EFFECT OF FOOD SIMULATING LIQUIDS ON BULK-FILL COMPOSITES: A DYNAMIC ANALYSIS APPROACH

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ABSTRACT

Objective: To determine the effect of food simulating liquids on visco-elastic properties of bulk-fill restoratives using dynamic mechanical analysis.

Material and Methods: Four dental composites were evaluated which included a conventional composite (Filtek Z350 [FZ]), two bulk-fill composites (Filtek Bulk-fill [FB] and Tetric N Ceram [TN]) and a bulk-fill giomer (Beautifil-Bulk Restorative [BB]). Test specimens (12 x 2 x 2mm) were fabricated using customized stainless steel molds. The specimens were light-cured, removed from their molds, finished, measured and randomly divided into six groups. The groups (n=10) were conditioned in the following mediums for 7 days at 37°C: air (control), artificial saliva (SAGF), distilled water, 0.02N citric acid, heptane, 50% ethanol-water solution. Specimens were then assessed using dynamic mechanical testing in flexural three-point bending mode and their respective mediums at 37°C and a frequency range of 0.1 to 10 Hz. The distance between the supports were fixed at 10mm and an axial load of 5N was employed. Data for elastic modulus, viscous modulus and loss tangent were subjected to ANOVA/Tukey's tests at significance level $p<0.05$.

Results: Significant difference in visco-elastic properties was observed between composite materials and conditioning mediums. With the exception of bulk-fill giomer restorative (BB), the highest elastic modulus was observed after conditioning in heptane. For BB, conditioning in air gave the highest elastic modulus. Excluding FB, the lowest elastic modulus was noted after exposure to ethanol. FB showed the lowest elastic modulus after conditioning in distilled water. No apparent trends were noted for viscous modulus. Excluding BB where exposure to citric acid gave the greatest values, loss tangent was the highest when the composites were conditioned in ethanol. For all materials, air and heptane had the lowest loss tangent values.

Conclusion: The effect of food simulating liquids on the visco-elastic properties of the evaluated bulk-fill composites was material and medium dependent. The UDMA-based bulk-fill composite (FB), however, appeared to be more resistant to degradation effects of ethanol when compared to BisGMA-based conventional and bulk-fill composites.

ABSTRAK

Objektif: Untuk mengenalpasti kesan cecair simulasi makanan ke atas sifat likat-kenyal pengisian restoratif secara pukal dengan menggunakan analisa mekanikal dinamik.

Bahan-bahan dan Kaedah: Empat komposit pergigian telah dinilai termasuk satu komposit konvensional (Filtek Z350 [FZ]), dua komposit pengisian pukal (Filtek Bulk-fill [FB] dan Tetric N Ceram [TN]) dan satu giomer pengisian pukal (Beautifil-Bulk Restorative [BB]). Spesimen ujian (12 x 2 x 2 mm) telah dihasilkan menggunakan acuan keluli tahan karat yang dibuat khas. Spesimen telah dicahaya-sembuh, dikeluarkan dari acuan, dirapikan, diukur dan dibahagikan secara rawak kepada enam kumpulan. Setiap kumpulan (n=10) telah disimpan di dalam media-media berikut selama 7 hari pada suhu 37°C: udara (kawalan), saliva artifisial (SAGF), air suling, asid sitrik 0.02N, heptana, 50% larutan etanol. Spesimen kemudiannya dinilai menggunakan ujian mekanikal dinamik dalam mod fleksural di dalam media masing-masing pada suhu 37°C dan pelbagai frekuensi antara 0.1 hingga 10 Hz. Jarak antara penyokong telah ditetapkan pada 10 mm dan beban paksi 5N telah digunakan. Data untuk modulus elastik, modulus likat dan kehilangan tangen telah dianalisa menggunakan ujian ANOVA/Tukey pada aras keertian $p < 0.05$.

Keputusan: Perbezaan ketara dalam sifat likat-kenyal telah diperhatikan di antara bahan-bahan komposit dan media pensuasanaan. Kecuali giomer pengisian pukal (BB), modulus elastik tertinggi diperhatikan selepas pensuasanaan di media heptana. Bagi BB, pensuasanaan di udara memberi modulus elastik tertinggi. Tidak termasuk FB, modulus elastik yang terendah dicatatkan selepas pendedahan kepada etanol. FB menunjukkan modulus elastik yang paling rendah selepas pensuasanaan di dalam air suling. Bagi modulus likat pula, tiada aliran yang jelas. Tidak termasuk BB, di mana pendedahan kepada asid sitrik memberikan nilai terbesar, kehilangan tangen adalah yang tertinggi apabila komposit telah disuasanakan dalam etanol. Bagi semua bahan, udara dan heptana mempunyai nilai kehilangan tangen yang terendah.

Kesimpulan: Kesan cecair simulasi makanan terhadap sifat likat-kenyal komposit pengisian secara pukal adalah bergantung kepada jenis bahan dan media. Isian komposit pukal (FB) berdasarkan UDMA, bagaimanapun, tampak lebih tahan kesan degradasi etanol berbanding isian komposit konvensional dan pukal berdasarkan BisGMA.

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LIST OF SYMBOLS AND ABBREVIATIONS

°C : Degree Celsius

AFM : Addition Fragmentation Monomers

AUDMA : Aromatic Urethane Dimethacrylate

BB : Beautifil-Bulk Restorative

Bis-EMA : Ethoxylated Bisphenol-A-glycidyl Methacrylate

Bis-GMA : Bisphenol-A Glycidyl Dimethacrylate

Bis-MPEPP : Bisphenol-A Polyethoxy-Dimethacrylate

C=O : Carbon Oxygen Bond

$CaCl_2 \cdot 2H_2O$: Calcium Chloride Dihydrate

DDDMA : 1,12-Dodecanediol Dimethacrylate

DMA : Dynamic Mechanical Analysis

E' : Elastic Modulus or Storage Modulus

E" : Viscous Modulus or Loss Modulus

FB : Filtek Bulk-Fill

F-Br-Al-Si : Fluoro-Boro-Alumino-Siliciate

FSLs : Food Simulating Liquids

FTIR : Fourier Transform Infrared

FZ : Filtek Z350

GPa : Giga Pascal

Hz : Hertz

ISO : International Organization for Standardization

$J^{1/2}m^{-3/2}$: Solubility Parameter Unit (Joule per meter)

KCl : Potassium Chloride

KH_2PO_4 : Potassium Dihydrogen Phosphate

KSCN : Potassium Thiocyanate

mm : Millimeter

MMA : Methyl Methacrylate

N : Normality

NaCl : Sodium Chloride

$NaHCO_3$: Sodium Bicarbonate

$NaSO_4 \bullet 10H_2O$: Sodium Sulfate Decahydrate

NH_4Cl : Ammonium Chloride

nm : Nanometer

O-H : Oxygen Hydrogen Bond

pH : Potential Hydrogen (measurement of acidity)

PPRF : Pre-Polymerized Resin Fillers

SEM : Scanning Electron Microscope

S-PRG : Surface Modified Pre-Reacted Glass

$\tan \delta$: Loss Tangent or Tan Delta

TEGDMA : Triethylene Glycol Dimethacrylate

TN : Tetric N Ceram Bulk-Fill

UDMA : Urethane Dimethacrylate

μm : Micrometer

CHAPTER 1: INTRODUCTION

1.1 Introduction

Dental composites can be broadly classified according to their usage into restoratives, sealants, cements or provisional materials (Ferracane, 2011). Dental composite technology has progressed significantly over the past decade (Leprince et al., 2013; Shah & Stansbury, 2014). Despite this, polymerization shrinkage and depth of cure remain a clinical challenge (Deliperi & Bardwell, 2002; Park et al., 2008; Jang et al., 2015). The incremental layering technique had traditionally been used to reduce polymerization shrinkage stresses and to facilitate curing light penetration. Besides being time-consuming to perform, air entrapment, contamination and bond failure can also occur between layers (Park et al., 2008; Jang et al., 2015). Bulk-fill composite restoratives, that can be light polymerized in 4 to 5mm increments, overcome the need for conventional composite layering and incremental packing procedures (Leprince et al., 2014). Their superior depth of cure is achieved through advancements in photo-initiator dynamics and increased material translucency that allows for greater light penetration (Fleming et al., 2008; Flury et al., 2012; Lassila et al., 2012). Bulk-fill composites thus facilitate the restoration of large and deep cavities, reducing both technique sensitivity and clinical time (Benetti et al., 2015).

The mechanical properties of bulk-fill composites have been the subject of some disagreement. While some authors have reported lower mechanical properties than conventional highly-filled composites, others have stated otherwise (Ilie et al., 2013; Leprince et al., 2014; El Gezawi et al., 2016). Mechanical properties of dental composites are usually evaluated using static tests designed for elastic and not visco-elastic materials (Whiting & Jacobsen, 1980). As dental composites are visco-elastic in nature, static tests provide limited information on material structure and their destructive nature does not allow for re-testing of specimens (Jacobsen & Darr, 1997). Conversely, dynamic tests permit specimen re-testing after particular treatments and allow for variations in temperatures, frequencies and displacements within the elastic limits of the tested material (Jacobsen & Darr, 1997). Dynamic tests are also more clinically relevant than static ones as dental composites are primarily subjected to dynamic loads intra-orally (Mesquita & Geis-Gerstorfer, 2008).

DMA (Dynamic Mechanical Analysis) involves the application of oscillating forces to a sample and response analysis of the material's deformation to the applied force. Analysis of the responses allows for quantification of elastic modulus, viscous modulus and loss tangent (Menard, 2008). Elastic modulus examines the ability of a material to return or store energy and reflects its stiffness. Viscous modulus relates to the energy absorbed by a material without recovering elastically yet this energy is used in raising segmental molecular vibrations or for translating chain positions. Viscous modulus shows the tendency of a material to flow (von Fraunhofer & Sichina, 1994; Tamareselvy & Rueggeberg, 1994). Loss tangent, which is a dimensionless property, is the ratio between viscous modulus to elastic modulus and indicates the material's damping or how efficiently the material loses energy. The energy is lost as heat and has been related to molecular mobility (Menard, 2008; Vouvoudi & Sideridou, 2012). DMA can be used in several deformation modes including three point bending, four point bending, compression, tension, bulk, shear and torsion. Guidelines on using DMA for composite testing were established in 2009, based on a statistical review of three point bend DMA testing on different materials (Swaminathan & Shivakumar, 2009).

Dental composites are affected by their surrounding chemical environment and can be degraded by certain food ingredients and organic acids (Yap et al., 2000b). In addition to being constantly bathed in saliva, they are subjected to dynamic functional and parafunctional forces. Collectively, these factors may cause dissolution and softening of the resin matrix, filler damage and de-bonding (Wu et al., 1984; Drummond, 2008) and may affect the visco-elastic properties of dental composites leading to restoration complications or failure (Marghalani & Watts, 2013). Food simulating liquids (FSLs) listed in the Food and Drug Administration (USA) guidelines have been used to study dental composites (Food and Drug Administration, 1976). Citric acid and ethanol solution simulate certain vegetables, fruits, candies, beverages including alcohol and syrups. Heptane is used to mimic greasy foods like vegetable oils, butter and fatty meats. Distilled water and artificial saliva were included to imitate the wet oral environment provided by water and saliva (Yap et al., 2000b, 2005; Akova et al., 2006; Vouvoudi & Sideridou, 2012). FSLs have been found to affect the strength of dental composites in in-vitro studies. Whilst conditioning in ethanol generally weakens dental composites (Krishnan & Yamuna, 1998; Yesilyurt et al., 2009), exposure to heptane was equivocal with authors reporting both increased and decreased strength (Yap et al., 2000b; Akova et al., 2006). These studies were all conducted on conventional materials and few, if any, had determined the impact of food substances on the strength of bulk-fill composites. The latter is clinically meaningful as bulk-fill composites may behave differently from their conventional counterparts considering the variances in filler and resin technology.

Although the static flexural properties of composite restoratives had been widely reported, studies investigating the effect of FSLs on bulk-fill composites using dynamic testing methods are still limited.

1.2 Aim of the study

To assess the effect of FSLs on the visco-elastic properties of bulk-fill composites.

1.3 Objectives of the study

1. To determine the effect of FSLs on the visco-elastic properties of bulk-fill composites.
2. To compare the performance of the various bulk-fill composites after exposure to the different FSLs.

1.4 Null hypotheses

1. Visco-elastic properties of evaluated bulk-fill composites are not affected by FSLs.
2. No difference in visco-elastic properties exists between the various evaluated bulk-fill composites irrespective of conditioning mediums.

CHAPTER 2: LITERATURE REVIEW

2.1 Continuum of tooth colored restoratives

Tooth-colored restoratives have witnessed major advancements over the past few years due to the pursuit of more aesthetic alternatives to amalgam (Burke, 2004). Such materials form a continuum linking resin-based composites to glass ionomer cements as well as hybrids of these materials in between. Resin based composites are hydrophobic materials containing inert glass and polymer while glass ionomer cements tend to be hydrophilic materials depending on the reaction between glass and acid forming polysalt matrix (Bonsor & Pearson, 2013). Those restoratives are continually being improved to enhance their clinical application, manipulation and longevity (Leprince et al., 2013; Baig & Fleming, 2015).

