Volumetric change due to polymerization in dental resins as measured with an electronic mercury dilatometer.

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A thesis submitted in fulfillment of the requirements for the degree of Magister Scientiae Dentium in the Department of Restorative Dentistry and the Oral and Dental Research Institute, University of the Western Cape.

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DECLARAITION FOR NO CONFLICT OF INTEREST

I declare that “Volumetric change due to polymerization in dental resins as measured with an electronic mercury dilatometer.” is my own work, that it has not been submitted before for any qualification or examination in any other university, and that all the sources I have used or quoted have been indicated and acknowledged by complete references. I have no competitive interest in any of the companies that manufacture any of the dental materials I tested on the modified electronic mercury dilatometer. No shares/stock is held nor will I have any financial gain or loss with the publication with any manuscript pertaining to this research. No funding have been received from any of the dental material companies. Winner of Pameijer Scholarship 2012.

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Signed: ………………………………..

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ABSTRACT

Volumetric change due to polymerization in dental resins as measured with an electronic mercury dilatometer.

Objectives: To determine the total volumetric change and the relative speed of shrinkage of bulk fill flowable composites during polymerization. **Background:** The volumetric change that occur during the polymerization of dental composite restorations are considered to be one of the most significant contributing factors when considering the failure in composite restorations. Volumetric shrinkage of more than 2% is considered to be enough to result in the occurrence of secondary caries resulting in fracture of restorations and failure in the adhesive layer of a resin restoration. The total volumetric change of dental resins can be attributed to three main factors: Firstly, the polymerization reaction that results in the formation of a polymer chain. Secondly, the increase of the exothermic thermal effects produced by the polymerization reaction and thirdly, light irradiance energy that is transferred to the dental resin. **Materials and Methods**: A specially designed electronic mercury dilatometer at the UWC Oral and Dental Research Institute was used to determine the volumetric change. The light intensity was set at 500mW/cm^2. The mercury dilatometer measured the volumetric change every 0.5 seconds during the 35 second irradiation exposure time. The materials tested were Z250 as the control and four bulk fill flowable composites. The volume of voids within the cured material samples were assessed with a Micro-3D ct reconstruction (General Electric Phoenix) **Results**: The sequence of total volumetric change from least to most were: Z250 < Filtek bulk fill < Xtra-Base bulk fill < SDR < Venus bulk fill. The speed/rate of shrinkage of the bulk fill flowable composites were faster than that of Z250, while the 2 bulk fill flowables with the highest shrinkage speed (SDR and Venus) also had the highest total volumetric change. Of the different materials tested the volumetric change of Z250 (1.13%) was the lowest and significantly less ($p<0.05$) than that of SDR (1.56%) and Venus (1.72%). The Kruskal-Wallis multiple comparison test indicated that the material with the highest filler content (Z250) also showed the lowest shrinkage (1.13%) but this effect of the filler content could not be seen in the bulk fill flowable composites. The volume of the voids within the test specimens were determined and were represented as a percentage of the cured volume (49.087mm^3). Venus had the largest percentage of voids (1.18%) in the test specimen (specimen volume: 49.087mm^3), followed by Z250 with 0,5248%, Xtra base with 0,00015%, SDR with 0,00059% and Filtek bulk fill with 0,00069%. **Conclusions**: The volumetric changes and rate of shrinkage were higher for all 4 bulk fill flowable composites than for Z250. Furthermore, the speed of shrinkage based on the polymerization reaction differed between the materials. SDR and Venus flowables had the fastest rate and highest volumetric change. The small percentage of voids within the materials seemed not to have affected the volumetric change negatively.

Clinical significance: The manufacturers of bulk fill flowable composites advocate filling layers of 4mm. However, because of the high shrinkage values found in this study the use of the standard 2mm layer increments is recommended.

Keywords: Bulk fill flowable composites, Mercury Dilatometer, Volumetric change, Polymerization shrinkage, Filler particles, Resin Matrix – bis-GMA, TEGDMA, UDMA.

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ABBREVIATIONS

BHT: Butylated hydroxytoluene

bis-GMA: 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane)

EBADMA &EPBADMA: Ethoxylated bisphenol A dimethacrylate

ETMA: Ethyltriglycol methacrylate

HPMA: 3-Hydroxypropyl methacrylate

IQR: Interquartile range

Procrylat: 2,2-bis[4-(3-methacryloxypropoxy)phenyl]propane

PMMA: Polymethyl methacrylate

SDR: Smart Dentin Replacement

Si-OH: Silane coupling

TEGDMA: Triethyleneglycol dimethacrylate

UDMA: Urethane dimethacrylate

UV absorption: Ultra violet absorption

UDMA: Urethane dimethacrylate

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Volumetric change in dental restorative materials is the result of polymerization shrinkage as a result of polymerization reactions between monomers to form polymers (Venhoven, 1993. Loshaek, 1953. Patel, 1978). This volumetric change that takes place has been and remains a factor for concern for dental restorative resins. After polymerization has been completed the difference between the initial volume and the resultant volume is the volumetric change that took place. During the polymerization process the state of the non-polymerized composite change from the plastic to a viscous gel point. The gel point is where no more viscous flow can occur and finally the rigid post–gel phase is reached (Davidson, 1997). The collective decrease in volume, results in the volumetric change due to polymerization. Volumetric shrinkage cause forces on the cavity walls (Schneider, 2010). The percentage of volumetric shrinkage that takes place in part, will mainly determine the long term success of a restoration (Feiler, 1995).

This volumetric shrinkage became used under the umbrella term "polymerization shrinkage" in the literature. The organic matrix of the dental restorative material contains the monomer constituents. The organic matrix undergoes polymerization and the resultant volumetric change/shrinkage. Ever since 1935, when the first real step was made towards resin restorative materials volumetric shrinkage has been a problem. Dr. Bowen achieved a breakthrough in 1956 when he added filler particles and coupling agents reducing volumetric shrinkage. Polymerization shrinkage of even 2 percent in resin composites may generate enough tension to destroy the marginal integrity between the filling and the tooth structure which could result in a micro-leakage gap, post-operative sensitivity and/or the failure of the restoration (Feiler, 1995. Meredith, 1997. Alomari, 2001. Abbas, 2003).

Shortly after restoration placement post operative sensitivity can set in. Long term effect of volumetric change can result in restoration fracture and micro-leakage (Sakaguchi, 1992. Craig, 2002:68). Clinicians are always looking for restorative materials that will result in easier restoration placement that last longer and save time on placement. For these reasons the importance of volumetric shrinkage comparisons between the bulk fill flowable composites from different manufacturers marketed as bulk fill composites were considered for investigation. It is believed that such a comparative study will both provide information about the volumetric changes of the resin materials as well as provide an independent set of results on their volumetric changes, since there are no results available on the recently launched bulk fill resin materials (Ilie, 2011. Scientific Compendium SDR, 2011). The handling protocol of some new resins state “bulk fill” of 4mm layers. This independent comparison of volumetric change is important to see if the degree of volumetric shrinkage is low enough to revert away from the traditional 2mm layering technique to the 4mm increments as per manufacturer’s instructions.

This study is therefore very important considering that the properties of the bulk fill flowable composites contradict the findings in the literature of what characteristics a flowable composite should display. The literature suggests that in general - the higher the monomer content the more flowable the material. This aforementioned fact in turn results in the higher volumetric shrinkage and a faster conversion rate to the gel phase (Rees, 1989. Rueggeberg, 1995. Davidson, 1997. Condon, 2000. Silikas, 2000. Stansbury, 2000. Ge, 2005. Pfeifer, 2008. Goncalves, 2010).

The main academic aim of this study is to improve clinicians' understanding of how volumetric change, as a direct result from polymerization of the bulk fill flowable composites, compares to a well established composite. The results will provide guidance on how volumetric change influences the longevity of the restorative material. Polymerization shrinkage due to volumetric change could possibly be influenced by many factors. By subjecting all the restorative resins to the same testing environment standardization can be established.

The null hypothesis is that the apparent improvements made to the volumetric change of the bulk fill flowable composites will not be statistically significant to warrant a 4mm bulk layering compared to the widely accepted 2mm layering technique. The modified electronic mercury dilatometer will provide more insight to the volumetric change due to polymerization shrinkage. This volumetric change can be influenced by external factors such as temperature and pressure changes. The modified electronic mercury dilatometer is able to assess the polymerization process of the bulk fill flowable composite alone, without being affected by additional external influences. One such external influence that may have an effect upon volumetric change is the heat transfer from the curing unit. However, this effect is removed by the software of the modified electronic mercury dilatometer. Because the polymerization shrinkage occurs over a time period of about 35 seconds the computer records the progression of polymerization every 0.5 seconds up to the 35 second limit. The result can be viewed and compared between the different restorative resins. This provides insight into the slope of volumetric change/shrinkage for different time intervals. This information in conjunction with the total volumetric change due to polymerization shrinkage provides insight into the performance of the bulk fill flowable composites compared to the well established composite restorative materials. Some manufactures of the bulk fill flowable composites claim that a modulator was added to provide more control during the polymerization resulting in a 20% decrease of polymerization shrinkage (Scientific Compendium SDR, 2011:8). The material constituents are considered when the slopes that result from the volumetric change are compared.

The well established data from the literature for Z250 by 3M ESPE will be used as the control for the electronic mercury dilatometer. The results from the bulk fill resin restorative materials can then be compared to the results obtained from Z250.

The electronic mercury dilatometer used by the author has been shown to be an accurate apparatus for the determination of volumetric change

(Oberholzer, 2002). Mercury dilatometers on the contrary are sensitive to temperature fluctuations and the resultant pressure changes (Rees, 1989). For these reasons the desktop computer monitors the various system parameters continuously. The dilatometer may be programmed to analyze the pressure in the closed system for any chosen amount of time. For this study five seconds was chosen as sufficient time to establish whether any environmental changes were present. The modified electronic mercury dilatometer is housed in an incubator at a constant 25°C±1°C and has a thermostat monitoring the temperature (Rees, 1989. Puckett, 1992). Should any pressure fluctuations occur within the closed system in the five second interval prior the start of the experiment and the polymerization activation by the dental curing light the test specimen will not be polymerized and the computer will reject that reading.

1.2 LITERATURE REVIEW

1.2.1 Overview

Most formulations of the organic resin matrix contain base monomers like bis-GMA, EBPADMA, UDMA and TEGDMA. An increase in molecular weight leads to matrixes with lower shrinkage and improved strength. This is why the modification of bis-GMA was investigated (Ge, 2005). Surface modifications were required to firstly reduce the filler surface energy. This reduction of the surface energy is important for the filler dispersion and the reduction in hydrophilicity. By decreasing the hydrophilicity less water sorption occurs leading to color stability of the restoration. Secondly the surface modification aid in the covalent attachment between the matrix and the filler particles - this increases the strength of the chemical bond (Cramer, 2011).

Total volumetric change of dental resins are a combination of firstly, the polymerization reaction that results in the formation of a polymer chain from monomers. Secondly, the increase of the exothermic heat produced by the polymerization reaction and thirdly, light irradiance energy that is transferred to the dental resin (Hansen, 1993. Knezevi´c, 2001. Uhl, 2003. Sideridou, 2004. Knezevi´c, 2005. Bouillaguet, 2005. Mucci, 2009. Dogan, 2009).

Research was first conducted by Thompson et al (1979) to investigate the expanding co-polymers termed “Spiro-orthocarbonates (SOCs)” and “epoxies”. Unfortunately the bis-GMA from the adhesive bonding systems was not compatible with the composites made from the SOC’s (Thompson, 1979). In 1993 Eick et al set out to synthesize these expanding co-polymers. These co-polymers of Spiro-orthocarbonates

(SOCs) and epoxies were envisaged to result in non-shrinking matrixes for dental composites (Byerley, 1992. Eick, 1993). The expanding organic matrix will form part of the dental composites of the future due to the resultant 0.1-0.8% volumetric expansion (Eick, 1993). The water sorption within the oral cavity negatively affects the physical properties of SOC's. When the properties of Z250 and the SOC's material preparations are compared the water sorption of the SOC's (<50µg/mm³) are much higher than that of Z250 (13.02µg/mm³). The resultant tensile strength is lower for SOC's (29-48 MPa) than that of Z250 (49.95-66.35 MPa) (Sideriduo, 2003. Andresa, 2005). This drawback is the reason why SOC's have not been used in dental resins. Since 1993, there have been no further published articles on expanding co-monomers for the employment in dental composite resins.

During the early 90's Silorane ring opening monomers were investigated (Figure 1). There is however a lower shrinking composite on the market called Silorane by 3M. The oxaspirocyclic core of the monomer provides ring opening during polymerization, resulting in volumetric expansion. Unfortunately silorane materials *(Figure 1)* do not expand enough to overcome all the volumetric shrinkage and are not compatible with bis-GMA based monomers and therefore have their own adhesive system (Sadhir, 1992. Rockiki, 1992).

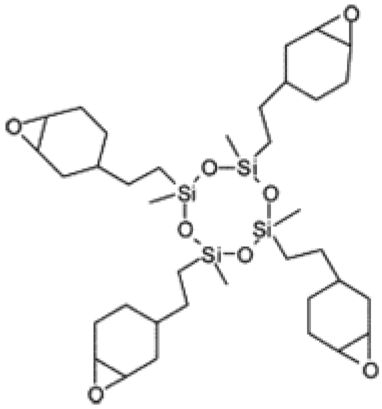


Figure 1: Silorane monomer

1.2.2 History of the development of dental composite materials

Around the 1840's Joseph Redtenbader discovered the acrylic acid. The acrylic resin was only developed into denture base materials in 1935 in Germany. During 1878 the introduction of aesthetic silicate cements was made by Fletcher. Followed by indirect acrylic fillings and then in the late 1930's unfilled direct resin fillings began to appear (Lee, 1985). During the 1940's and 1950's polymethyl methacrylate (PMMA) replaced silicates, but the large polymerization shrinkage during curing lead to microleakage due to 25% volumetric shrinkage *(Figure 2).*

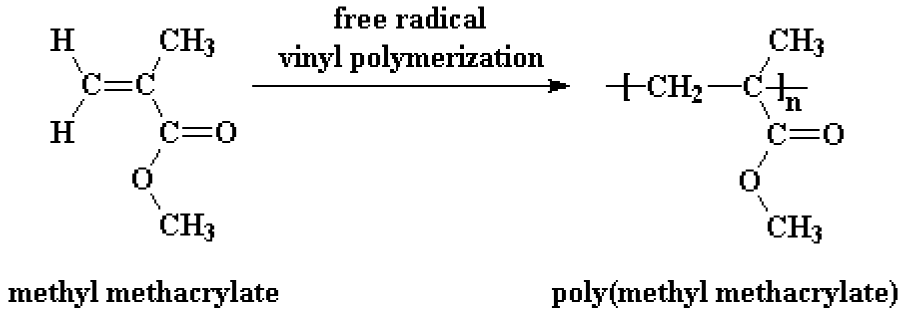


Figure 2: Free Radical polymerization of methyl methacrylate to poly (methyl methacrylate)

Quartz filler was added in an attempt to decrease the shrinkage and provide physical properties closer to that of tooth structure. Filler particles resulted in a decrease of the volumetric change due to polymerization, but the material still had poor wear, microleakage and staining of the restorations continued. The reason for the poor wear and staining was that the filler particles easily broke loose from the organic matrix as a result of the lack of a coupling agent between the filler particles and the PMMA resin matrix.

In 1956 Bowen introduced the first real step in improving resin dental materials when he experimented with quartz fillers in an epoxy resin *(Figure 3).*

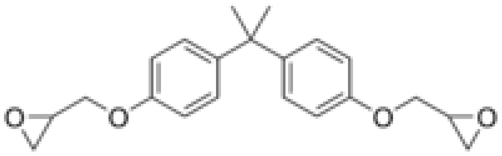


Figure 3: Epoxy resin

This combination of quartz and epoxy resin was successful in the laboratory but not in the oral environment due to the sensitivity of the epoxy to contamination of saliva, resulting in the material not curing. The epoxy group was abandoned and replaced with a dimethacrylate group called bis-GMA and became known as Bowen’s resin *(Figure 4)* (Bowen, Inventor 1956a).

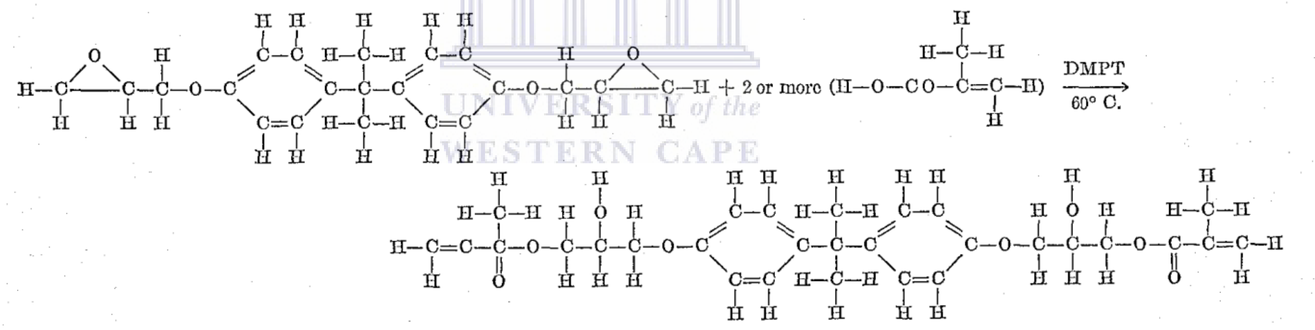


Figure 4: Diglycidyl ether of bisphenol A and dimethacrylate react to produce bisphenol A-glycidyl methacrylate (Bowen RL, Inventor 1956b).

The bis-GMA acrylic resin was found to be suitable as a binder of resin and filler for reinforcing the dental composite material (Paffenbarger, 1953). Polymerization shrinkage of bis-GMA was only a third of methyl methacrylate and as a non-volatile agent it also hardened rapidly in oral conditions (Bowen, 1956b). The commercially developed resin composite was born based on bis-GMA. It was complex in regard to its constituents. Bis-GMA was used in combination with other organic liquid monomers to form the organic matrix. The Inorganic filler portion of the resin composite consisted of filler particles in various shapes and sizes with polymerization initiators and inhibitors. Silane coupling agents joined the surfaces of the filler particles and the resin matrix. Stabilizers would aid in the prevention of discoloration, provided a shelf life and aided in the UV absorption (Bowen, 1968).

A short coming of bis-GMA based composites was the incomplete conversion of the methacrylate combination groups during polymerization (Ruyter, 1978). This lack of conversion in the polymerized cross linked polymer resulted in an un-reacted methacrylate amount of 30-50% (Ruyter, 1984).

1.2.3 Physical and Mechanical properties of dental composites

The volumetric change that results in the shrinkage of a dental restoration can affect the stress and strain that a restoration can absorb as well as the bond longevity on the cavity walls. Dental restorative resins have two very important functions. The first is restoring the damaged tooth structure that occurred from the disease process called dental caries. Secondly restorative materials are essential to restoring functionality of the tooth in terms of occlusion, mastication and aesthetics. The force applied to the restoration and tooth structure is measured in Newton (N) (Craig, 2002:68).

The concept of strength is an ideal mechanical property that can be described by any one or more of the following four properties *(Figure 5):*

1. Proportional limit: This is the limit just before where stress is not proportional to strain.

2. Elastic limit/strain: The maximum stress that a material will withstand without permanent deformation.

3. Plastic deformation/strain: Should the stress on the material become larger than the strain it can handle – failure will occur resulting in fracture.

4. Yield strength: A specific amount of stress that is required to produce a given amount of plastic strain (Anusavice, 2002:59).

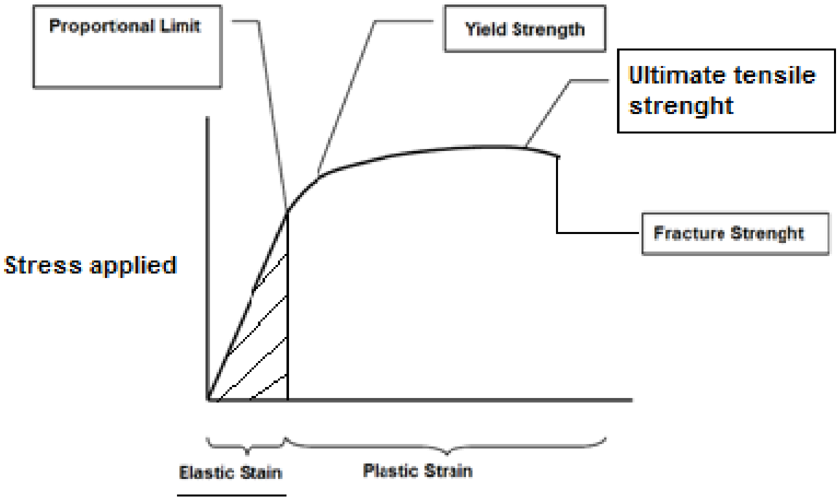


Figure 5: Stress-strain curve as determined by the application of tensile stress

Stress and strain are the two most important reactions of forces applied to a resin material. Stress and strain measure mechanical properties of materials

Strain is the amount of deformation that occurs when a force is exerted on a material. Strain can be measured in terms of change in length or as a percentage of the cross sectional area of the original dimensions.

Stress that occur on a restoration upon mastication is measured as the “Force” applied over the “cross sectional area”. Tensile stress, compressive stress and shear stress are all stresses that can occur in a material. Ultimate tensile strength is a measure of the total stress required to fracture a material. Strength of a material is not defined as the forces between individual atoms. Strength is rather the collective of inter-atomic forces over the entire specimen of material.

1.2.4 Chemistry of Dental Resins

Polymers comprise of long chains of monomer molecules. The carbon atom *(Figure 6)* or silicon atom *(Figure 7)* form the backbone of the chain.

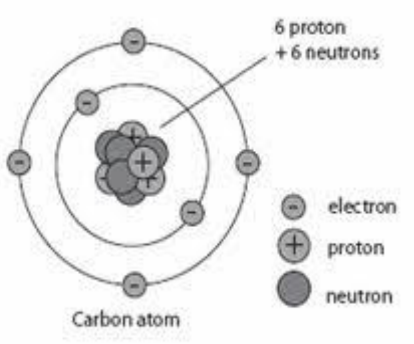


Figure 6: Carbon atom.

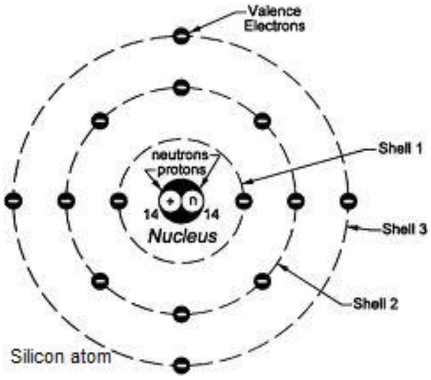


Figure 7: Silicon atom

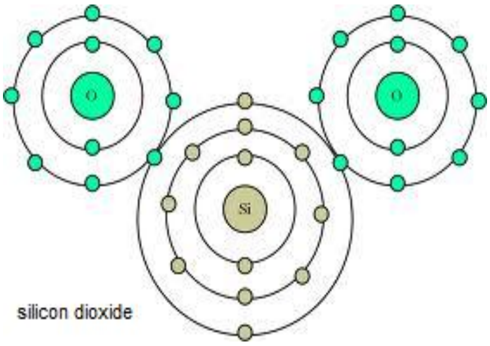


Figure 8: SiO_2

Carbon based polymers are known as organic polymers. Silicon dioxide also known as silica (SiO_2) is an inorganic polymer *(Figure 8).* The C-atom forms four sp^3 hybrid orbitals. In dental resins four valence electrons for the C-atom are required and form a hybrid configuration sp^3. Spatial structure of the polymers affects the flow of a material as well as the potential final size of a polymer. This change in size from multiple monomers to the final linked polymer is how the volumetric change occurs due to polymerization (Craig, 2002:186). Silicon dioxide serves as the base of the dental ceramics and dental resins. Silica (SiO_2) *(Figure 8)* can exist naturally in various forms namely quartz, cristobalite and fused silica. Silica can be manufactured in several forms including fused quartz, crystal, fumed silica (or pyrogenic silica), colloidal silica, silica gel and aerogel (Philips, 1982:395).

Polymerization is the process where smaller molecule chains (monomers) are activated/initiated to link together and form a larger macromolecule called a polymer *(Figure 9).*

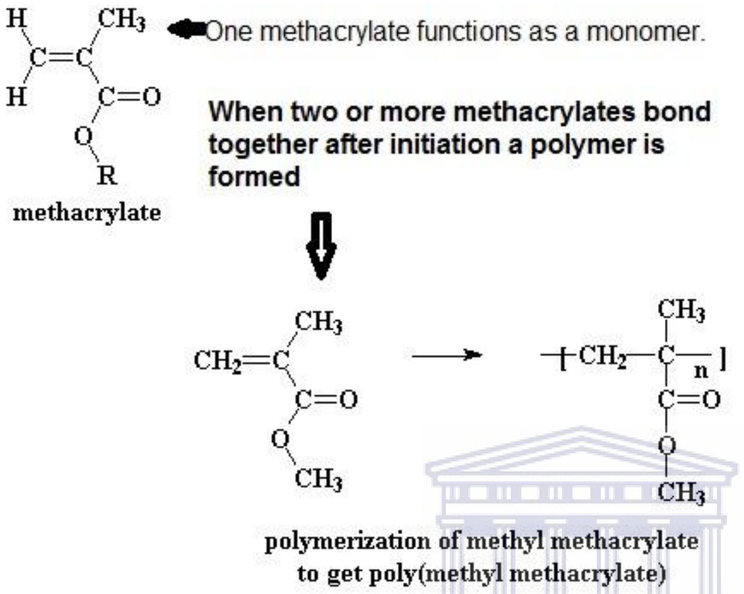


Figure 9: Two or more Methacrylate Monomers bind together to form a Poly (Methyl Methacrylate) polymer.

Anatomic arrangement and anatomic structure greatly affects the length of the chain that forms during polymerization. Greater physical properties are achieved with the longer final polymer chains (Anusavice, 2002:146). During the curing process known as polymerization, resin composites undergo shrinkage resulting in volumetric change. This polymerization process occurs through a free-radical mechanism (Silikas, 2000). During polymerization various polymer chains with side chains can form. Polymerization can occur in different directions namely cross linked, linearly linked and in a branched fashion *(Figure 10).* Cross linking of molecules result in a large molecule in comparison with molecules that link in a linear or branched fashion. The linear and branched linkage results in a more separate link. Therefore cross-linked molecules do not absorb as much fluids as the linear and branched molecules. Long linear molecules with only a few cross linkages have been found to undergo less polymerization shrinkage (Craig, 2002:186).

