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An Experimental Fibre-Reinforced Dental Resin Composite

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Abstract

Fibre-reinforced dental resin composites (FRCs) have shown increased fracture resistance and tensile strength compared with particulate filled composites (PFC). However, clinically successful restorative materials require adequate bond strength and wear resistance along with high strength.

An experimental FRC (ST) was developed and tested as a dentine replacement. It has randomly distributed E-glass fibres above their critical length of 0.5-1.6 mm. This work aimed to evaluate the possibility of using ST as a single restorative material by assessing its three-body wear resistance and surface contact fatigue. The polymerisation shrinkage, water sorption, and bond strength of ST were also assessed.

Two commercially available materials; an FRC (Build It FR) and PFC (Z250) were used as comparators. ST showed significantly lower wear resistance and higher contact fatigue. No significant difference was found regarding polymerisation shrinkage but ST had significantly higher water sorption, lower shear bond strength (SBS) to human dentine.

SBS of the interfacial layers within and between the dental resin composites was evaluated after 24 hours and 1 year of water storage in the absence of an oxygen inhibition layer. Build It/Z250 showed a significantly higher SBS at both time intervals. The presence of an oxygen inhibited layer increased the interfacial strength in all groups except ST/Z250.

ST formulations were varied in resin/diluent (Bis-GMA/TEGDMA) ratios, filler loading and fibre lengths for development. Wear testing found changing the Bis-GMA/TEGDMA ratio from 60/40 to 70/30 decreased the wear resistance regardless of filler loading and fibre length.

In summary, wear resistance of ST and its variants was insufficient to recommend its use as a single restorative material without a surface veneer of PFC. As a dentine replacement, ST was only comparable with Z250 and Build It in polymerisation shrinkage and SBS between composites in the absence of an oxygen inhibition layer.

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Last, and certainly not least, is my family whose unwavering support and belief in me has been vital in every aspect of my life. To them I owe more than words could ever express.

Author's Declaration

I declare that the work presented in this thesis is original, has been carried out by the author and has never been presented in part or in full to any university in support for any application for any degree.

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Chapter 1. Introduction

1.1 **Introduction**

Dental resin-based composite restorations are increasingly used to restore teeth in many clinical situations (Stein *et al.*, 2005). Compared with dental amalgams, dental resin composites possess better aesthetic properties, show reasonably satisfactory clinical results, and allow more conservative dental treatments to be carried out (Gao *et al.*, 2008; Ferracane, 2011). Particulate filled composites (PFC) are among the most commonly used dental resin-based composite materials. Despite their widespread use and acceptance, they have several drawbacks such as polymerisation shrinkage and an increased tendency to wear in high stress areas when compared with dental amalgam (Chan *et al.*, 2010; Ilie and Hickel, 2011). Using a composite restoration in a large posterior cavity or for a build-up is considered a contraindication by many members of the dental community, with the concern being for fracture of the restoration along with its excessive wear (Ferracane, 2006; Ferracane, 2011).

Using fibres to reinforce dental resin composite has shown an improvement in the strength of the resulting material (Pandey *et al.*, 2004; Callaghan *et al.*, 2006). They are already in use for several dental applications such as tooth stabilisation, splinting, and endodontic posts (Pandey *et al.*, 2004). In an attempt to overcome some of the shortcomings of conventional dental resin-based composites regarding strength while building upon existing fibre reinforcing knowledge, an experimental fibre reinforced composite material was developed in Finland at the University of Turku. It uses a poly(methylmethacrylate) (PMMA)-dimethacrylate based semi interpenetrating polymer network (semi- IPN) polymer matrix with randomly distributed 8 mm long E glass fibres (Garoushi, 2006). This material will be referred to as ST in this work.

In collaboration with the University of Turku, the production of ST was moved from the University laboratory to a Finnish company which manufactures fibre reinforcements for various dental uses, Stick Tech. ST; the latest material in a range already tested by Stick Tech with promising results as a core material; an increase in fracture resistance when used in a PRC/FRC combination (Garoushi *et al.*, 2006b; Garoushi *et al.*, 2007b; Garoushi *et al.*, 2007c; Garoushi *et al.*, 2007e), improved load bearing capacity of onlays and fixed partial dentures (Garoushi *et al.*, 2006c; Garoushi *et al.*, 2006d) as well as an improvement of static compression (Garoushi *et al.*, 2007a). This work will assess the effect of the incorporation of 8 mm E-glass fibres into a semi-IPN dental restorative material as a single restorative material by testing its surface contact fatigue and three body wear resistance as well as further assess several material properties when using ST as a core/dentine replacement.

Chapter 2. Literature Review

2.1 **Literature Review**

Introduction

The purpose of this review of literature is to give a brief overview about the development of dental resin composites, their components, and properties. Particular emphasis is given to properties of dental resin composites which cause problems during and after the placement of a restoration. These are:

a) Polymerisation Shrinkage;
b) Water sorption;
c) Bond Strength;
d) Fatigue;
e) Wear Resistance.

2.2 **Composites**

A composite is defined as a material consisting of two or more chemically distinct constituents with a distinct interface separating them. Ideally, the resulting material would have physical properties better than any of its constituents (Migliaresi and Alexander, 2004). Composites consist of a one or more discontinuous phases embedded within a continuous phase. The discontinuous phase is usually harder and stronger than the continuous one and it is called the reinforcement or reinforcing material, whereas the continuous material is termed the matrix (McCabe and Walls, 2008).

As with other composites, a dental resin composite consists of two main components; typically a polymer resin matrix and inorganic fillers. The polymer resin allows the composite to be moulded at ambient temperatures and to achieve polymerisation setting in a relatively short time, thus facilitating its usage chair-side in a dental clinic. The principal aim of adding fillers is to produce a material with properties similar to that of the tooth structure being replaced. The fillers, which may be in particulate or fibrous form, are incorporated into the composite to improve its hardness, rigidity, strength and reduce the coefficient of thermal expansion when compared to that of the resin matrix (McCabe and Walls, 2008; Chan *et al.*, 2010; Cramer *et al.*, 2011). An added benefit of markedly lowering the setting contraction occurs if the filler volume occupies a significant portion of the overall composite material (McCabe and Walls, 2008; Chan *et al.*, 2010).

The first tooth coloured filling material used was silicate cement, which was introduced in the 1870s (Schulein, 2005; Puckett *et al.*, 2007). It had a composite structure and its formulation was based on alumino-fluoro-silicate glasses and phosphoric acid. The matrix was the aluminium phosphate salt formed from the partial dissolution of the glass particles and the dispersed phase consisted of residual glass particles. However, this material was too brittle for restoring posterior teeth and even when used anteriorly only lasted a few years (Rueggeberg, 2002; Puckett *et al.*, 2007). The earliest acrylic filling materials were based on the monomer methyl methacrylate (MMA) (Anusavice, 1996). This was in the 1940s when polymer chemistry was associated with the need to create ‘unbreakable materials’ for combat aircrafts in World War II (Minguez *et al.*, 2003; Vasudeva, 2009). The first polymer based dental restorations were auto-polymerisable also known as self-polymerising, and consisted of a poly(methylmethacrylate) (PMMA) powder, MMA monomer, benzoyl peroxide and n,n-dimethylparatoludine. Upon mixing, the polymer powder formed a dispersed phase and the monomer polymerised to form the continuous phase, thus classifying these materials as composites (Rueggeberg, 2002; Puckett *et al.*, 2007). There were a variety of problems associated with the use of these early dental composites, including poor wear resistance, high volumetric shrinkage during polymerisation which lead to marginal leakage and a significant incidence of secondary caries, and high potential for discoloration (Brown, 1997; Combe and Burke, 2000). In the early 1950s, inorganic filler particles were added to resolve the polymerisation shrinkage problem. The resulting materials did show a decrease in the polymerisation shrinkage as well as a decrease in the coefficient of thermal expansion and water sorption (Patel *et al.*, 1987; Patel and Braden, 1989). Despite the improved polymerisation contraction, the materials did exhibit high wear and discoloration. The early materials were also unable to sufficiently withstand the loads generated in the oral cavity or adhere to the dental structures (Bowen and Marjenhoff, 1992). The second generation composite filling materials were the resin-based materials incorporating glass particles into the acrylic resin which increased the mechanical and abrasion resistance while reducing the volumetric contraction (Bowen and Marjenhoff, 1992). From then on, the development of so called “resin composites” started (Rueggeberg, 2002).

In the early 1960s, Bowen developed a new dimethacrylate resin: bisphenol-A-glycidyl-methacrylate (Bis-GMA), which was beneficial in terms of mechanical properties compared to both the silicate cements and methyl-methacrylate-based resins in use at the time. Bis-GMA had a relatively high molecular weight and a stiff, partially aromatic molecular structure which had low polymerisation shrinkage (6.1 vol.% compared to 21 vol.% of methylmethacrylate), rapid hardening, low volatility, a high refractive index, good adhesive and mechanical properties of the cured resins (Soderholm, 1984; Stansbury, 2000a; Moszner *et al.*, 2008). Combining Bis-GMA with inert particles as filling materials which were chemically bound to the resin via vinyl-silane bonds resulted in less volumetric contraction during polymerisation and a higher resistance to wear than in any of the unfilled resins (Bowen, 1963). The great acceptance of these materials by the dental community was due to several improved mechanical and physical properties; a greater resistance to wear, a decrease in polymerisation contraction and coefficient of thermal expansion, better colour matching and relative ease of handling (Leinfelder, 1987; Rueggeberg, 2002). Since the new resin composites had better physical properties, dentists began using them as restorations in both posterior and anterior teeth. Unfortunately, their excessive susceptibility to wear and high incidence of secondary caries made them inadequate replacements for amalgam fillings in posterior teeth (Osborne *et al.*, 1973; Rueggeberg, 2002).

Early Bis-GMA based composite systems were made up of two pastes with chemically activated polymerisation. The reaction involved combining benzoyl peroxide (the initiator) with a tertiary amine (the activator), producing free radicals at room temperature (Minguez *et al.*, 2003; McCabe and Walls, 2008). As the two pastes were mixed manually, air bubbles often became incorporated into the restoration, thus weakening it. The entire process of placing a composite restoration in a tooth was extremely technique sensitive (Anusavice, 1996). Some of the problems associated with placing composite restorations were resolved by the introduction of light activated materials and their subsequent incorporation into the polymerisation systems. UV lights were first used but had a limited depth of cure due to their low power light sources. The development of catalysts triggered by visible light solved this problem and allowed greater depth of polymerisation compared with UV light (Rueggeberg, 2002; Minguez *et al.*, 2003). One of the main advantages of light activated materials was that it increased working time for the dentist, allowing the placement of the material inside the cavity and appropriate moulding before exposure to the light and initiation of the polymerisation reaction (Rueggeberg, 2011).

The resin itself was modified and in some cases changed to help improve the characteristics of the final product. For example, Bis-GMA was altered by the replacement of the hydroxyl groups with ethoxy groups, to create what is known ethoxylated Bis-GMA composites. These materials are reported to offer less tackiness and “pull-back” when they are placed into preparations and greater ease of handling compared with Bis-GMA based composites (Rueggeberg, 2002). Urethane dimethacrylate (UDMA) was developed in 1974 by Foster and Walker and is now used in the matrix for dental resin composites either as a replacement for or in combination with Bis-GMA as it has been reported to have less polymerisation shrinkage compared with Bis-GMA (Ferracane and Greener, 1986; Vasudeva, 2009).

Further development of dental resin composites paralleled that of composites in various other industries, where both particulate and fibre reinforcement were used (Rueggeberg, 2002; Petersen, 2005). The use of fibre reinforcement in silicate glass and glass-ceramic matrices started in the 1970s (Roether and Boccaccini, 2005). In order to be characterised as a fibre rather than a particle, the length of the fibre must be much greater than its cross-sectional dimensions (Vallittu, 1996; Zhang and Matinlinna, 2011). Initially, fibre reinforced composite materials were used in weight critical aero-space components. Their high strength-to-weight ratio, coupled with oxidation resistance made them ideal candidates for general high-temperature aero-space applications, such as rocket nozzle inserts (Boccaccini, 2005). Since then, a great variety of composite systems employing different types of ceramic and metallic fibre reinforcements have been developed (Roether and Boccaccini, 2005; Zhang and Matinlinna, 2011). Currently, with biocompatible fibres and matrix systems, fibre reinforced composites have found applications as biomaterials. The main fibres used in biomedical composites are carbon fibres, polymer fibres, and glass (Boccaccini, 2005; Mallick, 2008).

In 1969, the first paper on the fabrication and characterisation of an experimental composite with a pure silica matrix reinforced with carbon fibres was published (Boccaccini, 2005). The 1970s and 1980s saw major developments in these systems. Carbon fibres are flexible, lightweight and high in strength (Chand, 2000; Minus and Kumar, 2005). Their main advantages are an elastic modulus up to 900 GPa, strength up to 4.5 GPa, and low density. Hence they are stronger and stiffer than steel (Chand, 2000; Minus and Kumar, 2005). One of their main disadvantages is their poor shear strength (Asmussen *et al.*, 1999). The interfacial properties in carbon fibre composites depend primarily on the chemical bonding and physical structure at the interface as well as the type of carbon fibre used. Changing the matrix chemistry influences the interfacial strength (Black *et al.*, 1998). Unfortunately, the *in vivo* results of using carbon fibres to reinforce biomaterials did not replicate the favourable *in vitro* wear test indications. Many patients presented with osteolysis and failure of the tibial inserts (Migliaresi and Alexander, 2004). This led to the withdrawal of several of the early devices from the market.

Unlike carbon fibres, polymer fibres are not comparably stiff or strong reinforcements for other polymers. Two possible exceptions are aramid fibres and ultrahigh-molecular-weight polyethylene (UHMWPE). Aramid fibres are light and strong while resisting impact and abrasion damage. Their compressive strength is 1/8 of their tensile strength, making their applications in medicine limited possibly due to concerns about their biocompatibility and moisture uptake (Migliaresi and Alexander, 2004). They have been used in ligament prostheses (Wening *et al.*, 1994) as well as in denture reinforcements (Vallittu, 1996).

Glass fibres are the most common of all reinforcing fibres used commercially for polymeric matrix composites and are used in several dental applications (Ravindra *et al.*, 1997). Their main advantages are low cost, high tensile strength, high chemical resistance and good insulating properties. The main disadvantages associated with these fibres are their low tensile modulus and relatively high density compared with the other fibres (Ravindra *et al.*, 1997; Migliaresi and Alexander, 2004). They also show a higher sensitivity to wear and a low fatigue resistance. Depending on the chemical composition of the glass they are commercially available in different grades: A, C, E, R, S. At one time 'A' or alkali glass was quite common as the basic material for glass fibre production. Today this has been virtually superseded by 4E' glass. E stands for electric (Migliaresi and Alexander, 2004 ; Zhang and Matinlinna, 2011). E-glass has a very low alkali content borosilicate glass which provides good electrical and mechanical properties, coupled with good chemical resistance. Another glass produced in commercial quantities for fibres production is the C-glass, a special chemical resistant glass. This is used in the manufacture of surfacing layers to provide additional chemical resistance over E-glass. For specific application 'R' and 'S' glasses are available as fibres. These are high strength glasses used mostly for aerospace applications (Black *et al.*, 1998).

Several fibre reinforced composite implants and devices for orthopaedic and dental applications have been developed (Baidya *et al.*, 2001). The orthopaedic applications include total knee replacements, hip replacements, spine rod, spine disk, intramedullary nail, as well as bone plates and screws. The requirement of the mechanical properties in these orthopaedic implant materials is extremely high to withstand the fatigue loading when in use. The usage of fibrous composite materials has been increasing in both volume and applications (Fujihara *et al.*, 2004).

In dentistry, fibres were used in an attempt to reinforce standard polymethacrylate dentures in the 1960s and 1970s. The fibres used were either glass or carbon and although the resulting materials had improved mechanical properties, their clinical acceptance was poor (Patel *et al.*, 1995). That was mainly due to the proposed reinforcing process requiring manual placement of the fibres into dental resins. The fibres were difficult to handle, easily damaged and easily contaminated (Duncan *et al.*, 2000; Freilech, 2000; Freilich *et al.*, 2000). Add the fact that the resulting mechanical properties did not improve as much as was expected and reason behind the clinicians' lack of acceptance was clear. There were two reasons cited for lack of improvement in mechanical properties. The first one was the low concentration of incorporated fibres, often less than 15%. The second was poor wetting of the fibre bundles led to insufficient coupling between the resin and the fibres as well as possible gap formation (Jancar and DiBenedeto, 1993). Two main approaches for fibre reinforcement have evolved since that time. The first involves the dentist or laboratory technician applying a low viscosity resin to the fibre bundles. This approach is more time consuming than the alternative, yet it allows versatility in selecting the resin and fibres to be used. The alternative approach involves using fibre bundles that have already been impregnated with resin in a controlled manufacturing process (Duncan *et al.*, 2000; Freilech, 2000; Freilich *et al.*, 2000; Pandey *et al.*, 2004).

When compared to amalgam restorations, FRCs exhibit superior aesthetics. They also have highly favourable mechanical properties and are superior to most alloys in their strength-to-weight ratio, do not corrode and have better bonding properties (Freilech, 2000; Freilich *et al.*, 2000; Pandey *et al.*, 2004).

2.2.1 Components and their effect on properties

The properties of a composite are influenced greatly by the properties of their constituent materials, their distribution, content and interactions (Chen, 2010; Ferracane, 2011). A composite's properties may be the volume fraction sum of the properties of all its components or may be the product of the constituents acting synergistically due to geometric orientation, providing properties in the composite that are not accounted for by a simple volume fraction sum(Migliaresi and Alexander, 2004).

Currently available dental composites are complex, tooth-coloured filling materials composed of synthetic polymer matrices, particulate and/or fibre ceramic reinforcing fillers, and silane coupling agents which bond the reinforcing fillers to the polymer matrix (Ferracane, 2011). Each of the components of the composite is critical to the success of the final dental restoration. The rheological properties of a composite, such as viscoelasticity and flow, govern the ease of placement and shaping as well as the adhesion to tooth surface. These factors, in turn, can influence factors such as the length of time required to place a restoration as well as its longevity (Lee *et al.*, 2003; Lee *et al.*, 2006; Ellakwa *et al.*, 2007).

1) Resin matrix

In the majority of contemporary composite filling materials, the organic resins are made up of mixtures of cross-linking dimethacrylates. These are used due to the fact that they form of a polymer network, which results in a number of desirable effects; the mechanical properties of polymer networks are superior to those of linear polymers, polymerisation occurs faster due to the gel effect and the cross-linked polymer matrix is not water soluble (Moszner *et al.*, 2008).

A large proportion of the commercially available dental composite materials are based on Bis-GMA, which, as mentioned previously, is a dimethacrylate monomer formed as a reaction of bisphenol A and glycidyl methacrylate. Bis-GMA has a relatively high molecular weight (512 g/mol) and stiff, partially aromatic molecular structure, which makes it a superior dimethacrylate (Moszner *et al.*, 2008). However, high molecular weight monomers are limited by their viscosity, increased stickiness, and undesirable general rheology which compromise the handling characteristics of the resulting restorative materials. In order to achieve a more suitable viscosity, the Bis-GMA is thinned with a monomer such as triethylene glycol dimethacrylate (TEGDMA) (Ferracane, 1995; Vasudeva, 2009). TEGDMA increases vinyl double-bond conversion (Chen, 2010). Other shortcomings of Bis-GMA include its low degree of carbon double bond conversion at ambient temperature, resulting in a relatively high amount of residual unreacted monomer which can leach into the oral fluids (Cramer *et al.*, 2011). There have been numerous monomers described in the literature which demonstrate partially improved properties compared with Bis-GMA. An example is the recently introduced siloranes. The silorane molecule represents a hybrid that is made of both siloxane and oxirane structural components. The matrix is formed by the cationic ring-opening of the silorane monomers rather than the cross linking of methacrylates. The cyclosiloxane backbone is hydrophobic while the cycloaliphatic oxirane sites have high reactivity and shrink less during polymerisation than methacrylates (Eick *et al.*, 2007). Some researchers found that siloranes had better marginal integrity and less marginal leakage than methacrylates (Thalacker *et al.*, 2004; Thalacker *et al.*, 2005), while others did not show any significant difference (Van Ende *et al.*, 2010).

Partially aromatic urethane dimethacrylates synthesized by the addition of OH-group containing methacrylates, such as 2-hydroxyethyl (HEMA) or hydroxypropyl methacrylate (HPMA), with α,α,α′,α′-tetramethyl-m-xylylene diisocyanate (TMXDI), can be used as cross-linkers in composites (Moszner *et al.*, 1999; Cramer *et al.*, 2011). TMXDI combines the favourable properties of aromatic and aliphatic diisocyanates with stiffness and a low tendency to discolour. Urethane dimethacrylates are commonly used in dentistry as resin monomers for dental composites (Peutzfeldt, 1997; Cramer *et al.*, 2011). The most commonly used dental monomer of this type is 1,6-bis-(2-

methacryloyloxyethoxycarbonylamino)-2,2,4-trimethylhexane (UDMA), which is synthesized by the addition 2 mol HEMA with 1 mol 2,2,4-trimethylhexamethylenediisocyanate (TMDI). Bis-GMA has a volumetric shrinkage of 6.1%, a molecular weight of 512 g/mol and a viscosity of 1.0–1.2 kPa s at 23 ◦C, while UDMA's molecular weight is 470 g/mol and its polymerisation shrinkage 6.5 % vol (Moszner *et al.*, 2008). Its viscosity (8–10 Pas at 23 °C) is significantly lower than Bis-GMA. The polymerisation of UDMA alone results in more flexible materials. In addition, the refractive index of UDMA is relatively low, which significantly decreases the curing depth of composites containing radiopaque glass fillers (Moszner *et al.*, 2008). Ethoxylated bisphenol-A-dimethacrylate (Bis-EMA) has a higher molecular weights and fewer double bonds *per* unit of weight, thus they normally have less shrinkage than TEGDMA. Therefore, TEGDMA has been replaced by UDMA and Bis-EMA in several products to reduce shrinkage, ageing, and the negative effects of environmental factors such as moisture, acid, and temperature changes (Yap *et al.*, 2000a). A modified urethane dimethacrylate resin has been found to reduce shrinkage due to its relatively high molecular weight compared with Bis-GMA and traditional UDMA (895 g/mol vs. 512 g/mol vs. 471 g/mol, respectively) (Ferracane, 2011). A review of the developments in dental monomers is beyond of the scope of this work and the reader is referred to two of the published reviews about the topic (Moszner and Salz, 2001; Vasudeva, 2009).

A different matrix type recently used in an attempt to improve upon existing dental resin composites is a semi-interpenetrating polymer network (semi-IPN) with glass fibres among the reinforcing fillers used. A manufacturer (StickTech Ltd, Turku, Finland) has introduced a PMMA – Bis-GMA based semi-IPN as a matrix for an experimental FRC. An IPN is a combination of two or more network polymers, synthesized in juxtaposition (Sperling, 1994). Despite the nomenclature, most IPNs do not interpenetrate on a molecular scale. They may however, form finely divided phases of nanometers in size (Sperling, 1994; Vallittu, 2009). Many IPNs have dual phase continuity, which means that "two or more polymers in the system form phases that are continuous on a macroscopic scale" (Sperling, 1994). The rationale behind the use of IPNs or IPN-like structures is in the mechanical interlocking at nanometer level of resin adhesives to IPN-like polymers and adhesives. This interlocking will allow more efficient stress transfer from the restoration to tooth rather than debond the restoration, in effect improving the longevity of the restoration (Vallittu, 2009).

A semi-IPN is one in which one or more polymers are cross linked and one or more polymers are linear or branched. A schematic representation of an IPN and a semi-IPN is shown in Figure 1 (Sperling, 1994). Dimethacrylate or multifunctional monomers form the cross-linked part of the semi-IPN while the monofunctional MMA forms the linear part of the system. Solid PMMA is often used in porous polymer form in preimpregnated glass fibre reinforcements. After polymerisation, the result is two or three of the following phases: semi-IPN phase, cross-linked matrix and linear polymer phase. Thus, the entire polymer may not be a semi-IPN, but there are microstructures of IPN in the resulting dental resin composite (Vallittu, 2009). The semi-IPN, in theory, should also improve the handling properties of FRCs (Garoushi *et al.*, 2006a). This is by allowing ease of placement along with ease of repair. As semi-IPN FRCs are still experimental materials, their handling has yet to be commented upon in the published literature.