2.1.1 Composite resins

Arising out of a material's science perspective, enamel and dentine are an exemplar of natural composite materials since they both incorporate organic and inorganic materials (Nanci, 2013; Seredin et al., 2017). Similarly, dental composite resins mainly consist of organic and inorganic phases. Resin-based dental composites were introduced for over fifty years where they kept evolving to become one of the paramount materials in restorative dentistry (Ferracane, 2011; Bayne, 2013). The main components of dental resin composites are organic resin polymer matrix, inorganic fillers, coupling agents (filler-matrix interface) and some minor additives including polymerization initiators, stabilizers and coloring pigments (Chung et al., 2004; Chen et al., 2011). Since 1963, rapid progress of composite resins has been witnessed in their composition in an attempt to improve their overall properties in clinical service. A summary of the evolution of dental composite over more than 50 years is shown in the schematic diagram in Figure 2.1 (Bayne, 2013).

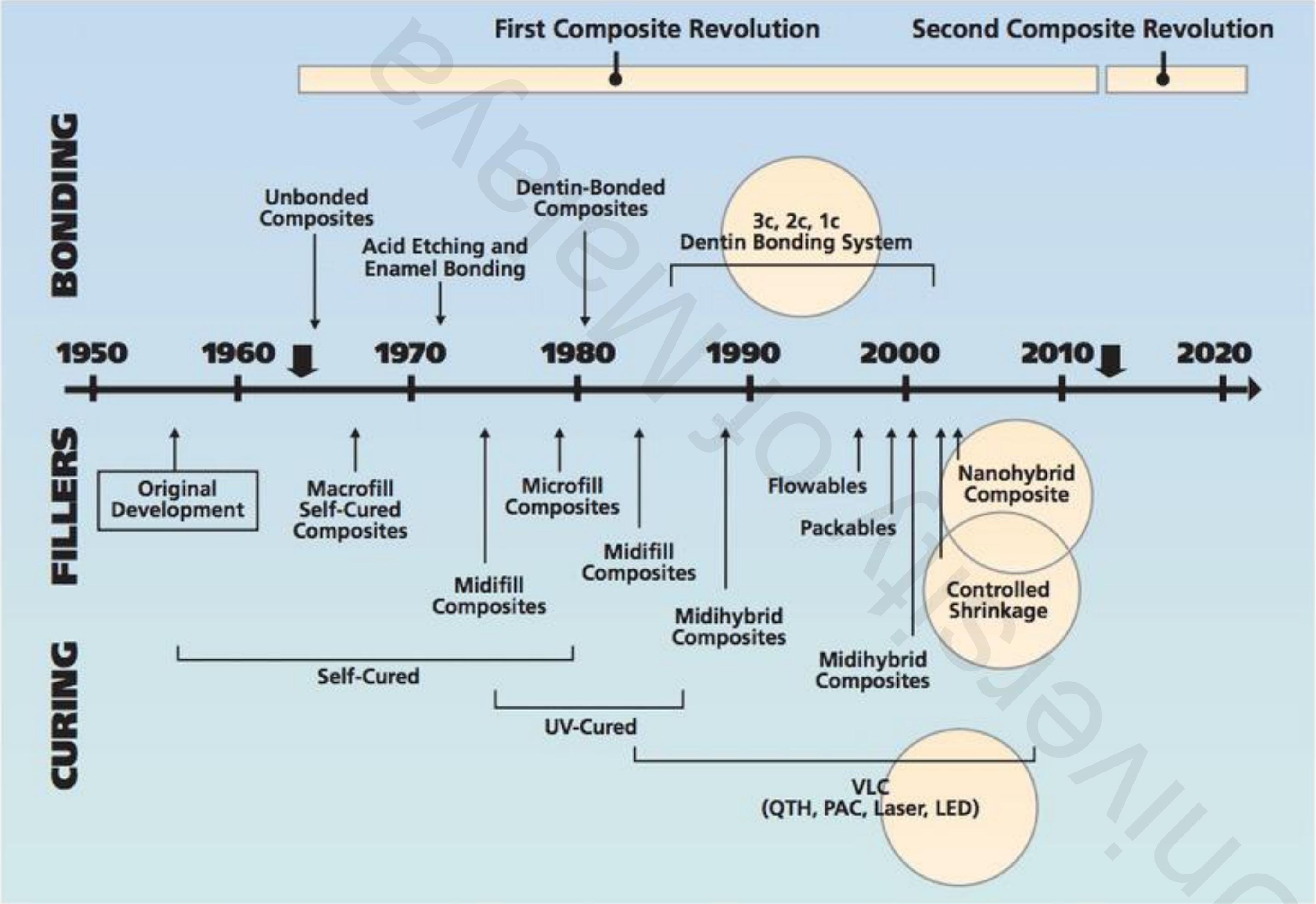

Figure 2.1: Evolution of composite resins (Bayne, 2013).

2.1.2 Classification of composite resins

Composite resins can be generally categorized according to their clinical application into cements, sealants, provisional materials, veneers, denture teeth, core buildups, intra-coronal and extra-coronal restorations (Ferracane, 2011; Sakaguchi & Powers, 2012). In accordance to their consistency, composite resins can be divided into either flowable or packable materials. Flowable composite commonly has low filler content of the mixture leading to its decreased viscosity while packable composite mostly has higher filler size and content causing its thicker consistency and packability (Choi et al., 2000; Baroudi & Rodrigues, 2015). Flowable composites, although having lower mechanical properties, can be used in areas with limited forces or as cavity liners for their flow and ease of adaptability (Sakaguchi & Powers, 2012; Baroudi & Rodrigues, 2015). On the other hand, highly filled packable composites are better suited for posterior fillings where they can withstand the frequent masticatory forces (Moszner & Salz, 2001; Cramer et al., 2011).

Composite resins can be characterized with respect to the fillers incorporated within, specifically the size. Furthermore, they can be classified according to type and distribution of their reinforcing fillers (Ferracane, 2011; Rahim et al., 2011). Subsequently, depending on the filler size, composite resins can usually be either macro-filled, micro-filled, nano-filled, micro-hybrid or nano-hybrid (Sakaguchi & Powers, 2012; Shah & Stansbury, 2014). The latter classification, however, is largely variable between different manufacturers due to the continuous and rapid modifications in the filler technology (Ferracane, 2011).

2.1.3 Composition of composite resins

2.1.3.1 Organic resin matrix

The resin matrix basically consists of synthetic monomers forming a cross-linked structure called the polymeric matrix after being cured. The monomer system is thought to be the base foundation of the organic resin matrix (Dhuru, 2004). Usually the monomers that are used, come in liquid form and are transformed to solids after polymerization. The degree to which the monomers are converted into polymers is termed the degree of conversion (Peutzfeldt & Asmussen, 1996; Bayne, 2005). Despite the fact that the mechanical properties of composite resins are mainly affected by the fillers, the resin matrix is a key contributor to the strength, stiffness and abrasion resistance of the composites (Peutzfeldt, 1997).

Initially, the monomers used in dental composite resins were methylmethacrylate (MMA). However, in 1962, Bowen developed a new monomer replacing MMA. The monomer was an aromatic dimethacrylate oligomer and a product from the reaction between Bisphenol-A and glycidyl methacrylate (Bis-GMA) (2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl] propane) (Bowen, 1962). Originally, Bis-GMA was synthesized from reacting bisphenol-A and glycidyl methacrylate, however, subsequently, it was prepared from the diglycidyl ether of bisphenol-A mixed with methacrylic acid leading to more advantageous effects (Lavigueur & Zhu, 2012). Until now, Bis-GMA is the prevalent monomer used in most of the commercially available composite resins (Gajewski et al., 2012).

Most manufacturers still use Bis-GMA on account of its high molecular weight which in turn leads to its low polymerization shrinkage (Hervás-García et al., 2006). Nonetheless, because of its high viscosity, the content of inorganic fillers that can be used with Bis-GMA is restrained since the content of filler is inversely proportional to the monomer viscosity (Peutzfeldt, 1997). As a result, other dimethacrylate monomers have been introduced to be mixed with Bis-GMA to dilute it, producing a more practicable mixture. These monomers mainly include ethoxylated bisphenol-A dimethacrylate (Bis-EMA), triethylene glycol dimethacrylate (TEGDMA) and urethane dimethacrylate (UDMA) (Hervás-García et al., 2006; Ferracane, 2011). Figure 2.2 shows the molecular structures of the most commonly used monomers (Gajewski et al., 2012).

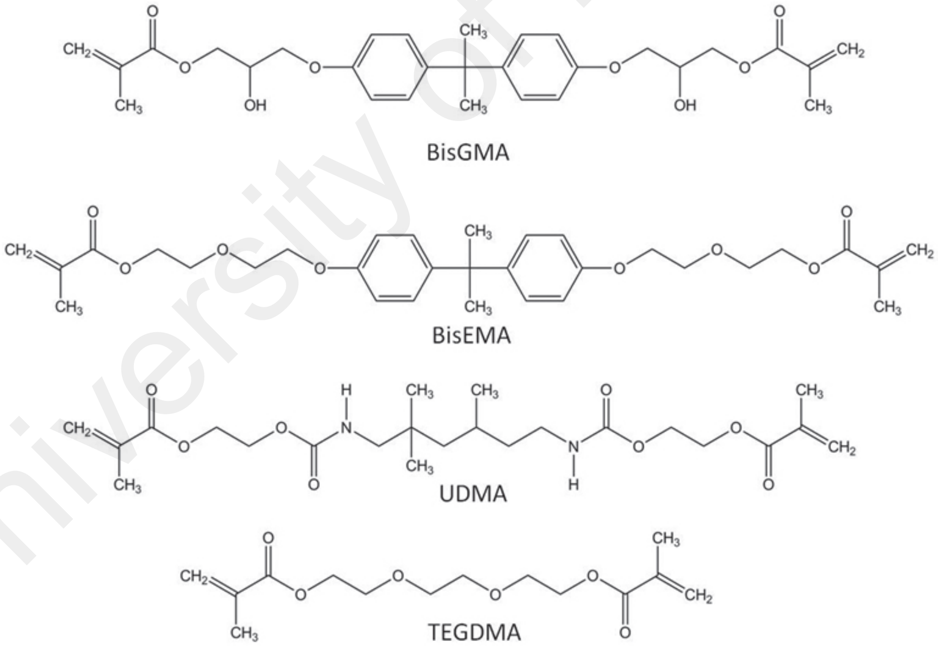

Figure 2.2: Molecular structures of the most commonly used monomers (Gajewski et al., 2012).

2.1.3.2 Inorganic filler

Inorganic fillers are particles that are formulated to reinforce the composite resin, reduce the stresses from polymerization shrinkage, lower the thermal expansion and lessen the degree of swelling resulting from water sorption (Munksgaard et al., 1987; Anusavice, 2003b). Moreover, it has been shown that fillers can provide increased stiffness, improved workability and better aesthetics for composite resins (Braem et al., 1989; van Dijken et al., 1989). However, even though adding fillers into the composite resins enhance their properties, there are limits to the percentage of fillers that can be incorporated. This is because the more fillers added, the more viscous the material becomes leading to difficulty in handling and manipulation (Lutz et al., 1983).

Due to the significant effects that fillers have on the performance of composite resins, especially the physical and mechanical properties, extensive amount of research have been carried out in order to improve their formulation (Hervás-García et al., 2006; de Moraes et al., 2009). The necessity for creating a greater balance of properties between the previously mentioned contradictory requirements has led to the development of different restorative composite resins, each for a different clinical situation (Anusavice, 2003b). Figure 2.3 shows the chronological development of the dental composite resins formulations based on the filler particles modifications (Ferracane, 2011).

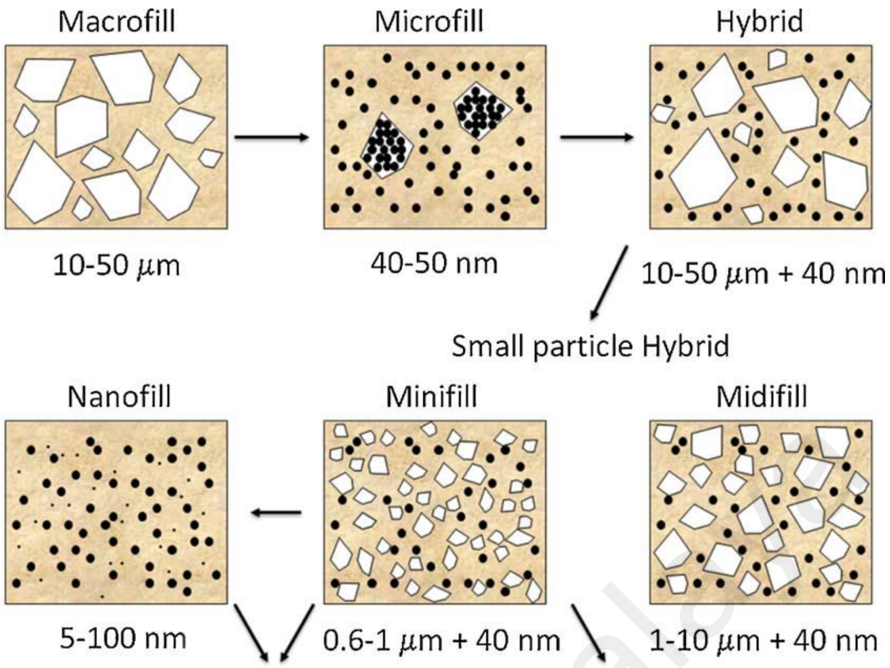

Figure 2.3: Chronological development of the dental composite resins formulations based on the filler particles modifications (Ferracane, 2011).

2.1.3.3 Coupling agent

Coupling agent is primarily a bonding agent applied to the inorganic filler particles in order to ensure chemical bonding to the organic resin matrix (Anusavice, 2003b). Although fillers incorporation plays a significant role in enhancing the composite resins, poorly bonded fillers to the resin matrix do not strengthen the resin but can in fact weaken the material. Hence, using an effective coupling agent is excessively important for a successful composite resin since it also permits the transmission of stresses from the more flexible polymer matrix to the more rigid filler particles (Peutzfeldt, 1997; Anusavice, 2003b; Ferracane, 2011).

