



**UNIVERSITY of the  
WESTERN CAPE**

**Water sorption and solubility of resin filled composites.**

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**3313723**

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at the Faculty of Dentistry

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## DECLARATION

I hereby declare that the study: "*Water sorption and solubility of resin filled composites*" is my own work, that has not been submitted before for any degree or examination in any university, and that all the sources I have used or quoted have been indicated and acknowledged by complete references.

October 2015

Signed:



Hana Ali Alharari Omar



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## DEDICATION

To my lovely husband and kids who always supported me and believed in me

(I love you)

To my parents who provided me with all what I needed to reach this level of  
education

To my in-laws, brothers and sisters thank you for all your love and support.



## ABSTRACT

Resin filled dental composite materials has been introduced into dental practice since mid-1960s as an aesthetic restorative material for anterior teeth (Bowen, 1962 cited in Peutzfeldt, 1997). Since then, they have undergone several developments in order to enhance the longevity and performance of these materials. Resin filled dental composites consist of three main components namely, organic resin matrix which consists of a monomer, an initiator system and a stabilizer system, inorganic filler such as quartz, silica, etc. and coupling agent such as organo-silane coupling agent that chemically bonds the inorganic fillers to the organic resin matrix (Phillips, 1973). The properties and the performance of the resin filled dental composites are basically dependent upon the components of the materials. Some properties are related to the resin matrix, whereas others are related to the inorganic fillers and coupling agent. Furthermore, properties such as polymerization shrinkage and water sorption are dependent on both the inorganic fillers and the organic resin matrix (Asmussen, 1975; Hashinger and Fairhurst, 1984; Munksgaard et al., 1987).

**Aim and objectives:** The aim and the objectives of this study was to compare the water sorption and solubility of four bulk-fill dental resin composite materials namely, two conventional viscosity bulk-fill (Surefil bulk fill composite and Tetric N Ceram Bulk Fill) and two low viscosity bulk-fill flowable dental composite materials (Filtek Bulk Fill flowable restorative and Surefil SDR Flow). **Materials and methods:** Four types of bulk-fill composite restorative materials (2 bulk-fill conventional viscosity (Surefil bulk fill composite and Tetric N Ceram Bulk Fill) and 2 bulk-fill flowable low viscosity (Filtek Bulk Fill flowable restorative and Surefil SDR Flow) were used to analyse the water sorption and solubility for each resin composite type. Thirty

specimens for each type of material were prepared, giving the total number of specimens to be 120 (n=120). To standardize this study Vita shade A2 was used for all the material types. All specimens were prepared in a Teflon mould with internal diameter of  $15\pm 1$ mm and thickness of  $1\pm 0.1$ mm in accordance with ISO 4049. The light curing unit used for all specimens was Elipar™ S10, (3M ESPE, Germany) at an output of  $1200 \text{ mW/cm}^2$  and used according to the manufacturer's instructions. Prior to curing, the intensity of the light was checked using Cure Rite visible curing light meter (Caulk, USA) to ensure light output consistency between specimens and was found to be  $1200 \text{ mW/cm}^2$ . All the specimens were first removed from the Teflon mould as prepared and described previously and placed in an oven at  $37 \text{ }^\circ\text{C}$  until their weights were constant and these weights were recorded as  $m_1$  by using an analytic balance (OHAUS, TS400D, USA). Ten specimens of each type of resin filled composite were then immersed individually in glass containers filled with 10 ml distilled water and placed in the oven at  $37\pm 1 \text{ }^\circ\text{C}$  for 24 hours, 7 days, 14 days respectively. The specimens were removed; surface water was blotted with tissue paper until free from visible moisture and weighed using the analytic balance (OHAUS, TS400D, USA). The resultant weights were recorded as  $m_2$ . The specimens were then placed in a desiccator containing silica gel (Associated Chemical Enterprises, ZA) and freshly dried for two hours in an oven at  $58 \text{ }^\circ\text{C}$  and then weighted to obtain  $m_3$ . According to Oysaed and Ruyter formula (Oysaed and Ruyter, 1986), the water sorption and solubility was calculated using the following equation:

1. Water sorption (SP) =  $m_2 - m_3 / v$ .

2. Water solubility (SI) =  $m_1 - m_3 / v$  - where v is the volume of the specimen.

For monomer leakage high performance liquid chromatography (HPLC) was used to identify monomers. The water that contained stored specimens was transferred to a refrigerator immediately after the specimens were removed until HPLC analysis was carried out to determine the amount of monomers that leached out of the cured composite specimens. **Results:** A significant difference between the materials ( $p < 0.05$ , ANOVA Analysis of Variance) showed that Surefil SDR Flow composite had the lowest overall mean water sorption values (10.191) over the three time intervals (24 hrs, 7 days and 14 days) which was significantly smaller than the other means, followed by Filtek Bulk Fill flowable restorative composite (11.135) and Tetric N Ceram Bulk Fill composite (16.419). The highest water sorption mean value was recorded for Surefil bulk fill composite (21.515). The overall means of water solubility for the two bulk-fill flowables i.e. Filtek Bulk Fill flowable restorative and Surefil SDR Flow were smaller than bulk-fill conventional viscosity Surefil bulk fill and Tetric N Ceram Bulk Fill. However, all the test materials displayed no statistically significant increase in water solubility over the time period ( $p > 0.05$  two way ANOVA test). The amounts of eluted monomers from bulk-fill conventional viscosity materials (Surefil bulk fill and Tetric N Ceram Bulk Fill) were higher than bulk-fill flowable materials (Surefil SDR Flow and Filtek Bulk Fill flowable restorative). Of all the monomers tested UDMA eluted more than Bis-GMA and TEGDMA. Overall UDMA monomer eluted the most, followed by Bis-GMA and the TEGDMA. **Conclusion:** Within the limitation of this study, the results of this study did not support the null hypothesis that there is no significant difference in the water sorption. The bulk-fill low viscosity flowables showed lower water sorption than the conventional viscosity bulk-fills. Surefil SDR Flow was significantly lower than the other materials followed by Filtek Bulk Fill flowable restorative and Tetric N-Ceram Bulk Fill and the highest overall

means were recorded for Surefil bulk fill. For water solubility the overall means for the flowables of Filtek and SDR were smaller than Surefil and Tetric N-Ceram. For monomer elution three monomers were detected of which UDMA monomer eluted the most, followed by Bis-GMA and the TEGDMA. With regards to the elution of monomers, it was found that 3 monomers named UDMA eluted more than Bis-GMA and TEGDMA.



## Keywords:

Resin filled composite

Bulk-fill composite

Flowable composite

Packable composite

Water sorption

Solubility

Monomer elution



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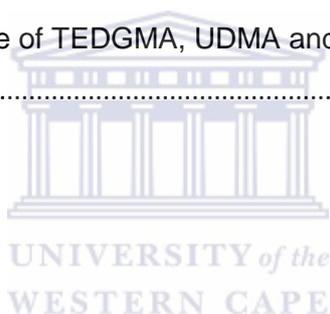
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# Chapter 1

## 1.1. Definition of terms

For the purpose of this study, the following terms are defined as follows:

- **Resin filled composite:** is the result of inter-atomic or molecular interaction between two or more components, the overall properties of which are superior to those of the individual components alone (Dogon, 1990). It is also defined as a multiphase material that exhibited the properties of both phases and results in a new enhanced material (Roberson et al., 2002). Rawls and Esquivel-Upshaw (2003) defined resin filled composites as a highly cross linked polymeric material reinforced by a dispersion of glass, crystalline, or resin filler particles or/ short fibres bonded to the matrix by saline coupling agent
- **Flowable composite:** a hybrid composite with reduced filler level and narrower particle size distribution that increases flow and promotes intimate adaptation to prepared tooth surface (Anusavice, 2003).
- **Packable composite:** a hybrid resin composite designed for use in posterior area, where a stiffer consistency facilitates condensation in posterior teeth (Anusavice, 2003).
- **Bulk-fill composite:** is an advanced composite technology which allows for directly placing posterior restorations in a single increment of 4mm (Vasquez, 2012).
- **Water sorption:** a diffusion controlled process that may cause chemical degradation of the material leading to several drawbacks, such as de-bonding of the filler polymer-matrix and release of the residual unreacted monomers (Giannini et al., 2014).
- **Water solubility:** is reflected by the amount of leached unreacted monomers and the loss of filler particles (Giannini et al., 2014). It is the maximum amount

of the chemical that will dissolve in pure water at a specified temperature. Above this concentration, two phases will exist if the organic chemical is a solid or a liquid at the system temperature: a saturated aqueous solution and a solid or liquid organic phase. Aqueous concentrations are usually stated in terms of weight per weight (ppm, ppb, g/kg, etc.) or weight per volume (mg/L, moles/L, etc.) (Lyman et al., 1990)

- **High performance liquid chromatography (HPLC):** is a type of liquid chromatography used to separate and quantify compounds that have been dissolved in solution (Kupiec, 2004).



## Chapter 2

### Literature review

#### 2.1. Introduction

Resin filled dental composite materials have been introduced into dental practice since mid-1960s as an aesthetic restorative material for anterior teeth (Bowen, 1962 cited in Peutzfeldt, 1997). Since then they have undergone several developments in order to enhance the longevity and performance of these materials. Typically, resin filled dental composites consist of three main components namely:

1- Organic resin matrix which consists of a monomer, an initiator system and a stabilizer system.

2 - Inorganic filler such as quartz.

3 - Coupling agent such as organo-silane coupling agent that chemically bonds the inorganic fillers to the organic resin matrix (Phillips, 1973).

The properties and the performance of the resin filled dental composites are basically dependent upon the components of the materials. Some properties are related to the resin matrix such as colour stability and softening tendency, whereas others are related to the inorganic fillers and coupling agent such as abrasion resistance, coefficient of thermal expansion, strength and stiffness (Asmussen, 1983; Asmussen, 1984; Soderholm, 1984; Braem et al., 1989). Furthermore, properties such as polymerization shrinkage and water sorption are dependent on both the inorganic fillers and the organic resin matrix (Asmussen, 1975; Hashinger and Fairhurst, 1984; Munksgaard et al., 1987).

Variation in filler size, amount, morphology, volume, distribution and chemical composition has resulted in a large variety of resin filled dental composites categories such as macrofilled, microfilled, hybrid, microhybrid, nanofilled, nanohybrid, flowable and packable (Lutz and Phillips, 1983; Willems et al., 1992; Bayne et al., 1994).

The oral environment plays an important role in modifying the properties of resin filled dental composites, as water sorption and solubility compromise the mechanical and physical properties of the materials (Roulet and Walti, 1984). Water sorption and solubility result in release of components of dental composites such as residual monomers which are essential factors in assessing the biocompatibility of resin filled dental composites (Moharamzadeh et al., 2007).

Although, they were first introduced as a restorative materials for the anterior teeth, currently resin filled composites are being used more and more as a restorative in posterior teeth (Helvatjoglu-Antoniades et al., 2006). Resin filled composite materials are widely used today because of their aesthetic properties as well as their ability to adhere to tooth structure.

Resin filled composite materials consist of organic polymeric matrix and inorganic filler particles coupled by coupling agent in addition to other additives. According to the filler size, resin filled dental composites are classified as hybrid, macrohybrid, microhybrid. With the introduction of nanotechnology in dentistry, nanofilled and nanohybrid resin composites are currently being used in dental practice (Roulet and Walti, 1984). Flowable and bulk-fill composites are new categories of resin filled composites that have been recently introduced in dentistry (Helvatjoglu-Antoniades et al., 2006).

Flowable composite is a resin filled composite that is described as a low viscous resin composite and is characterised by fluidity that was recently introduced to the market place. It has either less filler loading or a greater proportion of the diluent monomers and this type of dental composite offers better adaptation to the internal cavity walls, higher flow, greater elasticity and easier insertion than the previously available products (Bayne, 1999). The filler content of the earlier flowable composites was found to be 20-25% less than the universal composite materials but with similar particle sizes of the traditional hybrid composites. By reducing the filler content the viscosity of the material is reduced (Bayne et al, 1998). Flowable dental composites are being used for a variety of applications such as pit and fissure sealants, liners, margin or void repair and even class I and V restoration. The clinical application and performance of these materials require further investigation because of their inferior mechanical properties compared to the traditional hybrid composites (Attar et al., 2003).



Packable composites are characterised by stiffer consistency because of their higher filler content and distribution compared with conventional composites. Unlike the conventional composites, packable composites are recommended to be used as stress bearing posterior restorations because of their improved handling properties and they can be applied by utilizing a technique similar to that used for amalgam application (Helvatjoglu-Antoniades et al., 2006). There are a wide variety of filler types and a different filler contents that are being used in the packable composites, which may contribute to the variability in the results of the mechanical properties of the materials (Manhart et al., 2000).

Bulk-fill composites are new resin based composite materials that have been introduced recently in attempt to speed up the restoration and to save time. The first

bulk-fill materials in the market were introduced as packables e.g. Surefil (Dentsply, USA).

Oral environment plays an important role in modifying the properties of resin filled composite as water sorption and solubility could negatively affect their physical and mechanical properties (Yap, Teoh and Tan, 2000; Sarker, 2000).

Water sorption by resin based dental composites is described as a diffusion controlled process that may cause chemical degradation of the material leading to several drawbacks, such as de-bonding of the filler polymer-matrix and release of the residual unreacted monomers. Water solubility of resin based dental composites is reflected by the amount of leached unreacted monomers and the loss of filler particles (Giannini et al., 2014).

Water sorption and solubility properties are basically dependant on the composition of the dental composite materials like monomer type, efficiency of the filler-matrix bonding, filler characteristics (content, size, shape and inter-particle spacing) and degree of curing (Kim et al., 2002).

Water sorption by resin filled dental composites may cause expansion of the composite filling, which decreases any gap formed by polymerisation shrinkage, thus compensate for any material shrinkage (Yap et al.,2000). This might be considered as a positive effect of water sorption on marginal gap formation following polymerisation shrinkage, although further investigation is needed to provide direct evidence (Ruttermann et al., 2007). However, polymerisation shrinkage takes place within minutes after curing the composite, whereas water sorption that results in composite expansion and consequently results in full compensation of the polymerisation shrinkage takes a longer period of several weeks (Yap et al., 2000).

## **2.2. Resin filled composite**

### **2.2.1 History of resin filled composite**

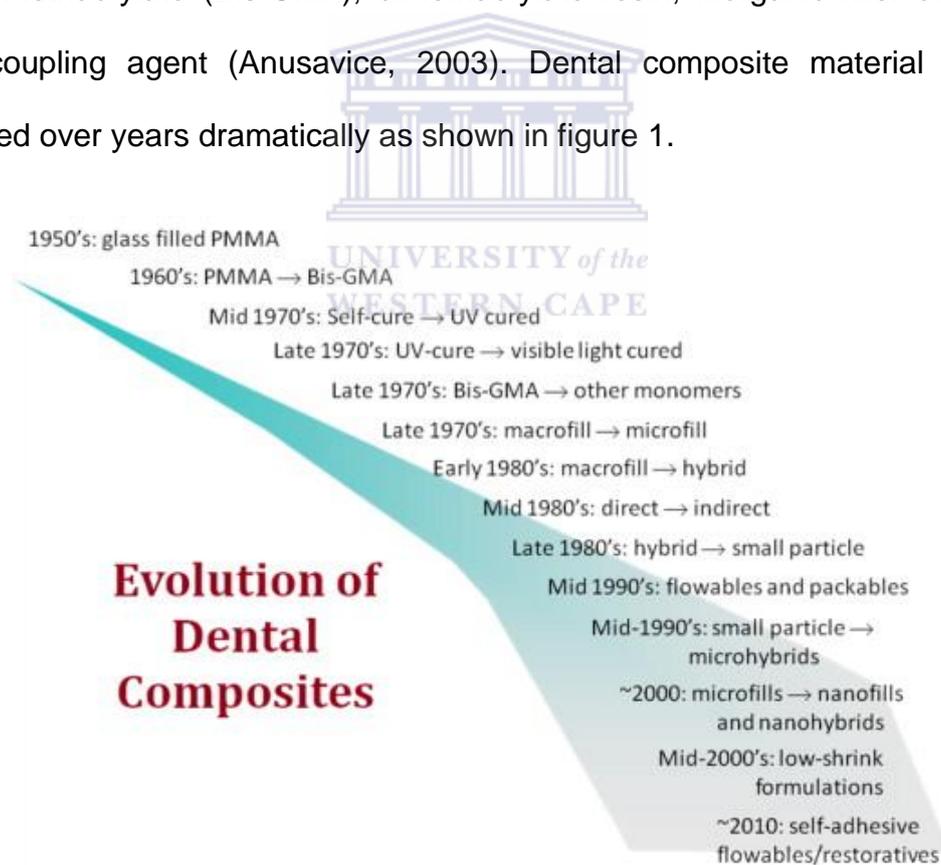
Acrylic acid was discovered by a German chemist, J. Redtenbacher in 1843. By 1900, methacrylic acid in addition to its esters as methyl methacrylate were synthesised and polymerized by addition mechanism to form polymethyl methacrylate (Luskin, 1967 cited in Peutzfeldt, 1997).

During World War II, the discovery of benzoyl peroxide tertiary amine redox initiator-accelerator system that allowed methyl methacrylate to polymerize at ambient temperature laid the foundation for direct filling resin synthesis and its development (Czapp et al, 1941 cited in Peutzfeldt, 1997). There were many expectations of the new methyl methacrylate, but none of these expectations were fulfilled as there were many drawbacks associated with this material, such as discolouration, pulp damage, high incidence of recurrent caries, high coefficient of thermal expansion and polymerization shrinkage (Coy, 1953 cited in Peutzfeldt, 1997).

As a result of the limitation of methyl methacrylate, R. L. Bowen, an American scientist developed other synthetic resins known as epoxy resins (Bowen, 1956 cited in Peutzfeldt, 1997). These resins seemed to harden at room temperature with less shrinkage and produced an insoluble polymer that has the ability to adhere to most solid surfaces. Better results in terms of coefficient of thermal expansion, colour stability and adhesion to tooth structure were obtained from the first dental resin composite materials which consisted of epoxy resin with aggregates of fused quartz, (Bowen, 1956 cited in Peutzfeldt, 1997). However, epoxy resins were discontinued because of slow hardening, which resulted in preventing their use as direct restoration (Peutzfeldt, 1997).

Bowen synthesized a new monomer known as Bis-GMA in 1956 from bisphenol A and glycidyl methacrylate and it was similar to epoxy resins with the exception that the methacrylate group replaced the epoxy group (Bowen, 1965 cited in Peutzfeldt, 1997). The new monomer was superior to methyl methacrylate in terms of molecular weight and chemical structure giving rapid hardening, lower volatility, lower polymerization shrinkage and stiffer resins. Consequently, Bis-GMA has started a new era of dental resin composite synthesis and development (Bowen 1962 cited in Peutzfeldt, 1997).

This new type of dental composite was developed in 1962 consisted of bisphenol A glycidyl methacrylate (Bis-GMA), dimethacrylate resin, inorganic filler and organic silane coupling agent (Anusavice, 2003). Dental composite material has since developed over years dramatically as shown in figure 1.



**Figure 1: Stages of resin filled composite development (Ferracane, 2011).**

## **2.2.2. Chemical composition of resin filled composite.**

Basically, dental composite materials have three main components, namely polymeric matrix, which is usually a methacrylate, fillers such as quartz, alumina, silicate, and coupling agent such as silane to create a bond between the fillers and the polymeric matrix (Smith, 1985 cited in Santerre, Shajii and Leung, 2001).

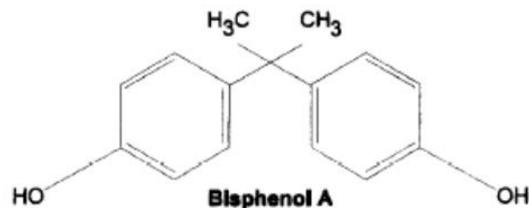
Ideally, resin based composite materials consist of 15-25% w/w of organic monomeric matrix, 75-85% w/w of a mixture of different inorganic fillers, in addition to other additives (Klapdohr and Moszner, 2005).

### **2.2.2.1. Polymeric matrix.**

Polymer is a large molecule that is made up by repetitive bonding together of smaller molecules known as monomers and polymerization is a term that is used to describe the process by which the monomers are joined together and converted to a polymer. In general, the monomers that are used in dentistry are in liquid form and converted to solids during a polymerization process and the extent to which monomers are changed to polymers is known as degree of conversion (Peutzfeldt, 1997).

The predominant resin monomer consists of complex methacrylate resins, where the methacrylate group is coupled with Bis-phenol A (figure 2) derivatives (Bowen et al., 1985 cited in Santerre et al., 2001). An experimental dimethacrylate was first synthesised by glycidyl methacrylate reaction (Bowen and Marjenhoff, 1992) and then later was synthesised by glycidyl ether of Bis-phenol A and methacrylic acid chemical reaction which resulted in formation of 2,2 bis[4(2 hydroxy-3methacryboxy propoxy)-phenol] propane, which is known commercially as Bis-GMA (Sandner and

Schreiber, 1992). The molecular weight of Bis-GMA is 512 g/mol and the initial viscosity is 1.200Pa (Gajewski et al., 2012).



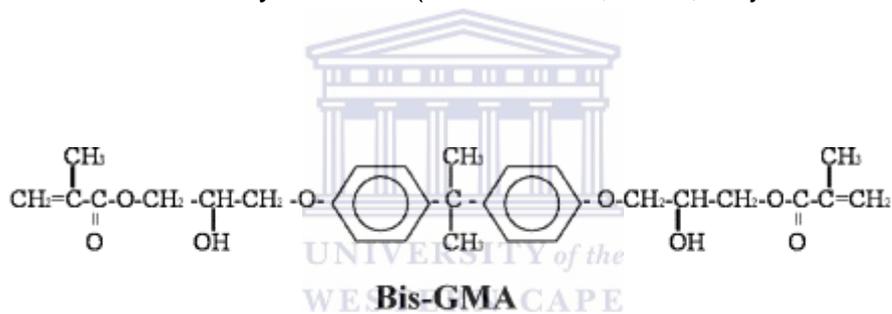
**Figure 2: Bisphenol A (Staples et al., 1988).**

Smith (1985, cited in Santerre et al., 2001) described Bis-GMA (figure 3) as a viscous, non-volatile monomer which has the ability to incorporate high filler load, providing what is known as reinforced composite resin. Bowen and Marjenhoff (1992) stated that Bis-GMA had lower polymerisation shrinkage while Sander et al. (1997) stated that the hydrogen bond between hydroxyl groups resulted in high viscosity which is considered a setback of Bis-GMA. As a result of that a diluent monomer was needed to reduce the viscosity of Bis-GMA and to allow easy handling and manipulation. The aim of diluting Bis-GMA is to lower the viscosity, the lower viscosity of monomer, the more filler can be incorporated which in turn improves many properties of the polymerised dental resin such as stiffness, strength and coefficient of thermal expansion. However, dilution of Bis-GMA has adverse effects like raised polymerisation shrinkage (Peutzfeldt, 1997).

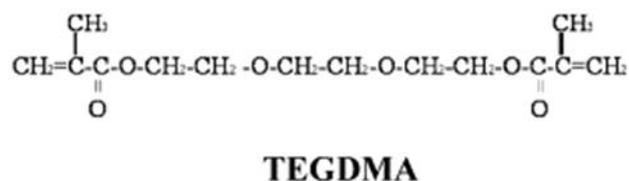
Triethylene glycol dimethacrylate (TEGDMA) (figure 4) is one of the most common monomers that have been used with Bis-GMA (Smith, 1985 cited in Santerre et al., 2001). Both Bis-GMA and TEGDMA have two reactive double bonds, in which when polymerised, covalent bonds will be formed between the polymer chains, which is

known as a cross-link. The cross-linking is responsible for improving the physical and mechanical properties of the matrix, which in turn will result in composite with physically and mechanically improved properties (Rawl and Esquivel-Upshaw, 2003). TEGDMA is described as highly flexible, low molecular weight and low viscosity monomer and all the previously mentioned characteristics contribute to high mobility during polymerisation (Sideridou et al., 2008). The molecular weight of TEGDMA is 286 g/mol and the initial viscosity is 0.01 Pa (Gajewski et al., 2012).

There are other different diluent monomers such as ethylene glycol dimethacrylate (EGDMA) and urethane dimethacrylate (UDMA) (figure 5) with molecular weight of 470 g/mol and initial viscosity of 23 Pa (Pucket et al., 2007; Gajewski et al., 2012).