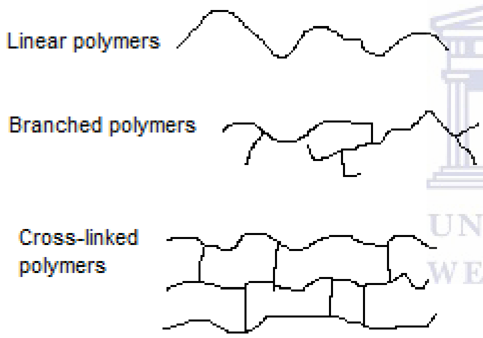


Figure 10: Representations of linear-, branched– and cross-linked polymers.

Polymerization is the formation of macromolecules by chemically joining monomers together. Two reactions can lead to polymerization namely Addition Polymerization and Condensation Polymerization. (Anusavice, 2002:154). Condensation polymerization joins two or more molecules together. The result is a byproduct for example alcohol, water, halogen acids and ammonia. The resulting byproduct is why the term condensation polymerization can be used. Dental resins are not formed via the condensation polymerization process and will therefore not be discussed in detail (Phillips, 1982:164). Dental resins make use of addition polymerization *(Figure 11).* Addition polymerization is when the monomers are activated one at a time and form a growing chain in sequence. (Anusavice, 2002:154). The following steps can be identified:

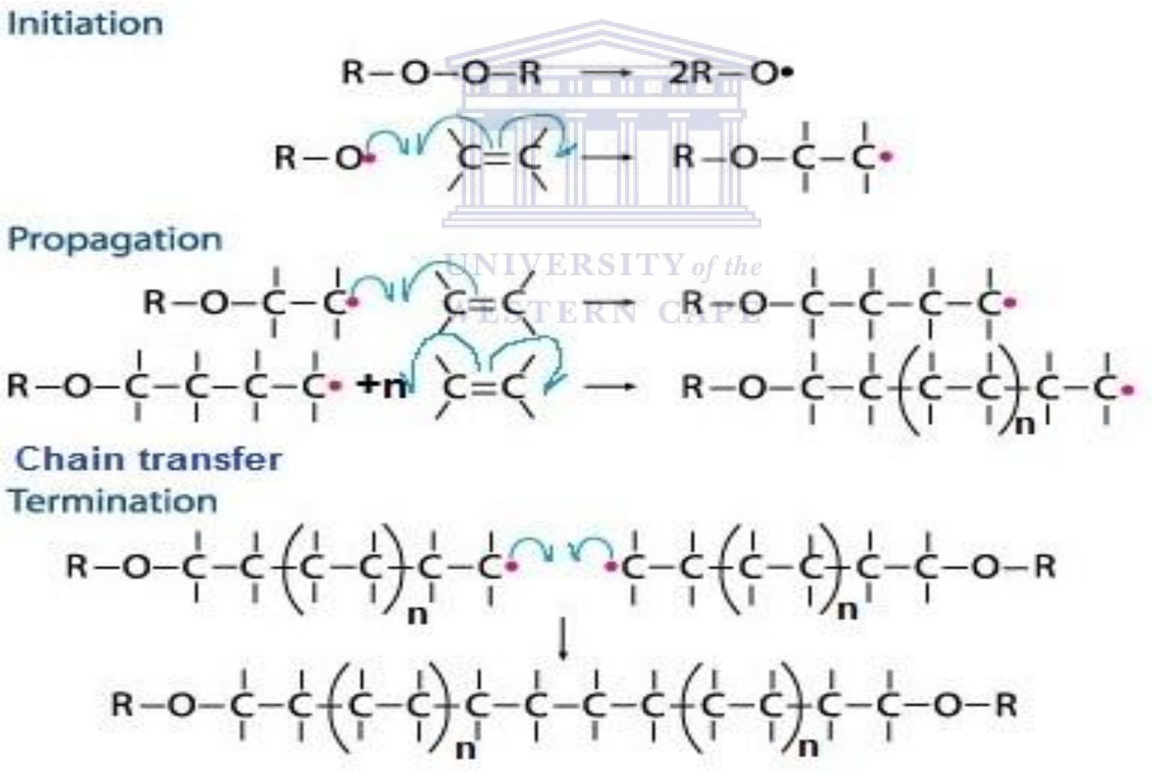
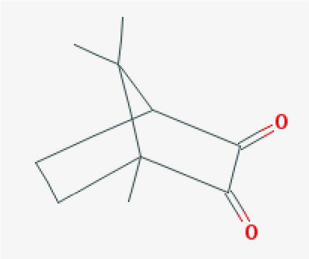


__Figure 11: Example of addition polymerization from Initiation to termination__

1.2.5 Stages of addition polymerization *(Figure 11)*

Addition Polymerization has four stages in the chain reaction: initiation/induction, propagation, chain transfer and termination. **Initiation/Induction** is controlled by activation and initiation of the polymerization process. Both an unsaturated double bond in the resin matrix and a source of free radicals are required for induction of polymerization. Activation of the free radicals requires a source of energy. This source of energy is supplied by the application of a dental curing light with a peak wavelength at 468 nm in the case of bis-GMA dental resins. The camphorquinone *(Figure 12)* or an organic amine is the initiators that provide the initial free radicals to start polymerization. The camphorquinone is activated at a minimum wave length of 400-500 nm.

	
Molecular Formula: $C_{10}H_{14}O_2$	Molecular Weight: 166.21 g/mol
Figure 12: Camphorquinone	

A free radical is any atom or group of atoms possessing an unpaired electron. The initiation process occurs when the electron from the free radical from the camphorquinone pairs with one electron of the un-saturated double bond, leaving one electron from the double bond unpaired. Only 0.2% per weight or less of champhorquinone (CQ) is required to initiate the polymerization process. Another initiator system that can be employed is the aliphatic amine initiators. Aliphatic amines are added to the resin in a concentration of 0.15%wt. The organic amine has a double bond that accelerates the polymerization reaction with champhorquinone (Stanbury, 2000). Aliphatic amines are used in light cured resins and are more colour stable compared to the aromatic amines in chemical cured resins. Ultraviolet (UV) absorbers minimize colour changes caused by oxidation. Inorganic oxides in small quantities have to be added to match various tooth shades (Craig, 2002:236). Inhibitors are required to minimize or prevent polymerization during storage and during the placement of the resin in the tooth. This inhibition is required until the activator is added/provided - usually blue light. The inhibitor reacts with the free radicals that occur until all the initiator has been used by the free radicals. Then only will the initiation of polymerization by the propagation step occur. Butylated hydroxytoluene (BHT) is an example of an inhibitor. Concentration of 0.01 wt % is sufficient. The degree of conversion (DC) is reduced as the layers of resin increase in thickness. **Propagation:** During propagation the electron of the free radical from the un-saturated double bond, formed by the induction process, is available to bond with another un-saturated double bond resulting in yet another free radical to continue this growth of the polymer molecule. During the curing process resin composites undergo dimensional shrinkage, inherent manifestation in materials polymerizing through a free-radical mechanism (Silikas, 2000). The polymerization process continues to grow the polymer through propagation until chain transfer, termination or depletion of the compounds stop the polymerization process *(Figure 13).*

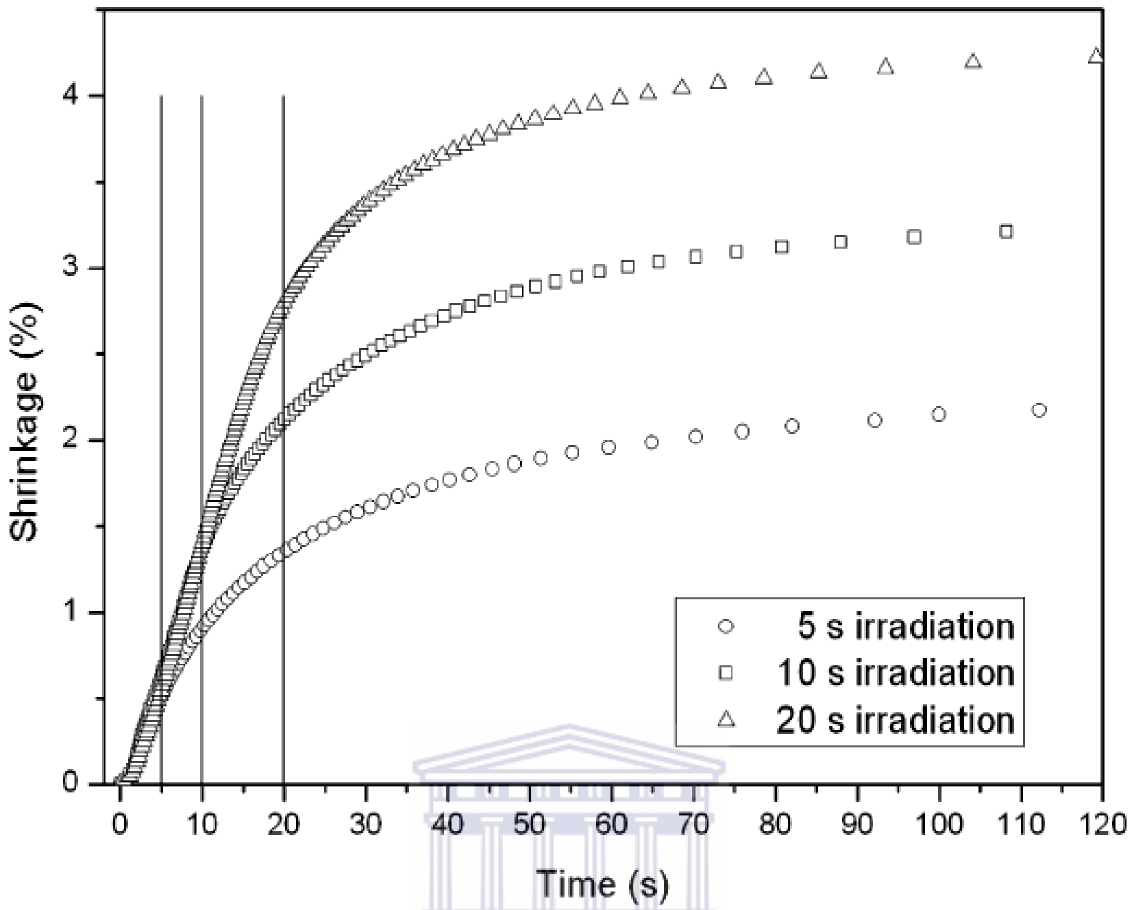


Figure 13: A typical diagram obtained during irradiation initiation (for 5, 10 and 20 seconds) of a dental resin and the percentage shrinkage that occur due to this polymerization reaction (Mucci, 2009).

Figure 13 indicates that the irradiance source provides the activation of the free radicals via the camphorquinone at 11,5mW/cm² for a set time period of 5, 10 or 20 seconds. Each vertical line demarcates the length of irradiance exposure. Note that the polymerization process continues irrespective when the irradiance source has been turned off *(Figure 13).*

This clearly indicates the process of propagation (Mucci, 2009). **Chain transfer** can occur in two ways. It occurs when a free radical approach the methyl methacrylate molecule where there is active propagation and then a hydrogen atom is transferred to it. The growth of this macromolecule will now terminate with the new double formation resulting from the transferred hydrogen atom. The remaining free radical without its hydrogen atom can continue to participate in the chain growth of propagation at another un-saturated double bond. Another type of chain transfer is when the un-saturated double bond interacts with an active propagation. The resulting free radical now approaches the previously un-saturated chain and this chain now becomes active to continue propagation. The original propagation molecule now becomes passive. **Termination** can result from either method of chain transfer. Usually in addition polymerization direct coupling of two free radical chain ends result in termination. Alternatively direct coupling of both free radical molecules can combine and become deactivated by the formation of a covalent bond *(Figure 14).*

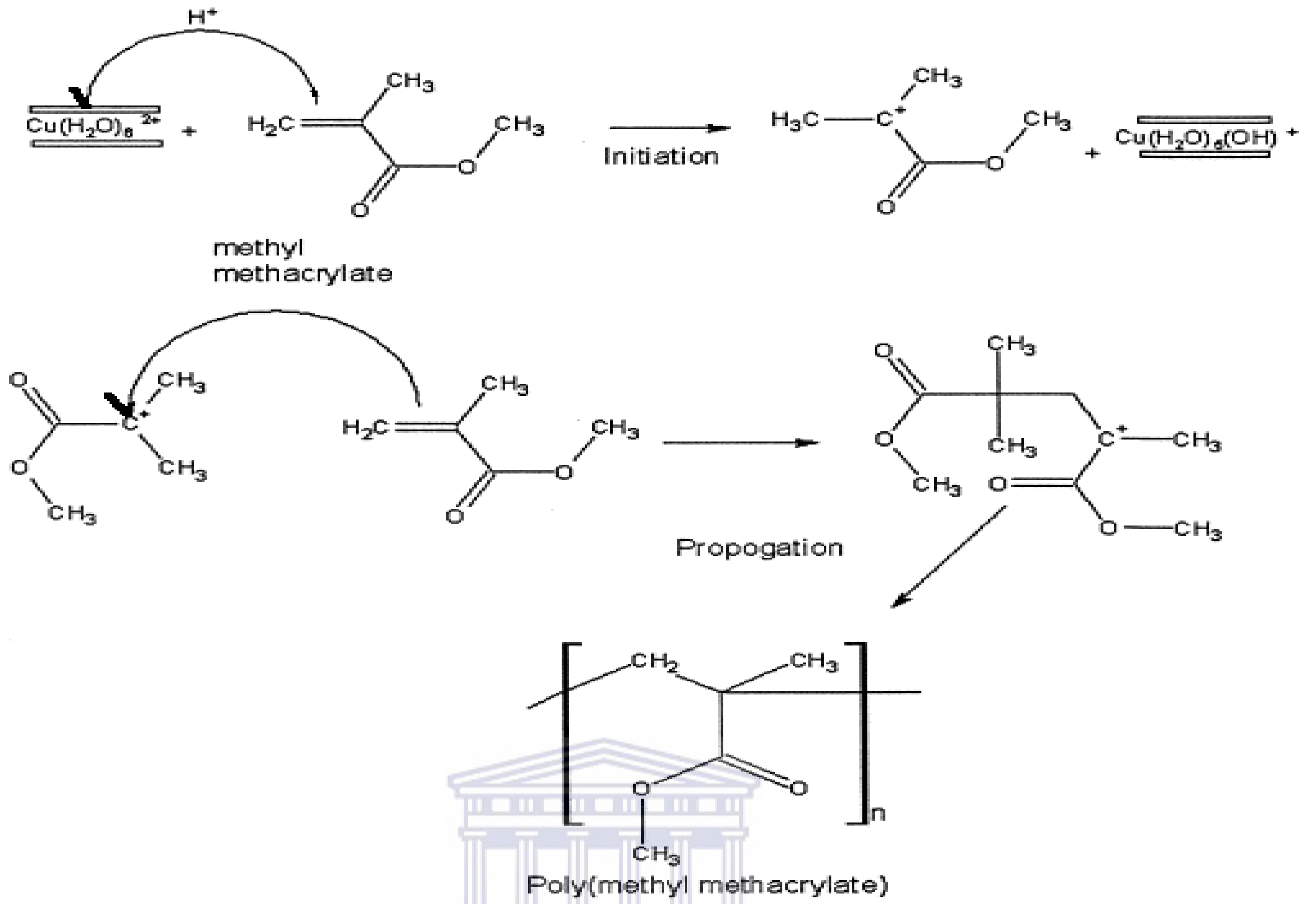
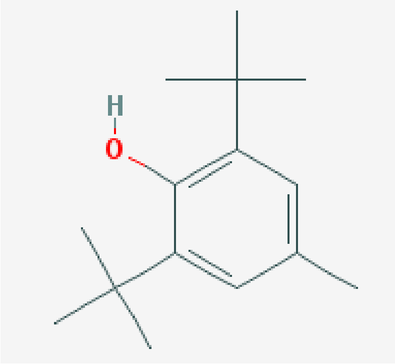


Figure 14: Representation of the polymerization reaction of Methyl Methacrylate to Poly-Methyl Methacrylate

Without the addition of inhibitors like butylated hydroxytoluene (BHT) in the composite material polymerization is inevitable to occur while the material is in storage *(Figure 15).* Hydroquinone is an inhibitor that inhibits polymerization completely in the absence of an initiator and retards polymerization in the presence of an initiator. Oxygen from the atmosphere can react with free radicals in the resin matrix and retard the reaction and degree of polymerization (Phillips, 1882:164).

	
Molecular Formula: $C_{15}H_{24}O$	Molecular Weight: 220.35046 g/mol
Figure 15: BHT (Butylated Hydroxytoluene)	

1.2.6 Organic resin matrix

The resin matrix can consist of various combinations of monomers, co-monomers, photo-initiators, co-initiators, inhibitors, ultraviolet absorbers, colour pigments, photo stabilizers and modulators. Oligomers most commonly employed and known in dental composites is bisphenol A-glycidyl methacrylate (bis-GMA). The full chemical name is 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane *(Figure 16);* Urethane dimethacrylate (UDMA) *(Figure 17)* and Triethyleneglycol Dimethacrylate (TEGDMA) *(Figure 18)* (Gugenberger, 2000). The organic matrix that is most utilized in dental resins are the bis-GMA (and the diluents TEGDMA combination) (Antonucci, 1997).

The volumetric changes of un-filled bis-GMA /TEGDMA combinations are much higher than the commercially available composites. The reason is the inorganic filler particles do not partake in the polymerization process as they are inert and therefore, reduces the volumetric change (Mucci, 2009).

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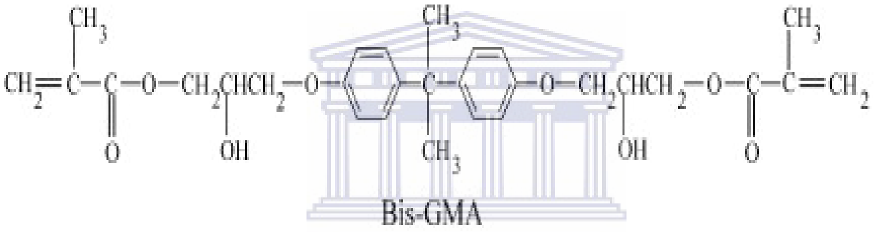
<tr><td colspan="2"> </td></tr>
<tr><td>Molecular formula: $C_{29}H_{36}O_8$</td><td>Molecular weight: 512.59g/mol</td></tr>
<tr><td colspan="2">Figure 16: Bis-GMA (2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane)</td></tr>
</table>

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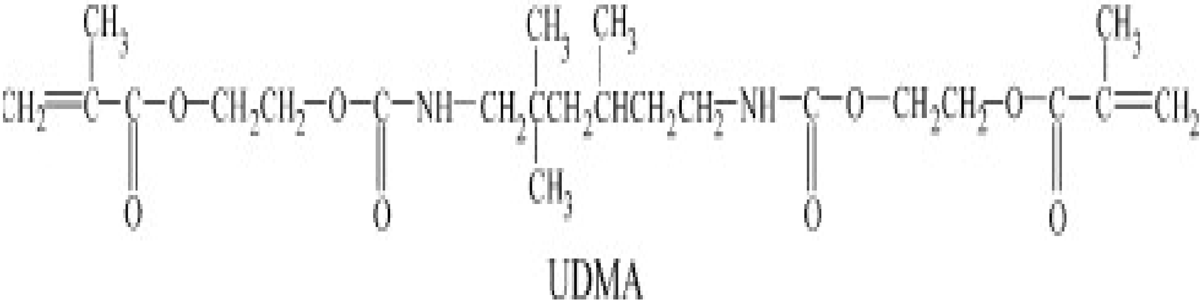
<tr><td colspan="2">

$$CH_2{=}\overset{CH_3}{\overset{|}{C}}-\underset{\underset{O}{\|}}{C}-O-CH_2CH_2-O-\underset{\underset{O}{\|}}{C}-NH-CH_2\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_2-NH-\underset{\underset{O}{\|}}{C}-O-CH_2CH_2-O-\underset{\underset{O}{\|}}{C}-\overset{CH_3}{\overset{|}{C}}{=}CH_2$$</td></tr>
<tr><td>Molecular Formula: $C_{22}H_{36}N_2O_8$</td><td>Molecular Weight: 470.55 g/mol</td></tr>
<tr><td colspan="2">*Figure 17: UDMA (Urethane dimethacrylate)*</td></tr>
</table>

<table>
<tr><td colspan="2">

$$CH_2{=}\overset{CH_3}{\overset{|}{C}}-\underset{\underset{O}{\|}}{C}-O-(CH_2CH_2O)_3-\underset{\underset{O}{\|}}{C}-\overset{CH_3}{\overset{|}{C}}{=}CH_2$$</td></tr>
<tr><td>Molecular Formula: $C_{14}H_{22}O_6$</td><td>Molecular Weight: 286.32 g/mol</td></tr>
<tr><td colspan="2">*Figure 18: TEGDMA (Triethyleneglycol dimethacrylate)*</td></tr>
</table>

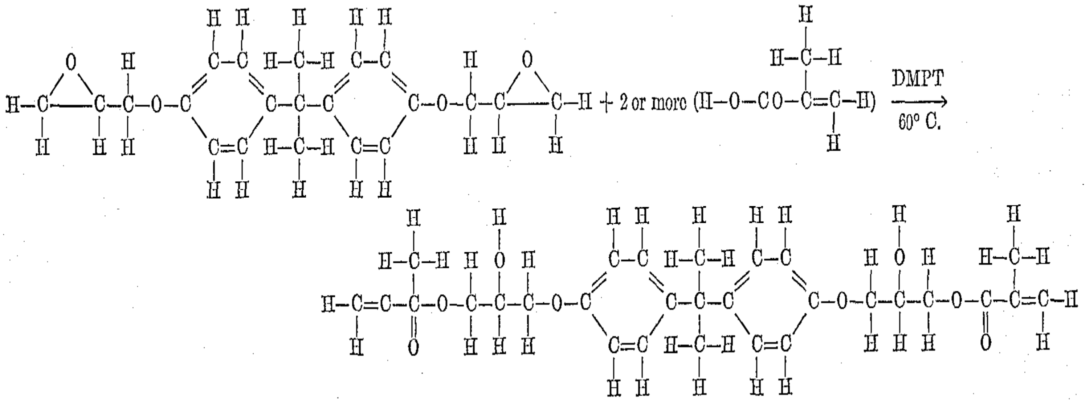
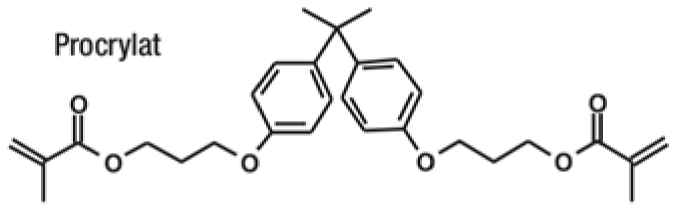


Figure 19: Aromatic ester of dimethacrylate

Figure 19 represents an aromatic ester dimethacrylate that is synthesized from an epoxy resin (ethylene glycol of bisphenol A) and methyl methacrylate (Anusavice, 2002:166). The two molecules of glycidyl methacrylate are added to one molecule of bisphenol-A completing the synthesis of bis-GMA *(Figure 16)* (Anusavice, 2002: p233). The two –OH groups of bis-GMA *(Figure 16)* form hydrogen bonds between the monomers and therefore makes it extremely viscous. Bis-GMA has two aromatic methacrylate groups reducing the rotation of the bis-GMA molecule. Therefore only one methacrylate group participate during polymerization. The other methacrylate group that does not participate continues to form a branch or pendant group along the polymer chain. Cross linking can, but not always occur with adjacent chains via the other methacrylate group (Anusavice, 2002:166). This is why procrylate *(Figure 20)* has been used in Filtek bulk fill. Procrylate has a reduced viscosity due to the lack of the pendant hydroxyl (-OH) groups.

	
	Molecular weight: 480.59 g/mol
Figure 20: Procrylat (2,2-bis[4-(3-methacryloxypropoxy)phenyl]propane)	

Viscosity is the resistance a fluid has against flow. The SI physical unit of viscosity is the Pascal-second (Pa·s). The SI unit is defined: If a fluid with a viscosity of one Pa·s is placed between two plates and one plate is pushed sideways with a shear stress of one Pascal, it moves a distance equal to the thickness of the layer between the plates in one second (Serway,1996). Honey (2-10 Pa·s) for example has a higher viscosity than water (0.001 Pa·s 25°C) (Kestin, 1987. Li, 2013).

The high viscosity of bis-GMA (628 Pa·s 25°C) and molecular weight (512.59 g/mol) results in lesser degree of freedom and a decreased contraction rate in the bis-GMA molecule than in other less viscous monomers like bis-EMA 50-800 Pa·s, UDMA 5- 10 Pa·s, TEGDMA 0.1 Pa·s (Moszner, 2002).

Viscosity is the resistance against the flow of the resin dental material while still in its plastic form. After activation of the polymer the plastic material become rigid to remain in its solid state. The constituents of the resin material in terms of filler content and resin matrix play a large role in the viscosity of the material (Anusavice, 2002: Chapter 3).

The conversion of the organic matrix and filler content by weight play the largest role in polymerization irrespective the mode of the light source used. This is true provided the intensity of the curing unit is more than 400mW/cm^2 (Yazici, 1999. Nalcaci, 2007). The degree of conversion has been shown by Braga et al (2002) to be proportional to the volumetric shrinkage of the composite (Braga, 2002).

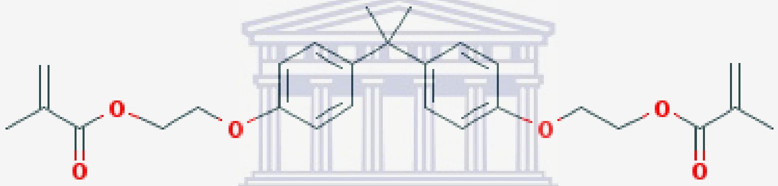
Shrinkage values for bis-GMA and TEDMA alone without any filler particles were reported as 52% and 12.5% respectively (Stansburg, 1992. Braga, 2005). Composites generally shrink between 2% and 3% (Labella, 1999).

In an attempt to make the bisphenol A-glycidyl methacrylate (bis-GMA) less viscous it can be blended with triethyleneglycol dimethacrylate

(TEGDMA) to achieve a consistency that can be manipulated easier in the clinical setting.

TEGDMA also has a lower viscosity and increased flexibility for reacting with both methacrylate groups and has been used extensively to reduce the viscosity of bis-GMA. dimethacrylate (eg. TEGDMA) results in extensive cross-linking of the base monomer leading to an increase in strength and rigidity (Anusavice, 2002:402). TEGDMA has high shrinkage due to high double bond formation during polymerization, therefore TEGDMA is used in very small quantities (1-5%) compared to bis-GMA (20-60%) (Stansbury, 2001). Bis-GMA and UDMA have nearly five times the molecular weight compared with methyl methacrylate.