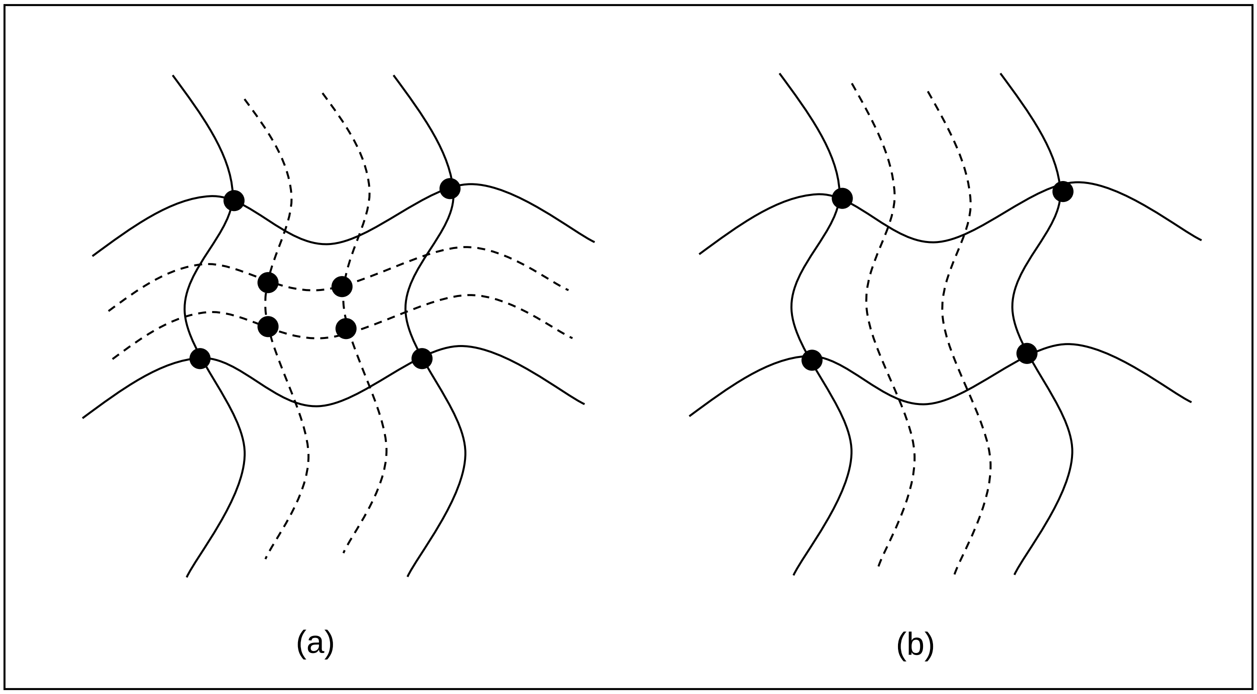


Figure 1. Schematic representation of (a) an IPN and (b) a semi-IPN.(adapted from Sperling, 1994).

2) Fillers

Bowen originally used large particles of quartz as fillers (Rueggeberg, 2002; Vasudeva, 2009). The main advantages of using quartz were its availability and its excellent optical match to the polymer resin. However, quartz was found to be rather abrasive to tooth tissue and was also radiolucent, making it difficult to detect on radiographs. Another drawback to the original quartz filler was that the particles were large and hard in relation to the surrounding polymer matrix. This meant that as the surface of the composite was abraded, the polymer would wear away more quickly than the fillers, leaving them raised and exposed from the surface. There was also the risk of the large filler being torn from the material during finishing and polishing or mastication. The polymerised restoration's surface was considerably different to the enamel it was meant to mimic. It was rough and difficult to polish. Consequently, the final restoration had compromised aesthetics and it lacked smoothness (Ferracane, 1995; Combe and Burke, 2000).

Since Bowen's first attempts, the filler component of composite dental restorative materials has developed considerably (Ferracane, 2011; Ilie and Hickel, 2011). In the 1970s, microfilled composites containing amorphous silica were introduced, with the mean particle size being 0.05µm. The small size of the particles allowed these composites to be polished without preferential abrasion, thus producing smooth surfaces and excellent aesthetics. Microfine silica is also softer than quartz. However, like quartz, these fillers are not radiopaque (Ferracane, 1995). Radiopaque particles such as strontium and barium silicate, lithium and aluminum silicate, and ytterbium triflouride were later incorporated (Ferracane, 1995; Lin *et al.*, 2000). Although these materials were more aesthetically pleasing, the microfilled composites in particular had a tendency to fracture in areas of stress concentration (Ferracane, 1995; Ferracane, 2011). Currently used fillers in dental resin composites include quartz, colloidal silica, and silica glass containing barium, strontium, and zirconium. They increase the strength and modulus of elasticity of the final restoration while reducing polymerisation shrinkage, the coefficient of thermal expansion, and water absorption (Chen, 2010; Ilie and Hickel, 2011).

An increase in filler load has observable effects on the final restoration. Flowable composites, for example, have a low filler load (45–67% by weight) and they exhibit typical shrinkage values of 4.0–5.5% vol. Many hybrid composites have higher filler load (74–79% by weight) and consequently have less volumetric shrinkage, averaging between 1.9% to 3.5% vol. Highly filled systems, such as packable posterior composites or materials with optimised filler load of up to 82% by addition of nano particles (ranging in size from 0.1 to 100 nm), demonstrate shrinkage values as low as 1.7% vol. However, there is a limit to the amount of filler which can be incorporated. The filler load can only be increased until the resin no longer allows for the complete wetting and incorporation of the filler particles (Roberson *et al.*, 2006).

Fibres as fillers are a more recent addition to dental resin composites. The main purpose of incorporating fibres into the composite resin is to increase its strength. Effective fibre reinforcement depends on several factors, including fibre length, form, orientation and concentration in the resin matrix (Ladizesky *et al.*, 1993; Stipho, 1998; Dyer *et al.*, 2004) adhesion to the polymer matrix (Vallittu, 1995). For fibres to effectively reinforce a polymer matrix, it is essential that stress transfers from the polymer matrix to the fibres (Vallittu *et al.*, 1994; Petersen, 2005). This is done by ensuring that the reinforcing fibres' length is equal to or greater than the critical fibre length (Lc). Critical fibre length is dependent on the fibre diameter (d), its ultimate strength (σ^*_f) and on the fibre-matrix bond strength (τ_c). It has been calculated using the following equation (Fu and Lauke, 1996; Petersen, 2005):

Equation 1.Critical Length (Lc)

$$\mathbf{Lc = \sigma * fd/2Tc}$$

When the length of the fibre (L) is much higher than Lc (normally L = 15Lc), a fibre is termed continuous. Shorter fibres are termed discontinuous. If the length of the fibre is significantly shorter than Lc, the matrix will deform around the fibre in such a way that there is almost no transference of stress to the fibre and little reinforcement. This makes the FRC no different to the PFC regarding strength gained from the fillers (Callister, 2007). The critical fibre lengths of E-glass with a Bis-GMA polymer matrix will vary between 0.5 and 1.6 mm when measured using fibre fragmentation test (Garoushi *et al.*, 2007d).

Fibres may be aligned parallel to each other, perpendicular to each other (woven or two ply) or be randomly distributed. Unidirectional fibres are anisotropic, i.e. offer reinforcement in a one known direction. Woven fibres are orthotropic and offer support in two directions. Short, randomly oriented fibres provide an isotropic reinforcement effect, i.e. in all directions. The theoretical reinforcement gained by adding randomly oriented fibres is 20% compared with that of unidirectional fibres (Murphy, 1998; Garoushi *et al.*, 2006e).

Fibre loading also influences the final restoration. Studies have shown that as fibre loading increases, the properties of the material become more similar to those of the fibres (Garoushi *et al.*, 2006e).

3) Interfacial phase

Fillers are commonly bonded to the surrounding matrix chemically (Ferracane, 2011). Bowen (1963) showed that silica powder treated with silane agents yielded an improvement in the strength of the Bis-GMA-based resins, with the final product exhibiting properties similar to those of hard tooth tissues. He also stated that the reinforced resin exhibited lower water solubility and much less susceptibility to disintegration in water than did the untreated silica-based composites. The Vickers hardness, flexural and compressive strengths of two composites following the silane treatment of hydroxyapatite filler particles was studied and it was found that all the properties improved after silanization of the fillers. This was believed to be due to an enhanced dispersion of the filler in the matrix, and the existence of a chemical bond between the two phases (Labella *et al.,* (1994). If the bond between filler and matrix is not robust, gaps or micro cracks or both can form, contributing to the degradation of the material and decreasing its longevity (Santerre *et al.*, 2001). Fillers are normally silane treated with a 0.025% - 2% aqueous solution. Silane coupling agents contain a silicon-containing compound linked to a reactive organic structure with a vinyl group that can subsequently react with the resin matrix. The methoxy groups on the silicon component can be hydrolysed by water to form silanol groups, which can then react on the filler surface in monomeric or oligomeric forms (Soderholm *et al.*, 1984). Subsequent drying would complete the process, linking the coupling agent molecules to each other and to the filler surface by siloxane bonds. The coupling agent y-methacryloxypropyltrimethoxy silane is a commonly used filler treatment agent in dentistry (Santerre *et al.*, 2001).

In FRC, the interfacial phase has been defined as a three-dimensional region that exists between the fibre surface and bulk-matrix (Gao *et al.*, 2008). Its' properties differ from those of either the fibre reinforcement or the matrix resin and govern the load transfer between matrix and fibre (Kessler and Bledzki, 2000; Khanna *et al.*, 2003). As in PFC, silane coupling agents play a key role in effective coupling between the fibres and the matrix. The better the filler-resin interface in FRCs, the better the fatigue, impact and hardness of the resulting composites (Keusch and Haessler, 1999; Gao *et al.*, 2008).

2.2.2 Classification Systems

Dental composites are generally classified according to their activation reaction and to the particle size/type and distribution of the fillers.

2.2.2.1 Mode of Activation

Dental resin composites may be classified based on their mode of activation. These are:

1. ***Chemically activated***

   Chemically activated products are frequently supplied as two pastes which must be combined. Each paste has premixed resin and filler. One of the pastes contains approximately 1% of an initiator such as benzoyl peroxide, while the other contains an aromatic tertiary amine activator such as N,N-diemthyl-*p*-toluidine or *p*-tolyl diethanolamine (McCabe and Walls, 2008). The setting reaction is free radical addition polymerisation.

   Other methods in which chemically activated material may be supplied include:

   - Encapsulated materials in which a thin membrane separates the filler and peroxide from the monomers and comonomer containing the activator.

Once the seal is broken, the reactive components come into contact with one another and are mixed mechanically.

- Paste/liquid materials in which the liquid contains the chemical activator and monomers while the paste contains the monomers, comonomers, fillers and peroxide.
- Powder/liquid systems in which the powder contains the filler particles and peroxide initiator whilst the liquid contains monomer, comonomer and chemical activator (McCabe and Walls, 2008).

2. ***Light activated***

   Light activated materials are generally supplied as a single paste which contains monomers, comonomers, and an initiator (McCabe and Walls, 2008). The initiator is unstable in the presence of ultraviolet (UV) or high intensity visible light. The use of UV activated materials has decreased significantly since the dangers of long term exposure to UV light were highlighted, making visible light activated dental resin composites much more commonly used (Stansbury, 2000b). The initiator used is a mixture of a diketone, commonly camphorquinone (CQ), and an amine, such as dimethylaminoethyl methacrylate (DMAEMA). Camphorquinone absorbs blue light wavelengths (400 – 500 nm) and forms free radicals in the presence of an amine (Stansbury, 2000b; Cramer *et al.*, 2011). Inhibitors are also added to resin systems to prevent accidental or spontaneous polymerisation of the monomers by exposure to room light for example. Inhibitors (≈0.01% wt) in the resin system have two main functions; extending the shelf life of the material and ensuring sufficient working time.

3. ***Dual cured***

   These materials combine the chemical and light curing modes of activation.

2.2.2.2 Filler size and distribution

Several authors have classified composites according to their filler size and distribution (Willems *et al.*, 1992b; Anusavice, 2003; Sturdevant, 2006). They all broadly classify resin composites into the following groups:

1. Conventional (traditional) composites have a particle size of 1 – 50 µm and typically contain 60 – 80% fillers by weight.
2. Microfilled composites have a particle size of 0.01-0.1µm with a filler loading of 30-60% by weight.
3. Hybrid composites contain a blend of both the conventional glass or quartz particles along with some submicron particulate silica with filler loadings on about 75% conventional size and 8% submicron size. Thus the total filler content of 83% or more may be achieved. (McCabe and Walls, 2008).
4. Nanocomposites are a relatively new class of composite resin with filler particle size between 0.1-100 nm (Beun *et al.*, 2007; Ferracane, 2011). Nanohybrids are resin composites with nanofiller in a prepolymerised form and are considered a class of nanocomposites (Senawongse and Pongprueksa, 2007).It is worth noting that microfilled composites, with an average reinforcing particle size of 40 nm are thought to be the first nanocomposites. However, due to the lack of recognition of the concept of “nano” at the time of their development, they were not recognised as nanofilled materials (Ferracane, 2011).

The classification systems mentioned previously do not take FRCs into account. An FRC may be considered a hybrid composite by some, but it does not necessarily have the filler loading that a hybrid composite is expected to have. FRCs are also often used as dentine replacements or cores with a veneering layer rather than a stand-alone restorative material. A classification which does allow for FRCs is shown in the diagram below, adapted from Callister (2007).

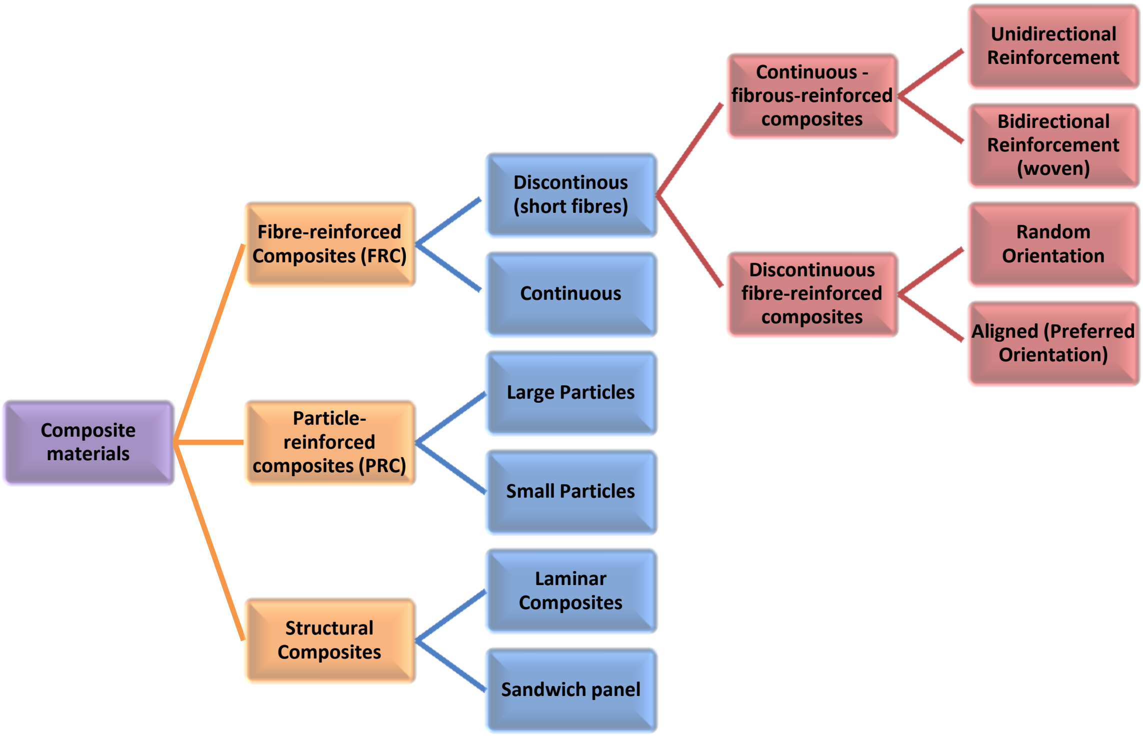


Figure 2. Composite Classification (adapted from Callister 2007).

Another classification system for dental resin composites comes from the International Organization for Standardization (ISO). The ISO standard 4049 for resin-based restorative materials classifies materials as being of two types depending on application. Type I is claimed to be suitable for the restoration of cavities involving the occlusal surface by the manufacturers while Type II includes all the other polymer-based filling and restorative materials. Materials are further sub-divided into three classes:

1. Class 1 comprises all self-curing materials whose setting reaction is activated by mixing an initiator and an activator.
2. Class 2 materials’ setting is affected by the application of energy from an external source, such as blue light or heat. These materials are divided into:
    - Class 2 group 1: materials whose use requires the energy to be applied intra-orally;

  - Class 2 group 2: materials which require the energy to be applied extra-orally.
3. Class 3 materials are dual cured, i.e. they have a self-cure chemical mechanism but are also cured by external energy application.

2.3 **Properties of Dental Composites**

2.3.1 Polymerisation Shrinkage

In general, dental resin composites shrink as they polymerise (Rueggeberg, 2002). This is due to a decrease in the distance between the atoms as the monomers react to establish a covalent bond as well as the reduction in the amount of free volume (Braga *et al.*, 2005; Schneider *et al.*, 2010). The curing reaction of dental resin composites often involves visible-light initiated polymerisation of dimethacrylate monomers to form a highly cross-linked polymer and consists of three steps; initiation, propagation and termination (Schneider *et al.*, 2010; Cramer *et al.*, 2011). The process occurs rapidly and is complex. Essentially, the blue curing light (400–550 nm) activates CQ and converts it to an excited state. Once excited, CQ reacts with a coinitiator to form free radicals and begin the activation and initiation phases of the polymerisation process (Schneider *et al.*, 2010). When the free radical reacts with a monomer molecule, an active centre is created and propagates the polymerisation process. The propagation process involves polymer chain growth by rapid sequential addition of monomer to the active centres via covalent bonds until the maximum degree of conversion of C=C double-bonds into C–C bonds is achieved & the process is terminated (Schneider *et al.*, 2010). The filler volume fraction, composition and degree of conversion of the resin matrix all play a role in determining the amount of volumetric shrinkage in a dental resin composite (Braga *et al.*, 2005; Cramer *et al.*, 2011).

Bis-GMA's volumetric shrinkage is approximately 5% - 6.1% (de Gee *et al.*, 1985; Patel *et al.*, 1987) while TEGDMA's is approximately 12.5%. The volumetric shrinkage reported for currently commercially available dental resin composites has been reported to be within the ranges of 1 – 5% (Ferracane, 2005), 1 - 6% (Schneider *et al.*, 2010) or 1-3% (Heintze and Zimmerli, 2011). The shrinkage values reported are considered approximate, because they are dependent upon the extent of the polymerisation reaction. (Labella *et al.*, 1999; Braga *et al.*, 2005). The difference in the value of the volumetric shrinkage is due to several factors, among which is the presence of inorganic filler in dental resin composites. In general, a higher filler volume fraction leads to a decrease in polymerisation shrinkage (Puckett *et al.*, 2007). For example, a hybrid composite has filler particles which occupy approximately 60% of its volume and shrinks between 1-3% on average. Low viscosity (flowable) composites present volumetric shrinkages of up to 5%, mainly due to their reduced inorganic content, which is typically below 50 % by vol (Weinmann *et al.*, 2005; Puckett *et al.*, 2007). However, microfilled composites show similar shrinkage values to hybrid composites despite an inorganic content of typically about 40 % by vol. This is due to the presence of pre-polymerised composite particles, sometimes referred to as ‘organic fillers’, which render them similar to hybrid composites in terms of the actual volume fraction of polymerising resin (Puckett *et al.*, 2007).

The addition of fibres to the composite matrix has been studied to a lesser degree. One study found that placing unidirectional fibres to reinforce the restoration resulted in higher shrinkage (0.41%) when compared with a commercially available PFC (0.32%), while biaxial fibre reinforced material shrank least of all (0.03%) (Anttila *et al.*, 2008). Another found that the shrinkage stress of fibre reinforced dental resin composites (2.45±0.11) was significantly less than that of a PFC (2.04±0.09) (Garoushi *et al.*, 2008a). This could be explained by the orientation of fibres in the material. When the fibres are all oriented in the same direction, the shrinkage appears to increase. Materials with randomly oriented fibres in the material showed a much lower shrinkage volume. This is believed to be due to the formation of a 3-dimensional network in the presence of randomly oriented fibres (Anttila *et al.*, 2008; Garoushi *et al.*, 2008a). However, it has been found that, similar to PFCs, the addition of nanofiller particles to an FRC decrease the polymerisation shrinkage significantly (Garoushi *et al.*, 2008b).

Shrinkage is an inherent property of dimethacrylate-based resin composite formulations (Braga *et al.*, 2005; Schneider *et al.*, 2010). The concentration of diluent monomers in the Bis-GMA based resin composites affects shrinkage. Higher TEGDMA/Bis-GMA ratios in experimental dental resin composites have resulted in higher contraction stress values and volumetric shrinkage (Feilzer and Dauvillier, 2003); (Kahler *et al.*, 2008; Amirouche-Korichi *et al.*, 2009; Goncalves *et al.*, 2010; Goncalves *et al.*, 2011) as illustrated in Figure 3. This is due to an increased volumetric shrinkage as a result of enhanced conversion. As diluents generally have lower molecular weight than the host monomers, diluent monomers increase the density of polymerisable carbon double bonds, which may lead to more shrinkage. Furthermore, the mobility in the reaction environment is increased due to the lower viscosity of the diluent, allowing a more efficient conversion (Feilzer and Dauvillier, 2003). The volumetric shrinkage of composites has also been shown to be proportional to their degree of conversion. Increasing degree of conversion of the polymer matrix increases volumetric shrinkage and elastic modulus simultaneously (Silikas *et al.*, 2000; Braga and Ferracane, 2002).

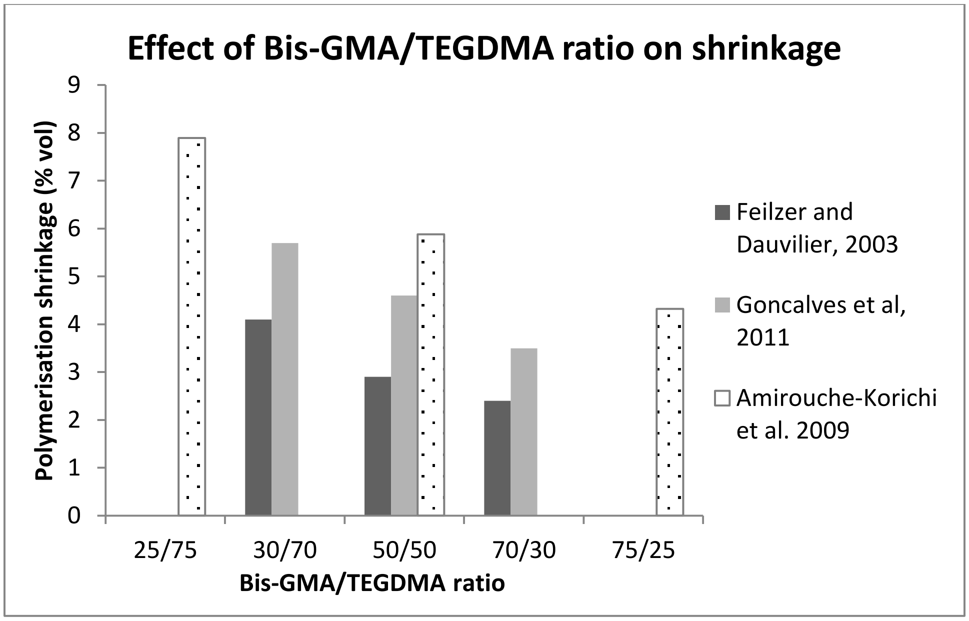


Figure 3. Effect of Bis-GMA/TEGDMA ratio on polymerisation shrinkage (based on Feilzer and Dauvilier, 2003, Amirouche-Korichi et al.2009 and Goncalves *et al*.,2011).

The polymerisation shrinkage of dental resin composites may also be altered by changing the chemistry of the monomers used. While the polymerisation reaction of the commonly used methacrylates involves the conversion of carbon double bonds (C=C) into carbon single bonds (C-C), other monomers use a ring-opening reaction to facilitate inter-monomer bonding and crosslinking (Schneider *et al.*, 2010; Cramer *et al.*, 2011). One such monomer is silorane. The term silorane derives from the novel monomer composed of a cyclic siloxane core with 4 oxirane reactive groups. Recently, it has been shown that silorane based composites have lower polymerisation shrinkage (≤ 1 %) than those based on Bis-GMA monomers (Guggenberger and Weinmann, 2000; Weinmann *et al.*, 2005; Eick *et al.*, 2007; Schneider *et al.*, 2010).

The clinical importance of polymerisation shrinkage lies in two main areas. If the material is not bonded to a cavity wall, a gap will form due to the shrinkage and subsequently micro leakage will result. When the material is bonded to a cavity wall, polymerisation stresses develop which are then transferred to the tooth-composite interface (Ferracane, 2005; Schneider *et al.*, 2010). These stresses will appear as tensile forces at the interface as the composite attempts to shrink toward the bonded surface, but is constrained by the rest of its mass, which is also bonded to an opposing surface. The constrained polymer matrix will flow from any free surfaces in an attempt to relieve these stresses (Schneider *et al.*, 2010). In addition, localised interfacial failures or weaker bonded areas will provide sites for stress relief. It has been shown that bond strengths of composite to tooth structure vary in magnitude along the interface (Kinomoto *et al.*, 2000). If the local contraction stresses exceed the local bond strength, stress relieving gaps may form. These gaps are not always associated with the margin and therefore will not be easily observed (Hannig and Friedrichs, 2001). Other localised failures, such as tooth deflection leading to fracture (Alomari *et al.*, 2001) and cracks in the tooth structure (Kanca and Suh, 1999), may also occur in an attempt to relieve internal stresses. It is expected that most of the residual stresses will be relieved as the polymer network absorbs water and time is provided for molecular reorganisations and relaxations (Ferracane, 2005).

A number of methods have been proposed for measuring the contraction of dental composites during polymerisation. Several are based on measuring the volumetric changes by using dilatometry, such as a mercury dilatometer and a water dilatometer (Feilzer *et al.*, 1988; Rees and Jacobsen, 1989; Lai and Johnson, 1993). These systems measure the volumetric change by measuring the volume changes of a liquid in a reservoir surrounding the test substance through a thin capillary column. This is determined in a manner similar to a thermometer, via the change in the column of fluid (water or mercury) after polymerisation of the sample. A drawback to dilatometry is its sensitivity to temperature changes, as even very minimal temperature fluctuations can affect the volume of liquid itself due to thermal expansion and/or contraction. Thus, a great deal of error may be introduced when attempting to measure the volumetric shrinkage of a small sample of composite, particularly where exothermic setting conditions may affect temperature. It is also difficult to light cure dental composites through a liquid medium along with the concern about environmental contamination when using a mercury dilatometer (Lee *et al.*, 2005).