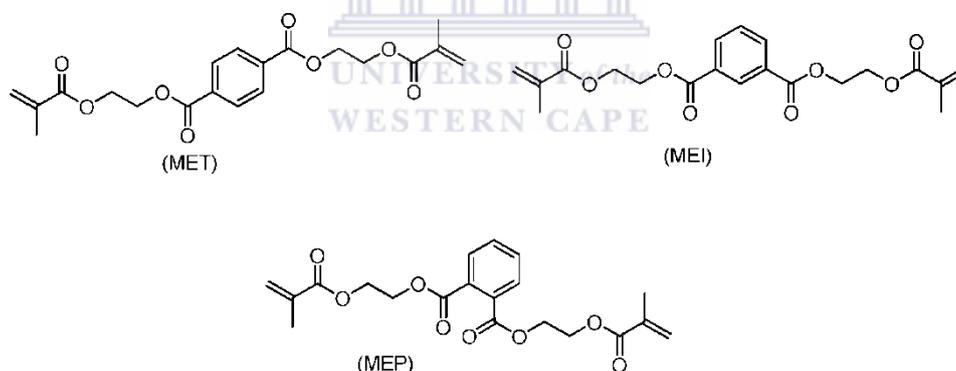
**Figure 3: Monomer Bis-GMA (Ferracane, 2006).**



**Figure 4: Monomer TEGDMA (Ferracane, 2006).**



As Bis-GMA is too viscous to be used without being thinned, it is not colour stable and cannot be purified because it is a mixture of high molecular weight optical isomer. A unique monomer system known as eutectic monomers system was made based on the theory that certain isometric crystalline dimethacrylates are able to make a eutectic that is liquid at room temperature. Three aromatic diesters were synthesized and purified, namely Bis (2-methacryloxyethyl) esters of phthalic (MEP), isophthalic (MEI) and terephthalic (MET), and it was found that their mechanical properties were comparable with those of Bis-GMA, but further improvements were needed in colour stability and polymerisation shrinkage (Bowen, 1970; Barton et al., 1973 cited in Peutzfeldt, 1997). Even though, the eutectic monomers (figure 6) appeared to be practical alternatives for Bis-GMA, neither of them has been used in commercial resin materials (Peutzfeldt, 1997).



**Figure 6: Eutectic monomers (Peutzfeldt, 1997).**

There were attempts to minimise water sorption by introducing non hydroxylated homologues of Bis-GMA which are also known as hydrophobic monomers. The utilisation of these monomers led to improved maintenance of the mechanical properties as a consequence of long exposure to water. However, utilisation of these monomers did not improve wear resistance and did not result in high mechanical

properties and this may be attributed to the significant reduction in hydrogen bonding of non-hydroxylated homologues (Atsuta et al., 1971 cited in Peutzfeldt, 1997).

Fluoro-carbon containing polymers are extremely hydrophobic, have low surface energy and very difficult to wet. It is assumed that dental composites with this type of monomers will show decreased microleakage and in order to test this assumption, a polyfluorinated monomethylacrylate (PFMA) was incorporated into an experimental resin composite material. The resultant dental composite showed high contact angles with water, reduced water sorption, higher resistance to staining and reduced microleakage. On the other hand, it showed increased polymerisation shrinkage and undesired physical and mechanical properties compared to dental composite based on Bis-GMA (Douglas et al., 1979 cited in Peutzfeldt, 1997). Many other fluorinated polymethacrylate have been synthesised in attempts to improve physical and mechanical properties and decrease polymerisation shrinkage of dental resin which is based on low surface energy and low water sorption monomers. One of them has comparable viscosity to the viscosity of Bis-GMA in addition to its ability to be incorporated with other monomers. It was found that experimental resin composites based on fluorinated multifunctional methacrylate prepolymers, such as PFMA showed high contact angles with water, at the same time it exhibited improved aesthetic and mechanical properties but this type of monomers have not been used commercially despite the promising results (Antonucci, 1986).

The first type of urethane dimethacrylate monomers was synthesised from hydroxyalkyl methacrylate and diisocyanates (Foster and Walker, 1973 cited in Peutzfeldt, 1997). The molecular weight of this monomer is almost equal to the molecular weight of Bis-GMA, but it is less viscous. It can be used alone or in

combination with other monomers such as Bis-GMA or TEGDMA (Ruyter and Oysaed, 1987).

Patel et al. (1987) reported that Bis-GMA has a volumetric shrinkage of 5% and adding diluent monomers will increase this value and because polymerisation shrinkage is considered one of the main factors that affect the longevity of dental resin, this motivated a research for non-shrinkage resin system based on bicyclic compound in ring opening polymerisation (Bailey, 1975 cited in Peutzfeldt, 1997). In this monomer, the Van Der Waals bond distance is changed into covalent distance and ring structures are opened during polymerisation. Bailey (1990) reported a variety of bicyclic monomers such as spiro-orthocarbonate, trioxibicyclo-octanes and spiro-orthoesters among others, that would undergo double ring opening with no change in volume. Thompson et al. (1979) reported that spiro-orthocarbonate when used as a component in dental composites; it resulted in doubling of the adhesive strength of the resin to the etched enamel.

New monomers with antibacterial properties have been synthesised in order to develop antibacterial resin composites, and they consist of methacrylate group and dodecylpyridinium bromide (MDPB) and they are considered the most promising as MDPB could copolymerise with conventional dental monomers, the antibacterial part of this molecule is bounded chemically to the resin matrix after curing. Imazato et al. (1993) and Imazato et al. (1994) reported the inhibitory effect on surface growth of *Streptococcus mutans*, but without releasing the antibacterial component and without having any adverse effect on curing and the mechanical properties.

Large numbers of methacrylate monomers in dental resin remain unreacted in cross linked polymer which may impair the physical, chemical and mechanical properties.

For this reason a new monomer system with potential for better conversion is needed (Ruyter, 1985 cited in Peutzfeldt, 1997). Stanbury and Antonucci (1992) theorised that the use of a more reactive diluent monomer is a practical measure to address the relatively low degree of conversion. Monomers such as  $\alpha$ -methylene- $\gamma$ -butyrolactone (MBL), which is the cyclic analogue of methyl methacrylate and evaluated to be used as a comonomer with Bis-GMA was found to be highly mobile having favourable properties and more reactive compared to methyl methacrylate. MBL has beneficial effect on the degree of conversion of the experimental resin as the degree of conversion was increased and mechanical properties were improved. It was concluded that MBL polymers resulted in materials with improved performance.

Rawl et al. (1997) described the use of liquid crystalline monomers as a resin which shrinks less to overcome the polymerisation shrinkage of dental composites.

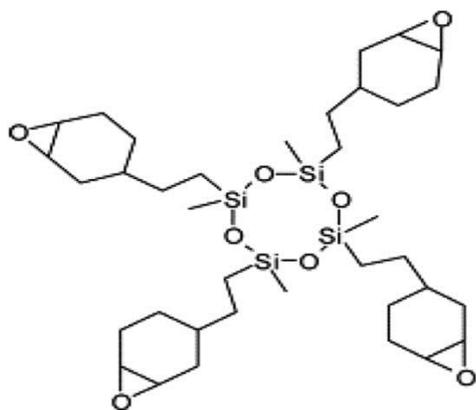
The use of ring-opening system like oxirane based resin cured by visible light has been the focus of the modern development in dental composite research to overcome the shrinkage of methacrylate resin. This type of resin has showed many desired properties such as higher strength, lower polymerisation shrinkage, improved depth of cure, acceptable glass transition temperature and equivalent hardness when compared to the conventional methacrylate resin based dental composite (Eick et al., 2002).

Silorane (figure 7) is another monomer system for dental composite described by Weinmann et al. (2005) and obtained by a chemical reaction between oxirane and siloxane molecules. It was claimed that the main advantage of this new monomer is combining the low polymerisation shrinkage property of the ring-opening oxirane

molecule and the increased hydrophobicity property of the siloxane molecule. It was reported that the lowest polymerisation shrinkage and the highest ambient colour stability in dental composite were provided by silorane technology. In addition to high reactivity, the mechanical properties compared well with successful methacrylate dental composite (Weinmann et al., 2005). These properties were attributed to the hydrophobic nature of silorane resins which absorb less water and dyes in daily diet, and this adds to its advantages by being less sensitive towards exogenic discolouration than the hydrophilic materials (Weinmann et al., 2005).

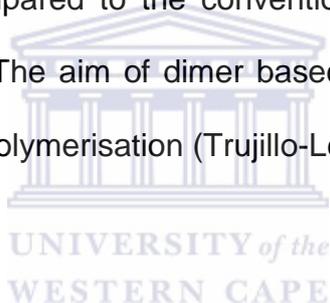
Palin et al. (2005) found that the silorane resin based dental composite exhibited favourable properties such as lower water sorption and solubility, when compared to the conventional methacrylate resin based dental composite. It is concluded that the silorane resin has potentially improved the hydrolytic stability of the silorane resin based dental composite.

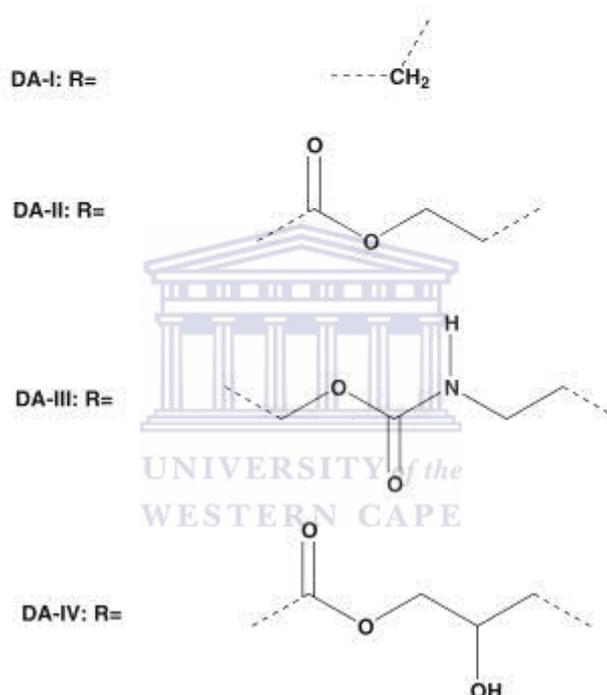
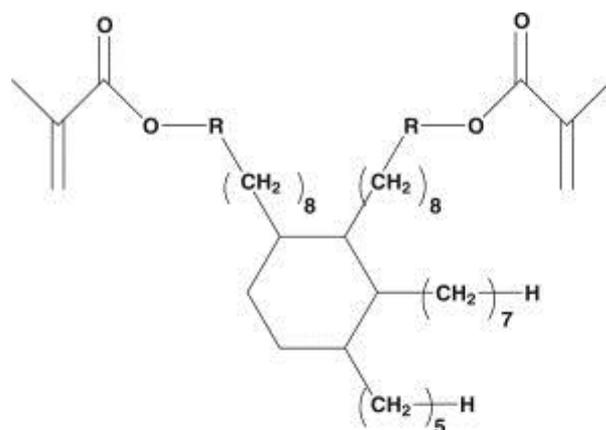
Furthermore, silorane resins were found stable in simulated biological fluids using aqueous solutions containing either porcine liver esterase, dilute hydrochloric acid or epoxide hydrolase, these findings enhance the potential of using silorane monomer in dental composite materials (Eick et al., 2006).



**Figure 7: Silorane monomer (Weinmann et al., 2005).**

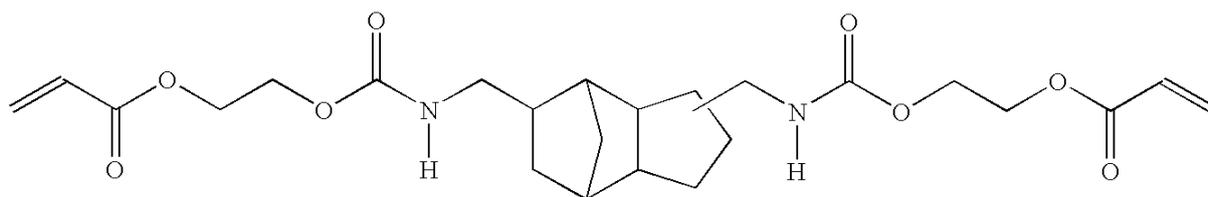
Trujillo-Lemon et al. (2006) stated that the new monomer dimer acid dimethacrylate (figure 8) had higher molecular weight, lower viscosity, and lower concentration of initial double bond when compared to the conventional dimethacrylate monomers such as Bis-GMA or UDMA. The aim of dimer based monomers was to overcome the volume shrinkage during polymerisation (Trujillo-Lemon et al., 2006).





**Figure 8: Dimer acid dimethacrylate (Trujillo-Lemon et al., 2006).**

Tricyclodecane (TCD) urethane based monomers are new methacrylic acid derivatives and incorporated to the recently introduced dental composites. The dental composites which contain TCD urethane based monomers (figure 9) have shown lower shrinkage and polymerisation stresses, when compared to the dental composites containing the conventional dimethacrylate monomers (Kurokawa et al., 2007).



**Figure 9: TCD Urethane monomer (Ille and Hickel, 2011).**

Monomers commonly used in resin filled composites are summarised in Table 1.

Monomer	Chemical nomenclature	Molecular weight (g/mol)	Molecular formula	Viscosity (Pa)
<b>Bis-GMA</b>	2,2-bis-4-2(hydroxi-3-metacriloxiprop-1-oxi)propane	512	C <sub>29</sub> H <sub>36</sub> O <sub>8</sub>	1200
<b>TEGDMA</b>	Triethylene glycol dimethacrylate	286	C <sub>14</sub> H <sub>22</sub> O <sub>6</sub>	0.01
<b>UDMA</b>	1,6-bis-(metacriloxi-2-etoxicarbolamino)-2,4,4-trimethylexane	470	C <sub>23</sub> O <sub>38</sub> N <sub>2</sub> O <sub>8</sub>	23
<b>Bis-EMA</b>	2,2-bis-4-2(hydroxi-3-methylacriloxietoxi)-phenylpropane	540	C <sub>39</sub> H <sub>14</sub> O <sub>8</sub>	0.9

**Table 1: Monomers used in dental composites (Gajewski et al., 2012).**

### 2.2.2.2 Fillers

In composites, the fillers are considered the major constituents by weight and volume (Dogon, 1990). The fillers are the inert, inorganic components of the resin composites. Barium, silica and quartz are examples of inorganic fillers which are

used in most commercial resin composites (Södreholm, 1985 cited from Santerre et al., 2001).

Dogon (1990) stated that the physical properties of dental composite, such as reduction of water sorption, polymerisation shrinkage, increased strength and modulus of elasticity were improved by adding fillers into the resin matrix. Roulet et al. (1987) stated that the radio-opacity was provided by adding heavy metals into the fillers.

Initially, the filler particles were limited in size as a result of the limited ability of grinding and sieving quartz, ceramic and glass particles. The size of particles ranged between 1-100  $\mu\text{m}$ . Later, various methods such as hydrolysis and precipitation have been used to produce what is called pyrolytic silica with size range from 0.06-0.1 $\mu\text{m}$  (Puckett et al., 2007). Recently, sol-gel chemistry is used to produce particles from silicate precursors which are then polymerised to make particles with size range between micrometres ( $\mu\text{m}$ ) and nanometres ( $\text{nm}$ ) (Puckett et al, 2007). The production of submicron size particles has led to the production of nanocomposite materials, in which the particles size approaches the size of polymer matrix molecules. The nanocomposite materials show improved physical and mechanical properties at higher filler load (Chen et al., 2006). On the other hand, Curtis et al. (2008) stated that the enlarged surface area to volume ratio of the fillers in nanofilled composites resulted in increased water sorption and filler-matrix interface degradation which negatively influenced the mechanical properties when compared to microhybrid composite materials.

In general, the resin filled composite materials contain many different types of fillers, for example ytterbium fluoride ( $\text{YbF}_3$ ) which serves as radiopacifier and yttrium

fluoride ( $YF_3$ ) which serves as fluoride source (Klapdohr and Moszner, 2005). The nano-size fillers could be categorised as fused aggregates of primary nanoparticles with cluster size may exceed 100 nm, or discrete isolated nanoparticles with dimension of 5-100 nm (Ilie et al., 2009).

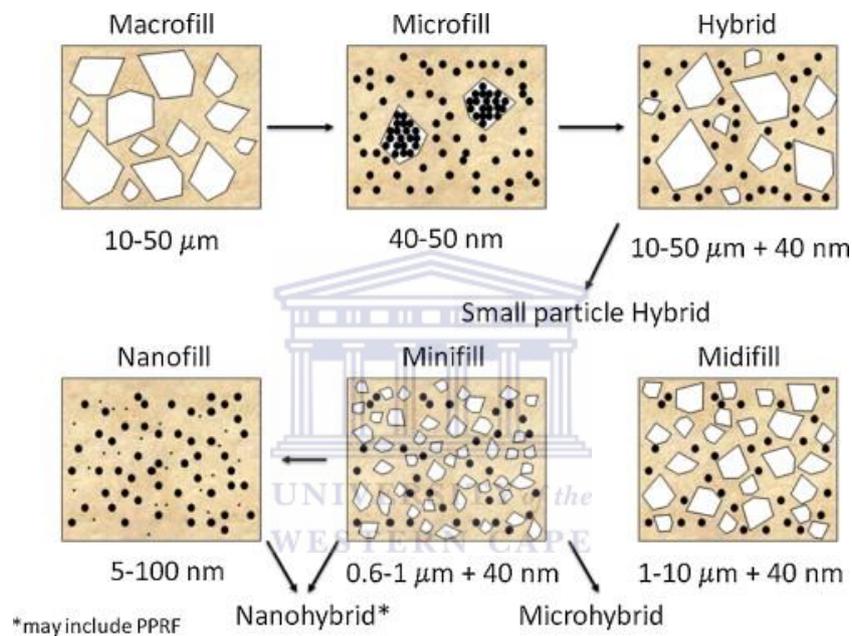
Turssi et al. (2005) conducted a study that showed that the size and the shape of filler particles significantly affect the wear resistance in which utilizing nano-sized fillers in dental composites usually results in improved properties. Samuel et al. (2009) discussed the use of mesoporous silica fillers to eliminate the need to use a silane coupling agent between fillers and matrix. Additionally, he conducted a study to evaluate the use of silica particles with interconnected porous structures and non-porous silanised silica particles. The results showed that the use of two different filler mixtures has led to optimising the filler load and mechanical reinforcement. Tian et al. (2008) stated that the use of nanofibrillar silicate crystals on one hand resulted in improved mechanical properties. On the other hand, it resulted in difficulties in obtaining uniform dispersion of nano-particles in the resin matrix.

A composite material with caries inhibition property and improved mechanical properties was obtained by utilizing the combination of calcium phosphate nanoparticles and silicon nitride whiskers (Xu et al., 2009). Additionally, quaternary ammonium polyethylenimine (PEI) nanoparticles were introduced to the dental composites, the antimicrobial effect of PEI nanoparticles lasted for only one month and these particles did not significantly affect the mechanical properties of dental composites (Beyth et al, 2006).

It is crucial to report that the risks related to utilizing nanoparticles are not well known yet in resin filled composites, the nanofillers are firmly embedded and bound to the

matrix, and therefore they should possess no harmful effect to the human health. As composite fillings wear over time, nanoparticles released from the filling may pose a potential health risk and nanofilled resin dental composites needs to be investigated and assessed profoundly (Brayner, 2008).

Figure 10 shows the developments in the fillers of resin filled dental composites that took place over time.



**Figure 10: The chronological development of the state of the art of dental composite formulation based on filler particle modifications (Ferracane, 2011).**

### 2.2.2.3. Silane coupling agent

Surface treatment of filler particles is necessary in order to reduce the surface energy of the fillers, which in turn results in enhanced filler particle dispersion and reduced hydrophilicity. In addition to that filler surface modifications provide a functional interface which permits covalent bonding between the organic matrix and the inorganic fillers (Cramer et al., 2011).

One of the most widely used coupling agents in dental composite is methacryloxypropyltrimethoxy silane (MPS). The hydrolysed trialkoxy silane group of the coupling agent interact with the filler silanol groups as well as with themselves to form an array of imperfectly arranged hydrogen and covalent bonded attachment which in turn yield a multi layered, dense interface (Cramer et al., 2011).

#### **2.2.2.4 Others**

Inhibitors such as hydroquinone mono-methyl ether (MEHQ) are added to resin matrix in amount of 200-1000 ppm to prevent the incidence of premature polymerisation during the storage of dental composite. In addition, inhibitors are needed to prevent uncontrolled polymerisation by the ambient light during the use of the dental composite (Klapdohr and Moszner, 2005). Ultra-violet (UV) photostabilisers such as 2-hydroxybenzophenone are added to resin matrix in amounts of 0.1-0.5% w/w to prevent photo-degradation, and to result in colour stability of the dental composite (Klapdohr and Moszner, 2005).

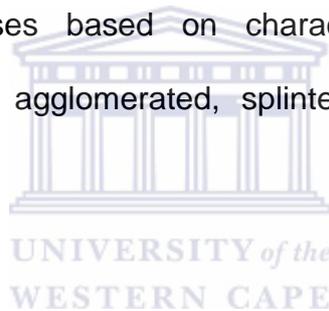
Pigments such as ferric oxide (red), ferric hydroxide (yellow) are added in amounts of 0.001-0.05% w/w, in which a mixture of different inorganic components is used to imitate the colour of natural teeth and to meet the aesthetic demands of the patient (Klapdohr and Moszner, 2005).

Chlorhexidine diacetate (CHXA) is added as an antimicrobial agent to some dental composites and with raising the hydroxyethylmethacrylate (HEMA) content this leads to decrease the light curing polymerisation. On the other hand, by adding CHXA the water sorption, expansion and the controlled diffusion of CHXA release is increased. It is noteworthy that biofilm formation with this type of dental composites is delayed compared to the conventional dental composites without CHXA (Leung et al., 2005).

It was reported that there were some problems accompanying the introduction of antimicrobial agents to the dental composites such as the reduced ability of the dental composites to the light cure and the antimicrobial properties are not permanent as they decrease with time (Jandt and Sigusch, 2009).

### **2.2.3 Classification of resin filled composite**

Lutz and Phillips (1983) introduced the conventional classification which is based on the filler size distribution and the amount of incorporated fillers. This system classifies composites into traditional, hybrid (mixture of ground glass and microfill particles) and microfilled composite (table 2). The microfilled composite are further sub-classified into sub-classes based on characterisation of the type pre-polymerised resin filler, e.g. agglomerated, splintered and spherical (Lutz and Phillips, 1983).



Filler	Composite	Particle size
Macrofiller (ground silica)	Macrofilled composite	1-50 $\mu\text{m}$
	Hybrid composite	1-20 $\mu\text{m}$ glass 0.04 $\mu\text{m}$ silica
Microfiller (pyrogenic silica)	Hybrid midfilled composite	0.1-10 $\mu\text{m}$ glass 0.04 $\mu\text{m}$ silica
	Homogenous microfilled composite	0.04 $\mu\text{m}$ silica
	Heterogeneous microfilled composite	0.04 $\mu\text{m}$ silica Prepolymerised resin particles containing 0.04 $\mu\text{m}$ silica
Microfiller-based complexes	Heterogeneous microfilled composite	0.1-2 $\mu\text{m}$ glass 0.04 $\mu\text{m}$ silica

**Table 2: Classification of resin based composites in accordance to filler size (Lutz and Phillips, 1983; Klapdohr and Moszner, 2005; Phillips, 2003).**

Willems et al. (1992) proposed a classification system based on the volume fraction of filler and filler size, this system distinguishes between microfine composite, densified composite, traditional composite, miscellaneous composite and fibre-reinforced composite. Additionally, the densified composite were subdivided into mid-way and compact filled composites. There is also a sub classification of ultrafine and fine with each category.

A simpler classification system was proposed by Bayne, Heymann and Swift (1994) based on the size of the largest fillers, in which dental composites are classified into microfill (0.01-0.1  $\mu\text{m}$ ), minifill (0.1-1  $\mu\text{m}$ ) and midfills (1-10  $\mu\text{m}$ ).

The size, shape and the amount of fillers influence the properties of dental composites. For example, the spherical fillers are incorporated in a higher amount

when compared to irregular fillers of the same size but the spherical fillers result in a higher wear rate (Venhoven et al., 1996).

