FABRICATION AND CHARACTERISATION OF FLOWABLE COMPOSITE INCORPORATED WITH NANOHYBRID SILICA EXTRACTED FROM RICE HUSK

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LIST OF SYMBOLS

cm	Centimetre
g	Gram
GPa	Gigapascal
h	Hour
HV	Hardness according to Vickers
Hz	Hertz
kN	Kilonewton
kV	Kilovolt
min	Minute
mL	Millilitre
mm	Millimetre
$mm\ min^{-1}$	millimetre per minute
$mm\ s^{-1}$	millimetre per second
µm	Micrometre
MPa	Megapascal
nm	Nanometre
Pa·s	pascal-second
s	second

LIST OF ABBREVIATIONS

ADA	American Dental Association
AFM	Atomic force microscopy
ATR	Attenuated total reflection
BET	Brunauer-Emmett-Teller
Bis-GMA	Bisphenol A glycidyl methacrylate
CQ	Camphorquinone
DMAEMA	2-(Dimethylamino)ethyl methacrylate
FEA	Finite element analysis
FESEM	Field emission scanning electron microscope
FTIR	Fourier-transform infrared spectroscopy
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
LED	Light emitting diode
MDDMS	(3-Mercaptopropyl)methyldimethoxysilane
MPS	[3-(Methacryloyloxy)propyl]trimethoxysilane
MPTMS	(3-Mercaptopropyl)trimethoxysilane
SD	Standard deviation
TEGDMA	Triethylene glycol dimethacrylate
TEOS	Tetraethyl orthosilicate
TEM	Transmission electron microscope
UDMA	Urethane dimethacrylate
UTM	Universal testing machine

FABRIKASI DAN PENCIRIAN *FLOWABLE* KOMPOSIT YANG DIMASUKKAN DENGAN SILIKA NANOHYBRID YANG DIEKSTRAK DARIPADA SEKAM PADI

ABSTRAK

Kajian ini bertujuan untuk menghasilkan *flowable* komposit tempatan yang digunakan sebagai bahan tampalan gigi yang berkos rendah dan mesra alam dengan menggunakan pengisi silika nanohybrid yang berasal daripada sekam padi. Beberapa *flowable* komposit eksperimen difabrikasi dengan mencairkan Bis-GMA dengan TEGDMA pada perkadaran yang berlainan. Hanya nisbah 50:50, 45:55 dan 40:60 Bis-GMA: TEGDMA yang dikodkan sebagai EF50B, EF45B dan EF40B telah dipilih kerana konsistensi yang wajar. Sifat-sifat aliran, fizikal dan mekanikal *flowable* komposit eksperimen telah dibandingkan dengan tiga *flowable* komposit komersial (Revolution Formula 2, Tetric N-Flow dan G-aenial Universal Flo) yang bertindak sebagai tanda aras. Data dianalisa secara statistik dengan 'one-way ANOVA' (p=0.05) diikuti dengan ujian post-hoc Scheffe atau Dunnett T3. Tiada perbezaan yang ketara didapati antara aliran *flowable* komposit eksperimen (EF50B dan EF45B) dan *flowable* komposit komersial (Tetric N-Flow dan G-aenial Universal Flo). Selain itu, tiada terdapat perbezaan yang signifikan antara EF40B dan Revolution Formula 2. Jarak pengaliran EF50B dan EF45B tidak menunjukkan perbezaan yang signifikan jika dibandingkan dengan Tetrik N-Flow. Umumnya, kekasaran permukaan semua *flowable* komposit eksperimen menunjukkan tiada perbezaan statistik yang ketara bila dibandingkan dengan semua *flowable* komposit komersial kecuali G-aenial Universal Flo. Mereka mempunyai permukaan licin yang setanding di bawah mikroskop elektron

imbasan (SEM). Tidak terdapat perbezaan kekerasan Vickers yang ketara dikesan antara semua *flowable* komposit eksperimen dengan Revolution Formula 2 dan juga antara EF50B dan Tetric N-Flow. Kekuatan lenturan EF50B dan EF45B tidak menunjukkan perbezaan yang ketara berbanding dengan Revolution Formula 2. Kesemua *flowable composite* yang diuji telah memenuhi syarat minimum (50 MPa) untuk bahan pergigian yang tidak bertujuan untuk digunakan di dalam situasi yang melibatkan permukaan oklusal. Kekuatan mampatan semua *flowable* komposit eksperimen adalah jauh lebih rendah daripada *flowable* komposit komersial. Modulus lenturan semua *flowable* komposit eksperimen tidak menunjukkan perbezaan yang ketara dengan Revolution Formula 2. Tiada perbezaan yang signifikan didapati antara modulus mampatan semua *flowable* komposit eksperimen dengan Tetric N-Flow dan juga antara EF45B dan EF40B dengan Revolution Formula 2. Di antara *flowable composite* eksperimen, pencairan Bis-GMA menunjukkan peningkatan pada aliran, jarak pengaliran dan kekuatan mampatan sementara penurunan pada kekerasan Vickers, kekuatan lenturan, modulus lenturan dan modulus mampatan. Walau bagaimanapun, tidak ada kecenderungan yang diperhatikan pada kekasaran permukaannya yang disebabkan oleh pencairan itu. Secara keseluruhan, *flowable* komposit eksperimen mempunyai sifat-sifat aliran, fizikal dan mekanikal yang boleh diterima dan boleh menjadi bahan tampalan gigi yang berpotensi berasaskan teknologi hijau.