2.1.4 Polymerization shrinkage of composite resins

In spite of their consequential improvements, resin-based composites experience several considerable drawbacks that shorten their life spans. These include complications related to their mechanical properties, depth of cure and polymerization shrinkage stress (Chen et al., 2011; Jang et al., 2015). Polymerization shrinkage stress is usually disseminated to the interface between the tooth and the filling which may lead to de-bonding, gap formation, microleakage and secondary caries (Braga et al., 2005; Lavigueur & Zhu, 2012). In addition, it can cause cuspal deflection and enamel cracks due to the damaging stresses on the tooth (Ferracane, 2005). All of the aforementioned factors may ultimately induce postoperative sensitivity and eventual premature failure of composite restorations (Park et al., 2008; Zorzin et al., 2015). Hence, it became a necessity to develop several strategies to decrease the produced stresses especially for the posterior composite restorations which are technically challenging and time consuming (Roulet, 1997).

2.1.5 Incremental layering technique

Various strategies have been generated to help decrease the stresses in dental composite resins, including modifications in the material's formulation or the curing system (Ferracane, 2005). Among the strategies incorporated to minimize the stresses from polymerization shrinkage are controlled light curing protocols, indirect resin restoration, using flowable resin liners and incremental layering technique (Park et al., 2008; Jang et al., 2015). The latter has been advocated to be used in large cavities where composite is placed in multiple layers not exceeding 2 mms; decreasing the effect of polymerization shrinkage, averting the limitation of curing depth and improving the aesthetics by utilizing multi-layering of color (Kovarik & Ergleb, 1993; Fleming et al., 2008; Furness et al., 2014). However, the incremental layering technique still has a number of disadvantages, including the incorporation of voids or contamination between layers leading to bond failure, difficulty in placement in limitedly accessible cavities as well as the lengthy time consumed to perform such technique clinically (Park et al., 2008; Jang et al., 2015).

2.1.6 Bulk-fill composite resins

Bulk-fill composites were introduced to overcome the issues of curing depth and polymerization shrinkage. They allow for the placement of materials in 4-5 mm increments without increasing shrinkage or compromising curing (Jang et al., 2015). That is achieved by means of novel resins, modified initiator systems; to ensure better curing depth compared to conventional composites, polymerization boosters; to allow fast curing, unique fillers and filler control; to act as shrinkage stress reliever (Fleming et al., 2008; Lassila et al., 2012; Yap et al., 2016). Furthermore, they incorporate the usage of special modulators and light sensitivity fillers to provide expanded working time by acting as a protective shield against operatory light, thus they don’t polymerize fast under ambient light. The mechanical properties of bulk-fill composites have been the subject of some disagreement. While some authors have reported lower mechanical properties than conventional highly-filled composites, others have reported values that are close to conventional composites (Ilie et al., 2013; Leprince et al., 2014; El Gezawi et al., 2016).

Various studies were carried out to assess the mechanical and physical properties of bulk-fill composites. A study which investigated different parameters as flexural strength, modulus of elasticity, degree of cure and Vickers hardness revealed promising results of such materials (Czasch & Ilie, 2013). Those modified versions of composite resins were reported to show values of polymerization shrinkage, compressive creep, nanoindentation as well as surface hardness that are analogous to those of the conventional composite resins utilizing layering technique (Ilie & Hickel, 2011; Flury et al., 2012). Moreover, bulk-fill composites showed degree of conversion up to 76-86% at an increment of 1 mm and up to 64% at an increment of 4 mm. These values are very much alike to the traditional composite resins which have a degree of conversion of 55-60% at an increment of 1 mm (Alshali et al., 2013; Vidhawan et al., 2015).

Despite the fact that some studies have reported similarity in the flexural strength when analyzing the different bulk-fill composites (Ilie et al., 2013), some other studies stated the presence of considerable inconsistency while comparing bulk-fill composites to conventional composites (Leprince et al., 2014). Hence, it was assumed that the modulus of elasticity and flexural strength of bulk-fill composites is variable between different materials depending on the filler type, filler loading and resin matrix utilized (Vidhawan et al., 2015). Usually, the modulus of elasticity of bulk-fill composites were reported to be within a range from 3.3 to 9.4 GPa (Leprince et al., 2014) although some studies reported values of up to 15 GPa for some bulk-fills which were still less than those of conventional composites reaching up to 20 GPa (El-Safty et al., 2012).

2.1.7 Giomers

Giomers, also known as PRG composites, are the latest composite-glass ionomer hybrid material (Saku et al., 2010). Giomers, unlike compomers, do not require water absorption after photo-polymerization for fluoride release (Tay et al., 2001; Ikemura et al., 2003). Differences between giomers, compomers and glass ionomers are displayed in Table 2.1. Giomers are based on surface pre-reacted glass ionomer (S-PRG) technology in which acid-reactive fluoride containing glass is pre-reacted with polyacids in the presence of water, freeze-dried, milled, silanized, ground, and used as fillers. The S-PRG fillers release fluoride, sodium, strontium, silicate, aluminum and borate ions (Wang et al., 2011). In addition to fluoride release and recharge, giomers also possess tooth demineralization inhibition and antiplaque formation properties (Gonzalez et al., 2004; Itota et al., 2004; Saku et al., 2010). Similar to other resin-based composites, giomers need bonding agents to adhere to tooth structure and are light-polymerized (Kooi et al., 2012).

A considerable number of studies have investigated the clinical performance of giomers clinically. A three-year clinical study showed no significant difference in the performance between giomers and micro-filled composites when used in Class V cavities (Matis et al., 2004). Furthermore, a clinical study including Class I and II restorations showed satisfactory clinical performance without restoration failures after thirteen years (Gordan et al., 2014). Other studies have also appraised the characteristics of giomers in-vitro. Giomers were reported to have considerably higher flexural strength when compared to resin modified glass ionomers (Sulaiman et al., 2007). In addition, they were reported to be harder when compared to mini-filled composites, compomers and ormocers (Yap et al., 2004). Another in-vitro study was done to evaluate the fluoride release from giomers and compomers where it was reported that giomer have significantly higher fluoride release and recharge than compomers (Dhull & Nandlal, 2009).

Table 2.1: Comparison between giomers, glass ionomers and compomers properties (Kataoka, 2016).

Category	Fluoride release	Recharge	Water sorption	Aesthetic	Bioactive or biointeractive
Giomer	Yes	Yes	No	Yes	Yes
Glass-ionomer	Yes	Yes	Yes	No	Yes
Compomer	Yes	No	Yes	Yes	No

2.2 Effects of food simulating liquids on tooth colored restoratives

2.2.1 Effect of oral environment on dental composites

Dental composite restorations are subjected to both physical and chemical degradation intra-orally. The surrounding environment in the oral cavity has a significant part in characterizing the final properties of the dental composites (Kao, 1989; Lee et al., 1996). Amongst the affecting factors in the oral environment are temperature changes, dynamic and static loading, chemicals and humidity from saliva and breathing (Marghalani & Watts, 2013). Accordingly, the matrices of dental composites are prone to softening and dissolution by the diverse food substances and liquids. In addition, filler damage and de-bonding can also occur, leading to leaching of fillers and ensuing in decreased restoration durability and longevity (Wu et al., 1984; Drummond, 2008). De-bonding, leaching out of fillers and their different effects on the properties of composites depend on the medium that they are subjected to (Krishnan & Yamuna, 1998). Therefore, various food simulants have been used for accelerated aging and testing mechanical and physical properties of dental composites (Krishnan & Yamuna, 1998; Vouvoudi & Sideridou, 2012).

2.2.2 Food simulating liquids

Food simulating liquids (FSLs) that are commonly employed in in-vitro studies include those listed in the Food and Drug Administration (USA) guidelines (Food and Drug Administration, 1976). A few of those liquids exist in the oral cavity while some mimic the ingredients of commonly used food and beverages (Vouvoudi & Sideridou, 2012). Distilled water and artificial saliva are used to replicate the wet oral environment presented by water and saliva. Citric acid mimics certain vegetables, fruits, candies, beverages and syrups while heptane imitates greasy foods like vegetable oils, salad dressing, butter and fatty meats. Ethanol-water solution simulates alcoholic drinks and used for accelerated aging of composites (Yap et al., 2000b, 2005; Akova et al., 2006; Vouvoudi & Sideridou, 2012). Studies revealed that the solubility parameter value of a food simulant can cause the maximal softening when it is equivalent or close to that of the matrix of composite resin, which in turn leads to decrease in the mechanical and physical properties of the composite (McKinney & Wu, 1985).

2.2.3 Effect of FSLs on various dental materials

It goes without saying that not only composite resins are degraded by FSLs but most of the various used dental materials as well. The influence of FSLs on mechanical and physical properties of soft lining materials had also been assessed in several studies (Jepson et al., 2000; Mante et al., 2008; Leite et al., 2010; Liao et al., 2012). Researchers have usually appraised the preservation of the visco-elasticity of the lining materials by measuring the change in hardness over time (Jepson et al., 2000; Mante et al., 2008). Generally, storage in ethanol-water solution demonstrated a remarkably different behavior than that in either distilled water or artificial saliva. There was a rapid uptake of ethanol from the ethanol-water solution followed by extraction of the ethanol miscible plasticizer and finally further uptake process (Liao et al., 2012). Additionally, employing a soft liner sealer was proved to decrease the degradation effect of artificial saliva on the methacrylate-based soft lining materials used (Mante et al., 2008).

The effect of FSLs on dentine bonding adhesive systems was also evaluated in in-vitro studies. Bonding agents are essential for optimum adhesion of the composite resin material to the natural tooth structure (Lee et al., 1996). The adhesion of most used bonding agents to dentine is due to the micromechanical bonding rather than chemical bonding (Van Meerbeek et al., 1992; Breschi et al., 2009). Therefore, it was a necessity to assess the effect of food solvents on the strength of the bond-interface formed between the tooth structure and different bonding agents (Lee et al., 1994). In addition, the effect of the solvents on the microstructure of the adhesive bonding agents themselves was examined using scanning electron microscope (SEM) and the fracture sites were inspected using Fourier transform infrared (FTIR) microscopic evaluation to further envisage the different effects whether related to the structure of bonding agents or the bonding interface (Lee et al., 1995, 1996).

With regards to the bonding interface, (Lee et al., 1994) reported a decrease in shear bond strength for all the tested bonding systems when stored in saliva compared to storage in air. For 75% ethanol-water solution, it was found out that the alcohol attack was mainly occurring in the composite system and reporting the maximum softening among the used food solvents. Considering the chemical similarity between the adhesive bonding systems to the composite resins, 75% ethanol caused degradation of resins as well (Lee et al., 1995). However, this occurred by means of decreasing in the amount of O-H bonds and increasing of C=O groups which suggested that the degradation is dependent on the chemical structure of the dentine bonding systems. SEM studies determined that fractures develop inside the bonding agent after conditioning for one week whereas they develop within both the bonding agent and the composite resin after conditioning for a period of two weeks or more (Lee et al., 1996).

Furthermore, studies on glass ionomers along with composite resins as well, were carried out to assess the effect of the chemical food solvents on the diverse materials since they have different compositions (Wu et al., 1984; McKinney et al., 1987; Kao, 1989; McKenzie et al., 2003). Generally, the most degradation for either the glass ionomers or the composite resins was observed after conditioning in a 75% or 50% ethanol-water solution having a solubility parameter values of approximately 3 or 3.7 x 10^4 $J^{1/2}m^{-3/2}$ respectively (Burrell, 1975; Kao, 1989). Those findings were in agreement with those done for composite resins alone (Wu et al., 1984; McKinney &

Wu, 1985). However, conditioning in 100% ethanol-water solution denoted increase in hardness which was attributed to possible dehydration. In addition, based on their findings, they suggested that urethane dimethacrylate matrix might be more susceptible to disintegration by food solvents than Bis-GMA matrix (Kao, 1989).

Likewise, researchers have investigated the effect of storage in the various food simulants on different resin luting cements (Nicholson et al., 2001; Bagheri et al., 2010). The shear punch strength test was performed to assess the mechanical properties of the different dental cements after conditioning in the various media for different time periods and varied temperature range. Shear punch test was used for its simplicity, reliability and that it can be used for diverse types of dental materials while giving results of great clinical significance, for instance the resistance to loads during mastication (Yap et al., 2003). The effect of food simulants on the shear punch strength was reported to be material dependent. Some materials reported significant decrease in strength over time while others weren’t significantly reduced. Hence, it was advised to use those significantly affected cements with caution since retention of restorations might be negatively affected (Bagheri et al., 2010).

2.2.4 Effect of FSLs on composite resins

Needless to say that exposure to FSLs extremely influence the mechanical and physical properties of dental composites (Krishnan & Yamuna, 1998). Moreover, ageing of dental materials in different aqueous solvents in order to simulate the oral environment has revealed faster degradation process (Shin & Drummond, 1999). Thus, their usage permits the assessing of fast wear of dental composites in a short period of time as well as appraising chemical affinity and elution processes (Vouvoudi & Sideridou, 2012). Although the effects of those simulants on composites are varied, they are all commonly related to degradation of polymer networks in view of the elution of unreacted fillers (Medeiros et al., 2007).