There are many proposed systems for the classification of resin filled dental composite materials. The most commonly used classification system is based on the size of the filler particles. The following broad system (microfilled, hybrid, packable) was used by Puckett et al. (2007). Additionally, the flowable, nanofilled, and microhybrid were addressed as a sub-classification.

It is important to note that the term (hybrid) is not used in this classification, because of the fact that almost all composites now are hybrid as they contain filler particles of two or more size ranges. The concept of incorporating a variety of filler sizes instead of a monomodel formulation, is consistent with the fact of reducing the inter-particle spacing in other words filling the spaces between the larger filler particles with the smaller filler particles and this improves the wear resistance, hardness and the strength of the resin filled composites (Lim et al., 2002).

#### **2.2.4 Flowable composites**

Flowable composites were first introduced in 1990s as an important advancement in restorative dental materials (Rada, 1998). Bayne et al. (1998) reported that the Flowable composites were made up with 20-25% lower filler loading than the conventional composites, or a greater proportion of diluent monomers and they are described as low viscosity resin composites. These materials offer easier insertion, better adaptation to internal cavity walls, higher flow and greater elasticity. Their use is advised to be restricted to low stress clinical application and their handling properties also varied widely, as the flow of some materials was difficult to control

while others did not flow any more than the universal composite control (Bayne et al, 1998).

The first generation of flowable resin composites had low modulus of elasticity which limited their use to be used only as liners and the second generation of flowable materials was introduced in 2000 and it promised improved mechanical properties and proposed to be used as bulk restorations, but the recent available clinical reports have not showed the expected results of improved clinical performance. Additionally, Loguercio et al. (2005) and Celik et al. (2007) reported no improved clinical performance of flowable composites when used in non-carious lesions whether used alone or as a liner. Furthermore, Ozelet al. (2008) and Han et al. (2009) did not recommend their application in critical stress areas.

A common clinical technique for flowable composites to be used as a liner, is to be in conjunction with the high modulus and high viscous packable composites, but the effect of possible restoration flexure when it is supported by low modulus flowable, and the higher than expected polymerisation shrinkage of flowable are not known (Bayne et al., 1998).

Attar et al. (2002) reported that the radio-opacity of some of flowable composites when used under posterior restorations was lower than the desirable. Malmstrom et al. (2002) conducted an *in vitro* study that showed the use of flowable composites resulted in reduced occurrence of voids and restoration microleakage, whereas Jain and Belcher (2000) reported no apparent advantages of flowable materials over universal hybrid composites. Hassan (2014) conducted a study to evaluate the mechanical properties of two flowable composites compared with two conventional composites; the study showed that the flowable had low mechanical strength

comparing with the conventional composites and this result supports the suggestion of the application of flowable composites should be avoided in high occlusal loading areas.

Flowable composites are being used currently for a wide range of applications such as liners, pit and fissure sealant, repairing materials for voids and margins and even as a restoration for class I and V. There are newer formulations of flowable materials such as flowable compomers and polyacid-modified resin composites (Attar et al., 2003).

### **2.2.5 Packable composite**

Packable composites are a new class of highly filled composite resin with a filler distribution which resulted in a different consistency compared to the hybrid composites. Packable composites are characterised with more viscosity and less stickiness compared to conventional composites. For this reason they claimed to be suitable to be placed in stress bearing areas as an amalgam alternatives and their application is similar to amalgam (Leinfelder et al., 1999).

The first few packable composites were introduced in early 1980s with altered filler characteristics such as filler size, shape, level or microfiller content. Unfortunately, porosity and insufficient wetting of particles by resin resulted from increasing the amount of filler particles beyond what had been used in conventional composites, and these early packable composites had high viscosity that made them difficult and sometimes impossible to be extruded through the small-bore syringe (Sturdevant et al., 1993).

According to Manhart et al. (2000) packable composites are also called condensable composites and may offer some technical advantages over the conventional composites, as they could allow easier and convenient application in posterior teeth, and their mechanical properties are significantly different but not consistently better than the properties of the conventional hybrid composites. Peumans et al. (2001) and Klein et al. (2002) explained that the better handling characteristics of the packable composites resulted from their high viscosity property which in turn resulted in easy establishment of the proximal contour of the restoration.

According to Condon and Ferracane (1997) heavily filled composites have had higher wear resistance, higher strength and higher fracture toughness when compared with composites that have lower filler content, but Willems et al. (1992) pointed out that the filler content should not exceed 70%, because of technical difficulties and poor handling characteristics.

Choi et al. (2000) conducted a study that showed that the properties of packable composites were similar to the non-packable posterior composites, and polymerisation shrinkage of packable composites was similar or higher than that of non-packable composites. Additionally, Cobb et al. (2000) compared the physical properties of the packable composites to the conventional hybrid composites and concluded that the physical properties of the packable composites were not superior to those of the conventional hybrid composites, in addition to that, the large filler particles may have caused long term problems such as surface roughness and increased wear.

There are studies which show that the clinical performance of packable resin composites placed using different adhesive systems had satisfactory results as a

restoration for posterior teeth after two years (Ernst et al., 2002; Ernst et al., 2003; Lopes et al., 2003).

### **2.2.6. Bulk-fill composite**

Bulk-fill composite are new resin based composite material that has been introduced recently, as a time saving restorative material for posterior application in attempt to speed up the restoration process by enabling the clinician to cure 4-5 mm thick increment in one step without negatively affecting polymerisation shrinkage, cavity adaptation and degree of conversion instead of time consuming layering technique (Ilie et al., 2013).

Bulk-fill composite has better adaptation with cavity walls resulting in self-levelling effect. However, in spite of the stated improved adaptation to the cavity walls microleakage analysis showed similar performance for flowable and conventional resin based composites (Ilie et al., 2013).

Increased polymerisation shrinkage stress at the tooth-material interface is the main concern of curing thick increments. However, bulk-fill materials in their experimental version revealed the lowest shrinkage stress and shrinkage rate value compared to regular flowable, microhybrid and nanohybrid methacrylate resin based composites and silorane based microhybrid resin based composite, thus the problems related to polymerisation shrinkage like gap formation, secondary caries, pulpal irritation and post-operative sensitivity could be minimised (Davidson et al., 1984 cited in Ilie et al., 2013; Leinfelder, 1995; Chen et al., 2001). Regarding the mechanical properties, the bulk-fill are proved to be more rigid (high modulus of elasticity) and more plastic (higher creep and plastic deformation) when compared with flowable composites, and generally have lower mechanical properties than microhybrid and nanohybrid

resin filled composites (Ilie and Hickel, 2011, Czasch and Ilie, 2013). However, other studies showed that bulk-fill composites showed creep deformation within the range of conventional composites. Additionally, flexure strength, water sorption and biocompatibility of bulk-fill composites were comparable to conventional resin based composites (Fleming et al., 2008; El-Safty et al., 2012).

Bulk-fill composite showed significantly reduced cuspal deflection in standardised class II cavity compared with a conventional resin based composite restored in an incremental filling technique (Moorthy et al., 2012).

### **2.2.7. Biocompatibility**

Biocompatibility is defined as “the ability of biomaterial to perform its desired function with respect to a medical therapy, without eliciting any undesirable local or systemic effects in the recipient or beneficiary of that therapy, but generating the most appropriate beneficial cellular or tissue response to that specific situation and optimising the clinically relevant performance of that therapy” (Williams, 2008).

There are many factors that could greatly affect the cytotoxic effects of dental materials in mammalian cells, such as sample preparation, aging method and curing conditions (Schweikl et al., 2005).

Several published researches discuss the adverse effects linked to the release of unpolymerised components from dental composites such as hypersensitivity (Moodley, 2005; Grobler et al., 2008), cytotoxicity (Alhiyasat, Darmani, and Milhem, 2005), estrogenicity (Wada et al., 2004), genotoxicity (Schweikl, Schmalz, and Weinmann, 2004) and alteration of immune response (Kostoryz et al., 2001). Yet, the clinical prevalence of these undesired adverse effects remains controversial.

Recently, many materials with new polymerisation chemistry, improved aesthetic and other properties are available in the market. However, the biological liabilities of many of them especially over the long term use are still inadequately defined (Eick et al., 2002).

Studies show significant cytotoxicity of resin composites in cell cultures, and the cytotoxicity occurs as a result of the residual monomers and oligomers (Caughman et al., 1991; Lefebvre and Schuster, 1994). On the other hand, there is lack of significant pulpal irritation after placing properly sealed resin composite restoration (Cox et al., 1987). This poor link between the results obtained from *in vivo* pulp test and *in vitro* cytotoxicity evaluation has been explained by the rapid release of the unbound components (Ferracane and Condon, 1990).

The release of substances from polymeric materials could occur by two mechanisms. Firstly, by elution of unbounded monomers by solvents after polymerisation and secondly, by degradation of polymerised materials over time which eventually results in creation of leachable components (Göpferich, 1996).

There are many factors that could greatly affect the cytotoxic effects of dental materials in mammalian cells, such as sample preparation, aging method and curing conditions (Schweikl et al., 2005).

Ferracane and Condon (1990) stated that the residual monomers and other additives could be released from polymerised dental composite restorations into the surrounding oral tissues in which about 75% of the leachable components were extracted within few hours, and 95% were extracted within 48 hours and it was concluded that dental resin filled composites do not represent a chronic source of unreacted monomers to the oral tissues.

Alhiyasat et al. (2005) conducted a study to compare the cytotoxicity of three composites (Tetric ceram, Filtek Z250, Admera) with their flowable products. Fibroblast cells were used for testing the cytotoxicity as they are the most common type of cells in dental pulp which makes them the most probable target of any chemical component that could be released from dental composite especially if the odontoblastic layer had been damaged. The results of the study showed that the least cytotoxic dental composite was Tetric ceram followed by Filtek Z250 and Admira (Voco). Compared to their flowable products, the flowables showed the highest toxicity and this may be attributed to the chemical difference in the composition (Alhiyasat et al., 2005). Flowable materials contain higher monomer content and lower filler content. High performance liquid chromatography analysis (HPLC) showed that there was a high concentration of TEGDMA and lower concentration of Bis-GMA in the extracts of the materials. UDMA was released from both Tetric Ceram and Filtek Z250 but not from Filtek flow. Bis-GMA was only detected in the extracts of Filtek Z250. Small amounts of Bisphenol A were detected in both Filtek Z250 and Tetric flow extracts. Wataha et al. (2003) conducted a study that showed similar results. Yoshii (1997) and Thialig et al. (2000) reported that TEGDMA had a toxic effect on different cell lines.

Wataha et al. (1999) pointed out that the release of the residual monomers from dental composites due to incomplete polymerisation or biodegradation is the responsible factor for the cytotoxicity of dental composite. On the other hand, Spahl et al. (1998) stated that there are about 30 components that have been eluted from set dental composite such as organic monomers, co-monomers, inorganic fillers and additives were detected.

It was proved that TEGDMA which is a co-monomer in dental composites could promote the growth and proliferation of cariogenic microorganisms and this may explain the incidence of secondary caries that develop beneath the dental composite restorations (Khalichi, Cvitkovitch and Santerre, 2004). Additionally, TEGDMA was identified as a mutagenic compound inducing gene mutation in mammalian cells. The gene mutation could be as result of covalent binding to DNA (Schweickl et al., 1998). Additionally, TEGDMA, MMA and HEMA caused an increase in the number of micronuclei in the Chinese hamster lung fibroblasts (V79) which is considered as an indicator of clastogenic activities.

Brackett et al. (2006) conducted an *in vitro* study to evaluate the cytotoxic effects of several types of dental composites (nanofilled, traditional hybrid, ormocer) on the cell mitochondrial activities of mouse fibroblasts. Initially, all dental types were highly cytotoxic. With time some materials showed improvement (conventional hybrid) which can be explained by the lower biological risk from the leached components, whereas other materials did not improve with time (nanofilled) and this could be attributed to the on-going leaching of components which have biological liabilities. Even though the clinical relevance of *in vitro* studies is usually questioned the persistent cytotoxicity of some dental composites should not be ignored, as it could be an indicator of serious clinical risks.

The biological effects of resin monomers (Bis-GMA, UDMA and TEGDMA) of several dental composites on the three dimensional human oral mucosal model were assessed. It was found that the TEGDMA based resin composites caused severe damage to the oral mucosal models in comparison to Bis-GMA and UDMA. Additionally, the viability of these models decreased significantly when exposed to TEGDMA comparing with Bis-GMA and UDMA. Furthermore, the amount of released

interleukin 1 $\beta$  cytokines secreted by immune cells and usually associated with inflammations and infections was increased, while Bis-GMA and UDMA did not result in any remarkable alteration. These findings indicate significant mucotoxicity of TEGDMA containing composite compared to Bis-GMA and UDMA (Moharamzadeh et al., 2008). In a previous study conducted by Moharamzadeh et al., (2007) interleukin 1 $\beta$  was undetectable and this could be attributed to the use of a different cell culture namely monolayer culture of human gingival fibroblasts.

The cytotoxicity of 35 dental composite monomers in human and animal fibroblast culture were assessed and it was found that the most toxic materials were TEGDMA, UDMA and Bis-EMA respectively (Geurtsen et al., 1998). Storing dental composites in organic solvents resulted in decreasing their toxic effects on fibroblast cultures and this could be explained by the removal of leachable toxic components from dental composites by the organic solvents (Rathbun et al., 1991).

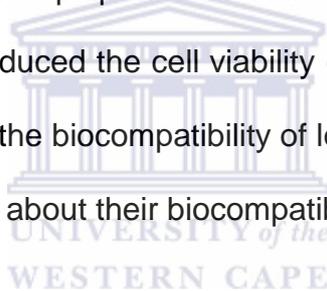
The toxic effects of monomers on isolated human gingival fibroblasts were studied. In one study, the cytotoxicity of the monomers increased as the following HEMA >TEGDMA >UDMA >Bis-GMA (Reichl et al., 2006). Another study showed similar results that the cytotoxicity of monomers released from dental composite to the human gingival fibroblasts increased as the following TEGDMA >UDMA >Bis-GMA (Moharamzadeh et al., 2007).

Wisniewska-Jarosinska et al. (2011) conducted a study to investigate the cytotoxicity and genotoxicity of UDMA as a monomer and TEGDMA as a co-monomer. Both compounds when combined resulted in decreased cell viability, damaged DNA and induced apoptosis. UDMA and TEGDMA could induce cytotoxic and genotoxic

effects individually. However, the combination of both UDMA and TEGDMA did not produce a remarkable increase in cytotoxicity and genotoxicity.

In a study aimed to compare the biocompatibility of the oxirane based dental composites to the methacrylate based dental composites, both were found to be comparable. In the same study, the mutagenic potential of silorane was investigated in different systems and found much lower than oxirane based materials (Schweickl et al., 2002).

In an in vitro study evaluating the cytotoxicity of four low shrink dental composites (Filtek Silorane, Kalore, Bisco Reflections and Kerr Premise) with new monomer technology, using bovine dental pulp-derived cells (bDPDCs) showed that these materials were not toxic but reduced the cell viability (Yalcin et al., 2014). This study is important as it shed light on the biocompatibility of low-shrink dental composites as there is insufficient information about their biocompatibility.



## 2.2.8 Water sorption and solubility

Water sorption by resin based dental composites is described as a diffusion controlled process that may cause chemical degradation of the material leading to several drawbacks, such as de-bonding of the filler polymer-matrix and release of the residual unreacted monomers, whereas water solubility of resin based dental composites is reflected by the amount of leached unreacted monomers and the loss of filler particles (Giannini et al, 2014).

Martin and Jedynakiewicz (1998) stated that after polymerisation of resin-based composite restorations, the materials become more interactive with the surrounding environment. One of the most important interactions is the interaction with water as it diffuses into the resin matrix resulting in two opposing phenomena, the composite shrinkage and swelling. According to Barden and Pearson (1981) water sorption would result in elution of unreacted monomers, which in turn will result in loss of weight and shrinkage. On the other hand, Hirasawa et al. (1983) and Fan et al. (1985) claimed that water sorption would result in swelling and weight increase of the materials as the solvent diffuses into the polymeric network and separate chains which creates swelling. However, as the polymeric network already contains porosity and free volume near crosslinks, it is possible for the water to be absorbed without causing a difference in volume. Furthermore, water sorption is accompanied with loss of unreacted components that would cause volume reduction (Hermesch et al., 2003). This change in the nature of the polymerised dental composite by water sorption will in turn result in alteration of properties such as reduced wear and abrasion resistance, discolouration and the expected clinical performance of the dental composite materials will be also negatively affected.

Water uptake and internal plasticisation of the resin matrix of dental composite will result in relaxation of viscoelastic stresses of dental composite (Lagouvardos et al., 2003), and studies showed that the hygroscopic expansion of dental composites will occur after some time and it will partially or totally compensate for the polymerisation shrinkage (Versluis et al., 2011).

The American Dental Association (ADA) specification no.27 states that “the water sorption of all materials shall be less than or equal to 40  $\mu\text{g}/\text{mm}^3$  within a seven day period of water storage” (ADA, 2003). As dental composites are identified as restorative materials, they must comply with the International Organisation of Standards (ISO) 4049 for a maximum value of 40 $\mu\text{g}/\text{mm}^3$  for water sorption within a period of seven days of water storage (ADA, 2003).

The effect of water sorption phenomenon on the behaviour of resin filled composite could be influenced by several factors including polymer matrix composition, the type, the content of the filler and the size and shape of filler particles (Soderholm et al., 1984; Sideridou et al., 2003; Berger et al., 2009). Thus, the water sorption phenomenon is a multi-factorial process and influenced by more than one factor not just by the media of immersion. Studies show that the type of monomer could influence water sorption process, as Bis-GMA based resin showed greater water sorption comparing with UDMA (Sideridou et al., 2003). On the other hand, Bis-EMA showed the lowest value because it does not contain the hydroxyl group of Bis-GMA or urethane linkage of UDMA which are hydrophilic in nature (Braden and Davy, 1986; Sideridou et al., 2003). Additionally, water sorption is greater for Bis-GMA based resins that contain high concentration of TEGDMA because of the hydrophilic ether linkage group of TEGDMA (Beatty et al., 1993).

Venz and Dickens (1991) conducted a study to investigate water sorption characteristics of dental resins and composites; the study showed difference in long term water sorption for the dental resins and composites that composed of different monomers. The sorption was reported in the following order: TEGDMA > Bis-GMA > UDMA. The difference was attributed to the presence of hydrophilic ether linkage in TEGDMA, urethane linkage in UDMA and hydroxyl group in Bis-GMA. The water enters the polymeric network through intermolecular spaces and porosity. The density of the polymer network and the potential for polar interaction and hydrogen bonding are the factors that determine the extent and rate of water uptake.

Ortengren et al. (2001) conducted a study to evaluate water sorption and solubility of different composites and cements for up to 6 months and revealed that most of the materials reached saturation within 7-60 days with only one composite that continued to uptake water throughout the experiment. The results of Ortengren et al. (2001) study matched the results of Ferracane (1997) study, and it was noteworthy that the water sorption was lower for the highly filled composite, but the rate of water uptake and time to reach saturation were being equivalent.

A study of water sorption and solubility of nanofilled composites conducted by Al-Shekhli and Hakimzadeh (2012) using seven commercial light cured composites of which three were nanofilled (Tetric Evo Ceram, Premise and Filtek Supreme XT) showed that the Premise light cure composite has the highest mean value  $26.666 \mu\text{g}/\text{mm}^3$  and the Tetric Evo Ceram light cure composite had the lowest mean value  $18.343 \mu\text{g}/\text{mm}^3$ .

The chemical composition of the resin matrix of Premise light cure composite containing ethoxylated Bis-GMA is considered a weak resin matrix to provide

adequate resistance to water sorption (Al-Shekhli and Hakimzadeh, 2012). The filler particle system could also influence the water sorption behaviour in the resin composite. Microfilled resin composite (Silux Plus) with a silica filler particle of 0.04  $\mu\text{m}$  in size showed a more dramatic reduction in the modulus of elasticity after immersion in water as a result of water accumulating at the filler-matrix interface (Kalachandra and Wilson, 1992). Samples of dry fillers identical to the fillers of the dental composite used in the experiment were weighted then immersed in distilled water, dried and weighted again. There was no change in the final weight. This result indicates that water sorption process does not take place at the filler particle level themselves. This strengthens the conclusion that the water sorption process takes place at the filler particle-matrix interface. Additionally, it was concluded that the water uptake process depends on the nature of the filler, polymerisation process and the use of coupling agent (Kalachandra and Wilson, 1992).

Janda et al. (2007) conducted a study to investigate the differences in water sorption and solubility values between different types of dental composites such as hybrid, packable, ormocer, compomer and flowable composite restorative materials. The study showed no correlation between the filler load and solubility as the packable composite showed the lowest solubility value which was close to zero. However, there was a significant correlation between water sorption and filler load. The lowest water sorption values were recorded with the composite with the highest filler load, and the highest water sorption values were recorded with the composite with the lower filler load in which compomer Dyract AP and Solitaire 2 (filler load 44-56 vol. %) showed the highest water sorption values. For Dyract AP, this was explained by the hydrophilic nature of its resin matrix (UDMA) and for Solitaire 2 the high water sorption value was attributed to two factors which are the hydrophilic resin matrix

(HPMA) and the presence of porous SiO<sub>2</sub> fillers.

The results obtained from Janda et al. (2007) study matches the results of Yap et al. (2002) study, in which it was also reported that there was a significantly lower water sorption and solubility values for the highly filled microhybrid (filler load 66 vol.%) when compared to microfilled and microhybrid restorative composites. Yap et al. (2002) attributed the lower water sorption of highly filled microhybrid to both high filler content and the resin matrix composition.

Al-Shekhli and Hakimzadeh (2012) suggested that there are two possibilities to explain the greater water sorption values that occurred in the Premise nanofilled composite. The first possibility was attributed to the larger surface area to volume of the nanofilled composite particles, which allowed more water accumulation at the filler particles-polymeric matrix interface. This matches the results of another study in which Curtis et al. (2008) also found that the water uptake in nanofilled composite is attributed to the large surface area to the volume and this influenced the mechanical properties negatively. Whereas the other possibility is that the water accumulation at the interface may have caused water diffusion through the aggregates of the fillers to the micro-voids, which may present between the aggregates as a result of lacking the 5-20 nm particles (Santos et al., 2002). Da-Silva et al. (2008) pointed out the degree of conversion may also indirectly influence the water sorption values as the nanofilled particle size may have resulted in a light scattering effect which may result in reduction in the light intensity and decrease the degree of conversion.

Dental composites showed higher water sorption in 75% ethanol/water solution than in distilled water and artificial saliva and this is because ethanol penetration into resin matrix is easier and faster than water penetration (Zhang and Xu, 2008). This

indicates that the use of different immersion media may affect the water sorption and solubility.

Palin et al. (2005) investigated the effect of water sorption and solubility for short-term (0.1, 0.5, 1, 4, 24 and 48 hrs.) and medium-term (1, 4, 12 and 26 weeks) on the mechanical properties of novel low-shrinkage dental composites with different types of monomers, two methacrylate composites (Z100 and Filtek), an experimental oxirane dental composite and silorane dental composite. The study revealed that after 0.5 hr. and subsequent short and medium-term water immersion there was a reduction in the sorption values of two methacrylate dental composites in comparison to oxirane dental composite. However, the lowest water sorption and solubility values were exhibited by silorane dental composite following short and medium water storage, and based on this study silorane showed improved behaviour regarding water sorption and solubility.

### **2.2.9. Elution of monomers**

The majority of the unreacted methacrylate groups in dental resins are not capable of being eluted into aqueous media as they are part of dimethacrylate groups that have reacted on one end, and are therefore connected to the main chain by a covalent bond. Yet, significant amount of unreacted monomers are released (Ferracane, 2006). Inoue and Hayashi (1982) have suggested that 10% of unreacted monomers are elutable in dental composite and a similar percentage of 8% of unreacted monomers are elutable was suggested by Ferracane (1994).

Tanaka et al. (1991) conducted a study that showed that Bis-GMA continued to elute in very small concentrations for more than one week. The results of Tanaka's study matched the findings of a study by Ferracane and Condon (1990) in which the rate of

leachable component elution reached 50% of the maximum in water and 75% in ethanol/water solution within the first three hours of immersion. The rapid elution was attributed to the ease of mobility of the low molecular weight substances and to the limited number of leachable molecules as a result of further curing reaction following initial light exposure. The percentage of elution was estimated to be 1.5% for dental composite in water (Ferracane and Condon, 1990), which was greater than the results obtained from other studies (Inoue and Hayashi, 1982; Fan et al., 1985; Oysaed and Ruyter, 1986). The difference in the results was attributed to placing the specimens in this study in a solvent for ten minutes before being light cured. In addition, the specimens were purposely under-cured to some degree. Munksgaard et al. (2000) conducted a study that revealed that the inadequately light cured composite showed higher monomers elution.