FABRICATION AND CHARACTERISATION OF FLOWABLE COMPOSITE INCORPORATED WITH NANOHYBRID SILICA EXTRACTED FROM RICE HUSK

ABSTRACT

This study was aimed to fabricate a local, low-cost and eco-friendly flowable composite in the application of tooth filling by using nanohybrid silica filler derived from rice husk. Several experimental flowable composites were made by diluting the Bis-GMA with TEGDMA at different proportions. Only 50:50, 45:55 and 40:60 ratio of Bis-GMA:TEGDMA coded as EF50B, EF45B and EF40B respectively were selected due to their desirable consistency. The flow, physical and mechanical properties of the experimental flowable composites were compared with three commercial flowable composites (Revolution Formula 2, Tetric N-Flow and G-aenial Universal Flo) as the benchmarks. Data was statistically analysed by one-way ANOVA (p=0.05) followed by Scheffe or Dunnett T3 post-hoc test. No significant differences were observed between the flowability of experimental flowable composites (EF50B and EF45B) and the commercial counterparts (Tetric N-Flow and G-aenial Universal Flo). Furthermore, there was also no significant difference between EF40B and Revolution Formula 2. The drip distance of EF50B and EF45B showed no significant differences when compared to Tetric N-Flow. Generally, surface roughness of all the experimental flowable composites showed no statistically significant differences to all the commercial flowable composites except G-aenial Universal Flo. They had a comparable smooth surface under scanning electron microscope (SEM). No significant differences were detected between the Vickers hardness of all the experimental flowable composites with Revolution Formula 2 and also between

EF50B and Tetric N-Flow. Flexural strength of EF50B and EF45B had no significant difference in comparison to Revolution Formula 2. All the tested flowable composite had passes the minimum requirement (50 MPa) for restorative material that are not intended to be used involving occlusal surfaces. Compressive strength of all the experimental flowable composites were significantly lower than that of commercial flowable composites. Flexural modulus of all the experimental flowable composites had no significant difference with Revolution Formula 2. No significant differences were found between the compressive modulus of all the experimental flowable composites with Tetric N-Flow and also between EF45B and EF40B with Revolution Formula 2. Among the experimental flowable composite, the dilution of Bis-GMA showed an increasing trend on the flowability, drip distance and compressive strength while decreasing trend on the Vickers hardness, flexural strength, flexural modulus and compressive modulus. However no trend were observed for their surface roughness due to the dilution. Overall, the experimental flowable composites had an acceptable flow, physical and mechanical properties and can be a potential green based dental filling.

CHAPTER 1

INTRODUCTION

1.1 Research background

Flowable composite is a type of tooth coloured restorative material with a lower viscosity compared to the other type of resin composites. Its introduction in the late 1960s offered an enhancement to the putty-like conventional resin composites which at the time demonstrated a lack of handling and manipulation ability (Bayne *et al.*, 1998). The flow property of the flowable composite gives high wettability, easier insertion, better adaptation to the internal cavity wall and greater elasticity than previous products, namely the putty-like conventional resin composites (Payne, 1999; Hervas-Garcia *et al.*, 2006). Figure 1.1 shows the visual comparison of the flowable composite and conventional resin composite. Flowable composite comes with a dispensing mode in which it can be delivered through small gauge needle. Restoring tiny cavities, tunnels and irregularities with difficult access are made possible with this needle like application where it flows well into the intended site (Yamamoto *et al.*, 2007). Thus, tooth restorations become easier, less time consuming and more efficient with this technology. In dentistry, flowable composite is considered as one of the versatile dental material, with a wide range of application including its role in preventive resin restorations, all classification of anterior and posterior restorations, lining and pit and fissure sealants, repairing fractured ceramic, porcelain, and denture, filling up defect in temporary restoration and splinting fractured and mobile tooth (Margolis, 2011; Baroudi and Rodrigues, 2015).

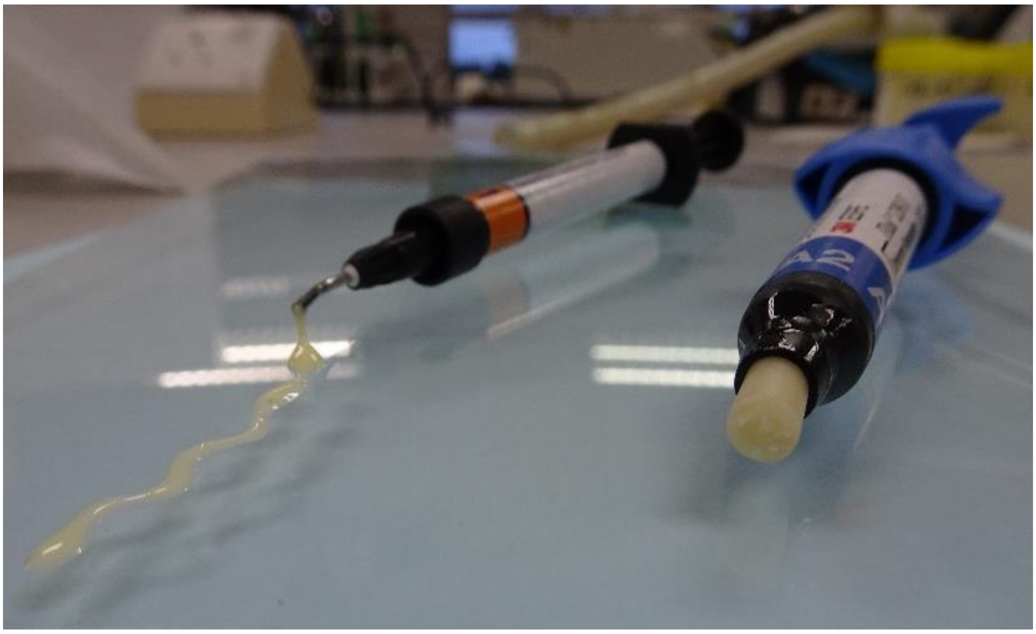

Figure 1.1 Visual comparison of flowable composite (on the left side) and conventional resin composite (on the right side).