Studies have shown that conditioning in the various aqueous media for long storage periods may provoke several negative effects on the main components of composite resins (Calais & Söderholm, 1988; Martos et al., 2003). Those effects include softening of the organic resin matrix, leakage of the inorganic filler particles and degradation of the silane coupling agent, the actual bonding interface between the fillers and the resin matrix (Ferracane & Marker, 1992; Xu, 2003; Shah et al., 2009). Storage in distilled water has revealed decrease in the mechanical properties of composites that might be imputed to the water sorption by the resin matrix which induces swelling of the cross-linked polymer network (Shin & Drummond, 1999).

A study was done by McKinney and Wu (1985) to establish the effect of FSLs on the surface hardness and wear resistance of composite resins (McKinney & Wu, 1985). The different composites evaluated showed degradation after storage in the food simulating liquids where the greatest degradation was generally after storage in 75% ethanol-water solution which has a solubility parameter value around 3 x 10^4 $J^{1/2}m^{-3/2}$. It was assumed that any food ingredient or oral component having an approximate solubility parameter value would cause damage to Bis-GMA based composite resins (Wu et al., 1984; Burrell, 1975). On the other hand, conditioning in heptane, generally, showed a slight but significant increase in the surface hardness for the composites evaluated (McKinney & Wu, 1985). Conditioning in 100% ethanol-water solution revealed reduction in surface hardness and fracture toughness in studies while increased toughness was demonstrated in different studies (McKinney & Wu, 1985; Pilliar et al., 1987; Truong & Tyas, 1988). The disparity in findings might be due to the diversity in the techniques used to measure fracture toughness, different storage periods, or the different composition of the materials evaluated (Ferracane & Marker, 1992).

Subsequent studies were performed to further assess the mechanical and physical properties of dental composite resins. Conditioning in ethanol was found to generally weaken composites (Krishnan & Yamuna, 1998; Yesilyurt et al., 2009). On the other hand, exposure to heptane was equivocal with authors where some reported increasing strength while others observed decreasing strength (Yap et al., 2000b; Akova et al., 2006). The disparity in findings in the different studies may be attributed to the differences in the chemical compositions between the materials evaluated (Akova et al., 2006). The effect of food simulants was material dependent in general for the other aqueous solvents. There were still considerable differences in the strengths between the different materials evaluated when stored in distilled water and citric acid (Yap et al., 2000b).

Recently, the effect of FSLs on visco-elastic properties of composite resins were appraised in a few studies in order to better envision the clinical performance of those materials when exposed to food simulants (Vouvoudi & Sideridou, 2013; Sideridou et al., 2015). Dynamic tests were used since they resemble the cyclic load from mastication and chewing better than the regular static tests, which entitled those recent studies to be more clinically relevant (Vouvoudi & Sideridou, 2012). Conditioning of composite resins for 1 and 7 days in air led to a notable post curing whereas storage in distilled water and artificial saliva provoked post curing as well as plasticization. Nonetheless, storage in 75% ethanol-water solution showed a more intensive effect where it led to post curing, plasticization along with degradation and hydrolysis of the organic matrix (Vouvoudi & Sideridou, 2012, 2013). Conditioning in heptane for 30 days showed plasticization and seemingly deterioration of the organic matrix and the coupling agent bond (Sideridou et al., 2015).

Correspondingly, the effects of food simulants and acidic media on surface hardness and roughness of giomers were assessed in some studies. In view of the pre-reacted glass fillers incorporated in those materials, it was assumed that they might act in a different manner than the conventionally used composite resins (Mohamed-Tahir et al., 2005; Kooi et al., 2012). It was revealed that the influence of pH of the different acidic media on the surface hardness was material dependent and that each material allegedly had a certain pH level where maximum softening and degradation occurred. Giomers were reported to have reduced surface hardness when compared to conventional composite resins; however, they were harder than compomers (Mohamed-Tahir et al., 2005). Generally, giomers were similar to other composites in terms of being degraded by food simulants. Surface hardness was considerably affected by citric acid and 50% ethanol-water solution where surface roughness was mainly affected by citric acid (Kooi et al., 2012).

2.3 Static and dynamic testing of dental composite resins

Not long ago since the composite resin materials have been adopted as materials of choice for posterior fillings whether Class I or II, which exhibit a considerable amount of loading. Also, they have been used for anterior fillings which necessitates remarkable aesthetic properties (Tanimoto et al., 2011). Clinically, dental composite resins are usually subjected to mechanical forces either static loading from habits like clenching or dynamic loading while chewing food which may lead to failure of the restorations during function (Marghalani & Watts, 2013). Thus, several studies in the dental field have been conducted to improve the mechanical and physical properties of composite resins and by that elongating their clinical life in the oral cavity. Besides the aforementioned, much effort has been continuously made to maintain good aesthetic properties as well (Drummond, 2008).

2.3.1 Elastic modulus parameter

Recently, studies have been focusing on producing mechanical and physical properties of dental composite resins that resemble those of the natural tooth to a great extent. Nonetheless, differences between composite resin and tooth structure still prevail mainly in terms of polymerization shrinkage, thermal expansion and elastic modulus (Estafan & Agosta, 2003). Elastic modulus is a valuable parameter that can give beneficial information about the materials behavior. It is usually quoted as a general and wide-ranging indicator of the performance of composite resins (Jacobsen & Darr, 1997; Helvatjoglu-Antoniades et al., 2006). The elastic modulus of composite resins increases as the polymerization process continues. Thus, the degree of polymerization doubtlessly affects the changes in the elastic modulus throughout polymerization (Sakaguchi et al., 2002; Helvatjoglu-Antoniades et al., 2006).

Composite resins are usually subjected to excessive masticatory forces specially when placed in high stress-bearing areas as in posterior teeth (Marghalani & Watts, 2013). As long as the load applied to the composite lies below its elastic limit, no permanent deformation takes place. But as the load increases and surpasses the elastic limit, permanent deformation eventually occurs (Anusavice, 2003a). Elastic modulus in general represents the stiffness and rigidity of the material. Therefore, composite resins having low elastic modulus will be easily elastically deformed under load (Helvatjoglu-Antoniades et al., 2006). Elastic modulus along with adhesive properties play a major part in limiting microleakage, postoperative sensitivity, secondary dental caries as well as displacement of filling (Sabbagh et al., 2002).

Accordingly, appraising the elastic modulus of composite resins is essential for choosing the appropriate material for the different clinical applications (Jacobsen & Darr, 1997; Anusavice, 2003a). Composite resins with low elastic modulus are mostly better used for non-stress bearing areas such as cervical cavities (Class V) or Class III so that they can flex with the teeth when occlusally loaded. Whereas, composite resins with higher elastic modulus are more favorable for Class I, II and IV where they can withstand the masticatory forces in such stress-bearing areas (Lambrechts et al., 1987; Sabbagh et al., 2002; Yap et al., 2002). However, composite resins having excessively high elastic modulus are incapable of absorbing occlusal vertical forces. That leads to transmitting the stresses to the cavity walls which eventually might cause catastrophic fracture of the brittle tooth structure (Mesquita et al., 2006).

In addition, overly stiff composites are unable to flow and counteract the stresses from volumetric contraction that are produced throughout the polymerization process (Mesquita et al., 2006). Hence, the bonding interface between the composite resin and the tooth structure might be affected leading to tooth fracture and failure of the restoration (Davidson & Feilzer, 1997). In theory, the elastic modulus of composite resins ought to be similar to that of the dental tissue they are replacing, either enamel or dentine. This would decrease the unlike movement between the composite and the tooth during function, thus reducing risk of failure (Nakayama et al., 1974).

On the other hand, enamel and dentine have different elastic moduli where enamel is around 82 GPa and dentine is about 18 GPa (Craig, 1979; Willems et al., 1992). Generally, since enamel and dentine must be replaced concurrently, two different materials, each with a modulus resembling the tissue replaced, should be used. However, a more realistic approach would be selecting one of them as a standard (Mesquita et al., 2006). Composite resins are visco-elastic in nature which would be a mismatch to the enamel at the normal temperature of oral cavity, yet will rather be a more convenient match to dentine that exhibit visco-elastic response (Korostoff et al., 1975; Watts, 1994). Thereupon, dentine should be selected as the standard dental tissue in terms of comparing its elastic modulus to that of the available composite resins.

2.3.2 Elastic, viscous and visco-elastic behaviors of materials

Theoretically, a material is one of two extremes, either totally elastic or totally viscous. A perfectly elastic material would comply with Hooke's law that explains the stress in a specimen solely as a function of deformation but not time. While a perfectly viscous material would comply with Newton's law of viscosity that explains the stress in a specimen as a function of rate of deformation (Colo et al., 1997; Mesquita & Geis-Gerstorfer, 2008). However, in reality, materials do not act as either absolutely elastic or totally viscous except in rare cases like steel or water. In the majority, all other materials including polymers and composite resins can be characterized as visco-elastic materials (Saber-Sheikh et al., 1999).

Basically, visco-elasticity describes a material's gradual response to applied force where it attain a final value after some time delay (Ferry, 1980). This can be explained by the requisite for enough time by the polymeric molecular chains of a material to be completely accustomed to the exerted stress. Hence, the faster the load applied, the less the time allowed for a material to adapt to the stress (Menard, 2008). For a visco-elastic material, after removal of an applied force, part of the material returns to its original form which can be related to the elastic property. On the other hand, the other part experiences permanent deformation which can be attributed to the viscous property (Mesquita & Geis-Gerstorfer, 2008). The typical form of deformation of a polymer after applying continuous stress followed by recovery after stress removal is presented in Figure 2.4.

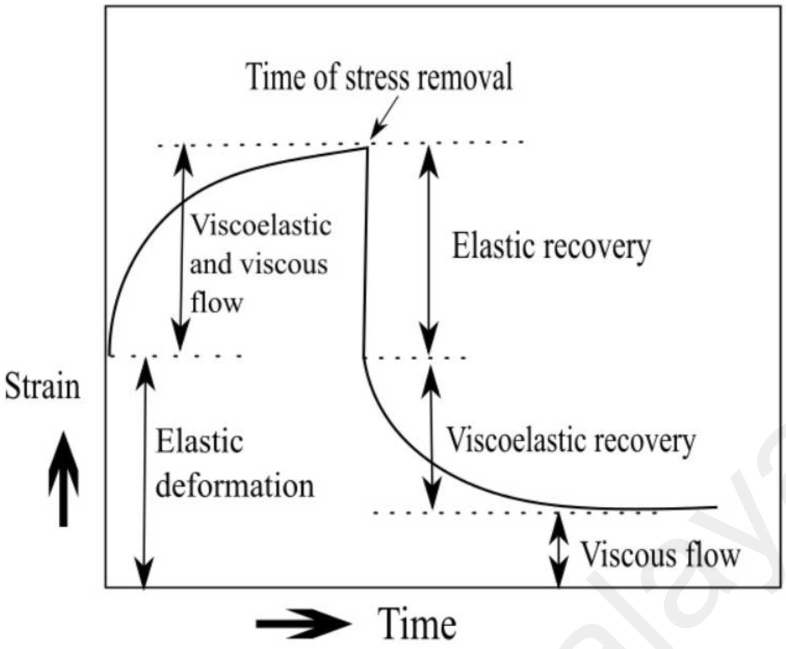

Figure 2.4: Typical form of deformation of a polymer after application of constant stress and recovery on stress removal (Vaidyanathan & Vaidyanathan, 2001).

2.3.3 Static vs. dynamic testing

In vitro assessment of mechanical properties of composite resins tend to be quite difficult in virtue of being highly rigid materials, their visco-elasticity and requisite of using clinically realistic specimen sizes (Whiting & Jacobsen, 1980). Generally, the mechanical properties of dental composite resins have been evaluated through static tests including flexure, compression, tension, shear and hardness tests (Tanimoto et al., 2011). However, static tests give restricted information on the structure of the materials since the acquired information pertain to a longer duration than that of mastication. Moreover, despite being valuable in assessing the utmost strength, those static tests are not well fitted for appraising the visco-elastic properties of composite resins (Jacobsen & Darr, 1997; Saber-Sheikh et al., 1999). Furthermore, static tests have destructive nature where the specimens are usually ruined; which in turn hinder the ability of re-testing the specimens (Jacobsen & Darr, 1997).

Even though the static behavior of composite resins have been interpreted in several studies, their dynamic behavior is inadequately appreciated owing to the limitations of testing in a universal testing machine (Tanimoto et al., 2011). Dynamic testing is usually preferable since they can more competently simulate the cyclic masticatory forces that the composite resins are exposed to in-vivo (Saber-Sheikh et al., 1999). These more relevant tests are more suited to assess the visco-elastic materials giving information about both the elastic and the viscous portions of a material at the same time (Colo et al., 1997). Hence, in the current study, a dynamic mechanical analysis (DMA) approach was employed to better assess both the elastic and viscous behaviors of the evaluated composite resins.

2.3.4 Dynamic Mechanical Analysis (DMA) concept

DMA is a technique that has been utilized to obtain valuable information regarding the visco-elastic behavior of a material including composite resins based on the change of time, frequency and temperature. DMA could be simplified as “applying an oscillating force to a sample and analyzing the material’s response to that force.” (Menard, 2008). Through using DMA, a specimen with a precise dimension is subjected to a strain in the form of sinusoidal mechanical deformation and the equivalent force is measured. This is either done at a constant frequency or a range of frequencies over a certain temperature range or is carried out at a constant temperature over a definite time period (Waters et al., 1997). Figure 2.5 illustrates a schematic diagram showing how a typical Perkin-Elmer DMA works (Menard, 2008).