High performance liquid chromatography (HPLC) is used to measure the release of unreacted monomers in immersion solutions. In a study conducted by Zhang and Xu (2008), it was revealed that the highest amount of monomer elution was recorded in 75% ethanol/water solution, followed by distilled water and finally followed by artificial saliva. This study showed the amount of eluted unreacted monomer, triethylene glycol dimethacrylate (TEGDMA) in two types of dental composites in distilled water and artificial saliva was higher than the other monomer (Bis-GMA). In 75% ethanol/water solution, the elution of unreacted Bis-GMA is much higher than TEGDMA, as Bis-GMA is highly soluble in organic solvent like ethanol (Zhang and Xu, 2008). An older study conducted by Zou and Zheng (1999) on solubility showed similar results in which the highest solubility values were recorded in ethanol/water solution. It was found that the solubility values in distilled water were slightly lower than the values recorded in artificial saliva (Zou and Zheng, 1999 cited in Zhang and

Xu, 2008). Spahl et al. (1998) attributed this phenomenon to air void formation following unreacted monomer and filler elution which could result in solubility acceleration.

Örtengren et al. (2001) studied water sorption, solubility and identification of any released monomers in six different types of composite resin materials, by using high performance liquid chromatography ultra-violet analysis (HPLC-UV) to identify leaked substances in the liquids of which the materials were immersed in for specific periods of time. These authors found that the monomer TEGDMA was found as the main substance in the stored water and quantifiable quantity was registered after 4 hours of storage. These results are similar to other studies (Oysaed et al., 1988; Ruyter, 1995). The monomer elution processes from dental composites have many adverse effects regarding the clinical performance of the dental composites as restorative materials and the biocompatibility of the dental composites.

According to Ferracane (1994) the release of unbounded substance from polymerised resin composite is influenced by some factors, like monomer-polymer conversion, the composition and solubility parameters of the solvent and the chemical characteristic and the size of the leachable substance.

Göpferrich (1996) stated that the micro-structure of the bulk of composite resin is changed as a result of progressive degradation by formation of pores through which the degradation products, additives and the residual monomers can be released.

There are two mechanisms that explain the water degradation in resin-filled composite and monomers elution. According to Bastoli et al. (1990) the first mechanism is that the water absorption causes swelling and weakness of the resin matrix which in turn initiates elution of the monomers. The second mechanism was

explained by Soderholm et al. (1984) stating that the degradation of silane interface caused by water is the responsible factor for the reduction of properties of the resin based composites. It is known that the condensation reaction between the silane coupling agent and the silanol group of silica fillers surface result in formation of siloxane bridge bond and covalent bond. Water infiltration results in hydrolysis and degradation of siloxane bond, which in turn initiates filler de-bonding at the interface (Soderholm et al., 1996). The degradation of filler-matrix interface was caused by interfacial micro-cracks initiation. This finding supports the results of scanning electron microscopy (SEM) images of Curtis et al. (2008) study. The SEM images exhibited the existence of micro-cracks at the filler-resin matrix interface, which may be caused as a result of either resin matrix degradation or silane layer degradation (Calais and Soderholm, 1988).

Gajewski et al. (2012) conducted a study aimed to compare water sorption (SR), solubility (SL), degree of conversion (DC) and the mechanical properties between different monomers used in dental composites. The study showed increased water sorption with decreased degree of conversion. Bis-EMA showed the lowest water sorption due to the hydrophobic property of the molecule and the highest degree of conversion. Bis-GMA and UDMA showed similar water sorption values despite difference in degree of conversion due to their hydrophilicity property as both molecules are the most hydrophilic molecules (Gajewski et al., 2012). Water solubility of Bis-GMA was not the highest among the other monomers despite its significantly high water sorption. On the other hand TEGDMA showed higher solubility despite its greater degree of conversion and lower water sorption possibly because of the presence of low molecular weight oligomers that was able to leach. The lowest water solubility (SL) and sorption (SR) was reported with Bis-EMA

because of its higher degree of conversion (DC) and hydrophobic property of the monomer (table 3).

Monomer	DC after 10 min (%)	DC after 24 h (%)	SR ( $\mu\text{g}/\text{mm}^3$ )	SL ( $\mu\text{g}/\text{mm}^3$ )
Bis-GMA	21.7	34.5	51.2	9.5
TEGDMA	74	82.5	28.8	27.5
UDMA	59.6	72.4	42.3	20.4
Bis-EMA	65.5	75.5	21.3	2.1

**Table 3: Relation between solubility (SL), sorption (SR) and degree of conversion (DC) for Bis-EMA (Gajewski et al., 2012).**

Mustaza et al. (2014) conducted a study to compare different properties of silorane based composite (Filtek Silorane) with two methacrylate based dental composites (Filtek Supreme XT and Esthet X HD) in terms of water sorption, solubility and other properties by using different immersion media (distilled water, artificial saliva, 25% ethanol, Coke and coconut oil). The study revealed that the Filtek Silorane absorbed water linearly and very slowly in the different immersion media throughout the entire length of the experiment (until there was no further water uptake was recorded by the different samples). Filtek Supreme XT and Esthet X HD showed similar water absorption profile in the different immersion media. Filtek Supreme XT in distilled water and Esthet X HD in soft drinks like Coke start to lose weight indicating leaching of constituents, whereas in coconut oil no weight change (water uptake) was recorded in all types of dental composites. In Mustaza's study, there was little difference in weight change of Filtek Silorane when compared to Esthet X HD and Filtek Supreme XT. Additionally, there was no significant difference in solubility of these dental composites. Whereas Palin et al. (2005) found that silorane based

dental composite exhibited significantly lower water sorption and solubility than the methacrylate based dental composites. It is crucial to report that in Palin's study, the samples were disc shaped of 15 mm x 2 mm dimensions, whereas in Mustaza's study the samples were smaller dimensions of 6 mm x 2 mm discs.

Dental composites are widely used aesthetic restorative dental materials. However, water sorption and solubility are considered one of the main setbacks of dental composites as water sorption and solubility could cause changes in the composition of dental composites. This in turn results in dramatic alteration of the expected clinical performance, mechanical properties and even the biocompatibility of dental composites by biodegradation and release of monomers.

Since the newer bulk-fill composites have altered filler content and resin matrix to enable depth of cure at larger increments, the water sorption and solubility may possibly be affected. Therefore, the aim of this research was to determine whether this altered filler and monomer composition has an effect on water sorption and solubility of these newer bulk-fill dental composites which were recently introduced into the market.

## Chapter 3

### Aim and Objectives

#### 3.1. Aim

The aim of this research was to study the water sorption and solubility of four bulk-fill dental resin filled composite materials namely, two conventional viscosity bulk-fill and two low viscosity bulk-fill flowable dental composite materials.

#### 3.2. Objectives

1. To measure the water sorption of four bulk-fill dental resin filled composite materials when stored in distilled water for 24 hours, 7 days and 14 days.
2. To measure the water solubility of four bulk-fill dental resin filled composite materials when stored in distilled water for 24 hours, 7 days and 14 days.
3. To compare the water sorption and solubility of the four types of bulk-fill dental resin filled composites.
4. To compare the water sorption and solubility of the low viscosity bulk-fill flowable with that of the conventional viscosity bulk-fill composite.
5. To identify the release of monomers as a result of water solubility within the aqueous environment through high performance liquid chromatography analysis (HPLC).

#### 3.3. Hypothesis

There is no difference in the water sorption and solubility of the four different types of resin filled composite materials tested.

## Chapter 4

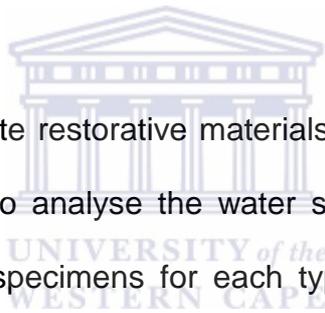
### Materials and Methods

#### 4.1. Study design

A quantitative research approach was used to do a comparative study of the water sorption and solubility of two types of bulk-fill dental composite materials namely, conventional viscosity bulk-fill and low viscosity bulk-fill flowable resin filled composites.

#### 4.2. Sample size

Four types of bulk-fill composite restorative materials (2 bulk-fill conventional and 2 bulk-fill flowable) were used to analyse the water sorption and solubility for each resin composite type. Thirty specimens for each type of material were prepared, giving the total number of specimens to be 120 (n=120).



### 4.3. Resin filled dental composite materials

The four dental composites used in this study as given by the manufacturers are shown in table 4.

Material	Classification	Monomers	Fillers	Filler %	Manufacture
Surefil bulk fill composite	Bulk-fill conventional viscosity	UDMA, Bis-GMA	Silicon dioxide, Ba-B-F silicate	77% (wt), 58% (vol)	DENTSPLY (USA)
Tetric N Ceram Bulk Fill	Bulk-fill conventional viscosity	Bis-GMA, UDMA, Bis-EMA	Barium aluminium silicate glass, Ytterbium fluoride, spherical mixed oxides	61% (vol),	Ivoclar Vivadent (Germany)
Filtek Bulk Fill flowable restorative	Bulk-fill low viscosity flowable	Bis-GMA, Bis-EMA, UDMA	Zirconia/silica, Ytterbium trifluoride	64.5% (wt), 42.5% (vol).	3M-ESPE (Germany)
Surefil SDR Flow	Bulk-fill low viscosity flowable	UDMA, DMA	Barium and strontium alimino-flouro-silicate glasses	68% (wt.), 45% (vol).	DENTSPLY (USA)

**Table 4: composition of composites with filler percentage.**

#### 4.3.1. Surefil High Density Posterior Restorative (Dentsply, USA)

Surefil is a bulk-fill composite (figure 11) and marketed as a packable composite.

The composition of the material according to the manufacturers is as follows:

-Resin matrix: urethane modified bis-GMA dimethacrylate and polymerisable dimethacrylate resin.

-Inorganic fillers: barium boron fluoro alumino silicate glass.

-Fillers: 77% by weight and 58% by volume.



Figure 11: Surefil High density Posterior Restorative (Dentsply, USA).

#### 4.3.2. Tetric N-Ceram Bulk-fill (Ivoclar Vivadent, Germany)

Tetric N-Ceram Bulk Fill is a bulk-fill composite of conventional viscosity (figure 12).

The composition of the material according to the manufacturers is as follows:

-Resin matrix: Dimethacrylate (19-20% by weight)

-Inorganic fillers (53-55% by volume or 75-77% by weight): barium glass, prepolymer, ytterbium trifluoride and mixed oxides. The particle size of the inorganic fillers is between 0.04 and 3  $\mu\text{m}$  and the mean particle size is 0.6  $\mu\text{m}$

-Additives.

-Catalysts.

-Stabilisers.

-Pigments.



Figure 12: Tetric N-Ceram Bulk Fill (Ivoclar Vivadent, Germany).

**Figure 12: Tetric N-Ceram Bulk Fill (Ivoclar Vivadent, Germany).**

#### **4.3.3. Filtek™ Bulk-Fill Flowable Restorative (3M ESPE, Germany)**

Filtek Bulk-fill Flowable Restorative is classified as a bulk-fill low viscosity flowable composite (figure 13). The composition of the material according to the manufacturers is as follows:

-Resin matrix: Bis-GMA, UDMA, Bis-EMA(6) and procrylate resins.

-Inorganic fillers (42.5% by volume and 64.5% by weight): yttrium trifluoride with a range of particle size from 0.1 to 0.5  $\mu\text{m}$  and zirconia/silica with particle size 0.01 to 3.5  $\mu\text{m}$ .



**Figure 13: Filtek Bulk Fill Flowable Restorative (3M ESPE, Germany).**

#### 4.3.4. Surefil SDR Flow by Dentsply (USA)

Surefil SDR Flow is a bulk-fill flowable composite (figure 14). The composition of the material according to the manufacturers was as follows:

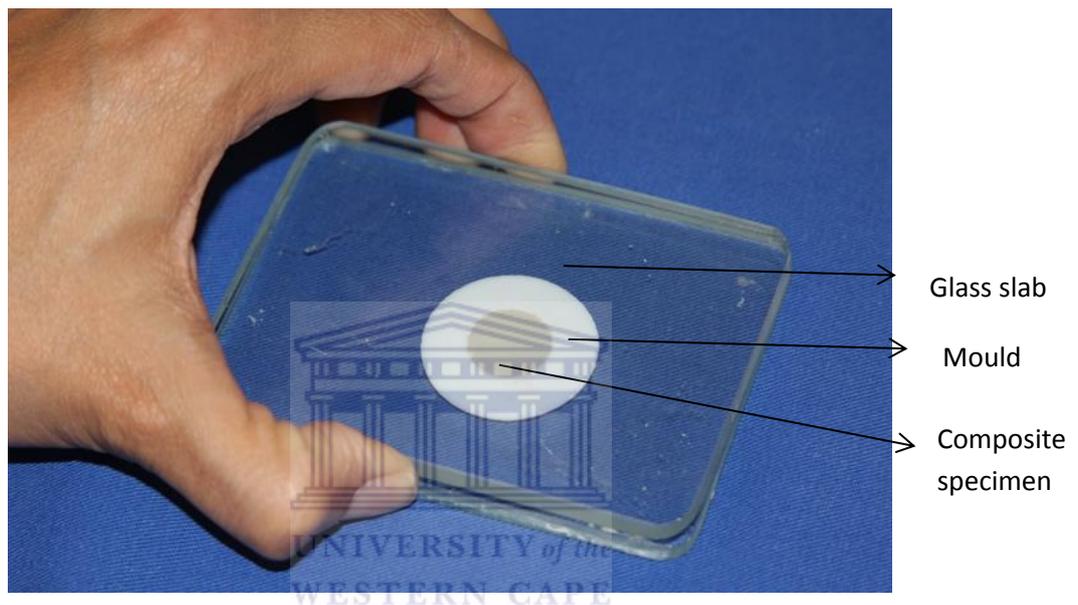
- Resin matrix: SDR patented urethane dimethacrylate resin, dimethacrylate resin and di-functional diluent resin.
- Inorganic fillers (68% by weight and 45% by volume): barium and strontium alumino-fluoro-silicate glasses.
- Photoinitiating system.
- Colourant.



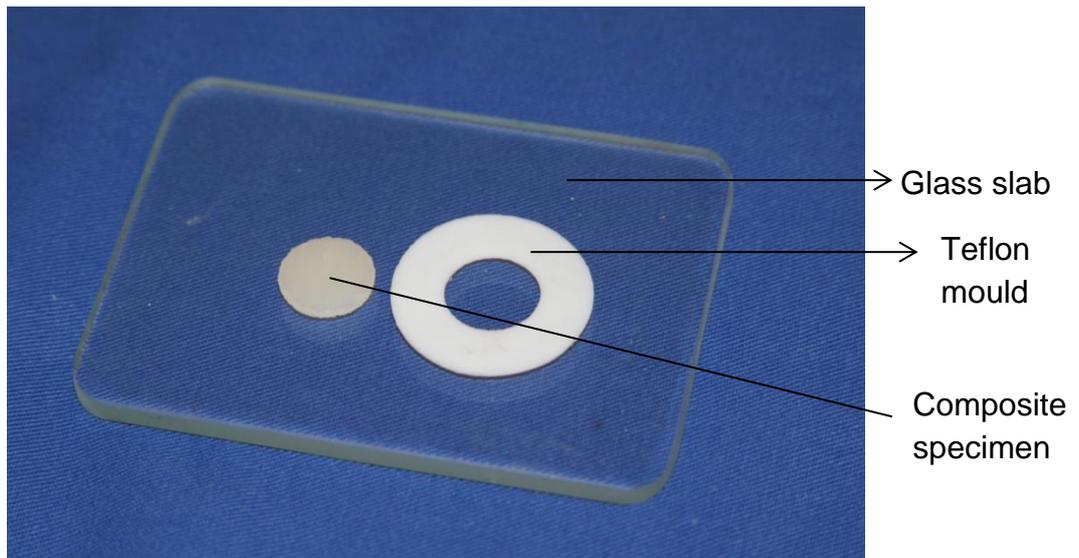
Figure 14: Surefil SDR Flow (Dentsply, USA).

#### 4.4. Specimen preparation

To standardize this study Vita shade A2 was used for all the material types. All specimens were prepared in a Teflon mould as shown in figure 15 and 16 with internal diameter of  $15\pm 1\text{mm}$  and thickness of  $1\pm 0.1\text{mm}$  in accordance with ISO 4049 for water solubility and water sorption studies.

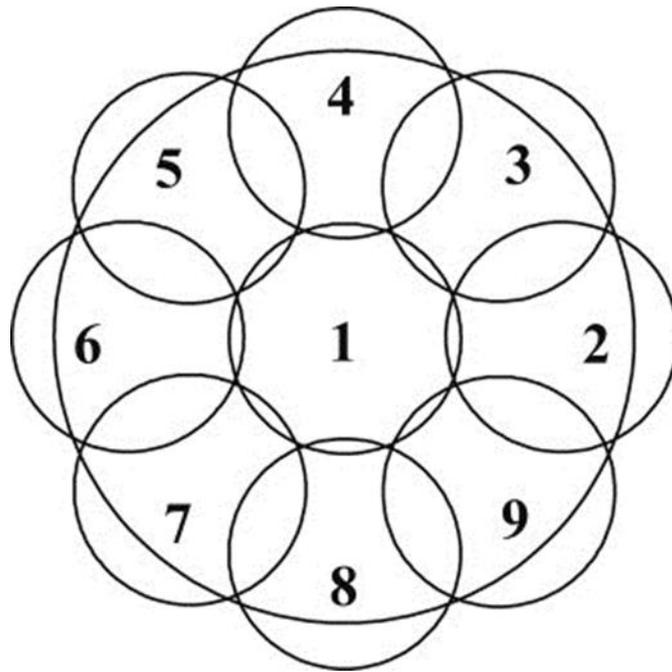


**Figure 15: Specimen preparation**



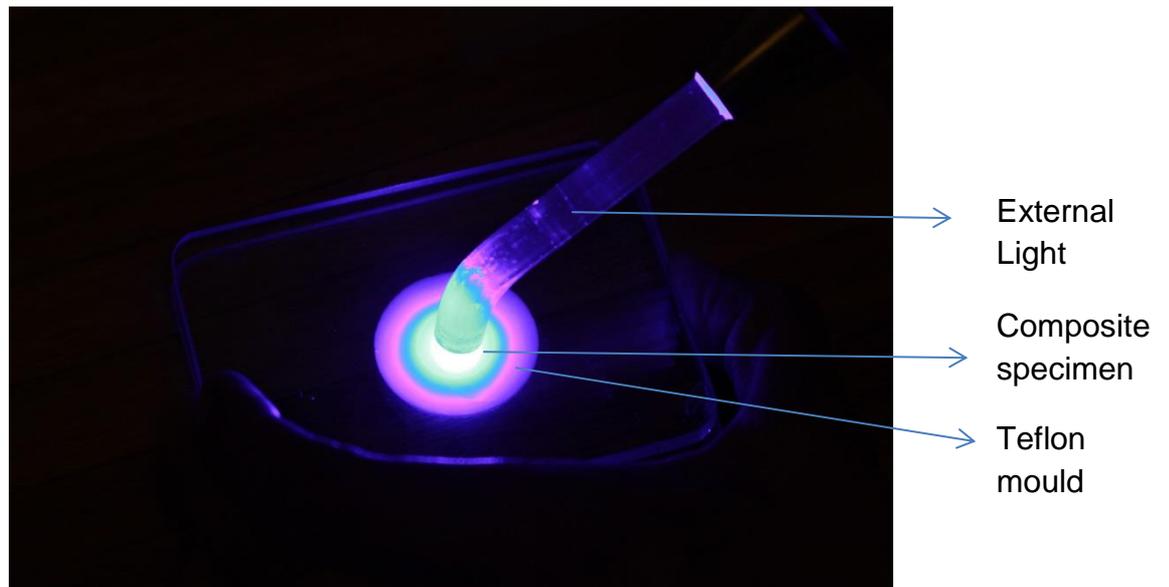
**Figure 16: The Teflon mould and the composite specimen**

The mould was filled with the test material and a sheet of polyester film and two glass plates were positioned on the top and bottom of the material to standardize the thickness of the specimens. The glass plate was removed and the specimens were light cured following the light curing pattern as suggested by ISO 4049 guideline (figure 17), and by placing the external light source directly on the specimens (figures 18 and 19).

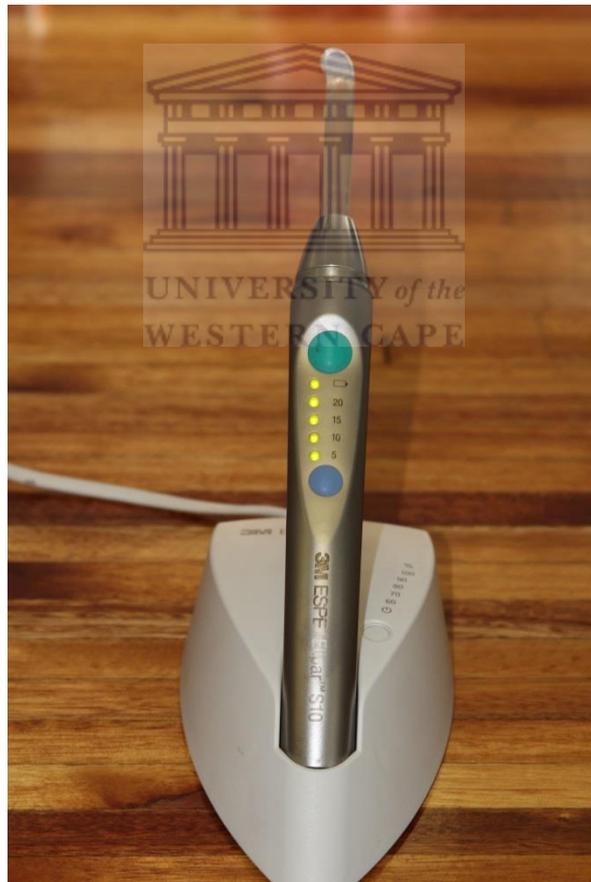


**Figure 17: light curing pattern of the specimen (Janda et al., 2007).**





**Figure 18: Specimen preparation.**



**Figure 19: Elipar™ S10 LED light curing unit (3M ESPE, Germany).**

The light curing unit used for all specimens was Elipar™ S10, (3M ESPE, Germany) at an output of  $1200 \text{ mW/cm}^2$  and used according to the manufacturer's instructions.

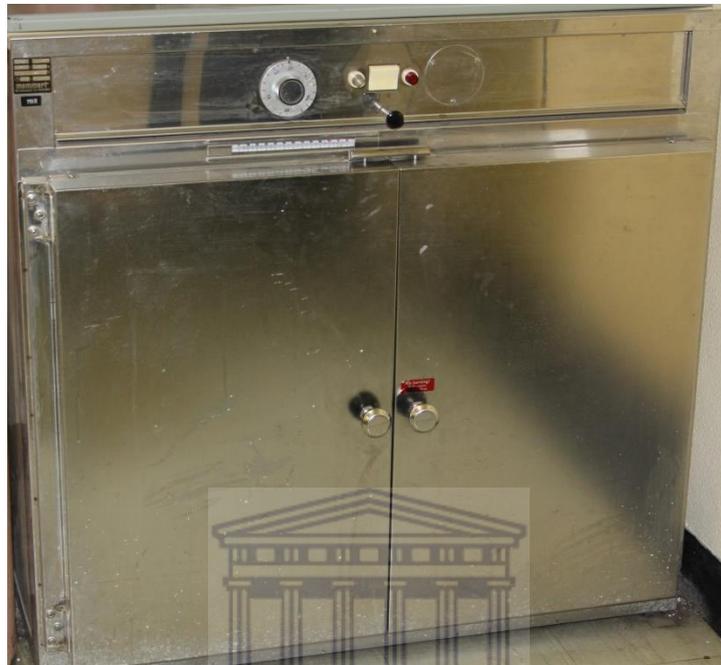
Prior to curing the intensity of the light was checked using Cure Rite visible curing light meter (Caulk, USA) to ensure light output consistency between specimens and was found to be 1000 mWatt/cm<sup>2</sup> and rechecked after every 10 specimens.