In an alternative to dilatometry, Walls *et al* (1988) monitored the distortion of a transparent cover slip on the surface of a range of light cured composites during setting to calculate their polymerisation shrinkage. This study gave results comparable to those reported by using mercury dilatometry (Wassell, 1992). If the height of the composite specimen was less than one twelfth of its diameter, the axial contraction was found to be of the same order as the volumetric changes. However if the height was increased, the axial contraction revealed only the linear polymerisation contraction (Feilzer *et al.*, 1989). The bonded disc technique was then developed by Watts and Cash to study light cured biomaterials (Watts and Cash, 1991; de Gee *et al.*, 1993; Venhoven *et al.*, 1993). This method was also confirmed to have good agreement with dilatometric volumetric strain values obtained on identical material batches in round-robin studies (Watts and Marouf, 2000).The optimum specimen geometry for the bonded disc technique was a ratio between 7:1 and 9:1 for specimen diameter: height (Watts and Marouf, 2000). Since then, the bonded disk technique has been widely used by dental laboratories for its relative ease and precise results (Bryant and Mahler, 2007; Garoushi *et al.*, 2008a; Garoushi *et al.*, 2008b; Lee *et al.*, 2008).

Another method for measuring the polymerisation shrinkage of dental resin composites is to measure the density change of composites before and after polymerisation using a pycnometer and an analytic balance (Puckett and Smith, 1992; Cook *et al.*, 1999). The method itself is simple without the need for any specialised equipment but it is difficult to observe the continuous change in volume. Other investigators have used laser beam scanning or video-imaging techniques to measure polymerisation shrinkage (Fano *et al.*, 1997; Sharp *et al.*, 2003). These techniques record the external dimensions of the composite specimen continuously. The average material shrinkage is obtained by determining its overall shape change during the polymerisation process. 3D micro-CT imaging techniques have also been used to measure polymerisation shrinkage of dental composites (Sun and Lin-Gibson, 2008).

Modified digital image correlation has also been used to measure the polymerisation shrinkage of dental composites (Li *et al.*, 2009). The original technique is normally used to measure the flow of fluids and the surface strain distribution in materials testing (Kang *et al.*, 2007). A series of images of the specimen are taken using a charged couple device (CCD) camera. The movements of individual spots on the surface of the specimen during polymerisation are tracked and analysed using specialist software. The strains can then be derived from the displacement fields. In addition, the composite sample does not have to be in direct contact with a rigid medium that would provide a significant constraint (Li *et al.*, 2009). Laser speckle contrast analysis (Sato *et al.*, 2004a; Sato *et al.*, 2004b), mathematical and computational models have also been developed for research applications (Atai and Watts, 2006).

2.3.2 Water Sorption

The phenomena of sorption and solubility may lead to undesirable consequences in a dental resin composite. Over time, the absorption of water can lead to deterioration of the physical/mechanical properties. This is mainly due to a hydrolytic breakdown of the bond between silane and filler particles, filler–matrix debonding or even hydrolytic degradation of the fillers (Soderholm *et al.*, 1984). Flexural strength, tensile strength, modulus of elasticity and wear resistance are all negatively affected (Soderholm and Roberts, 1990; Sarrett *et al.*, 1991; Sideridou *et al.*, 2003). Water sorption may also cause expansion of the restoration. Micro-cracks may form within the polymerised material (Santos *et al.*, 2002). There is concern that these effects may lead to a shortened service life of dental restorations (Ferracane, 2006). Interestingly, not all the effects of water sorption are negative; the expansion caused by water sorption may also help to overcome stress on the tooth/restoration interface from polymerisation shrinkage (McCabe and Rusby, 2004).

The extent to which a resin composite material is affected by the aqueous environment in the mouth is related to its chemistry and structure (Ilie and Hickel, 2011). Some important chemical characteristics include the hydrophilicity of the polymer and the difference in solubility parameter between the polymer and the solvent (Ferracane, 2006; Cramer *et al.*, 2011). Important structural parameters include the cross-linking density and the porosity of the network. In addition, the presence of reinforcing fillers may significantly influence the sorption and solubility of the final restoration (Ferracane, 2006).

Even though monomers such as Bis-GMA and UDMA and their resultant polymers are not considered to be very hydrophilic, they do absorb water (Ferracane, 2006). Differences in water sorption were studied in polymer networks composed of various monomers, with the results being that TEGDMA absorbed more water than Bis-GMA which absorbed more water than UDMA (Kalachandra and Turner, 1987; Imazato *et al.*, 1999; Ruttermann *et al.*, 2010). This difference was due to the presence of hydrophilic ether linkages in TEGDMA, hydroxyl groups in Bis-GMA, urethane linkages in UDMA, and the presence of ester groups in all (Venz and Dickens, 1991). Researchers have also found the lowest water sorption for ethoxylated Bis-GMA (Bis-EMA) resins which did not contain the hydroxyl groups of Bis-GMA or the urethane linkages of UDMA (Sideridou *et al.*, 2003).

The quality of the polymerised network also plays a crucial role in determining the extent to which molecular uptake and swelling occur when a polymer is submerged in water or any other solvent. Water enters the polymer network through porosities and intermolecular spaces. The extent and rate of water uptake is dependent upon the density of the polymer network and the potential for hydrogen bonding and polar interactions. Other factors that may influence water sorption include the degree of conversion of the polymer, as well as the quantity of pendant molecules existing within the network (Ferracane, 2006).

The presence of fillers in a polymer network can greatly affect solvent uptake and dissolution, possibly in inverse relation to their concentration as they reduce the overall volume of the absorbing polymer (Ferracane, 2006). The water sorption for a range of commercially available dental composites and compomers has been shown to vary between 1.0 and 3.5 μg/mm^3, with the level of sorption being much higher (6–7 μg/mm^3) for resin modified glass ionomers (Toledano *et al.*, 2003). When studying the percentage of water sorption in commercially available dental restorative materials, the lowest water sorption was noted in dental resin composites (0.17%), followed by compomers (1.2%) with the highest being found in resin-modified glass ionomers (7.0%) (Musanje *et al.*, 2001). The water uptake of a variety of composites and resin cements was measured for up to 6 months. Saturation of most of the materials was reached within two months, with the more highly filled materials showing lower water sorption. Therefore, the assumption could be made that a typical dental composite restoration will become saturated with its solvent environment within one to two months of placement (Ferracane, 1997; Ortengren *et al.*, 2001).

There is no clear consensus in the literature regarding the effect of adding fibres to a dental resin composite's water sorption. While some researchers found that adding fibres to an already highly filled dental resin composite decreased the water sorption (Miettinen *et al.*, 1999; Polat *et al.*, 2003), others noted an increase in the amount of water sorption with the addition of fibres (Lassila *et al.*, 2002; Anttila *et al.*, 2008). Some authors even found no difference as a result of the fibre addition (Pastila *et al.*, 2007). Once again, the orientation of the fibres may play a role, but this has not been specified in any of the studies.

The ISO specifies how to measure water sorption as well as its acceptable level in dental resin composites. ISO 4049:2000 requires that for a dental resin composite, water sorption ≤ 40 μg mm^{-3} for disc shaped specimens. The specimens are made at room temperature (22 – 23°C), then stored 37°C in a vacuum desiccator followed by 2 h storage at 22–23°C and weighed to within ±0.1 mg. This cycle is repeated until a constant mass is achieved. The volume of the specimen is then determined by measuring the specimen's diameter from two perpendicular planes and the thickness from five measurements, one at the centre and four at equally spaced points on the specimen's circumference. Then the specimens are stored for 7 days in water at (37 ± 1) °C. They are then dried until there is no water visible on the surfaces. Then they are weighed to obtain mass. After that, the specimens are stored at (37 ± 1)°C in a desiccator and weighed every 24 h until mass was constant. Water sorption is then calculated in µg mm^{-3} according to the formula $W_{sp} = (m_2 - m_3)/V$, where m_1 is the mass of specimen prior to water storage in µg; m_2 is the mass of specimen after water storage at 37°C for 7 days in µg; m_3 is the mass of specimen after water storage and drying in µg; and V is the volume of specimen in mm^3.

2.3.3 Degree of Conversion

The extent of polymerisation within the composite is most commonly defined in terms of the degree of conversion from monomer to polymer (McCabe and Walls, 2008). While it is desirable for a dental resin composite to convert all of its monomer to polymer during polymerisation, there is a significant portion of unreacted carbon-carbon double bonds (C=C) within the set material at or near oral temperature. The dimethacrylate monomers used in restorative materials exhibit a degree of conversion ranging from 55% to 75% under conventional irradiation conditions (Ferracane and Greener, 1986; Silikas *et al.*, 2000; Stansbury and Dickens, 2001; Baroudi *et al.*, 2007; Galvão *et al.*, 2010). The release of the unreacted monomers may stimulate the growth of bacteria around the restoration and promote allergic reactions in some patients (Carmichael *et al.*, 1997; Hansel *et al.*, 1998; Sideridou *et al.*, 2003). The unreacted monomers may also act as a plasticiser and decrease the mechanical properties of the restoration (Lovell *et al.*, 1999).

An ideal composite would exhibit minimal polymerisation shrinkage with a high degree of conversion (Dewaele *et al.*, 2006; Amirouche-Korichi *et al.*, 2009). As an increase of monomer conversion leads to the increase of polymerisation shrinkage, this ideal seems to be almost impossible to attain. The degree of conversion has a linear correlation with volumetric shrinkage in dental resin composites (Rueggeberg and K.

Tamareselvy, 1995; Silikas *et al.*, 2000; Braga *et al.*, 2005). Experimentally, an approximately linear correlation was also exhibited between degree of conversion and Knoop hardness. A high degree of conversion is also related to high hardness (Chen *et al.*, 2005; Silva *et al.*, 2007), while a low degree of conversion will lead to low hardness, excessive wear, low strength and low marginal retention (Ferracane *et al.*, 1998; Uhl *et al.*, 2002; Versluis *et al.*, 2004).

The use of the high intensity halogen lamp as an activator for the polymerisation reaction is very common (Yearn, 1985; Rueggeberg *et al.*, 1994; Obici *et al.*, 2004). Light of an appropriate wavelength activates photo-polymerisation of methacrylate groups producing a highly cross-linked polymer matrix. Light from the curing source should ideally be able to adequately polymerise the top as well as deeper composite regions. However, as light passes through the composite, it is absorbed and scattered, reducing its effectiveness to initiate polymerisation, and consequently resulting in variation of degree of conversion with depth (Peutzfeldt *et al.*, 2000; Mendes *et al.*, 2005a; Mendes *et al.*, 2005b). In deeper regions, where significant light attenuation occurs, the curing unit that delivers light at a more specific wavelength and with high enough power should provide higher degree of conversion.

In an attempt to maintain a high degree of conversion while reducing polymerisation shrinkage, several variations to the continuous use of high intensity halogen lamp have been suggested. Such variations include stepped light (Bouschlicher *et al.*, 2000; Obici *et al.*, 2002; Obici *et al.*, 2004), exponential light (Caldas *et al.*, 2003), light emitting diode (LED) (Kurachi *et al.*, 2001; Obici *et al.*, 2004) and intermittent light (Obici *et al.*, 2002). Another method employs the plasma arc curing (PAC) lamps, which provide a high intensity in a short time (Peutzfeldt *et al.*, 2000).

It has been reported that the values for the degree of conversion at the surface of a dental resin composite and at 1 and 2 mm deep were not significantly different regardless of light-curing unit or exposure method, but were less at greater depths (Vandewalle *et al.*, 2004; Obici *et al.*, 2006). Some found that two-step curing protocols might generate lower degrees of conversion (Lu *et al.*, 2005; Lopes *et al.*, 2009). Other studies found no difference between the alternate curing method and the continuous curing method (Koran and Kurschner, 1998; Sakaguchi and Berge, 1998 ; Silikas *et al.*, 2000; Tarle *et al.*, 2006).

The monomers used in a dental resin composite also play a role in the degree of conversion achieved. As the commonly used monomer Bis-GMA is much more rigid than the dimethacrylate TEGDMA, the degree of conversion in Bis-GMA and TEGDMA copolymers has been found to decrease with an increasing content of Bis-GMA (Peutzfeldt, 1997; Asmussen and Peutzfeldt, 2001; Sideridou *et al.*, 2002; Emami and Soderholm, 2009). When comparing binary mixtures, it was found the degree of conversion in resin mixtures with a higher percentage of TEGDMA was significantly higher than those with a high concentration of Bis-GMA. The degree of conversion was significantly higher for binary mixtures of UEDMA and TEGDMA, and significantly lower for 100 wt% Bis-GMA. The degree of conversion values were between 53.1%±0.9% (100% Bis-GMA) and 85.6%±1% (80% UEDMA-20% TEGDMA) (Emami and Soderholm, 2009). Despite the resultant decrease in degree of conversion, an increasing content of Bis-GMA did not result in reduction in strength or in hardness according to the authors. This lack of correlation between conversion and hardness, or strength may be explained by the fact that the flexible TEGDMA is substituted by the much stiffer Bis-GMA in the polymer network (Vasudeva, 2009).

Some studies on the formation of polymers from dimethacrylates of mono-, di-, tri-, and tetraethyleneglycol have shown that the reactivity of the monomers increases with increasing distance between the methacrylate groups (Floyd and Dickens, 2006). Long chain, flexible dimethacrylates of oligoethyleneglycols have been found to exhibit relatively high degrees of conversion. This has been attributed to their stereochemistry (Floyd and Dickens, 2006). An increase in filler loading has been reported to show a decrease in the degree of conversion (Halvorson *et al.*, 2003). Other researchers also found a decrease, but it was of no statistical significance (Amirouche-Korichi *et al.*, 2009). The explanation for that may lie in the fact that the influence of fillers is more related to their size than to their volume (Atai and Watts, 2006). Turssi *et al* (Turssi *et al.*, 2005) found no effect on degree of conversion with different filler shapes.

The photoinitiators in a light cured dental resin composite also play a role in degree of conversion. Camphorquinone (CQ) has been largely used as a photoinitiator since the introduction of visible-light activated resin composites (Schneider *et al.*, 2008). CQ exhibits a broad light absorption, between 400 and 500 nm, peaking at 468 nm (Nomoto, 1997; Fujibayashi *et al.*, 1998; Obici *et al.*, 2006). The spectral emission from quartz tungsten halogen curing lights ranges between 380 and 510 nm), with a wavelength peak near 480 nm (Fujibayashi *et al.*, 1998; Obici *et al.*, 2006). LED curing lights produce a narrower wavelength range (450–490 nm) (Nomoto, 1997) with a peak near 466 nm (Fujibayashi *et al.*, 1998). The association of CQ with an electron/proton donor substance, usually a tertiary amine, may increase its reactivity (Stansbury, 2000b; Jakubiak *et al.*, 2003). The photoinitiator concentration is a factor that influences radical formation in CQ/amine systems. This concentration varies among commercially available brands (Shintani *et al.*, 1985; Alvim *et al.*, 2007; Schneider *et al.*, 2008). Higher concentrations of photoinitiators have been found to improve the degree of conversion (Peutzfeldt and Asmussen, 1989; Cook, 1992; Yoshida and Greener, 1994; Rueggeberg *et al.*, 1997; Moin *et al.*, 2001; Schroeder and Vallo, 2007). However, that is only true to a certain threshold (approximately 1%), above which no benefits are observed (Jakubiak *et al.*, 2001) and aesthetics may be affected due to CQ's yellow colour (Schneider *et al.*, 2008). It has been reported that, in experimental dental resin composites, the degree of conversion increased as CQ concentration increased from 0.3 to 0.6 wt. % of the total resin matrix. Above that limit, the degree of conversion actually decreased (Jakubiak *et al.*, 2001; Moin *et al.*, 2001).

To measure the degree of conversion of dental resin composites, Fourier transform infrared spectroscopy (FTIR) has been widely used and is considered a reliable method due to the availability of equipment and numerous sampling techniques (Imazato *et al.*, 2001; Stansbury and Dickens, 2001; Amirouche-Korichi *et al.*, 2009). This method detects the ($C{=}C$) stretching vibrations, centred around 1638 cm^{-1}, directly before and after curing of materials (Imazato *et al.*, 2001; Stansbury and Dickens, 2001; Amirouche-Korichi *et al.*, 2009). The ratios of the infrared spectra of aliphatic (1638 cm^{-1}) to aromatic (1608 cm^{-1}) $C{=}C$ double bonds absorption peaks are used to calculate monomers conversion (Silikas *et al.*, 2000).

Another vibrational technique used is Raman spectroscopy (Shin *et al.*, 1993). For the monomers and polymers used in dental resins, most of the vibrations should have both infrared and Raman activity. The use of Raman spectroscopy has been limited due to the poorer sensitivity of Raman spectroscopy compared with IR spectroscopy and the existence of broadband fluorescence which interferes with the Raman signal of interest. Raman spectroscopy can detect concentrations of about 1%, whereas IR spectroscopy can be used for concentrations of approximately 0.1% (Shin *et al.*, 1993).

A hybrid technique called FT-Raman spectroscopy was developed which eliminates the disadvantages of Raman scattering as a tool for characterisation of impure polymer systems such as dental resins (Hirschfeld and Chase, 1986). Its advantages compared with traditional Raman scattering methods are: (1) samples of any thickness and geometry can be investigated because the incident radiation can be focused on the sample and the scattered radiation collected with suitable collection optics; (2) many inorganic fillers such as silica are poor Raman scatterers and thus appear as weak, broad features in the Raman spectra; and (3) the sensitivity of Raman scattering to the highly symmetrical C=C vibration of the dimethacrylate resins used in dentistry (Shin *et al.*, 1993).

Differential thermal analysis (DTA) using a split fibre optic light source has also been reported to be a convenient method of measuring the degree of conversion of light-activated composites (McCabe, 1985). The heat of reaction of a composite specimen after different polymerisation times was determined. A second exposure to the polymerising light was made 10 minutes later. This enabled the percentage conversion for the initial exposure to be calculated. When compared with FTIR, it showed good agreement in measuring degree of conversion (Imazato *et al.*, 2001).

2.3.4 Bond Strength

Bonding and adhesion are two terms that are often used interchangeably. Adhesion may be defined as a molecular or atomic attraction between two contacting surfaces promoted by the interfacial force of attraction between the molecules or atoms of two different species; adhesion may occur as chemical adhesion, mechanical adhesion (structural interlocking), or a combination of both types (Soderholm, 2007). Adhesive bonding has defined as “the process of joining two materials by means of an adhesive agent that solidifies during the bonding process” (Anusavice, 2003).

One of the first known dental adhesives was an acidic cement used by the Maya Indians for attaching semi-precious stones to the buccal surface of their anterior teeth (Van Meerbeek *et al.*, 2006). It is believed that the concepts of modern adhesive dentistry began in 1955 when Buonocore published a paper in which he demonstrated that etching enamel with phosphoric acid could increase bond effectiveness in terms of both the marginal seal and the bond strength (Buonocore, 1955).

The first dental adhesive systems were based on Bis-GMA, thus making them extremely hydrophobic. Consequently, bonding to dentine was practically impossible when compared to enamel. Since then, bonding systems have developed to include more hydrophilic monomers, allowing adhesives to bond to both enamel and dentine. The 3 step etch-and-rinse adhesive systems are currently considered the gold standard for bonding (De Munck *et al.*, 2005; Soderholm, 2007; Van Meerbeek *et al.*, 2010). A detailed account of the evolution of dental bonding systems is outside the scope of this literature review. There are several papers which deal with this topic for more information (Van Landuyt *et al.*, 2007; Breschi *et al.*, 2009).

To bond to enamel, the surface is pretreated with an acid to render it microporous and then infiltrated with a low viscosity resin (Walls *et al.*, 2001). To bond to dentine, two main processes must be undertaken. They are the removal of the mineral phase from the dentine substrate without altering the collagen matrix and then filling the voids left by the mineral with an adhesive resin that undergoes complete *in situ* polymerisation, i.e formation of a hybrid layer, also known as a resin-reinforced layer (Nakabayashi *et al.*, 1982a; Spencer *et al.*, 2010). The ideal hybrid layer is a 3 dimensional polymer/collagen network that provides both a continuous and stable link between the bulk adhesive and dentine substrate. There is evidence in the literature to suggest that this ideal objective has yet to be achieved (Sano *et al.*, 1999; Spencer and Swafford, 1999; Hashimoto *et al.*, 2000; Hashimoto *et al.*, 2002; Spencer *et al.*, 2006). Instead of serving as a stable connection between the bulk adhesive and subjacent intact dentine, the hybrid layer is often called the weakest link in the adhesive/dentine bond (Breschi *et al.*, 2008; Spencer *et al.*, 2010). A poor bond between a restoration and tooth structure often results in post-operative sensitivity, marginal staining and recurrent caries (Heintze *et al.*, 2009).

Both *in vitro* and *in vivo* studies have suggested several factors which inhibit the formation of a durable adhesive/dentine bond (Ferracane, 2006; Wang *et al.*, 2007; Ye *et al.*, 2007; Breschi *et al.*, 2008). These factors include:

a) Incomplete resin infiltration;
b) Inadequate monomer/polymer conversion rates of the infiltrating adhesive;
c) Incomplete solvent evaporation;
d) Water sorption and hydrolysis of the adhesive resin.

Both resin permeability and monomer elution are related to incompletely polymerised bonding systems, one method proposed to improve polymerisation was to extend the curing time of the adhesive beyond 20 s the time period recommended by manufacturers. It has been reported that extending the curing times of simplified adhesives beyond those recommend by the manufacturers did result in improved polymerisation and reduced permeability, thus making it a vailable option for improving the performance of the adhesive (Cadenaro *et al.*, 2005; Breschi *et al.*, 2008). Including photoinitiators that are compatible with hydrophilic components may also improve the inadequate monomer/ polymer conversions (Ye *et al.*, 2009). The incorporation of hydrophilic monomer blends in simplified adhesives (two-step etch-and-rinse and one-step self-etch adhesives) has been shown to significantly reduce bond longevity, a hydrophobic coating seems to be key to reduce water sorption and stabilise the hybrid layer over time (Breschi *et al.*, 2008). To reduce incomplete resin infiltration and inadequate solvent evaporation several other strategies could also be used. These include using a rubber dam to limit moisture contamination by saliva or water as well as careful attention to the handling, management, and storage of the adhesive to prevent solvent evaporation before and during the application of the adhesive (Spencer *et al.*, 2010). The use of MMP inhibitors as additional primer has been reported to reduce interfacial aging *in vivo* and *in vitro*. This is inhibiting the activation of the dentine enzymes which are responsible for the degradation of collagen fibrils in the absence of bacterial contamination (Hebling *et al.*, 2005; Carrilho *et al.*, 2007).

Depending on the size of the bond area, bond strength may be measured using a macro- or micro-test set-up. The macro-bond strength, with a bond area larger than 3 mm^2, can be measured in shear, tensile, or using a push-out protocol (Van Meerbeek *et al.*, 2010). Dental adhesive bond strength tests typically involve the application of a load causing a distributed stress to develop at the bonded interface or within the substrate or tooth, ultimately leading to the fracture of the specimen. There are a number of methods used to measure the bond strength of adhesives to enamel and dentine (Burke *et al.*, 2008). One of the most straightforward ways of accomplishing that goal is through the use of a planar shear bond strength test. This is done by applying a load to a cylindrical resin composite material bonded to a substrate. The load may be applied through a blade contacting the bonded specimen and running parallel with the bonded surface, distributed axially along the composite cylinder or cosine distributed along the interface simulating a wire loop. The stress distribution is influenced by the load and specimen design as well as the stiffness of the materials used. A non-uniform stress distribution has been measured along the interface, which brings into question the accuracy of bond strength relative to the measurement of true maximum strength forces (Ferracane *et al.*, 2009). In an attempt to standardise testing procedures, specific jigs have been prepared, such the Ultradent jig (Ultradent, Salt Lake City, UT, USA) and the more recent SDI rig (SDI, Bayswater, Victoria, Australia) (Van Meerbeek *et al.*, 2010). Despite attempting to standardise the jig used during testing, their use is not widespread yet. Even if the jigs were standardised, several variables still exist which influence the final result. They include those related to the nature of the teeth used (i.e. dentine substrate), the stiffness of the dental resin composites tested and bonding area (i.e. composite stiffness), the storage conditions of the bond assemblies (i.e. thermo-cycling), and the test design (i.e. crosshead speed) (Leloup *et al.*, 2001; Van Meerbeek *et al.*, 2010). The variation in so many variables makes comparing test results from different laboratories almost impossible.

Tensile bond strength testing involves a tensile load being applied perpendicular to the adhesive surface and uniaxially along the specimen. Specimen alignment is difficult to control and due to plastic and elastic deformations, asymmetric stress concentrations and load applications, the results are variable. Stress concentration also depends on the height of the composite sample. At 3 mm or higher, the stresses are concentrated at the adhesive interface while a cylinder height of less than 3 mm moves stress away from the interface and onto unpredictable locations (Ferracane *et al.*, 2009).