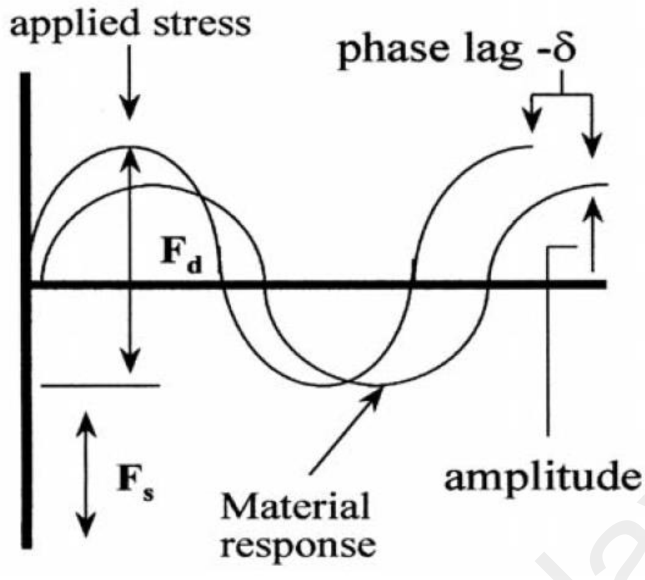

Figure 2.5: How a typical Perkin-Elmer DMA works (Menard, 2008).

Fs: Static or clamping force whereas **Fd:** dynamic or oscillatory force. "DMA produces an oscillatory force causing sinusoidal stress to be applied to the sample which generates a sinusoidal strain. By analyzing the amplitude of deformation and the lag between stress and strain, visco-elastic properties can be calculated."

Another method that can be used via the DMA is applying a pre-determined force amplitude to the specimen then calculating the resulting strain in the form of deformation. A slower response indicates a more viscous material while a faster one demonstrates a more elastic material (Nahm, 2001). In a nutshell, a strain represents the alteration in the length of a material after application of force whereas a stress describes the internal force in a material that is equivalent yet opposing to the exerted load (Waters et al., 1997).

Parameters that can be derived from DMA include elastic or storage modulus (E'), viscous or loss modulus (E'') and loss tangent (tan δ). Elastic modulus embodies how stiff and rigid the material is and indicates its ability to store elastic energy amidst a loading cycle. Viscous modulus relates to the energy absorbed by the material which does not recover elastically yet this energy is utilized in raising segmental molecular vibrations and in terms of viscous flow as well (von Fraunhofer & Sichina, 1994; Tamareselvy & Rueggeberg, 1994). Loss tangent is a dimensionless property that quantifies the material’s capability to damp mechanical energy within the material via conversion into heat and is defined by the ratio of E'' to E'. Hence, a purely elastic material has a loss tangent which is equal to zero. When applying a sinusoidal stress to a completely elastic or viscous material, deformation occurs precisely in phase or lag 90° behind the stress applied respectively. For visco-elastic materials, the ensuing strain will be delayed behind the stress by an angle s, where s is $< 90°$ (Jacobsen & Darr, 1997; Waters et al., 1997).

2.3.5 DMA and dental materials

In view of its versatile configurations and great clinical relevance in assessing the visco-elastic materials, DMA has been used in a number of studies to examine the dynamic mechanical properties of dental materials in general and composite resins in particular. Visco-elastic properties of some denture base resins as well as soft liners have been assessed from a dynamic analysis approach. Waters et al. utilized dynamic mechanical analysis to examine the deformation parameters of different silicone rubber materials that are employed during manufacturing of facial prostheses (Waters et al., 1997). Saber-Sheikh and others investigated the time dependent, visco-elastic behaviors of some dental soft lining materials using DMA. They reported that rubbery-like soft liners had low modulus and were insensitive to temperature whereas leathery-like ones had high modulus and were very sensitive to temperature (Saber-Sheikh et al., 1999).

Likewise, the dynamic mechanical properties of several composite resins have been characterized using DMA in some studies. Tamareslvy and Rueggeberg assessed the visco-elastic properties of two dental restorative co-polymers to clarify the effect of dependent group length and adding a crosslinking agent (Tamareselvy & Rueggeberg, 1994). Jacobsen and Darr examined a series of polymeric dental composite materials cured by primary and secondary methods by both static and dynamic testing (Jacobsen & Darr, 1997). Vaidyanathan and Vaidyanathan assessed the deformation under stress and recovery following removal of stress for three different composite resin systems including micro-filled, mini-filled and mid-filled types (Vaidyanathan & Vaidyanathan, 2001). Lovell et al. evaluated the influence of curing rate on the mechanical properties of commonly used dimethacrylate dental resin where it was revealed that the properties of highly cross-linked dimethacrylates in terms of double bond conversion were not affected by rate or method of cure (Lovell et al., 2001).

Another study by Sakaguchi et al. was carried out to examine the capability of using DMA of tubular geometry in a flexural three-point bend fixture so that the storage modulus development of a light activated polymer matrix composite could be monitored (Sakaguchi et al., 2002). Mesquita et al. evaluated the visco-elastic properties of direct and indirect composite resins via dynamic mechanical analysis in various temperature and frequencies ranges after storage in either air or distilled water (Mesquita et al., 2006; Mesquita & Geis-Gerstorfer, 2008). Park et al. reported a study where the visco-elastic properties of dentine adhesives utilizing a new monomer were evaluated using DMA (Park et al., 2009). Subsequently, they assessed the effect of addition of iodonium salt to different photo-initiator systems on their dynamic mechanical properties (Park et al., 2010).

Vouvoudi and Sideridou examined the dynamic mechanical properties of nano-filled composite resins where a wide range of temperature was used while maintaining a fixed frequency of 1 Hz (Vouvoudi & Sideridou, 2012). Later they assessed the effect of FSLs on the visco-elastic properties of different commercial nano-hybrid composite resins (Vouvoudi & Sideridou, 2013). In conclusion, there were limited, if any, studies that characterized the dynamic mechanical properties of bulk-fill resin composites after conditioning in different FSLs. Therefore, in our study, the effect of FSLs on the visco-elastic properties of bulk-fill composites were assessed using DMA.

CHAPTER 3: MATERIALS AND METHODS

3.1 Materials

The materials evaluated and their technical profiles are shown in Table 3.1 as well as in Figures 3.1-3.4. They included a conventional composite (Filtek Z350 [FZ]), two bulk-fill composites (Filtek Bulk-Fill [FB] and Tetric N Ceram Bulk-Fill [TN]) and a bulk-fill giomer (Beautifil-Bulk Restorative [BB]). The conventional composite served as a comparison for the bulk-fill materials.

Figure 3.1: Nano-hybrid composite resin, Filtek Z350 (FZ) [Control].

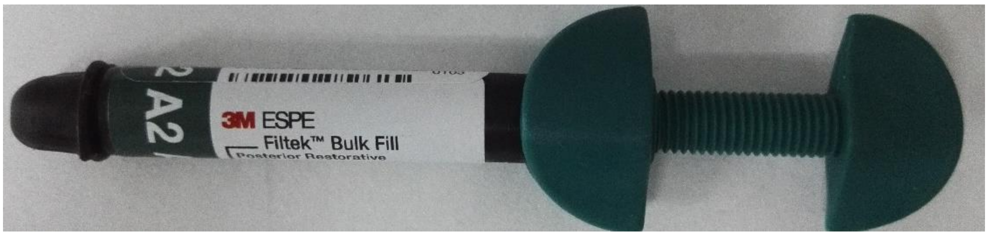

Figure 3.2: Bulk-fill restorative, Filtek Bulk-fill (FB).

Figure 3.3: Bulk-fill restorative, Tetric N Ceram Bulk-fill (TN).

Figure 3.4: Bulk-fill giomer restorative, Beautifil-Bulk restorative (BB).

Table 3.1: Technical profiles and manufacturers of the materials evaluated.

Material (Abbreviation)	Manufacturer	Type	Resin	Filler	Filler content % by weight / % by volume	Lot No./ (Shade)
Filtek Z350 (FZ) [control]	3M ESPE, St Paul, MN, USA	Nanohybrid restorative	Bis-GMA Bis-EMA UDMA TEGDMA	Zirconia/Silica cluster and Silica nanoparticle	78.5/63.3	N771467 (A2)
Filtek Bulk-Fill (FB)	3M ESPE, St Paul, MN, USA	Bulk-fill restorative	AUDMA AFM DDDMA UDMA	Zirconia/Silica cluster, ytterbium trifluoride	76.5/58.4	N693019 (A2)
Tetric N ceram Bulk-Fill (TN)	Ivoclar, Vivadent Inc., NY, USA	Bulk-fill restorative	Bis-GMA Bis-EMA UDMA	Barium glass filler, ytterbium fluoride and spherical mixed oxide	77/55	S38368 (A2)
Beautifil-Bulk Restorative (BB)	SHOFU Inc., Koyoto, Japan	Bulk-fill giomer restorative	Bis-GMA UDMA Bis-MPEPP TEGDMA	S-PRG based on F-Br-Al-Si glass	87/74.5	051623 (A2)

AUDMA= Aromatic urethane dimethacrylate
AFM= Addition-fragmentaion monomers
Bis-EMA= Ethoxylated bisphenol-A-glycidyl methacrylate
Bis-GMA= Bisphenol-A glycidyl dimethacrylate
Bis-MPEPP= Bisphenol-A polyethoxy-dimethacrylate
DDDMA= 1,12-dodecanediol dimethacrylate
F-Br-Al-Si= Fluoroboroaluminosiliciate
S-PRG= Surface modified pre-reacted glass
TEGDMA= Triethylene glycol dimethacrylate
UDMA= Urethane dimethacrylate
*(Abbreviation) depicts the code for study materials

3.2 Specimens preparation

Sixty beam-shaped test specimens (12 x 2 x 2 mm) of each of the various composites were fabricated using customized stainless steel molds. The composites were placed in one increment and excess material was removed by compressing the molds between two mylar strips with glass slides. The top surface of the composite specimens were light polymerized through the glass slide with two overlapping irradiations of 10 s each using a calibrated LED curing light (Demi Plus, Kerr, CA, USA) with an output irradiance of 1330 mW/cm^2 and wavelength range of 450-470 nm. The glass slide was removed and the composite specimens were light cured for another 10 s. The mylar strips were subsequently discarded and the composite beams were removed from their molds. Any minor material excess or ‘fins’ were gently removed by fine polishing discs (Sof-Lex, 3M ESPE, USA). Following ISO 4049, the composite specimens were examined by naked eyes, without magnification, for the presence of voids or air bubbles and any defective specimens were replaced. The final dimensions of the specimens and the parallelism between their opposite surfaces were verified with a digital caliper (Mitutoyo Corporation, Kawasaki, Japan) and measured at three different points of the specimen (right, left and center) (International Organization for Standardization, 2000; Swaminathan & Shivakumar, 2009).

3.3 Storage mediums and time

The composite specimens for each material were randomly divided into six groups of ten (n=10) and conditioned in the following mediums for 7 days at 37°C: air (control), artificial saliva (SAGF), distilled water, 0.02N citric acid, heptane, 50% ethanol-water solution as shown in Figure 3.5. Containers used to house the various solutions were sealed to minimize evaporation. Composition of the artificial saliva (SAGF) used is reflected in Table 3.2 (Gal et al., 2001). The pH of the artificial saliva was adjusted to 6.8 to resemble natural saliva pH when it is released from the salivary ducts (Vouvoudi & Sideridou, 2012).

Table 3.2: Composition of the SAGF medium (Gal et al., 2001).

Components	Concentration (mg L^{-1})
NaCl	125.6
KCl	963.9
KSCN	189.2
KH_2PO_4	654.5
Urea	200.0
$NaSO_4 \cdot 10H_2O$	763.2
NH_4Cl	178.0
$CaCl_2 \cdot 2H_2O$	227.8
$NaHCO_3$	630.8

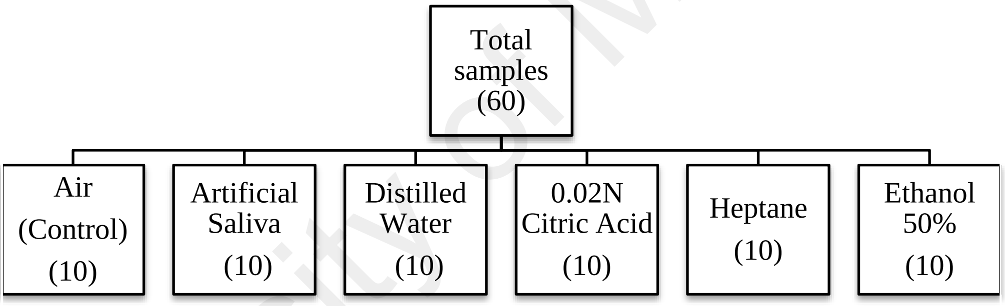

Figure 3.5: Grouping of samples according to conditioning mediums (per material).

3.4 Dynamic Mechanical Analysis (DMA) testing

After the 7 days conditioning period, the composite specimens were subjected to dynamic mechanical testing (DMA RSA-G2, TA Instruments, New Castle, USA) (Figure 3.6) in their respective conditioning mediums at 37°C. The dynamic testing device was set up in flexural mode. Specimens were loaded using a three point bending configuration with an axial load of 5 N and a span length of 10mm inside an immersion cup enclosed in an environmental chamber. Loading frequency was set at 0.1 to 10 Hz to represent a range from close to "static" testing (0.1 Hz) to the upper limit of normal chewing frequency while temperature was fixed at 37°C to mimic temperature in the oral cavity (Bates et al., 1976; Sideridou et al., 2009). Throughout the experiment, elastic modulus, viscous modulus and loss tangent data were computed as follows (Menard, 2008) and plotted against loading frequency (Figure 3.7):

Elastic modulus: $E' = (\sigma^\circ / \varepsilon^\circ) \cos \delta = (f_o / b\mathrm{k}) \cos \delta$ (1)

Viscous modulus: $E'' = (\sigma^\circ / \varepsilon^\circ) \sin \delta = (f_o / b\mathrm{k}) \sin \delta$ (2)

Loss tangent: $\mathrm{Tan}\ \delta = E'' / E'$ (3)

where σ° is the maximum stress at the peak of the sine wave, ε° is the strain at the maximum stress, f_o is the force applied at the peak of the sine wave, b is the sample geometry term and k is the sample displacement at the peak.

