in liquid resin, monomers transform into a solid polymer network. The composite resin is applied in layers, with each layer meticulously shaped and contoured. A curing light (visible blue light) initiates the polymerisation reaction, activating photoinitiators within the resin. This reaction forms long polymer chains, converting the liquid resin into a solid, resilient material that adheres mechanically to the prepared tooth surface.

Dental composite resin was initially introduced as a revolutionary advancement in restorative dentistry. It has recently become popular in aesthetic prospects and has been extensively utilised for its advantages. By replicating the natural colour of teeth, dental composite resins are excellent for restoring front teeth, fixing chips or discolouration, closing gaps, and enhancing smiles for a more natural appearance. Dental composite resins facilitate a conservative treatment approach. Unlike traditional restorative materials like amalgam (metal fillings), they require minimal tooth preparation, preserving more natural tooth structure (Cho et al., 2022).

They can be used for a wide range of dental restorations, including fillings (known as composite fillings or tooth-coloured fillings) (Haque et al., 2019), bonding procedures (Jensen, 2015), veneers, inlays, onlays (Bartlett & Ricketts, 2011), and even full-mouth reconstructions (Beriain et al., 2022; Mehta et al., 2021). Furthermore, dental composite resins are generally considered biocompatible materials, meaning they are well tolerated by the body and have minimal adverse effects on oral tissues. (Mousavinasab, 2011a). Advances in dental materials science have led to the development of composite resins with improved mechanical properties, such as increased strength, wear resistance, and longevity. (German, 2022; Rodríguez et al., 2019; Zhou et al., 2019). These advancements have expanded the scope of applications for composite resins, making them suitable for use in high-stress areas of the mouth.

1.2 Research background

The polymer composite resin is the main component in dental restoring applications. Restoration material from ancient times was obtained from bone, bee waxes, gum, and powdered pearls. In 1826, August Taveau of Paris used mercury and silver to form a silver paste, which was used in dental restoration, known as amalgam. Later, in 1833, amalgam was commercially used in the United States, but the major drawback was the excess of mercury, which was misused (Singh et al., 2017). In 1963, Dr William solved the problem by developing a new formulation of amalgam that enhanced the long-term marginal integrity (Bharti et al., 2010). However, this type of restoration material has caused a problem due to its release of low mercury in vapour, which is also hazardous to health and causes allergic reactions.

The use of acrylate resin was invented in 1947 when methacrylate resin was used to overcome the problem of silicate cement (Shulein, 2005). The issues related to silicate cement were their solubility, pulp irritation, and desiccation. Even though using acrylate resin has improved the material's mechanical properties and provided aesthetic restoration, its major drawback is polymerisation shrinkage. To overcome this polymerisation shrinkage problem, the researcher used the ring-opening polymerisation method to develop a new monomer known as silorane (Malathi & Reddy, 2020) A silorane-based resin has been developed, employing ring-opening polymerisation of silorane molecules incorporating siloxane and oxirane, in contrast to the conventional free radical polymerisation process involving acrylated monomers. The utilisation of ring-opening polymerisation in these resins shows promise in mitigating the issues associated with polymerisation shrinkage commonly encountered in dental procedures (Yu et al., 2015).

However, this silorane material had some drawback, which is cavity wall adaptation and curing deep cavities (Ende et al., 2010). Moreover, silorane material is costly compared to acrylate material, which may not be preferable (Öztürk-Bozkurt et al., 2016). Thus, researchers are being urged to find alternative materials with improved properties of polymerisation shrinkage for dental application use. Low-shrinkage acrylate-based resins are dental composite materials designed to reduce the polymerisation shrinkage during curing.

In low-shrinkage acrylate-based resin, incorporating monomers with bulkier molecular structures can help reduce polymerisation shrinkage while preserving essential physical and mechanical properties. These bulkier monomers occupy more space within the resin matrix, limiting the overall volume change during polymerisation and thus reducing shrinkage stress on the tooth-restoration interface (Marx & Wiesbrock, 2021a). Furthermore, incorporating a higher volume fraction of fillers into the resin matrix can effectively minimise the polymerisation shrinkage. This is because the presence of fillers creates physical barriers that limit the contraction of the resin matrix during curing, resulting in less shrinkage stress being transmitted to the tooth-restoration interface (Taylor et al., 1998). The type, size, and distribution of fillers can influence the effectiveness of shrinkage reduction.