Without this combination of the less viscous TEGDMA, more viscous monomers with bis-GMA the wet ability of the filler will be very low (Schmalz, 2009). The two free hydroxyl-groups of bis-GMA results in it being hydrophilic. An important aesthetic factor for a restoration is colour stability and therefore the fluid absorption must be limited for the restoration to remain aesthetically pleasing. Bis-GMA has a high affinity for water and in order to make the hydrophilic bis-GMA more hydrophobic, less hydroxyl groups must be present. This can be achieved through ethoxylation of the bis-GMA. Ethoxylation result in a less hydrophilic resin. Ethoxylation of bisphenol-A is when ethoxy groups are added to bisphenol-A at various ethoxylation degrees. The final methacrylation process results in a material that is less susceptible to fluid absorption. This is known as ethoxylated bis-GMA. Bis-EMA *(Figure 21),* bis-EMA(6) *(Figure 22),* EBADMA and EPBADMA are all examples of ethoxylated bis-GMA. Bis-EMA is less viscous than the bis-GMA due to the lack of hydroxyl groups (Filho, 2007).



Molecular Formula: $C_{27}H_{32}O_6$	Molecular Weight: 452.53 g/mol

Figure 21: Bis-EMA (Ethoxylated bis-phenol A dimethacrylate)

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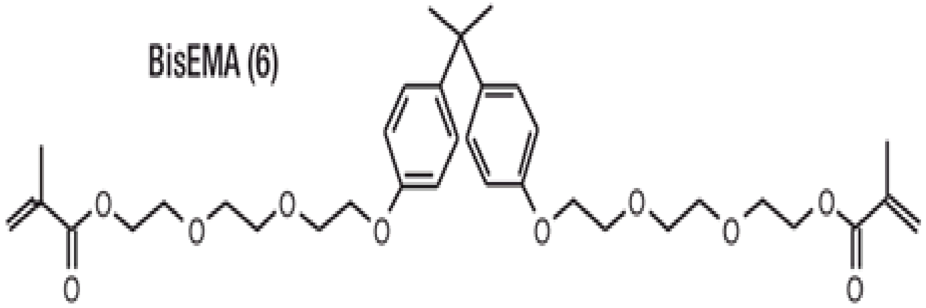
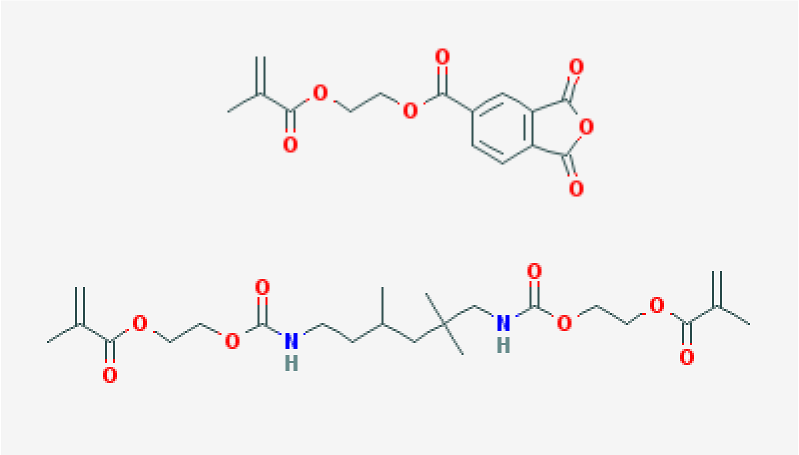
<tr><td colspan="2">
</td></tr>
<tr><td></td><td>Molecular weight: 496.58 g/mol</td></tr>
<tr><td colspan="2">Figure 22: Bis-EMA(6) (2,2-bis[4-methacryloxypolyethoxyphenyl)propane]</td></tr>
</table>

A base monomer has a larger molecular weight resulting in less polymerization shrinkage and the lower viscosity monomer has a greater degree of freedom to assist in improving the handling properties and the formation of copolymer chains. The organic matrix that is utilized most in dental resins is the combination of bis-GMA with UDMA and the diluent TEGDMA.



Molecular Formula: $C_{38}H_{50}N_2O_{15}$

Molecular Weight: 774.8 g/mol

Figure 23: TEGDMA/UDMA copolymer (1,2-Ethanediylbis(oxy-2,1-ethanediyl) 2-methyl-2-propenoate polymer with 7,7,9(or 7,9,9)-trimethyl-4,13-dioxo-3,14-dioxa-5,12-diazahexadecane-1,16-diyl 2-methyl-2-propenoate)

Due to the high water sorption of this combination and the low conversion rate that results in the decreased polymerization shrinkage the service life of these composites are affected. When the organic matrices of bis-GMA, EBADMA and UDMA combined with TEGDMA were compared by Antonucci (1993) at similar diluent concentrations, UDMA resins had significantly more polymerization shrinkage than bis-GMA and EBADMA. However, the higher concentration of EBADMA that could be achieved in the organic matrix combination with TEGDMA resulted in the lowest polymerization shrinkage. The UDMA and

EBADMA resin systems with the addition of relatively small amounts of TEGDMA show higher degrees of conversion and lower polymerization shrinkages than the 50% bis-GMA and 50% TEGDMA combinations. This was a great leap forward in a reduction of polymerization shrinkage and water sorption (Antonucci, 1993). UDMA reduces water sorption and polymerization shrinkage while enhancing the mechanical properties against wear of the resin matrices (Yap, 2000).

Non-functional monomers can contribute to a lower degree of shrinkage. 3-hydroxypropyl methacrylate (HPMA) and ethyltriglycol methacrylate (ETMA) are examples of non-functional monomers. In order for the non-functional monomers to result in a decrease in volumetric change the levels of HPMA and ETMA must theoretically be as high as 40% in weight to be considered a good mixture with bis-GMA. However, in reality at this high level volumetric shrinkage is promoted (Labella, 1998).

TEGDMA has a long flexible chain and when selected as a diluent with bis-GMA the combination results in plasticity without compromising neither strength nor hardness. UDMA is a monomer chain with one or more urethane group and two methacrylate end groups. UDMA can be added to resins to improve resistance to wear and reduce the absorption of water. To prevent hydrogenation over time TEGDMA is mixed with UEDMA (Filho, 2007). UDMA is a monomer with less shrinkage and better flexural strength than bis-GMA and have a decreased viscosity. UDMA has a molecular weight that is relatively close to bis-GMA. UDMA has a higher conversion rate than bis-GMA due to its weaker intermolecular bonds resulting in an increased flexibility (Sideridou, 2003. Floyd, 2006. Cynthia, 2006).

Conversion is the process that occurs during polymerization where the monomers become a polymer. Conversion rate is the rate at which the double bonds open to provide a free radical to participate in the polymerization process. The rate of conversion determines the rate of volumetric change. Resin based composites has a degree of conversion between 35% on 77% (Schmalz, 2009). The constituents of the organic resin matrix play a large role in the polymerization stress and conversion rate. The filler content however play an important role in polymerization shrinkage and the modulus of elasticity. According to Goncalves et al (2011) shrinkage and conversion are significantly related to polymerization stress. The suggestion was made that if the matrix is altered to achieve a reasonable degree of conversion a lower polymerization stress can be achieved without changing the filler content

(Goncalves, 2010). The degree of conversion is a large determining factor of volumetric shrinkage (Bouschlicher, 2000).

The degree of conversion is proportional to volumetric shrinkage and determined by the organic matrix combination (Braga, 2005). Because of the filler particles not taking part in polymerization they still influence the percentage shrinkage and many physical properties. Polymerization stress has a direct correlation with polymerization shrinkage. Polymerization stress and polymerization shrinkage shows an inverse relationship to the filler content (Goncalves, 2010). The larger the degree of conversion the larger the polymerization shrinkage (Asmussen, 1998).

This means that a restoration that employs lower polymerization shrinkage will not ensure sufficient force distribution in the restoration to the filler particles. In order to increase the strength of the bond between the filler particle and the resin matrix a silane coupling (Si-OH) agent must be added around the filler particle. They assist in transferring forces from the matrix to the more rigid filler particles. In order to bind the filler to the organic matrix a coupling agent must be added around the filler. The most effective coupling agent for resin materials containing bis-GMA, TEGDMA, UDMA is an organosilane called 3-

(trimethoxysilyl)propyl methacrylate because it binds to the filler particles as well as the organic matrix *(Figure 24)* (Ozcan, 2004).

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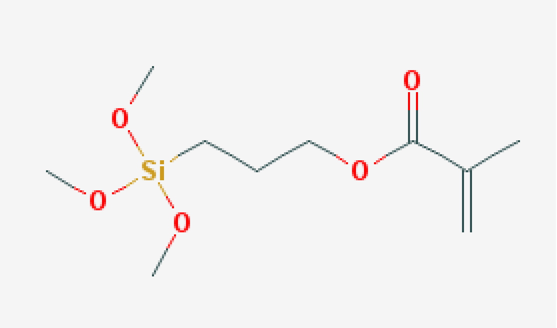
<tr><td colspan="2">
</td></tr>
<tr><td>Molecular Formula: $C_{10}H_{20}O_5Si$</td><td>Molecular Weight: 248.34 g/mol</td></tr>
<tr><td colspan="2">*Figure 24: 3-(trimethoxysilyl)propyl methacrylate)*</td></tr>
</table>

Stresses from masticatory forces can only transfer from the inorganic filler particle to the organic matrix if a coupling agent is present around the filler particle. Due to the stiffness of the bis-GMA molecule it has a lower rotation and therefore less matching with other reactive methacrylate groups during polymerization – this results in a lower degree of conversion.

Titanates and zirconates can also be used as coupling agents for composite filler particles. Currently it is only used in the petrochemical industry for fiber glass and various adhesive composite materials. They are different from silanes used for dental composites in the fact that titanates and zirconates are coupling agents that work via proton (H^+) bonds with no condensation process unlike silanes that require hydroxyl (OH^-) group to bond to on various substrates with a hydrolyzing reaction *(Figure 25).*

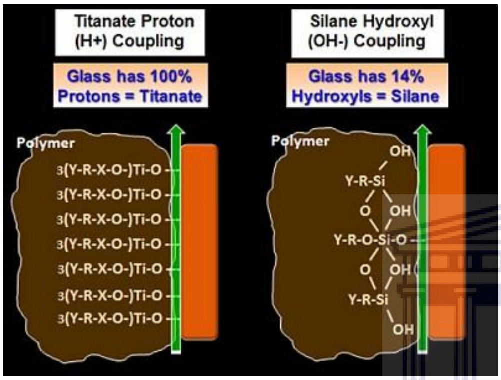


Figure 25: Indicating Titane and Silane coupling to glass

(http://www.4kenrich.com/content/home-page/titanates-zirconates-silanes.html)

Coupling agents for dental composites are made with methoxy groups ($-OCH_3$) *(Figure 25).* Methoxy is one of the constituents of organosilanes. The methoxy groups react with the inorganic filler by hydrolyzing with the methoxy group. The methoxy groups also react with the unsaturated organic matrix groups of the oligomer during polymerization (Craig, 2002:33).

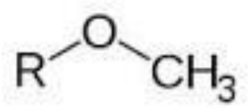


Figure 26: Methoxy group

This coupling process between the coupling agent around the filler particle and the organic matrix is completed when the covalent bonds are formed. The better the coupling the better the performance of the resin material (Anusavice, 2002:403). Organosilanes are designed to chemically bind to the matrix and the filler phases. Coupling agents in dental resins result in improved force distribution within the dental resin and therefore, decrease the occurrence of filler fracture during function of the restoration (Brown, 1980. Calais, 1988. Mohsen, 1995). Coupling agents decrease water sorption due to the hydrophobic nature of silane coupling agents (Nishiyma, 1991). Poly-functional silanes were produced in an attempt to improve long term hydrolytic stability at the polymer and silica interface. The nanocomposites require an increased volume percentage of organosilanes in order to coat the increased surfaces area. This is one reason why nanocomposites have a decreased water sorption (Nishiyma, 1987. Calais, 1988. Wilson, 2005. Wilson, 2006).

1.2.7. The importance of volumetric change due to polymerization shrinkage

During the curing process resin composites undergo dimensional shrinkage, inherent manifestation in materials polymerizing through a free-radical mechanism (Silikas, 2000). Composites generally shrink between 2% and 3% (Labella, 1999). After polymerization is triggered contraction stress start to build-up within seconds due the speed of polymerization even though a low initial conversion rate was achieved (Calheiros, 2004). The composite is rigid but conversion continues resulting in internal stresses and polymerization stress to increase (Kannurpatti, 1997). Several studies with curing lights attempted to reduce these internal stresses. The technique used was called the soft start technique. The light curing process was started a lower intensity and the light intensity gradually increase. The strain within the dental resin decrease, due to the rigid set of the resin material being reached slower (Sakaguchi, 1998. Watts, 1999. Silikas, 2000. Emami, 2003).

Unfortunately the reduction in reaction rate of polymerization did not relate in the reduction of contraction stress on the cavity walls, since the volumetric change remains the same as with traditional curing technique of full intensity from the first second (Bouschlicher, 2000. Braga, 2002). Reducing the intensity of the light emission to allow slow reaction rates have an impact on the visco-elastic properties of the composite material, since there is an increased conversion of more diluent monomers with an increased density of carbon double bonds (Feilzer, 2003).

The decreased viscosity of TEGDMA compared to bis-GMA also result in an increase of conversion (Ferracane, 1986). Therefore, conversion and its resulting volumetric change are the most important factors in contraction stress development in cured composites.

Due to an increase in filler content of packable posterior composites the contraction stress became directly proportional to filler content regardless of the matrix (Condon, 2000. Chen, 2001. Calheiros, 2000).

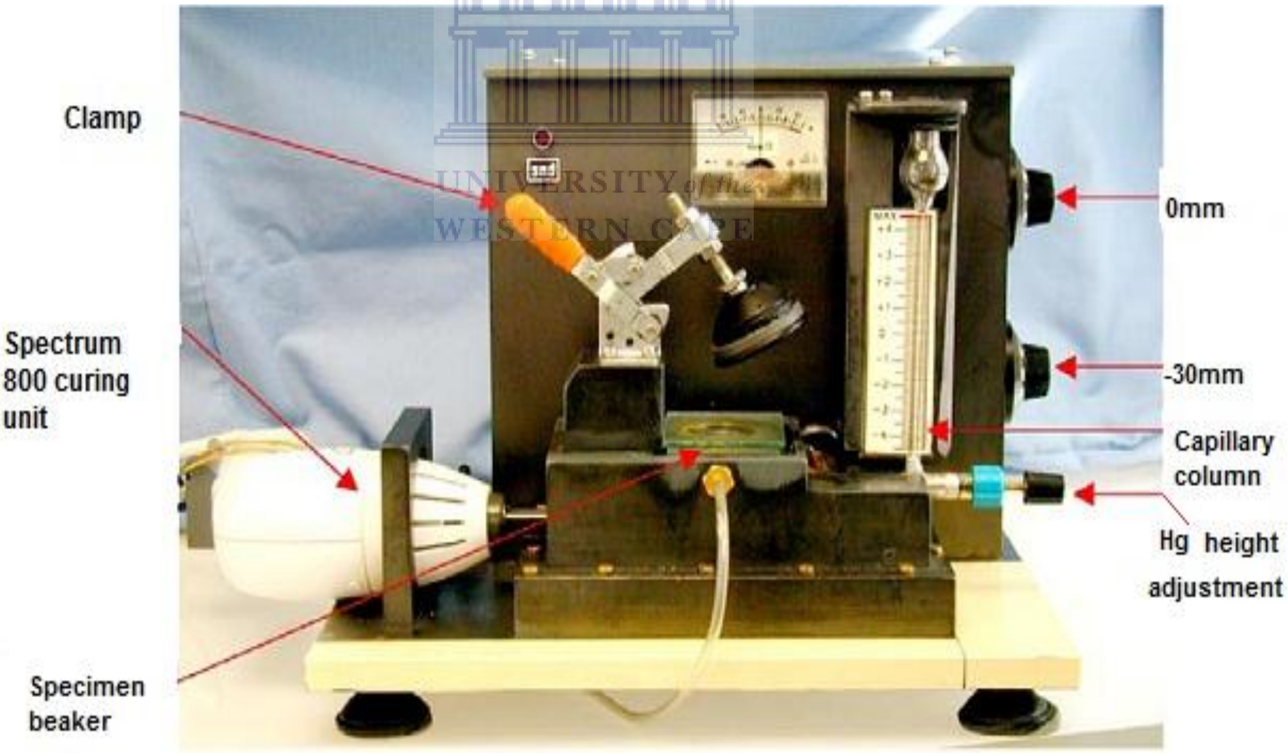
Therefore, the filler content decreases the volumetric shrinkage to some extent, improving the overall properties of the dental resin.

1.2.8. Methods of measuring volumetric change

Volumetric change is the determining factor in the degree of polymerization shrinkage and various techniques became available to measure the exact volumetric changes that occur during polymerization.

Different techniques can be utilized to determine volumetric change due to polymerization shrinkage. Volumetric techniques employed are the mercury dilatometer, water dilatometers and a pycnometer (De Gee, 1993. Cook, 1999. Watts, 1991). Linear techniques are Watts or ACTA. Jacquot et al (2001) developed a new linear technique where resin was extruded in a cylindrical shape (6mm long and 2mm in diameter) on a Teflon surface with two fluorescent zones 3mm apart. A one millimeter area in diameter was used as a reference point for the barycentres. The shrinkage is deduced by comparing the two barycentres under an optical microscope with specially developed computer software (Jacquot, 2001).

The mercury dilatometer *(Figure 27)* has a capillary tube where the volumetric change can be visualized during polymerization of the composite but due to concerns over mercury vapors a water dilatometer was developed. However, it was found that water clung to the sides of the capillary tube due to the difference in the surface tension of water and that of glass which could cause readings to be inaccurate. Normally the disadvantage of the dilatometers is that they are extremely sensitive to variations in temperature (Lai, 1983. Penn, 1986). However, Oberholzer et al (2001) developed the electronic mercury dilatometer for use at the University of the Western Cape Oral and Dental Research Institute *(Figure 27)* (Oberholzer et al, 2001). One of the advantages of this dilatometer was that the change of the mercury height in the capillary could be measured electronically, instead of manual viewing-removing human error. Furthermore, the electronic dilatometer enables measurements to be made on samples regardless of their shape and size. It was concluded that the exothermic reaction from the small sample used was negligible and did not affect the volumetric change. The additional volumetric change that occurs due to the light source could also be determined and the real volumetric change calculated (Oberholzer, 2001).



<u>*Figure 27: Modified Mercury Dilatometer as constructed by Stellenbosch Electronic Services (Oberholzer, 2002).*</u>

The mercury dilatometers are sensitive to fluctuation in room temperature as well as the heat radiating from the curing light has an effect on the liquid in the dilatometer, which in turn influences the reading. In 1993, De Gee introduced a modified linometer that was not sensitive to temperature fluctuations. De Gee compared the results from his modified linometer to that of mercury dilatometers and found no significant difference (De Gee, 1993). Cook at al developed a gas pycnometer that was useful in materials where water altered the volumetric shrinkage. The disadvantage was that only a final amount of volumetric shrinkage could be determined (Cook, 1999). Yu–Chih Chiangac et al (2010), developed a method to experimentally determine and visualize the direction of polymerization shrinkage – namely high-resolution micro-computed tomography. This method is currently only used to determine direction of volumetric shrinkage (Chiangac, 2010). The result for volumetric shrinkage obtained from video imaging has been shown to be comparable to that of a mercury dilatometer (Sharp, 2003). The dimensional change that is measured by the electronic mercury dilatometer is linear and the volumetric change is the total shrinkage that occurred between pre- and the post gel phases (Loshaek, 1953. Pucket, 1992. Lai, 1993. Attin, 1995. Rueggeberg, 1995).

From the literature it became clear that it was difficult to compare results obtained from different methods of testing. The various instrumentations available for the determination of volumetric change resulted in variations of results. Therefore, for the same product different shrinkages were obtained on different testing instruments (Venhoven, 1933. Patel, 1978. Jorgensen, 1985. Munksgaard, 1987. Walls, 1988. Feilzer, 1989. Grajower, 1989. Watts, 1991. De Gee, 1993. Uno, 1994).

Sakaguchi et al, 2004 analyzed four methods of measuring polymerization shrinkage and strain of composites. The study found that the results in all four methods as presented in the published literature (linear transducer, dilatometer, strain gage and the bonded disk method) were statistically different. It was determined that the variations came about with the exothermic reaction that occurs during polymerization and the heat generated by the light curing units (Sakaguchi, 2004). However, the mercury dilatometer has been used in many polymerization shrinkage studies and proved to be very accurate (Loshaek, 1953. Lai, 1983. Pucket, 1992. De-Gee, 1993. Attin, 1995. Rueggeberg, 1995). The modified mercury dilatometer used by the author has the added advantages over normal mercury dilatometers in that it is also able to measure and record the polymerization every 0.5 seconds. This is important since other mercury dilatometers can only provide the total percentage polymerization shrinkage (Oberholzer, 2001). With a data range of 0.5 second intervals of the polymerization process, the speed of polymerization can be analyzed by analyzing the gradient of the data - represented in the graphs created by the electronic mercury dilatometer (Davidson, 1997. Oberholzer, 2001). Rosin et al, 2002, demonstrated that the dilatometer, linometer and buoyancy methods showed the same statistically significant results (Rosin, 2002). However, an electronically controlled mercury dilatometer was developed to further increase the accuracy of the results of the volumetric change measurements (Oberholzer, 2001). This electronic mercury dilatometer can detect any change in volume of a sample of any size and shape. The advantage was that the change of the mercury height in the capillary is measured electronically with a computer instead of manual viewing (Oberholzer, 2001).

1.2.9. Inorganic filler particles

Filler content vary widely from one composite to another. Examples of filler particles include: borosilicate or strontium glass, lithium or barium, aluminum silicate or colloidal silica (Anusavice, 2002:101). Filler particles like barium, strontium and lanthanum glass provide the required radiopacity *(Figure 28)* for clinical diagnosis on radiographs, since radiolucent restorations from previous years made caries diagnosis more challenging *(Figure 29)* (Phillips, 1982:226).

Figure 28: Composite restorations that are radiopaque

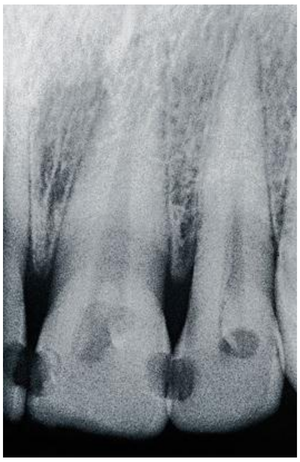


Figure 29: Composite restorations that are radiolucent

Filler content of a dental composite can be described in percentage (%). The percentage of filler particles in a resin can be expressed as filler by weight (wt. %) or filler by volume (vol. %). Filler particles constitute the inorganic constituent of a resin filling. The fillers have various sizes and can vary generally from 0.005-50 µm *(Figure 30).* Manufacturers have developed filler particles that contain fluoride (YbF3). The increase in filler load of a dental resin can be achieved by pre-polymerized filler particles. These particles were produced in an attempt to decrease the volumetric shrinkage of dental resins (Schmalz, 2009:99).

Glass or quartz is used for the production of the fine particles as well as the colloidal silica for the microfine particles (Anusavice, 2002:23).

A classification of resin based composites is very difficult due to the wide variety of resin based materials and their clinical applications. The organic and inorganic content of the resin material provide the physical handling properties and determines the viscosity. Dental resins can be classified according to composite type, class of composite, filler size *(Table 1)* and filler morphology. The term flowable composite was derived from the less viscous composites to which surfactants were added to decrease viscosity and to increase flow. A new composite restorative material with the viscosity of a flowable composite and a perceived polymerization shrinkage rivaling composites (according to the manufacturers) emerged. This product was released as a “bulk fill flowable composite”. According to the manufacturers of SDR, Filtek bulk fill, Xtra base and Venus bulk fill - these “bulk fill“ restorative materials can be placed in 4mm bulk fill layers, whereas for the traditional dental composites and original flowable composites 2mm layers were advocated.

Table 1: Classification of dental composites based on filler size (Anusavice, 2002; p418)

Class of composite	***Particle size***
Traditional (macro filled)	1-50µm glass, amorphous silica
Hybrid (large particle)	1-20µm glass, 0.04µm silica
Hybrid (mini filler/SPF)	0.1-10µm glass, 0.04µm silica
Packable hybrid (1990)	Midifiller / Minifiller hybrid, but with lower filler fraction
Flowable hybrid	Midifiller hybrid, but with finer particles size distribution
Homogeneous microfill	0.04µm silica
Heterogeneous microfill	0.04µm silica, Pre-polymerized resin particles containing 0.04µm Silica

Braga et al 2004 indicated that composites that are still available commercially could be classified into three main groups namely microfilled, microhybrid and nanocomposites. This classification was based on filler content (Braga, 2004). For a composite to be classified under the umbrella term “hybrid” at least 7-15% fumed silica in the form of micro-filler (less than 0.1 μm) must be added.

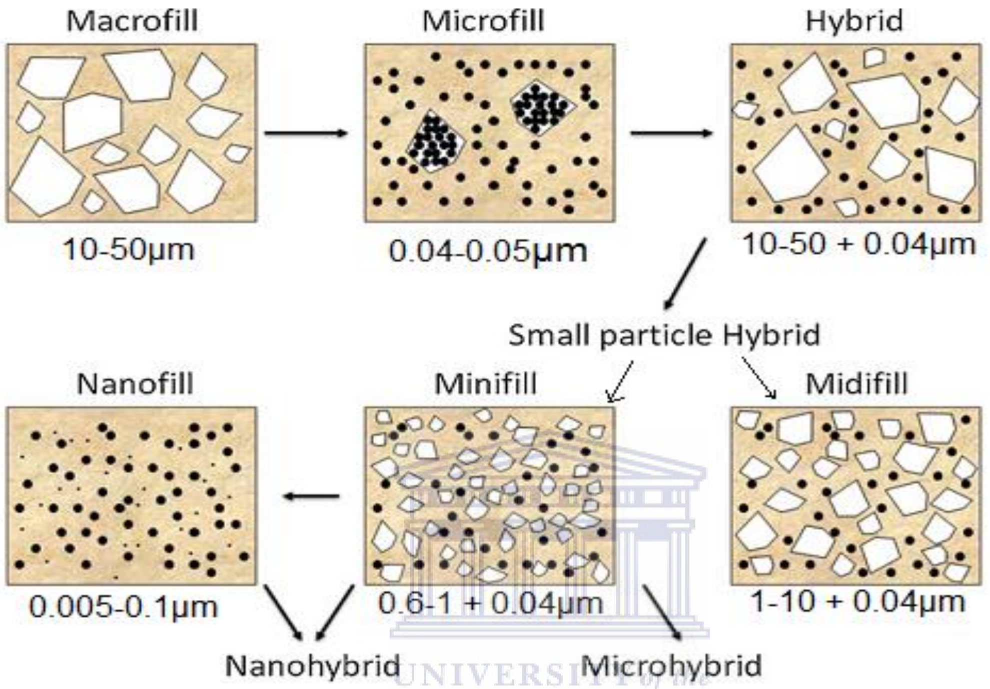


Figure 30: Visual representation of the classification of dental composites based on filler size (as adopted by Ferracane, 2011).