Generally, flowable composite or any type of resin composite are composed of three main chemical ingredients which are filler, monomer and silane coupling agent that are safe and accepted to be used in dentistry (ADA Council on Scientific Affairs, A. 2003). The viscosity of flowable composite can be lowered by two methods, namely lowering the filler content or diluting the base monomer (Lee *et al.,* 2003; Baroudi *et al.,* 2007; Ferracane, 2011; Baroudi and Mahmoud, 2015). The fillers act as a reinforcement to strengthen the composite, while monomers function as a dispersing medium for the filler and silane coupling agent is used to bond the filler and matrix. Several type of particles and fibres were used as fillers, however silica is the most common one (Moszner and Klapdohr, 2004; Shouha *et al.,* 2014; Bijelic-Donova *et al.*, 2016; Habib *et al.*, 2016). The monomer system is based on methacrylate chemistry and many types of them had been used (Peutzfeldt, 1997; Moszner and Salz, 2001; Cramer *et al.,* 2011) yet still a combination of Bisphenol A glycidyl methacrylate (Bis-

GMA) and Triethylene glycol dimethacrylate (TEGDMA) or Urethane dimethacrylate (UDMA) are the mostly used monomer. Silane coupling agent like 3-(Trimethoxysilyl)propyl Methacrylate (y-MPS) have bifunctional chemical groups; one forms reaction with filler and the other forms interaction with the monomers. The size, shape, loading and type of filler (Turssi *et al.*, 2005; Ilie and Hickel, 2009), mixture of monomers (Sideridou *et al.*, 2002; Floyd and Dickens, 2006; Barszczewska-Rybarek, 2009; Gonçalves *et al.*, 2011) and silanisation process (Antonucci *et al.*, 2005; Aydınoğlu and Yoruç, 2017) were known to affect the performance of the composites clinically, physically and mechanically. As the composites need to withstand harsh oral condition and masticatory forces, numerous researches and developments had been done on these three systems; filler, monomer and silane coupling agent to improve their physical and mechanical properties.

Commercial flowable composite can be considered as an expensive dental material following the improvements as a result of ongoing researches and developments that take place in the dental material field. The price for one syringe consisted of approximately 0.5-2 ml of the composites can be in the range of RM 50 to RM 200 depending on the brands and manufacturers. Most of the flowable composites that were used in clinics particularly in Malaysia were imported from USA, Japan and Germany and this may be the reason for its high price. Furthermore, the silica filler used in the composites are synthesised using expensive chemical precursors such as sodium alkoxide and tetraethyl orthosilicate (TEOS) which may contribute to the high price as well. Furthermore, the chemical precursors used are also toxic (Bageru and Srivastava, 2017) which may cause harm to the environment and human. The expensive flowable composites may contribute to the high cost of dental treatment worldwide. In addition, it is reported that 2.3 billion people worldwide (FDI, 2016) and 6 out of 10 Malaysian primary school children particularly (Ministry of Health, 2014) had experienced dental caries. Therefore, dental treatment is in need. However lack of affordable dental material may limit the treatment (Peterson *et al,* 2010; FDI, 2015). Thus, researchers had been encouraged to find solutions to the problem.

In order to solve the problem mentioned, local researchers had work on the one part of the chemical that is being used in the flowable composite which is the filler. They had successfully synthesised green based nanohybrid silica filler from natural renewable resource which is suitable to be used in fabrication of resin composite (Zulkifli *et al.,* 2013; Noushad *et al.*, 2014). The nanohybrid silica was extracted from rice husk using sol-gel method. As a by-product from agricultural activity, rice husk can be found abundantly in Malaysia and yet it is a cheap and excellent source of silica (Athinarayanan *et al.*, 2015). Consequently, resin composite from the silica of the rice husk which had a putty-like consistency were developed (Noushad *et al.*, 2016). As an extension to the previous findings, modifications had been further made in order to improve the consistency of composite resin from rice husk. As the desired consistency achieved through the fabrication of flowable composite, the evaluation on the flow, physical and mechanical properties were subjected to further testings.

1.2 Problem statements and justification

1. In Malaysia, there is no local flowable composite that have been produced and commercialised yet. A local product can provide an affordable material for patients and clinics.

2. Conventional resin composite that incorporate the green nanohybrid silica filler derived from rice husk had been developed, however no

flowable composites is yet invented from the same resource. It would be beneficial if one can further formulates the flowable composites and expands the uses of the nanohybrid silica.

3. The newly developed flowable composites fabricated using the nanohybrid silica derived from rice husk need to be characterised in order to meet the clinical requirements in terms of their flow, physical and mechanical properties prior to its application in clinic.

To solve the problems, this study aimed to produce local, low cost and eco-friendly experimental flowable composites with the incorporation of nanohybrid silica filler derived from rice husk. A series of experimental flowable composites were made by diluting Bis-GMA with TEGDMA. Their flow, physical and mechanical properties were characterised.

1.3 Research objectives

1.3.1 Main objective

To fabricate experimental flowable composites incorporated with nanohybrid silica filler derived from rice husk and characterise their flow, physical and mechanical properties in comparison to the commercial flowable composites.

1.3.2 Specific objectives

1. To formulate experimental flowable composites from nanohybrid silica derived from rice husk.

2. To study the flow properties of the flowable composites

3. To investigate the physical properties of the flowable composites.

4. To evaluate the mechanical properties of the flowable composites.

1.4 Research hypothesis

1. The fabrication of the experimental flowable composites will be successful.

2. The flow properties of the flowable composites has no significant difference from commercial flowable composites.

3. The physical properties of the experimental flowable composites has no significant difference from commercial flowable composites.

4. The mechanical properties of the experimental flowable composites has no significant difference from commercial flowable composites.

1.5 Scope of study

This research is limited to the fabrication of experimental flowable composites that incorporated nanohybrid silica derived from rice husk and a combination of Bis-GMA and TEGDMA as the filler and monomers respectively. Silica was selected among other type of filler because it's the main type of filler in most of dental composite. Whereas the nanohybrid size of the filler was selected due to most of the flowable composite nowadays use nanohybrid filler type as it can produce good quality restoration in term of strength and esthetic value. Their flow, physical and mechanical properties were measured and compared with three commercially available flowable composites, Revolution Formula 2, Tetric N-Flow and G-aenial Universal Flo. The studied characterisation on the flowable composite were chosen due to their relevancy to dental clinician usage in which the important properties of flowable composite such as flow, surface properties, and mechanical properties are required.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The previous chapter stated the background, problem statements, aim and objectives of this study, where it all revolves around producing ecofriendly flowable composite from rice husk that have a comparable physical and mechanical properties with the one in the market. It is hope that the material can be further used for restoring defected tooth, thus the understanding of the properties and function of the flowable composite is required.