The microtensile bond strength tests apply a tensile load to specimens with adhesive cross-sectional areas of approximately 1 mm^2. Usually one of three specimen designs (hourglass, stick or dumbbell) is fixed to a testing jig to allow the measurement of ultimate fracture strength. The hourglass-shaped specimens better concentrate stress at the interface, but involve a more invasive specimen procedure with an increased risk of pre-test failure compared with the other two specimen designs. The stress distributions for the dumbbell and stick shape specimens are similar. There is a risk of flaw introduction due to the mechanical shaping of the specimens (Sadek *et al.*, 2006; Ferracane *et al.*, 2009). There are several advantages of using the microtensile technique, the most obvious of which is the need for fewer teeth as a single tooth will produce multiple specimens. Better control of which region of dentine is being used and better stress distribution at the true interface has also been reported (Pashley *et al.*, 1999; Scherrer *et al.*, 2010). Another advantage of micro-tensile testing is the possibility to test the bonding effectiveness to clinically relevant tooth substrates such as carious (Nakajima *et al.*, 1995; Van Meerbeek *et al.*, 2003) and sclerotic dentin (Tay *et al.*, 2000; Van Meerbeek *et al.*, 2003). Microtensile bond strength is inversely related to the bonded surface area (Pashley *et al.*, 1999; Van Meerbeek *et al.*, 2003). Despite measuring much higher bond strengths than macro-testing methods, the majority of the failures occurred at the interface between tooth substrate and adhesive. The main disadvantage is the technique sensitive, labour intensive and fragile specimen preparation technique. Inadequate technique could introduce microfractures or flaws into the specimens where none existed, weakening the bond and reducing the bond strength (Ferrari and Cardoso, 2002; Van Meerbeek *et al.*, 2003; Van Meerbeek *et al.*, 2010). All this has led to the belief that microtensile tests may give results with a lower coefficient of variation compared with macrotensile testing. However, a high coefficient of variance exists in such tests, up to 100% reported by some authors (Armstrong *et al.*, 2003; Burrow *et al.*, 2004; Scherrer *et al.*, 2010). Variables such as specimen shape (hourglass, dumbbell or stick), flaws in the adhesive (such as air bubbles), or flaws created during specimen preparation all contributed to the high coefficient of variance. Recently, microtensile and macrotensile adhesive tests were compared and no difference was found in the coefficient of variation for most of the adhesives tested in the literature (Scherrer *et al.*, 2010).

The microshear bond strength test uses cylindrical composite specimens with a cross sectional area of approximately 1 mm^2, with a typical diameter of 0.7 mm (Nakabayashi *et al.*, 1982a; Van Meerbeek *et al.*, 2010). This means that several specimens can be bonded to the same substrate and there is potential for regional mapping of bond strength across the substrate. This test combines the ease of manipulation with the ability to test several specimens per tooth. However, the very fine composite (cylinder) with a typical diameter of 0.7mm, in combination with a relative thick adhesive layer, may result in considerable bending and variable and non-uniform loading conditions (Armstrong *et al.*, 2010). This means that stress measurements may be more difficult and less accurate as an area of relative stress intensifies due to the smaller specimen size combined with load application which is directed very close to the interface. These factors are rather challenging when dealing with low modulus resin composites (Ferracane *et al.*, 2009; Van Meerbeek *et al.*, 2010). The same Finite Element Analysis findings apply for both shear and microshear bond strength tests; (1) a stress distribution which is not uniform and (2) a nominally measured bond strength that severely underestimates the true stress the specimen resisted at fracture (Armstrong *et al.*, 2010). It has been reported that microshear results may actually be less representative that macroshear (Placido *et al.*, 2007).

Bond strength testing in shear has been reported as the most frequently used test (Heintze, 2007) followed by tensile and microtensile tests. The simplicity of specimen preparation and fewer pre-test failures contribute to shear bond strength's popularity (Placido *et al.*, 2007; Salz and Bock, 2010; Scherrer *et al.*, 2010). Others have reported micro-tensile bond-strength tests were the most frequently used, followed by macro-shear, micro-shear, and then macro-tensile bond-strength tests (Van Meerbeek *et al.*, 2010). The difference may reflect more researchers moving towards micro-tensile testing. The bond strength obtained from micro shear and microtensile tests are usually higher than their macro-scale counterparts, 1-3 times higher in microshear and 2-5 times higher in microtensile results (Scherrer *et al.*, 2010). This may be explained by the increased likelihood of flaws existing in larger samples, making it more probable for such a sample to encounter a strength limiting flaw during testing (Burrow *et al.*, 2004; Scherrer *et al.*, 2010).

Reporting on bond strength data may be done simply by reporting the means and standard deviations of the results of testing. Due to the high coefficient of variance reported, a better predictor of clinical performance would be to describe the fraction of the specimens to survive or fail at a given load. Weibull probability of survival analysis has been developed as, among other things, an engineering design method for components made from such materials as ceramics. Weibull described this fraction, the survival probability, which relates the probability (P_f) of failure to stress (σ), using the following equation (McCabe and Carrick, 1986) :

Equation 2. Weibull Probability (P_f)

$$P_f = 1 - \exp\left\{- \left(\frac{\sigma - \sigma_u}{\sigma_0}\right)^m\right\}$$

where σ_u, σ_0 and m are constants. The constant σ_u is the lowest level of stress at which P_f approaches zero. It is customary to assume that $\sigma_u = 0$. The constant σ_0 is a difficult parameter to visualise and is normally referred to as a normalising parameter (McCabe and Carrick, 1986). The constant m is the Weibull Modulus and is a measure of the variability of the results. A high value of m indicates a close grouping of fracture stress values whilst a low value indicates a wide distribution with a long tail at low stress levels (McCabe and Carrick, 1986; Burrow *et al.*, 2004). The ISO technical specification 11405; 2003 recommends reporting the Weibull probability analysis along with the mean bond strengths.

To date, no *in vitro* method has been validated as the gold standard for clinical adhesive performance. Clinical trials are still considered by many to be the only valid method for evaluating the performance and efficacy of dental adhesives (Ferracane *et al.*, 2009; Van Meerbeek *et al.*, 2010). However, designing clinical trial for materials which are not intended for direct exposure to the oral environment such as core build up materials is a challenge.

The addition of a layer of FRC at the tooth/restoration interface has shown an improvement in shear bond strength compared with bonding a PFC without the addition of an FRC material (Tezvergil *et al.*, 2005; Tezvergil-Mutluay *et al.*, 2008).

2.3.5 Hardness

Hardness is defined as the resistance of a surface to penetration or deformation. The deformation may be the result of indentation, scratching, abrasion, or machining (Callister,2007). Early hardness tests were constructed solely on the ability of one material to scratch another. Quantitative hardness tests were later developed which depended on an indenter being forced into the surface of the test material. Various methods of measuring hardness are available based on surface indentation (McCabe and Walls, 2008). They include the following:

- Rockwell, in which the indenters may be spherical or conical. Spherical and hardened steel balls are used for soft and medium hardness values while a conical diamond (Brale) indenter in used for the hardest materials;
- Brinell, which uses a spherical indenter;
- Vickers, in which a diamond indenter of pyramidal shape with a square base is used;
- Knoop, in which a diamond indenter of pyramidal shape with an elongated base is used.

The common principle of measuring the area or depth of indentation is used by all the tests mentioned above. A microscope is used for measuring due to the small size of the indentations (McCabe and Walls, 2008). The tests differ in the indenter material and geometry, along with the force applied and its duration.

In the Rockwell test, the hardness number is determined by the difference in depth of penetration resulting from the application of an initial minor load, followed by a larger major load. Specimen thickness should be at least ten times the indentation depth while allowance should be made for at least three indentation diameters between the center of one indentation to another or to the edge of the specimen .

In the Brinell test, standard loads used range between 500 – 3000 kg in 500 kg increments. The Brinell hardness number is a function of both the diameter of the indentation and the magnitude of the load. The diameter of the indentation will vary with depth due to the indenter's spherical shape (Callister, 2007). The measured diameter is then converted into a hardness number based on a calibrated conversion chart. As in the Rockwell test, there is a minimum specimen thickness and space requirements between indents.

The Barcol test is based on a hand-held instrument which is designed to apply a fixed load of approximately 10 kg to the flat-ended steel indenter. The depth of indenter penetration into the surface is measured by means of a dial gauge which is in units of Barcol Hardness (Wassell *et al.*, 1992).

In the Vickers test, a pyramidal indentation is made under specified conditions of load and time. The hardness number is derived by dividing the surface are of the indentation measured in mm^2 by the applied force. Standard loads are between 5 – 10 kg, low loads are between 200 g – 5 kg, while microhardness measurements are made at loads of 200g or less. The hardness number is qualified by giving the indenter load and its duration of action. For example, a Vickers hardness n umber of 670 made at 9.807 N (1 Kg force) applied for 20s would be written: 670 HV 1/20. One of the advantages of using Vickers hardness tests is that it appears to be independent of the applied force. However, it is difficult to measure the hardness of dental resin composites. Exposed filler particles on sectioned or lapped specimens cause reflections which make it difficult or impossible to view the indentation. Consequently, for routine testing, the indentation is generally made on the surface polymerised against a smooth matrix (Wassell, 1992) ; Callister, 2007).

The Knoop test employs a principle similar to that of the Vickers test with the exception of the proportions of the indenter. A Knoop test uses a pyramidal indenter with diagonals seven times longer than they are wide. This allows the study of materials in which the hardness measurements are dependent on surface orientation (Wassell, 1992).

Material hardness is used to give an indication of the material's ability to resist scratching. It is often used to give an indication of the abrasion resistance of a material when the material will be subjected to abrasive wear (McCabe and Walls, 2008).

Measuring hardness in dental resin composites is challenging due to the fact that each of the constituents will have a different hardness. A common approach to overcoming this challenge is the use of micro- indentation hardness measurements. Both the Knoop and Vickers tests are known as micro-indentation-testing regimes based on the size of their indenters. They allow measurement of small, selected regions of a specimen, smaller than the filler particles or phases being measured.

Nano-indentation is another method used. The instruments used function as load and displacement sensing systems in which information is derived from the penetration of indenter on loading as well as from the elastic recovery of the specimen upon unloading (Angker and Swain, 2006).

Indentation into specimens proceeds by loading either continuously or incrementally until a preset maximum force is reached. The specimen is then unloaded in a similar manner. Several cycles of partial loading and unloading may also be utilised in the testing regime. An additional hold period at maximum load is frequently incorporated to allow for creep relaxation before unloading, enabling a more reliable estimate of the elastic modulus from the unloading slope. Using these techniques, testing of soft hydrated tissue with highly elastic recovery behaviour, such as carious dentine, is possible (Angker *et al.*, 2005; Angker and Swain, 2006). Either spherical or pyramidal indenters may be used. The most common one is a pyramidal indenter with an equilateral triangular base (Berkovich indenter). The indentation is normally carried out in a continuous load/unload cycle. Hardness is determined as a function of penetration depth (Angker and Swain, 2006).

Field and Swain (1993) showed that indentation with a spherical indenter has advantages, such as the ability to follow the transition from elastic to plastic behaviour of the test material. The smooth, blunt tip ensures the initial penetration at contact is limited, which is of particular use in soft materials. The degree of penetration is controlled by the choice of indenter radius (Angker and Swain, 2006).

A dental resin composite's hardness increases with an increase in volume filler loading (Manhart *et al.*, 2001; Cadenaro *et al.*, 2005; Hebling *et al.*, 2005; Carrilho *et al.*, 2007; Zhou *et al.*, 2009; Davidsen *et al.*, 2011). When comparing the filler morphology and loading of dental resin composites in relation to hardness, it has been reported that dental resin composites which contain round filler particles had higher filler loading and hardness when compared to those with irregularly shaped fillers or a mixture of pre-polymerised and irregularly shaped fillers (Cadenaro *et al.*, 2005). Some have found the highest hardness to be for FRCs (Hebling *et al.*, 2005). However, this may or may not be due to the presence of fibres as the FRC tested had the highest filler loading.

Bis-GMA/TEGDMA levels, an increase in Bis-GMA improved hardness (Burette *et al.*, 2008; Bednarek *et al.*, 2009). Changing the tertiary amine associated with the initiator has also been found to increase hardness. Using 2-dimethylaminoethyl methacrylate (DMAEMA) has increased hardness when compared to aromatic amines (Sepulchre *et al.*, 2006).

2.3.6 Fatigue

Fatigue is a form of failure that occurs when a structure is subjected to variable and dynamic stresses repeatedly (Callister, 2007). Individually, the stresses encountered would not cause a fracture when the material is measured in direct compressive, tensile or flexural tests. The term fatigue is used because this type of failure often occurs after repeated cycles of stress or strain. This type of failure is used to determine the fatigue limit, also called the endurance limit, below which fatigue failure will not occur. Another important parameter is fatigue life, which is the number of cycles to cause failure at a specified stress level (Callister, 2007; McCabe and Walls, 2008).

Understanding the fatigue process, together with knowledge of the fatigue limit and fatigue life of dental materials, helps to produce better materials, determine their longevity and ideal applications. Several factors may participate in fatigue-induced damage, including the strength of various phases, interfacial strength and direction of load application. Void formation, matrix deformation and cracking, filler debonding, and filler failure are all among the types of damage which may occur. The dominant mechanism is influenced by the mode of load application. For example, in cyclic fatigue, voids are more likely to form at the fibre-matrix interface than during monotonic loading (Horst and Spoormaker, 1997).

Clinical fatigue is mainly driven by cyclic forces, such as those which occur during mastication forces (Baran *et al.*, 2001; Fujii *et al.*, 2004; Drummond, 2008). *In vitro* cyclic fatigue studies demonstrated slow crack propagation in dental resin composites (Draughn, 1979; Lohbauer *et al.*, 2003). A significant decrease in strength performance due to stress corrosion under load or due to viscoelastic creep was reported after the applied combination of water ageing and cyclic loading (Choi *et al.*, 2000; Manhart *et al.*, 2000b; Manhart *et al.*, 2000a). Fracture was detected both at the resin-filler interface and within the resin itself (Lohbauer *et al.*, 2003).

The fatigue strength of a resin composite varies according to its composition. Some authors reported that adding UDMA to a Bis-GMA/TEGDMA matrix improved the fatigue life of a dental resin composite (Papadogiannis *et al.*, 2007). Others found a uniform Bis-GMA matrix with UDMA and EMA had the highest fatigue strength, but attributed it to the uniform distribution of the particles within the dental resin composite rather than the components of the matrix (Vanmeerbeek and Louis, 2006).

In PFCs, debonding at the filler/matrix interface occurs at low static stresses, producing a rough fracture surface. The crack propagation in dental resin composites is mainly through the matrix and its adhesion to the filler particles (Lohbauer *et al.*, 2006). The crack propagation in resin composite materials is around or through second-phase particles and it depends on the filler content and the interparticle distance (Drummond, 1989). Higher localised polymerisation stresses might build up around filler particles, thus leading to reduced crack growth susceptibility (Drummond, 1989; Lohbauer *et al.*, 2006).

In FRCs, cracks quickly reach the fibre interface during their propagation through the matrix. The crack may then bifurcate and travel for considerable distances along the interface (Baran *et al.*, 2001; Garoushi *et al.*, 2007f; Drummond, 2008). This illustrates the fact that the direction of crack propagation is affected by the microstructure of the dental resin composite, not only by the direction of the load applied. Similarly, the microstructure also plays a role in determining the speed of crack propagation. The strength gradient at the interface between matrix and filler will determine the crack-growth rate rather than the crack propagation rate determined for the matrix alone (Baran *et al.*, 2001). Following the failure of the local matrix and interface surrounding a dispersed fibre, the fibre itself ruptures. The load is then transferred to neighbouring fibres, which rupture. Fracture of the body of the material takes place after a critical density of single-fibre failures is attained. Failures may also be localised within a specific domain, and this damage is termed "brush-like cracking", from which ultimate failure of the body proceeds (Bolotin and Bolotin, 1999; Baran *et al.*, 2001). When sufficient micro-crack damage has accumulated, via the mechanisms described above, a macro-crack is initiated. The presence of the macro-crack changes the compliance of the bulk composite. This change is often useful in defining fatigue life, since the load-bearing capacity of the composite structure deteriorates well before actual failure through the specimen. FRCs have generally shown lower fatigue resistance in compression rather than in tension, possibly due to the cooperative-buckling of adjacent fibres and matrix shear (Baran *et al.*, 2001).

Specimens may be cyclically tested in tension-tension, flexure, torsion, shear, or compression. Contact fatigue, such as that induced by cyclic loading of an indenter into the surface of a material, has also been used because of its relevance for the study of wear processes in the oral cavity (McCabe *et al.*, 2002).

Fatigue is often tested using the staircase method (Draughn, 1979) where the investigator pre-determines the number of cycles and then tests the material. If the specimen survives, a higher stress is chosen and the experiment is repeated. If the specimen fails, a lower stress is chosen, and the experiment is repeated. The results of different materials at the same stress level are compared. This test may be used in compressive testing or in tensile testing, which involve testing cylindrical or beam specimens of materials to destruction through cyclic loading under wet or dry conditions (Yoshida *et al.*, 2003; Lohbauer *et al.*, 2006). A concern with this method is that its use virtually implies a fatigue limit. This limit is seldom rationalised, and the choice of too low a limit will preclude observation of changes in fatigue mechanism. Cross-over behaviour, in which some materials perform best at high stress levels while others perform best at low stress levels, such as has been observed in compression testing of polymer-based composites, could remain unobserved if the cycle limit were to be set too low (Baran *et al.*, 2001). It is also worth noting that the bulk failure observed when specimens undergo catastrophic failure may not be related to loss of surface material by ‘fatigue wear’. Secondly, experimental procedures designed to cause bulk fracture by fatigue normally produce a large scatter in the results (McCabe *et al.*, 1997; Baran *et al.*, 2001). McCabe *et al* (2000) found that the static strength of materials did not correlate with fatigue values, and also that contact fatigue is different from flexural fatigue. Surface contact fatigue is used to measure the wear due to surface contact rather than the fatigue that leads to catastrophic failure.

For surface contact fatigue measurements, several measuring techniques may be used. One of them involves using a rolling ball device; a ruby ball rolls across the surface of the specimen in a circular motion while distilled water drips onto the surface, removing debris. As the ball rolls, the surface is subjected to a complex pattern of changing stress primarily involving both compression and shear. Subsurface cracks grow until they reach the surface, where they can be observed as open fissures (McCabe *et al.*, 1997). At this stage, the fissures may become filled with water, and crack propagation, leading to material loss, may be accelerated by the loading and the development of large hydrodynamic pressures within cracks. This mechanism also may play a part in the bulk fatigue process if materials are able to absorb water into porosities and other subsurface defects, thus explaining the effect that porosity can have on the compressive fatigue limit of composites (McCabe *et al.*, 2000). Another method involves subjecting specimens to cyclic compression cycles under varying loads (Padipatvuthikul *et al.*, 2010).The degree of surface damage may then by determined by light microscopy (Padipatvuthikul *et al.*, 2010).

Resin-matrix composites with intermediate levels of filler loading (30 – 50%) have optimum contact fatigue resistance, which implies that simple properties such as hardness and strength do not have a direct correlation with contact fatigue (McCabe *et al.*, 1997; McCabe *et al.*, 2000). This goes against the view that filler content needs to be maximised to increase hardness and reduce abrasive wear, with very low and very high filler volumes markedly reducing fatigue life. Low volumes of filler could be explained by the high deformations of the specimen beneath the rolling ball which may lead to micro-cracking. Higher filler volumes may be explained by the increased brittleness leading to more rapid crack propagation. Consequently, a balance between good abrasive wear and fatigue resistance for good performance of composites must be found. Greater flexibility and compliancy was shown to be advantageous; hardness and brittleness were not. Filler silanation was also found to optimise contact fatigue life (McCabe *et al*. 2000).

The surface quality was also demonstrated to have an effect on fatigue life. The presence and location of flaws at or near to the surface of the restoration was shown to be a key factor in reduced fatigue resistance. Air bubbles, in particular at or near the surface of the restoration, had a marked effect on both the inherent resistance to contact fatigue and its dependence on applied load (Fujii *et al.*, 2004).

2.3.7 Wear Resistance

Wear is defined as the continuous loss of substance resulting from mechanical interaction between two contacting surfaces, which are in relative motion (Burette *et al.*, 2006). Enamel wears at a rate of 30 to 40 µm a year, although the wear does not increase on a yearly basis (Lambrechts et al, 1989; (Heintze, 2009). It has a wear pattern which is high initially and then plateaus after approximately two years , which is similar to the pattern displayed by dental resin composites (Heintze, 2009).

The clinical importance of wear in contemporary dental resin composite restorations lies in the fact that wear may cause a loss of contour of the final restoration, exposure of cavity margins and enhanced visibility of the restoration. This is in addition to staining due to an increase in the surface roughness (Heintze, 2009). There is also the concern that, besides the leaching of monomer components, micro- and nano-sized inorganic filler particles of composite resins that are worn, swallowed or inhaled and accumulated into tissues could be linked to diseases of the liver, kidney and intestine (Gatti, 2004). There is, however, no scientific evidence to date that the absorbed particles pose a health risk to the patient (Gatti, 2004). Wear can be classified into adhesive, abrasive, wear due to fatigue, and wear due primarily to chemical action of the environment. The wear that occurs in the oral cavity is a combination of all the types of wear rather than any single type (McCabe *et al.*, 2002).

Adhesive wear occurs when two surfaces are brought into contact under load, which determines the occurrence of local welding at the tips of the major asperities of the surfaces (Turssi *et al.*, 2005). During relative sliding between the surfaces, the welded junctions are sheared, which may cause the transference of material from one surface to another. Transferred material often resides on a surface and may even transfer back to the original surface. The formation of adhesive wear particles can contribute to further abrasive wear processes taking place between the surfaces involved. Saliva is a lubricant in the oral cavity and limits adhesive wear (Turssi *et al.*, 2003).

Abrasive wear detaches material from a surface as a result of the presence of hard particles between or embedded in one or both of the two surfaces in relative motion, or by the presence of hard protuberances on one or both of the relatively moving surfaces (McCabe *et al.*, 2002; Turssi *et al.*, 2003). In the oral cavity, abrasive wear can be divided into two types (McCabe *et al.*, 2002). The first type is known as two-body wear. It may occur on the occlusal or proximal contact surface of the restoration or tooth due to the direct contact of opposing or adjacent tooth surfaces. This type of wear is of importance to clinicians when dealing with patients who have parafunctional habits, such as grinding or clenching (Turssi *et al.*, 2003). Placing a posterior composite restoration in patients with bruxing habits is still considered a contraindication by some due to the accelerated rate of wear, fracture or chipping that has been found on the occlusal contact areas of the dental resin composites placed in these patients (van Dijken, 2000; Manhart *et al.*, 2004). Wear due to fatigue is caused by intermittent loading resulting in repeated stressing and de-stressing, which may in time lead to the formation of microcracks at or below the surface (Turssi *et al.*, 2003). This type of wear is often observed with rolling rather than sliding of surfaces. The second type of abrasive wear is three-body wear, which occurs in the presence of a food bolus or toothpaste (Mair *et al.*, 1996; McCabe *et al.*, 2002; Mendes *et al.*, 2005a). Three body wear is believed to be more clinically relevant than two body wear as the amount of time that restorative materials contact an opposing tooth or restoration is limited when compared with the amount of contact with a third body such as a bolus of food or toothpaste (McCabe *et al.*, 2002).

Posterior dental resin composites materials typically wear between 0.1 to 0.2 mm more than enamel over 10 years (Anusavice, 2003). However, the resin matrix and filler particles of resin composites do not abrade to the same degree (Sarac *et al.*, 2006). Nanocomposite resins with higher filler content and smaller particle size are smoother than hybrid resin composites and show a reduced wear rate compared to microfilled ones (Yap *et al.*, 2004).

Many variables influence the extent and rate at which dental resin composites wear. These include the properties of the filler, the matrix, and the interface; the relative hardness of the filler to that of the abrasive and the filler content. The wear of dental resin composites in the oral environment has been related largely to filler particle size and inter-particle spacing (Bayne *et al.*, 1992; Manhart *et al.*, 2000b). Due to the fact that the matrix is softer and less wear-resistant than the inorganic filler, it is preferentially abraded by food, toothpaste, etc. The filler particles are exposed as the polymer matrix wears down, allowing them to be plucked from the surrounding matrix during the next abrasion cycle. Smaller particles minimise the space and the extent of filler plucking and surface degradation during chewing, thus reducing the rate of abrasive wear (Ferracane, 1995). Larger fillers adversely affect wear rates when compared to smaller fillers (Turssi *et al.*, 2003; Turssi *et al.*, 2005). This is due to the fact that per unit volume, larger fillers are not as well retained in the resin and that they protrude further into the surface. That protrusion would cause their preferential breakage, leaving larger gaps in the material and propagating the wear process. However, the relationship between wear and particle size may not be a linear one (Ferracane, 2011). Some researchers have reported the wear resistance of nanocomposites to be either the same or less than that of microfilled dental resin composites (Turssi *et al.*, 2006), while others found that nanocomposites showed an increase in wear resistance (Yap *et al.*, 2004). Clinical trials have confirmed the success of composites in small to moderate posterior occlusal cavities, showing wear rates in contact-free areas of 10-20 µm or less per year when the average particle size is less than 1.0 µm (Kawai and Leinfelder, 1995; Suzuki *et al.*, 1995). It was concluded that wear decreases significantly when the inter-particle spacing is between 1.3 – 1.5 µm, which is the average size of food fibres (Venhoven *et al.*, 1996).

Those results led to the further development of very heavily filled small-particle composites. In essence, the size of the filler particle was reduced and the filler loading increased. Doing so resulted in an appreciable reduction in the amounts of stress around each particle. The overall result was a significant reduction in loss of anatomical form (Leinfelder, 1988). Other studies noted a decrease in wear resistance with a higher filler load and smaller filler size (Li *et al.*, 1985; Hu *et al.*, 2003). The surface wear of experimental composite resins with fillers below a percentage of 48 wt% increased significantly (Condon and Ferracane, 1997; Lührs and Geurtsen, 2009). In addition to using larger concentrations of smaller filler particles, manufacturers began using particles of reduced hardness. Most manufacturers now use a variety of barium glass rather than the original hard quartz particles. The softer filler particles partially absorb masticatory forces, rather than transmit them all to the underlying resin matrix. This resulted in substantially more wear resistant dental resin composites materials (Lührs and Geurtsen, 2009).