Filler particles can be manufactured by a grinding, burning and the sol-gel processes. Milling/grinding of quartz and various glasses produce filler particle sizes from 0.1-100 μm. Microfilled composites have filler particles of 0.04-0.05μm *(Figure 30).* Due to the reduced size of the microfilled composites, a larger surface area resulted, that must be coated with organic resin. The microfilled filler particles are produced by a process called pyrolytic or precipitation (Craig, 2002:234). Grinding quartz and/or various glasses produced filler particles for the traditional composites with an average size of 8-12 µm. The traditional composites had filler particles as large as 50-100 µm (Anusavice; 1991:222). Silicon tetrachloride is burned in an oxygen (O_2) and hydrogen (H_2) environment resulting in silicon dioxide (SiO_2) and hydrochloric acid (HCl). The SiO_2 spherical particles are 0.02-0.04 µm. This filler particle is known as pyrogenic silica. The Sol-Gel process results in porous silica particles around 1 µm in size. The organic resin matrix penetrates well into the particles and is easy to polish (Anusavice, 2002:403).

Amorphous silica is not crystalline like quarts but has the same composition. The advantage is that silica is not as hard and abrasive as quartz making it a good alternative for resin restorations to reduce the wear of the opposing tooth (Anusavice, 2002:403). Microhybrid composites have irregularly shaped glass or quartz particles with a filler load that can be as high as 77-84% in weight. Glass content can vary between combinations of borosilicate, lithium or barium, aluminium, silicate, strontium or zinc glass (Craig, 2002:234). Barium, strontium, zirconium have the same reflective indices of light refraction as the resin matrix. This light refraction is important for conversion of the resin matrix during light irradiation.

Certain ceramic filler particles cannot be used in dental resins. The reason is that their refractive indexes of the filler particles are not similar to the tooth structure as well as the resin matrix to ensure depth of cure aesthetics. Filler composition, filler size and the light intensity affect the depth of cure. Manufacturer instructions indicate the light intensity as well as the curing time for composites of various shades. Amorphous silica and quartz has no extra metals as a constituent and therefore do not weaken or leach over time, unlike the glasses of barium, strontium and zirconium. This leaching effect is used as an advent and that is why fluoride is added to barium, strontium, zirconium glass (Craig, 2002:142).

The filler weight and size influence several properties.

1. Reinforce the resin matrix improving wear, water sorption and strength.
2. Reduction in polymerization shrinkage, since the filler particle in inert.
3. Co–efficient of thermal expansion is decreased to be closer to that of the tooth.
4. Material viscosity and workability improved.

5. Due to less free monomer there will be decreased staining and softening of the material.
6. Strontium (Sr) and barium (Ba) are added to filler particles to increase radiopacity (Anusavice, 2002:403).

Filler particles are bound to the organic resin matrix with an appropriate coupling agent improve the properties of a resin material. High inorganic filler content were associated with lower polymerization stress that leads to a reduced volumetric shrinkage (Goncalves, 2010). Irrespective of the organic matrix used a high filler loading is important for various properties of the resin material. Organic resin matrix combinations of bis-GMA /TEGDMA with variable filler content were tested to determine the importance of the filler particle size and filler load effect on polymerization shrinkage and volumetric change. Goncalves et al used a mercury dilatometer to determine the volumetric change. The study concluded that the resin matrix had a strong influence on polymerization stress, conversion rate and reaction rate. Filler content however showed a stronger influence on shrinkage and the modulus of elasticity. Filler content also indicated a loss of the tangent relationship with the conversion rate. The conversion rate was an effect of the matrix rather than the shrinkage effect that was affected by the filler content. It was concluded that polymerization stress can be altered by the bis-GMA /TEGDMA ratio and filler content with variable results with every combination.

The ideal combination would be high filler content with sufficient bis-GMA /TEGDMA to have an ideal conversion rate to allow the lowest possible polymerization shrinkage resulting in a decreased polymerization stress (Goncalves, 2003). UDMA reduce water sorption and polymerization shrinkage while enhancing the mechanical properties against wear of the resin matrices.

CHAPTER 2

RESEARCH METHODOLOGY AND MATERIALS

2.1 Overview

This is a comparative study comparing the polymerization shrinkage of the materials under standardized conditions. The research hypothesis is that Bulk Fill flowable composites will have a smaller polymerization shrinkage compared to composites. The importance of this study is to establish an independent comparison of the polymerization shrinkage of especially the new bulk fill flowable composites with resin composites. The information available for the bulk fill flowable composites are supplied to the clinicians by the various materials manufactures. Measuring the volumetric change accurately provide insight into the true volumetric change due to polymerization shrinkage. Voids within dental restorations may play various roles and requires further exploration.

2.2 Methods: Electronic Mercury Dilatometer *(Figure 27)*

The volumetric change due to polymerization shrinkage over a total period of 35.0 seconds was measured every 0.5 seconds. All samples were cured for 35.0 seconds at 500mW/cm^2 with a Dentsply/Caulk Spectrum 800 halogen curing light in order to standardize the curing process. The output was monitored with a Caulk (Milford, Germany) radiometer to ensure 500mW/cm^2± 50mW/cm^2. Calibration of the modified mercury dilatometer was done prior to the testing of every specimen. Ten specimen samples, of each material were tested. The Teflon specimen holder has a hole with a diameter of 5.0 mm and a height of 2.5 mm resulting in the specimen volume in the Teflon holder of 49.087mm^3 *(Figure 31).* A brief synopsis of the steps to complete one experiment follows: The prepared specimen was placed in the dilatometer and the clamp closed. The calibration was achieved by adjusting the mercury column and the 0mm as well as the -30mm calibration knobs. The curing light was activated by the computer when the mercury dilatometer had a stable environment for 5.0 seconds. The polymerization shrinkage of the resin material and the resultant volumetric change was measured every 0.5 seconds. When the next specimen was tested, additional distilled water was added to establish the correct volume of water to achieve a stable environment. This “newly filled water” was also kept constant at 25^{0}C ± 1. The dilatometer was kept in a temperature controlled incubator at the 25°C ± 1 (Jin, 2002). The baseline effect of the curing unit was established prior to each set of experimental set-ups and the data corrected accordingly (Oberholzer, 2001). This correction resulted in the volumetric shrinkage that is presented for each material to be the true volumetric change due to polymerization only. Therefore, only the effect of polymerization shrinkage for the conversion of monomers to polymers remained (Oberholzer, 2001. Halvorson, 2002. Jin, 2002).

2.3 Detailed calibration of the electronic mercury dilatometer *(Figure 27)*

The capillary column on the mercury dilatometer where the calibration of the 0mm and -30mm were viewed has a diameter of 0.6mm *(Figure 31).* The mercury could not rise by itself in the capillary column, since the angle of contact of the meniscus is obtuse. The height of the mercury could be adjusted by the mercury height adjustment tap *(Figure 27, 31).*

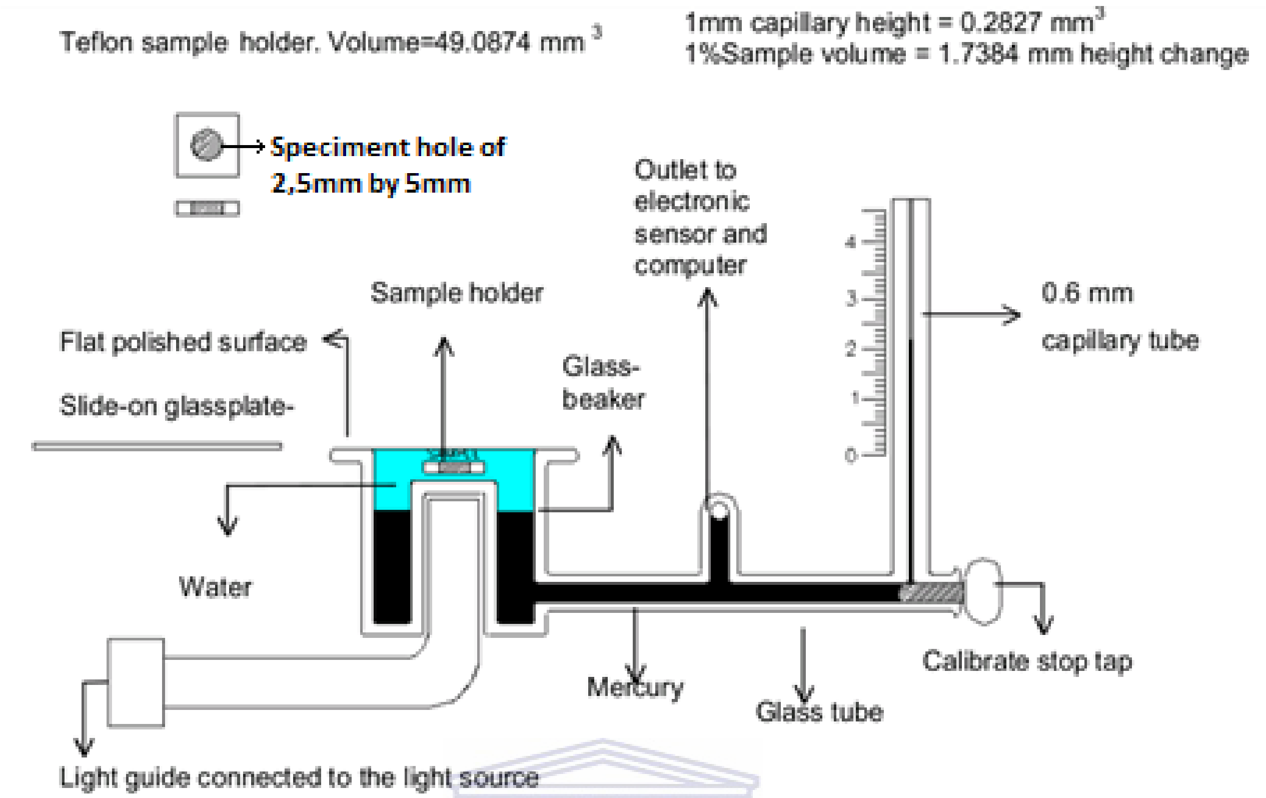


Figure 31: Modified Mercury Dilatometer line diagram as constructed by Oberholzer, 2002.

The measurements obtained from the mercury dilatometer are recorded by the computer. If manual viewing were to be used on the capillary column a 1mm height change in the capillary tube result in a volume change of 0.2827mm^3. The Teflon specimen holder has a hole with a diameter of 5mm and a height of 2.5mm resulting in the specimen volume in the Teflon holder of 49.087mm^3 *(Figure 31).* The Teflon holder itself has a known volume of 0,049 mm^3. At the base of the Teflon holder a thin 0.5mm glass slide was placed with a smear layer of silicone gel to achieve an environment where the test material can be maintained during the experiment. The test specimen was irradiated through the 0.5mm glass. The light attenuation through the glass into the test specimen was not negatively affected (Miyazaki, 2007). The material was extruded into the Teflon holder in a radiograph developing box. The specimen was then placed in the dilatometer and the clamp closed *(Figure 27).* The mercury column was adjusted with the tap A to the right of the measurement scale to the 0mm mark.

In order to view the results of the volumetric change the computer and the mercury dilatometer has to be calibrated. The graph parameters have to be set and this forms the basis of the calibration process. Time (in seconds) was represented by the value on the X-axis and the percentage of volumetric change was represented by the value on the Y-axis *(Figure 32).* There were two adjustment dials that form an essential part of the dilatometer calibration (0mm and -30mm dials) with the computer *(Figure 27).* The 0 mm calibration dial was also used to calibrate the computer to the “zero” baseline and then the 0 mm dial was locked. Tap A was then used to set the mercury column down to -0.30 mm. The -0.30 mm dial was used to calibrate the computer to ensure the volumetric change that results in shrinkage can be read directly from the graph that was developed by the software of the computer. However, if the volumetric change was expected to be 4%, the calibration must have been set at 0 mm and at -0.45mm. After locking the -0.30 mm knob, Tap A is used to adjust the mercury column to 0mm again. The calibration process is now complete and the measurement may begin by using the mouse of the computer to click on the “start measurement” icon. There was a 5 second delay prior to when the “start measurement” icon was clicked on the computer and the Spectrum 800 curing light (Dentsply/Caulk Division Milford, DE, USA) switched on. This 5 second precaution was to ensure that the calibrated environment is stable from any pressure changes. Should pressure changes occur within that 5 second monitoring time the computer will not allow the experiment to continue and the calibration process would have to be restarted. The successful completion of the 5 second monitoring period will allow the curing light to start the photo-polymerization of the test specimen. The electronic mercury dilatometer records the temperature and the volumetric change every 0.5 seconds, even during this 5 second monitoring period.

The computer records the volumetric change results in the form of a graph. The raw data can be viewed in Microsoft Excel format. The dilatometer is “electronic” due to the fact that the volumetric change is recorded and calculated electronically. The volumetric changes that occur during the experiment directly affect the diaphragm of the transducer. An output voltage is generated by the transducer and sent to the built-in processor. The processor relays the information to the computer via the RS232 port where the computer calculates the data and presents it to the operator in the form of a graph.

It was established that 90% of the total polymerization occur in the first 20 seconds, so 35 seconds should ensure sufficient curing light exposure to achieve conversion of the remaining 10% of the polymerizable reaction (Davidson, 1997).

The specimen test results were stored on the computer in Microsoft Excel format. Prior to opening the clamp Tap A was adjusted to + 30mm on the mercury column and the clamp was then released to remove the polymerized specimen. The surrounding temperature of the electronic mercury dilatometer was kept constant by means of an external incubator equipped with a thermostat, wherein the dilatometer is permanently operated from. The temperature of the dilatometer can be viewed on the computer as well as on the incubator prior and during the specimen test. Lai et al 1993 described that the important factor while using their water dilatometer was a constant temperature. This environment can be maintained by placing the dilatometer in an incubator with its own thermostat to ensure a constant temperature was maintained (Lai, 1993).

2.4. Materials tested

The control composite was the well established Z250 by 3M (ESPE). The four newly available bulk fill flowable composites were tested and compared with Z250. The bulk fill flowable composites consisted of Smart Dentin Replacement (SDR) by Dentsply/Caulk (Milford, Germany), Venus bulk fill by Haraeus Kulzer (Hanau, Germany), Filtek bulk fill flow by 3M ESPE (Massachusetts, USA) and Xtra base bulk fill flowable by Voco (Cuxhaven, Germany) *(Table 2).* The manufacturers of these four bulk fill flowable composites advocated a material placement thickness of 4mm. The composite as well as the traditional flowable composite instruction guidelines indicated a layering technique of 2mm.

All the samples were subjected to the same volume of $49.087mm^3$ material in order to standardize the findings of the polymerization shrinkage.

The following table indicates the materials used for the purpose of this thesis. Special note has to be given to the varying concentration and type of organic and inorganic matrixes,

Table 2: Information on the various resin composites and % volumetric change found.

Dental material	**Inorganic filler**	**Organic resin matrix**	**Filler size µm**	**% filler wt.**
Z250 (3M ESPE) Lot 176833 exp 2013-05	Zirconia/ silica	bis-GMA (1-10%), UDMA (1-10%), bis-EMA (1-10%), TEGDMA (<5%).	0.01-3.5 (Average size 0.6)	78
SDR (Dentsply/ Caulk) Lot 110429. exp. 2013-04	Barium-alumino-fluoro-borosilicate glass; Strontium alumino-	SDR patented urethane (<25%), TEGDMA (<10%), EPBADMA (<10%)	Average size 4.2	68

	fluoro-silicate glass			
Venus Bulk Fill (Haraeus Kulzer) Lot 010031 exp. 2014-08	barium-alumina-fluoro-silicate, YbF3, Silica.	UDMA (Concentration % not available from the suppliers), EPBADMA (Concentration % not available from the suppliers)	0.02 - 5	65
Filtek Bulk Fill (3M ESPE) lot N356852 exp. 2015-	YBF3 filler Zirconia / silica	UDMA (10-20%), bis-GMA (1-10%), bis-EMA (6) (1-10%), procrylat resins	0,1 -5 0,01 -3,5	64,5

02		(10-20%), TEGDMA (<1%)		
Xtra Base bulk flow (Voco) Lot 1201096	(Concentration % not available from the suppliers)	bis-GMA (10-25%), UDMA (10-25%)	(Concentration % not available from the suppliers)	75

Table 3: Molecular weight of individual monomers with full chemical names displayed

Resin present in material	**Molecular weight g/mol**
UDMA (urethane dimethacrylate)	470,55
Smart Dentine Replacement-UDMA	849
TEGDMA3 (6-dioxaoctamethylene-	286,32

dimethacrylate)	
bis-GMA (bis-phenol glycidylmethacrylate)	512,59
bis-EMA 6 (bisphenol A polyethylene glycol diether dimethacrylate).	496.58
EBADMA (2-propenoic acid 2-methyl- 1,1'-[(1-methylethylidene) bis(4,1-phenyleneoxy-2,1-ethanediyl)] ester	496.58
EPBADMA	452.53
Procrylate (2,2-bis[4-(3-methacryloxypropoxy)phenyl]propane)	480,59

2.4.1. Venus Bulk Fill - Haraeus Kulzer *(Table 2, 3)*

The organic resin matrix consists of UDMA and EBADMA. The inorganic filler particles are Ba–Al-F silicate glass, YbF3 and SiO_2. The sizes range from 0,02µm and 5 µm and is filled per weight to 65%. The universal shade advocated 550–1000 mW/cm^2 for a period of 20 seconds per 4mm bulk fill flowable composite.

2.4.2 Z250 - 3M *(Table 2, 3)*

The organic matrix contain: bis-GMA , UDMA and bis-EMA. This resin is filled with 78% weight silica/zirconia. The filler particle size distribution is 0.01 µm to 3.5 µm with an average particle size of 0.6 µm.

2.4.3 SDR-Dentsply *(Table2, 3)*

The organic resin matrix consists of a patented SDR-urethane dimethacrylate resin, ethoxylated bisphenol A dimethacrylate (EBPADMA), triethyleneglycol dimethacrylate (TEGDMA) and the photo-initiator is butylated hydroxyl toluene (BHT). The inorganic filler particles are barium–alumino–fluoro–borosilicate glass and strontium–alumino–fluoro–silicate glass filled to a level of 68% weight with an average size of 4.2 µm.

SDR directions for use indicate that 4mm increments are advised. 470nm spectral output activates the camphorquinone. 20 seconds cure with 550mW /cm^2 should be sufficient.

2.4.4. X-tra Base – Voco *(Table 2, 3)*

The organic resin matrix consists of a methacrylate matrix of bis-GMA and UDMA. The inorganic filler particles are 75% filled by weight.

Light output of 500–800mW/cm^2 for 10 seconds with the universal shade is advised per 4mm bulk fill.

2.4.5. Filtek Bulk Fill - 3M *(Table 2, 3).*

This organic resin matrix consists of UDMA, bis-GMA , bis-EMA and procrylat resins. The inorganic filler particles are ytterbium trifluoride filler particles sized 0.1-5 µm and zirconia/silica particles 0.01-3.5 µm. The filler content is 64.5% per weight.

2.5. Stereomicroscope

A Nikon SMZ-10 stereomicroscope (Japan) was used to view the voids in the cured samples. The Stereomicroscope was a set at 20 times magnification. Illumination was obtained from below the specimen and the voids were observed as round dark structures within the sample specimen.

2.6. Micro-3D ct reconstruction

The instrument used for this purpose is a General Electric Phoenix V|Tome|X L240 with an additional NF180 option. This is a system with two tubes. The first tube is a reflection (direct) type tube up to 240 kV. The second is a transmission tube up to 180 kV - meant for higher resolution work with a minimum focal spot size of 700 nm. In order to view the voids the transmission tube was used. The samples for void visualisation were all scanned at 140 kV, 80µA, 500 ms and 2000 images, with resolution 5.5 microns. Images were reconstructed with system integrated Datos software and analysis done with VGStudioMax 2.1. One randomly selected SDR ampule was selected to determine if there were any voids within the ampules. This ampule was scanned at 30 microns, 140 kV, 100 µA, with 500 ms per image and 1600 images in 1 rotation.

2.7. Data analysis.

The volumetric change that occurred every 0.5 seconds were measured by the electronic mercury dilatometer and stored on the computer in Microsoft Excel format. Data analysis was done by way of the Number Cruncher Statistical System (NCSS). The results were analyzed using the Tukey-Kramer multiple comparison test and the Kruskal-Wallis multiple comparison test.

CHAPTER 3

RESULTS

3.1. Overview

During the literature review it became clear that many authors use a sample size for volumetric change and polymerization shrinkage of ten (10) sample specimens of each material. In order to achieve a repeatable result a specimen holder of known volume with a specimen holding area of known volume was essential (Bausch, 1982. Davidson, 1997. Aw, 1997. Sakaguchi, 1997, 2004). The values obtained for volumetric change by the electronic mercury dilatometer used by the researcher are comparable with other mercury dilatometers from the literature. The statistical analysis of the total polymerization volumetric change is comparable with other mercury dilatometers since, the same statistical analysis to standardize the results from the electronic mercury dilatometer with the results from the literature (Lai, 1993. Sharp, 2003. Oberholzer, 2002. Sakaguchi, 2004).

3.2. Statistical analysis

The polymerization shrinkage slopes of all the bulk fill flowable composites and Z250 were calculated and compared in order to establish the possible differences that the constituents of the resin play in the rate of polymerization shrinkage. The graphical representation of volumetric change over time assists in the visualization of the polymerization process. The data obtained every 0.5 seconds could possibly provide valuable information to establish the possible improvements that the bulk fill flowable composites have made in comparison with the established composite materials from the literature.

Tukey-Kramer Multiple-Comparison Test *(Table 4)* and the Kruskal-Wallis one-way Anova on Ranks *(Table 5)* were used to analyze the volumetric shrinkage and rate of polymerization shrinkage obtained during the 0-35 second curing process. The Tukey-Kramer multiple-comparison test provided multiple comparison tests for all the pairwise differences between the means. The value Alpha=0.050 was considered significant**.** The total cumulative volumetric shrinkage was determined from the slopes with the Kruskal-Wallis Multiple-Comparison Z-Value Test. When the means and medians of each material were compared in Table 4 with the Tukey-Kramer multiple comparison test, it was noted that they were very close to one another indicate the total polymerization as per the mean *(Table 4)*.

The Tukey–Kramer Multiple comparison test indicates that there are differences in total percentages of shrinkage *(Table 4).* The results from the Tukey-Kramer can be treated further with the Kruskal-Wallis multiple-comparison test to indicate the magnitudes of the statistical significance are between the materials tested *(Table 5).* The slopes of polymerization shrinkage are analyzed using the Kruskal-Wallis one way Anova on ranks. This is done to determine if there are statistically significant differences between the rates of polymerization shrinkage of the materials.

3.3. Results of the volumetric change

The total polymerization shrinkage showing the slope of polymerization shrinkage over time *(Figure 32).* Z250 shrank 1.13% and Venus bulk fill had the largest shrinkage of 1.72%. The time period from 30.5 to where the curing light was switched off at 35 seconds represents the total cumulative shrinkage for the specimens tested. Z250 was used as the control group during the statistical analysis and the Tukey-Kramer *(Table 4)* indicates that all the bulk flowable composites differed from Z250. There are also differences between the bulk fill flowable composite materials. The magnitude of the differences is unknown and that is why the Kruskal Wallis multiple comparison test was completed *(Table 5).*

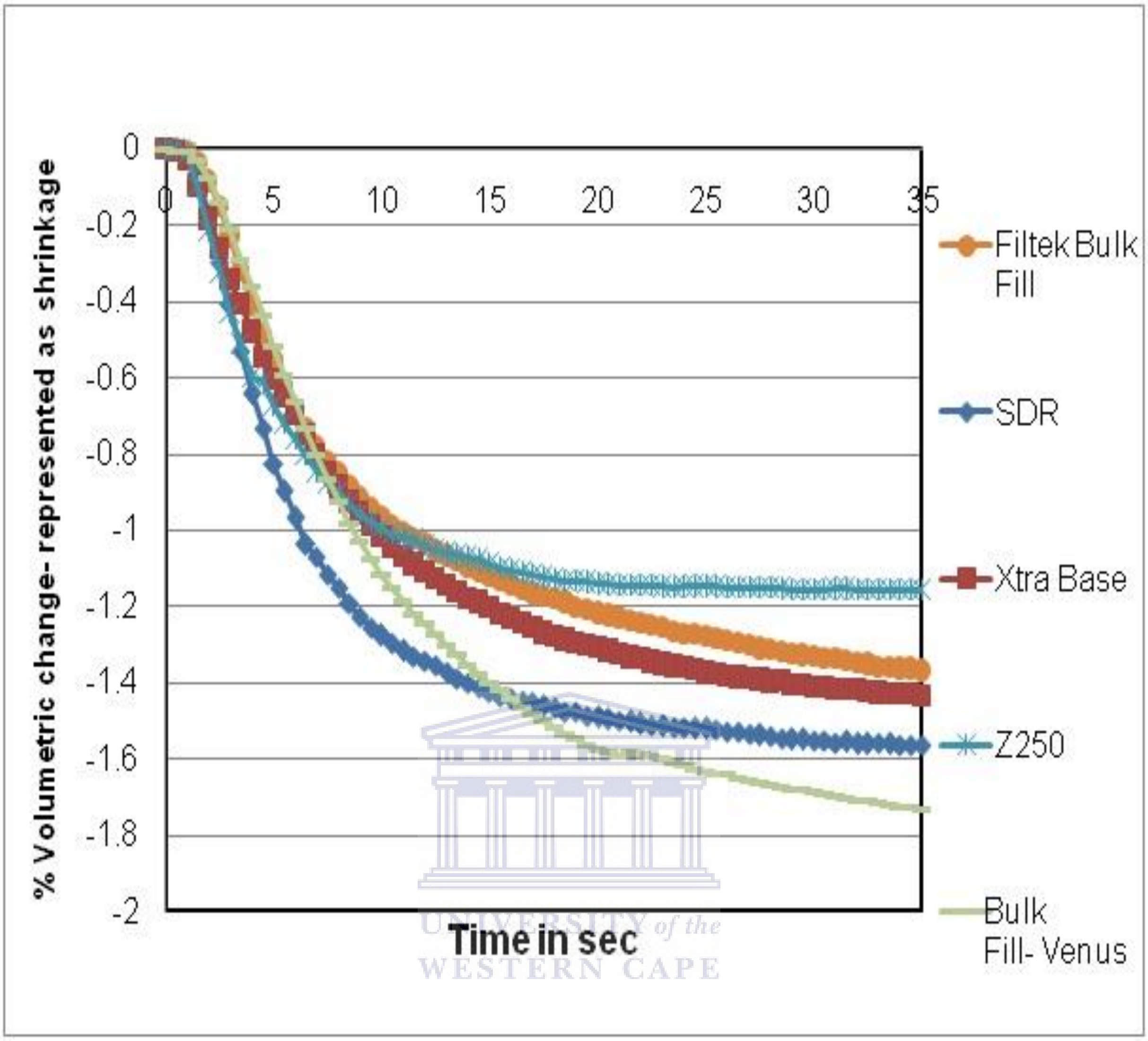


Figure 32: Average volumetric change of "Bulk Fill Flowable Composites"

Table 4: Tukey-Kramer multiple comparison test indicating differences between groups

Material group	**No. of test specimens**	**Mean**	**Materials that differed from "material group" column**
Venus bulk fill	10	-1.7153	X-tra base, 3m Filtek Bulk Fill, z250
SDR	10	-1.5604	Filtek Bulk Fill, z250
X-tra base	10	-1.4257	Venus bulk fill, z250
Filtek Bulk Fill	10	-1.3582	Venus bulk fill, SDR, z250
Z250	10	-1.1565	Venus bulk fill, SDR bulk, Xtra base, Filtek Bulk Fill

In order to determine exactly what the extent of these differences were the Kruskal–Wallis one way Anova on ranks indicated that between groups of materials there were statistical differences in polymerization shrinkage p-0.000001 *(Table 5).* There were statistical significant differences found between groups with the Kruskal-Wallis multiple comparison z-value test.