Thus, this chapter aim to review the properties, function and development on flowable composite as well as the test available to validate the flow, physical and mechanical properties of the flowable composite.

2.2 Flowable composite

While wide choice of materials are available on the market, resin composite is one of the versatile material preferred by clinician and mostly used in all classes and type of tooth restorations (ADA Council on Scientific Affairs, 2003). The vast use of resin composite or also known as the white tooth-coloured filling were mainly attributed to its aesthetic characteristic by having the ability to mimic tooth structure making the restoration appears natural. Furthermore, it has good mechanical strength and clinical longevity. Since it was first introduced in 1950, extensive researches and improvements had been done on resin composite with the aim to improve the physical and mechanical properties as well as clinical longevity (Cramer *et al.*, 2011; Ferracane, 2011). With the improvement, ideally, resin composite was ought to be used for all type of restorative situations and all areas of the mouth (Roeters *et al.*, 2005). However, to date, none can fulfil the criteria for an ideal requirement of the restorative material that suit all restorative situation. As a result of the advancement, various type of resin composites were introduced in the market which were formulated based on their particular clinical indications and requirements. There were anterior, posterior and universal resin composites which can be selected according to their indication and application. Another classification on these resin composites can also be based on their filler size (Lutz and Phillips, 1983). The latter classification categorised the resin composite into macrofill (10-50 µm), microfill (0.04-0.05 µm), hybrid (combination of filler at 10-50 µm and 40 nm), midifill (combination of filler at 1-10 µm and 40 nm), minifill (combination of filler at 0.6-1 µm and 40 nm) which is currently known as microhybrid, nanofill (5-100 nm) and nanohybrid (Ferracane, 2011; Ilie and Hickel, 2011). The filler size of nanohybrid is similar to microhybrid but with more portion of nano filler. Resin composite that possess the ability to produce smooth surface can be attributed to its submicron filler and nanoparticles which suits the anterior region restorations (Hervas-Garcia *et al.*, 2006).

Resin composite can also be classified according to their viscosity or consistency (Lee *et al.*, 2003; Roeters *et al.*, 2005; Ferracane, 2011). This category is divided into packable, universal and flowable composite. Among these three mentioned, packable or condensable composite had the highest viscosity and possessed the same consistency as amalgam (Roeters *et al.*, 2005). Universal composite that is indicated for general restorative uses, both at anterior and posterior site may have wide range of viscosity depending on their formulation (Ferracane, 2011). Having lower viscosity, flowable composite is indicated with the ability to flow into the cavity during its placement and stay when being light cured.

When it was first being marketed, flowable composite was famous merely due to marketing strategy by manufacturer rather than its clinical success (Bayne *et al.*, 1998). During those days, flowable composite had the same filler size as conventional hybrid resin composite but with 20-25 % less filler content (Bayne *et al.*, 1998; Baroudi *et al.*, 2007). Due to its lower filler content, it had low strength which made it unsuitable to be used in restoration that involved high loading stress area. Despite its poor clinical performance compared to conventional resin composite, it still preferred by many clinicians due to its flowability. One might ask the importance of flowability. In restorative dentistry, the defects or cavities on the tooth sometimes can be really small and deep with difficult access which can be in the size of 2 mm in diameter and 2 mm in depth (Ikeda *et al.*, 2009) where typical putty-like consistency resin composite may not be able to successfully load the cavity. On the other hand, flowable composite can flow and fill the cavity well ensuring a good adaptation to the tooth structure, in contrast to putty-like resin composite which might cause voids, porosities or gaps in the restoration (Opdam *et al.*, 1996b; Peutzfeldt and Asmussen, 2004). Moreover, the use of flowable composite eases the placement procedure and shorten the treatment time as opposed to manually packing the putty-like consistency resin composite. Opdam and colleagues stressed that handling characteristics affect the application and manipulation of the material (Opdam *et al.*, 1996a).

Research and improvement had been done on flowable composite to improve its clinical performance (Baroudi and Rodrigues, 2015). As the result, new generation of flowable composites were used for a wide range of application in restorative dentistry.

In order to study the physical and mechanical properties of a given material, it is paramount to discuss the clinical applications of the material as it is very much related to the science behind it. Prior to the clinical application discussion, an overview on the type of tooth cavities would give a better understanding on the situation.

2.3 Type of tooth cavities

Tooth cavities are caused by bacterial infection that leads to demineralization and destruction of the dental hard tissue. Figure 2.1 demonstrated the type of carious lesion based on G.V Black classification. The classification identifies caries according to their location on the tooth surface and is divided into six class as follow:

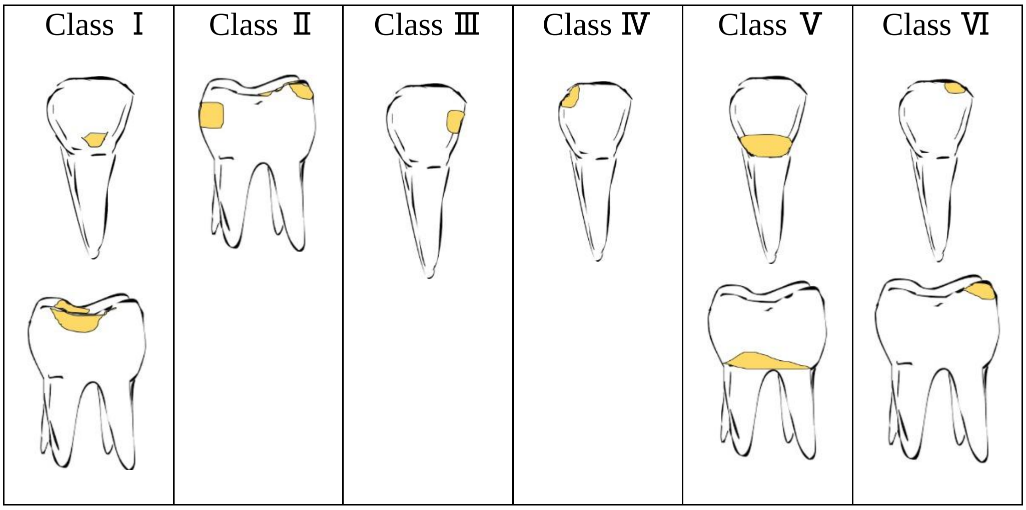

Figure 2.1 Type of carious lesion according to G.V. Black classification.

Class Ⅰ: caries that occur at the pit and fissure

Class Ⅱ: caries that occur at the proximal surface of posterior teeth.

Class Ⅲ: caries that occur at the proximal surface of anterior teeth but not affected the incisor line.

Class Ⅳ: caries that occur at the proximal surface of anterior teeth and extend to the incisor line.

Class Ⅴ: caries that occur at the cervical third of the teeth.

Class Ⅵ: caries that occur at the top surface or cusp tips of the teeth.

2.4 Clinical indications of flowable composite

2.4.1 Pit and fissure sealant

Flowable composite had been used extensively to seal pit and fissure of the tooth (Bagherian and Shiraz, 2018). The flowability of flowable composite enables it to flow well and adapt to the grooves of the pits and fissures. Based on the systematic review and meta-analysis done by Bagherian and Shiraz (2018), most of clinical studies reported that flowable composite showed a better clinical performance in comparison to other sealant materials. Over the time, sealant will eventually wear and abrade due to masticatory action and eventually needed to be reapplied at six months interval. Studies reported that flowable composite had showed better retention rates than conventional sealant (Jafarzadeh *et al.*, 2010; Erdemir *et al.*, 2014). Beun *et al.* (2012) measured the elastic modulus, flexural strength and Vickers hardness of eight commercially available flowable composites in comparison to four conventional sealants. They found out that flowable composite had a superior result for the tested parameters (Beun *et al.*, 2012). The highest value of elastic moduli, flexural strength and Vickers hardness for flowable composite group were 8.5 GPa, 116.1 MPa and 59.9 VHN respectively, while for sealant group were 3.6 GPa, 82.6 MPa and 28.5 VHN respectively. The superiority was possibly due to higher filler loading compared to the sealant.

2.4.2 Preventive resin restoration

Preventive resin restoration or minimally invasive class Ⅰ restoration involved pits and fissures areas which are infected by caries. After the caries is being removed, the needle application of flowable composite is very helpful as it enables the flowable composite to penetrate the small sites and flow well to the prepared cavity. A review had suggested the use of flowable composite in preventive resin restoration as it possessed the advantages of both sealant and conventional composite (Simonsen, 2005). From a survey that was sent to pediatric dentist, Savage *et al.* (2009) found out that most of the clinician preferred flowable composite compared to other restorative materials to restore preventive resin restoration. The selection was most probably due to flowable composite is easy to use as it flow well into the site and also possessed higher mechanical strength compared to sealant.

2.4.3 Cavity liner

Flowable composite is used as the first increment or liner for restoration of class Ⅰ, Ⅱ and Ⅲ cavities before filling up the rest of the cavities with conventional composite. This step is crucial as the flowable composite seal the margin and irregularities of the prepared cavity surface. Furthermore, due to its low viscosity, flowable composite can properly wet the cavity surface. Studies showed that microleakage was less when flowable composites had been used as liner before placement of conventional composite (Leevailoj *et al.*, 2001; Korkmaz *et al.*, 2007; Sadeghi and Lynch, 2009).

2.4.4 Class V abfraction lesions

Class V abfraction is defined as the chip of tooth surface resulted from the microfracture of enamel and dentin at cervical area (Nascimento *et al.*, 2016). During masticatory action, tooth is flexed, and masticatory forces are concentrated at the cervical area which caused the chip. Stiff or high flexural modulus restorative material may not be able to resist the flexure of the tooth (McCoy *et al.*, 1998). In one of the study, the retention rates of conventional resin composite was only approximately 70 % after 3 years of restoration (McCoy *et al.*, 1998). On the other hand, it is beneficial to use flowable composite as it does allow some degree of flexion due to its low flexural modulus characteristic. This has been displayed by Cieplik *et al*. (2017) who had treated 50 patient that were diagnosed with class V abfraction lesion using two type of flowable composites. After 5 years, the performance of both flowable composites were good as their retention rates were 94.7 % and 84.2 % (Cieplik *et al.*, 2017) and were better than reported by McCoy *et al.* (1998). Therefore, flowable composite may treat class V abfraction lesions better than conventional resin composite.

2.4.5 Other indications

Flowable composites can be used to bond orthodontic bracket or braces to tooth structure. In an *in vivo* study, Ryou *et al.* (2008) evaluated the shear bond strength, flow and flexural strength of flowable composites in comparison to an orthodontic bonding system (Transbond XT) and a resin composite (Filtek Z250). By having adequate bonding strength, flexuaral strength and good flowability, the flowable composites in the study had successfully bond the orthodontic bracket to the enamel (Ryou *et al.*, 2008). In tooth splinting, orthodontic wire, ribbon and retainer are used to stabilize the tooth and flowable composites is used to bond the mentioned appliances to the tooth structure (Tabrizi *et al.*, 2010; Purayil *et al.*, 2015). In a recent case report, flowable composites was successfully used to bond 2-unit cantilever fibre-reinforced composite bridge (Johari *et al.*, 2016).