The low stress abrasive wear behaviour of short E-glass FRCs with and without fillers was studied and it was found that a higher weight fraction of glass fibres (45% vol) improved the wear resistance when compared with composites containing fewer glass fibres (40% vol) (Chand *et al.*, 2000). Others found that the wear rate in composites with longer fibres was lower compared with that of shorter fibre with the same weight per cent (Callaghan *et al.*, 2006). Longer fibres in general provide better strengthening mechanisms compared with that of short fibres and thus more wear resistance. They also found that PFCs wore less than FRCs (Callaghan *et al.*, 2006).

One of two main approaches have been adopted to assess the *in vitro* wear resistance of dental resin composites; by either attempting to closely simulate oral conditions by simulating all the processes that occur during mastication and assessing the resulting wear (DeLong and Douglas, 1983; Condon and Ferracane, 1996; Raabe *et al.*, 2009) or by isolating certain mechanisms or factor (Wassell *et al.*, 1994; Hu *et al.*, 1999a; Yap *et al.*, 2000b). Many of the simplified wear simulation devices assess test two-body wear, in which the surfaces move against each other in direct contact (Lee *et al.*, 2011).

A range of devices have been used to simulate the two body wear that occurs in the occlusal contact area, such as the reciprocating sliding-wear test (Wassell *et al.*, 1994), two-body wear rotating counter sample (Hu *et al.*, 1999b) and the oscillating friction and wear test rig, MTM Leuven (Willems *et al.*, 1992a). A key challenge with many of these wear testers is the choice of abrader used to produce the two body wear. An enamel abrader may appear ideal at first glance. However, it will cause the morphology and physical characteristics among the specimens to vary due to the natural heterogeneity which exists in enamel. In an effort to overcome this lack of homogeneity, the antagonists used typically consist of steatite (Wassell *et al.*, 1994) or stainless steel (Hu *et al.*, 1999a). As the mechanical and chemical properties of stainless steel are different from that of human enamel, the value of using it as an antagonist has also been questioned (Hu *et al.*, 1999a; Turssi *et al.*, 2003). However, considering that both natural enamel and synthetic materials have shown shortcomings, the choice of abrader has been made arbitrary (Turssi *et al.*, 2003). The shape of the abrader is another consideration. Cylindrical abraders tend to plough the surface of the specimen, thus hastening wear and altering the wear mechanisms which would otherwise operate (Turssi *et al.*, 2003), while spherical abraders may help to avoid such problems (Wassell *et al.*, 1994). A pin-on-disk wear-test rig has also been frequently used to simulate two-body wear between the sample and the antagonist (Hahnel *et al.*, 2011; Lee *et al.*, 2011). Deionised water is considered a reasonable substitute for salivary lubrication despite the fact that it has dissimilar rheological properties compared with human saliva. Saliva decreases the wear rate in comparison to distilled water (Kaidonis *et al.*, 1998).

Wear simulators have been proposed, based on the existing biophysical knowledge of the human masticatory system (Kawai and Leinfelder, 1995; Condon and Ferracane, 1996; Hu *et al.*, 1999a). The abrasive media used for *in vitro* wear tests has to be mild to simulate the texture and abrasiveness of the food bolus. To that aim, several materials have been used such as rice, poppy seeds, millet seeds and PMMA beads.

Among the most commonly used wear machines are the Oregon Health and Sciences University (OHSU) simulator (Condon and Ferracane, 1996) and the Academic Centre for Dentistry Amsterdam (ACTA) wear machine (de Gee and Pallav, 1994). The ACTA wear machine has two wheels which rotate in different directions, with about 15% difference in the circumferential speed (de Gee and Pallav, 1994). Test specimens are placed on the circumference of one wheel and antagonist specimens on the other. This allows several wear experiments to be run simultaneously. During the wear test, the antagonist wheel wears a track into the test specimen leaving an area on either side as a reference. The loss of material is determined by profilometry (ISO TS 14569-2:2000). The OHSU determines both two and three body abrasive wear on the same specimen (Condon and Ferracane, 1996). This is achieved by forcing an enamel cusp into contact with a specimen through a layer of food-like slurry and then applying a 20 N load to the specimen. The cusp is then slid across the surface over a linear path, producing three body abrasive wear. At the end of the path, the load is increased to 70N to produce localised two body wear. This sequence is repeated for 50,000 cycles and the wear patterns are analysed using a profilometer. Each zone of wear is analysed separately as are the antagonists (ISO TS 14569-2:2000).

A recently developed device, still in prototype form that attempts to simulate wear in the mouth is the chewing robot (Raabe *et al.*, 2009). It attempts to replicate the mandibular movements when chewing a bolus of food and is capable of replicating natural mandibular movements and a range of chewing forces, including the occlusal forces occurring during TMJ dysfunction and bruxism (Raabe *et al.*, 2009). The chewing robot aims to create chewing patterns and tooth-food-tooth interaction dynamics as an emergent property rather than tracking a set of force and position trajectories, with the future view of three body wear and a combination of different wear mechanisms (Raabe *et al.*, 2011).

A device used to simulate three body wear is the toothbrush simulator, which was developed after examining aspects of *in vivo* toothbrushing conditions, such as load and stroke rate (de Gee *et al.*, 1985; Momoi *et al.*, 1997; Sarkar, 2000; Turssi *et al.*, 2001). The wear resistance was evaluated by a variety of means such as weight loss (Chadwick *et al.*, 1990; Hu *et al.*, 1999a) , profilometrical tracings (Kawai and Leinfelder, 1995; Suzuki *et al.*, 1995) photomicrographs, or 3D laser scanning (Manhart *et al.*, 2000a). Adjusting variables such as brushing force and speed affected the wear resistance of both enamel and dentine. An increase in speed or force decreased wear resistance (Parry *et al.*, 2008). Comparison between test results from different laboratories is difficult due to use of a wide range of dentifrices, toothbrushes, substrate properties and testing conditions (McCabe *et al.*, 2002). Thus, it is recommended that the relative wear rates are compared.

In vivo, wear is measured using either direct or indirect methods. The major direct method is anatomical form section of the qualitative criteria developed by Ryge, also called the U.S. Public Health Service, or USPHS, criteria (Cvar and Ryge, 2005).The restorations are visually inspected using a dental probe and mirror if needed. The restoration categorised as one of the following:

a. continuous with existing anatomical form;
b. discontinuous with existing anatomical form, but the material is not sufficient to expose the dentin or base;
c. discontinuous with the existing anatomical form and sufficient material has been lost to expose the dentin or base.

There are two key shortcomings to the USPSH criteria: (a) the requirement for good calibration and inter- and intra-examiner agreement among the evaluators, and (b) the limited discriminating capacity of these scales (Kreulen and van Amerongen, 1991; Turssi *et al.*, 2006). In 2007, a new set of clinical criteria for the evaluation of restorations was published. The criteria and the grading were both approved by the Science Committee of the FDI World Dental Federation in 2007 and in the General Assembly 2008 as “standard criteria” that should be applied when restorative materials and/or operative techniques are to be clinically investigated (Hickel *et al.*, 2010). The evaluation of a restoration is categorised into three groups: esthetic, functional and biological criteria. Each group is divided into subgroups and the overall rating is determined by the subcategory scores. The final score in each group is dictated by the worst score among those of the subcategories. For example, if one property/category is deemed unacceptable, the overall score of that restoration is also unacceptable. Therefore, when summarising the three categories (esthetic, functional and biological) in one overall rating, the worst score prevails and gives the final score. The criteria were modified in certain areas, including assessment of wear, after usage by clinicians. The term “occlusal contour” was added to this criterion, as an alteration in the occlusal contour may be a sign of material degradation or wear. Wear can be assessed qualitatively by the evaluator or quantitatively on replicas with special sensors and computer software. In both instances, baseline and follow-up images/ replicas are needed in order to assess possible alterations. Therefore, the criterion has been effectively divided into (a) “qualitatively” and (b) “quantitatively” measured wear (Hickel *et al.*, 2010). The wear criteria are summarised in Table 1.

Assessment Score	**Occlusal contour and wear** **a) qualitatively** **b) quantitatively**
1. Clinically excellent / very good	a. Physiological wear equivalent of enamel. b.Wear corresponding to 80-120% of enamel
2.Clinically good	a. Normal wear only slightly different from that to enamel. b. 50-80% or 120-150 % wear compared to that of corresponding enamel
3. Clinically sufficient / satisfactory (minor shortcomings, no unacceptable effects but not adjustable w/o damage to the tooth)	a. Different wear rate than enamel but within the biological variation. b. < 50 % or 150- 300 % of corresponding enamel
4. Clinically unsatisfactory / (but repairable)	a. Wear considerably exceeds normal enamel wear; or occlusal contact points are lost. b. Restoration >300 % of enamel wear or antagonist > 300 %.
5.Clinically poor (replacement necessary)	a. Wear is excessive. b. Restoration or antagonist > 500 % of corresponding enamel.

Table 1. FDI wear criteria and gradings (adapted from Hicknel *et al.,* 2010).

Impressions and casts have been the predominant indirect methods for wear investigations designed to measure the vertical loss of height of resin composite restorations. They are either based on visual evaluations by dentists or physical measurements by machines (Goldberg *et al.*, 1984; Bryant, 1990). The faster and less expensive methods are the visual evaluation techniques, which involve the categorisation of replica models with a set of standard casts. The machine dependent methods are more time consuming and expensive, but are more accurate (Mehl *et al.*, 1997; Folwaczny *et al.*, 2000). Some examples of mechanical devices used include: stereomicroscopes, stereomicroscopes employing the stereophotogrammetry technique, interferometers, mechanical profilometers, computerised three-dimensional measuring microscopes, laser profilometers, and the scanning electron microscope (Kreulen and van Amerongen, 1991; Perry *et al.*, 2000). These wear analysis methods specify how much composite wear has occurred, whereas the visual methods provide inaccurate examination of dental restorations due to the lack of exact measurements or low resolutions (Folwaczny *et al* , 2000). Digital mapping of tooth surfaces seems to be the most accurate method for indirectly analysing restoration wear (Perry *et al.*, 2000). In general, the more sophisticated digital techniques provide better accuracy and more extensive information regarding the entire occlusal surface wear of restored teeth (Mehl *et al* , 1997). However, they are too expensive and time-consuming to be used in clinical studies involving many patients (Turssi *et al.*, 2003).

In general, the size of spherical filler particles has been shown to have a significant effect on wear resistance (Turssi *et al.*, 2005). When dental resin composites with identical filler loadings (56.7 vol %) were compared with the OHSU machines, the composites with the smallest particles had the lowest amount of wear. Wear increased with an increase in the particle size. However, this relationship does not necessarily hold true for nanocomposites. While some authors have found nanocomposites showed significantly less wear and a more uniform surface topography (Teixeira *et al.*, 2005), others have found that microhybrids exhibited a higher wear resistance (Yesil *et al.*, 2008; Barucci-Pfister and Gohring, 2009). This was attributed to the possibility that the nanometre-sized filler particles were too small to offer any preferential load support and the wear properties of the materials were not purely dependent on particle size (Turssi *et al.*, 2006). Dental resin composites with irregularly shaped filler particles also displayed more wear resistance than those with more regular fillers in the range of 1000 nm (Turssi *et al.*, 2005). This has been attributed to irregular particles having a higher specific area for adhesion, with spherical particles being able to debond and be pulled out more easily (Xu *et al.*, 2004; Turssi *et al.*, 2005) An increase in filler fraction also results in an increased wear resistance, with a lower limit of approximately 48% (Condon and Ferracane, 1997; Lim *et al.*, 2002). Using a pin on disk method, FRC were found to have a wear rate similar to PFC (Callaghan *et al.*, 2006) with a higher loading of longer fibres showing the best wear results within the FRCs tested (Callaghan *et al.*, 2006). However, using a three body wear simulator found that the more heavily loaded the fibres in an FRC, the lower the wear resistance (Suresha *et al.*, 2007).

Summary

Fibre reinforced materials are used extensively in industry, when strength and lightness are needed. Reinforcing dental resin composite restorative materials with fibres has shown an improvement in polymerisation shrinkage compared with PFCs by some authors. A higher bond strength was also noted, thus leading to the possibility that an FRC used as a reinforcing core material may help overcome some of the existing limitation of dental resin composites.

Chapter 3. Aims and objectives

3.1 **Aims**

This work has the following aims:

1. To assess the possibility of using ST as a direct restorative material. This was done by evaluating its three body wear and surface contact fatigue. The effects of variation in resin and filler composition were also determined. Two commercially available materials, one PFC (Z250 *3M ESPE*) and one FRC (Build It FR *Jeneric Pentron*), were chosen as comparators.
2. To determine the suitability of ST as a potential core material for direct resin composite restorations, veneered by a PFC. The work focuses on:
   a) Polymerisation shrinkage and water sorption;
   b) the effectiveness of bonding to dentine;
   c) the effectiveness of bonding between layers of the same material or between different materials.

3.2 **Objectives**

The objectives of this project are:

1. To assess ST as a single restorative material in comparison to Z250 and Build It FR regarding :
   a) Three-body wear resistance
   b) Surface contact fatigue

2. To assess the effect a change in ST's resin formulation and fibre lengths will have on:
   a) Two-body wear resistance;
   b) Surface contact fatigue.

3. To assess ST as a core material ,with regard to Z250 and Build It FR in terms of the following properties:
   a) Polymerisation Shrinkage;

b) Water sorption;
c) Shear bond strength and modes of failure when bonding:
    i) to human dentine;
    ii) to lapped composite surfaces;
    iii) to air inhibited composite surfaces;

3.3 Programme of work

The programme of work is in two parts:

1. Testing the possibility of using ST as a single restorative material as well as assessing the effect of changes in fibre length and resin constituents on wear resistance. This was done by testing the surface contact fatigue and three body wear. Chapter 4 detail the materials, methods and results of this segment of the work while chapter 7 discusses the results;
2. Material characterisation by determining the polymerisation shrinkage, water sorption and interfacial strength of ST. Chapters 5 and 6 detail the materials, methods and results of this portion of the project while chapter 7 discusses the results.

Chapter 4. Material Testing as a Single Restorative Material

4.1 **Testing as a Single Restorative Material**

Assessing wear resistance is vital if the material will be exposed directly to the oral environment. ST's surface contact fatigue and three body wear resistance were assessed 24 hours after water storage and compared with Build It and Z250. All the materials were also tested after 1 year of water storage to evaluate any changes due to water storage.

In an attempt to further develop ST by Stick Tech, the Bis-GMA/TEGDMA ratio was changed as was the filler loading and fibre length. The surface contact fatigue and three body wear of these materials was assessed to ascertain the effect of the changes. A total of seven different formulations were tested. The materials and their components are listed in Table 2.

Material	**Manufacturer**	**Lot Number (s)**	**Composition (% by weight)**
Z250 (PFC)	Filtek Z250 3M ESPE Dental Products St Paul, MN,USA	9WF 20090327	18 % Resin consisting of BIS-GMA, UDMA, and Bis-EMA 82 % Filler (silica and zirconia particles , with particles ranging from 0.01 to 3.5 µm)
Build It (FRC)	Build IT FR Core material (dual cured) Pentron Clinical, Wallingford, CT, USA	157279	32% Resin (mixture of Bis-GMA, UDMA and HDDMA) 68% Fillers [Mixture of bariumborosilicate, calcium alumino-fluro-silicate, silica and chopped glass fibres (10 – 40 µm in length)]
ST (An Experimental FRC)	StickTech, Finland	D7.002 D7.003	21% Resin (PMMA + Bis-GMA/TEGDMA =60/40 + initiators) 19% Everstick fibres (8mm) 60% Filler (silica particles) 79% Total inorganic material content (fibres and fillers together)
ST 1	StickTech, Finland	NA	21% Resin (PMMA+ Bis-GMA/TEGDMA=60/40 + initiators) 19% Fibres (3-5 mm) 60% Filler
ST 2	StickTech, Finland	NA	21% Resin (PMMA+ Bis-GMA/TEGDMA=60/40 + initiators) 19% Fibres (25 mm) 60% Filler
ST 3	StickTech, Finland	NA	26% Resin (PMMA+ Bis-GMA/TEGDMA=70/30 + initiators) 22% Everstick fibres (10 mm) 52% Filler

ST 4	StickTech, Finland	NA	26% Resin (PMMA+ Bis-GMA/TEGDMA=70/30 + initiators) 22% Everstick fibres (15 mm) 52% Filler
ST 5	StickTech, Finland	NA	26% Resin (PMMA+ Bis-GMA/TEGDMA=70/30 + initiators) 22% Everstick fibres (20 mm) 52% Filler
ST 6	StickTech, Finland	NA	23.5 % Resin (PMMA+ Bis-GMA/TEGDMA=70/30 + initiators) 21.5% Everstick fibres (20 mm) 55 % Filler
ST 7	StickTech, Finland	NA	19 % Resin (PMMA+ Bis-GMA/TEGDMA=70/30 + initiators) 21% Everstick fibres (20 mm) 60 % Filler

Table 2. Names, Manufactures' and Components of Commercial and Experimental Materials Used.

4.2 **Surface contact fatigue**

4.2.1 Materials and Methods

Table 2 displays the names and constituents of the materials used in this study.

Sample holders were made by drilling a hole 10 mm in diameter and 2 mm deep into square Perspex (poly(methyl methacrylate)) blocks (Bay Plastics Ltd, Tyne and Wear, UK). The cavity created was then slightly overfilled with a test dental resin composite, covered by a mylar strip (polyethylene terephthalate matrix strip, Goodfellows, Cambridgeshire, UK), and compressed with another Perspex block using hand pressure to ensure a flat surface. The composite was then light cured using a halogen light curing unit (Visilux 2 light cure, 3M ESPE Dental Products, USA) for 60 seconds, finished using 500 through to 1000 grit silicon carbide paper (Tri-M-ite Wet or Dry paper,3M,St Paul USA) on a lapping machine (Metaserve prerotary grinder, Betchworth, England) and then stored in distilled deionised water in a 37°C oven before being tested. 10 specimens were made of ST, Build It and Z250; half of which were tested 24 hours after water storage in a 37°C oven, while the other half were stored for a year, then tested.

During the year in which ST was water stored, ST1-ST7 were developed by Stick Tech. 5 specimens of each of those formulations were tested after only 24 hours of water storage.

Each specimen was placed in the rolling ball (RB) device (Thrive Seiko Co Ltd, Japan) (Figure 4). A weight of 300 grams was placed on the weight carrier. A 2 mm diameter ruby ball (Goodfellows, Cambridgeshire,UK) was inserted into the rotor groove and the weight brought the specimen, ball and rotor into contact. The rotor was rotating at a speed of 720 rpm. Distilled water was continuously dripped onto the specimen to remove debris.

Each specimen was tested for 500,000 cycles, with an impression taken every 100,000 cycles, using Microset (a synthetic rubber replicating compound, Microset, UK). The impression was then scanned using a non-contact laser profilometer (Uniscan OSP 100, AG Electro Optics UK) to give a three dimensional image of the surface. The impression was used to negate the possibility of the laser light penetrating the dental resin composite samples. The scans of the wear tracks were then assessed using Wyko Vison32 software (1999©Veeco Instruments Inc., NY, USA). The depth of four perpendicular points was measured on the wear track. This was done by using the X profile on the scan and measuring from the highest to the lowest point. Figure 6 to Figure 9 show the four points measured. The average depth of the four points was then used as the depth of the individual wear track.

The tested samples were also assessed using an environmental scanning electron microscope (Philips XL 30 ESEM-FEG, Philips, UK). The samples were viewed at a low vacuum of 0.5 torr and the images were obtained using a gaseous secondary electron detector.

100,000 was the minimum number of cycles which gave a measurable wear track in Build It, Z250 and ST according to our pilot studies. Thus, it was the starting point of the surface contact fatigue testing.

SPSS Statistics 17 was used for the analysis of the data. A Shapiro Wilk test was done to test the normality of the data distribution. As the data was normally distributed, a one-way ANOVA (at a significance level of 0.05) was applied to results of the material and Tukey’s post hoc test was used to determine which materials caused a significant difference if found. Two-way ANOVA was used to determine if water storage had an effect.

Figure 4. Rolling ball machine basic components.

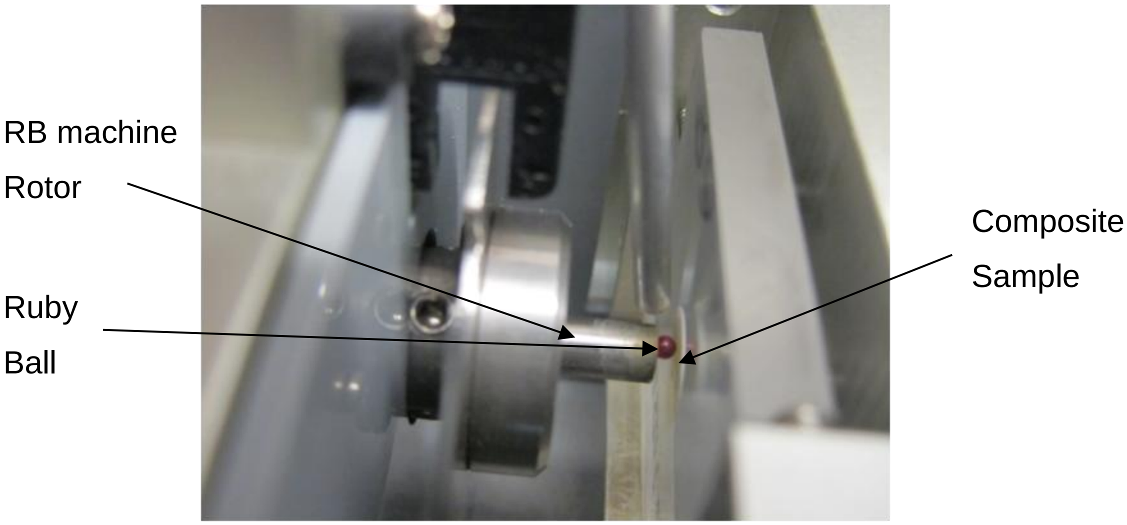
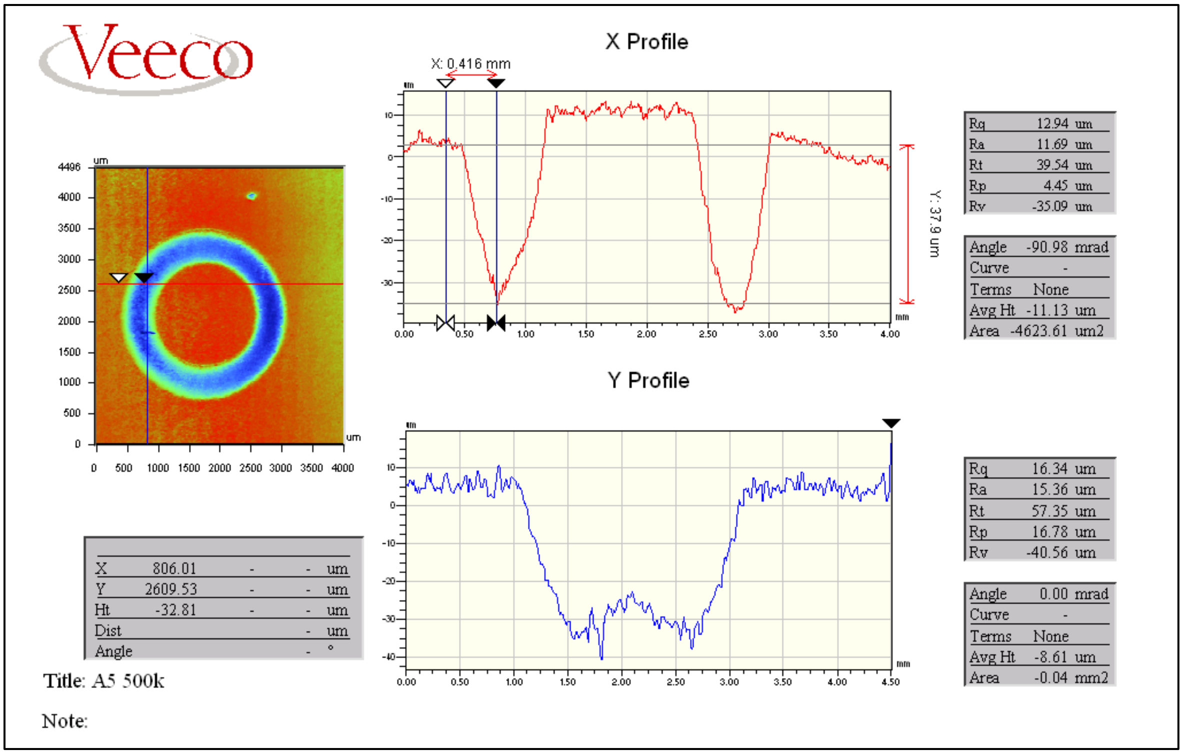


Figure 5. Composite sample in rolling ball machine.