1.3 Problem statement

Polymerisation shrinkage is a critical issue associated with conventional composite resins in dentistry. As the resin undergoes polymerisation and transitions from liquid to solid, it contracts, decreasing volume. This phenomenon, known as polymerisation shrinkage, can result in several challenges. Polymerisation shrinkage can create gaps or voids between the composite resin and the tooth structure, causing marginal leakage (Schricker, 2017a). Marginal leakage refers to the infiltration of bacteria and fluids along the margins of the dental restoration, which can lead to secondary caries and compromise the longevity of the restoration (Ben-Amar et al., 1978). A study involving Navy and Marine recruits with satisfactory posterior amalgam or composite restorations at the time of enlistment found that composite restorations had a 64 % higher risk of failure compared to amalgam restorations. One of the main contributing factors to this failure was polymerisation shrinkage (S. Yadav et al., 2019).

This can lead to post-operative sensitivity, discomfort, and potential damage to the pulp tissue within the tooth (Sabbagh et al., 2018). Furthermore, the shrinkage stress generated during polymerisation shrinkage can exceed the bond strength between the composite resin and the tooth structure, leading to debonding or fracturing of the restoration (Schneider et al., 2010; Soares et al., 2017). This can compromise the integrity of the restoration and necessitate replacement or repair. These restoration failures often necessitate costly replacements, repeated dental visits, and additional chair time, placing a significant burden on both patients and healthcare providers.

From a patient perspective, such failures can cause discomfort, sensitivity, anxiety, and a reduced quality of life, especially when multiple interventions are required.

Minimising polymerisation shrinkage in dental composite resins is essential for overcoming common problems in restorative dentistry. Although various strategies have been proposed, such as modifying curing protocols, altering filler compositions, and designing new monomer systems , there is still no clear consensus in the literature on the most effective approach. While some researchers support the development of silorane- or ormocer-based resins, others emphasise modifications within acrylate-based systems. These differing perspectives underscore the need for further investigation into low-shrinkage acrylate-based formulations**.** Hence, developing low-shrinkage composite resins can mitigating these issues and enhancing the overall quality of dental care (Albeshir et al., 2022b). By reducing polymerisation shrinkage, these advanced materials achieve superior marginal adaptation and sealing, thus lowering the risk of complications and prolonging the lifespan of dental restorations.

Acrylate-based low-shrinkage resins, characterised by their unique chemical properties and versatility, emerge as promising candidates for low-shrinkage dental composites (Albeshir et al., 2022a; Alhussein et al., 2023; Ma et al., 2023). The low-shrinkage property is achieved through carefully selecting monomers and additives and optimising the polymerisation process. By minimising shrinkage, these resins help mitigate issues such as internal stresses, void formation, and dimensional changes, which can compromise the integrity and performance of the final product.

1.4 General objective

The general objective of the study is to develop an experimental low-shrinkage dental composite resin by combining novel low-shrinkage diacrylated polyethylene glycol (DAPEG) monomers with different silica filler loadings synthesised from tetraethyl orthosilicate (TEOS).

1.5 Specific objectives

1. To synthesise silica filler from TEOS and to characterise the former using Fourier Transform Infrared (FTIR) spectroscopy, Field Emission Scanning Electron Microscopy (FESEM), and particle size analysis.
2. To synthesise novel low-shrinkage diacrylated polyethylene glycol (DAPEGs) monomers and characterise their chemical structures, thermal behaviours, and key performance metrics (including density, gel content, degree of conversion, depth of cure, and polymerisation shrinkage) using techniques such as Fourier Transform Infrared spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR), Field Emission Scanning Electron Microscopy (FESEM), and Differential Scanning Calorimetry (DSC).
3. To develop an experimental low-shrinkage dental composite resin using synthesised new DAPEG monomers and synthesised silica filler from TEOS with different filler loadings and to characterise its structural morphology and thermal behaviour using Fourier Transform Infrared (FTIR) spectroscopy, Field Emission Scanning Electron Microscopy (FESEM), and Thermogravimetric Analysis (TGA).
4. To evaluate the mechanical and physical properties of the newly developed dental composite with silica-TEOS loading using flexural testing, compressive testing, polymerisation shrinkage testing, and dimensional stability (water absorption and thickness swelling)

1.6 Research questions

1. How do the physical properties of new DAPEG monomers, such as density, content gel, degree of conversion, depth of cure, and polymerisation shrinkage, correlate with their performance?
2. How does silica filler load impact the structural morphology and thermal behaviour of experimentally newly developed low-shrinkage dental composite resins?
3. Do the mechanical and physical properties of newly developed low-shrinkage dental composite resins improve by increasing silica-TEOS filler loading?

1.7 Hypotheses

1. The physical properties of new DAPEG monomers, including density, gel content, degree of conversion, depth of cure, and polymerisation shrinkage, will be closely correlated with their overall performance with optimal physical properties leading to superior material characteristics.
2. Silica-TEOS filler loading will significantly impact the structural morphology and thermal behaviour of experimentally newly developed low-shrinkage dental composite resins.
3. The newly developed low-shrinkage dental composite resins will exhibit enhanced mechanical and physical properties by increasing silica-TEOS filler loading.