The sample geometry for a three point bending bar was calculated as follows:

$$4B_s H_s{}^3 / L_s{}^3 \quad (4)$$

where B is the width in millimeters, H is the height in millimeters, L is the distance between support in millimeters and s denotes for the specimen.

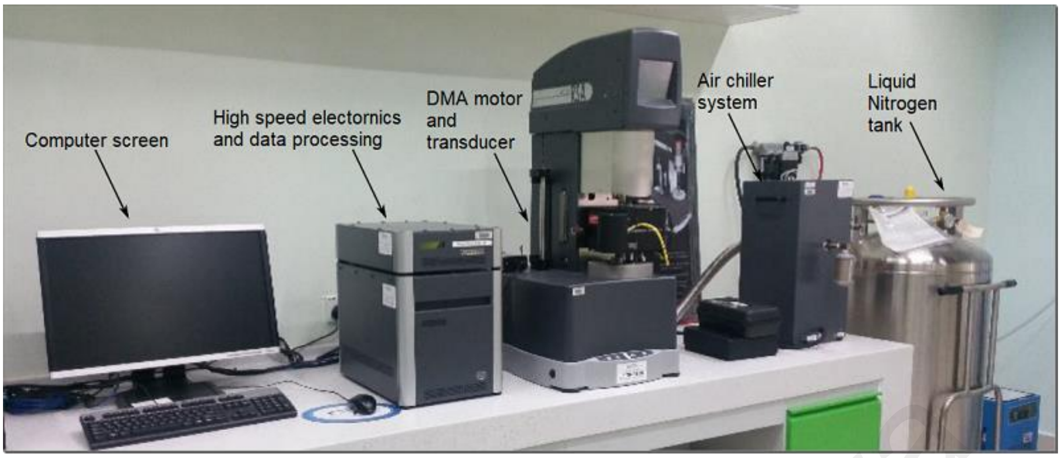

Figure 3.7: DMA RSA-G2, TA Instruments, New Castle, USA.

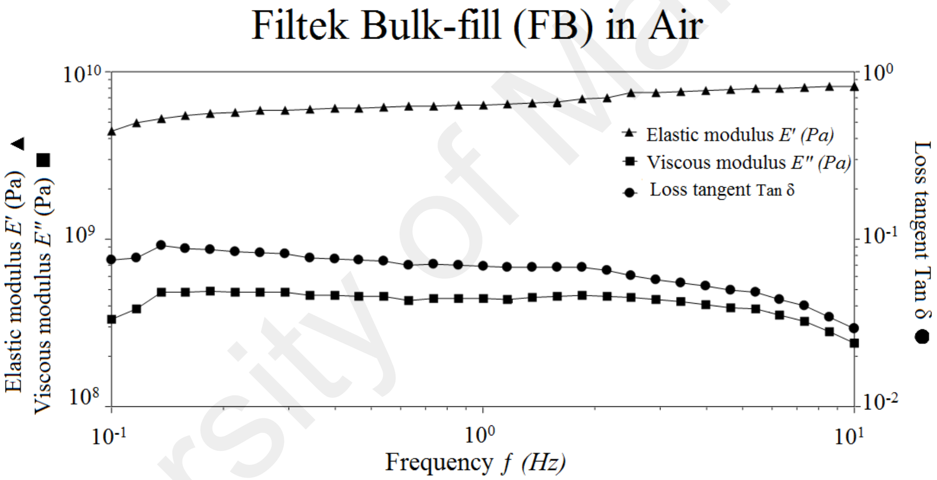

Figure 3.6: Elastic modulus, viscous modulus and loss tangent plotted against frequency for Filtek Bulk-Fill (FB) in Air.

3.5 Statistical analysis for visco-elastic properties

SPSS statistical program (Version 12.0.1, SPSS Inc., Chicago, USA) was used to analyze the data obtained. Normality testing was done using Shapiro-Wilk test. As data was found to be normally distributed, parametric analysis was permissible. Homogeneity of variance was assessed using Levene's test and equal variances were assumed. The interactions between the independent variables (materials and conditioning mediums) and each of the dependent variables (elastic modulus, viscous modulus and loss tangent) were evaluated using two-way ANOVA for mean values of each dependent variable. One way ANOVA followed by Tukey's post-hoc tests were used to determine inter-medium and inter-material differences for mean values of elastic modulus, viscous modulus and loss tangent. All statistical analyses were carried out at significance level $p<0.05$.

CHAPTER 4: RESULTS

Two-way ANOVA revealed significant interactions (p<0.001) between materials and mediums for elastic modulus, viscous modulus and loss tangent. As the effect of FSLs on visco-elastic properties of the evaluated bulk-fill composites was material and medium dependent, the null hypotheses were rejected.

4.1 Elastic modulus

The mean values of elastic modulus for the various materials and conditioning mediums are reflected in Table 4.1 whereas Figure 4.1 compares the mean values of elastic modulus of materials when grouped according to mediums. Results of statistical analysis of elastic modulus based on materials and mediums are shown in Tables 4.2 and 4.3 respectively.

Table 4.1: Mean elastic modulus [E′ (GPa)] values for the various restorative materials with standard deviations (in parentheses).

Material/ Medium	Filtek Z350 (FZ)	Filtek Bulk-Fill (FB)	Tetric N Ceram (TN)	Beautifil-Bulk (BB)
Air (Control)	6.29 (0.29)	6.20 (0.72)	5.00 (0.37)	5.79 (0.36)
Artificial Saliva	5.48 (0.56)	6.09 (0.49)	3.76 (0.40)	5.51 (0.53)
Distilled Water	5.75 (0.42)	5.47 (0.45)	4.77 (0.54)	5.28 (0.62)
Citric Acid	5.19 (0.42)	5.86 (0.50)	3.72 (0.48)	5.04 (0.56)
Heptane	7.11 (0.49)	6.83 (0.57)	6.22 (0.37)	5.18 (0.43)
Ethanol	4.49 (0.48)	6.04 (0.37)	3.68 (0.18)	4.61 (0.47)

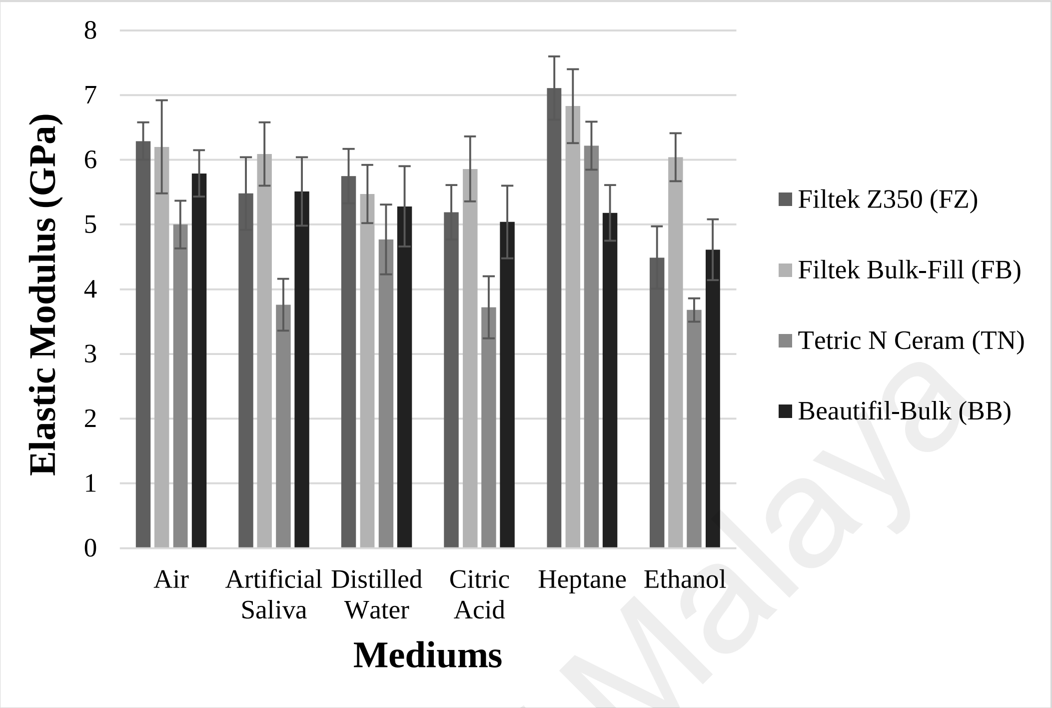

Figure 4.1: Mean elastic modulus values E′ (GPa) after storage in the different mediums.

4.1.1 Elastic modulus comparison between mediums based on materials

With the exception of BB, the highest elastic modulus was observed after conditioning in heptane. For BB, elastic modulus peaked after conditioning in air. For FZ, FB and TN, elastic modulus after exposure to heptane was mostly significantly greater than all other mediums. Elastic modulus for BB in air was only significantly greater than in citric acid and ethanol. Excluding FB, the lowest elastic modulus was noted after exposure to ethanol. FB showed the lowest elastic modulus after conditioning in distilled water. Table 4.2 shows the results of statistical analysis of elastic modulus values based on materials.

Table 4.2: Results of statistical analysis for elastic modulus (E′) values based on materials[a]

Material	Differences
FZ	Heptane > Air (control), Water, Saliva, Citric acid > Ethanol Air (control) > Saliva, Citric acid
FB	Heptane > Saliva, Ethanol, Citric acid, Water, Air (control) > Water
TN	Heptane > Air (control), Water > Saliva, Citric acid, Ethanol
BB	Air (control), Saliva, Water > Ethanol Air (control) > Citric acid

Abbreviations: FZ, Filtek Z350; FB, Filtek Bulk-Fill; TN, Tetric N Ceram; BB, Beautifil-Bulk
[a]Results of One way ANOVA and Post Hoc's Tukey's test ($p<0.05$); > indicates statistical significance.

4.1.2 Elastic modulus comparison between materials based on mediums

For all mediums, either FZ or FB had the highest elastic modulus (Figure 4.1). With the exception of heptane, TN exhibited the lowest elastic modulus for all mediums. When exposed to heptane, BB had the lowest elastic modulus. Elastic modulus of TN was significantly lower than FZ and FB for all mediums. TN also had significantly lower elastic modulus than BB when conditioned in air, artificial salvia, citric acid and ethanol solution. Table 4.3 shows the results of statistical analysis for elastic modulus values based on conditioning mediums.

Table 4.3: Results of statistical analysis for elastic modulus (E′) values based on conditioning mediums[a]

Medium	Differences
Air	FZ, FB, BB > TN
Artificial Saliva	FB > FZ > TN BB > TN
Distilled Water	FZ, FB > TN
Citric Acid	FB > FZ, BB > TN
Heptane	FZ, FB > TN > BB
Ethanol 50%	FB > BB, FZ > TN

Abbreviations: FZ, Filtek Z350; FB, Filtek Bulk-Fill; TN, Tetric N Ceram; BB, Beautifil-Bulk
[a]Results of One way ANOVA and Post Hoc's Tukey's test ($p<0.05$); > indicates statistical significance.

4.2 Viscous modulus

The mean values of viscous modulus for the various materials and conditioning mediums are reflected in Table 4.4 whereas Figure 4.2 compares the mean values of viscous modulus of materials when grouped according to mediums. Results of statistical analysis of viscous modulus based on materials and mediums are shown in Tables 4.5 and 4.6 respectively.

Table 4.4: Mean viscous modulus [E″ (GPa)] values for the various restorative materials with standard deviations (in parentheses).