#### **4.5. Water sorption and solubility in dental composites**

For the water sorption and solubility, 30 specimens were prepared from each of the four types of dental composites namely, bulk-fill conventional composites (Surefil bulk-fill composite, Tetric N Ceram), bulk-fill flowable composites (Filtek Bulk-fill flowable restorative, SDR Bulkfill Flowable).

The water sorption and solubility tests were performed according to ISO 4049 (2009). All the specimens were first removed from the Teflon mould as prepared and described previously and transferred to an incubator (figure 20) at 37 °C until their weights were constant and these weights were recorded as  $m_1$  by using an analytic balance and weighted again to ensure the weight was constant (OHAUS, TS400D, USA) (figure 21). Minor differences in the weight may be attributed to mould size variations of  $\pm 1$  mm in the diameter measurements. Ten specimens of each type of resin filled composite were then immersed individually in ten glass containers filled with 10 ml distilled water (figure 22) and placed in oven at  $37 \pm 1$  °C for 24 hours. This was repeated for an additional 10 specimens to be left for 7 days and an additional 10 specimens were placed in 10 glass containers to be left for a period of 14 days. Samples were transferred into separate glass vials and stored in a lightproof desiccator with anhydrous self-indicating silica gel at 37° C. After 22 h, the samples were moved into another desiccator maintained at room temperature (23° C) for 2 h and then weighed to an accuracy of 0.01 mg using a calibrated electronic analytical balance (Ohaus Analytical Plus, Ohaus Corporation, USA). This cycle was repeated

until the mass loss of each specimen was not more than 0.1 mg in any 24 h period to ensure the completion of post-irradiation polymerisation and dehydration. This constant mass  $m_1$  was the initial mass of the specimen.



**Figure 20: Incubator in which specimens were placed until their weights were constant**

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**Figure 21: Analytic balance (OHAUS, TS400D, USA).**

The containers were clearly labelled with the name of the material and the duration time of water immersion i.e. for 24 hours, 7 days or 14 days (figure 22). The specimens were placed in containers in a vertical position with each containing 10 ml of distilled water. After the specified time period of 24 hours, 7 days and 14 days, the specimens were removed; surface water was blotted with tissue paper until free from visible moisture and weighed using the analytic balance (OHAUS, TS400D, USA). The resultant weights were recorded as  $m_2$ . The specimens were then placed in a desiccator containing silica gel (Associated Chemical Enterprises, ZA) (figure 23) and freshly dried for two hours and placed in an oven at 58 °C and then weighted to obtain  $m_3$ .



**Figure 22: Water sorption test.**



**Figure 23: Specimens in a desiccator containing silica gel.**

According to Oysaed and Ruyter formulation (Oysaed and Ruyter, 1986), the water sorption and solubility are calculated using the following equation:

1. Water sorption (SP) =  $m_2 - m_3 / v$ .

2. Water solubility (SI) =  $m_1 - m_3 / v$ .

Where,

- $m_1$  = the mass of the specimen in  $\mu\text{g}$  before immersion in distilled water.
- $m_2$  = the mass of the specimen in  $\mu\text{g}$  after immersion in distilled water.
- $m_3$  = the reconditioned mass of the specimen in  $\mu\text{g}$  after being introduced into the silica gel desiccator.
- $v$  = the specimen volume in  $\text{mm}^3$  and was measured using an electronic calliper (Vernier, Grip) to measure the diameter and thickness of specimens at the centre and 4 equally spaced points on the circumferences and the volume calculated using the equation  $v = \pi r^2 h$  ( $\pi = 3.14$ ) and  $r$  was half the diameter of the specimen and  $h$  was the mean thickness of the specimen.

## 4.6 Monomer elution

The high performance liquid chromatography (HPLC) was used to identify unreacted monomers that may leach into the water from the four types of dental composites by analysing the water in which the specimens were immersed.

HPLC was chosen for this part of the study as it is considered a powerful and commonly used method for the analysis of resin monomers. Additionally, it is preferred to the other methods because it gives a greater level of control over the separation process when compared to other methods such as gas chromatography (GC).

### 4.6.1. Monomer leakage and high performance liquid chromatography (HPLC)

The water contained in the stored specimens was transferred to a refrigerator immediately at temperature  $1.6\text{ C}^\circ$  after the specimens were removed until analysis was carried out.

The analysis of the organic substance released from the test samples, as well as the reference substances Bis-GMA, TEGDMA, UDMA and Bis-EMA (SIGMA ALDRICH) (figure 24) of the known compounds in the matrix were carried out by Agilent 1200 Series HPLC system (Agilent Technologies, USA) as illustrated in figure 25.



**Figure 24: Monomers (Bis-GMA, UDMA, TEGDMA and Bis-EMA) (SIGMA ALDRICH).**



**Figure 25: Agilent 1200 Series HPLC system (Agilent Technologies, USA).**

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#### **4.6.2. HPLC method development for TEGDMA, Bis-GMA and UDMA**

##### **Reference for materials used**

- TEGDMA.
- Bis-GMA.
- UDMA.

##### **HPLC apparatus**

Agilent 1200 Series HPLC system equipped with a quaternary pump, photodiode array detector (PDA), in-line degasser, column oven and PC with Chemstation software (Agilent OpenLab CDS Chemostation Edition LC and CE version A.01.04(033)).

## Reagents

- Acetonitrile HPLC grade.
- Formic acid, HPLC grade.
- Water, in-house deionised water.
- Reference compounds (TEGDMA, Bis-GMA, UDMA).

## Mobile phase

Mobile phase A: H<sub>2</sub>O (0.1% Formic acid).

Mobile phase B: Acetonitrile (0.1% Formic acid).

Solvents filtered and degassed by membrane filtration prior to use.

## Mobile phase preparation

1L of a 0.1% Formic acid aqueous solution was prepared and the solvent degassed using vacuum filtration through a 0.45 µm HVLP Millipore (Bedford, MA, USA). The acetonitrile eluent also containing 0.1% formic acid was prepared in a similar manner.

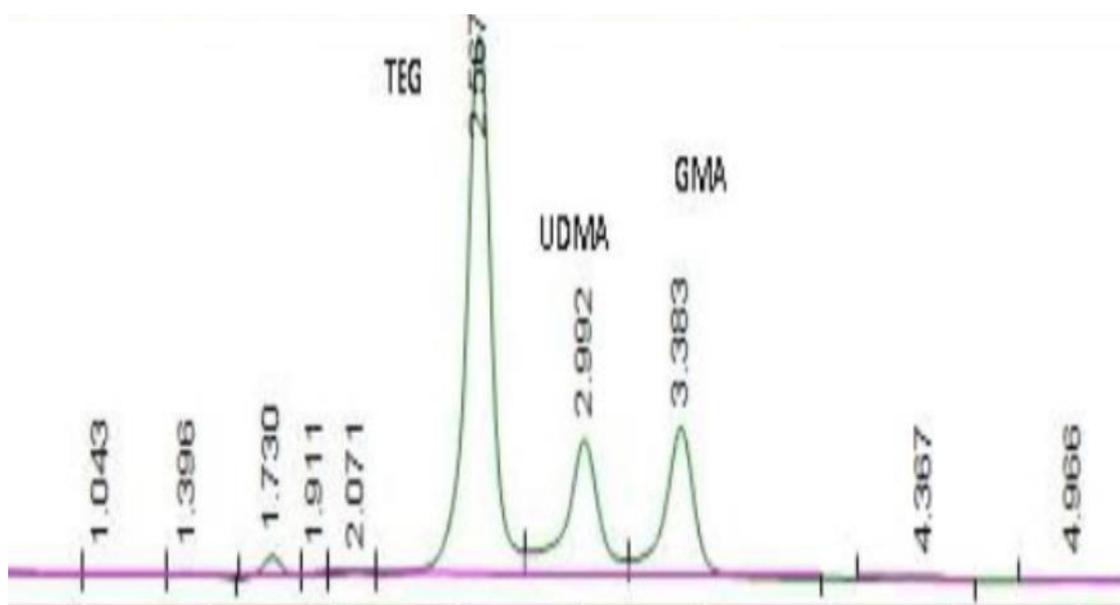
## Final chromatographic parameters

The mobile phase for this study was carried out as follows:

Chromatographic conditions:

- Column: Discovery Supelco, 5 µm, 4.6×150 mm.
- Temperature: 45 °C.
- Mobile phase A: H<sub>2</sub>O (0.1% Formic acid).
- Mobile phase B: Acetonitrile (0.1% Formic acid).
- Flow rate: 1.0 mL/min.
- Detector: PDA at 210 nm.
- Injection volume: 10 µL.
- Run time: 7 min.

The typical chromatogram for TEGDMA, UDMA and Bis-GMA is shown in figure 26.



**Figure 26: Typical HPLC chromatogram for TEGDMA, UDMA and Bis-GMA reference standards at 210 nm.**

Retention times of the reference compounds (TEGDMA, UDMA, Bis-GMA) at the final chromatographic conditions (shown in table 5)

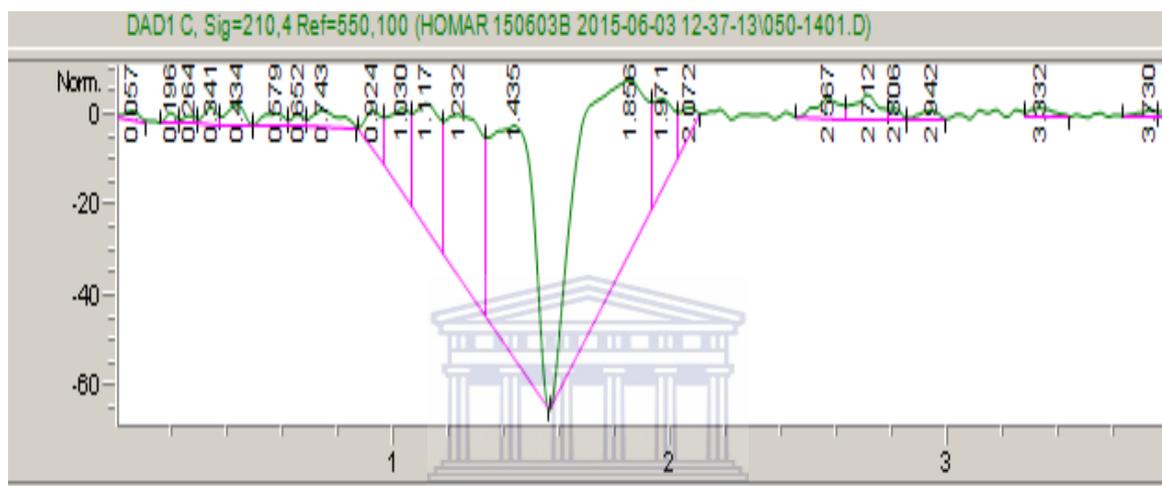
Compound/reference	Retention time (RT)
TEGDMA	2.567 min.
UDMA	2.992 min.
Bis-GMA	3.383 min.

**Table 5: The retention time of reference compounds at the final chromatographic conditions.**

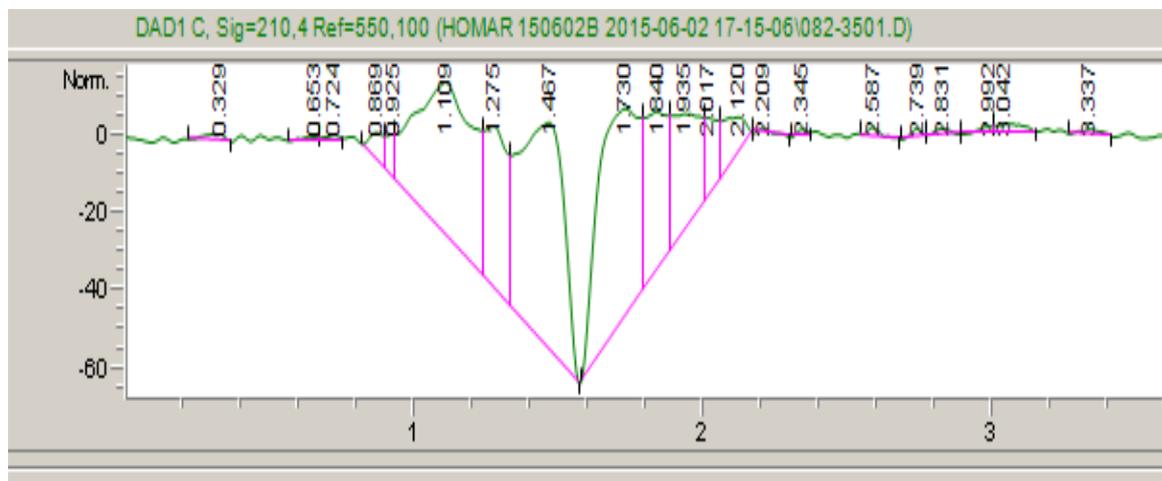
#### Preparation of calibration standards

Stock solutions for the calibration curves were prepared by accurately weighing out a certain amount of the reference compounds and dissolving in a mixture of acetonitrile and water to achieve concentrations of between 46.7-140 µg/ml for

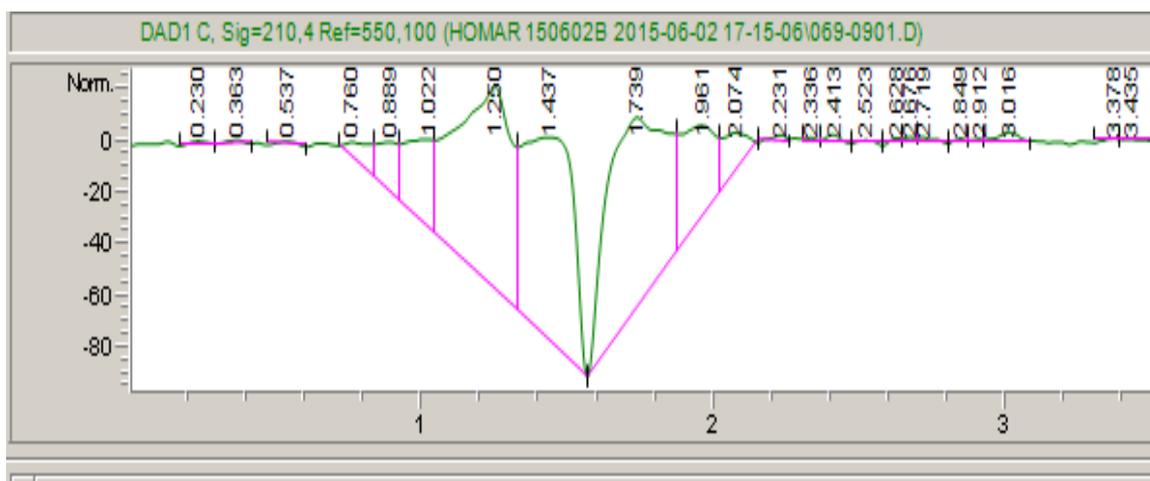
TEGDMA, 33.3-100 µg/ml for UDMA and 23.3-70 µg/ml for Bis GMA. The calibration standards were assayed in triplicate and calibration lines were constructed by linear regression plots of peak area and peak height against concentration were illustrated in figures 1, 2, 3, 4, 5 and 6 in the appendix. Figures 27, 28, 29 and 30 show the references chromatograms of all 3 monomers i.e. TEGDMA, UDMA and Bis-GMA in the test materials



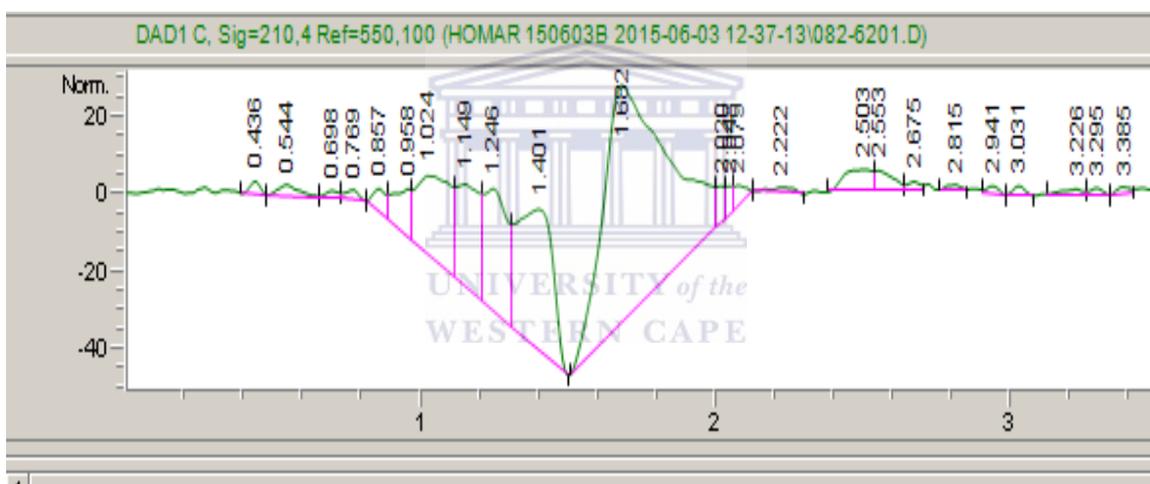
**Figure 27: Reference chromatogram of TEGDMA (2.567), UDMA (2.942) and Bis-GMA (3.332) in SDR water sample.**



**Figure 28: Reference chromatogram of TEGDMA (2.587), UDMA (2.992) and Bis-GMA (3.337) in Tetric N-Ceram water sample.**



**Figure 29: Reference chromatogram of TEGDMA (2.5230, UDMA (2.912) and Bis-GMA (3.378) in Filtek water sample.**



**Figure 30: Reference chromatogram of TEGDMA (2.553), UDMA (2.941) and Bis-GMA (3.385) in Surefil water sample.**

#### 4.6.3. HPLC method development for Bis-EMA

A different HPLC method was needed for Bis-EMA as the peaks of Bis-EMA and UDMA were coinciding in the first method which make distinguishing between them impossible. For this reason an alternative method was developed for Bis-EMA monomer where Bis-EMA can be visualized alone.

### **Reference for material used:**

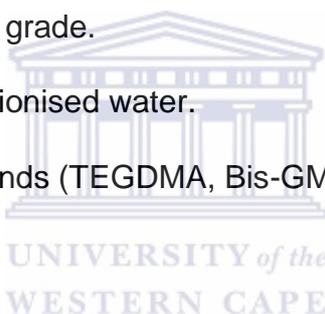
- Bis-EMA.

### **HPLC apparatus**

Agilent 1200 Series HPLC system equipped with a quaternary pump, photodiode array detector (PDA), in-line degasser, column oven and PC with Chemstation software (Agilent OpenLab CDS Chemstation Edition LC and CE version A.01.04(033)).

### **Reagents**

- Acetonitrile HPLC grade.
- Formic acid, HPLC grade.
- Water, in-house deionised water.
- Reference compounds (TEGDMA, Bis-GMA, UDMA, Bis-EMA).



### **Mobile phase**

Mobile phase A: H<sub>2</sub>O (0.1% Formic acid).

Mobile phase B: Acetonitrile (0.1% Formic acid).

Solvents filtered and degassed by membrane filtration prior use.

### **Mobile phase preparation**

1L of a 0.1% Formic acid aqueous solution was prepared and the solvent degassed using vacuum filtration through a 0.45 um HVLP Millipore (Bedford, MA, USA). The acetonitrile eluent also containing 0.1% Formic acid was prepared in a similar manner.

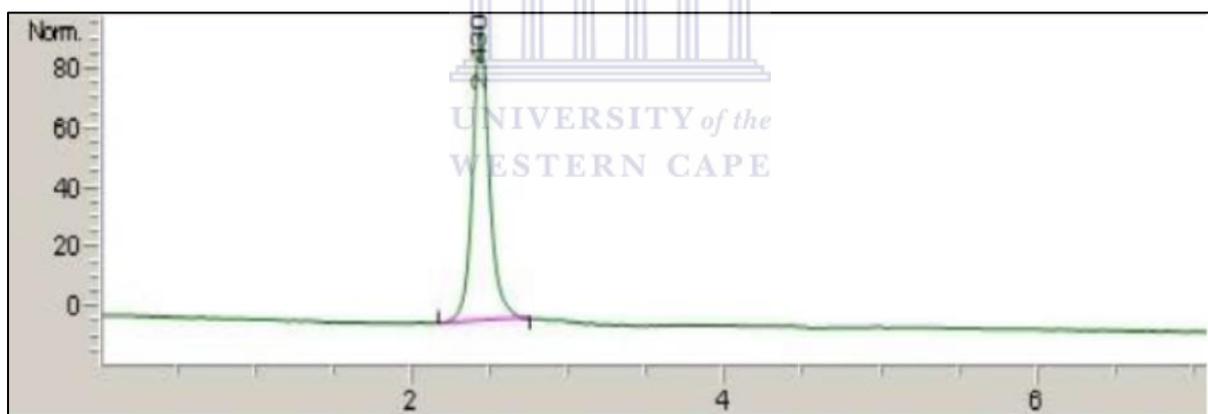
## Final chromatographic parameters

The mobile phase for this study was carried out as follows:

Chromatographic conditions:

- Column: Luna column, 5  $\mu\text{m}$ , 4.6 $\times$ 250 mm.
- Temperature: 45  $^{\circ}\text{C}$ .
- Mobile phase A: H<sub>2</sub>O (0.1% Formic acid).
- Mobile phase B: Acetonitrile (0.1% Formic acid).
- Flow rate: 0.8 mL/min.
- Detector: PDA at 210 nm.
- Injection volume: 20  $\mu\text{L}$ .
- Run time: 7 min.

The typical HPLC chromatogram for the Bis-EMA reference standard at 210 nm is shown in figure 31.



**Figure 31: Reference chromatogram for the Bis-EMA reference standard at 210 nm.**

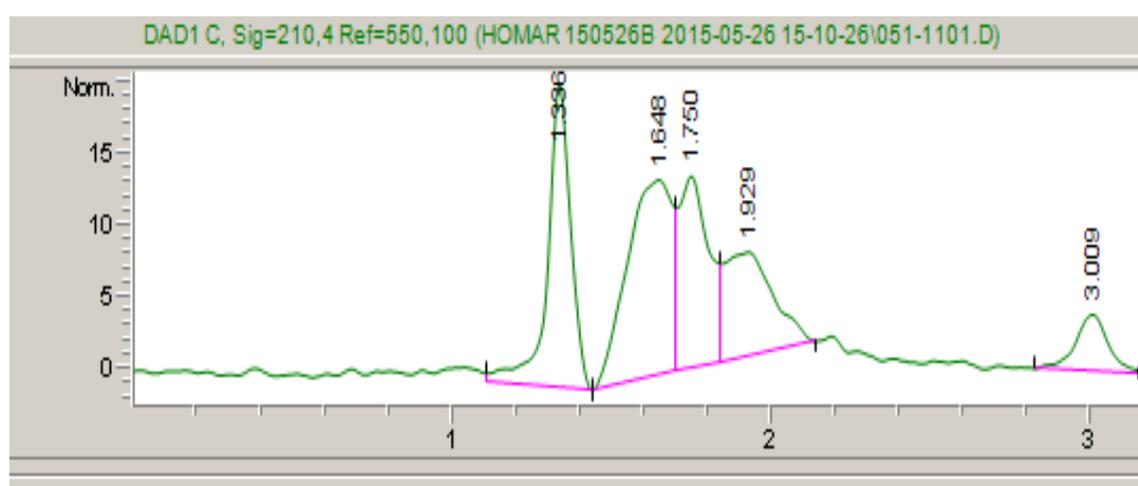
Retention time of the reference compound (Bis-EMA) at the final chromatographic conditions (shown in table 6):

Compound/reference	Retention time (RT)
Bis-EMA	2.430 min.

**Table 6: The retention time for the reference compound at the final chromatographic conditions.**

### Preparation of calibration standards

Stock solutions for the calibration curves were prepared by accurately weighing out a certain amount of the reference compound (Bis-EMA) and dissolving in water to achieve concentrations of between 60µg/ml and 180µg/ml for Bis-EMA. The calibration standards are assayed in triplicate and calibration lines were constructed by linear regression of plots of peak area and peak height against concentration as shown in figures 7 And 8 respectively in the appendix. Figure 32 illustrated the chromatogram of a Filtek sample after 7 days that showed no trace of Bis-EMA.