X	806.01	-	-	um
Y	2609.53	-	-	um
Ht	-32.81	-	-	um
Dist			-	um
Angle			-	°

Rq	12.94	um
Ra	11.69	um
Rt	39.54	um
Rp	4.45	um
Rv	-35.09	um

Angle	-90.98	mrad
Curve	-	
Terms	None	
Avg Ht	-11.13	um
Area	-4623.61	um2

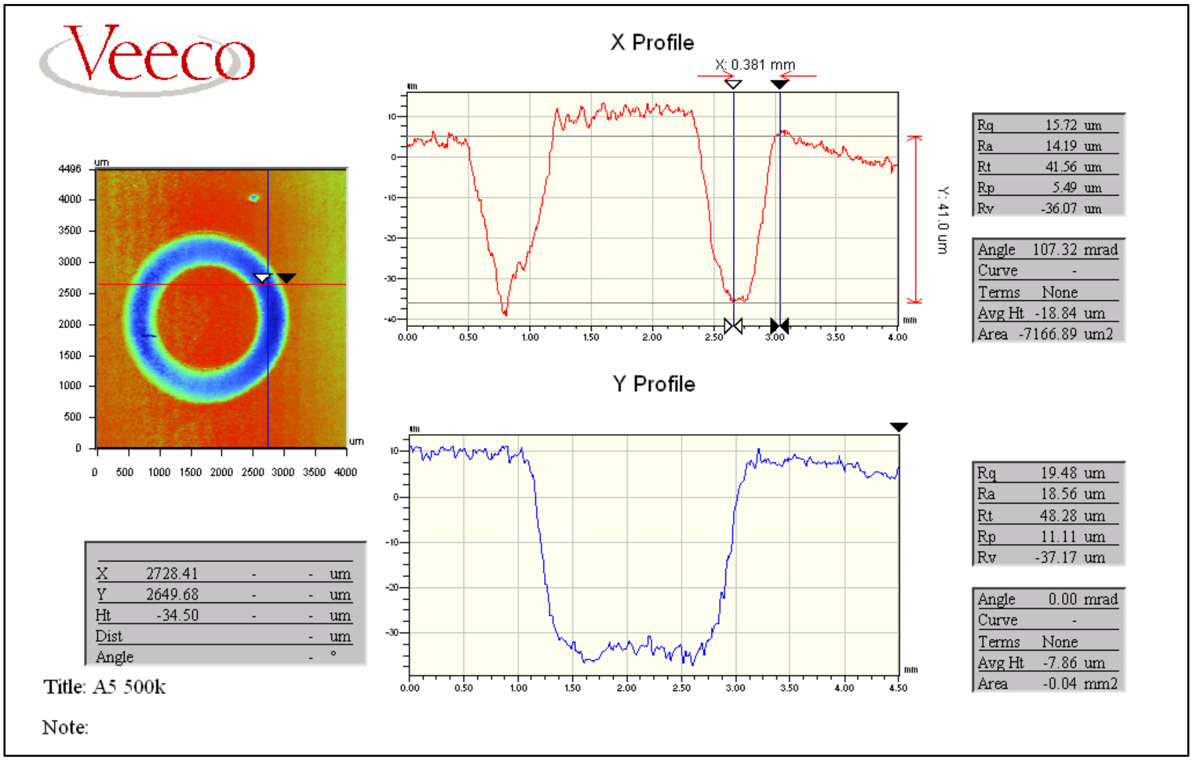
Rq	16.34	um
Ra	15.36	um
Rt	57.35	um
Rp	16.78	um
Rv	-40.56	um

Angle	0.00	mrad
Curve	-	
Terms	None	
Avg Ht	-8.61	um
Area	-0.04	mm2

Title: A5 500k

Note:

Figure 6. First point used in depth determination of Build It after 500,000 RB cycles



X	2728.41	-	-	um
Y	2649.68	-	-	um
Ht	-34.50	-	-	um
Dist			-	um
Angle			-	°

Rq	15.72	um
Ra	14.19	um
Rt	41.56	um
Rp	5.49	um
Rv	-36.07	um

Angle	107.32	mrad
Curve	-	
Terms	None	
Avg Ht	-18.84	um
Area	-7166.89	um2

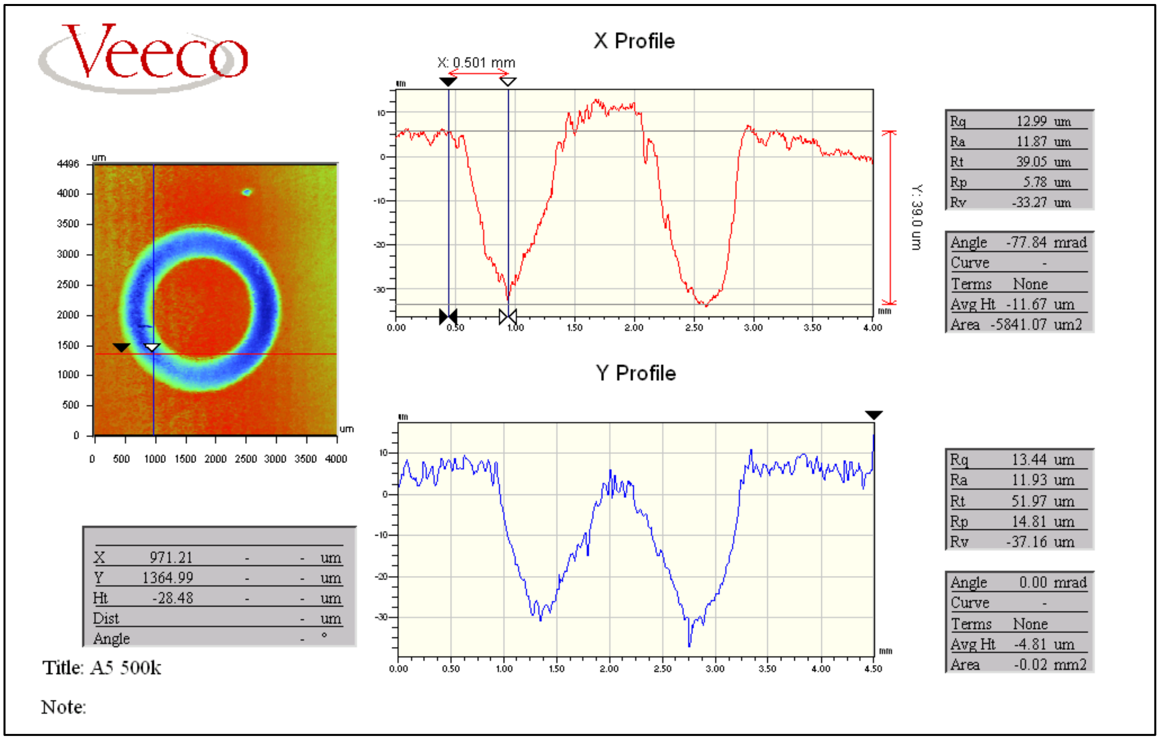
Rq	19.48	um
Ra	18.56	um
Rt	48.28	um
Rp	11.11	um
Rv	-37.17	um

Angle	0.00	mrad
Curve	-	
Terms	None	
Avg Ht	-7.86	um
Area	-0.04	mm2

Title: A5 500k

Note:

Figure 7.Second point used in depth determination of Build It after 500,000 RB cycles



X	971.21	-	-	um
Y	1364.99	-	-	um
Ht	-28.48	-	-	um
Dist			-	um
Angle			-	°

Title: A5 500k

Note:

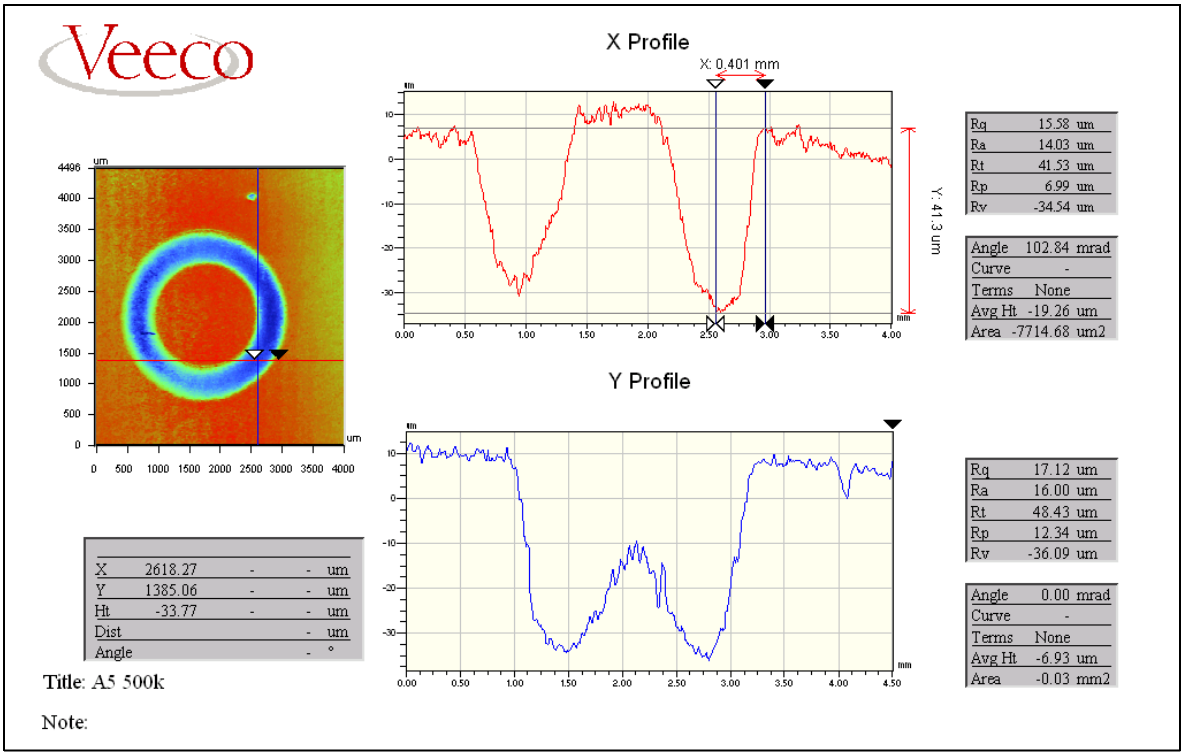
Rq	12.99	um
Ra	11.87	um
Rt	39.05	um
Rp	5.78	um
Rv	-33.27	um

Angle	-77.84	mrad
Curve	-	
Terms	None	
Avg Ht	-11.67	um
Area	-5841.07	um2

Rq	13.44	um
Ra	11.93	um
Rt	51.97	um
Rp	14.81	um
Rv	-37.16	um

Angle	0.00	mrad
Curve	-	
Terms	None	
Avg Ht	-4.81	um
Area	-0.02	mm2

Figure 8. Third point used in depth determination of Build It after 500,000 RB cycles



X	2618.27	-	-	um
Y	1385.06	-	-	um
Ht	-33.77	-	-	um
Dist			-	um
Angle			-	°

Title: A5 500k

Note:

Rq	15.58	um
Ra	14.03	um
Rt	41.53	um
Rp	6.99	um
Rv	-34.54	um

Angle	102.84	mrad
Curve	-	
Terms	None	
Avg Ht	-19.26	um
Area	-7714.68	um2

Rq	17.12	um
Ra	16.00	um
Rt	48.43	um
Rp	12.34	um
Rv	-36.09	um

Angle	0.00	mrad
Curve	-	
Terms	None	
Avg Ht	-6.93	um
Area	-0.03	mm2

Figure 9. Fourth point used in depth determination of Build It after 500,000 RB cycles

4.2.2 Results

ST compared with Build It and Z250

a) After 24 hours water storage

The number of cycles until degradation began to be apparent (nominally 5 µm mean track depth) was estimated. This was done by plotting the mean depths of wear after each 100,000 cycles against the number of cycles. The point at which the depth of the wear would be 5 µm (x) was then calculated, using the regression trendline equation which fits the points drawn. Figure 10 shows the plot, complete with regression equations for ST, Build It and Z250 after 24 hours of water storage. A log transformation of the number of cycles was used allow for a better correlation coefficient and regression analysis. Table 3 shows the estimated number of cycles calculated for each material tested 24 hours after water storage.

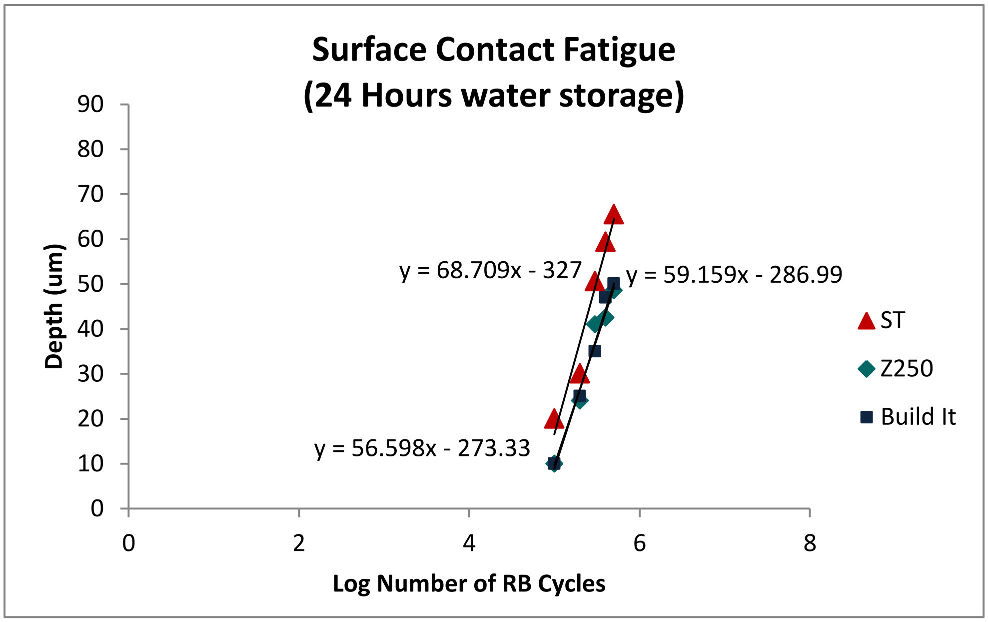


Figure 10. Trend lines for surface contact fatigue after 24 hours showing regression equations for ST, Z250, and Build It.

One-way ANOVA showed a significant difference between the groups (p≤ 0.001). Tukey's post hoc analysis showed that both Build It and Z250 could withstand significantly more cycles until wear was seen compared with ST.

b) After 1 year

The number of cycles until degradation began to be apparent was calculated as for the 24 hour groups. Figure 11 shows the plot, with regression equations for ST, Build It and Z250. Table 3 shows the estimated number of cycles calculated for each material tested 24 hours after water storage.

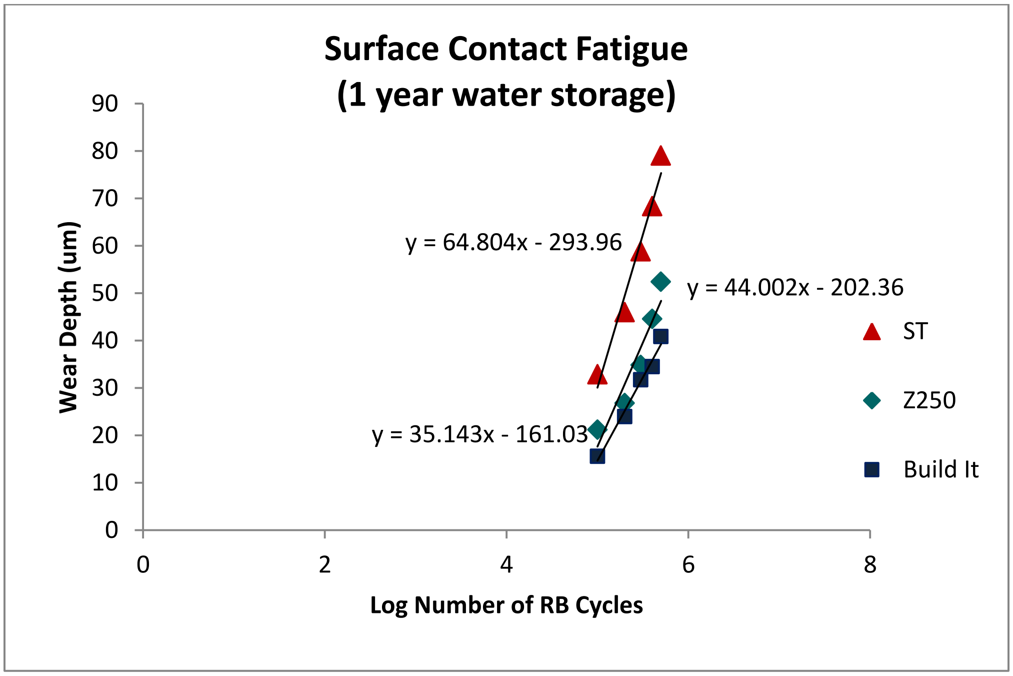


Figure 11. Trend lines for surface contact fatigue after 1 year showing regression equations for ST, Build It and Z250.

One-way ANOVA showed a significant difference between the three materials (p ≤ 0.001). Tukey's analysis showed that each of the materials was significantly different from the other. ST could withstand significantly fewer cycles than Z250, which could stand significantly fewer cycles than Build It.

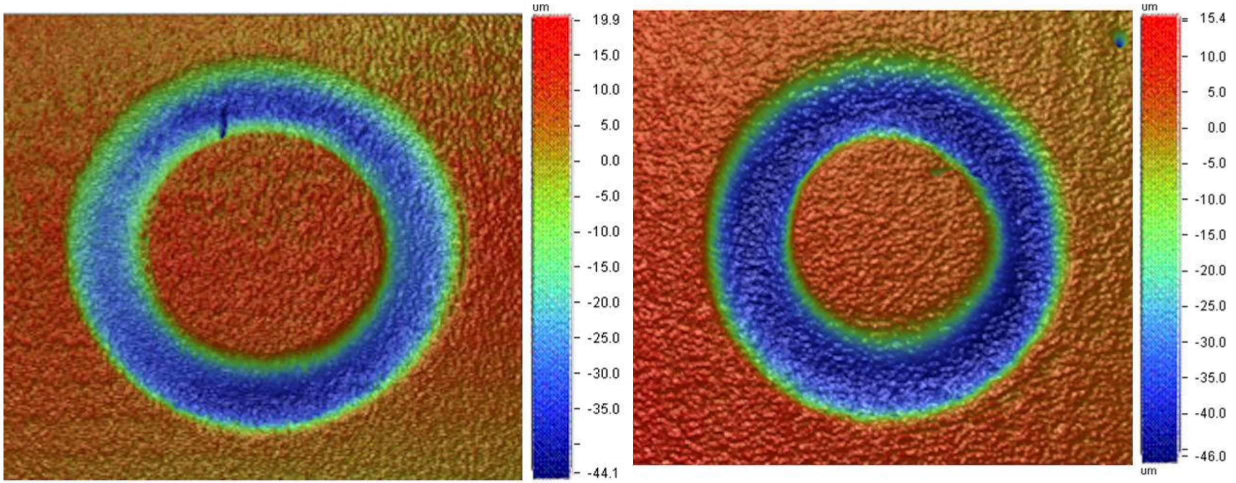
Material	**Wear Depth after 500,000 cycles in μm (SD) after 24 hours water storage**	**Estimated No. Of Cycles (24 hours water storage)**	**Wear Depth after 500,000 cycles in μm (SD) after 1 year water storage**	**Estimated No. of Cycles (1 year water storage)**
Z250	48.5(4.9)	82,730	52.3(6.6)	51,583
ST	65.5(13.7)	67,916	79(20.3)	41,041
Build It	47.5(5.4)	86,234	45.8(6.5)	53,190

Table 3. Estimated number of cycles until surface degradation begins after 24 hours and 1 year water storage.

- ***Representative Laser Profilometer Scans after 24 hours and 1 year water storage***

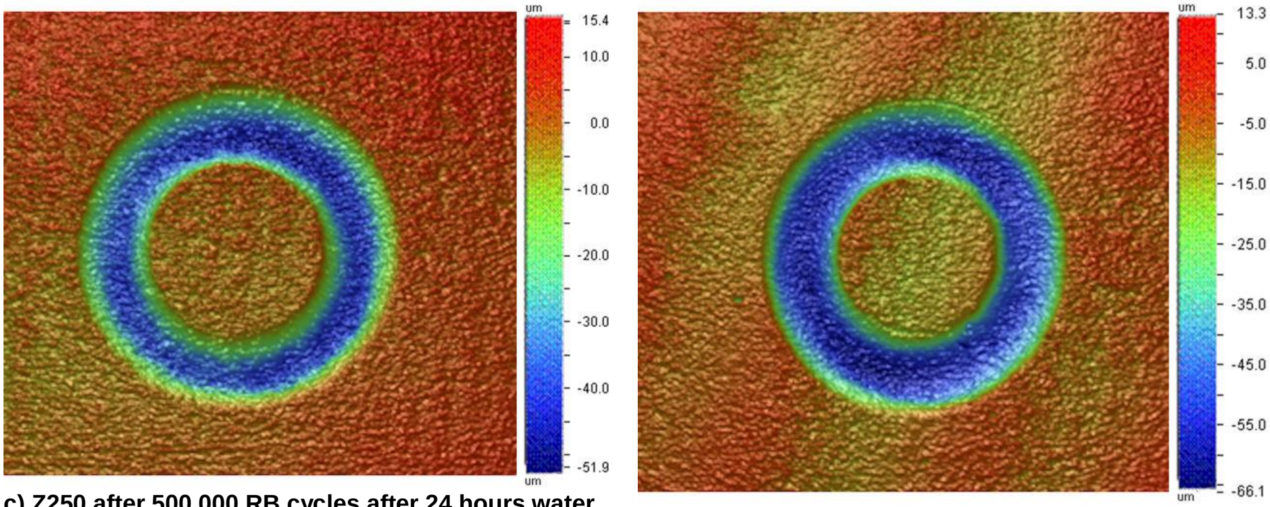
Figure 12 a to h are representative of the profiled three dimensional surfaces of the tested dental resin composites. The colours represent the depth of the wear track, with the darker blue representing a deeper track. Please note the legend to the right of each figure, to note the actual depth representation of each figure.

Upon analysis of the figures, it is worth noting that the wear track produced in ST lacks the homogeneity of depth and outline found in both Z250 and Build It. The effect of one year water storage is also clear in both the depth and width of the tracks created as all the materials have wider deeper wear tracks after 1 year water storage. ST also appears to have the most surface defects in the form of voids on the polished surface.



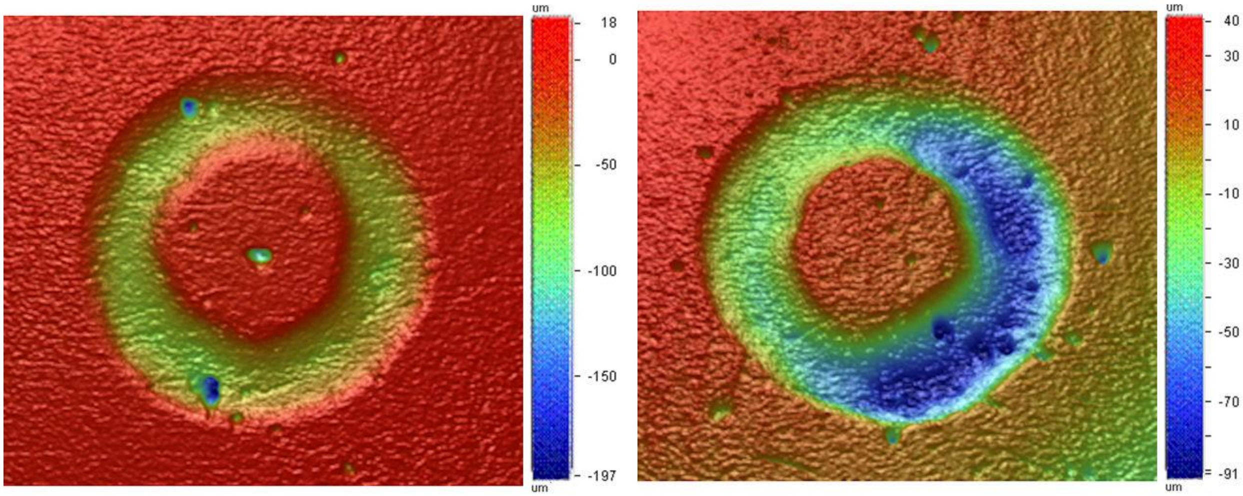
a) Build It after 500,000 RB cycles after 24 hours water storage (max depth 44.1 µm)

b) Build It after 500,000 RB cycles after 1 year water storage (max depth 46 µm)



c) Z250 after 500,000 RB cycles after 24 hours water storage (max depth 51.9 µm)

d) Z250 after 500,000 RB cycles after 1 year water storage (max depth 66.1 µm)



e) ST after 500,00 RB cycles after 24 hours water storage (max depth 197 µm)

f) ST after 500,000 RB cycles after 1 year water storage (max depth 91 µm)

Figure 12. laser profilometer images of the tested dental resin composites after 24 hours and 1 year water storage.

- ***SEM image analysis after 24 hours and 1 year water storage***

Figure 13 to Figure 24 represent the SEM images of the materials tested.

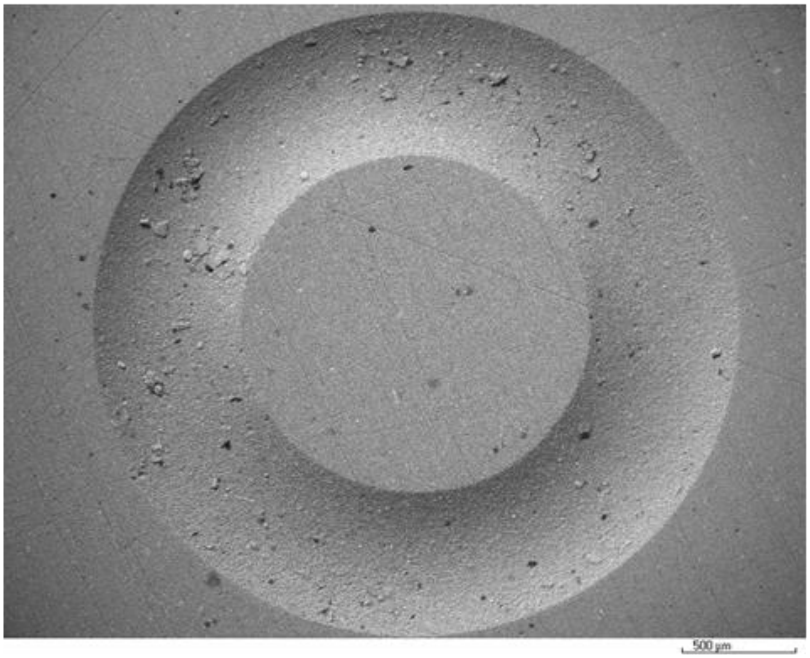


Figure 13. Build It after 24 hours water storage and 500,000 RB cycles (SEM image x35).
Note the homogenous wear track with what appear to be crushed particles within it.