Material/ Medium	Filtek Z350 (FZ)	Filtek Bulk-Fill (FB)	Tetric N Ceram (TN)	Beautifil-Bulk (BB)
Air (Control)	0.42 (0.04)	0.43 (0.06)	0.38 (0.04)	0.38 (0.04)
Artificial Saliva	0.47 (0.06)	0.46 (0.06)	0.36 (0.05)	0.43 (0.06)
Distilled Water	0.47 (0.05)	0.46 (0.05)	0.65 (0.07)	0.47 (0.05)
Citric Acid	0.48 (0.06)	0.51 (0.06)	0.33 (0.04)	0.48 (0.07)
Heptane	0.44 (0.05)	0.50 (0.04)	0.55 (0.06)	0.35 (0.05)
Ethanol	0.42 (0.05)	0.64 (0.06)	0.44 (0.05)	0.42 (0.06)

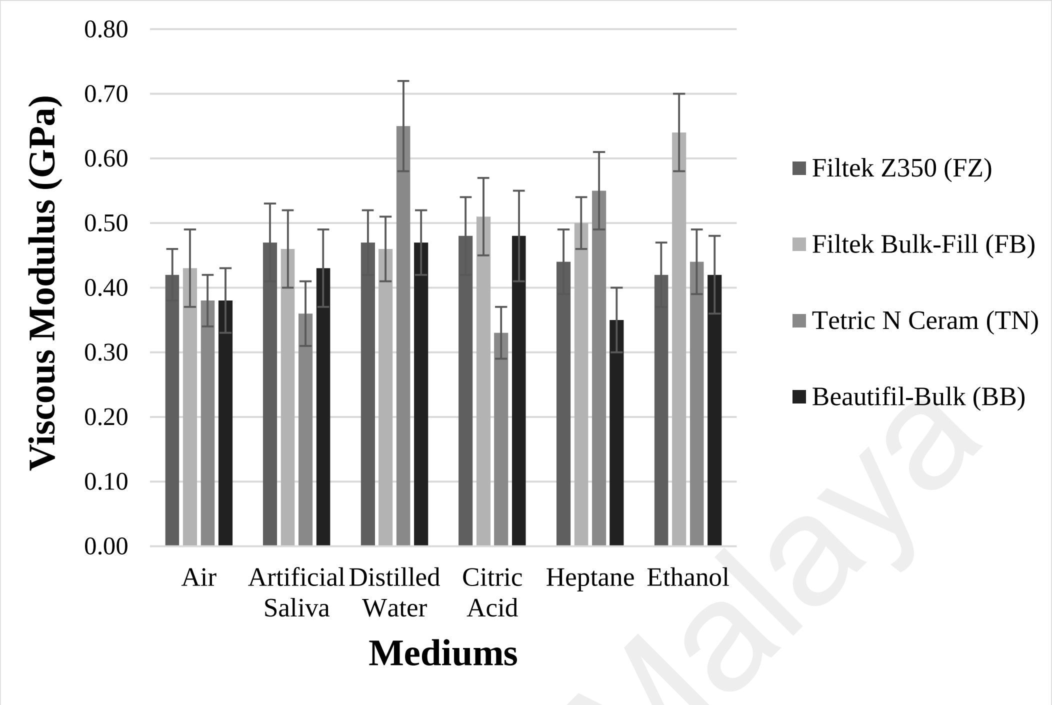

Figure 4.2: Mean viscous modulus values E″ (GPa) after storage in the different mediums.

4.2.1 Viscous modulus comparison between mediums based on materials

No significant difference in viscous modulus was observed between mediums for FZ. No apparent trends in viscous modulus were established for FB, TN and BB. Highest viscous modulus was observed after conditioning in ethanol, distilled water and citric acid for FB, TN and BB respectively. Lowest viscous modulus was detected in air, citric acid and heptane correspondingly. For FB, exposure to ethanol solution resulted in significantly higher viscous modulus than all other mediums. For TN, conditioning in water led to greater viscous modulus than heptane, ethanol, air, saliva and citric acid. The viscous modulus of BB conditioned in citric acid and water was significantly higher than in air and heptane. Table 4.5 shows the results of statistical analysis for viscous modulus values based on materials.

Table 4.5: Results of statistical analysis for viscous modulus (E″) values based on materials[a]

Material	Differences
FZ	No significant difference
FB	Ethanol > Citric acid, Heptane, Saliva, Water, Air (control)
TN	Water > Heptane > Ethanol > Saliva, Citric acid Water > Heptane > Air (control)
BB	Citric acid, Water > Air, Heptane
Abbreviations: FZ, Filtek Z350; FB, Filtek Bulk-Fill; TN, Tetric N Ceram; BB, Beautifil-Bulk [a]Results of One way ANOVA and Post Hoc's Tukey's test ($p<0.05$); > indicates statistical significance.	

4.2.2 Viscous modulus comparison between materials based on mediums

No significant difference in viscous modulus between materials was observed for the control (air) group. When conditioned in air, citric acid and ethanol, FB had the highest viscous modulus. For distilled water and heptane, maximum viscous modulus was observed for TN (Figure 4.2). The highest viscous modulus after conditioning in artificial saliva was noted with FZ. The lowest viscous modulus was observed with TN after exposure to air, artificial saliva plus citric acid, and with BB after conditioning with heptane and ethanol. When stored in distilled water, FB had the lowest viscous modulus. When conditioned in artificial saliva, distilled water and citric acid, no significant difference in viscous modulus was observed between FZ, FB and BB. TN had significantly lower viscous modulus than the other materials when conditioned in artificial saliva and citric acid but significantly higher viscous modulus when conditioned in distilled water. When exposed to heptane, BB had significantly lower viscous modulus than all the other materials. Table 4.6 shows the results of statistical analysis for viscous modulus values based on conditioning mediums.

Table 4.6: Results of statistical analysis for viscous modulus (E″) values based on conditioning mediums[a]

Medium	Differences
Air	No significant difference
Artificial Saliva	FZ, FB, BB > TN
Distilled Water	TN > FZ, BB, FB
Citric Acid	FB, FZ, BB > TN
Heptane	TN, FB > FZ > BB
Ethanol 50%	FB > TN, FZ, BB
Abbreviations: FZ, Filtek Z350; FB, Filtek Bulk-Fill; TN, Tetric N Ceram; BB, Beautifil-Bulk [a]Results of One way ANOVA and Post Hoc's Tukey's test ($p<0.05$); > indicates statistical significance.	

4.3 Loss tangent

The mean values of loss tangent for the various materials and conditioning mediums are reflected in Table 4.7 whereas Figure 4.3 compares the mean values of loss tangent of materials when grouped according to mediums. Results of statistical analysis of loss tangent based on materials and mediums are shown in Tables 4.8 and 4.9 respectively.

Table 4.7: Mean loss tangent (x10^{-3}) values for the various restorative materials with standard deviations (in parentheses).

Material/ Medium	Filtek Z350 (FZ)	Filtek Bulk-Fill (FB)	Tetric N Ceram (TN)	Beautifil-Bulk (BB)
Air (Control)	68 (5)	69 (4)	76 (5)	66 (7)
Artificial Saliva	88 (9)	84 (10)	95 (7)	73 (5)
Distilled Water	83 (5)	84 (6)	134 (12)	89 (6)
Citric Acid	91 (10)	85 (5)	94 (10)	101 (6)
Heptane	66 (4)	75 (3)	87 (5)	66 (8)
Ethanol	97 (3)	106 (5)	135 (9)	93 (3)

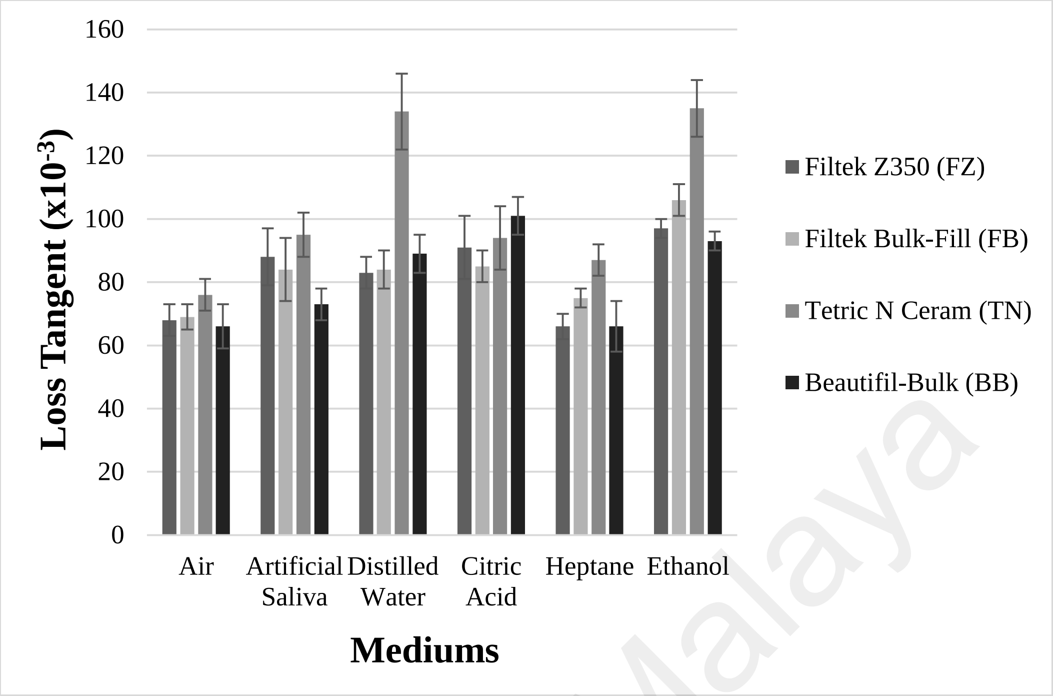

Figure 4.3: Mean loss tangent values (Tanδ) x10^{-3} after storage in the different mediums.

4.3.1 Loss tangent comparison between mediums based on materials

Apart from BB, all materials exhibited the largest loss tangent after exposure to ethanol solution. For BB, the greatest loss tangent was observed with citric acid. For all materials, air and heptane had the lowest loss tangent values. Conditioning in air and heptane generally resulted in significantly lower loss tangent values than in the other mediums. Table 4.8 shows the results of statistical analysis for loss tangent values based on materials.

Table 4.8: Results of statistical analysis for loss tangent (Tanδ) values based on materials[a]

Material	Differences
FZ	Ethanol > Saliva, Water > Air (control), Heptane Citric acid > Air (control), Heptane
FB	Ethanol > Citric acid, Water, Saliva > Heptane, Air (control)
TN	Ethanol, Water > Saliva, Citric acid > Air (control) Ethanol, Water > Heptane
BB	Citric acid > Water > Saliva, Air (control), Heptane Ethanol > Saliva, Air (control), Heptane

Abbreviations: FZ, Filtek Z350; FB, Filtek Bulk-Fill; TN, Tetric N Ceram; BB, Beautifil-Bulk
[a]Results of One way ANOVA and Post Hoc's Tukey's test ($p<0.05$); > indicates statistical significance.

4.3.2 Loss tangent comparison between materials based on mediums

Discounting citric acid, TN had the highest loss tangent for all mediums (Figure 4.3). BB had the lowest loss tangent for all mediums except for distilled water and citric acid where FZ and FB had the smallest loss tangent respectively. When conditioned in air, artificial saliva, distilled water, heptane and ethanol solution, the loss tangent of TN was generally significantly greater than the other materials. For citric acid, the loss tangent of BB was significantly greater than FB. When exposed to air and distilled water, no significant difference in loss tangent was observed between FZ, FB and BB. BB showed significantly lower loss tangent values than the other materials when conditioned in artificial saliva. When stored in heptane and ethanol, no significant difference in loss tangent was noted between FZ and BB but these materials had significantly lower values than TN and FB. Table 4.9 shows the results of statistical analysis for loss tangent values based on conditioning mediums.

Table 4.9: Results of statistical analysis for loss tangent (Tanδ) values based on conditioning mediums[a]

Medium	**Differences**
Air	TN > FB, FZ, BB
Artificial Saliva	TN > FB > BB FZ > BB
Distilled Water	TN > BB, FB, FZ
Citric Acid	BB >FB
Heptane	TN > FB > FZ, BB
Ethanol 50%	TN > FB > FZ, BB

Abbreviations: FZ, Filtek Z350; FB, Filtek Bulk-Fill; TN, Tetric N Ceram; BB, Beautifil-Bulk
[a]Results of One way ANOVA and Post Hoc's Tukey's test ($p<0.05$); > indicates statistical significance.

CHAPTER 5: DISCUSSION

5.1 Discussion of Materials and Methods

5.1.1 Materials evaluated

The materials evaluated included a conventional composite (Filtek Z350 [FZ]), two bulk-fill composites (Filtek Bulk-Fill [FB] and Tetric N Ceram Bulk-Fill [TN]) and a bulk-fill giomer (Beautifil-Bulk Restorative [BB]). The conventional composite served as a comparison for the bulk-fill materials. The bulk-fill materials selected represented the most recent advances in dental composite and photo-initiator technology. FB is a newly introduced camphorquinone based composite with two proprietary monomers. These are the aromatic dimethacrylate (AUDMA) and addition fragmentation monomers (AFM). There are very few, if any studies, done on FB. Most previous studies were conducted on its flowable counterpart, Filtek Bulk-Fill flowable. Likewise, few studies had also been conducted on TN which is an ivocerin based composite. Ivocerin is a recently patented photo-initiator that acts as a polymerization booster. On the other hand, BB is the first camphorquinone based bulk-fill giomer launched. Owing to its patented filler, S-PRG, this bulk-fill composite may act differently when compared to the other evaluated composites which utilize other fillers. Finally, FZ is a widely used nano-hybrid conventional composite that is well investigated in several studies. It was thus chosen as a control and as a direct comparison for FB.

5.1.2 Specimens dimensions and preparation

This study investigated the effect of FSLs on visco-elastic properties of bulk-fill dental composites using DMA. Test samples used for three point bend testing are usually based on ISO 4049 specifications which entail the use of 25 mm long specimens (International Organization for Standardization, 2000). Fabrication of these elongated composite specimens is technically challenging and requires the use of multiple overlapping light irradiations due to the relatively smaller light exit windows of most curing tips (dos Santos et al., 2012). Moreover, the ISO recommended length is not clinically realistic given the fact that the mesio-distal widths of molars are usually around 11 mm whereas the cervico-incisal widths of incisors are usually around 13 mm (Wheeler, 1965).

Even though the ISO 4049 specifications have been utilized in numerous studies, many other authors have employed the use of specimens of variable dimensions in their studies. Several studies have investigated the influence of specimen dimensions on flexural strength of composite resins. Although some studies had reported similar flexural strength values, others had observed higher strengths with shorter specimens (Peutzfeldt & Asmussen, 1991; Yap & Teoh, 2003; Muench et al., 2005; Calheiros et al., 2013; Calabrese et al., 2015). The use of mini-flexural test specimens (12 mm x 2 mm x 2 mm) had also been validated by (Yap & Teoh, 2003). Significant and positive correlations for flexural strength and modulus were observed between the mini- and ISO flexural tests. Besides being more clinically relevant, the mini-flexural test specimens also have the advantage of reduced fabrication time and material usage.