2.5 Composition of flowable composites

Fundamentally, the flowable composite or any type of resin composite consists of three major chemically different materials which are the fillers, monomers and coupling agent (Pereira *et al.*, 2005; Cramer *et al.*, 2011). These three basic ingredients are also the main factors that can affect the physical and mechanical properties of the flowable composites.

2.5.1 Filler

Filler plays an important role in resin composite. It acts as the reinforcement that provides the strength, colour, translucency, and opacity of the resin composite. A lot of researches had been done to produce a variety of filler with different properties with the objective to improve the performance of the resin composite (Cramer *et al.*, 2011; Habib *et al.*, 2016). The physical and mechanical properties of the resin composite are dependent on type, loading, size, shape or geometry and porosity of the filler (Habib *et al.*, 2016).

2.5.1(a) Filler type

Various type of fillers had been used for fabrication of resin composite such as quartz, silica, silicate glass, strontium, alumina, zirconia, barium and glass (Klapdohr and Moszner, 2005). Earlier resin composite formulation included quartz as their filler due to its hardness and inertness toward oral conditions. Quartz was produced by grinding or milling process which made the particle large (0.1-100 μm), coarse and irregular in shape. Because of the size and shape of the quartz, the resulted composite was difficult to be polished, lacked aesthetic value and possessed high wear rates. Having the same strength as quartz but with the ability to be polished better, amorphous silica that was produced from sol-gel or pyrogenic process was used as the replacement to the quartz (Habib *et al.*, 2016). Most of the resin composite nowadays comprised of the silica as the main filler with addition of other type of filler as the co-filler. Silicate glass is incorporated to provide translucency and optical properties to the resin composite. Strontium and barium helped with the diagnostic process after resin composite was placed in tooth structure by yielding the radiopacity. Moreover, alumina and zirconia were added to improve the strength of the resin composite.

The mostly used filler, silica nowadays were generally synthesised from chemicals such as sodium silicate, silicon tetrachloride, tetraethyl orthosilicate as the precursors. Although high purity silica with defined morphologies, and size can be produced from these chemicals (Rahman and Padavettan, 2012), they are also expensive, hazardous and toxic (Tanaka *et al.*, 1982; Kizer *et al.*, 1984; Nakashima *et al.*, 1994). As an alternative, silica can be extracted from rice husk (Baccile *et al.*, 2009). Rice husk contains high percentage of silica (Athinarayanan *et al.*, 2015) and it is abundantly available in rice-producing countries where it can provide a low-cost silica source. The silica had gained attention among researchers as it can be turned into high potential products with a low impact on the environment. Silica from rice husk with different type, structure, size, porosity and shape are being produced by number of researchers with an extensive range of application. For health purposes it was widely used as drug carrier(Salazar Hernández *et al.*, 2014; Iqbal *et al.*, 2018), bioactive glass for bone replacement and regeneration (Naghizadeh *et al.*, 2015; Leenakul *et al.*, 2016) and scaffold for tissue engineering (Özarslan and Yücel, 2016). While the wide uses of silica from rice husk are found in other field, it may have less attraction in dentistry, which warrant further researches to fully utilise this potentially sustainable material. Based on the literature, only a few researches were focusing on the use of silica from rice husk as filler for dental materials. Shamsudin and colleagues derived silica from rice husk and sintered it together with lime stone to produced wollastonite, $CaSiO_3$ which was intended to be used as implantable dental material (Shamsudin *et al.*, 2017). Saowapark and colleagues impregnated silica from rice husk in natural rubber that can be used as rubber dam sheet, rubber band on braces and elastomeric chains (Saowapark *et al.*, 2016). Local researchers had done a series of experimental researches to extract well-defined silica from rice husk for application as filler in dental composite (Noushad *et al.*, 2013; Zulkifli *et al.*, 2013; Noushad *et al.*, 2014; Noushad *et al.*, 2016). In these studies, silica particles with different size range and morphology were successfully developed by manipulating the pH, addition of solvent, feed rate, mixing speed and drying mechanism. From the studies, silica with ideal properties was selected and further used in fabrication of dental composite (Noushad *et al.*, 2016). The resulted dental composites had surface roughness of 0.057 mm, Vickers hardness of 39 VHN, flexural strength of 107 MPa, flexural modulus of 6.2 GPa and compressive strength of 191 MPa (Noushad *et al.*, 2016).

2.5.1(b) Filler loading

Generally, the higher the filler loading, the higher is the physical and mechanical properties of a material. An increase in filler loading had shown to greatly affect the viscosity, hardness, flexural and compressive properties of the resin composite. Al-

Ahdal and colleagues studied the viscosity of commercially resin composite while Lee and colleagues measured the viscosity of their own fabricated resin composite and both did demonstrate an increase in viscosity as the filler loading was increased (Lee *et al.*, 2006; Al-Ahdal *et al.*, 2014). Beun and colleagues also revealed that viscosity of experimental flowable composite in their study did increase with the increase in microfiller loading (Beun *et al.*, 2009). With the aim of improving the strength, Rahman *et al.* (2017) evaluated the hardness of glass ionomer cement composite with the incorporation of 1-20 wt.% of nanozirconia-silica-hydroxyapatite filler. They recorded an increase in the hardness with the filler addition up to 3-5 wt.% (Rahman *et al.*, 2017). Ilie *et al.* (2009) measured the flexural strength, flexural modulus, compressive strength, diametric tensile of several type of resin composite with different filler loading. Result from the study revealed that filler volume had the most significant influence on the mechanical properties followed by filler weight and filler type (Ilie and Hickel, 2009). Although higher filler loading had a higher strength, this is true up to a certain level. The flexural strength of resin composite in Ilie and colleagues' work showed an increase in the trend up to 80 wt.% filler loading while above this value the flexural strength appeared to decrease (Ilie and Hickel, 2009). The assumption was made that it was probably due to an increase in defect occurrence in high filler loaded resin composite (Ilie and Hickel, 2009). The same phenomenon was observed by Rahman *et al.* (2017) as addition of filler more than 7 wt.% did decrease the hardness of the glass ionomer composite. They postulated that it was due to overloading of filler which disrupted the monomer matrix (Rahman *et al.*, 2017). Not many studies were found that could relate filler loading with surface roughness and they showed that surface roughness may not be significantly influenced by filler loading (Han *et al.*, 2014; Yilmaz and Sadeler, 2016).