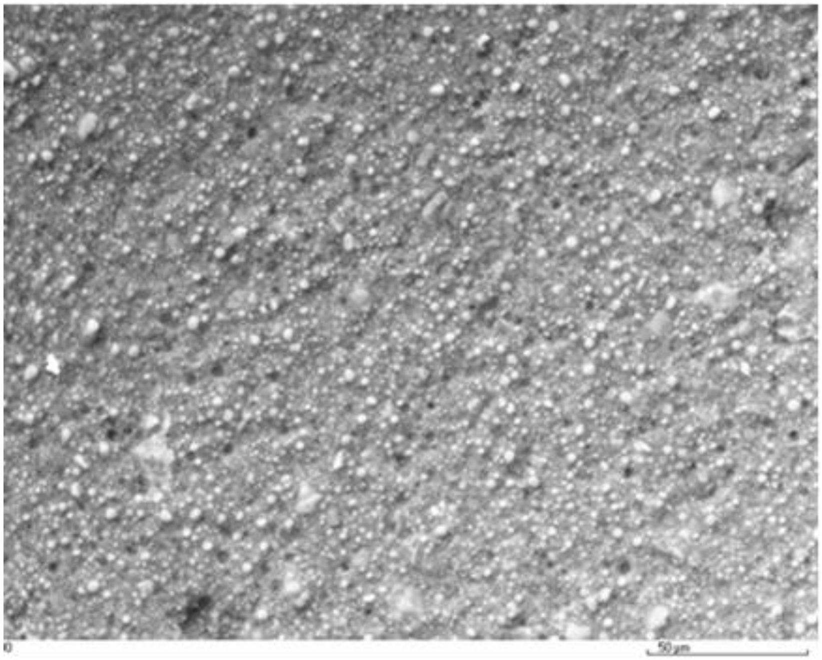


Figure 14. Build It after 24 hours water storage and 500,000 RB cycles (SEM image x500 inside wear track).
Note the integration of the filler particles into the matrix.

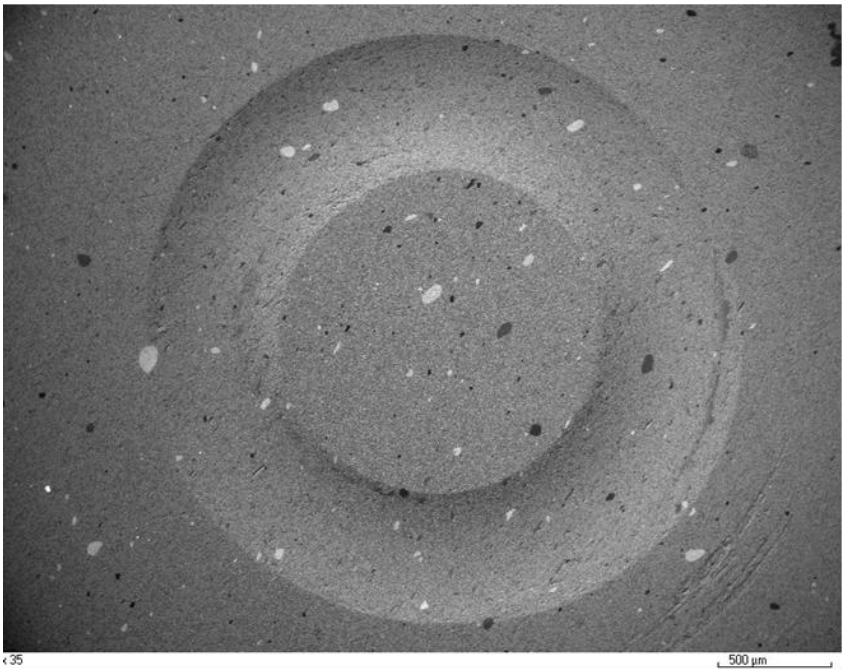


Figure 15. Build It after 1 year water storage and 500,000 RB cycles (SEM image x35). The wear track maintains its homogeneity.

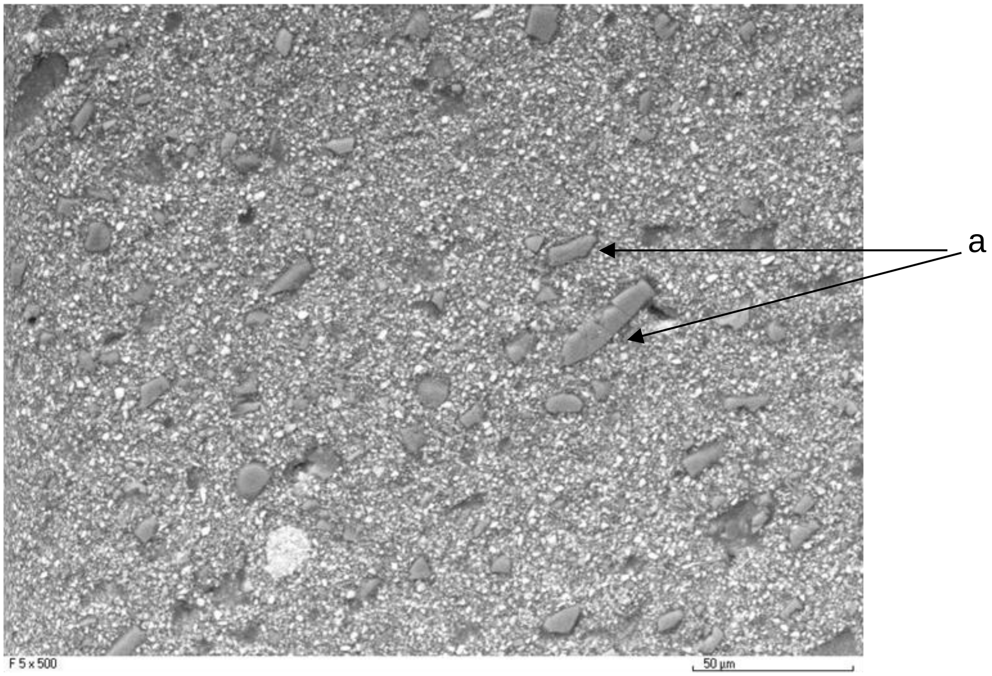


Figure 16. Build It after 1 year water storage and 500,000 RB cycles (SEM image x500 inside wear track).
Note the appearance of (a) crushed fibres which were not visible in the 24 hour image.

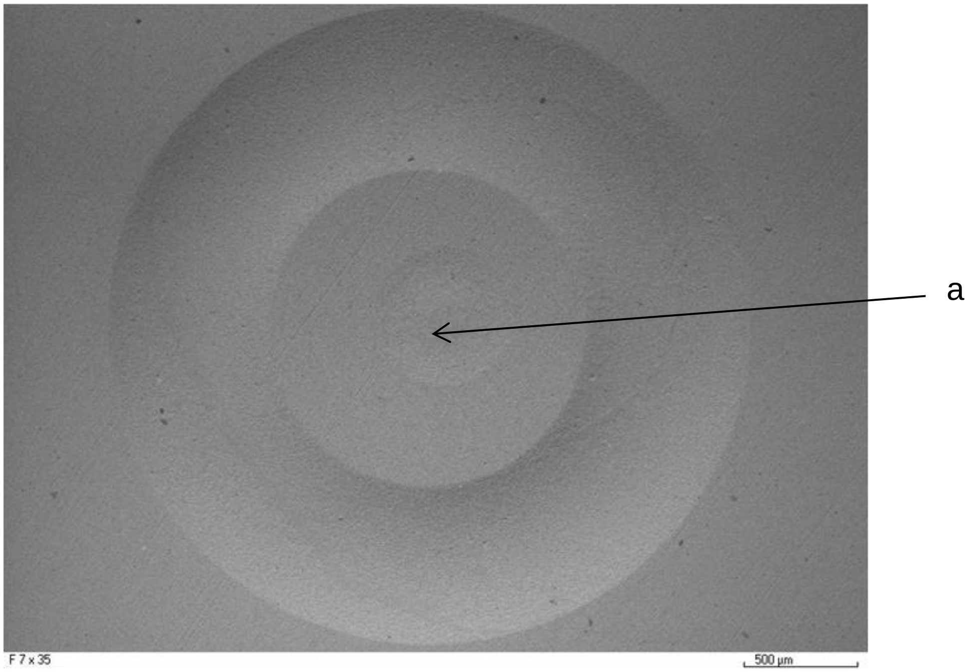


Figure 17. Z250 after 24 hours water storage and 500,000 RB cycles (SEM imagex35). Note (a) the depression caused by the RB machine rotor

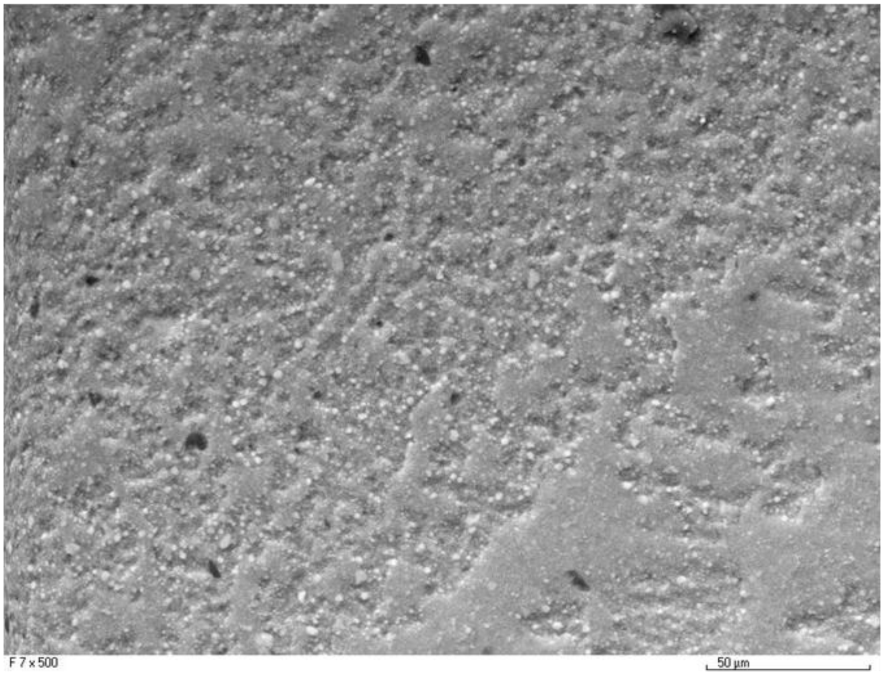


Figure 18. Z250 after 24 hours water storage and 500,000 RB cycles (SEM image x500 inside wear track).

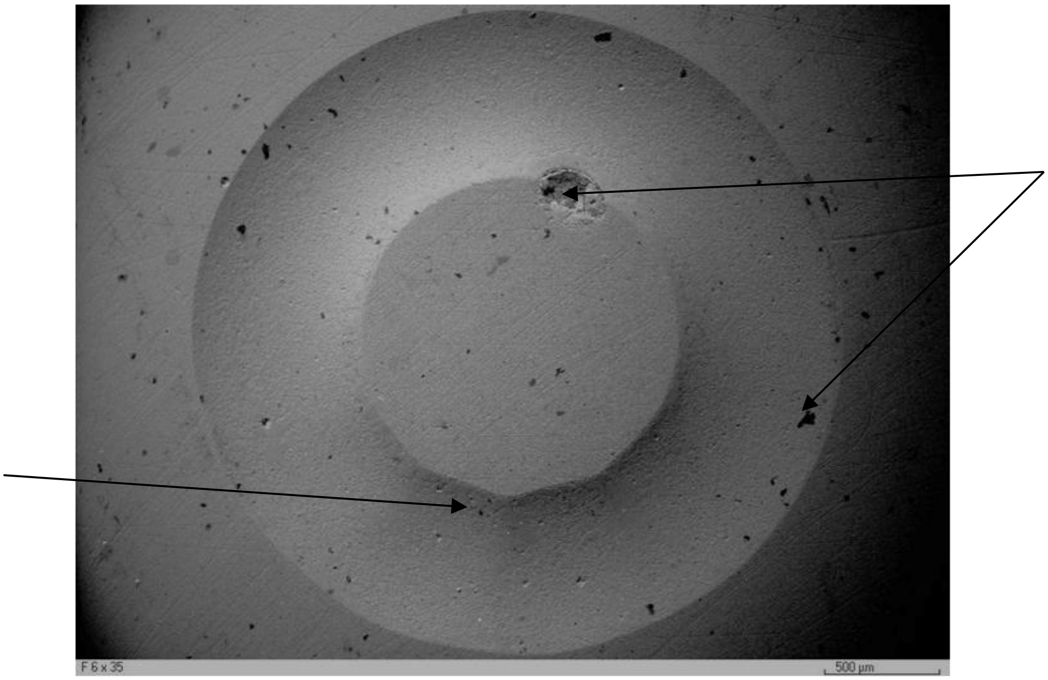


Figure 19. Z250 after 1 year water storage and 500,000 RB cycles (SEM image x35). Note the (a) voids on the surface and (b).the loss of homogeneity on the inner surface of the wear track

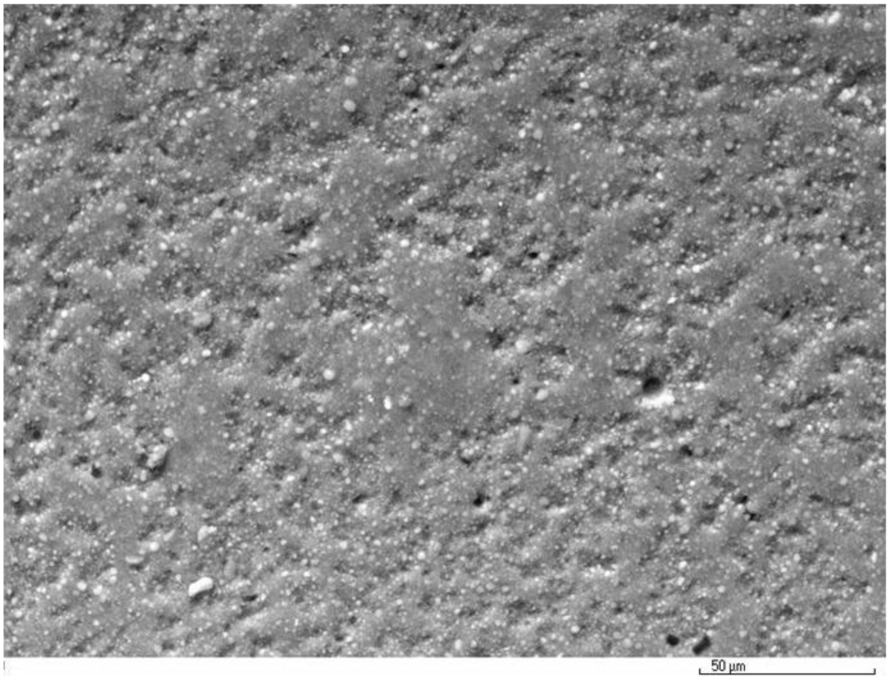


Figure 20. Z250 after 1 year water storage and 500,000 RB cycles (SEM image x500 inside wear track).

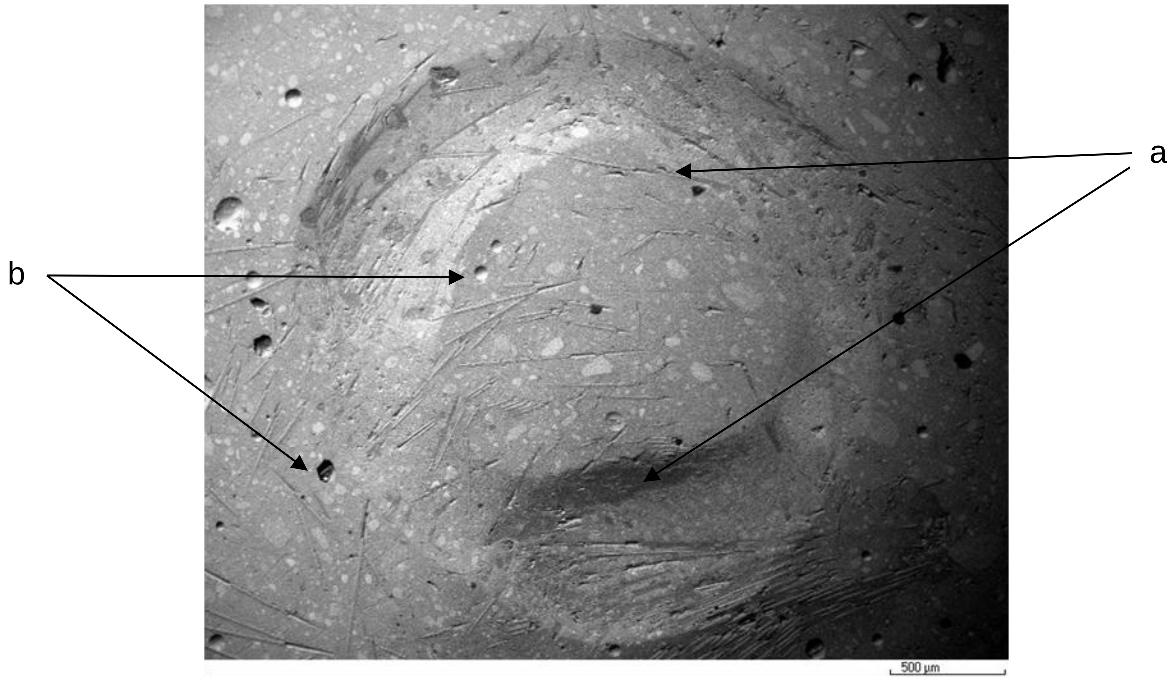


Figure 21. ST after 24 hours water storage and 500,000 RB cycles (SEM image x35).
Note (a) the lack of homogeneity and (b). the surface defects

Figure 22 ST after 24 hours water storage and 500,000 RB cycles (SEM image x500 inside wear track).
Note the (a) crushed fibres and (b) areas where fibres were plucked out

Figure 23. ST after 1 year water storage and 500,000 RB cycles (SEM image x35).

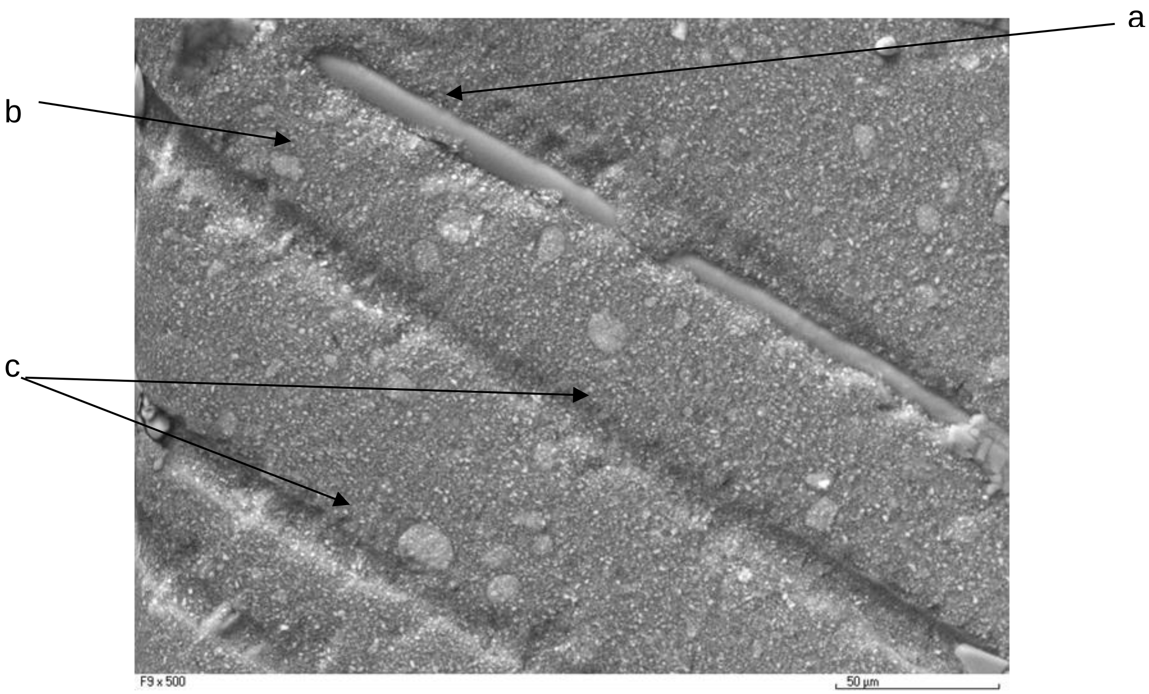


Figure 24. ST after 1 year water storage and 500,000 RB cycles (SEM image x500 inside wear track).
Note the (a) exposed fibre in the upper groove (b) the ground surface of the particulate filler and (c)the tracks where fibres were plucked out.

Different ST formulations

During the one year period of water storage of ST, Build It and Z250, seven different formulations of ST were manufactured in an attempt to clarify the relationship between the formulation and wear resistance of this FRC. These formulations could be grouped into:

1. Materials with a Bis-GMA/TEGDMA ratio of 60/40 which differed in fibre lengths from 3- 25mm. ST, ST1 and ST2 fell into that group.
2. Materials with a Bis-GMA/TEGDMA ratio of 70/30 which differed in fibre lengths from 10 – 20 mm. ST3, ST4 and ST5 fell into group.
3. Materials with a Bis-GMA/TEGDMA ratio of 70/30 which differed in filler loading. ST5, ST6 and ST7 fell into that group.

Each of the groups was tested and, as in the previous section, a plot was drawn to help determine the point at which degradation becomes apparent (5 µm). The results are shown in Table 4.

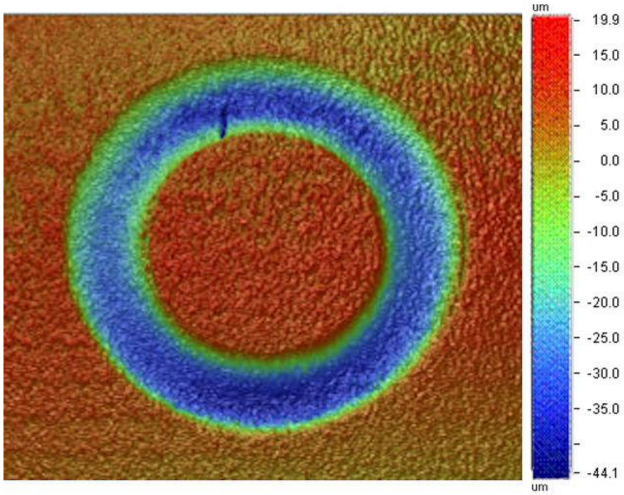
One-way ANOVA showed no significant difference in the depths of ST1 – ST7 after 500,000 cycles. The estimated number of cycles until degradation began varied as shown in Table 4. Upon calculating the estimated number of cycles, one-way ANOVA was done for the results after 100,000 cycles. No significant difference was found. When comparing ST to ST1-ST7, one-way ANOVA showed no significant difference after 100,000 cycles ($p = 0.051$).

Material	Estimated No of Cycles
ST	67,916
ST1	2,193
ST2	48,810
ST3	31,407
ST4	59,410
ST5	10,839
ST6	56,818
ST7	23,368

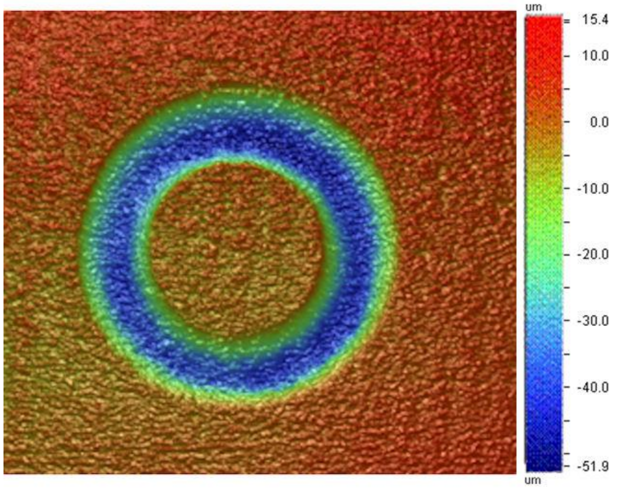
Table 4. Estimated Number of Cycles until surface degradation begins (5 µm) in ST and all its formulations after 24 hours water storage.

- ***Representative Laser profilometer scans after 24 hours water storage.***

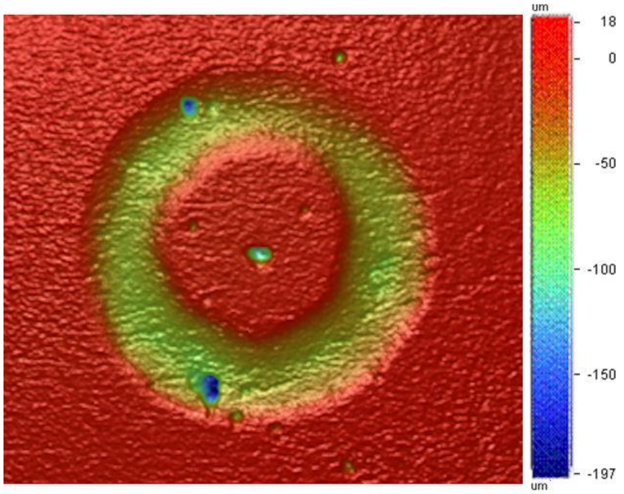
Figure 25 a- j displays representative images of the profiled three dimensional surfaces of all the dental resin composites tested after 24 hours water storage. While the colours represent the depth of the wear track, with the darker blue being a deeper track, the scale is not identical in all images. Please note the individual depth scales to the right of each image such that colour coding is particular to that image. The wear tracks in Build It and Z250 exhibit more homogeneity in outline and depth. Regarding the experimental dental resin composites, ST6 exhibits the least homogeneity regarding its depth and outline while ST3 appears to have improved outline and depth homogeneity.