The specimens were covered by a mylar strip in order to reduce the oxygen inhibition layer during polymerization. It has been reported that oxygen prevents surface polymerization of composite resins. Inhibition depths in air varied between 25 μm and 105 μm and it differed between composites (Finger & Jörgensen, 1976). The use of the mylar strips also ensures a smooth, regular and optimal surface finish and eliminates errors related to finishing and polishing procedures (Stanford et al., 1985). Nevertheless, it has to be noted that unpolished surfaces are usually matrix-rich which might lead to a higher degree of degradation by FSLs (Hachiya et al., 1984).

5.1.3 Storage medium and time setting

The composite materials were conditioned in the different mediums continuously for 7 days at 37°C prior to dynamic testing. This may appear somewhat extensive given the fact that restorations come into contact with foods and liquids only briefly and in a sporadic way during function. The current test results may therefore exaggerate the effects of food substances and liquids in-vivo. Continuous exposure may, still, occur in-vivo since chemicals are absorbed by adherent debris (such as calculus or food particles) at the margins or grooves of restorations. Moreover, the accelerated in-vitro rate provides an indication of the in-vivo performance of the composite resins (McKinney & Wu, 1985; Yap et al., 2000b; Akova et al., 2006). SAGF medium was chosen since its pH, buffering capacity, contents and viscosity simulated that of natural saliva. It has also been reported to be valuable for determining fluoride release and corrosion behavior of dental biomaterials (Gal et al., 2001).

5.1.4 DMA test setting

In this study, the DMA testing was set up in flexural mode. This test geometry allowed for adequate deflection of the composite specimens within the small load capacity of the DMA instrument. Dynamic testing was carried out in the various conditioning mediums at a fixed temperature of 37°C to mimic temperature in oral cavity and loading frequency of 0.1 to 10 Hz to represent a range from “close to static” testing (0.1 Hz) to the upper limit of normal chewing frequency (Bates et al., 1976; Sideridou et al., 2009). The synergistic effect of load application and medium exposure is anticipated to be different from just conditioning in a solvent and testing in air. The current DMA instrument set-up presents an improvement over regular static and even other dynamic testing that only allows for examination in air (Yap & Teoh, 2003). The visco-elastic properties of contemporary dental composites had been studied using

DMA and were reported to be valuable for predicting clinical performance under physiological mouth movements (Jacobsen & Darr, 1997; Mesquita et al., 2006; Sideridou et al., 2009; Vouvoudi & Sideridou, 2012).

5.2 Discussion of Results

Parameters that can be derived from DMA include elastic modulus (rigidity), viscous modulus (flow) and loss tangent (energy dissipation capacity). Figure 3.7 shows the typical plot attained when visco-elastic properties values were mapped against loading frequency. As frequency increases, elastic modulus increases while viscous modulus and loss tangent decreases. Findings corroborated previous DMA studies conducted on dental composite resins (Mesquita et al., 2006; Sideridou et al., 2009). The increased elastic modulus associated with frequency escalation can be attributed to the fact that frequency is inversely related to time. At higher frequencies, the composites do not have sufficient time to flow and hence internal friction is minimized leading to decreased capacity for energy dissipation. Consequently, elastic modulus is increased whereas viscous modulus and loss tangent are decreased since $Tan\ \delta = E''/E'$.

5.2.1 Effect of FSLs on elastic modulus

For the restoration of posterior teeth, dental composites with higher modulus and thus rigidity are desirable. Composites with low elastic modulus are more flexible and deform elastically under functional loads putting more stress on the remaining tooth structure and the tooth-restoration bond. Conversely, dental composite resins with very high elastic modulus are exceedingly stiff and unable to absorb occlusal forces. Functional stresses are transferred to the cavity walls leading to possible tooth fracture (Mesquita et al., 2006). Ideally, the elastic modulus of dental composites should be similar to or higher than dentine which is approximately 18 GPa (Craig, 1979; Willems et al., 1992). Regardless of conditioning mediums, none of the dental composites evaluated had such high elastic modulus. The highest modulus (7.11 ± 0.49 GPa) was observed with the conventional composite FZ when conditioned in heptane. In view of the aforementioned, dynamic testing with DMA is expected to play a greater role in the characterization of dental composites than the commonly used static tests.

Apart from the bulk-fill giomer BB, conditioning in heptane resulted in significantly higher elastic modulus than the other mediums. Findings reinforced that of Yap et al who reported highest composite strength after conditioning in heptane (Yap et al., 2000b). Heptane, a water-insoluble hydrocarbon, may prevent the leaching out of silica and other fillers that arises when conditioning in aqueous solutions. Another explanation maybe due to the fact that heptane decreases oxygen inhibition throughout post-curing that takes place for specimens stored in air (Söderholm, 1983; McKinney & Wu, 1985; Yap et al., 2000a). Akova et al, however, found that exposure to heptane decreased hardness and flexural strength of provisional restorative materials (Akova et al., 2006). Their study was, however, conducted on bis-acryl resin provisional materials and not on composite resins. The disparity in findings can be attributed to differences in materials evaluated and warrants further exploration.

For the bulk-fill giomer BB, the highest elastic modulus was observed in the control group (air) and no significant difference in elastic modulus was noted between conditioning in air, artificial saliva, distilled water and heptane. BB is based on pre-reacted glass ionomer (PRG) technology in which acid-reactive fluoride containing glass is reacted with polyacids in the presence of water, freeze-dried, milled, silanized, ground, and used as fillers (Wang et al., 2011). The surface-modified layer is said to protect the PRG fillers from water sorption and degradation and was upheld by the current study.

Conditioning in ethanol yielded the lowest elastic modulus for all the materials except for FB. With the exemption of FB, all composites evaluated utilized Bis-GMA as part of their resin matrix. Ethanol has a solubility index that is similar to that of Bis-GMA and increases its disintegration (El-Safty et al., 2012). The elastic modulus of FB was not drastically affected by ethanol as it employed the use of other proprietary monomers in place of Bis-GMA. FB incorporates two new monomers; a high molecular weight aromatic dimethacrylate (AUDMA) and addition fragmentation monomers (AFM) that act to decrease the polymerization shrinkage stress (Kalliecharan et al., 2016).

As reported by the manufacturers, AUDMA reduces the reactive groups in the resin which control the volumetric shrinkage and the rigidity of the final polymeric matrix. Whereas, AFM, containing a third reactive site cleaving through a fragmentation process, helps in providing a relaxation mechanism of the developing network and consequently leading to stress relief (3M ESPE, 2015). Nonetheless, the fragments can still react with each other or with other reactive sites which ensures preserving physical properties of the material. The aforementioned might in turn develop shorter and stiffer polymeric chains leading to less softening effect by ethanol (Braga et al., 2005). Moreover, UDMA was reported to have higher strength and elastic modulus when compared to other monomers used which might be owing to the stronger hydrogen bonding affinity, shorter crosslinks (in relation to Bis-EMA) leading to less free volume and less cyclization (in relation to TEGDMA) (Gajewski et al., 2012).

For all conditioning mediums, the elastic modulus of TN was in general the lowest. This can be attributed to TN’s relatively lower filler volume (55% as compared to 58.4 to 74.5% in the other composites). Findings were in agreement with those of El-Safty et al. who reported a significant positive correlation between elastic modulus and filler loading (El-Safty et al., 2012). Mesquita and others revealed a relation between elastic modulus and filler weight packing (Mesquita et al., 2006). However, despite the fact that TN has high fillers percentage by weight, its elastic modulus was yet significantly lower than the rest of the evaluated composites. That might be due to TN's low filler volume that does not seem to withstand its high filler weight. The stated above reiterates the major significance of percentage filler volume when it comes to composite characterization.

5.2.2 Effect of FSLs on viscous modulus

No significant difference in viscous modulus was observed between conditioning mediums for FZ. The flow of the conventional composite FZ was thus impartial to conditioning medium. For the bulk-fill materials, no apparent trends between mediums were perceived for viscous modulus. The variance is probably due to differences in resin matrix and filler particle composition of the bulk-fill composites. The latter also explains the alternations in viscous modulus between materials for the different conditioning mediums. For the control medium (air), no significant difference in viscous flow was observed between all composites. As viscous modulus was considerably lower than elastic modulus, the composites evaluated were primarily elastic when undergoing deformation. Thus, it seemed that the viscous modulus might be a less important factor to differentiate between the different materials and conditioning mediums in this particular study.

5.2.3 Effect of FSLs on loss tangent

Loss tangent reflects the energy dissipation capacity of the composites. For FZ, FB and TN, the highest loss tangent values were observed after conditioning in ethanol. For BB, conditioning in citric acid resulted in the highest loss tangent. As loss tangent is a function of both viscous and elastic modulus ($Tan\ \delta = E''/ E'$), any increase in viscous flow or decrease in elastic modulus would result in higher loss tangent values. As viscous modulus is much smaller than elastic modulus, loss tangent values will be predominantly influenced by changes in rigidity for all composites evaluated. The effects of ethanol on resin matrix degradation had been discussed earlier. As the polymer swells with solvent absorption, inter-chain interactions are reduced resulting in more energy dissipation and higher loss tangent (Vouvoudi & Sideridou, 2012). The increased energy dissipation capacity is also contributed in part by the softening of dental composites by ethanol (Soh & Yap, 2004).

Loss tangent was reported to be highly affected by the filler content of composite resins. Higher filler content had been associated with lower loss tangent (Papadogiannis et al., 2004). Typically, the greater the filler content, the lower the strain under continuous stress. The present study corroborated these studies when the composites were conditioned in heptane, ethanol and air (control). Moreover, with the exception of heptane, loss tangent values were higher in aqueous solutions than in the air, for all the materials evaluated, which was in agreement with previous studies (Papadogiannis et al., 2015). In aqueous solutions, the polymer swells with solvent absorption and inter-chain interactions are decreased resulting in more energy dissipation and higher loss tangent (Vouvoudi & Sideridou, 2012). Heptane, as previously discussed, might prevent the leaching out of fillers that arises in other aqueous solutions (McKinney & Wu, 1985; Yap et al., 2000a).

Giomer materials are significantly softened by citric acid due to susceptibility of the fluorosilicate glass fillers to degradation by weak acids (Mohamed-Tahir et al., 2005; Kooi et al., 2012). Softening and reduced stiffness of BB with exposure to citric acid explains the higher loss tangent values obtained. Excluding citric acid (where BB showed the highest loss tangent values), TN showed the greatest loss tangent amongst the composites for all mediums. This can be attributed to its lower elastic modulus arising from its relatively lower filler volume and higher resin content (Ilie et al., 2013). Apart from conditioning in distilled water and citric acid, BB with its greater filler volume content had the lowest loss tangent values. Composites with lower loss tangent will respond quicker to load, returning faster to their original shape (Mesquita et al., 2006). In addition, it can be contemplated that composites with lower loss tangents and higher elastic modulus may display better clinical outcomes in terms of deformation behavior, particularly in stress bearing areas (Papadogiannis et al., 2004).

5.3 Clinical relevance

The evaluated bulk-fill composite resins, like conventional composite resins, are degraded by FSLs especially ethanol. The UDMA-based bulk-fill composite (FB), however, appeared to be more resistant to the effects of ethanol when compared to BisGMA-based conventional and bulk-fill composites. Clinicians may need to take into consideration the dietary habits of patients when selecting composites for stress-bearing restorations.

5.4 Limitations of the study and future work

The present study had some limitations. Dynamic testing was carried out at a fixed temperature of 37°C. DMA testing over a wider temperature range representing intra-oral temperature changes from routine eating, drinking and breathing would help envisage sudden changes in mechanical properties during clinical service (Mesquita & Geis-Gerstorfer, 2008). Cyclic temperature changes had been shown to affect the hardness, water sorption and solubility of composite restoratives and may influence visco-elastic properties as well (Yap & Wee, 2002a, 2002b). Static testing to determine flexural strength and modulus should also be conducted. Data from static testing could then be correlated to dynamic testing to better appreciate the relationships between visco-elastic and elastic variables.

In the present study, a 7 days storage period was selected. Conditioning time in the various mediums may well be extended to assess the longer term effects of FSLs on visco-elastic properties (Mesquita et al., 2006; Vouvoudi & Sideridou, 2012). While the bulk-fill composites were conditioned in individual FSLs in the present study, simultaneous exposure to a variety of food substances occur in-vivo. The collective and cumulative effects of the various FSLs on the visco-elastic properties of bulk-fill composites are also warranted.

CHAPTER 6: CONCLUSION

Within the confines of this study, the following can be concluded:

1. The effect of FSLs on the visco-elastic properties of the evaluated bulk-fill composites was found to be material and conditioning medium dependent. Thus the null hypotheses were rejected.
2. Apart from the bulk-fill giomer restorative (BB), the highest elastic modulus was observed after conditioning in heptane. For BB, conditioning in air gave the highest elastic modulus. No apparent trends were noted for viscous modulus. Excluding BB where exposure to citric acid gave the greatest values, loss tangent was the highest when the composites were conditioned in ethanol. Loss tangent values were influenced by elastic modulus which was associated with filler volume content.
3. The UDMA-based bulk-fill composite (FB) appeared to be more resistant to degradation effects of ethanol when compared to BisGMA-based conventional and bulk-fill composites.
4. Dynamic testing is anticipated to play more significant roles in dental composite characterization in view of its presumed non-destructive nature, multiple deformation modes, versatile configurations and greater clinical relevance.

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