2.5.1(c) Filler size

Filler size has prominent effect on the aesthetic value and roughness of the resin composite. Earlier filler was grinded from mineral thus producing irregular and large particle with an average size between 0.2-5.0 µm and less than 0.1 µm for macrofill and microfill composite respectively (Moszner and Klapdohr, 2004; Ferracane, 2011). Due to the large particle size, the final product was rough, lack of aesthetic value and difficult to polish. Advanced in nanotechnology enabled the filler to be produced in smaller size in the range of nano which is less than 100 nm. The nano filler was synthesised via several techniques such as flame pyrolysis, flame spray pyrolysis and sol-gel process. The resin composite comprised of nano filler is known as nanocomposite and studies has showed that nanocomposite can offer a better aesthetic value. Mitra *et al.* (2003) formulated nanocomposite consisted of 20 and 75 nm filler and compared its physical properties with hybrid and microhybrid composite. They found out that nanocomposite had better polish ability, gloss retention and wear resistance (Mitra *et al.*, 2003). Lai *et al.* (2018) tested the surface gloss, roughness and color change of six commercial flowable composites after simulated toothbrushing. The result from the study showed that G-aenial Universal Flo which contained the smallest filler (16 and 200 nm) had the most excellent surface properties and the lowest surface roughness (Lai *et al.*, 2018). Filler size in the range of nano was also believed to affect the mechanical strength and viscosity of the resin composite. The smaller filler size gives a better mechanical strength as the filler can be loaded at a higher percentage (de Andrade *et al.*, 2011) and offers an increased viscosity as a result of stronger interaction to the monomer matrix due to their high total surface area (Klapdohr and Moszner, 2005; Lee *et al.*, 2006; Guo *et al.*, 2012).

2.5.1(d) Filler geometry

Filler may take different form of shape such as spherical, irregular, nanotubes, fibre and whisker. Generally, spherically shaped filler was implemented in most of the commercial flowable composite while some manufacturers still filled their formulation with irregular filler from conventional grinding process. Spherical filler provides better polish ability, homogeneity and strength. Literature highlighted that stress may be localized at the edge of the irregular filler and hence weakening the resin composite. Instead of spherical and irregular shaped, fillers with other geometry were studied as a co-filler to increase the mechanical strength of resin composite. They were added to the main filler in a small amount. Chen *et al.* (2012) formulated resin composite by adding 1, 2.5 and 5 wt.% halloysite nanotubes as co-filler to conventional glass filler. The addition of 1 and 2.5 wt.% halloysite nanotubes in their study did increase the flexural strength, elastic modulus and work of fracture of the resin composite. The suggested reasons for the increase in strength were suggested due to firstly, halloysite nanotubes were strongly bonded to the resin; secondly, halloysite nanotubes had a higher modulus than resin; and thirdly the halloysite nanotubes aid in stress transfer when the composite are stretched (Chen *et al.*, 2012). Li *et al.* (2015) synthesised ceramic microfibres by using electrospinning technique and impregnated them in combination with glass filler into resin composite at 2.5 and 5.0 wt.%. In comparison to resin composite without addition of the fibres, the flexural strength and modulus of the fibres impregnated resin composite were superior (Li *et al.*, 2015). Addition of 2.5 and 5.0 wt.% of ceramic nanofibres into the resin composite formulation in another study showed a significant superior flexural strength, flexural modulus and energy at break (Guo *et al.*, 2012). The potential of whisker or rod-like shape filler had been investigated by several studies (Xu *et al.*, 1999; Wu *et al.*, 2017). The incorporation of 0.4 μm silicon nitride whisker into resin composite that had been done by Xu *et al.* (1999) was able to increase the flexural strength of the resin composite by two-fold. By incorporating small amount of hydroxyapatite whisker into the silica nanoparticle filled resin composite, Liu *et al.* (2014) successfully increased the flexural strength, flexural modulus and work of fracture of their formulated resin composite. They believed that the increase of mechanical strength was due to better dispersion of the hydroxyapatite whisker (Liu *et al.*, 2014) which possibly attributed to its high aspect ratio that permits higher filler-matrix interfacial interaction. In general, apart from fibre shaped filler, other geometrically form of fillers such as nanotubes, rod-shape or whiskers filler were still undergoing investigation and development, and none were used in commercial resin composite.

2.5.1(e) Filler porosity

Most of the filler used in resin composite are usually solid or non-porous in nature. However, a few researchers hypothesised that porous filler is better than non-porous filler as the filler porosity provides micromechanical bonding with the monomers which can result in an increase in the mechanical strength of the resin composite. Zandinejad *et al.* (2006) measured the flexural strength and modulus of resin composite impregnated with either non-porous or porous glass filler. They proved that porosity could increase the mechanical strength of the resin composite in their study (Zandinejad *et al.*, 2006). In another study, Atai *et al.* (2012) reported that their experimental resin composite which contained sintered nanoporous silica showed higher flexural strength, flexural modulus, fracture toughness and diametral tensile strength compared to the counterpart that contained non-porous glass filler. The superior result demonstrated by the use of porous filler in their study was believed due to the monomer matrix which had diffused into the surface porosity of the filler and created micromechanical retention (Atai *et al.*, 2012). Other researchers may have different point of view as the porosity may also act as void or empty space which can weaken the strength of the resin composite. In contrast to the above two studies, Liu *et al.* (2009) concluded that porosity of the filler itself may not increase the mechanical strength of their resin composite. In the study, they compared the flexural strength of resin composite that consisted of either dense or porous filler with different composition; A2 filler comprised of calcium-mica, fluorapatite and nepheline while A5 composed of fluorapatite and nepheline only (Liu *et al.*, 2009). The result in their study showed that the flexural strength of resin composite that contained porous A5 filler was 33% lower than that of dense A5 filler (Liu *et al.*, 2009). Factors that lead to the inferior result for resin composite that contained porous filler were possibly due to the monomer matrix may not be completely filled in the pore structure of the filler (Liu *et al.*, 2009) and residual pore may act as void that decreased the strength. In another study, Samuel *et al.* (2009) evaluated the potential of mesoporous silica filler to improve the mechanical strength of resin composite in comparison to nonporous silica filler. They revealed that resin composite had better mechanical strength with the combination of mesoporous and nonporous filler as compared to when they were used alone (Samuel *et al.*, 2009). Due to high surface area of the mesoporous filler, the highest filler loading that can be achieved in the study was only 50 wt.% which could be considered as low in comparison to typical type of conventional resin composite (Samuel *et al.*, 2009).