1.8 Scope of study

This study synthesised acrylate-based monomers from polyethylene glycol (PEG) with varying molecular weights. Three types of PEGs were chosen: PEG 400, PEG 2000, and PEG 4000. Silica fillers were chemically synthesised from tetraethyl orthosilicate (TEOS). Both the synthesised monomers and fillers underwent comprehensive characterisation analyses. Subsequently, dental composites were fabricated using these low-shrinkage acrylated monomers and silica fillers to develop low-shrinkage dental composite resins. The significance of this study lies in its potential to advance dental materials science and enhance clinical outcomes in restorative dentistry. By synthesising low-shrinkage acrylated monomers from polyethylene glycol with varying molecular weights and incorporating them into dental composite resin formulations, this research aims to address a critical issue of polymerisation shrinkage in dental practice.

The findings of this study have the potential to innovate dental composite formulations by significantly reducing polymerisation shrinkage while maintaining or even enhancing mechanical properties. By systematically analysing the mechanical, chemical, and physical properties of the synthesised monomers and the resulting composite resins, this research will provide valuable insights into the relationship between molecular weight, monomer structure, filler content, and composite performance. Developing novel dental composite formulations with reduced polymerisation shrinkage and improved overall performance has far-reaching implications for clinical practice. These advanced materials can lead to more durable and long-lasting dental restorations, minimising the need for costly and time-consuming replacements or repairs. Moreover, by enhancing the clinical success of dental treatments, these innovative composite formulations can improve patient satisfaction and quality of life.

In summary, this study has the potential to make significant contributions to dental materials science by advancing our understanding of low-shrinkage acrylated monomers and their role in dental composite formulations. By developing novel materials with enhanced performance and reduced polymerisation shrinkage, this research can improve the clinical outcomes of restorative dentistry, benefiting both dental practitioners and patients alike.

1.9 Contribution to the body of knowledge

This study is the first to use DAPEG as a matrix in experimental dental composite resin. DAPEG can absorb water to counter polymerisation shrinkage; however, on its own, it undergoes excessive expansion, leading to negative shrinkage and composite breakage. The highest silica loading (60 % by weight) helps to control this excessive expansion, counteracting 1.58 % polymerisation shrinkage with 8.55 % expansion, as shown in Figure 4.15.

CHAPTER 2

LITERATURE REVIEW

2.1 Composite resin in dental restoration

Dental caries, commonly known as tooth decay or cavities, is a major oral health concern that affects individuals globally. This condition is typically identified by the presence of decay or cavities on any surface of the teeth. Dental caries can impact individuals of all ages, including both children and adults, and can involve both primary and permanent dentition. According to global reports on oral health, approximately 2 billion people suffer from dental caries in their permanent teeth, while an estimated 514 million children are affected by caries in their primary teeth (Watt, 2022). Standard treatment for dental caries aims to restore the affected tooth's structure by using filling materials to replace decayed tissue. Dental composite fillings are central to contemporary restorative dentistry, offering an effective solution for addressing tooth decay, cavities, and structural damage. Composite resin has become increasingly prominent among the materials used for this purpose. This chapter provides a comprehensive literature of its clinical applications, challenges, and recent advancements, offering a thorough understanding of the role of composite resin in modern dentistry.

The use of composite resin in dental filling restorations began in the 1960s, marking a significant development in restorative dentistry (Bowen & Rodgriguez, 1962). Initially known as "acrylic-based composites," these materials were primarily composed of acrylic resins. Due to their limited mechanical properties, they were predominantly used for anterior (front) dental restorations. As dental materials research developed in the 1970s (Bassiouny & Grant, 1978), emphasis shifted to the creation of resin-based composites (RBCs). The resin bisphenol-A glycidyl methacrylate (Bis-GMA) as referred to Figure 2.1, which one of the resins used in these RBCs. Dental composites' strength and durability were increased by using these type of resin resins due to its structure, where rigid aromatic rings add stiffness, making it more wear-resistant (Bowen, 1982).