The Bonferroni adjustment protects the statistical magnitude against Type I Error. The Bonferroni adjustment was made to the results from the Kruskal–Wallis multiple comparison test *(Table 5)*. This is done by dividing the priori alpha level by the number of comparisons that's made. The regular test showed no difference between Z250 and Filtek Bulk Fill. Bonferroni test showed no difference between Z250, Filtek Bulk Fill and X-tra base. With both the regular test and Bonferroni tests SDR and Venus bulk fill had results where the difference in shrinkage statistically significant with an Alpha=0,050 fixed p value (significance level 5%).

The regular test showed that only Filtek bulk fill was not statistically significant different when Z250 is the control group. In order to prevent a type 1 error the Bonferroni test was applied at Alpha= 0.050 with a significance level of 5%.

The Z-Value test had to be done with the Kruskal-Wallis multiple comparison z-value tests. When the regular test was considered with the Kruskal-Wallis multiple comparison test the z-value of 1.4958 for 3M Filtek Bulk Fill was not significantly different, but the Z-value of SDR, Venus bulk fill and X-tra base was.

The Bonferroni test was considered: Z250 compared to Filtek Bulk Fill 1.4958 and X-tra base 2.401 was not significantly different (Z-value

2.8070.) This means that only the results obtained from SDR and Venus bulk fill were statistically different from Z250.

Table 5: Kruskal-Wallis Multiple-Comparison Z-Value Test indicating significant differences based on the median

Average Shrinkage of material	**Filtek Bulk Fill**	**SDR bulk**	**Venus Bulk Fill**	**X-tra base**	**z250**
Filtek Bulk Fill	0	2.2629	4.0042	0.9052	1.4958
SDR bulk	2.2629	0	1.7413	1.3578	3.7588
Venus bulk fill	4.0042	1.7413	0	3.0991	5.5001
X-tra base	0.9052	1.3578	3.0991	0	2.401
Z250	1.4958	3.7588	5.5001	2.401	0
Regular Test: Medians significantly different if z-value > 1.9600 Bonferroni Test: Medians significantly different if z-value > 2.8070			Alpha=0.050 fixed p-value (significance level 5%)		

When considering the regular test with the Z-Value >1, 9600 it was noted that the Z-value of Filtek Bulk Fill was not statistically to X-tra Base 0.9052. Z-value of SDR 2.2629 is not statistically different when the Bonferroni correction was made >2.8070 when compared to Filtek Bulk Fill.

Therefore, all the bulk flowable composites differed from the Z250 control with an Alpha =0.050 fixed p-value (significance 5%).

The results from the Kruskal-Wallis multiple comparison test therefore concludes that: 3M Filtek Bulk Fill had a total polymerization shrinkage that was lower and statistical different with an Alpha=0.050 with Venus bulk fill and SDR bulk fill. The regular test of the z-value of Kruskal-Wallis multiple comparison confirmed this.

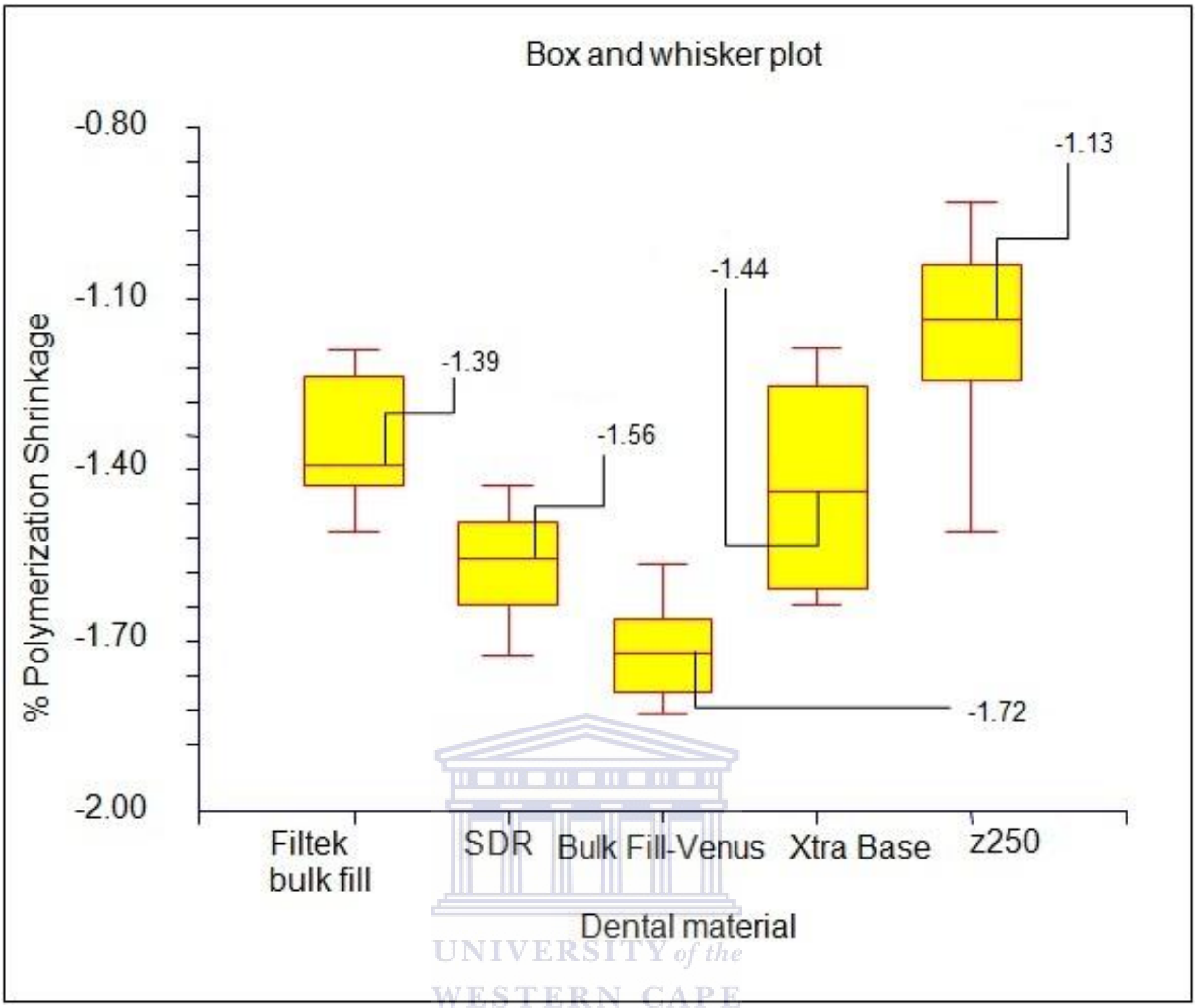


Figure 33: Box and whisker plot of total polymerization for the time interval 30.5-35 seconds.

The results from all the specimens were used to compile a box and whisker plot *(Figure 33)* data of the volumetric change over the 35 second period for each material was presented as Box and Whisker plots *(Figure 33).* Each box and whisker plot gave the maximum and minimum values of polymerization shrinkage for each of the ten samples of each bulk fill flowable composite tested. The median is represented by the solid line in each box and therefore the median value for the 10 samples.

The interquartile range (IQR) is important, since it indicates the central 50% of the data collected and represents the data set where other authors completing the same experiment will find 50% of their results (Schultz, 2009). When the box and whisker plots are analyzed and the interquartile range (IQR) of quartile 3 is deducted from quartile 1- it is seen that the range of spread for Filtek Bulk Fill and Z250 is the same at an IQR of 0.21 *(Figure 33).* This is closely followed by SDR IQR 0.18. X-tra Base has an IQR of 0.33 indicating a large spread of the data around the median. From all the results it is clear that Z250 had a shrinkage that was different from the flowable composites as a group according to Tukey-Kramer multiple comparison tests. The box and whisker plot indicates that the data ranges for Z250 are equally dispersed in the 25th and 75th percentile around the mean. The interquartile range for Filtek bulk fill indicated that most of the data were in the upper 75th percentile. The interquartile range of X-tra base was very large in comparison to all the other materials. The data range of Venus bulk fill was the lowest at 0.11- indicating that 50% of the data are spread more closely around the mean when compared to the aforementioned IQR results.

The symmetry of the box around the median indicated that the results are less variable between the 25th and 75th percentile. Therefore, the spread of polymerization shrinkage values are more evenly spread across the box plot form quartile one to quartile three.

The whiskers indicating the 10th and 90th percentile are close to equal in length with exception of Z250 that has a long 10th percentile whisker.

The box for Filtek bulk fill shows an upward positive skewness. The median is shifted towards the lower portion of box with the most of the polymerization shrinkage observations in the upper quartile as compared to the lower quartile. The spread of the data range is form 1.15% to 1.48%. The interquartile range for Filtek bulk fill is 0.21. The median is 1.388% shrinkage. This spread indicates that most of the shrinkage values are less than the mean and located in the 75th percentile. The box shows that SDR had zero skewness with the median middle clustered. The spread of the data range is form 1.42% to 1.72% shrinkage. The interquartile range is 0.18 and the median 1.553.

The box for Venus bulk fill shows zero skewness with the median middle clustered. The spread of the data range is from 1.80% to 1.53% shrinkage. The interquartile range is 0.11 and the median 1.7175%. The box for X-tra Base shows zero skewness with a large dispersion of data.

The spread of the data range is form 1.17% to 1.65% shrinkage. The interquartile range is 0.33 and the median 1.4355%. The box for Z250 shows zero skewness with the median middle clustered. The spread of the data range is form 0.99% to 1.48% shrinkage. The interquartile range is 0.21 and the median 1.133.

The Bonferroni test is considered when comparing SDR for statistical significant differences with the other bulk fill flowable composites. The Bonferroni test showed no differences in statistical significance for the total percentage shrinkage with the other three bulk fill flowable composites. The volumetric change of SDR was however statistically significantly larger than the Z250 composite.

Due to the dilatometer recording the volumetric change every 0.5 seconds the slopes of volumetric change can be analyzed for the speed of volumetric change.

3.4 Results from analyzing the rate of polymerization shrinkage slopes (Table 6)

The total volumetric change has been analyzed. The rate at which the polymerization process occurs is important, since it has been shown that materials with a faster rate of shrinkage has higher stresses on the cavity walls and within the material (Bragga, 2002, 2005. Condon, 2000. Davidson, 1984).

The rate of polymerization is assessed by analyzing the polymerization slopes *(Table 6)* of volumetric change *(Figure 32).* In order to determine the rate of polymerization, the incline of the slopes of volumetric change gives clues to the polymerization rate. During polymerization of the resin materials it was noted the shrinkage started from 1.5 seconds *(Figure 32).* In order to analyze the rates for the slopes of polymerization it was divided into time intervals *(Table 6).* The rate/speed of polymerization is illustrated by the angulations of the various slopes. In order to assess the rate of polymerization time intervals were chosen *(Table 6).* Due to the complex combinations of monomer systems the rate of polymerization and the volumetric change per time interval does not necessarily correspond. Therefore, the magnitude of the rate of polymerization must not be confused with the amount of volumetric change per time interval. It is important to note that the Tukey-Kramer Multiple comparison test indicated a difference between all the materials tested and Venus bulk fill during the 5.5 seconds and 20 seconds *(Table 4). Table 6* was compiled in order to establish and illustrate where the statistical differences in the rate of polymerization. From 0-1.0 second no polymerization took place, therefore the first time frame for the rate of polymerization was chosen as 1.5-5 seconds. During the first 1,5-5 seconds SDR bulk fill shrank faster than Z250, Filtek Bulk Fill, X-tra Base, Venus bulk fill *(Table 6).*

When the slopes of the bulk fill flowable composites were considered in respect to Z250 the slopes of the shrinkage rates over the first 5 seconds did not differ significantly *(Figure 32).* From 5.5 seconds to 20 seconds Venus bulk fill shrank faster than Z250, Filtek Bulk Fill, X-tra Base and SDR. When Z250 is looked at for the time period 25.5-30 seconds, it is seen that SDR had the same rate of shrinkage as Z250 (*Table 6).*
The rate of polymerization for Venus bulk fill was statistically more than all the materials tested for the time period 5.5-10 seconds *(Table 6).* From 5.5-25 seconds, Venus bulk fill shrank statistically faster than Z250 and SDR.

The conclusion of the slope analysis with the Tukey-Kramer multiple comparison test was that although the total polymerization differ - the slope of polymerization of bulk fill flowable composites (with exception of Venus bulk fill) were not statistically different form one another.

Table 6: The rate of polymerization shrinkage based on the summary of Tukey-Kramer multiple comparison test of incline slopes (Figure 32)

Material	**slope 1.5-5**	**slope 5.5-10**	**Slope 10.5-15**	**slope 15.5-20**	**slope 20.5-25**	**slope 25.5-30**
SDR	Filtek bulk fill, Venus bulk fill, X-tra base	-	-	-	-	-
Venus	-	Filtek bulk fill, X-tra base, SDR, Z250	Filtek bulk fill, SDR, Z250	SDR, Z250	SDR, Z250	Z250
X-tra base	-	-	Z250	-	Z250	-
Filtek bulk	-	-	-	-	Z250	Z250

Z250	-	-	-	-	-	-

3.5. Voids in the samples

3.5.1 Results

3.5.1.1 Z250

Average of the ten samples for Z250 showed a volumetric shrinkage of 1.13% (*Figure* 34, 35). Therefore, the total volume of voids recorded within the Micro-3D ct reconstruction of the polymerized sample of $49.087mm^3$ was $0.273260504mm^3$ for Z250. This volume of voids ($0.27mm^3$) was most likely present in the sample.

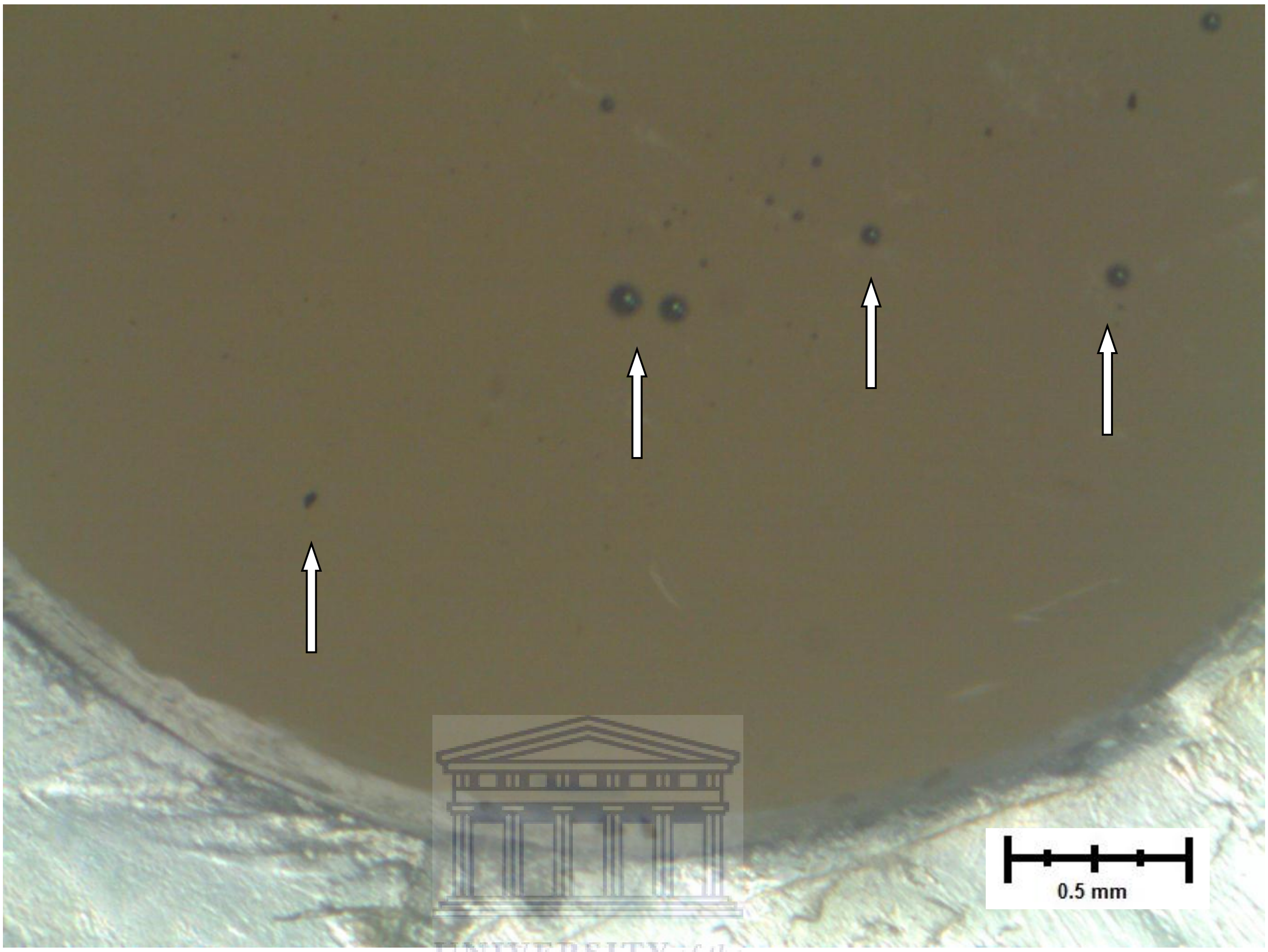


Figure 34: Stereomicroscope of Z250, voids appear as black spots

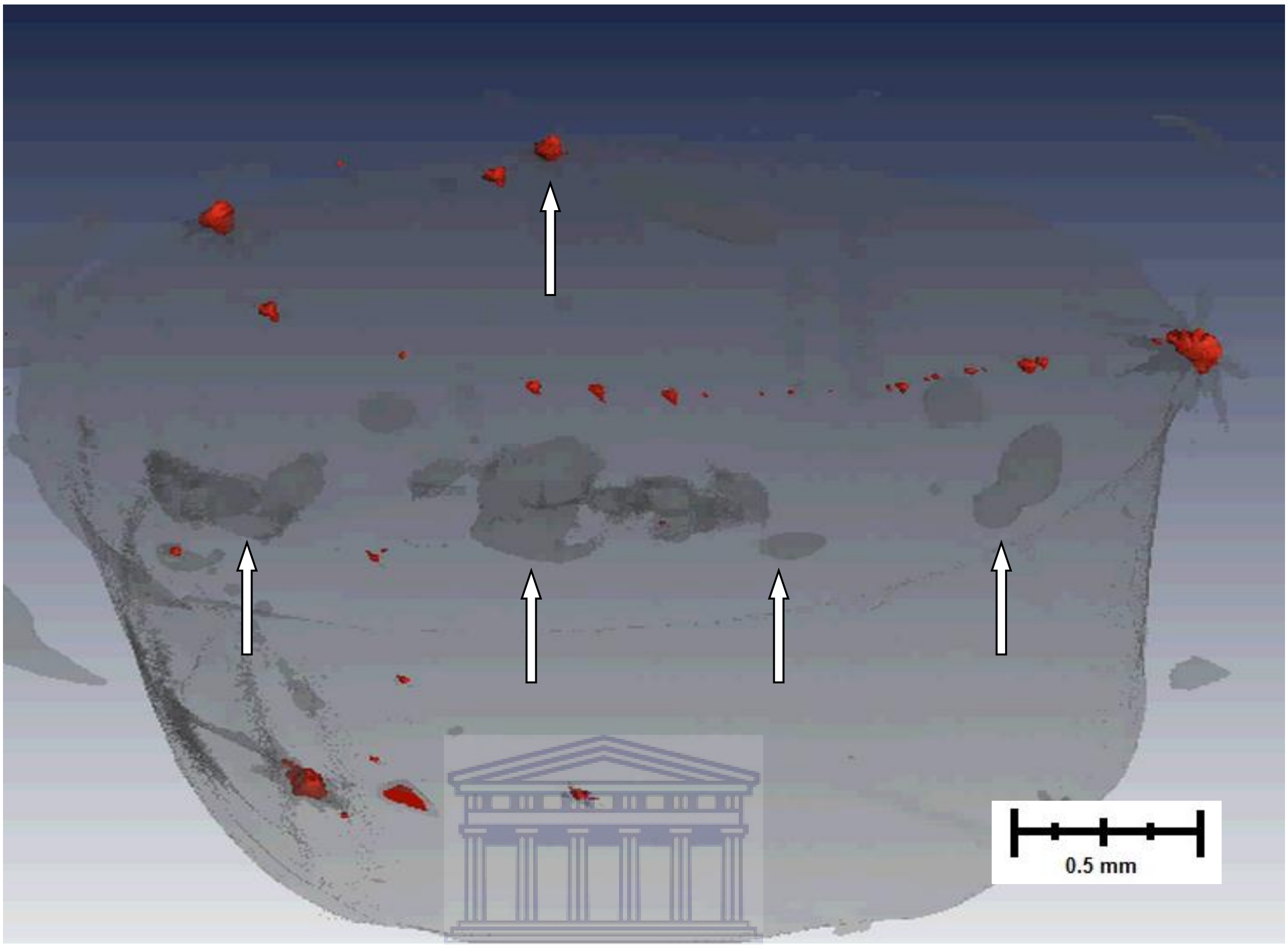


Figure 35: 3D micro-ct reconstruction of Z250, voids (gray) and filler particles 3.5 µm in size (red)

3.5.1.2. SDR

Average of the ten samples for SDR showed a volumetric shrinkage of 1.55% *(Figure 36, 37).* Therefore, the total voids recorded within the Micro-3D ct reconstruction of the polymerized sample of 49.087mm^3 were 0.000290302 mm^3 for SDR. This volume of 0.00029 mm^3 voids were likely present in the sample.

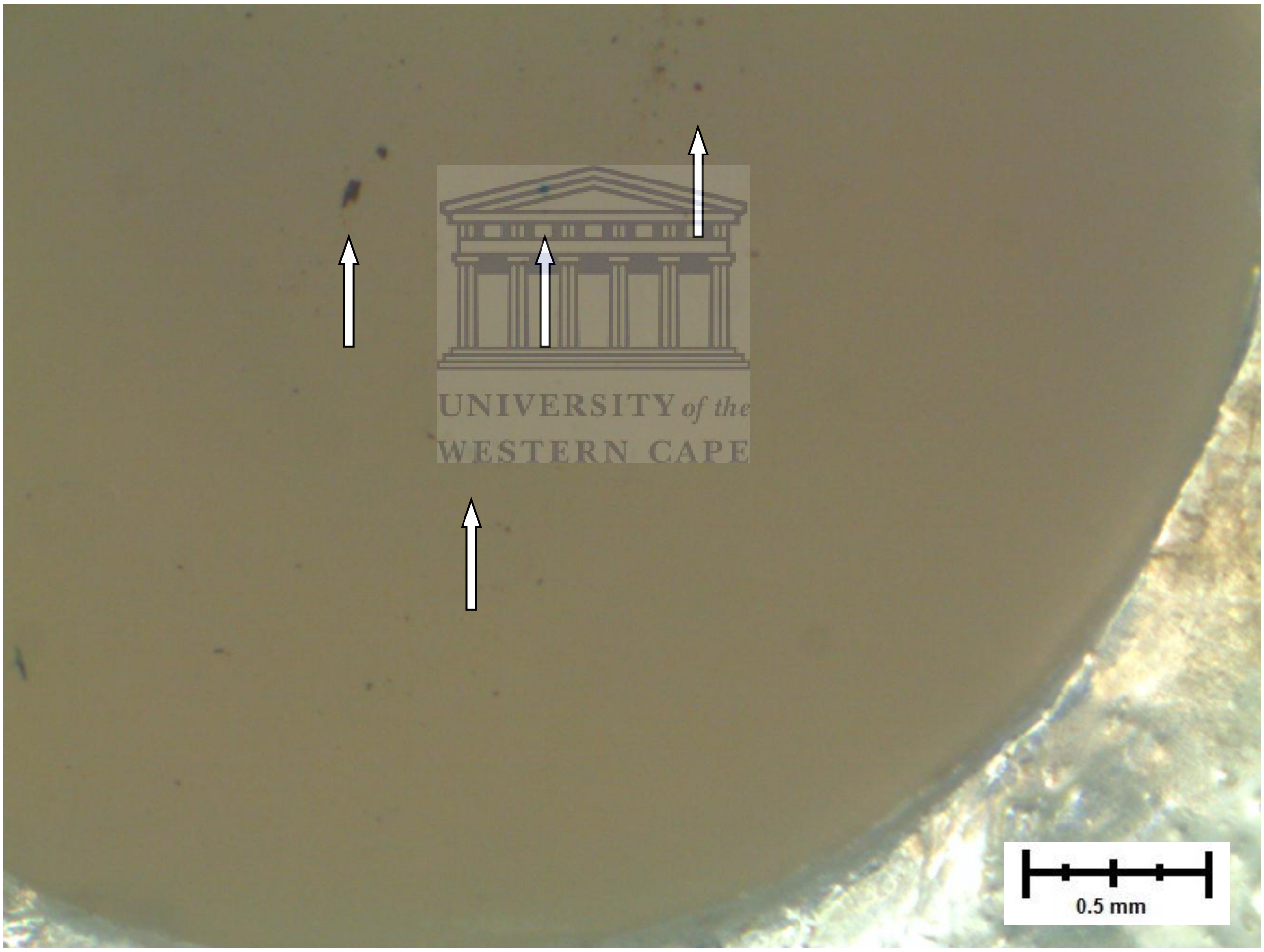


Figure 36: Stereomicroscope of SDR, voids appear as black spots

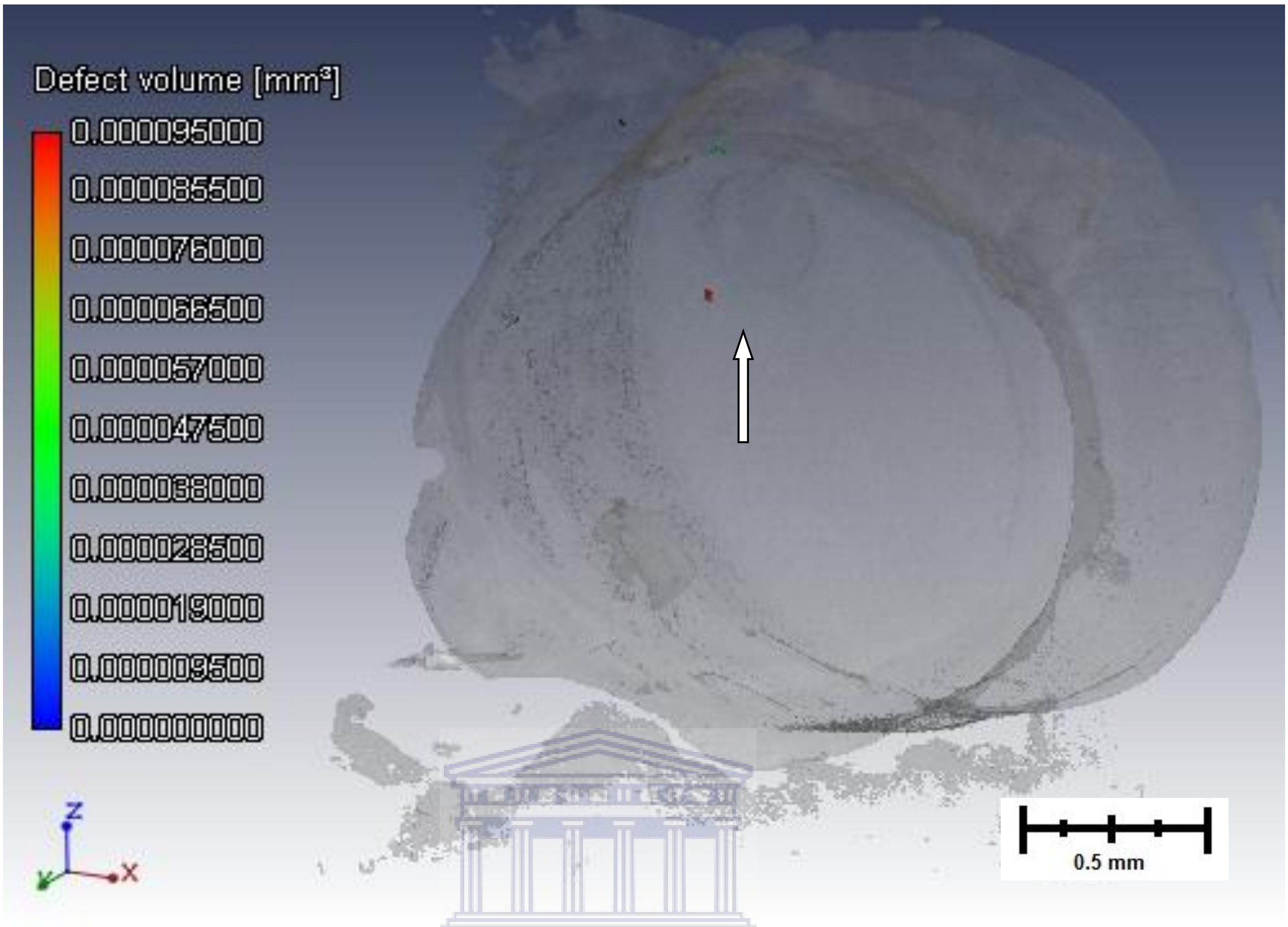


Figure 37: 3D micro-ct reconstruction of voids in 49,089 mm^3 of cured SDR, indicated in various colors

3.5.1.3. Venus Bulk Fill

Average of the ten samples for Venus bulk fill showed a volumetric shrinkage of 1.72% *(Figure 38, 39).* Therefore, the total voids recorded within the Micro-3D ct reconstruction of the polymerized sample of

49.087mm³ were 0.585846543 mm³ for Venus bulk fill. This volume of 0.58 mm³ voids were likely present in the sample.