**Figure 32: Filtek water sample showed no trace of Bis-EMA.**

## Chapter 5

### Results

#### 5.1. Data analysis

The results were transferred to Microsoft Excel 2010 spreadsheet (Microsoft Corporation, USA) and the data was analysed using SPSS Statistical Software Ver21 (IBM, USA). A non-parametric analysis was performed at significance level of  $p < 0.05$  to compare the water sorption and solubility of the various materials.

The results have been obtained in a typical 4x3 factorial experiment, where factor Material has four levels (Filtek Bulk Fill flowable restorative, SDR Flow, Surefil bulk fill composite, Tetric-N Ceram Bulk Fill) and factor Time has 3 levels (24h, 7days, 14days). A two way analysis of variance was used to analyse the results via linear models to determine statistically significant, if any, between immersion of the four materials in distilled water and water sorption over time, between immersion of the four materials in distilled water and water solubility over time, and between the two bulk-fill flowable materials and the two bulk-fill conventional viscosity composite materials in terms of water sorption and solubility. These variables are summarised in table 7. Only p values  $< 0.05$  were regarded as statistically significant differences.

Water sorption of the 4 materials.	vs	Time.
Water solubility of the 4 materials.	vs	Time.
Water sorption of the 2 bulk-fill flowable materials.	vs	Water sorption of the 2 bulk-fill conventional composite materials.
Water solubility of the 2 bulk-fill flowable materials.	vs	Water solubility of the 2 bulk-fill conventional composite materials.

**Table 7: Summary of variables being compared in the study.**

## **5.2. Water sorption**

The results for the water sorption part of the study are presented in tables 8, 9 and illustrated in figures 33, 34 and 35 where there was a significant difference between the materials ( $p < 0.05$ , ANOVA Analysis of Variance). SDR flowable bulk-fill composite showed the lowest overall mean water sorption values (10.191) over the three time intervals (24 hrs, 7 days and 14 days) which was significantly smaller than the other means, followed by Filtek bulk-fill composite (11.135) and Tetric N Ceram bulk-fill composite (16.419). The highest mean value was recorded for Surefil (21.515) . The interaction over time indicates that there were differences between the water sorption of the different materials as shown in figures 33 and 34. The overall water sorption mean values increased from 24 h to 7 days to 14 days.

Material	(24 hrs)		(7 days)		(14 days)	
	Mean value	Standard deviation	Mean value	Standard deviation	Mean value	Standard deviation
Filtek	11.135	5.06	17.740	3.23	19.250	5.47
SDR	10.191	1.82	11.512	3.49	11.701	1.19
Surefil	15.853	5.20	21.515	6.42	21.515	3.58
Tetric	16.419	4.17	21.326	2.18	16.513	3.67

**Table 8: The mean values and the standard deviation values of the water sorption of the four test materials over time.**

Factor	DF	Sum Sq	Mean Sq	F value	Pr (>F)
Material	4	1229.51	409.84	24.59	<0.001
Days	3	490.28	245.14	14.71	<0.001
Interaction	6	266.99	44.5	2.67	0.019

**Table 9: The results of a two way ANOVA of water sorption.**

Water sorption mean values increased from 24 h to 7days to 14 days in Filtek and SDR. Tetric N-Ceram water sorption increased from 24 h to 7 days and then showed a decrease at 14 days while Surefil increased from 24 h to 7 days and then remained the same from 7 days to 14 days (figures 33 and 34). The ANOVA analysis showed a significant material effect, a significant time effect and a significant interaction ( $p < 0.05$ , two way ANOVA test).

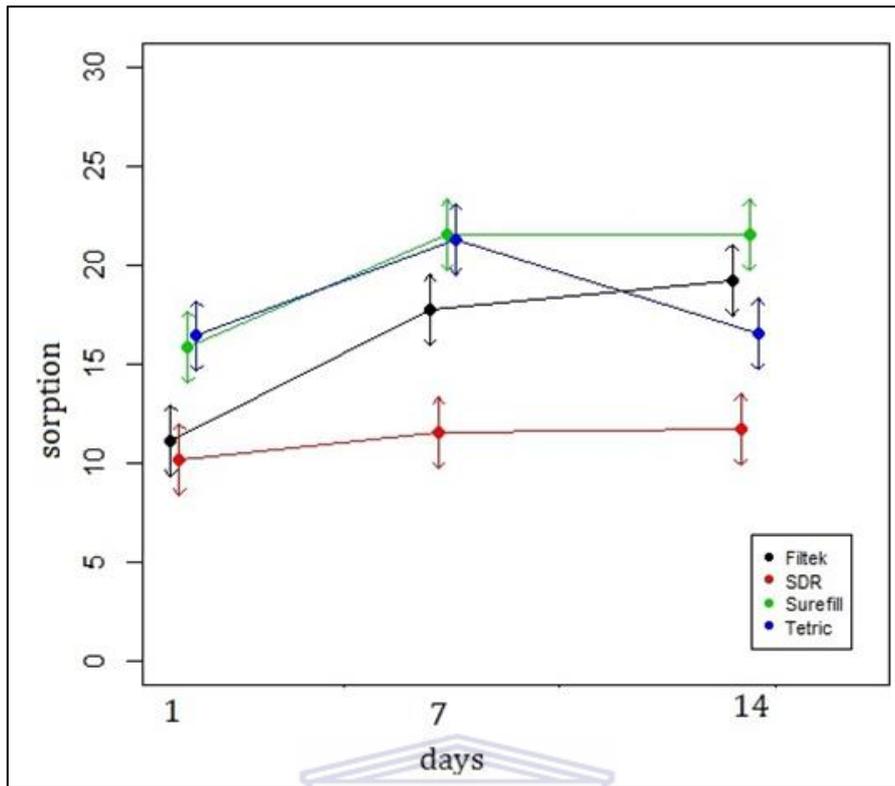


Figure 33: Mean values of water sorption for the four test materials over time.

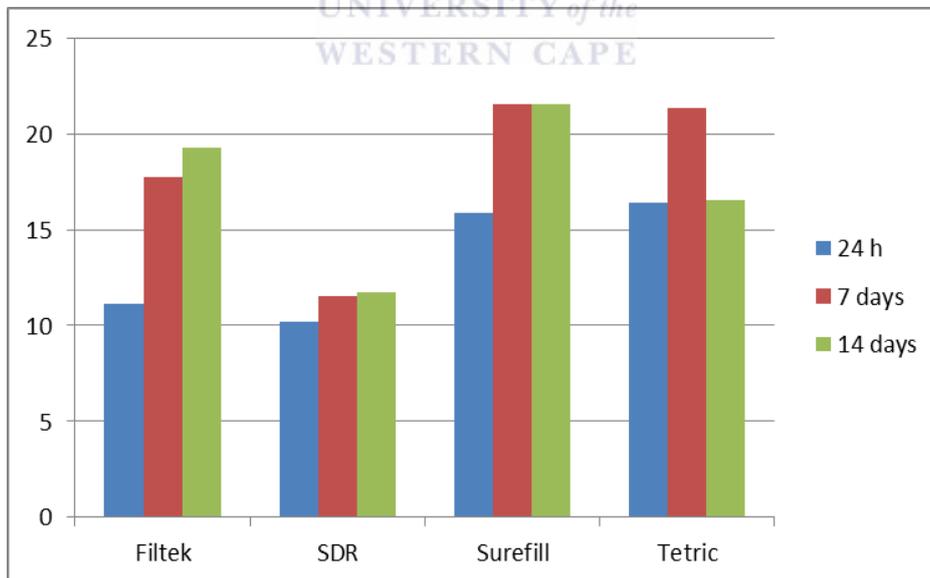
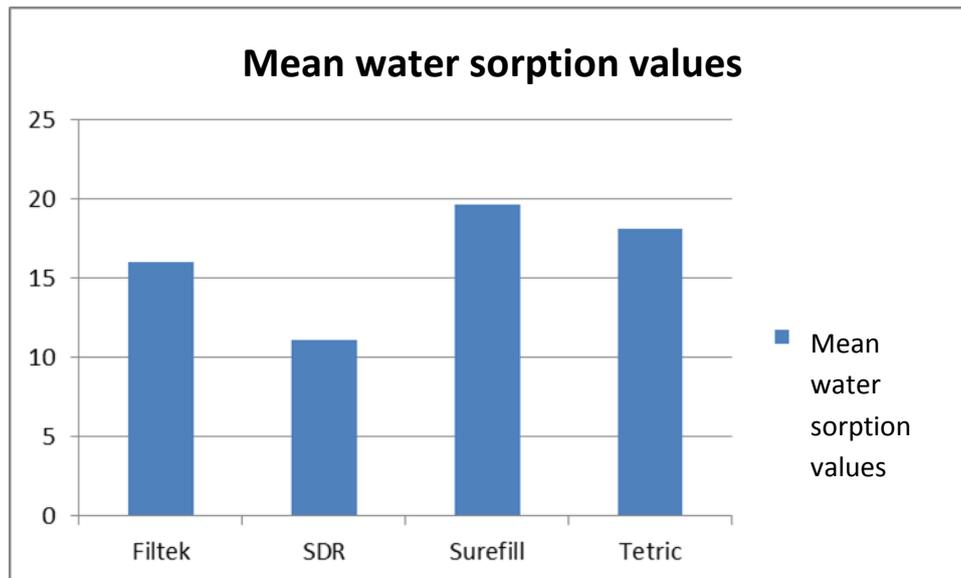


Figure 34: Mean values of water sorption for the four test materials over time.



**Figure 35: the overall mean water sorption values for the four test materials.**

Figure 35 shows the overall mean water sorption values of the four test materials, as Surefill showed the highest value followed by Tetric and Filtek while SDR had the lowest mean value.

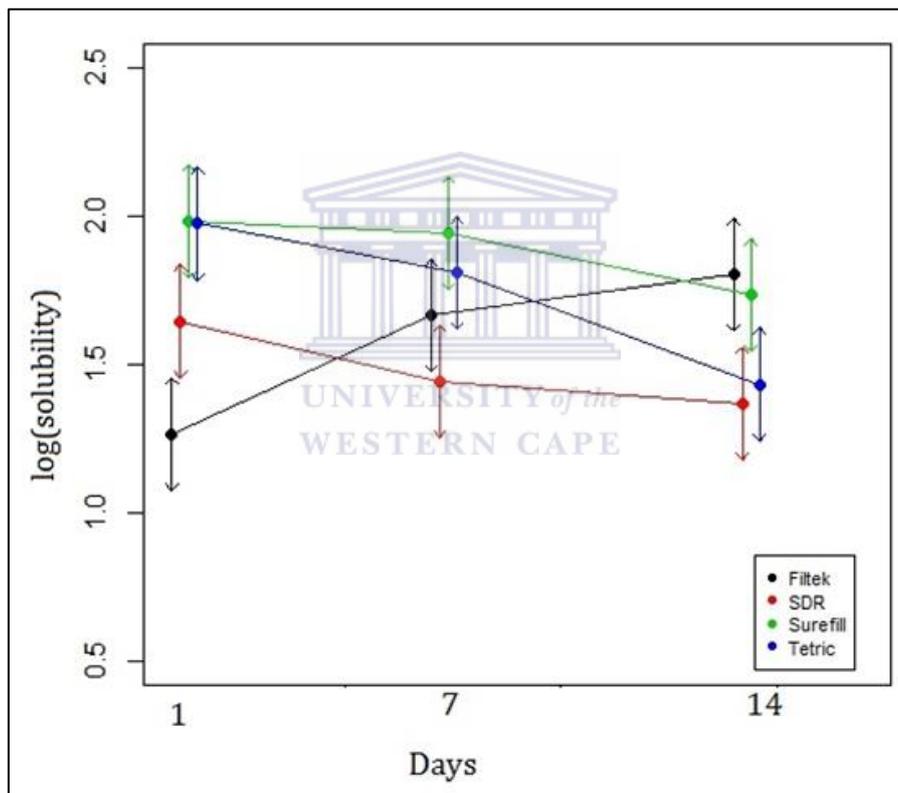


### **5.3. Water solubility**

The results for the overall water solubility means over time with  $\pm 1.4$  standard error limits are presented in table 10 and illustrated in figure 36, 37 and 38. The overall means for the two bulk-fill flowables i.e. Filtek and SDR were smaller than bulk-fill conventional Surefill and Tetric N-Ceram. However, all the test materials displayed no statistically significant increase in water solubility ( $p > 0.05$  two way ANOVA test)

Material	Days			Material mean
	24 h	7 days	14 days	
Filtek	1.266	1.664	1.803	1.578
SDR	1.646	1.443	1.369	1.486
Surefil	1.982	1.942	1.734	1.886
Tetric N-Ceram	1.975	1.808	1.433	1.739

**Table 10: Overall water solubility means.**



**Figure 36: Mean values of water solubility for the four test materials over time.**

The two way ANOVA analysis showed that Filtek means increased over time and the means of the other materials (SDR, Surefil and Tetric N-Ceram) decreased over time as shown in figure 36. The results of two way ANOVA analysis showed that there is a significant material effect and a significant interaction effect between the materials

was seen (  $p < 0.05$ ).

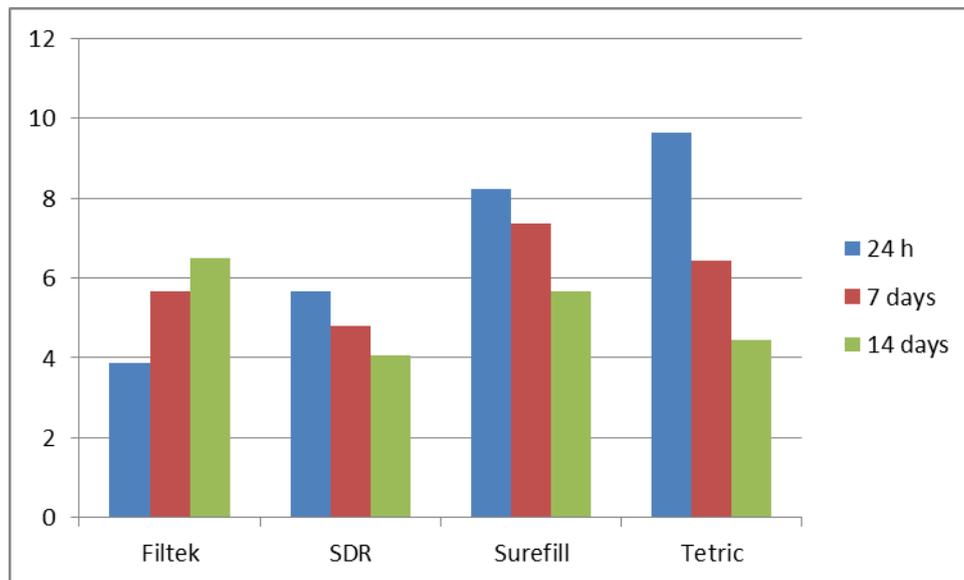


Figure 37: Mean values of the water solubility for the four test materials over time.

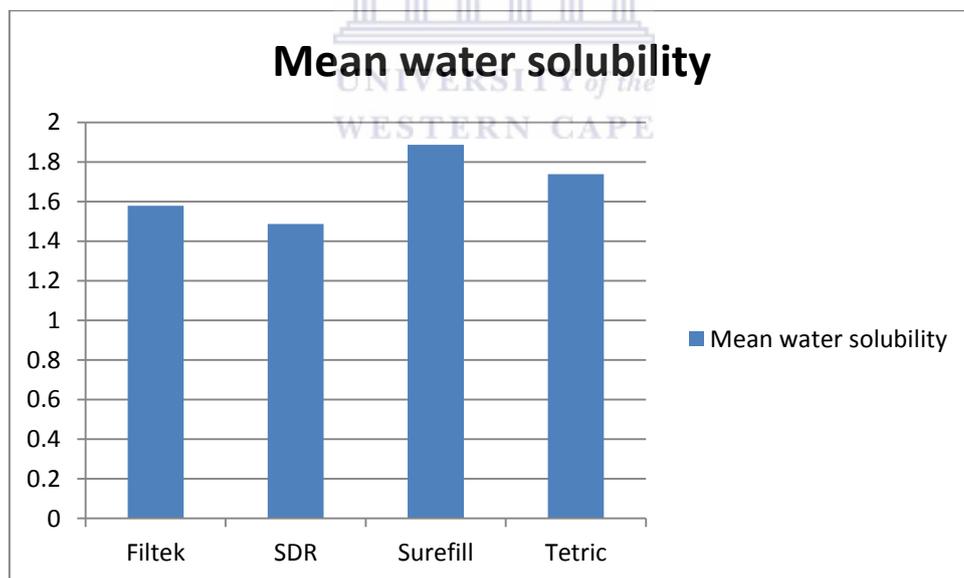


Figure 38: Mean water solubility values for the four test materials.

The exponentials of the means in table 11 were the geometric means of the original untransformed observations and may be compared with the means in table 12.

Material	24 hrs		7 days		14 days	
	Mean values	Standard deviation	Mean values	Standard deviation	Mean values	Standard deviation
<b>Filtek</b>	3.869	1.63	5.662	2.31	6.511	2.68
<b>SDR</b>	5.662	2.66	4.812	3.37	4.058	1.26
<b>Surefil</b>	8.209	4.31	7.360	2.73	5.662	0.00
<b>Tetric N-Ceram</b>	9.625	8.26	6.417	2.21	4.435	1.60

**Table 11: Mean values of water solubility of the four test materials over time.**

The mean values of the water solubility for the materials, time factors and interaction were calculated as the  $p < 0.05$  (two way ANOVA) were not statistically significant, and are presented as shown in table 12.

Factor	Df	Sum Sq	Mean Sq	F value	Pr (> F)
<b>Material</b>	4	2.809	0.936	5.075	0.003
<b>Days</b>	3	0.459	0.229	1.243	0.293
<b>Interaction</b>	6	3.406	0.568	3.077	0.008

**Table 12: The results of a two way ANOVA of water solubility.**

## 5.4. Monomers elution

Results for released monomers are shown in table 13. Organic substance released from the four test materials tested at different storage times (ND= Not detectable, D= Detectable). Where the number in the brackets indicates the number of the sample in which the monomer was either detected or not detected.

Correlation between the reference peaks and the retention times of the registered peaks was observed.

TEGDMA was the main monomer found in detectable (D) quantities in the stored water of Surefil, Tetric-N Ceram and in SDR after 24 hours, 7 days and 14 days.

Bis-GMA was found in detectable (D) amounts in the stored water of Tetric-N Ceram after 7 and 14 days and in Filtek after 14 days.

UDMA was mainly detectable (D) in Tetric-N Ceram after 7 and 14 days and in Surefil after 24 hours, 7 days and 14 days.

Bis-EMA was non-detectable (ND) in the stored water of the four test materials.

Material	Organic substance	24 hrs	7 days	14 days
Filtek	TEGDMA	ND (8)	ND (9)	ND (6)
		D (2)	D (1)	D (4)
	UDMA	ND (10)	ND (9)	ND (8)
			D (1)	D (2)
Bis-GMA	ND (8)	ND (8)	ND (5)	
	D (2)	D (2)	D (5)	
Bis-EMA	ND (10)	ND (10)	ND (10)	
SDR	TEGDMA	D (6)	ND (6)	ND (6)
		ND (4)	D (4)	D (4)
	UDMA	ND (9)	ND (6)	ND (6)
		D (1)	D (4)	D (4)
	Bis-GMA	ND (8)	ND (9)	ND (6)
		D (2)	D (1)	D (4)
Surefill	TEGDMA	QD (1)	D (6)	ND (8)
		D (7)	ND (4)	D (2)
		ND (2)		
	UDMA	D (6)	ND (7)	D (6)
		ND (4)	D (3)	ND (4)
	Bis-GMA	D (5)	D (5)	ND (7)
ND (5)		ND (5)	D (3)	
Tetric-N Ceram	TEGDMA	D (5)	ND (6)	ND (8)
		ND (5)	D (4)	D (2)
	UDMA	ND (7)	D (7)	D (7)
		D (3)	ND (3)	ND (3)
	Bis-GMA	ND (8)	ND (5)	ND (6)
		D (2)	D (5)	D (4)
	Bis-EMA	ND	ND	ND

**Table 13: Monomers elution from the four test materials over time. Organic substance released from the composite resin materials tested at different storage times (ND= Not detectable, D= Detectable. where the number in the brackets indicates the number of the sample in which monomer was either detected or not detected.**

### 5.4.1. TEGDMA monomer

Two way ANOVA analysis of the TEGDMA of the test materials showed that the standard deviations (SD) as shown in table 13 and figure 9 (appendix) varied considerably between the materials, for this reason it seemed advisable to transform the TEGDMA values into their logarithms. The results showed that there was a significant difference in the overall TEGDMA mean values between the test materials. The presence of TEGDMA in Filtek was significantly smaller than SDR and Surefil and TEGDMA in Tetric N-Ceram was smaller than Surefil (Filtek < SDR < Surefil < Tetric N-Ceram),  $p < 0.001$  ANOVA two way Analysis of Variance).

Materials	TEGDMA		Log <sub>e</sub> (TEGDMA)	
	Mean	SD	Mean	SD
Filtek	0.098	0.02	2.369	0.29
SDR	0.169	0.07	1.869	0.43
Surefil	0.205	0.10	1.699	0.48
Tetric N-Ceram	0.122	0.02	2.126	0.24

**Table 14: The overall mean and logarithm mean values of TEGDMA monomer in the test materials.**

### 5.4.2. UDMA

Two way ANOVA analysis of the UDMA of the test materials showed that the standard deviations (SD) as shown in table 14 and figure 10 (appendix) varied considerably between the materials, for this reason the values were transformed into their logarithms. The results showed that there was a significant difference in the overall UDMA means between the test materials. The amount of UDMA leaching out

of Filtek was significantly smaller than that of SDR, Surefil and Tetric N-Ceram ( $p = 0.001$ , ANOVA two way Analysis of Variance).

Materials	UDMA		Log <sub>e</sub> (UDMA)	
	Mean	SD	Mean	SD
<b>Filtek</b>	0.335	0.21	1.331	0.82
<b>SDR</b>	0.504	0.29	0.858	0.64
<b>Surefil</b>	0.735	0.40	0.409	0.43
<b>Tetric N-Ceram</b>	0.813	0.43	0.370	0.64

**Table 15: The overall mean and logarithm mean values of UDMA of the test materials.**

#### 5.4.3. Bis-GMA

The results of an ANOVA of log<sub>e</sub> of Bis-GMA showed that SDR was smaller than Filtek, Surefil and Tetric N-Ceram, but there was no significant difference in the overall mean values among the test materials ( $p = 0.8867$ ) as shown in table 15 and figure 11 (appendix).

Material	Bis-GMA		Log <sub>e</sub> (Bis-GMA)	
	Mean	SD	Mean	SD
<b>Filtek</b>	0.202	0.28	2.417	1.33
<b>SDR</b>	0.177	0.16	2.180	1.03
<b>Surefil</b>	0.213	0.22	2.140	1.33
<b>Tetric N-Ceram</b>	0.275	0.39	1.993	1.30

**Table 16: The overall mean and logarithm of the mean values of Bis-GMA of the test materials.**

The overall means for all the monomers that were eluted from the test materials are summarised in table 16 and illustrated in figure 42.

The amounts of eluted monomers from bulk-fill conventional viscosity materials (Surefil and Tetric N-Ceram) were higher than bulk-fill flowable materials (SDR and Filtek). Of all the monomers tested UDMA eluted more than Bis-GMA and TEGDMA. Overall UDMA monomer eluted the most, followed by Bis-GMA and the TEGDMA.

Material	TEGDMA	UDMA	Bis-GMA
Filtek	0.098	0.335	0.202
SDR	0.169	0.504	0.177
Surefil	0.205	0.735	0.213
Tetric	0.122	0.813	0.275

Table 17: The overall means of TEGDMA, UDMA and Bis-GMA for the test materials.