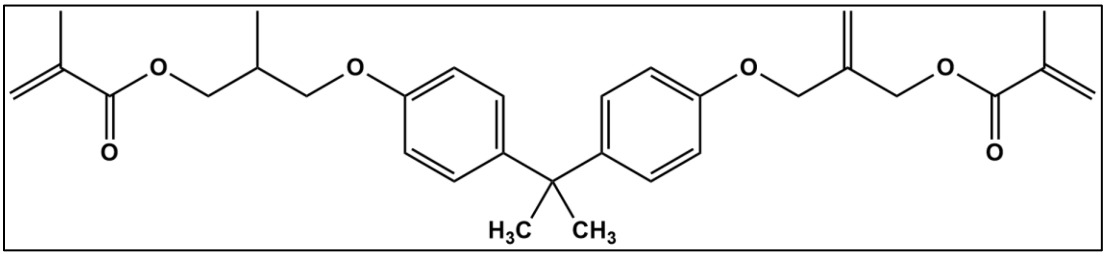

Figure 2.1 Chemical structure of Bis-GMA

The development of light-cured composites marked a significant advancement, as these materials feature light-activated initiators that enhance the control and efficiency of the curing process (Buonocore, 1970). Light-cured composites gained popularity due to their superior handling characteristics. Throughout the 1990s, ongoing advancements in resin formulations led to the introduction of hybrid composite materials, which combine both microfill and macrofill particles to enhance performance (Sub et al., 1990). The hybrid approach aimed to achieve a balance between strength and aesthetic properties. In the twenty-first century, advancements in resin technology continued, with recent research increasingly focusing on nanocomposites, which incorporate fillers and resins at the nanoscale for enhanced performance (Azmy et al., 2022). These materials, which offered enhanced strength and wear resistance (Althoey et al., 2023), also featured modified resin matrices to reduce shrinkage and improve the bond with tooth structure, thereby transforming dental fillings into a safer and more aesthetically pleasing option for patients and practitioners (Albeshir et al., 2022a; Thalacker, 2022).

Dental composite resin is used to replace decayed portions of tooth structure. Its primary advantage over conventional dental amalgam is its aesthetic appearance, which closely matches the natural colour of the teeth (Report, 2018). Dental composite resin is biocompatible and minimally invasive, preserving more healthy tooth structure than traditional amalgam fillings and it does not contain mercury, alleviating concerns associated with amalgam (Amirkalali, 2023). Dental composite resin materials are composed of a blend of organic polymers and inorganic filler particles, making them exceptionally versatile. They are highly regarded for their outstanding aesthetic qualities, such as colour matching and translucency, which enable them to blend effortlessly with natural teeth. Moreover, these materials possess superior mechanical properties, offering increased strength and durability compared to previous generations (Cramer et al., 2011). Additionally, their ability to bond directly to tooth structures further enhances their clinical effectiveness (Chan et al., 2010). In the clinical view, composite resin finds widespread use in various scenarios. Dentists employ it for cavity preparation, utilizing adhesive bonding techniques to create a strong bond between the resin and tooth structure (Sofan et al., 2017). Layering techniques enable precise replication of natural tooth anatomy (Chandrasekhar et al., 2017).

Composite resin is a flexible material used to fix different dental issues, such as cavities, broken teeth, and cosmetic improvements. Real-life examples show how effective and adaptable it is for a wide range of dental treatments. While dental composite resin offers numerous benefits, it is not without its challenges. One of the most significant issues is polymerisation shrinkage, which can cause the formation of marginal gaps between the tooth and the restoration. These gaps may lead to complications such as post-operative sensitivity, secondary caries, and compromised long-term durability of the restoration (Ensaff et al., 2001; Riva & Rahman, 2019; Suliman et al., 1994). However, advancements in material science and clinical techniques have significantly addressed many of these challenges. Clinicians can now reduce the impact of polymerisation shrinkage by employing incremental layering techniques and utilizing low-shrinkage composite materials, which help to minimise the risk of marginal gaps and enhance the overall success of the restoration (Chandrasekhar et al., 2017; Wang et al., 2022).

Recent advancements in composite resin materials have focused on enhancing their durability, handling characteristics, and aesthetic properties. Nano-filled and silorane-based composites represent cutting-edge options, offering improved wear resistance and reduced shrinkage (Hamama, 2019; Lin et al., 2020). Future trends in composite resin dentistry may involve the development of bioactive composites and the integration of digital technologies for more precise restorations (Flucke, 2022; Ibarretxe, 2022; Melo et al., 2023). Dental composite resin has emerged as a transformative force in dental filling restoration. Its historical evolution, favourable properties, and wide-ranging clinical applications have cemented its place as a versatile and patient-friendly choice. While challenges exist, ongoing research and technological advancements promise an even brighter future for composite resin in the field of restorative dentistry.

2.2 Composition in dental composite resin

Dental composite materials are a cornerstone of modern restorative dentistry, offering a versatile solution for repairing and restoring teeth while achieving natural aesthetics. These composite resins are carefully formulated, composed of several essential components, each component take a role in their performance and clinical success. Dental composite resin is comprised of several components: an organic resin (polymer matrix), inorganic filler, photoinitiators, co-initiator, and other additives. Resin (polymer matrix) acts as the "glue" or binder that holds the other components of a composite resin together. It is typically made from organic (carbon-based) materials, giving the composite structure and helping it bond well to the tooth. Most common resin matrix formulation in dental composite resin typically composed of bisphenol A-glycidyl methacrylate (Bis-GMA) and/or urethane dimethacrylate (UDMA). These methacrylate-based monomers provide the composite its adhesion properties and make it easy to shape before it hardens (sculptability).