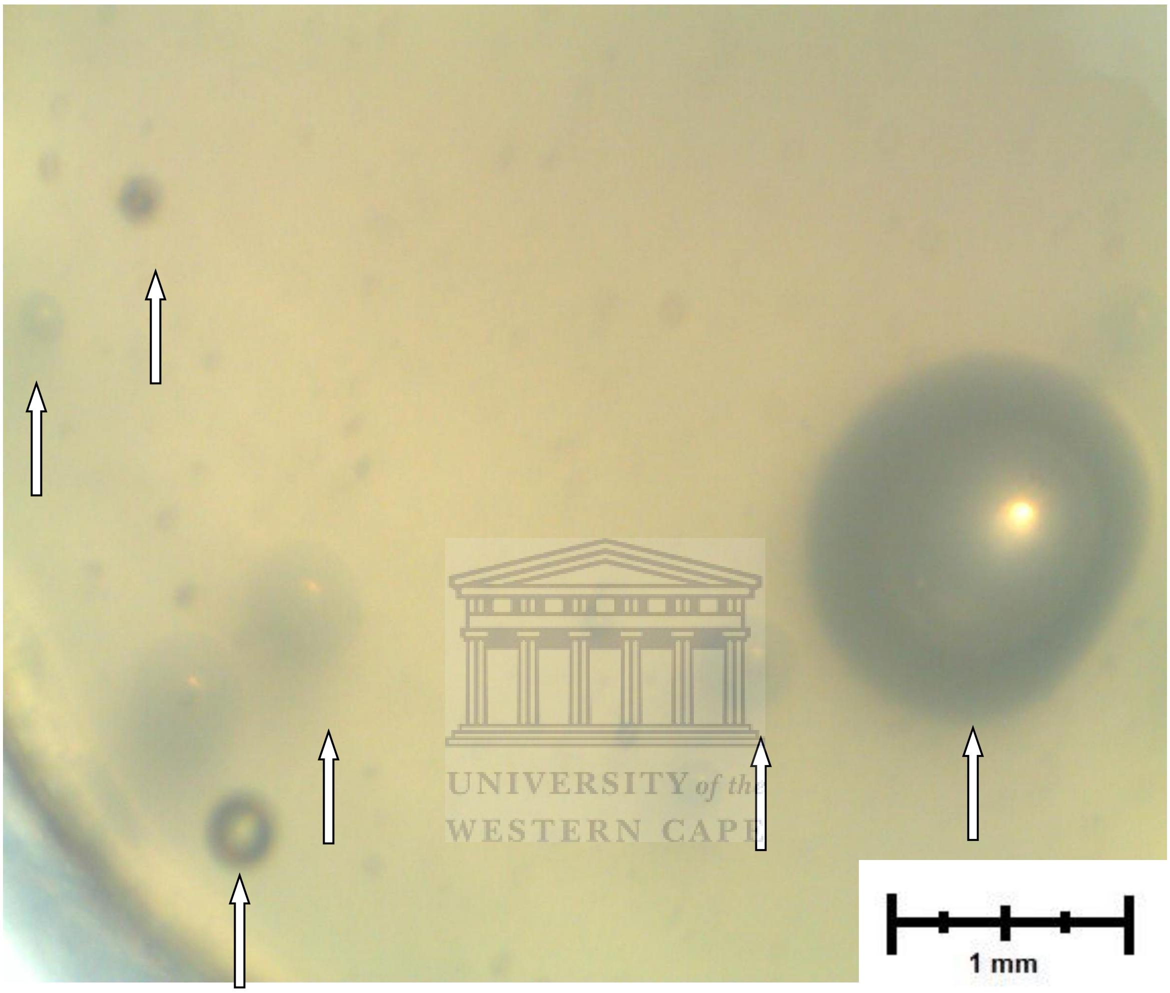


Figure 38: Stereomicroscope of Venus, voids appear as black spots

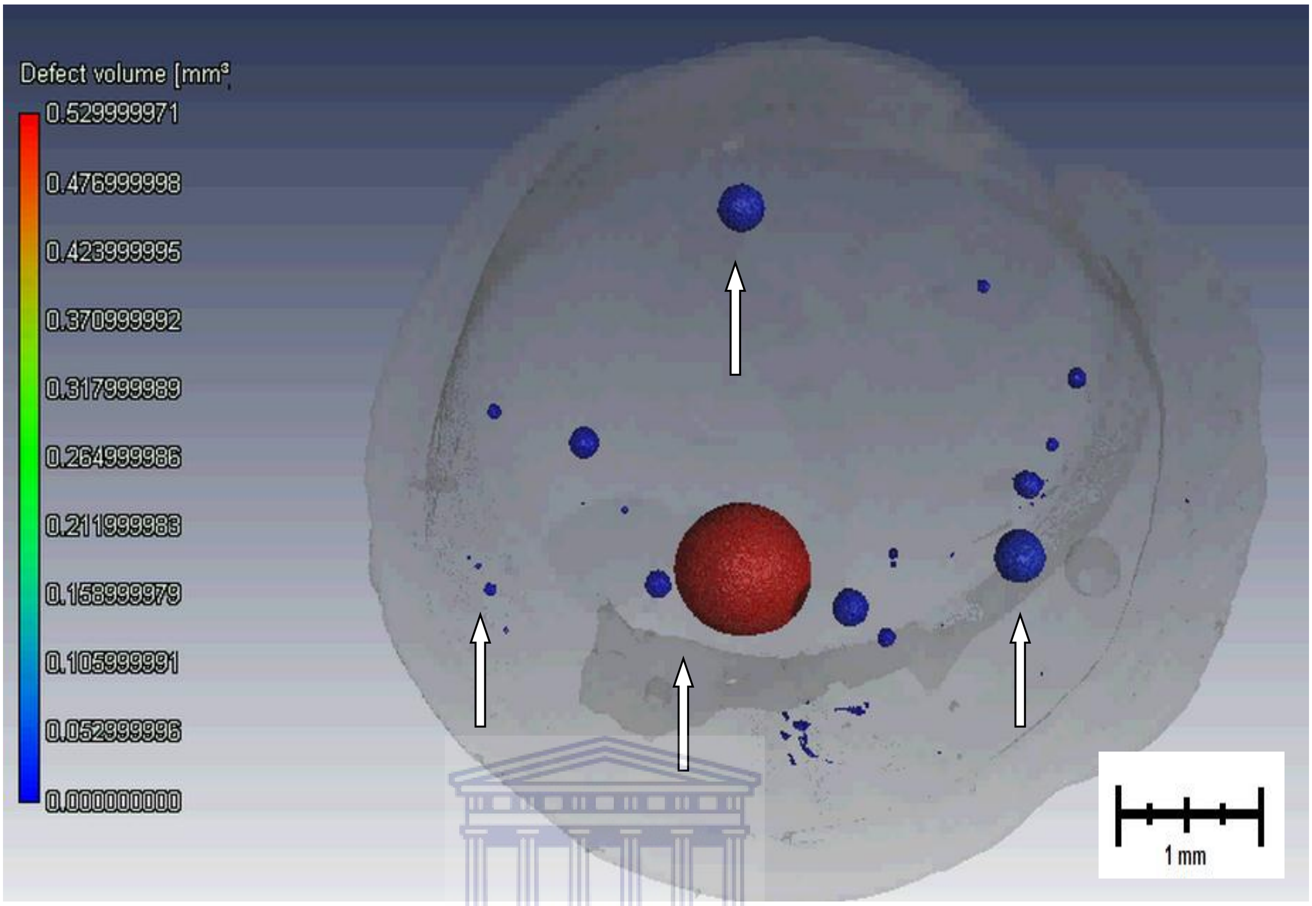


Figure 39: 3D micro-ct reconstruction of voids in 49,089 mm^3 of cured Venus bulk fill, indicated in various colors

3.5.1.4. Filtek Bulk Fill

Average of the ten samples for Filtek bulk fill showed a volumetric shrinkage of 1.39% *(Figure 40, 41).* Therefore, the total voids recorded within the Micro-3D ct reconstruction of the polymerized sample of 49.087mm^3 were 0.000344766 mm^3 for Filtek bulk fill. This volume of 0.00034 mm^3 voids were likely present in the sample.

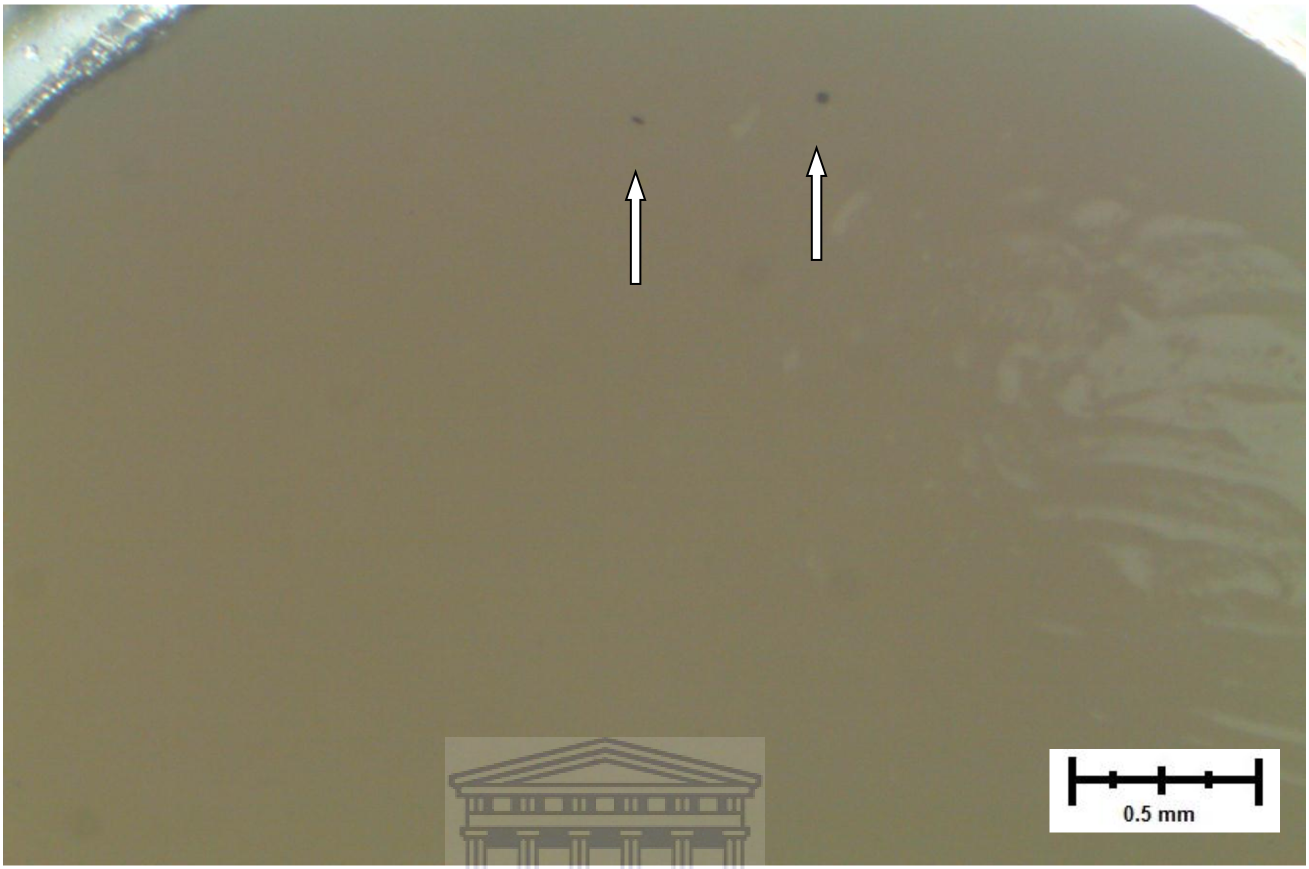


Figure 40: Stereomicroscope of Filtek bulk fill, voids appear as black spots

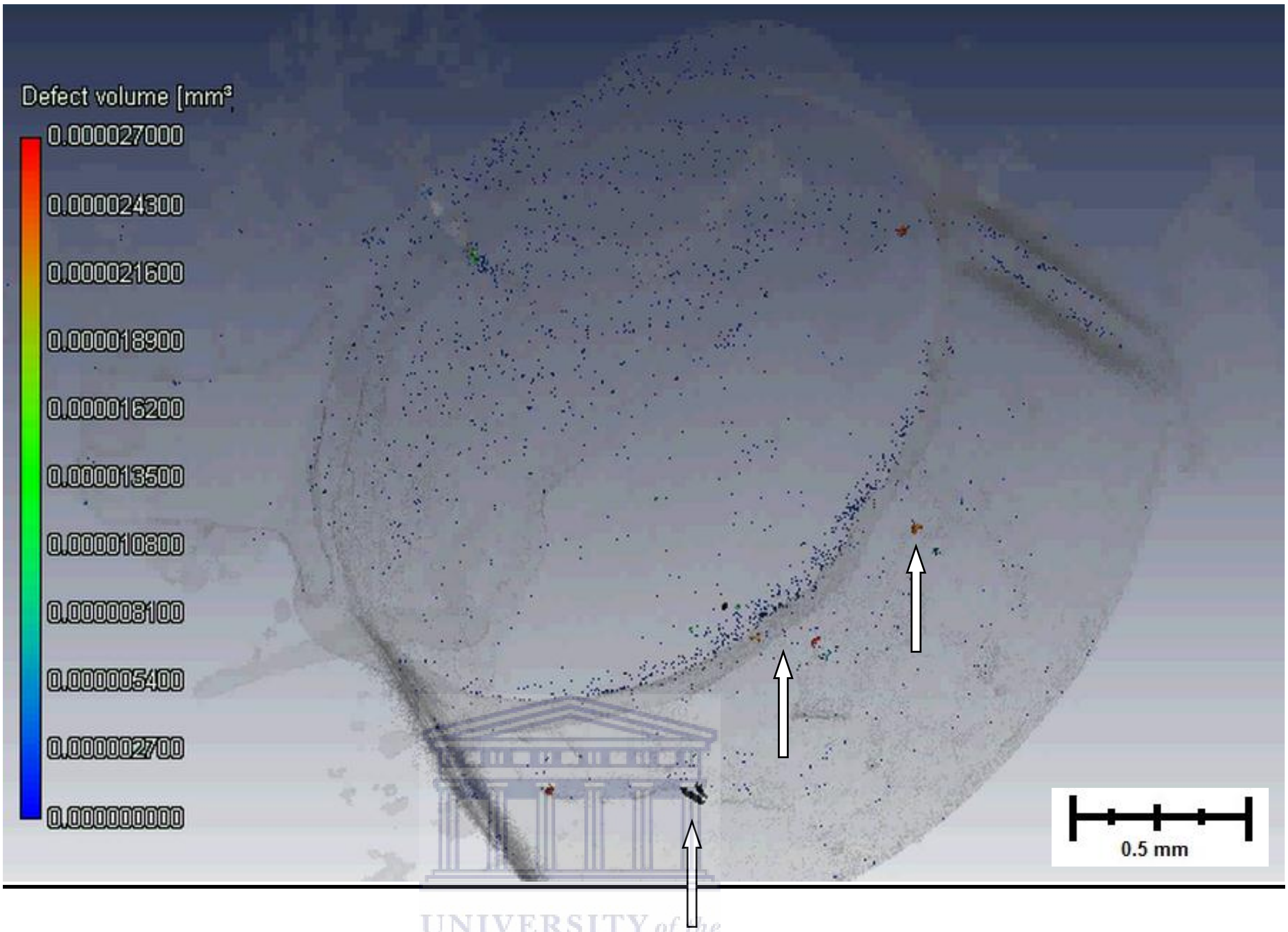


Figure 41: 3D micro-ct reconstruction of voids in 49,089 mm^3 of cured Filtek Bulk Fill, indicated in various colors

3.5.1.5. X-tra Base

Average of the ten samples for Filtek bulk fill showed a volumetric shrinkage of 1.44% *(Figure 42).* Therefore, the total voids recorded within the Micro-3D ct reconstruction of the polymerized sample of 49.087mm^3 were 0.000077806 mm^3 for Filtek bulk fill. This volume of 0.000077 mm^3 voids were likely present in the sample.

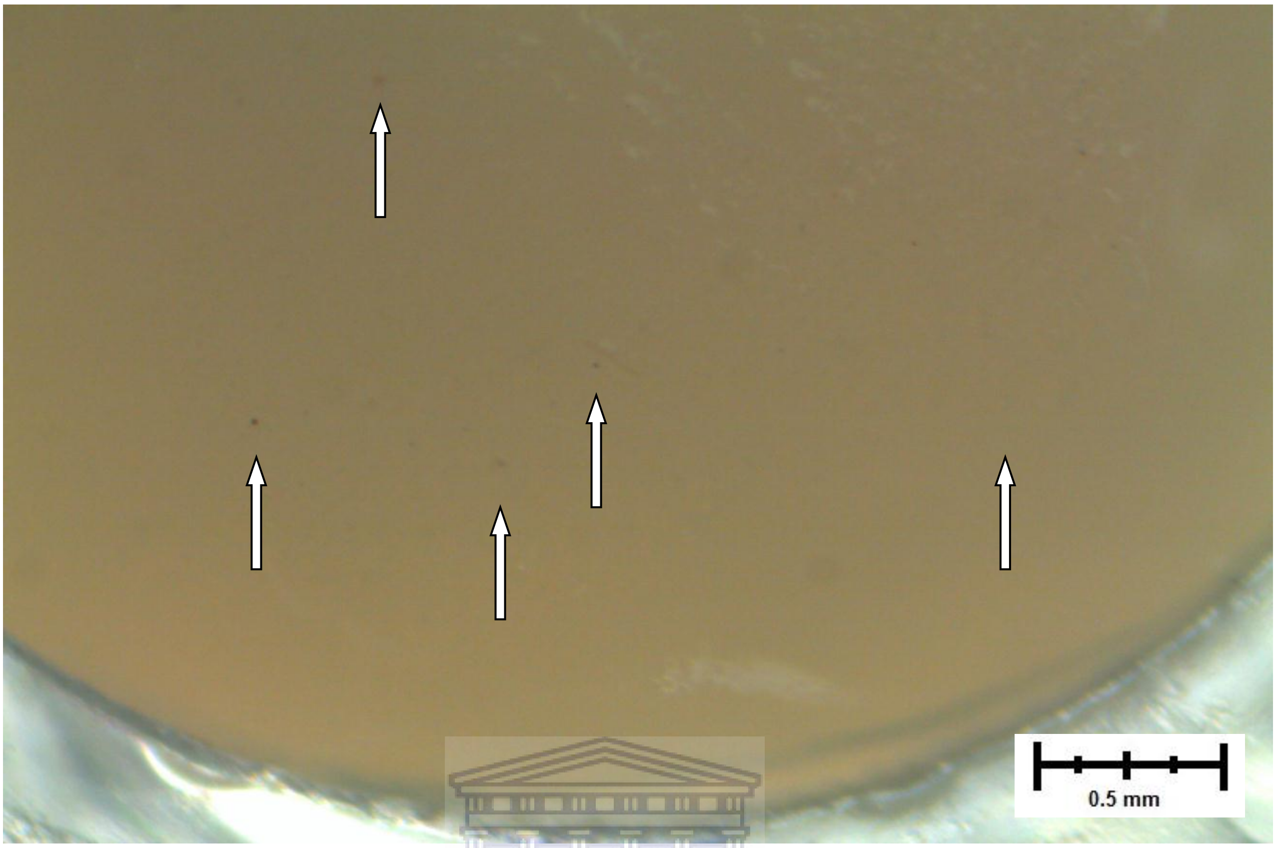


Figure 42: Stereomicroscope of X-tra base, voids appear as black spots

3.5.2. Voids in a SDR ampule

Figure 43 indicate the total flowable composite volume of 169.7 mm^3 in the SDR ampule. The total volume of voids within the ampule from the manufacturer was 4.1 mm^3. The volume of voids in the cured sample (49.087 mm^3) of SDR was 0,000290302 mm^3. This difference in void volume indicated that the thin dispensing tip results in the reduction of voids in the restoration. This will only ring true provided the metal tip is not submerged in the material that gets extruded into the prepared tooth cavity.

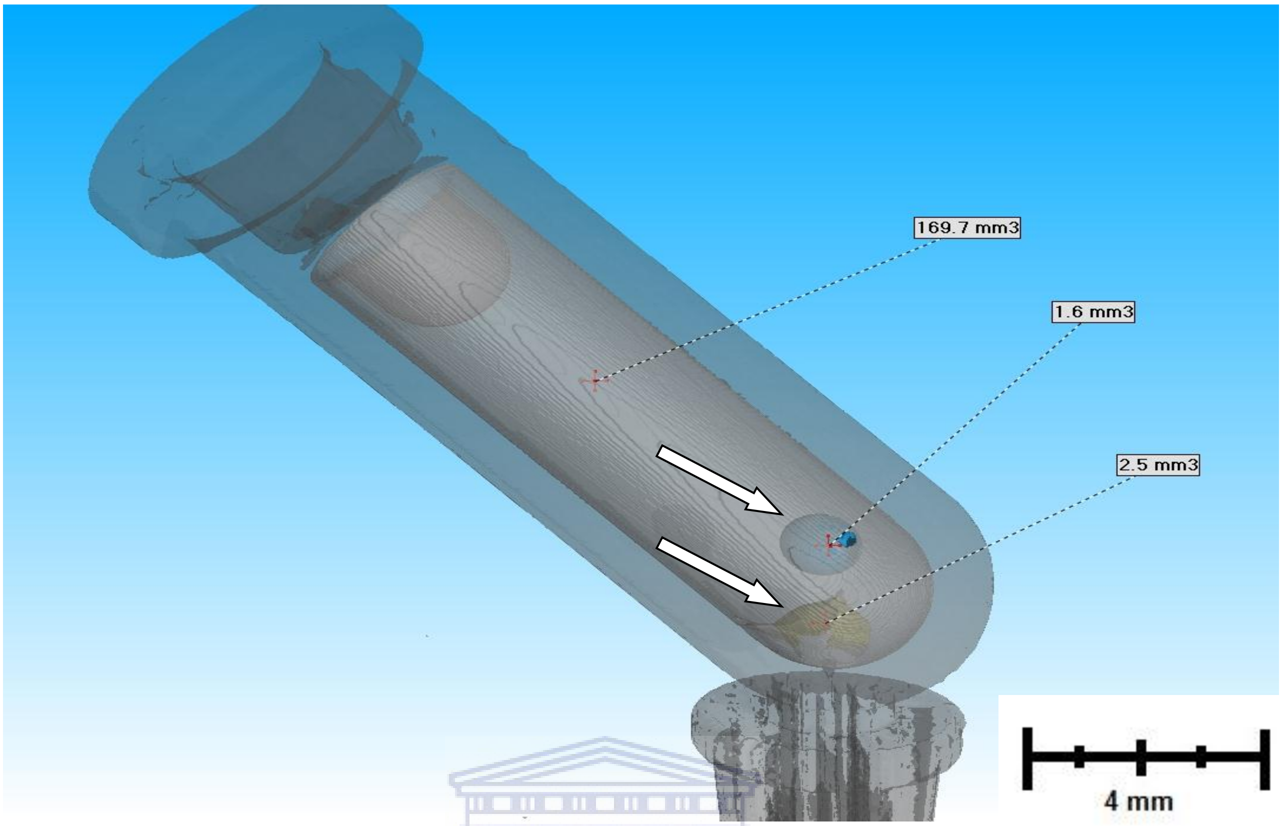


Figure 43: 3D micro-ct reconstruction of voids in a new ampule of SDR

CHAPTER 4

DISCUSSION

Dilatometry has been used extensively as a technique for the determination of volumetric change (De Gee, 1981. Soderholm, 1984. Reed, 1996. Oberholzer, 2001).