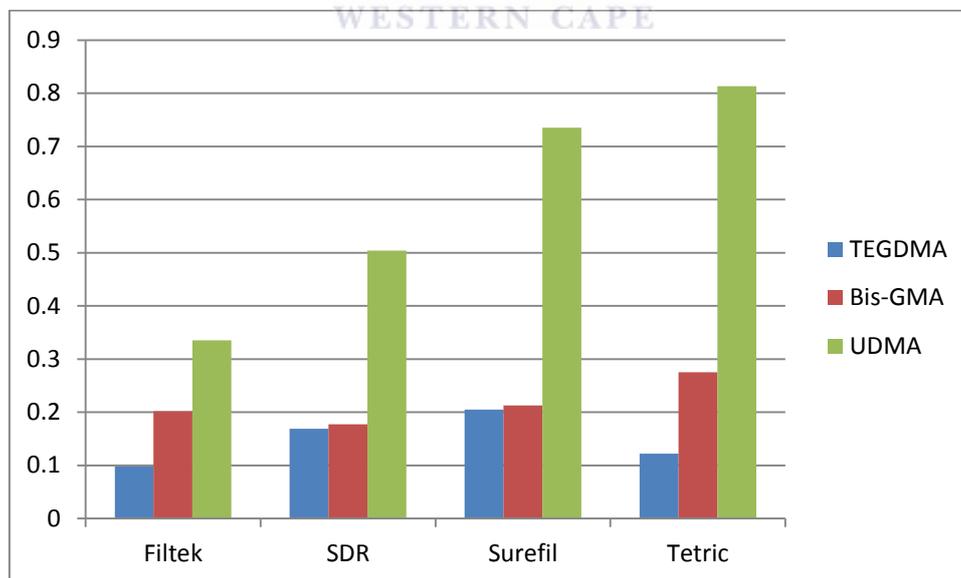
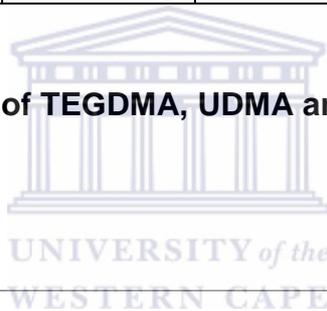


Figure 39: The overall mean value of TEGDMA, UDMA and Bis-GMA for the test materials.

## Chapter 6

### Discussion

#### 6.1. Introduction

Oral environment plays a significant role in modifying the properties of resin filled composites as water sorption and solubility could negatively affect their physical and mechanical properties (Yap, Teoh and Tan, 2000; Sarker, 2000).

Water sorption of resin based dental composites is described as a diffusion controlled process that may cause chemical degradation of the material leading to several drawbacks, such as de-bonding of the filler polymer-matrix and release of the residual unreacted monomers. On the other hand, water solubility of resin based dental composites is reflected by the amount of leached unreacted monomers and the subsequent loss of filler particles (Giannini et al., 2014).

Water sorption and solubility properties are basically dependant on the composition of the dental composite materials like monomer type, degree of curing, efficiency of the filler-matrix bonding and filler characteristics like content, size, shape and inter-particle spacing (Kim et al., 2002).

Water sorption by resin filled dental composites may cause expansion of the composite filling, which decreases any gap formed by polymerisation shrinkage, thus compensate for any material shrinkage (Yap et al., 2000). This might be considered as a positive effect of water sorption on marginal gap formation following polymerisation shrinkage, but further investigation is still needed to provide direct evidence (Ruttermann et al., 2007). However, polymerisation shrinkage takes place within minutes after curing the composite, whereas water sorption that results in

composite expansion and consequently results in full compensation of the polymerisation shrinkage takes longer period of several weeks (Yap et al., 2000).

Many resin filled composites are Bis-GMA based and the addition of diluent monomers like TEGDMA is important to reduce the high viscosity of Bis-GMA. These diluent monomers become coupled with the hydroxyl group of Bis-GMA which leads to high values of water sorption (Al-shekhli and Hakimzadeh, 2012). It is crucial to reduce water sorption as low as possible because it negatively affects the colour stability, wear and abrasion resistance and flexure strength (Al-shekhli and Hakimzadeh, 2012).

Resin filled composites are indicated as restorative materials that must comply with ISO 4049 guideline of water sorption and water solubility for maximum values of 40  $\mu\text{g}/\text{mm}^3$  and 7.5  $\mu\text{g}/\text{mm}^3$  respectively within seven day period of water storage (ADA, 2003). In this study we extended the time period to 14 days and evaluated both water sorption and solubility over 24hrs, 7 days and 14 days.

Water sorption and water solubility have been reported to be dependent upon the extent of polymerisation, chemistry of the monomers, fillers particle size and distribution and the interfacial properties between resin materials and fillers (Calais and Soderholm, 1988; Ferracane, 1994; Beatty et al., 1998). Water sorption and solubility in resin filled composite is a diffusion controlled process and mainly takes place in the resin matrix (Barden and Clarke, 1984).

Pearson and Longman (1989) showed less water sorption from composites based on UDMA because it is a hydrophobic monomer compared with Bis-GMA. Similarly, Barden (1984 cited in Ortengren et al., 2001) found that resin composites which are based on TEGDMA showed higher water sorption values compared with resin

composites based on UDMA and Bis-GMA.

Solubility of resin filled composites is affected by the type of fillers. Silane treatment of fillers and air voids within composite material are some factors that can lead to a reduction of material mass (Soderholm et al., 1984; Oysaed and Ruyter, 1986).

## **6.2. Water sorption and solubility**

Two classes of contemporary resin filled composites (bulk-fill conventional viscosity and bulk-fill low viscosity flowables) were selected to measure water sorption and solubility and the measurements were done according to ISO 4049 to investigate if the obtained values meet the standards limits.

In the current study, the obtained water sorption and solubility values fall within ADA and ISO guidelines, even for 14 days storage time which is double the recommended time.



Water sorption and water solubility have a significantly negative impact on wear and strength and subsequently on the clinical performance of the materials (Janda et al., 2007), and this justifies a comprehensive investigation of water sorption and solubility.

### **6.2.1. Water sorption**

Surefil and Tetric N-Ceram bulk-fill composites showed the highest amount of water sorption which may be attributed to the higher filler content (58% by volume for Surefil and 61% by volume for Tetric N-Ceram).

The organic matrix contains Bis-GMA which is considered a weaker monomer in providing adequate resistance against water sorption when compared to the other

monomers present in the other composites used in the current study (SDR and Filtek Flowable).

The mean value of water sorption in Tetric N-Ceram after 14 days was 16.513  $\mu\text{g}/\text{mm}^3$  with 3.675 standard deviation, which is similar to the results of Al-Shekhli and Hakimzadeh (2012) where the mean value of water sorption for Tetric EvoCeram after 15 days was 18.343 with 4.297 standard deviation. The mean water sorption for Surefil in this was 21.515  $\mu\text{g}/\text{mm}^3$  after 7 days and this value stabilized after 7 days with the same reading at 14 days. However, Yap et al. (2002) and Janda et al. (2007) showed lower values of 9.5  $\mu\text{g}/\text{mm}^3$  and 9  $\mu\text{g}/\text{mm}^3$  respectively for Surefil.

The filler particle system may enhance water sorption as Kalachandara and Wilson (1992) found that 0.04  $\mu\text{m}$  silica particles displayed reduction in the modulus of elasticity after storage in water at 37°C, which resulted in greater water accumulation at the matrix-filler interface which explains the higher water sorption that took place in Surefil material in the current study. Surefil is said to have three differently sized fillers namely midfiller, minifiller and microfiller and that the filler particle size in Surefil ranges between 0.8-20  $\mu\text{m}$  (Leinfelder et al., 1999; Reic et al. 2003).

There was a statistical difference in the mean values of the water sorption between the test materials with SDR significantly smaller than the other materials in the current study which may be attributed to a higher conversion of the monomers. The results of the current study are consistent with the results of Tiba et al. (2013) as the mean value of water solubility in Filtek was less than Tetric N-Ceram.

The chemistry of the monomers that is present in the matrix is the key to the hydrophilic nature of the polymer (Al-shekhli and Hakimzadeh, 2012). This may

explain the water sorption process over time. All the materials used in the current study except SDR flowable contain Bis-GMA which is weak resin monomer in terms of resisting water sorption as it contains hydroxyl group which results in increased water sorption (Peutzfeldt,1997). The polar nature of such a polymer matrix and presence of ether linkage are significant factors in water sorption in resin filled composites (Peutzfeldt,1997). Furthermore, Yap and Wee (2002) claimed that higher filler content may lead to increased water accumulation at the interface between the fillers and the matrix resulting in increased water sorption. This may explain the higher water sorption for Surefill and Tetric N Ceram in this study. The mean value of water sorption for Tetric N Ceram when stored in distilled water for 14 days was 16.513  $\mu\text{g}$ . Similar results were obtained by Alshekhli and Hakimzadeh (2012) where Tetric Evo Ceram showed water sorption of 18.343  $\mu\text{g}$ . Tetric Evo Ceram and Tetric N Ceram contain the same fillers and the same filler content (61% by volume).

The bulk-fill flowable materials used in this study showed increased water sorption over time from 24 hrs to 7 days to 14 days, although statistically not significant. Whereas in bulk-fill conventional materials there was noticeable increase in water sorption from 24 hrs to 7 days but stabilized from 7 days to 14 days especially for Surefil as illustrated in figures (33, 34 and 35) and table (8). Water sorption in resin filled composites takes place mainly in resin matrix and it is a diffusion-controlled process in which the diffusion coefficient decreases with the concentration of water in the matrix (Braden and Clarke, 1984 cited in Ortengren et al., 2001).

The results of this study did not support the null hypothesis that there is no significant difference in the water sorption. The bulk-fill low viscosity flowables showed lower water sorption than the conventional bulk-fills. SDR was significantly lower than the other materials, followed by Filtek, Tetric N-Ceram and the highest

overall means were recorded for Surefil.

### **6.2.2. Water solubility**

In the current study there was no statistical difference in the mean values of water solubility for the materials tested as illustrated in figures (36, 37 and 38) and table (10).

The overall mean of water solubility for Surefil and Tetric N-Ceram were consistent with results Boaro et al. (2013) where Filtek Supreme was used, and this was attributed to the slightly lower network density in the material, so the polymeric matrix was able to swell but there were not many unreacted monomers available to leach out.

Water sorption and solubility in bulk-fill resin filled composites was higher than bulk-fill flowable resin filled composites in the current study and this could be attributed to the higher filler content and weak resin monomer (Bis-GMA) content contained in bulk-fill resin filled composites as also claimed by Yap and Wee (2002).

Water solubility in the current study for all materials decreased over time from 24hrs to 7 days to 14 days for all test materials except Filtek which showed an increase over time. Although these were not statistical different, these findings were consistent with the results of Ortengren et al. (2001) which showed moderate increase in water solubility over time in general for some of the test materials. It is important to point out that the water solubility of one material (Vario-Link II composite) in Ortengren's study decreased over time and the solubility of another composite material (TPH Spectrum) slightly increased from 4 hr to 24 hr then decreased to 7 days. Ortengren et al. (2001) attributed the negative solubility values

in his study to the chemical reaction with water within the composite while Janda et al. (2007) attributed that to incomplete removal of the absorbed water during the drying process. In this study Tetric N Ceram showed an initial increase in water solubility and then a decrease at 14 days. However, Ferracane and Condon (1990) reported that approximately 50% of leachable components are eluted within three hours, and elution of nearly all leachable components was complete within 24hrs which may explain the decreasing loss of mass during the test period. Recently, Ferracane (2006) said that elution of components from set resin filled composites reaches completion within 1-3 days.

The results of this study supported the null hypothesis that there is no significant difference in solubility in the four different types of resin filled composite materials tested.

### **6.3. Monomers elution**



High Performance Liquid Chromatography (HPLC) analysis was used in this research to evaluate monomer release from the study materials as it is a very powerful chemical separation method and gives a greater level of control over the separation process since the monomers are soluble in the mobile phase.

Ferracane (1994) listed the factors for the release of unbound components from polymerised resin filled composites as follows:

- The monomer-polymer conversion as determinant of quantity of leachable components.
- The solubility parameters and solvent composition.

- The chemical characteristics and the size of the leachable substance as determinants of the diffusion through the polymer network.

Gopferich (1996) and Geurtsen (1998) stated that progressive degradation alters the bulk of the resin filled material by void formation through which the residual monomers can be released.

Conventional flowable composites contain higher amounts of monomers in non-polymerised form compared with conventional composites (Polydorou et al., 2007). In this study the results for the polymerised samples show the amount of released monomers from bulk-fill flowable composites, SDR and Filtek to be lower than bulk-fill conventional viscosity Tetric-N Ceram and Surefill. These results are in agreement with the study by Siderisou and Achilias (2005) and Polydorou et al. (2007). This may be attributed to the chemical structure of monomers used for the preparation of the resin filled composites as this directly affects the time needed for the elution and the amount of eluted monomers (Siderisou and Achilias, 2005).

Detectable amounts of TEGDMA were found in distilled water at different storage times and this is consistent with other studies that found detectable amounts of TEGDMA (Sphal et al., 1998; Orengrén et al., 2001). The lower molecular weight of TEGDMA (286 g/mol) explains the higher mobility and the faster elution than Bis-GMA (512 g/mol) and UDMA (470 g/mol) (Tanaka et al., 1991). The quantity of the measured amount of TEGDMA from the test materials was less than UDMA and Bis-GMA and this could be due to TEGDMA being a co-monomer is present in small percentage compared with Bis-GMA and UDMA. The higher amount of UDMA eluted from the test materials compared to the other materials tested in the current study indicate that the test materials contain larger amounts of UDMA than Bis-GMA and

TEGDMA and this finding is consistent with the results of monomers elution from in Sideridou and Achilias (2005). In the current study, the amount of released Bis-GMA from the test materials was higher than TEGDMA with similar results obtained in other studies (Komurcuoglu et al., 2005; Polydorou et al., 2007). Stanbury and Dickens (2001) explained that because of the chemical properties and reactive potential of Bis-GMA and TEGDMA the polymerisation shrinkage is expected to increase with the proportion of TEGDMA added since this monomer has a smaller molecular weight and greater molecular mobility and promotes a higher degree of conversion.

The detectable quantities of higher molecular UDMA and Bis-GMA released from the test materials in this study may be due to the initiator/ activator and inhibitor system used (Asmussen, 1982 cited in Ortengren et al., 2001) and the blend mix formulation Muller et al., (1997). Bis-EMA was not detectable in the storage water of the four test materials at any given point of time. These results are consistent with the results of Ortengren et al. (2001). This may be a result of the smaller amounts of Bis-EMA used in the composition of the materials or possibly due to the higher conversion rate of this monomer.

The amounts of eluted monomers either decreased or remain unchanged over time (table1 in the appendix) which is consistent with the finding of Zhang and Xu (2008). As only free unpolymerised monomers will elute, this is not time related but dependent on the free available monomers.

## Chapter 7

### Limitations of the study

Within the limitations of this study, possible factors that could have affected the outcomes of the study are as follows:

- Only 24 hrs, 7 days and 14 day time intervals were used for measuring water sorption and solubility.
- Results were based on a specimen size of 30 specimens per material, as 10 specimens each were used for 24 hrs, 7 days and 14 days, and results may be different if the specimens were increased.
- Only distilled water was used as an immersion medium, as artificial saliva and 70:30 ethanol/water solutions could also be used as immersion media.
- HPLC analysis is advised to be carried out immediately after removing the resin filled composite specimens from the distilled water, as some monomers may continue degrading when stored in distilled water for long time which may affects the accuracy of the results.

## Chapter 8

### Conclusion and recommendations

#### 8.1. Conclusion

The bulk-fill low viscosity flowables showed lower water sorption than the conventional bulk-fills. Surefil SDR Flow was significantly lower than the other materials, followed by Filtek Bulk Fill flowable restorative, Tetric N-Ceram Bulk Fill and the highest overall means were recorded for Surefil bulk fill

For water solubility the overall means of Filtek Bulk Fill flowable restorative and Surefil SDR Flow were smaller than Surefill bulk fill and Tetric N-Ceram Bulk Fill. However, there was no significant difference in solubility in the four different types of resin filled composite materials tested.

The amounts of eluted monomers from bulk-fill conventional viscosity materials (Surefil bulk fill and Tetric N-Ceram Bulk Fill) were higher than bulk-fill flowable materials (Surefil SDR Flow and Filtek Bulk Fill flowable restorative). Of all the monomers tested UDMA eluted more than Bis-GMA and TEGDMA.

#### 8.2. Recommendations

Based on the results of this study bulk-fill composites should be supplied as a dual cure material *i.e.* light-curing as well as self-curing composite material to ensure complete curing of the composites which in turn will reduce water sorption, water solubility and monomers elution.

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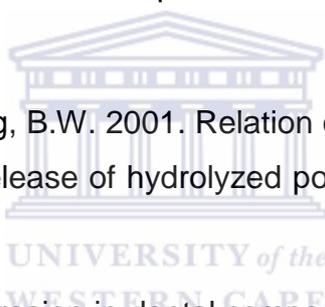
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## Chapter 10. Appendix

### 1. Water sorption and solubility

Material	Time	specimen	m1 ( $\mu\text{g}$ )	m2 ( $\mu\text{g}$ )	m3 ( $\mu\text{g}$ )	v ( $\text{mm}^3$ )	sorption	solubility
Filtek	24 h	1	449000	452000	449000	176.625	16.985	0
Filtek	24 h	2	478000	478000	478000	264.937	0	0
Filtek	24 h	3	421000	423000	420000	176.625	11.323	5.661
Filtek	24 h	4	422000	424000	422000	264.937	7.548	0
Filtek	24 h	5	448000	450000	447000	264.937	7.548	3.774
Filtek	24 h	6	440000	441000	440000	176.625	5.661	0
Filtek	24 h	7	458000	460000	457000	176.625	11.323	5.661
Filtek	24 h	8	436000	437000	435000	176.625	5.661	5.661
Filtek	24 h	9	456000	458000	456000	176.625	11.323	0
Filtek	24 h	10	425000	426000	424000	176.625	5.661	5.661
Filtek	7 days	11	454000	456000	453000	176.625	11.323	5.661
Filtek	7 days	12	446000	449000	446000	176.625	16.985	0
Filtek	7 days	13	412000	414000	412000	176.625	11.323	0
Filtek	7 days	14	448000	450000	447000	176.625	11.323	5.661
Filtek	7 days	15	428000	430000	427000	176.625	11.323	5.661
Filtek	7 days	16	413000	415000	412000	176.625	11.323	5.661
Filtek	7 days	17	408000	410000	407000	176.625	11.323	5.661
Filtek	7 days	18	492000	494000	489000	264.937	7.548	11.323
Filtek	7 days	19	438000	441000	437000	176.625	16.985	5.661
Filtek	7 days	20	435000	438000	434000	176.625	16.985	5.661
Filtek	14 days	21	436000	438000	435000	176.625	11.323	5.661
Filtek	14 days	22	431000	432000	430000	176.625	5.661	5.661
Filtek	14 days	23	425000	427000	425000	176.625	11.323	0
Filtek	14 days	24	442000	444000	441000	176.625	11.323	5.661
Filtek	14 days	25	445000	448000	444000	176.625	16.985	5.661

Filtek	14 days	26	427000	430000	426000	176.625	16.985	5.661
Filtek	14 days	27	431000	433000	429000	176.625	11.323	11.323
Filtek	14 days	28	425000	428000	424000	176.625	16.985	5.661
Filtek	14 days	29	430000	433000	428000	176.625	16.985	11.323
Filtek	14 days	30	464000	466000	463000	176.625	11.323	5.661
SDR	24 h	1	476000	478000	475000	176.625	11.323	5.661
SDR	24 h	2	456000	458000	456000	176.625	11.323	0
SDR	24 h	3	463000	464000	461000	176.625	5.661	5.661
SDR	24 h	4	464000	465000	462000	176.625	5.661	11.323
SDR	24 h	5	449000	451000	446000	176.625	11.323	16.985
SDR	24 h	6	458000	459000	457000	176.625	5.661	5.661
SDR	24 h	7	462000	463000	460000	176.625	5.661	11.323
SDR	24 h	8	457000	458000	456000	176.625	5.661	5.661
SDR	24 h	9	451000	453000	450000	176.625	11.323	5.661
SDR	24 h	10	453000	454000	452000	176.625	5.661	5.661
SDR	7 days	11	464000	468000	462000	176.625	22.646	11.323
SDR	7 days	12	451000	453000	450000	176.625	11.323	5.661
SDR	7 days	13	451000	454000	450000	176.625	16.985	5.661
SDR	7 days	14	475000	478000	474000	176.625	16.985	5.661
SDR	7 days	15	462000	466000	461000	176.625	22.646	5.661
SDR	7 dayd	16	444000	446000	443000	176.625	11.323	5.661
SDR	7 days	17	458000	460000	456000	176.625	11.323	11.323
SDR	7 days	18	500000	502000	498000	264.937	7.548	7.548
SDR	7 days	19	460000	462000	459000	176.625	11.323	5.661
SDR	7 days	20	450000	451000	449000	176.625	5.661	5.661
SDR	14 days	21	445000	448000	444000	176.625	16.985	5.661
SDR	14 days	22	480000	484000	479000	176.625	22.646	5.661
SDR	14 days	23	456000	459000	455000	176.625	16.985	5.661
SDR	14 days	24	480000	482000	479000	176.625	11.323	5.661

SDR	14 days	25	459000	461000	458000	176.625	11.323	5.661
SDR	14 days	26	459000	462000	458000	176.625	16.985	5.661
SDR	14 days	27	459000	463000	458000	176.625	22.646	5.661
SDR	14 days	28	469000	471000	468000	176.625	11.323	5.661
SDR	14 days	29	466000	468000	465000	176.625	11.323	5.661
SDR	14 days	30	455000	458000	454000	176.625	16.985	5.661
Suerfill	24 h	1	506000	507000	503000	176.625	5.661	16.985
surefill	24 h	2	556000	557000	554000	264.937	3.774	7.548
Surefill	24 h	3	597000	598000	596000	264.937	3.774	3.774
Surefill	24 h	4	573000	574000	572000	264.937	3.774	3.774
Surefill	24 h	5	551000	553000	550000	264.937	7.548	3.774
Surefill	24 h	6	698000	700000	697000	353.25	5.661	2.83
Surefill	24 h	7	537000	538000	536000	264.937	3.774	3.774
Surefill	24 h	8	613000	614000	611000	264.937	3.774	7.548
surefill	24 h	9	589000	590000	587000	264.937	3.774	7.548
surefill	24 h	10	538000	540000	537000	176.625	11.323	5.661
Suerfill	7 days	11	487000	489000	486000	176.625	11.323	5.661
surefill	7 days	12	580000	582000	580000	264.937	7.548	0
Surefill	7 days	13	588000	590000	583000	353.25	5.661	14.154
Surefill	7 days	14	600000	602000	599000	264.937	7.548	3.774
Surefill	7 days	15	582000	585000	581000	264.937	11.323	3.774
Surefill	7 dayd	16	568000	569000	567000	264.937	3.774	3.774
Surefill	7 days	17	507000	509000	506000	176.625	11.323	5.661
Surefill	7 days	18	549000	550000	549000	176.625	5.661	0
surefill	7 days	19	549000	551000	548000	264.937	7.548	3.774
surefill	7 days	20	537000	538000	536000	264.937	3.774	3.774
Suerfill	14 days	21	563000	566000	562000	264.937	11.323	3.774
surefill	14 days	22	556000	558000	555000	264.937	7.548	3.774
Surefill	14	23	605000	606000	603000	264.937	3.774	7.548

	days							
Surefill	14 days	24	604000	606000	603000	264.937	7.548	3.774
Surefill	14 days	25	605000	607000	604000	264.937	7.549	3.774
Surefill	14 days	26	579000	582000	578000	264.937	11.323	3.774
Surefill	14 days	27	616000	618000	615000	264.937	7.548	3.774
Surefill	14 days	28	598000	600000	597000	264.937	7.548	3.774
surefill	14 days	29	593000	596000	592000	264.937	11.323	3.774
surefill	14 days	30	617000	620000	616000	353.25	8.492	2.83
Tetric	24 h	1	501000	502000	500000	176.625	5.661	5.661
Tetric	24 h	2	546000	547000	541000	176.625	5.661	28.308
Tetric	24 h	3	514000	516000	513000	176.625	11.323	5.661
Tetric	24 h	4	517000	520000	517000	176.625	16.985	0
Tetric	24 h	5	558000	560000	558000	264.937	7.548	0
Tetric	24 h	6	517000	519000	516000	176.625	11.323	5.661
Tetric	24 h	7	512000	514000	500000	176.625	11.323	67.94
Tetric	24 h	8	548000	551000	545000	264.937	11.323	11.323
Tetric	24 h	9	549000	551000	548000	264.937	7.548	3.774
Tetric	24 h	10	595000	598000	590000	264.937	11.323	18.872
Tetric	7 days	11	530000	536000	528000	264.937	22.646	7.548
Tetric	7 days	12	523000	526000	522000	176.625	16.985	5.661
Tetric	7 days	13	506000	510000	505000	176.625	22.646	5.661
Tetric	7 days	14	553000	556000	551000	264.937	11.323	7.548
Tetric	7 days	15	550000	552000	549000	176.625	11.323	5.661
Tetric	7 dayd	16	511000	512000	509000	176.625	5.661	11.323
Tetric	7 days	17	534000	535000	533000	176.625	5.661	5.661
Tetric	7 days	18	568000	570000	567000	264.937	7.548	3.774
Tetric	7 days	19	590000	594000	588000	264.937	15.097	7.548
Tetric	7 days	20	550000	552000	549000	264.937	7.548	3.774
Tetric	14 days	21	652000	657000	651000	353.25	14.154	2.83

Tetric	14 days	22	592000	595000	590000	353.25	8.492	5.661
Tetric	14 days	23	580000	583000	579000	264.937	11.323	3.774
Tetric	14 days	24	613000	618000	611000	264.937	18.872	7.548
Tetric	14 days	25	637000	642000	636000	353.25	14.154	2.83
Tetric	14 days	26	666000	668000	664000	353.25	5.661	5.661
Tetric	14 days	27	630000	633000	629000	176.625	16.985	5.661
Tetric	14 days	28	580000	584000	579000	264.937	15.097	3.774
Tetric	14 days	29	596000	600000	595000	353.25	11.323	2.83
Tetric	14 days	30	587000	590000	586000	264.937	11.323	3.774



## 2. HPLC analysis

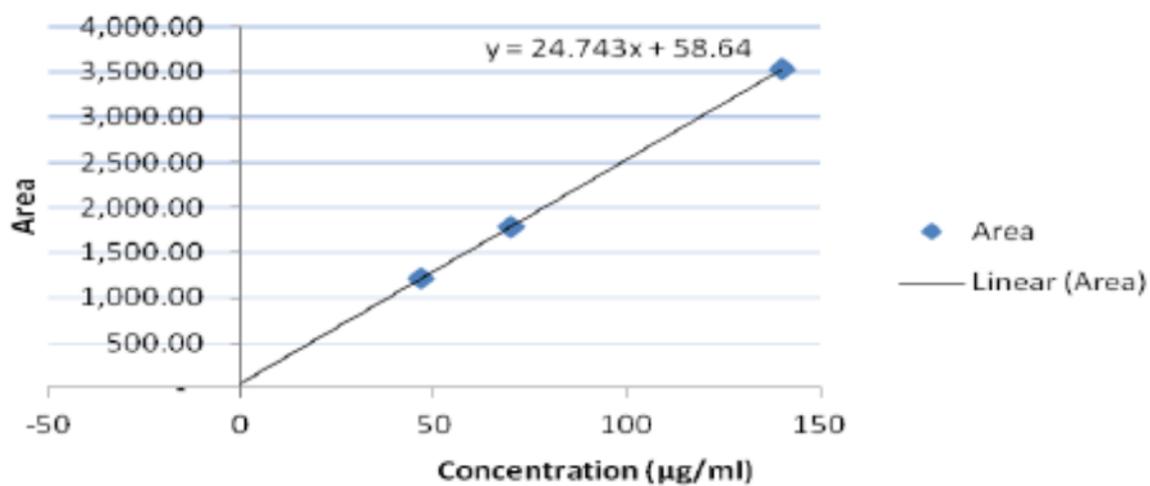


Figure 1: Area calibration curve of TEGDMA.