Filler is usually an inorganic material that added to the composition to enhance mechanical, physical, and aesthetic properties of composite resin (Elfakhri et al., 2022). Common examples of inorganic fillers include silica (silicon dioxide, SiO_2), zirconia (zirconium dioxide, ZrO_2), and barium sulphate ($BaSO_4$). They significantly improve the strength, wear resistance (Liu et al., 2021), radiopacity (Islam et al., 2023), and translucency of dental composites (Elfakhri et al., 2022). The type, size, and distribution of fillers can be customized to meet specific clinical requirements. Photoinitiator and co-initiator are added in small amount and responsible for the free radical polymerisation of monomers (Kowalska et al., 2021). Additives like inhibitor and pigments are added to prevent pre-curing polymerisation and to give colour, respectively. Figure 2.2 illustrates the composition of dental composite resin.

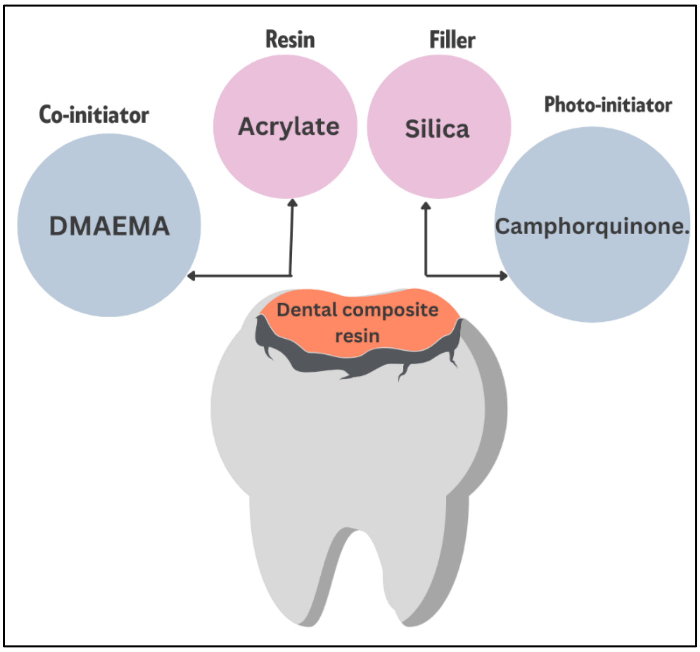

Figure 2.2 Dental composite resin composition

2.2.1 Resin matrix

In dental resin composites, the term "resin matrix" refers to a repeating chemical structure, or "monomer," that serves as the continuous phase for the filler dispersion that gives shape to the finished resin composite. Resin matrix in dental composite resin is typically composed of a single monomer or a mixture of monomers, often acrylated monomer such as bisphenol-A glycidyl methacrylate (Bis-GMA), urethane dimethacrylate (UDMA), triethylene glycol dimethacrylate (TEGDMA), and others. They are fluids and combined with other components like fillers, initiators, and additives to form the composite material. The filler particles, which are frequently inorganic materials like silica and calcium carbonate, are encased and joined by the resin matrix to form composite. This binding process increases the material's strength by evenly distributing stress.

Additionally, the function of resin matrix in dental composite materials is to facilitate adhesion and bonding to tooth structure and other dental materials (Sofan et al., 2017). The resin matrix in dental composites forms a strong bond with tooth structure through mechanical interlocking. This occurs when the composite is applied to the prepared tooth surface, and the resin flows into the microscopic irregularities of the tooth, creating a secure physical attachment (S. Zhang et al., 2023). As the dental composite resin is exposed to a specific wavelength of light (400-500 nm), curing process takes place. The resin matrix may contains light-activated initiators that enable it to cure or harden (Milosevic, 2016). This curing step is essential for stabilizing the composite material within the tooth cavity. During curing, a chemical transformation occurs. The C=C (carbon-carbon double) bonds present in the resin matrix polymerise, transforming into more stable C-C (carbon-carbon single) bonds (D. Watts, 2023). This polymerisation reaction solidifies the composite, ensuring that it becomes a durable and integral part of the tooth restoration.