Oberholzer et al., developed the dilatometer used in this study (Oberholzer, 2001). The main advantage of this dilatometer was that the change of the mercury height within the capillary could be measured electronically, instead of manual viewing. Furthermore, the electronic mercury dilatometer enables measurements to be made on samples regardless of their shape and size. The modified mercury dilatometer is more accurate than the water filled dilatometers as used by Lai, 1993. Lai suggested that it is necessary to employ a correction value to the shrinkage results of water filled dilatometers. The correction value was suggested by Lai (1993) because it was found by his study that the surface hardness of the material tested was softer than the samples tested under standard conditions, suggesting interference from the water on the surface layers of the dental resin. Yap et al (2000) set out to assess this claim from Lai (1993) and the results indicated that dental composite resins composites take hours, to even days to absorb water. Therefore, no correction for the percentage of conversion is required (Yap, 2000).

Pfeifer (2008) confirmed the studies on curing exposure by Halvorson (2002) that a variation of exposures up to and including 500 mW/cm^2 were able to provide sufficient irradiance to composites provided that an appropriate exposure time was provided (Halvorson, 2002. Pfeifer, 2008). The peak wavelength of Quartz–Tungsten–Halogen light–curing units (QTH) can range from 450nm to 490nm and the intensity 400–800mW/cm^2 (Craig, 2002:249). A standard curing intensity of 500mW/cm^2 was used. This curing light output setting was within the range of the material manufacturer's specifications. The output of the Spectrum 800 curing light was monitored with a Dentsply Caulk radiometer to ensure 500mW/cm^2 ±50mW/cm^2. Calibration of the modified mercury dilatometer was done prior every specimen (Figure 27, 31). The curing intensity of 500mW/cm^2 is widely used for volumetric change, polymerization shrinkage and material properties studies (Oberholzer, 2001. Sharp, 2003. Lee, 2005). Lee (2005) established that the volumetric shrinkage did not increase when the results were compared for volumetric change with the 400mW/cm^2 to the intensity of the 500mW/cm^2 and 600mW/cm^2 even though the time it took to reach the same final total volumetric shrinkage was decreased with the higher intensities (Lee, 2005). A strong correlation was observed between the shrinkage and the degree of conversion of the organic resin matrix (Lee, 2005). Only Venus bulk fill and SDR requested an intensity of 550mW/cm^2 or more according to the instruction manual. Dentsply used 500-550 mW/cm^2 in the comparative test of SDR and Venus Bulk Fill (Scientific Compendium SDR, 2011:21, 62, 66). Conversion rate resulting in carbon double bond formation can range from 55-75% under conventional irradiation conditions of 500mW/cm^2 (Stansbury, 2001. Baroudi, 2007). This was confirmed by Dentsply in their Scientific Compendium of SDR (2011:23, 24). Therefore, no material was advantaged nor disadvantaged by using 500mW/cm^2 intensity. Al-Quadah (2007) illustrated that the curing light as well as the thickness of the composite in millimeter can influence the amount of the temperature change that results in the tooth *(Al-Quadah, 2007).* A temperature increase of 5.5°C may result in irreversible pulpitis. Therefore, a pulpal temperature of 37°C ±1 and an increase to more than 42.5°C may result in possible irreversible pulpitis (Ebenezar, 2010). This is essential since the addition of heat from the curing light that takes place be considered in the influence of the volumetric change readings on various devices. Therefore, the increase in temperature should be considered for studies of volumetric change. Alnazzawia (2012) used 1200mW/cm^2 that provided significantly more energy and the results indicated that the exothermic reaction of polymerization and the heat transferred due to light irradiance showed a close correlation to one another and therefore not negligible (Alnazzawia, 2012).

The temperature change induced by the curing light is not considered a variable for the electronic mercury dilatometer used by the author, because the software of the modified electronic mercury dilatometer ensures that the temperature and the pressure in mmHg stay stable *(Figure 27, 31) (Oberholzer, 2001, 2002).* The software of the electronic mercury dilatometer was designed and calibrated with the Spectrum 800 curing unit by Stellenbosch Elektroniese Dienste (SED) to eliminate these variations in real time, as the polymerization takes place. The baseline effect of the curing unit was established prior each set of experimental set-ups to ensure that the data was corrected accordingly by the software (Oberholzer, 2001, 2002). This software correction of the heat generated by the curing light resulted in the volumetric shrinkage that is presented for each material to be the true volumetric change due to polymerization only. Therefore, only the effect of polymerization shrinkage between the monomers from a monomer to a polymer is presented in the results (Jin, 2002. Oberholzer, 2002). The dilatometer is kept at 25°C ± 1°C. The software correction corresponds well to a study done by Jin (2002). The effect from the curing light was found to be only 0.15% volumetric expansion or contraction when the baseline was established prior specimen tensting.

The design of the electronic mercury dilatometer included the calibration of the software with the Teflon specimen holder *(Figure 31)* and the Spectrum 800 curing light.

The volumes of the dental resins tested in linometers are larger (Sharp, 2003. Sakaguchi, 2004. Miller, 2006) than the volumes of dental resin tested in the mercury dilatometer of Oberholzer et al, (2001, 2002) and Mulder et al, (2013). The exothermic reaction was noticeable in the volumetric change results of linometers and therefore data correction had to have been done for Sharp (2003), Miller (2006) and Sakaguchi (2004). This difference between the results from Oberholzer and the volumetric change obtained by Watts, 1991 and De Gee, 1991 is the exothermic effect of polymerization, as these authors did not state that a data correction was considered for the results (De Gee, 1991. Watts, 1991). The results obtained by Oberholzer (2001, 2002) and Mulder (2013) are the volumetric change due to the polymerization of the monomers to the final polymer. This polymerization reaction that was expressed in the form of a graph and therefore represents the polymerization slopes *(Figure 32).* The specimen volume of the dental resins tested was 0.049mm³. Oberholzer (2001) concluded that the exothermic heat resulting from the reaction of polymerization in the small sample of dental resin used in the electronic mercury dilatometer was negligible and did not affect the volumetric change (Oberholzer, 2001. Uhl, 2003). The volume and the mass of the specimen holder and resin polymer remain constant during the curing cycle *(Figure 31)*. It is therefore predicted that the electronic mercury dilatometer is a device that was well designed for the accurate determination of the volumetric change in dental resins. Mercury dilatometers will be of value until volumetric change resulting from the polymerization from a monomer to a polymer reaches 0% (Li, 2004).

From the literature many factors might have an influence on the volumetric shrinkage of a material i.e. filler content, filler size, type of monomers, monomer content, organic matrix and type and organic matrix conversion factors (Condon, 2000. Davidson, 1984). Initially the comparison of bulk fill flowable composites with composites could be seen as an unfair comparison towards the bulk fill flowable composites. The reason for is that the lower viscosity dental materials like flowable composites have a larger polymerization shrinkage compared to composites (Oberholzer, 2000, 2004). But, due to the fact that the manufactures of the bulk fill flowable composites claimed lower polymerization shrinkage than composites and 4mm bulk fill layers, these statements became the hypothesis. Composites and traditional flowable composites are advocated to be used in 2mm layers (Meredith, 1997. Alomari, 2001. Abbas, 2003. de Las Casas, 2012. Mulder, 2013). However, the bulk fill flowable composites claim a 4mm layering technique in the instruction brochures. The highest percentage of volumetric change *(Figure 32)* for all 5 materials occurred approximately within the first 10.0 seconds. Furthermore, it can be seen that most (~90%) of the polymerization shrinkage for all 5 different materials took place in the first 20 seconds and the degree of polymerization was generally completed after 35 seconds of constant irradiation (Davidson, 1997). Davidson also reported that 90% of the shrinkage of composites took place during the first 20 seconds. However, when the sequence of shrinkage (Filtek < Xtra base < SDR < Venus) of the 4 bulk flowables was compared to their filler content no clear trend could be seen *(Table 2).* Furthermore, the sizes of the fillers alone did not seem to show a clear effect on the shrinkage values, although Z250 with an average filler size of 0.6 µm showed a lower shrinkage (1.13%) relative to SDR with a higher average filler size of 4.2 µm. Unfortunately, the average filler sizes of the other flowables were not stipulated by the manufacturers and their possible effects on shrinkage could not be discussed.

It was also reported that the higher the molecular weight of a molecule *(Table 3)* the lower the shrinkage (Ferracane, 1986, Condon, 2000, Braga, 2005, Cramer, 2011.) But when there are variations in the mixtures of chemicals with different molecular weights and in different ratios (like the flowables tested in this study) it would not be possible to illustrate clear trends. The effectiveness of the claimed SDR-UDMA could not be assessed, since there is no SDR material with normal UDMA. Based on the molecular weight of SDR-UDMA 849g/mol and non modified UDMA with a molecular weight of 470.55g/mol SDR-UDMA should have less volumetric change *(Figure 32).* To proof this addition of the modulator as a significant improvement on SDR bulk fill flowable composites the author feels that volumetric change for a SDR product with ‘normal’ UDMA should be done to establish the potential difference the patented SDR-UDMA makes. Thanks to the SDR-UDMA a claim of 20% reduction in polymerization shrinkage occur in SDR as tested by Dentsply against their Esthet•X flowable composites. (Scientific Compendium, 2011:8). Oberholzer et al (2004) indicated the volumetric change of Dyract flow (Dentsply) 3.5% and Z250 1.1% (Oberholzer, 2004). Mulder et al (2013) indicated SDR 1.56% and Z250 1.13%

(Mulder, 2013). This indicates that the volumetric change of flowable composites has improved from previous results. In order to establish the possible improvements of resin filling materials the constituents of the materials should be considered in conjunction with the polymerization shrinkage resulting in volumetric change. From the composition of the various materials it becomes apparent that the prediction on polymerization shrinkage due to volumetric change based on the constituents alone is difficult to make. Kleverlaan et al (2005) is of the view from their work that the elastic properties (i.e. E-modulus or tensile modulus) and the ability of the polymer to rearrange and relieve stress, i.e. flow, has been shown to influence the final contraction stress. These four parameters, shrinkage, contraction stress, tensile modulus and flow have shown an interesting interplay which depends on many factors such as filler load, type of filler particles, monomer system and pre-polymerized particles (Kleverlaan, 2005). The ratio of the viscous base monomer to the more flowable diluent monomers has also been found to be a large contributing factor to the percentage of polymerization shrinkage (Antonucci, 1993. Silikas, 2000). Braem et al (1986) showed this strong correlation between increasing the filler load and the resulting lower shrinkage due to a decrease in organic matrix diluents (Braem, 1986). However, in this study the influence that the ratio might have on the volumetric change, could unfortunately not be sensibly discussed as the manufacturers of the dental materials did not provide the exact ratio or percentage of different monomers contained in the dental materials *(Table 7).* By combining various monomers to create a multifunctional organic matrix - a reduction of polymerization shrinkage and water sorption can be achieved (Antonucci, 1993).

All the above-mentioned factors which might have varying influences on the speed and volume of shrinkage. This study proved that the only reliable way to establish and compare the performance of the materials in terms of shrinkages is by measuring the volumetric shrinkage.

Based on the rate of polymerization SDR, the resin material seems to reach the gel point in a similar fashion but does not reflect the differences in contraction stress (Labella, 1999). Polymerization rate can influence the contraction stress generated in resin composites. After polymerization is triggered contraction stress start to build-up within seconds due the speed of polymerization even though a low initial conversion rate was achieved (Calheiros, 2004). The first 1.5 seconds represent the incipient gel is formed. 5-10% of the conversion is completed here and demarcates the start of stress build (Bunyamin, 2008). Faster polymerization rates imply that the resin composite reaches the gel point more quickly and rapidly giving rise to stiffness instead of giving it time to let the resin composite flow. Venus bulk fill showed a 5% increase in conversion compared to SDR. The larger degree of conversion of Venus bulk fill translated into a larger volumetric change (Czash, 2013). Initially the large volumetric change of Venus was attributed to the voids in the sample that was clearly visible under stereomicroscope *(Figure 38, 39).* All the samples were inspected under Stereomicroscope and later Micro-3D ct reconstruction was used to assess the volume of the voids in the samples. Venus bulk fill have a filler content of 65%wt and a relatively viscous organic matrix based on the molecular weight *(Table 7).* The voids towards the surface became exposed as the shrinkage of the material took place in the electronic mercury dilatometer, resulting in volume loss and the dilatometer recording more shrinkage (Figure 32). The polymerization shrinkage of Venus bulk fill (1.72%) is the largest out of the materials tested. The presence of relatively large air bubbles/voids in Venus bulk fill compared to other bulk fill flowable composites that became exposed during polymerization shrinkage could be viewed in the data that was recorded every 0.5 seconds as irregularities (Figure 32). These irregularities could be seen on the polymerization graph at the 20-25 second interval exposure of the void was prone (Figure 32). It was established, when the voids become exposed during the volumetric change process in the mercury dilatometer, the void fills with water, resulting in a sudden volumetric change on the mercury column. During the experiment of polymerization irregularities were noted in the data for Venus bulk fill from the 20th to the 25th second time interval (Figure 32). Further investigation was required to ascertain the cause for the irregularities. For the purpose of void determination the author used ct scans produced by a Micro-ct 3D reconstruction unit (General Electrical). The effectiveness of this piece of equipment was established in 2009. In 2009 Yu–Chih Chiangac et al, developed a method to experimentally determine and visualize the direction of polymerization shrinkage – namely high-resolution micro-computed tomography (Chiangac, 2010). The total volume of bubbles in Venus was 0.585846543 mm^3 of the total polymerized sample volume (49.087mm^3) *(Figure 38, 39).* This volume was therefore too small to have an effect on the percentage of volumetric change. Although the voids played no role in volumetric change due to their small volume, void inclusion could be due to the manufacturing process of the restorative material or the operator during restoration placement. The solubility as well as the mass of the dental restoration is affected by the voids (éYSAED, 1986a). The formation of cracks can be potentiated when voids are incorporated in the restoration. The precipitation and swelling phenomena of composite restorative materials over time can give rise to voids and cracks (Drummond, 2008). Voids contribute to post-operative sensitivity, micro-leakage and secondary caries (Medlock, 1985. McCabe, 1987. Nordbo, 1993). Willems et al (1992) concluded that a midway-filled composite (Gem-CCI) had a higher surface roughness than the other materials tested. The reason was the inclusion of air bubbles/voids during the mixing process that was necessary prior use (Willems, 1992). Various techniques were investigated in an attempt to decrease void inclusion during placement of dental resins, to no statistical avail (Tagteken, 2007).

The viscosity and consistency play a role during the packing and adaptation process, resulting in void inclusion by the operator. When flowable composites were compared to hybrid composites, the results from the literature was not conclusive whether less voids are present in flowable composites compared to hybrid composites (Tagteken, 2007). The bulk fill flowable composites are very flowable and a scan was done of the Filtek bulk fill and the filler content assessed *(Figure 44).* The set-up for the ampule was done the afternoon and the scan could only have been done the following morning. *Figure 44* indicated a clear sedimentation of filler particles. The 3D micro-ct reconstruction revealed a filler content of 55.42%, whereas the manufacture states a volume filler content of 42.5% (Fitek bulk technical guide: p6). This large variation in filler content between what the manufactures state and what is in actual fact in the ampule, might affect the volumetric change of the dental resins.

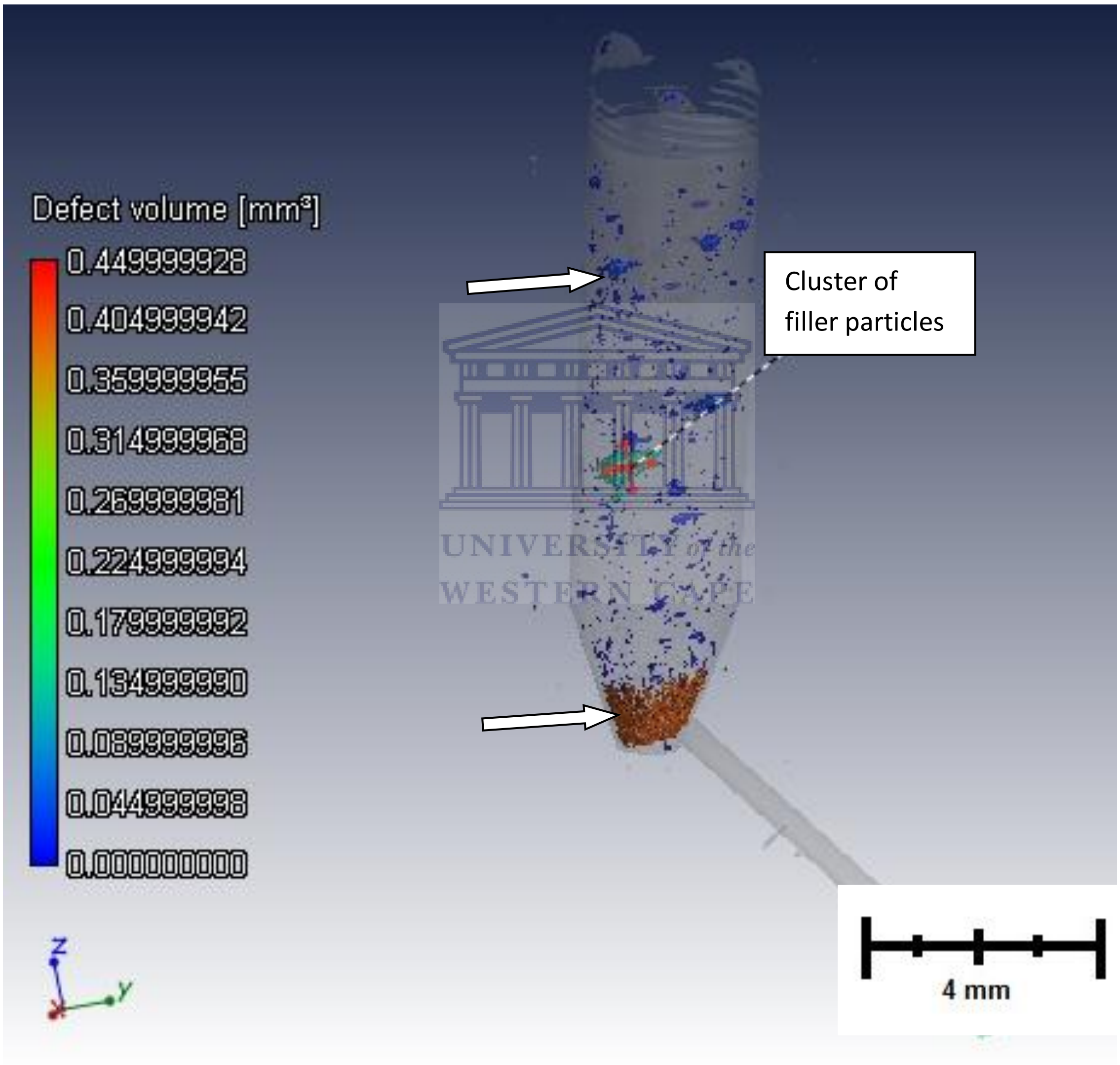


Figure 44: 3D micro-ct reconstruction indicating filler sedimentation in a new ampule of Filtek bulk fill flowable composite after 17 hours.

In general, the rate of polymerization shrinkage *(Figure 32)* for all the bulk fill flowable composites was faster than the control composite Z250. However, over the 5-15 second period, Venus and SDR shrank the fastest after which period they all levelled out to about the same slope and shrinkage rate (Figure 32). After about 15 seconds the shrinkage rate of SDR decreased at which stage Venus began to shrink at a faster rate than SDR. The speed of shrinkage (slopes) of the other two bulk flowables (Xtra-Base and Filtek) was about the same with Xtra-Base ending marginally larger total volumetric shrinkage value. Therefore, it can be seen that the two materials (SDR and Venus) with the fastest polymerization rates (highest slopes) also had the largest total volumetric shrinkage. The shrinkage value obtained for Z250 (1.13%) corresponds well with other published values of ~1.1% (Bouschlicher, 2000. Oberholzer, 2001, 2004. Kleverlaan, 2005. Goncalves, 2010, 2011). The literature also showed that in general the higher the monomer content and the more flowable, the higher the shrinkage (Rees, 1989. Davidson, 1997. Condon, 2000. Ge, 2005. Goncalves, 2010. Pfeifer, 2008.) and the faster the conversion rate to the gel phase (Reuggeberg, 1995. Penn, 1986. Silikas, 2000. Oberholzer, 2001. Stansbury, 2001). As long as there is volumetric change in composite resins polymerization shrinkage will remain very important in adhesive dentistry. Polymerization shrinkage can be modified and manipulated with various organic resin matrixes and inorganic filler combinations and types. Until this moment in time, there is no ideal composite on the market that fulfill in every ideal characteristic. Until composites become available that expand during polymerization volumetric shrinkage will be something to always consider. Therefore, the organic matrix will become increasingly important in the development of a composite with a low volumetric shrinkage or even a volumetric expansion upon polymerization.

Table 7: Organic matrix combinations of "Bulk Fill Flowable Composites" and Z250.

Resin present in material	**Molecular weight g/mol**	**Material containing the following combination resins**				
UDMA	470,55	Z250 1-10%		Filtek Bulk Fill 10-20%	Venus bulk fill (Unknown)	X-tra Base 10-25%

SDR-UDMA (Unknown)	849		SDR <25%			
TEGDMA	286,32	Z250 <5%	SDR <10%	Filtek Bulk Fill <1%		
Bis-GMA	512,59	Z250 1-10%		Filtek Bulk Fill 1-10%		X-tra Base 10-25%
Bis-EMA(6), EBADMA	496.582	Z250 1-10%		Filtek Bulk Fill 1-10%	Venus bulk fill (Unknown)	
EPBADMA	452.53938		SDR <10%			
Procrylate	480,59			Filtek Bulk Fill 10-20%		

The quest for the ideal material will continue as the applications and expectations evolve over time. Peutzfeldt (1997) investigated the organic matrix and determined that it is the main deficiency in the dental material since it contributes to polymerization shrinkage and insufficient wear characteristics under masticatory forces (Peutzfeldt, 1997).

The organic matrix that is utilized most in dental resins is the bis-GMA invented in 1935 and the more diluent TEGDMA in very small concentrations (Antonucci, 1997).

The base monomer (bis-GMA) has a larger molecular weight resulting in less polymerization shrinkage and the lower viscosity monomer (TEGDMA) has a greater degree of freedom to assist in improving the handling properties and the formation of copolymer chains (Stansbury, 2001).

The bisphenol-A back bone of bis-GMA provides less shrinkage and a higher modulus due to the high molecular weight (512,59g/mol). Studies on the matrix formation of the resin complex have shown that bis-GMA as the main monomer results in a decreased degree of conversion as the proportion of bis-GMA increase (Asmussen, 1998. Izabela, 2012).

The drawback of the bis-GMA is the hydrogen bonds of the hydroxyl groups that limit the degree of conversion and filler incorporation (Atai, 2006). Bis-EMA is an organic resin that can add strength and an increased hardness to a dental resin due to the lack of hydroxyl groups (Lovell, 1999). When looking at X-tra base, it is noted that only two base monomers are present, namely UDMA and bis-GMA. With a high filler weigh present in X-tra base (75%) wetting of the filler particles are important. The manufacturer withheld the resin concentration in X-tra base. From the literature it is clear that in order to achieve sufficient wetting of the filler particles, a lower viscosity resin like UDMA would have to be present in a larger ratio compared to the more viscous bis-GMA (Antonucci, 1997).

Therefore, the conclusion can be made that although a high filler load is present, the more viscous UDMA present in X-tra base will result in the higher polymerization shrinkage compared to Filtek bulk fill with lower filler loading systems, but a multitude of monomer combinations *(Table 7).*

The polymerization shrinkage of Filtek Bulk Fill of 1.13% compared to Venus bulk fill 1.72% and SDR 1.56% (Figure 32) indicates that although these three products have a filler weight and type in close relation to each other the organic resin matrixes differ vastly resulting in varying results. SDR had higher filler content than Filtek Bulk Fill and shrank more.

For a resin with only two monomers X-tra Base performed well with the high filler load of 75% with the second best shrinkage percentage after bulk fill flowable composite. When looking at X-tra Base with the high filler content of 75% and the polymerization shrinkage of 1.44% there would have to be a range of fillers ranging from 0.01-10 µm.

In an attempt to create base monomers with an increased conversion rate that is less viscous bis-GMA was ethoxylated. Dental polymers based on EBPADMA were subsequently produced. EBPADMA has a high molecular weight (452.53g/mol) and is relatively more hydrophobic than bis-GMA. EBPADMA is more flexible and have a lower viscosity than bis-GMA (Antonucci, 1993). When EBPADMA was added to bis-GMA/TEGDMA a lower polymerization shrinkage than the bis-GMA /TEGDMA combination was found. Bis-GMA and EBADMA are similar to EPBADMA since they are all derived from bis-GMA (Antonucci, 1993). Procrylate has a molecular weight of 480.59g/mol *(Figure 20. Table 3, 7).* The only differences with bis-GMA are the lower molecular weight and procylate lacks pendant hydroxyl groups. The subsequent result is a lower viscosity. Therefore, is served as a partial replacement for

TEGDMA (Filtek bulk fill flowable technical profile: page 8). The matrix of Z250 and Filtek bulk fill are remarkably similar. Filtek bulk fill has the additional monomer called procrylate. The UDMA, bis-EMA6 and procrylate enabled a lower viscosity for Filtek bulk fill than Z250 with a reduction in TEGDMA. This evolution of the resin matrix clearly indicates the importance of the combination and the percentage of each diluent *(Table 7).* With the results obtained and the similarities in filler type Filtek Bulk Fill seem to have a good balance in filler size and matrix combinations. Based on the contents of the organic matrix of SDR the result of having the third largest volumetric change was surprising. Especially considering the SDR-UDMA with a molecular weight of 849g/mol *(Figure 45, Table 7).* The modulator added in the SDR-UDMA is said to assist in the dissipation of energy and a more controlled polymerization chain formation. The result is less stress and polymerization shrinkage of the restoration tooth interface (SDR Scientific compendium, p11). The conclusion must be made that a larger percentage of the patented urethane and TEGDMA must be present in relation to the ratio of EBADMA- this was confirmed in the literature on SDR. (MSDS: DENTSPLY/International DENTSPLY/Caulk Safety Data Sheet 51C700). Should TEGDMA be reduced to 1% and procrylate added to 10-20% a better result should be obtained since the molecular weight will be higher, with the flowable viscosity maintained (Asmussen, 1998. Sideriduo, 2003).