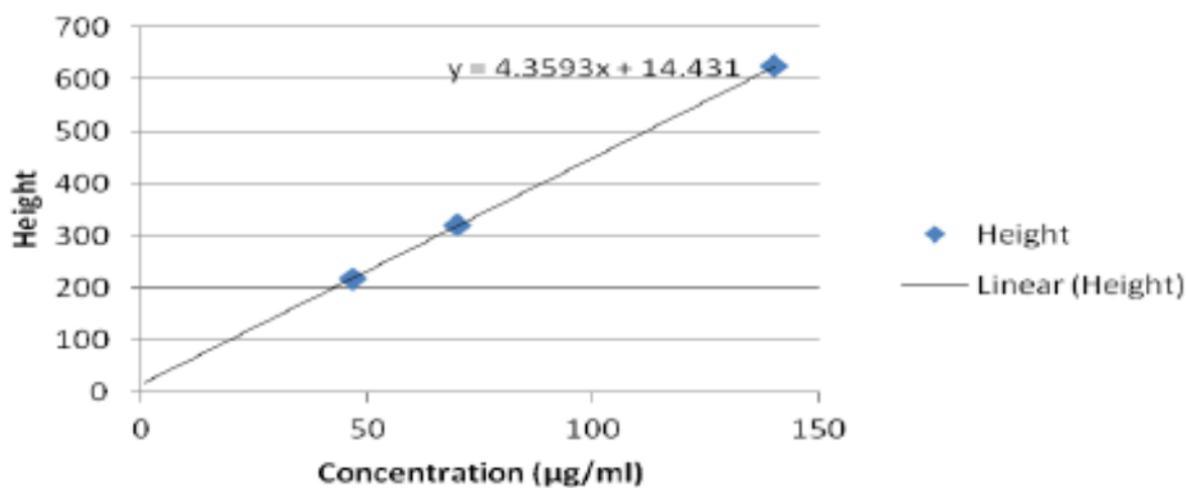


Figure 2: Height calibration curve of TEGDMA.

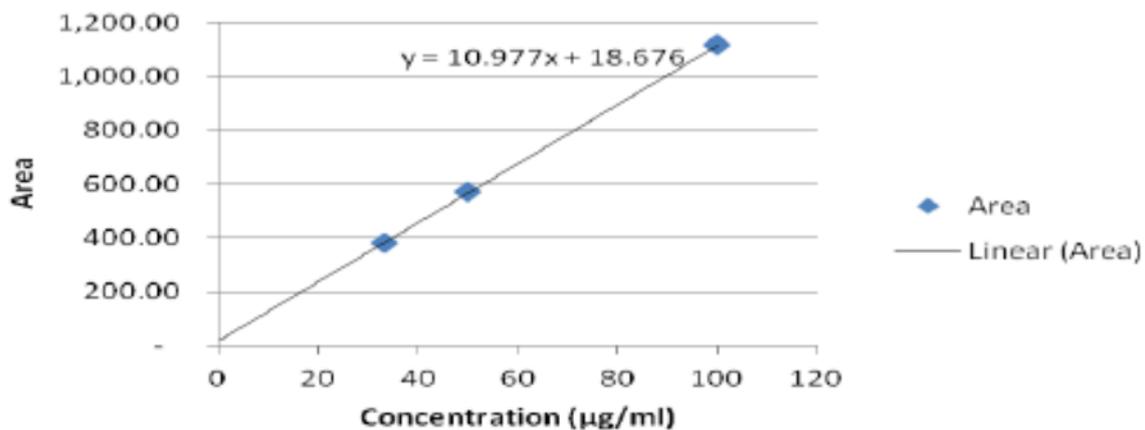


Figure 3: Area calibration curve of UDMA.

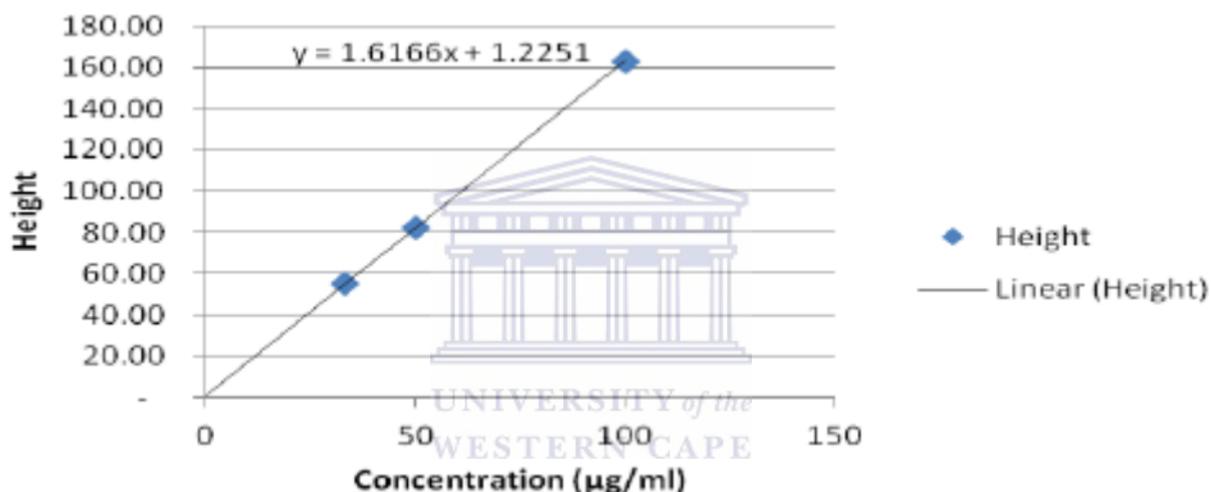


Figure 4: Height calibration curve of UDMA.

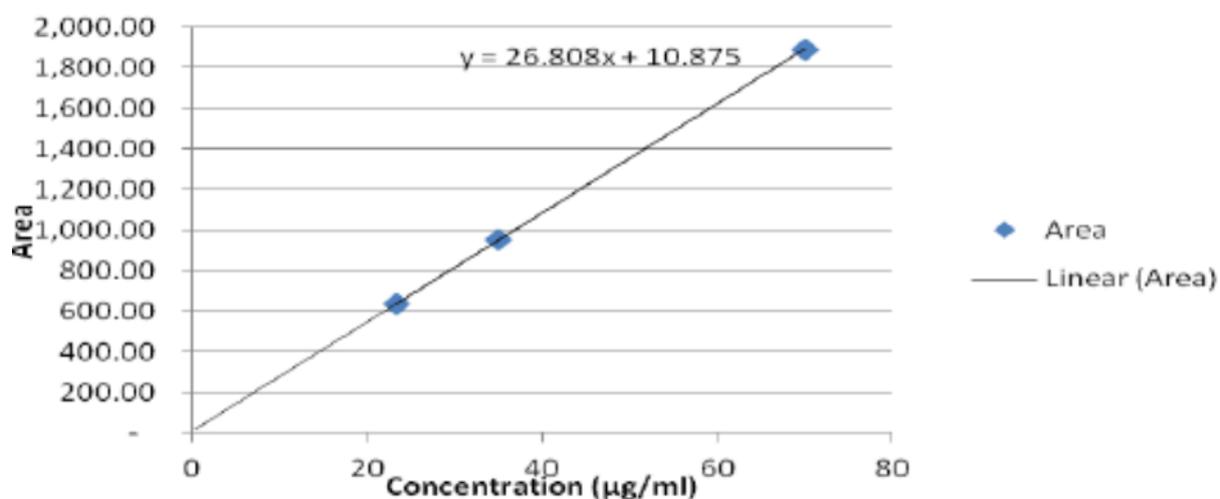


Figure 5: Area calibration curve of Bis-GMA.

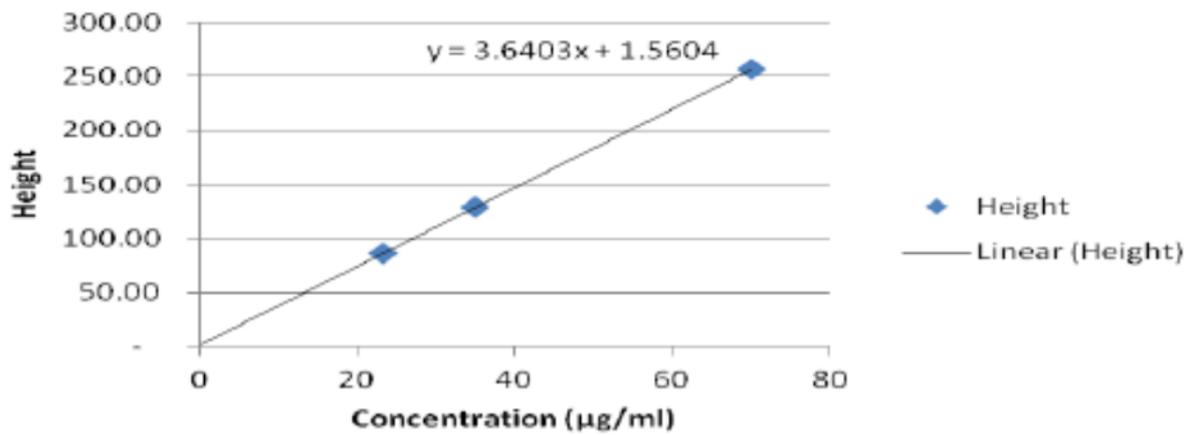


Figure 6: Height calibration curve of Bis-GMA.

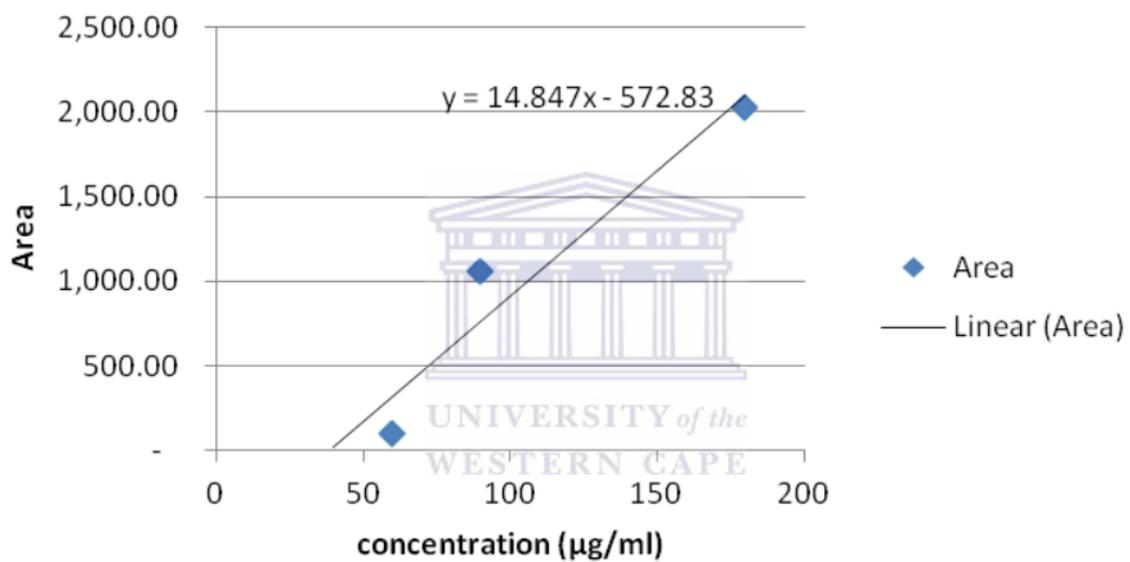


Figure 7: Area calibration curve of Bis-EMA.

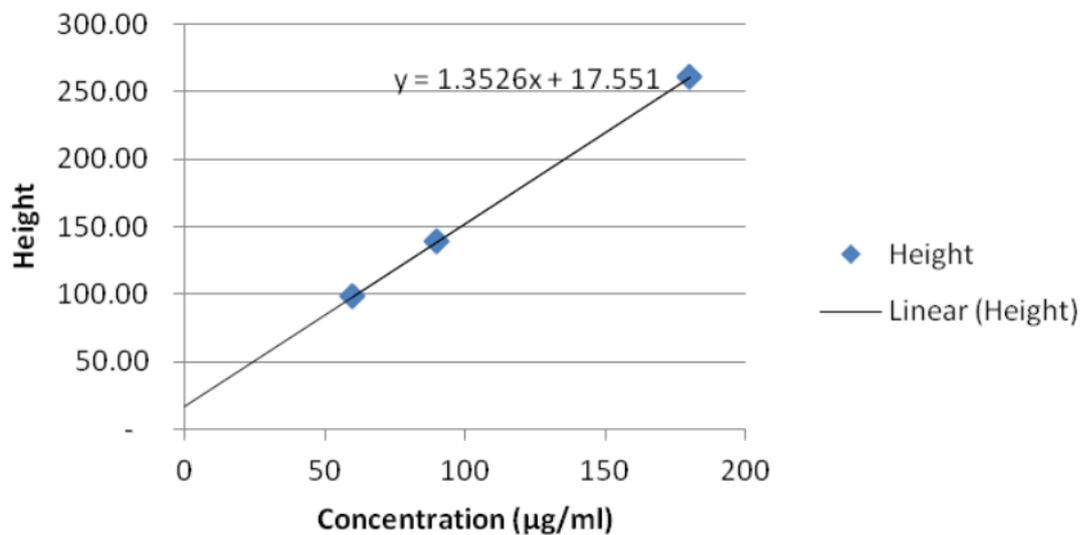


Figure 8: Height calibration curve of Bis-EMA.

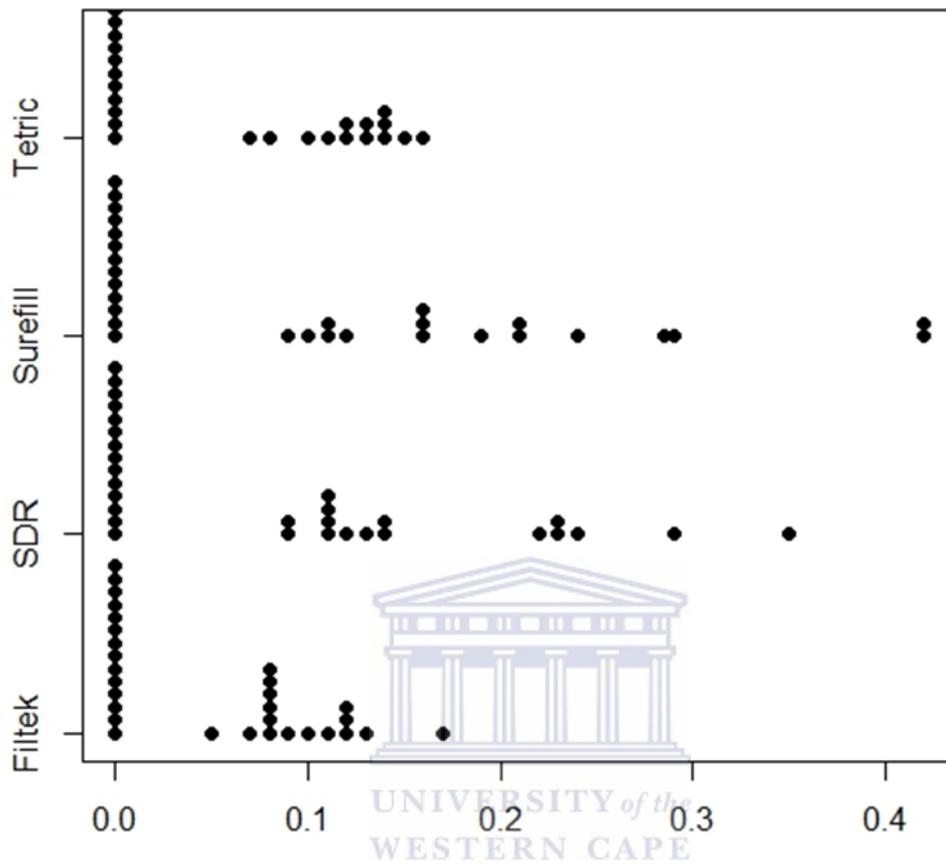


Figure 9: Overall mean values of the detectable amounts of TEGDMA of the test materials.

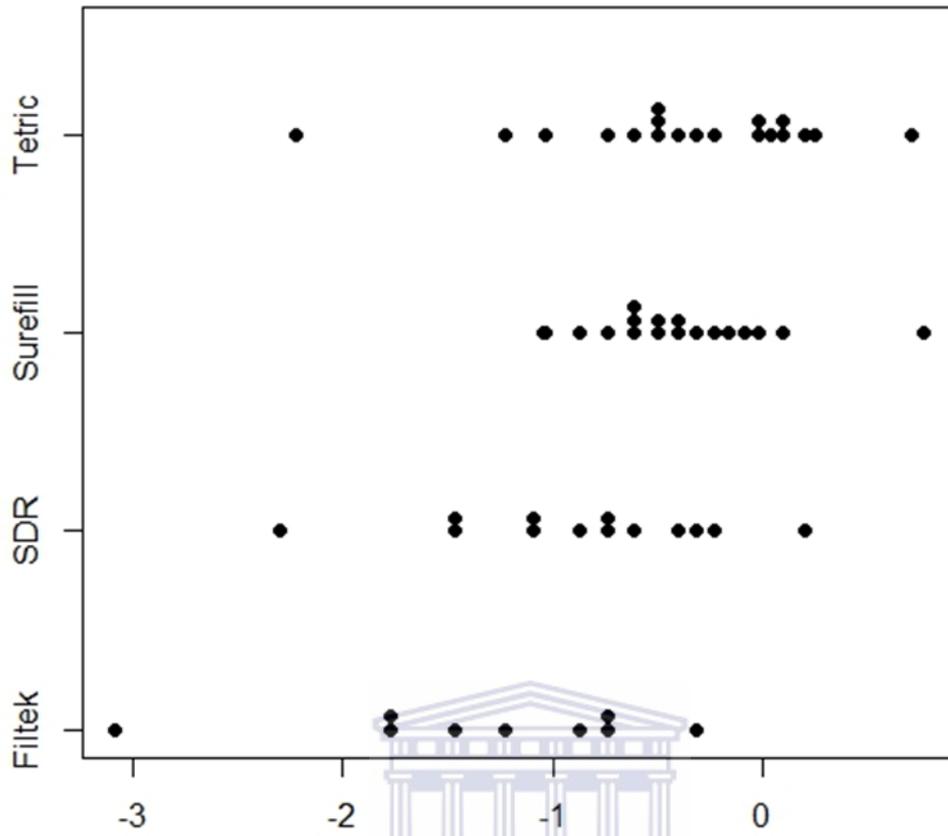


Figure 10: Overall mean values of detectable amounts of UDMA of the test materials.



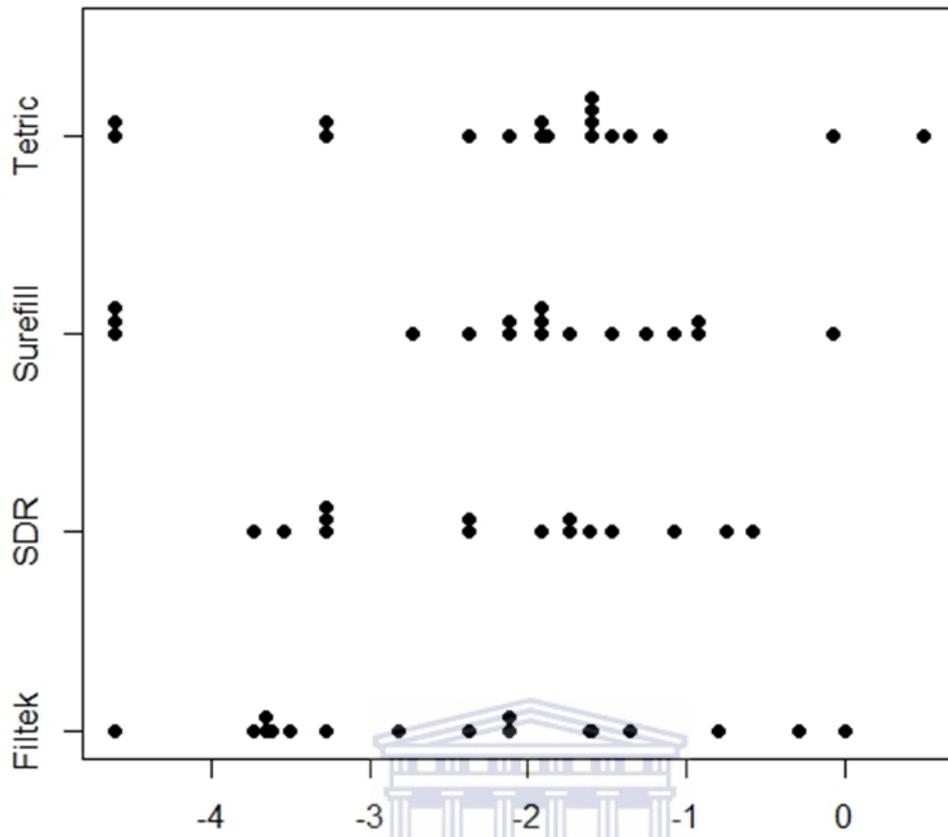


Figure 11: overall mean values of detectable amounts of Bis-GMA of the test materials.