Resin matrix also acts as an aesthetic material. The resin matrix can be designed to be translucent and resemble tooth enamel (LeSage, 2007). The aesthetic properties of the resin matrix are essential for achieving lifelike and visually appealing dental restorations. Furthermore, the resin matrix keeps the composite stable over time by minimising shrinkage during curing, which could otherwise cause gaps and leaks in the restoration. Researchers have actively pursued the development of low-shrinkage resin matrices as an innovative solution to tackle the persistent challenge of polymerisation shrinkage. This low-shrinkage resin will be discussed more in Chapter 2.2.2 (b). In conclusion, the resin matrix in dental composite resin is the polymer component consists of fillers and other additives, produces a flexible restorative material for dental application. It imparts physical and mechanical properties to the composite, including adhesion, strength, and aesthetics, making it a crucial element in modern dental restorations.

2.2.1(a) Acrylate based resin as dental filling restorative materials

There are numerous types of monomer options available; however, because they are intended to be utilised in humans, they must be biocompatible and stable in the oral environment. Historically, methyl methacrylate were utilised as monomers, but they had various drawbacks, including significant polymerisation shrinkage, deleterious effects on oral soft and hard tissue, and a slow hardening rate, which led to the discovery of Bisphenol A diglycidyl methacrylate (Bis-GMA) (Pratap et al., 2019b). It is formed by the o-alkylation of Bisphenol A (BPA) with epichlorohydrin, featuring a rigid core of phenyl rings and pendant hydroxyl groups that can form hydrogen bonding between themselves, resulting in high viscosity ($\eta = 1200$ Pa.s) and limited mobility. It is known for its excellent mechanical properties and durability.

The rigid aromatic rings in Bis-GMA (Figure 2.1) provides hardness to the composite. Bis-GMA is the predominant monomer utilized in resin-based dental materials, renowned for its widespread application (Gajewski et al., 2012). However, its high viscosity poses handling challenges and contributes to lower monomer conversion rates (Peutzfeldt, 1997). Despite these drawbacks, Bis-GMA offers advantages over smaller dental monomers like methyl methacrylate, including reduced shrinkage, higher modulus, and lower toxicity due to its diminished volatility and tissue diffusion (Sideridou et al., 2002). To reduce the high viscosity of Bis-GMA, triethylene glycol dimethacrylate (TEGDMA) is commonly used as a diluent to enhance handling, allowing for higher filler loading. Reducing the material's viscosity makes it easier to handle (Geurtsen & Leyhausen, 2001).

TEGDMA exhibits weak polar bond interactions between chains and possesses a flexible backbone structure, resulting in low viscosity. Unlike Bis-GMA, TEGDMA has a linear chain between its two methacrylate groups, contributing to its lower viscosity. However incorporating TEGDMA into the resin matrix can lead to reduced mechanical properties, and colour stability (Ok & Aykac, 2023). Urethane dimethacrylate (UDMA), developed by Foster and Walter in 1974, is synthesised from 2-hydroxyethyl methacrylate and 2,4,4-trimethylhexamethylenediisocyanate (Polydorou et al., 2009). Unlike Bis-GMA, UDMA lacks a phenol ring in its monomer chain, which results in higher flexibility and toughness. While UDMA exhibits higher viscosity than TEGDMA due to hydrogen bonding between amine (–NH–) and carbonyl (C=O) groups, it viscosity is still considerable than Bis-GMA (Khatri et al., 2003).

The presence of an aliphatic spacer group between methacrylates and urethane groups (–NHCOO–) contributes to the relatively high glass transition temperature (T_g) of UDMA's. UDMA-based resins demonstrate greater polymerisation rate and degree of conversion compared to Bis-GMA-based resins (Stansbury & Dickens, 2001). One significant benefit of acrylate is its rapid and efficient polymerisation upon light activation, enabling quick and predictable curing. Acrylated resins also demonstrates exceptional adhesion to both tooth structure and filler particles within the composite material (Allen, 1989). This strong bonding capability ensures durable restorations with excellent marginal integrity, minimizing the risk of microleakage and secondary caries formation (Zhou et al., 2023). Overall, the properties of acrylated resin contribute play a key role in the success and reliability of modern dental composite materials in restorative dentistry, providing clinicians with versatile and high-performance solutions for a various clinical application.

2.2.1(b) Low-shrinkage acrylated resins

There are several types of acrylate-based resins used in dentistry, each with their unique properties and applications. Some of them provide mechanical strength

(Kostić et al., 2022), flowability (Vouvoudi, 2022), dual curing (Konuray et al., 2018), biocompatibility (Sunarintyas et al., 2022) and anti-bacterial property (Khamooshi et al., 2022; Marra et al., 2012). However, methacrylate-based resins comes with a polymerisation shrinkage (Topa-Skwarczyńska & Ortyl, 2023a). It is caused by the conversion of monomers into a polymer network, where chemical bonds are formed, leading to a reduction in the intermolecular spacing. Details about polymerisation shrinkage is discussed in Chapter 2.4