In short the physical and mechanical properties of flowable composite was strongly depended on the filler type, loading, size, geometry and porosity. Generally the physical and mechanical properties is favor to silica based, high loaded, nano size, fiber shaped and dense filler.

2.5.2 Monomers

Monomer is the subunit of repeating chemical structure that acts as the matrix for the filler dispersion which give shape to the resulted resin composite. Many choices of monomers are available, nevertheless as they are intended to be used in human, they need to be biocompatible and stable in the oral environment. Historically, methyl methacrylate and epoxy were used as the monomer, however they possessed several problems such as high polymerization shrinkage, some negative implications on the dental soft and hard tissue as well as low hardening rate which then lead to the finding of Bis-GMA by R.L. Bowen (Peutzfeldt, 1997). The Bis-GMA were synthesised from bisphenol A and glycidyl methacrylate or from diglycidyl ether of bisphenol A and methacrylate acid which produce bulky and difunctional monomer with large molecular size and chemical structure. Hence, Bis-GMA is a strong and stiff monomer that have low volatility and polymerisation shrinkage and rapid hardening. The finding of Bis-GMA lead to the development of other methacrylate-based monomers such as UDMA and TEGDMA that were usually used in combination with Bis-GMA in commercial resin composites (Moszner and Salz, 2001; Hervas-Garcia *et al.*, 2006). Figure 2.2 shows the chemical structure while Table 2.1 shows the molecular weight and viscosity of the Bis-GMA, UDMA and TEGDMA. A major problem with Bis-GMA is that due to its rigid backbone structure and high molecular weight, it is too viscous to be used alone and limits the amount of filler to be dispersed. The lower the viscosity, the more filler can be loaded. Therefore, UDMA and TEGDMA which have a lower viscosity are commonly used as the co-monomers.

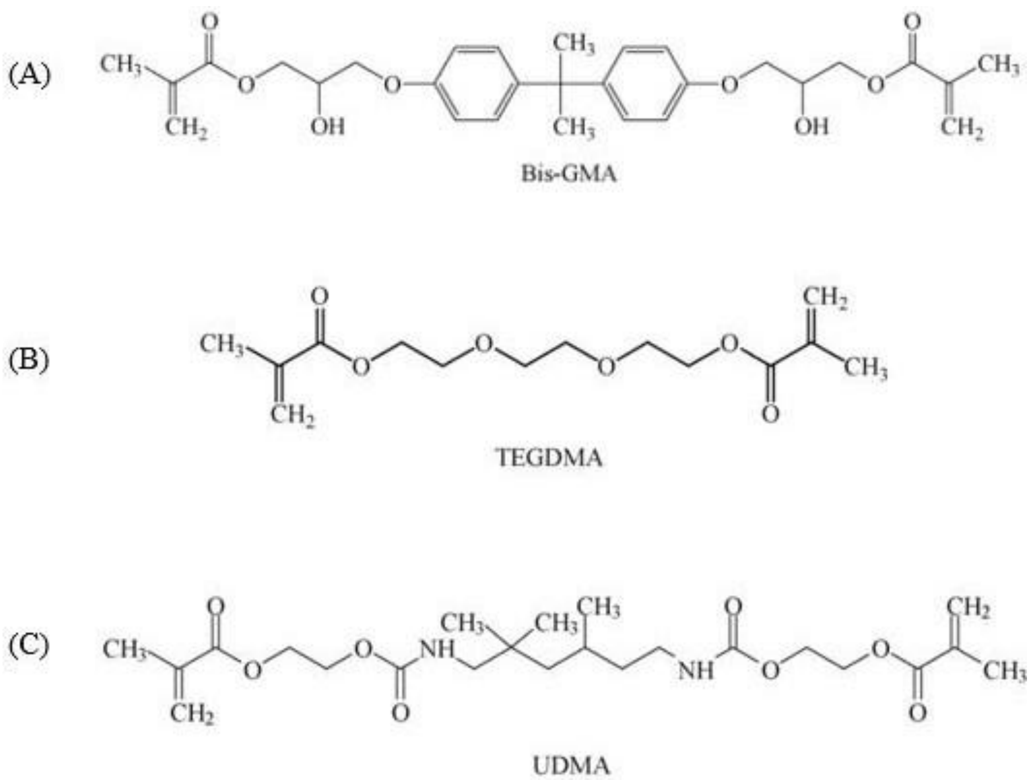

Figure 2.2 Chemical structure of Bis-GMA, TEGDMA and UDMA.

Table 2.1 Molecular weight and viscosity of Bis-GMA, TEGDMA and UDMA.

Monomer	Molecular weight (g/mol)	Viscosity (mPa·s)
Bis-GMA	512	500,000-800,000
TEGDMA	286	100
UDMA	470	5,000-10,000

The selection on the monomers with different type, chemical structure, functional group and molecular weight can significantly influence the physical and mechanical properties of the resin composite. In order to have the desirable flow property that suit for the flowable composite, the viscosity of the monomers mixture is