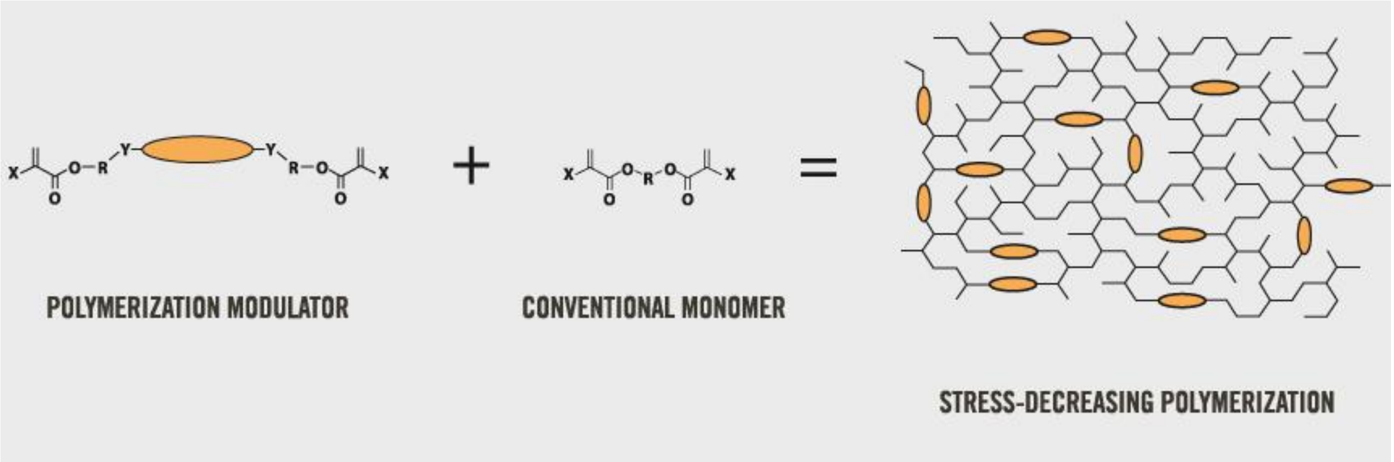


Figure 45: Illustration of the Dentsply patented modulator.

When looking at Venus bulk fill only two base monomers are present: UDMA and bis-EMA. Venus has a filler weight of 65%. Therefore, the conclusion can be made that there is more UDMA than EBADMA present resulting in the higher polymerization shrinkage compared to other bulk fill flowable composites. UDMA and bis-EMA(6) create a hard cross linked network and has a relatively high molecular weight while reducing the viscosity of resins, enabling less shrinkage than TEGDMA (Filtek bulk fill flowable technical profile: page 8).

X-tra base only have two monomers *(Table 7).* The manufacturers do not divulge the exact percentage of the resin combination and the total resultant molecular weights of the final matrices of all the dental resins tested. The inorganic filler particles are inert and therefore do not contribute to polymerization. The combination, size and filler type result in variations of the percentage filler particles in dental resins per weight/volume do however to a point reduce polymerization shrinkage.

Higher filler content by weight percentage has shown to reduce polymerization shrinkage (Silikas, 2000. Manhart, 2001. Calheiros, 2004).

When comparing the filler content and total percentage filler particles of the bulk fill flowable composites, with attention to note the overlapping similarities in filler type and size *(Table 2).* It would appear that based on the similarities of the filler type and size the differences in organic matrices may be an important factor in affecting the volumetric change. X-tra base and Venus bulk fill share the UDMA resin. X-tra base has bis-GMA and Venus bulk fill has EBADMA as the monomer. The ratio of UDMA and EBADMA are not provided and considering the viscosity of the Venus bulk fill it can be speculated the UDMA ratio is higher than the bis-GMA.

Goncalves (2010) indicated that filler type and load does play a significant role in the total polymerization shrinkage when filled per weight above 60% wt. Therefore, until the total molecular weight of the organic matrixes are known and compared in combination with the filler load a conclusion cannot be made to what organic matrix has the highest molecular weight (Goncalves, 2010).

It is these organic matrices that play a large role in the volumetric shrinkage as well as the exothermic reaction that occur during polymerization. The irradiance source does provide heat to the dental resin that changes the coefficient of thermal expansion resulting in an effect on the volumetric change (Alnazzawia, 2012). The literature concurs that as the filler content increases, the exothermic value decrease due to the inert characteristic of the filler particle (Soderholm, 1984. Versluis, 1996. Stansbury, 2000. Tezvergi, 2003. Sideridou, 2004. Park, 2010).

The shrinkage curve *(Figure 32)* for Venus over the whole 35 second period was the most fluent which indicated a steady shrinkage. The slopes of the shrinkage rates over the first 5 seconds did not differ significantly. However, , over the 5-15 second period, Venus and SDR shrank the fastest after which period they all leveled out to about the same slope and shrinkage rate.

After about 15 seconds the shrinkage rate of SDR decreased at which stage Venus began to shrink at a faster rate than SDR. The speed of shrinkage (slopes) of the other 2 bulk flowables (Xtra-Base and Filtek) was about the same with Xtra-Base ending marginally higher total volumetric shrinkage value.

By combining various monomers to create a multifunctional organic matrix - a reduction of polymerization shrinkage and water sorption can be achieved (Antonucci, 1993).

It was also reported that the higher the molecular weight of a molecule *(Table 3)* the lower the shrinkage (Braga, 2005. Condon, 2000. Cramer, 2011. Ferracane, 1986), but when there are variations in the mixtures of chemicals with different molecular weights and in different ratios (like the flowables tested in this study) it would not be possible to illustrate clear trends. Despite all the above-mentioned factors which might have varying influences on the speed and volume of shrinkage, this study proved that the only reliable way to establish and compare the performance of the materials is by measuring the volumetric shrinkage.

CHAPTER 5

CONCLUSION

In order to establish the possible improvements in resin filling materials the constituents of the materials has to be considered in conjunction with the polymerization shrinkage resulting in volumetric change. Voids/bubbles were noted in the cured samples and it was found that it was present in the ampules from the manufacturer *(Figure 44).* The presence of the voids played no role in volumetric change.

Factors that directly influence the amount of polymerization shrinkage are the inorganic filler particles and the organic resin matrix. The electronic mercury dilatometer is the ideal apparatus for this shrinkage measurement since the polymerization can be viewed every 0.5 seconds and visualized on the computer in the form a graph.

The author (Mulder, 2013) concluded that differences in the volumetric change amongst all four bulk fill flowable composites were found. However, the technical brochures on the bulk fill flowable composites advocate filling increments of 4mm layers. All the bulk fill flowable composites had a volumetric shrinkage greater than that of the Z250 control. Therefore, it can be concluded that it would be advisable to place layers of 2mm increments. (Meredith, 1997. Alomari, 2001. Abbas, 2003. de Las Casas, 2012. Mulder, 2013).

CHAPTER 6

RECOMMENDATIONS FOR FUTURE DEVELOPMENT AND SCOPE FOR RESEARCH

Monomer development

In an attempt to reduce shrinkage higher molecular weight monomers like the modified-UDMA (849g/mol) in SDR and dimethacrylate monomer analogs of bis-GMA was synthesized. In the case of SDR we will probably see another combination with SDR-UDMA. Molecular weight of bis-GMA is 512 g/mol and DtBp–bis-GMA 899 g/mol will continue to develop (Ge, 2005). Diluents like TEGDMA will be replaced with monomers that shrink less; 3M already started this with procrylate resins.

Higher levels of inhibitor like BHT will be added to reduce curing rate, contraction stress and rate of stress formation in experimental composites, but did not compromise the final degree of conversion (Goncalves, 2008. Schneider, 2010).

The nanogel filler particle can be added to 50% weight without altering the filler to organic matrix ratio –there will be a proportional decrease in polymerization shrinkage and stress with the use of these nanogel particles (Stansbury, 2010). Future developments include the inorganic filler particles and the addition of nanofibers, glass fibers, titania, nanoparticles. Silsesquioxane nanocomposites are organic/ inorganic hybrid molecule resulting in less shrinkage provided the concentration is between 4-8% (Mui, 2007). These are only but a few examples of what will hopefully see making their way into composites.

Since the inception of dental resins in 1950 improvements have occurred yearly, essentially it is the same recipe with improved ingredients and various matrix concentrations resulting in improved results.

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Annexure A – Published article

Oral Biology and Dentistry

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Volumetric change of flowable composite resins due to polymerization as measured with an electronic mercury dilatometer

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Abstract

Background: To determine the total volumetric change and the relative speed of shrinkage of bulk fill flowable composites during polymerization.

Materials and methods: A specially designed electronic mercury dilatometer was used to determine the volumetric change. The light intensity was 500mW/cm^2. The mercury dilatometer measured the volumetric change every 0.5 seconds during the 35 second irradiation exposure time. The materials tested were Z250 as standard and control. Four bulk fill flowable composites were tested.

Results: The sequence of total volumetric change was found to be: Z250 < Filtek bulk fill < Xtra-Base bulk fill < SDR < Venus bulk fill. The speed of shrinkage of the bulk fill flowables was faster than that of Z250, while the 2 flowables with the highest shrinkage speed (SDR and Venus) also had the highest total volumetric change. Of the different materials tested the volumetric change of Z250 (1.13%) was the lowest and significantly less ($p<0.05$) than that of SDR (1.55%) and Venus (1.72%). The material with the highest filler content (Z250) also showed the lowest shrinkage (1.13%) but this effect could not be seen in the flowables. In general, it was found that a 35 second irradiation period (with a light intensity of 500mW/cm^2) was satisfactory for complete polymerization of the resins.

Conclusions: The volumetric changes and speed of shrinkage were higher for all 4 bulk fill flowable composites than for Z250. SDR and Venus flowables had the fastest and highest volumetric shrinkage.

Clinical significance: The manufacturers of bulk fill flowable composites advocate filling layers of 4mm. However, because of the high shrinkage values found in this study it should be suggested that the standard 2mm layer increments still be used.

Keywords: Volumetric change, flowable composites, mercury dilatometer, polymerization, bulk fill

Introduction

During polymerization the distance between groups of atoms/molecules decreases with a resultant volume change that is known as shrinkage [1-3]. Polymerization shrinkage as low as 2% in composites may generate enough tension to destroy the marginal integrity between the restoration and the tooth structure which could result in micro-leakage, post-operative sensitivity and/or the failure of the restoration [4-6].

However, to minimize volumetric shrinkage, dental material manufacturers previously advised placing composite resins in increments not larger than 2-3mm before it is polymerized. Nowadays, manufacturers are becoming bolder with suggested increments of up to 4mm in regard to the bulk fill flowable composites [7-11]. This method of placement of bulk fill flowable composites, could pose a problem if the shrinkage of the material is too large and allows the disruption of the integrity of the tooth-restoration interface.

Various techniques are available to measure the volumetric change which occurs during irradiation with a curing light [12-15]. An electronic mercury dilatometer proved to be accurate in measuring polymerization shrinkage [1,12-18,35,39]. The volumetric shrinkage measured by the electronic mercury dilatometer is linear and the volumetric change is measured as the total percentage shrinkage that occurred between the pre- and post-gel phases. Examples of various volumetric measuring techniques are the mercury dilatometer, water dilatometer, linear techniques and the pycnometer. A disadvantage with the utilization of dilatometers is that they are extremely sensitive to variations in temperature [14,19]. Oberholzer et al., [15] described a specially designed electronically controlled mercury dilatometer which measured change in volume of the sample every 0.5 seconds.

Studies were completed on varying irradiation techniques to decrease polymerization shrinkage and polymerization stress. Some of these techniques resulted in a low initial conversion rate of the organic matrix. However, the moment the resin material became rigid, the internal stresses and polymerization stress started to increase [8,20]. It has been established that exposures not higher than 500 mW/cm^2, were able to provide a sufficient combination of irradiance and exposure time [15,21]. It was found that conversion rate resulting in carbon double bond formation can range from 55-75% under conventional irradiation conditions of 500mW/cm^2 [22,23].

In an attempt to decrease volumetric shrinkage, an increase

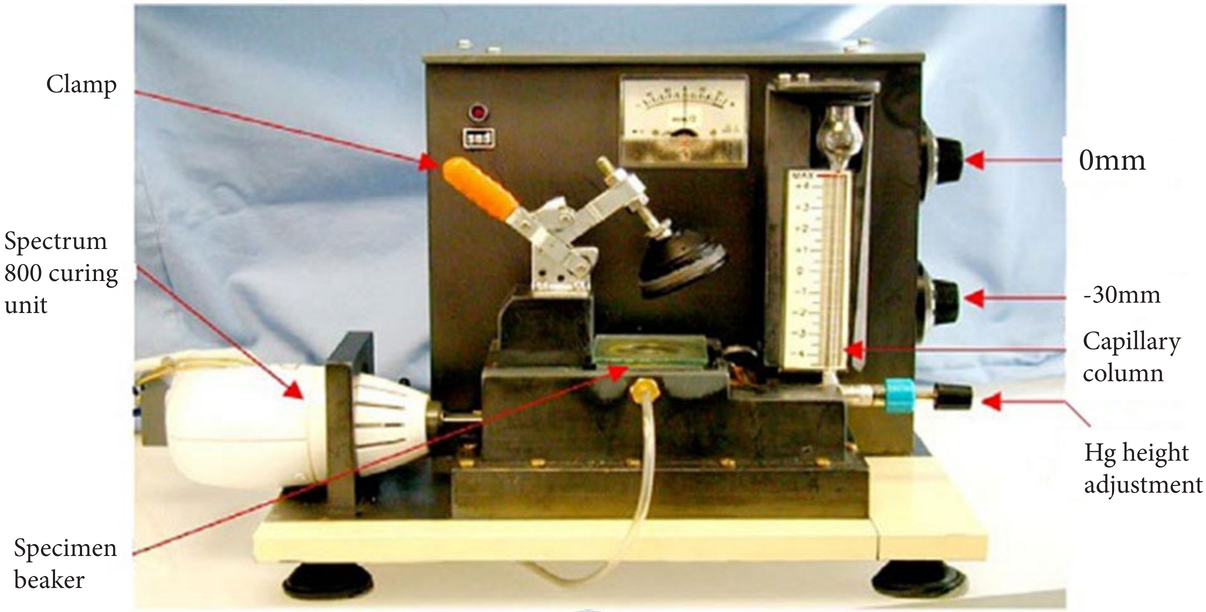

Figure1. Specially designed electronic mercury dilatometer.

in the molecular weight of the organic matrix was suggested [24-27]. Furthermore, by increasing the filler content the resulting contraction stress that developed was found to be directly proportional to the filler content regardless of the matrix [20,28]. Therefore, the purpose of this study was to determine the relative volumetric change and the speed of shrinkage of bulk fill flowable composites relative to the composite Z250.

Materials and methods

The composite Z250 by 3M ESPE (Massachusetts, USA) was used as the standard control material. Furthermore, the shrinkage over time of four newly developed bulk fill flowable composites was measured.

The bulk fill flowable composites consisted of Smart Dentin Replacement (SDR) by Dentsply/Caulk (Milford, Germany), Venus bulk fill by Haraeus Kulzer (Hanau, Germany), Filtek bulk fill flow by 3M ESPE (Massachusetts, USA) and Xtra base bulk fill flowable by Voco (Cuxhaven, Germany). Volumetric change was measured with a specially designed electronic mercury dilatometer (**Figure 1**) [15] .The volumetric change due to polymerization in the dental resin material is measured as a voltage change by a pressure sensitive transducer. An analog to digital converter creates data that is transmitted from the pressure sensor to RS232 format - where the computer creates a graph of volumetric change in Microsoft Excel, From the data collected every 0.5 seconds over the 35 seconds from the curing light irradiation period the graph has time in seconds on the X-axis and the percentage of volumetric change on the Y-axis. All samples were cured for 35.0 seconds at 500mW/cm^2 with a Dentsply/Caulk Spectrum 800 halogen curing light in order to standardize the curing process. The output was monitored with a Caulk (Milford, Germany) radiometer to ensure 500mW/cm^2± 50mW/cm^2. Calibration of the modified mercury dilatometer was done prior to every specimen test. Ten sample specimens of each material were tested. The Teflon specimen holder has a hole with a diameter of 5.0mm and a height of 2.5mm resulting in the specimen volume in the Teflon holder of 49.087mm^3. Briefly, the specimen was placed in the dilatometer and the clamp closed. The calibration was achieved by adjusting the mercury column. The curing light was activated by the computer when the mercury dilatometer had a stable environment for 5.0 seconds. The polymerization shrinkage of the resin material and the resultant volumetric change was measured every 0.5 seconds. The dilatometer was kept in a temperature controlled incubator at the 25°C ± 1°C [29]. The baseline effect of the curing unit was established prior to each set of experimental set-ups and the data corrected accordingly [21]. This correction resulted in the volumetric shrinkage that is presented for each material to be the true volumetric change due to polymerization only. Therefore only the effect of polymerization shrinkage from a monomer to a polymer remained [21,29,30].

Results

The total volumetric change for all ten samples of each material was presented as a combination in the Box and Whisker plot (**Figure 2**). Each Box and Whisker plot gives the maximum and minimum values. The intermediary box gives the range of 50% of the values and the solid line in each box indicates the median value for the 10 samples. The sequence of total volumetric change according to the shrinkage values

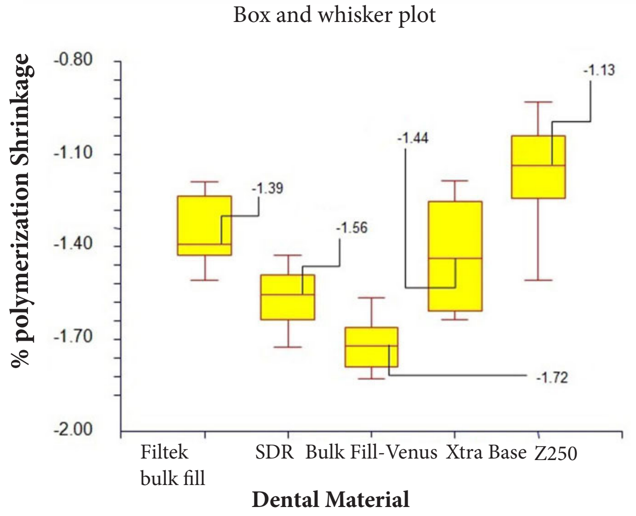

Figure 2. The Box and Whisker plot. The maximum, minimum and median values are provided.

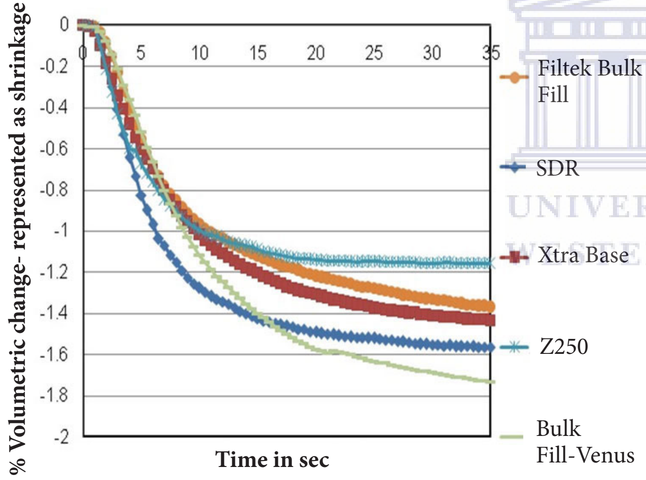

Figure 3. Volumetric change over a 35 second irradiation period (an average of 10 samples per material).

after 35 seconds was: Z250< Filtek < Xtra base< SDR< Venus. The Kruskal-Wallis multiple-comparison test was used to show statistical significant differences in the total volumetric change amongst materials. The results (**Figure 2**) indicated that SDR and Venus bulk fill had significantly more volumetric shrinkage compared to Z250. Z250 shrank 1.13% and Venus bulk fill had the largest volumetric shrinkage of 1.72%.

The Tukey-Kramer multiple comparison test on the rate of shrinkage slopes (**Figure 3**) showed that at a 1.5-5.0 second time period, the slope of SDR was significantly ($p<0.05$) steeper (shrank the fastest) than that of all the other materials. At the time slot (5.5-20.0 seconds) Venus shrank the fastest (steepest slope). For the 20.5-25.0 period Z250 shrank significantly slower than Filtek, Venus and Xtra base but not significantly slower than SDR. When the polymerization rate (slope) of Z250 was considered for the time period 20.5-30.0 seconds, it was found that the rate of polymerization shrinkage of all the bulk fill flowable composites tested were statistically significantly faster than that of Z250.

Discussion

Oberholzer et al., developed the dilatometer used in this study [15]. The main advantage of the dilatometer was that the change of the mercury height in the capillary could be measured electronically, instead of manual viewing. Furthermore, the electronic dilatometer enables measurements to be made on samples regardless of their shape and size. It was concluded [15] that the exothermic reaction from the small sample used was negligible and did not affect the volumetric change. The additional volumetric change that occurs due to the light source could also be determined and the real volumetric change calculated.

From the literature many factors might have an influence on the volumetric shrinkage of a material i.e., filler content, filler size, type of monomers, monomer content, organic matrix and type, and organic matrix conversion factors. The highest percentage volumetric shrinkage (**Figure 3**) for all 5 materials occurred approximately within the first 10.0 seconds. Furthermore, it can be seen that most (~ 90%) of the polymerization shrinkage for all 5 different materials took place in the first 20 seconds and the degree of polymerization was generally completed after 35 seconds of constant irradiation. Davidson [12] also reported that 90% of the shrinkage of composites took place during the first 20 seconds. However, when the sequence of shrinkage (Filtek < Xtra base < SDR < Venus) of the 4 bulk flowables was compared to their filler content (**Table 1**) no clear trend could be seen. Furthermore, the sizes of the fillers alone (**Table 1**) did not seem to show a clear effect on the shrinkage values, although Z250 with an average filler size of 0.6 μm showed a lower shrinkage (1.16%) relative to SDR with a higher average filler size of 4.2 μm. Unfortunately, the average filler sizes of the other flowables were not stipulated by the manufacturers and their possible effects on shrinkage could not be discussed. In general, the rate of polymerization shrinkage (**Figure 3**) for all the bulk fill flowable composites was faster than the control composite Z250.

The literature also showed that in general the higher the monomer content and the more flowable, the higher the shrinkage [12,25,31-35] and the faster the conversion rate to the gel phase [18,20,22]. Again, without the necessary information (**Table 1**) this could not be meaningfully discussed. The shrinkage curve (**Figure 3**) for Venus over the whole 35 second period was the most fluent which indicated a steady shrinkage which might have a positive effect on bond strength.

The slopes of the shrinkage rates over the first 5 seconds did not differ significantly. However, over the 5-15 second period, Venus and SDR shrank the fastest after which period

Table 1. Information on the various resin composites and % volumetric shrinkage found.

Dental material	Inorganic filler	Organic resin matrix	Filler size µm	% filler wt.	Shrinkage
Z250 (3M ESPE) Lot 176833 exp 2013-05	Zirconia/ silica	bisGMA (1-10%), UDMA (1-10%), BisEMA (1-10%), TEGDMA (<5%)	0.01-3.5 (Average size 0.6)	78	1.13%
SDR bulk flow (Dentsply/ Caulk) Lot 110429. exp. 2013-04	Barium-alumino-fluoro-borosilicate glass; Strontium alumino-fluoro-silicate glass	SDR patented urethane (<25%), TEGDMA (<10%), EPBADMA (<10%)	Average size 4.2	68	1.55%
Venus Bulk Fill (Haraeus Kulzer) Lot 010031 exp. 2014-08	barium- alumina-fluoro-silicate, YbF3, Silica.	UDMA (Not available), EPBADMA (Not available)	0.02-5	65	1.72%
Filtek bulk flow (3M ESPE) lot N356852 exp. 2015-02	YBF3 filler Zirconia / silica	UDMA (10-20%), bisGMA (1-10%), bisEMA (6) (1-10%), procrylat resins (10-20%), TEGDMA (<1%)	0.1-5 0.01-3.5	64.5	1.39%
Xtra Base bulk flow (Voco) Lot 1201096	Not available from manufacturer	bisGMA (10-25%), UDMA (10-25%)	Not available	75	1.44%

Table 2. Molecular weight of individual monomers.

Resin present in material	Molecular weight g/mol
UDMA (urethane dimethacrylate)	470.55
SDR-UDMA	849
TEGDMA3 (6-dioxaoctamethylene-dimethacrylate)	286.32
bisGMA (bis-phenol glycidylmethacrylate)	512.59
Bisema6 (bisphenol A polyethylene glycol diether dimethacrylate).	496.58
EBADMA (2-propenoic acid 2-methyl-1,1'-[(1-methylethylidene) bis(4,1-phenylene-oxy-2,1-ethanediyl)] ester	496.58
EPBADMA	452.53
Procrylate2,2-bis[4-(3-methacryloxypropoxy) phenyl]propane	480.59

they all levelled out to about the same slope and shrinkage rate. After about 15 seconds the shrinkage rate of SDR decreased at which stage Venus began to shrink at a faster rate than SDR. The speed of shrinkage (slopes) of the other 2 bulk flowables (Xtra-Base and Filtek) was about the same with Xtra-Base ending marginally higher total volumetric shrinkage value. Therefore it can be seen that the two materials (SDR and Venus) with the fastest polymerization rates (highest slopes) also had the largest total volumetric shrinkage. Our shrinkage value obtained for Z250 (1.13%) corresponds well with other published values of ~1.1% [21,33,36-39].

The ratio of the viscous base monomer to the more flowable diluent monomers has also been found to be a large contributing factor to the percentage of polymerization shrinkage [40]. However, in this study the influence that the ratio might have on the volumetric change, could unfortunately not be sensibly discussed as the manufacturers of the dental materials did not provide the exact ratio or percentage of different monomers contained in the dental materials (Table 1). By combining various monomers to create a multifunctional organic matrix - a reduction of polymerization shrinkage and water sorption can be achieved [40].

It was also reported that the higher the molecular weight of a molecule (Table 2) the lower the shrinkage [24-27], but when there are variations in the mixtures of chemicals with different molecular weights and in different ratios (like the flowables tested in this study) it would not be possible to illustrate clear trends.

Despite all the above-mentioned factors which might have varying influences on the speed and volume of shrinkage, this study proved that the only reliable way to establish and compare the performance of the materials is by measuring the volumetric shrinkage.

Conclusion

Differences in the volumetric change amongst all four bulk fill flowable composites were found. However, the technical brochures on the bulk fill flowable composites advocate filling increments of 4mm layers. All the bulk fill flowable composites had a volumetric shrinkage greater than that of the Z250 control. Therefore, it can be concluded that it would be advisable to place layers of 2mm increments.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

R Mulder: conceived idea, methodology, experiments.
SR Grobler, YI Osman: Supervision and assistance in the write-up of the literature review, discussion, statistical results.

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