Moszner & Salz (2001) conducted an extensive study on restorative composites, consisting of dimethacrylates, fillers, photoinitiators, and are cured using visible light. The study aimed to decrease shrinkage, enhance biocompatibility, and improve durability by using customized monomers (novel cyclic, liquid-crystalline, and ormocers) and improved fillers. Lu et al., (2005) investigated the common use of TEGDMA as a reactive diluent alongside Bis-GMA in dental resins to adjust viscosity, which, unfortunately, could result in water absorption and shrinkage. Their research delved into the potential of novel mono-(meth)acrylates as alternative reactive diluents to mitigate shrinkage and enhance double bond conversion in Bis-GMA-based copolymers. The findings indicated that specific highly reactive mono-(meth)acrylates demonstrated superior performance compared to TEGDMA. They exhibited faster curing rates, higher conversions, and reduced shrinkage, offering promising prospects for the improvement of dental resin materials.

Lu et al., (2005) used step-growth thiol-ene photopolymerisation to create improved dental restorative materials with reduced shrinkage and stress while maintaining adequate physical properties compared to dimethacrylate-based systems. The results highlight thiol-ene systems' advantages: lower shrinkage stress, faster polymerisation, increased functional group conversion, and reduced leachable, making them promising for dental restorations. Ge et al., (2005) created photopolymerisable formulations by employing dimethacrylate monomers with large substituent groups. The goal was to decrease polymerisation shrinkage while upholding conversion and mechanical properties. However, the bulky groups did not reduce shrinkage as anticipated, but they did improve double bond conversion, maintain mechanical properties, and foster more consistent copolymer networks.

Geiser et al., (2009) examined composites with nanosized SiO_2 in an acrylated hyperbranched polymer matrix. The addition of 20 % volume filler led to a significant 33 % reduction in cure shrinkage due to the replacement of polymer matrix with fillers. Wu et al., (2010) developed dental nanocomposites using polyhedral oligomeric silsesquioxane (POSS) to reduce shrinkage and enhanced mechanical properties. Yu et al., (2014) pioneered the development of BPA-free resin systems to address concerns surrounding Bisphenol A (BPA) derivatives in dental materials. Their findings demonstrated that these BPA-free resins achieved superior double bond conversion, similar or reduced polymerisation shrinkage, decreased water solubility, and lowered water sorption. Although there was a modest decrease in flexural strength and modulus, the BPA-free polymers exhibited enhanced fracture toughness, enhancing the longevity of dental materials.

Incorporating the monomer "Phene" into Bis-GMA/TEGDMA resin, as demonstrated by He et al., (2019), effectively mitigates polymerisation shrinkage while preserving the essential physical properties and wear resistance of resin composites. The most favourable outcomes were observed with a 20 % Phene composition. A recent research by Lamparth et al., (2021) addresses the issue of polymerisation shrinkage in dental composites by introducing new urethane-based addition-fragmentation chain transfer (AFCT) agents. These agents significantly reduce shrinkage stress in dimethacrylate resins, resulting in low-shrinkage materials with improved mechanical properties, including high flexural strength and modulus. Filemban et al., (2022) developed a novel dental resin composite to address shrinkage, bacteria, and remineralization concerns. By incorporating 2–5 % dimethylaminohexadecyl methacrylate (DMAHDM) and 20 % nanoparticles of amorphous calcium phosphate (NACP), mechanical properties were preserved. The low-shrinkage composite maintained a high degree of conversion (around 70 %) while decreasing shrinkage stress by 37 % compared to a commercial control. Grob et al., (2023) investigated the use of ethyl-2-(tosylmethyl)acrylate (ASEE) as a chain transfer agent for low-shrinkage dental composites. They tested ASEE-based composites with various initiator systems, revealing promising potential for low-shrinkage dental composites without affecting working time.

2.2.1(c) Polyethylene glycol in dental practice

Polyethylene glycol (PEG) is a polymeric compound composed of repeating ethoxy (ethylene oxide, $-CH_2-CH_2-O-)_n$ units. The number of these units, represented by "n," varies, resulting in PEGs with different molecular weights. It is a synthetic, water-soluble polymer that can vary in molecular weight, resulting in PEGs with different sizes and properties (Ramezani et al., 2022). PEG is widely used in various industries, including as a drug delivery agent and wound care in pharmaceuticals and medicine (Chen et al., 2023; D’souza & Shegokar, 2016; Hoang et al., 2020; Li et al., 2023; Armengol et al., 2022), as emulsifier, surfactant, and cleansing agent in cosmetics (Jang et al., 2015; Wang et al., 2017), and as foam stability, food packaging, lubricant in industrial applications (Dutta et al., 2023; Kobayashi et al., 2014; Shin et al., 2023; Xu et al., 2023), due to its versatility, biocompatibility, and solubility in both water and organic solvents. It serves a range of purposes, from drug formulation and wound care to lubrication and industrial processes, making it a valuable and versatile polymer.

In dental application, PEG was used as an antimicrobial material in oral environment because of its hydrophilicity and ability to reduce adhesion of proteins, platelets, and bacteria. PEG's effectiveness stems from forming a water layer on surfaces, reducing protein adsorption. It can be grafted to substrates or coupled with polyelectrolytes and has applications in coatings and composites for dental materials (Zhang et al., 2022). Application of PEG coatings to titanium mini-implants in orthodontics represents a significant breakthrough (Rodriguez-Fernandez et al., (2022). Having a bacteriostatic coating on orthodontic mini implants can help reduce the risk of infections and complications associated with implant placement. Bacterial colonization on implant surfaces can lead to peri-implantitis, which is a common issue in implant dentistry. By inhibiting the growth of bacteria, PEG coatings can contribute to better oral health outcomes for patients It serves as strong evidence supporting the feasibility of implementing bacteriostatic coatings on orthodontic mini-implants.

PEG also acts as a biocompatible lubricant, once functionalized with wheat germ agglutinin (WGA), it can stick to oral surfaces, reduce friction, and help relieve the discomfort of dry mouth (Blakeley et al., 2022). It does not have C=C double bonds, therefore incapable of the polymerisation and hardening process essential for dental materials. To make acrylated PEG with C=C double bonds, the two -OH (hydroxyl) groups at the ends of a PEG molecule are replaced with acrylate groups. This change allows the PEG to join with other molecules and form a strong, cross-linked structure. This modified form of PEG is useful in making materials like dental resins, where a durable and interconnected network is needed (Kazemi et al., 2023).

2.2.2 Fillers and reinforcements

Fillers in dental composite resin are defined as solid particles added to dental composite resin to enhance its properties. Fillers are typically made of inorganic materials like silica, glass, or ceramics. Fillers serve several purposes, including improving strength (Go et al., 2023), wear resistance (Chen et al., 2023), and radiopacity (Bazerbashi et al., 2023). Fillers vary in shape and size, with nanofillers being very small (nanometers) and microfillers being larger (micrometers). Large size of filler increase the overall stiffness and hardness of the composite (Elfakhri et al., 2022), reducing polymerisation shrinkage (Mohn, et al., 2020). Fillers also can be remineralizing (Bin-Jardan et al., 2023), antibacterial (Weiss et al., 2023), and self-healing (Elfakhri et al., 2022). Fillers can also be divided into two classes, according to their sizes (macro-size, micro-size, and nano-size) and shapes (particulates, fibres, whiskers, nanotube, and porous). Table 2.1 highlights the range and the sizes for fillers in dental composites (Elfakhri et al., 2022).

Table 2.1 Sizes and the ranges of fillers in dental composites (Elfakhri et al., 2022).

Size	Range
Macrofill	10-50 μm
Microfill	40-50 nm
Hybrid = Macrofill + Microfill	(10-50 μm) + (40 nm)
Midifill	(1-10 μm) + (40 nm)
Minifill	(0.6-1 μm) + (40 nm)
Microhybrid = Midifill + Minifill	(1-10 μm) + (0.6-1 μm) + (40 nm)
Nanofill	5-100 nm
Nanohybrid = Minifill + Nanofill	(0.6-1 μm) + (40 nm) + (5-100 nm)

Reinforcements are added to dental composite resin to provide additional strength, including fibres (e.g., glass or carbon) (Safwat et al., 2021) and particles (e.g., nano-hydroxyapatite) (Akhtar et al., 2021). Reinforcements enhance the mechanical properties of the composite, such as fracture toughness and flexural strength (Mangoush et al., 2020). Fibres can be randomly dispersed or aligned in a specific direction to control mechanical properties (Petersen et al., 2018; Suzaki et al., 2020; Tiu et al., 2023). Proper dispersion and alignment of reinforcements are critical for optimal performance. Reinforced composites are more durable and suitable for load-bearing applications. They are often used in crowns, bridges, and other restorative dental procedures (Martínez et al., 2020; Heo et al., 2020; Mohammadzadeh et al., 2016; Petersen et al., 2020). Table 2.2 shows the characteristic and comparison between filler and reinforcement in dental composite resin.

Table 2.2 Characteristics and comparison between filler and reinforcement.

Type	Uses	Type	Advantages	Disadvantages
Filler	Dental restoration	Particle (variable size)	Tooth appearance Reducing shrinkage Improving strength	Dispersion Agglomeration
Reinforcement	Bridge and crown	Particle and fibre	Load bearing application Strength Toughness	Alignment