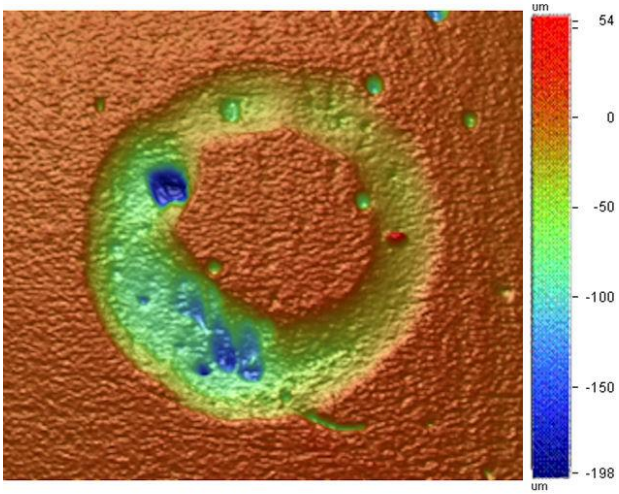
a) Wear track in Build It after 500,000 RB cycles after 24 hours water storage (max depth 44µm)



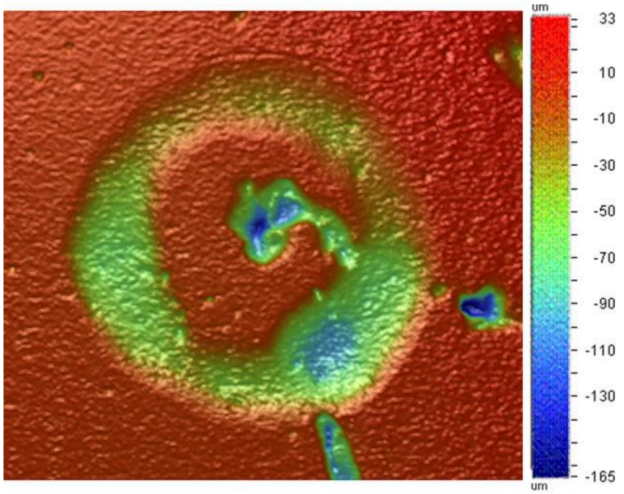
b) Wear track in Z250 after 500,000 RB cycles after 24 hours water storage (max depth 46µm)



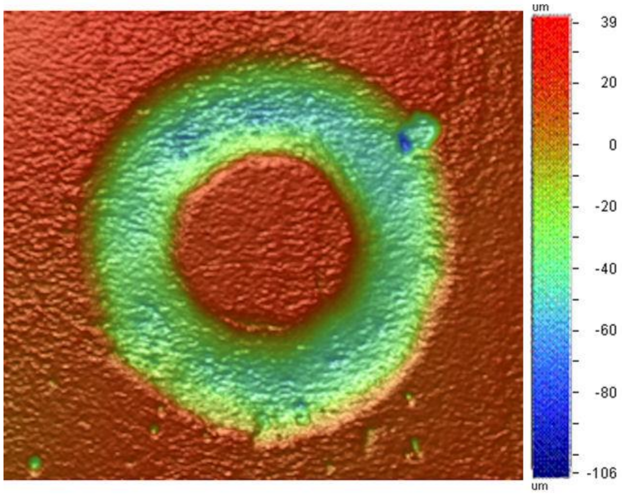
c) Wear track in ST after 500,000 RB cycles after 24 hours water storage (max depth 197µm)



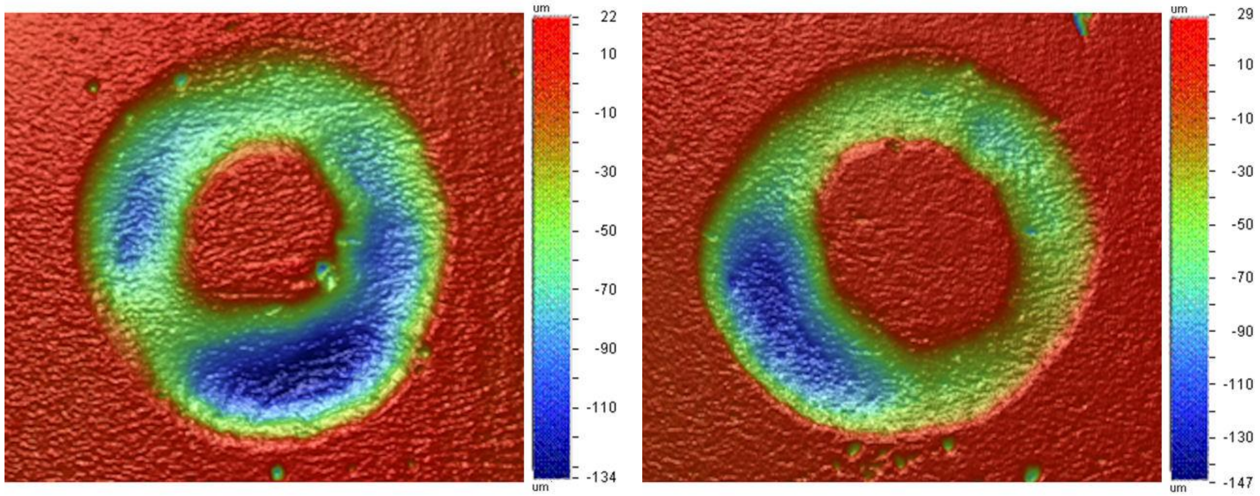
d) Wear track in ST1 after 500,000 rB cycles after 24 hours water storage (max depth 198µm)



e) Wear Track in ST2 after 500,000 RB cycles after 24 hours water storage (max depth 165 µm)

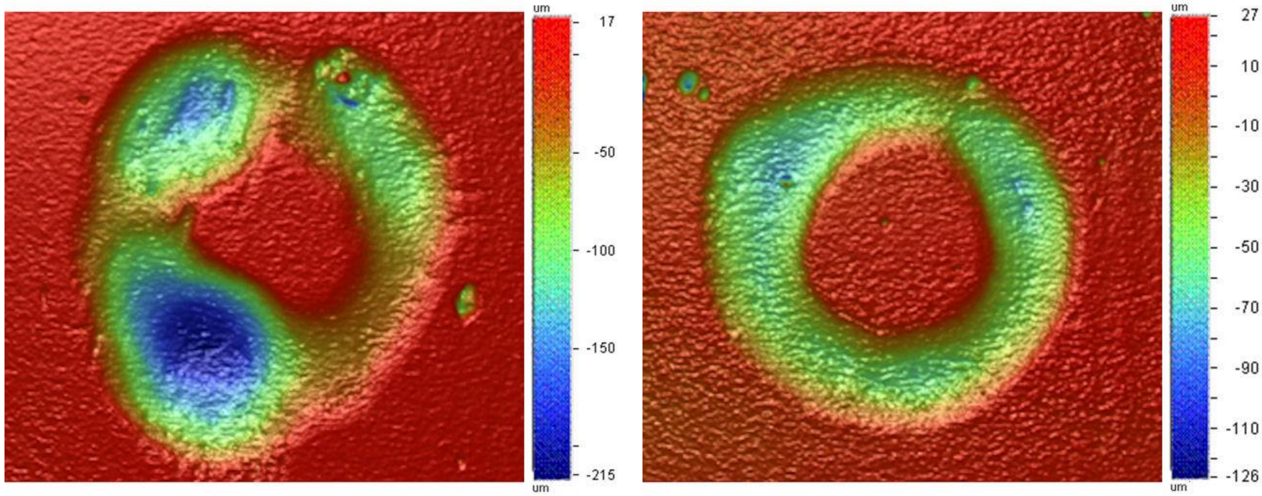


f) Wear track in ST3 after 500,000 RB cycles after 24 hours water storage (max depth 105 µm)



g) Wear track in ST4 after 500,000 RB cycles after 24 hours water storage (max depth 134 µm)

h) Wear track in ST5 after 500,000 RB cycles after 24 hours water storage (max depth 147 µm)



i) Wear track in ST6 after 500,000 RB cycles after 24 hours water storage (max depth 215 µm)

j) Wear track in ST7 after 500,000 RB cycles after 24 hours water storage (max depth 126 µm)

Figure 25. Representative Laser Profilometer scans after 24 hours water storage and 500,000 RB cycles.

4.2.3 Conclusions

1. After 24 hours water storage, ST degraded significantly earlier than either one of the comparator materials. That trend remained the same after 1 year water. storage, which significantly decreased the surface contact fatigue life of all three materials.
2. The different formulations showed no statistical improvement to ST's surface contact fatigue.

4.3 **Three Body Wear**

4.3.1 Materials and Methods

Table 2 lists the names, manufacturers and components of the materials used in this study.

To test three-body wear, a toothbrush wear simulator was used (Figure 26). Factors such as type of testing device, number of brush strokes, and dentifrice type have all been shown to affect toothbrush abrasion (Goldstein and Lerner, 1991; Yankell *et al.*, 1998). These were standardised to allow the characteristics of the composite materials being tested to be better evaluated.

Sample holders were made by drilling a hole, 12mm diameter and 2mm deep, into a rectangular Perspex block. The chosen material was then placed into the Perspex, covered with a transparent Mylar strip (polyethylene terephthalate matrix strip, Goodfellows, Cambridgeshire, UK), compressed by another Perspex block, using hand pressure to remove any gross excess of material. The specimen was then cured by a halogen light curing unit (Visilux 2 light cure, 3M ESPE Dental Products, USA) for 60 seconds. The samples were finished using 500 through to 1000 grit silicon carbide paper (Tri-M-ite Wet or Dry paper,3M,St Paul USA) on a lapping machine (Metaserve prerotary grinder, Betchworth, England) and then stored in distilled deionised water in a 37°C oven for 24 hours before being tested. 8 specimens were made of each ST, Build It and Z250; half of which were tested 24 hours after water storage in a 37°C oven, while the other half were stored for a year, then tested.

During the year in which ST was water stored, ST1-ST7 were developed by Stick Tech. 4 specimens of each of those formulations were tested 24 hours after water storage.

Upon removal from the oven, duct tape (Duckbrand, UK) was used to cover the sides of each specimen, leaving a central 3 mm wide strip to be tested (Figure 27). The specimen was then placed in the water bath of the toothbrush simulator (Figure 28) with a water/toothpaste slurry made of 60 grams of Colgate Cavity Protection fluoridetoothpaste and 30 mls of distilled water. The exposed strip of composite was parallel to the path of oscillation of the toothbrush simulator. Straight head soft toothbrushes with 0.007 mm diameter nylon filaments (Henry Schein, UK) were used. The wear rate was measured after a run of 50,000 cycles which corresponds to 5 years in the oral cavity as every 10,000 cycles simulates approximately one year of toothbrush wear (Goldstein and Lerner, 1991; Momoi *et al*., 1997). After each run, the duct tape was removed from the tested specimen. It was then washed, dried, and an impression was taken using Microset. The impressions were then profiled using a laser profilometer. The scans of the wear tracks were then assessed using Wyko Vison 32 software. The depth of three points was measured on the wear track (one in the center and one either side). This was done by using the X profile on the scan and measuring from the highest to the lowest point. Figure 29 to Figure 31show the points measured. The average depth of the points was then used as the depth of the individual wear track.

The tested samples were also assessed using an environmental scanning electron microscope (Philips XL 30 ESEM-FEG, Philips, UK). The samples were viewed at a low vacuum of 0.5 torr and the images were obtained using a gaseous secondary electron detector.

SPSS Statistics 17 was used for the analysis of the data. A Shapiro Wilk test was done to test the normality of the data distribution. As the data was normally distributed, a one-way ANOVA (at a significance level of 0.05) was applied to results of the material and Tukey’s post hoc test was used to determine which materials caused a significant difference if found. Two-way ANOVA was used to determine if water storage had an effect.

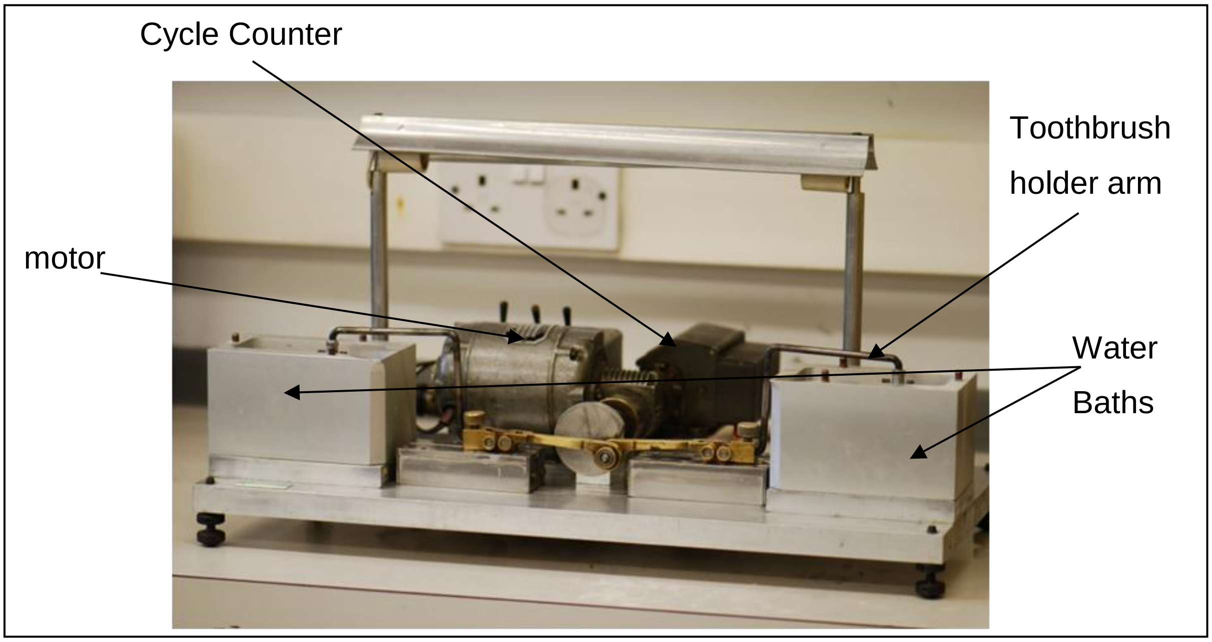


Figure 26. Manual toothbrush simulator components.

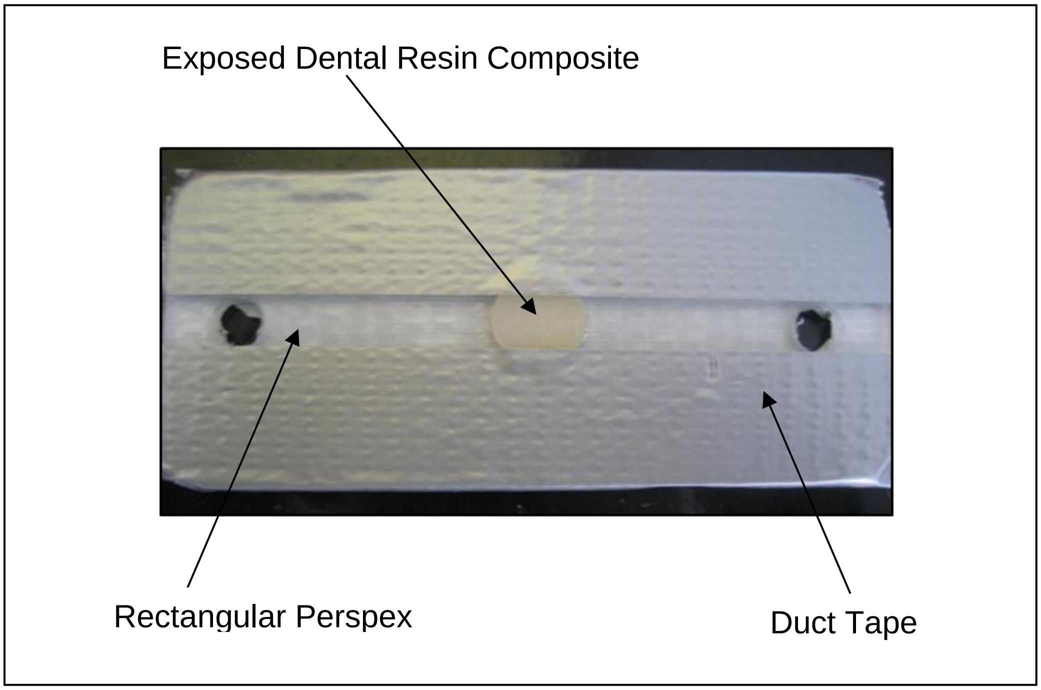


Figure 27. Prepared dental resin composite specimen before toothbrush testing.

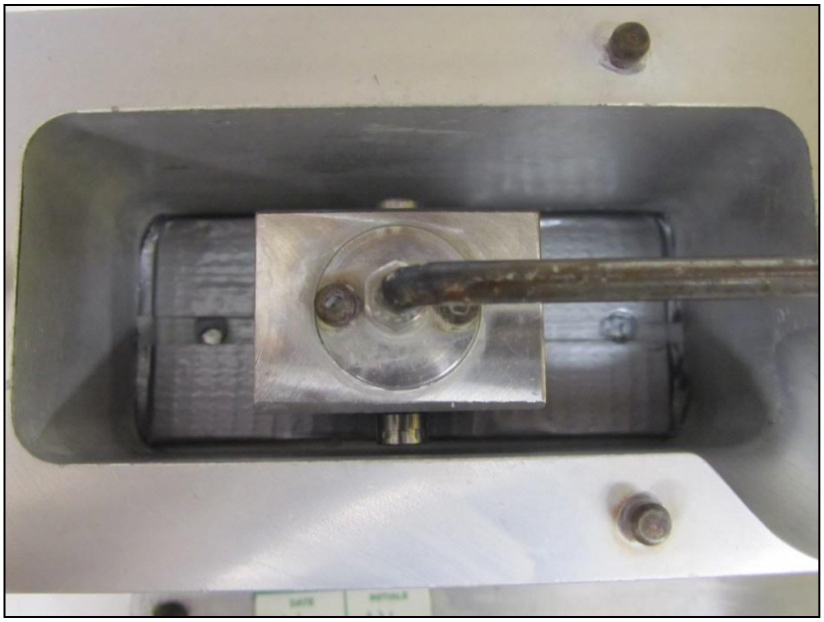
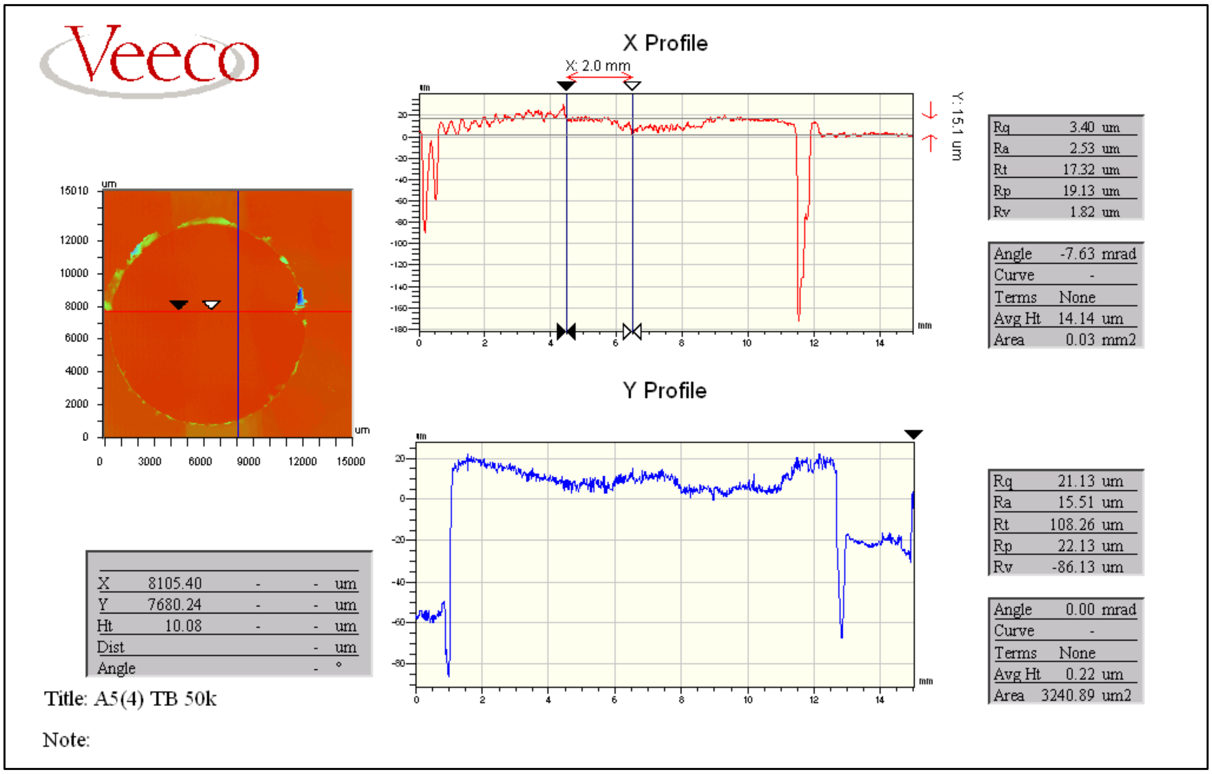


Figure 28. Composite specimen in a water bath of toothbrush simulator.



X	8105.40	-	-	um
Y	7680.24	-	-	um
Ht	10.08	-	-	um
Dist			-	um
Angle			-	°

Title: A5(4) TB 50k

Note:

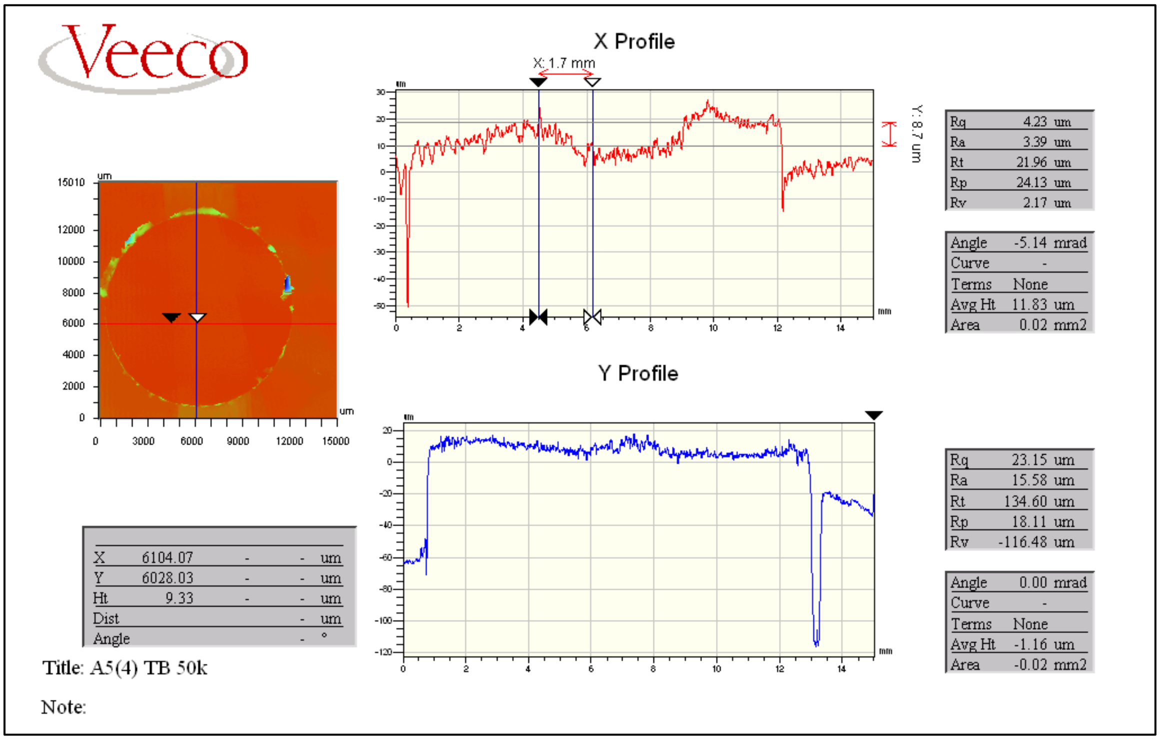
Rq	3.40	um
Ra	2.53	um
Rt	17.32	um
Rp	19.13	um
Rv	1.82	um

Angle	-7.63	mrad
Curve	-	
Terms	None	
Avg Ht	14.14	um
Area	0.03	mm2

Rq	21.13	um
Ra	15.51	um
Rt	108.26	um
Rp	22.13	um
Rv	-86.13	um

Angle	0.00	mrad
Curve	-	
Terms	None	
Avg Ht	0.22	um
Area	3240.89	um2

Figure 29. First point used in depth determination of Build It after 50,000 TB cycles



Rq	4.23	um		
Ra	3.39	um		
Rt	21.96	um		
Rp	24.13	um		
Rv	2.17	um		

Angle	-5.14	mrad
Curve	-	
Terms	None	
Avg Ht	11.83	um
Area	0.02	mm2

Rq	23.15	um
Ra	15.58	um
Rt	134.60	um
Rp	18.11	um
Rv	-116.48	um

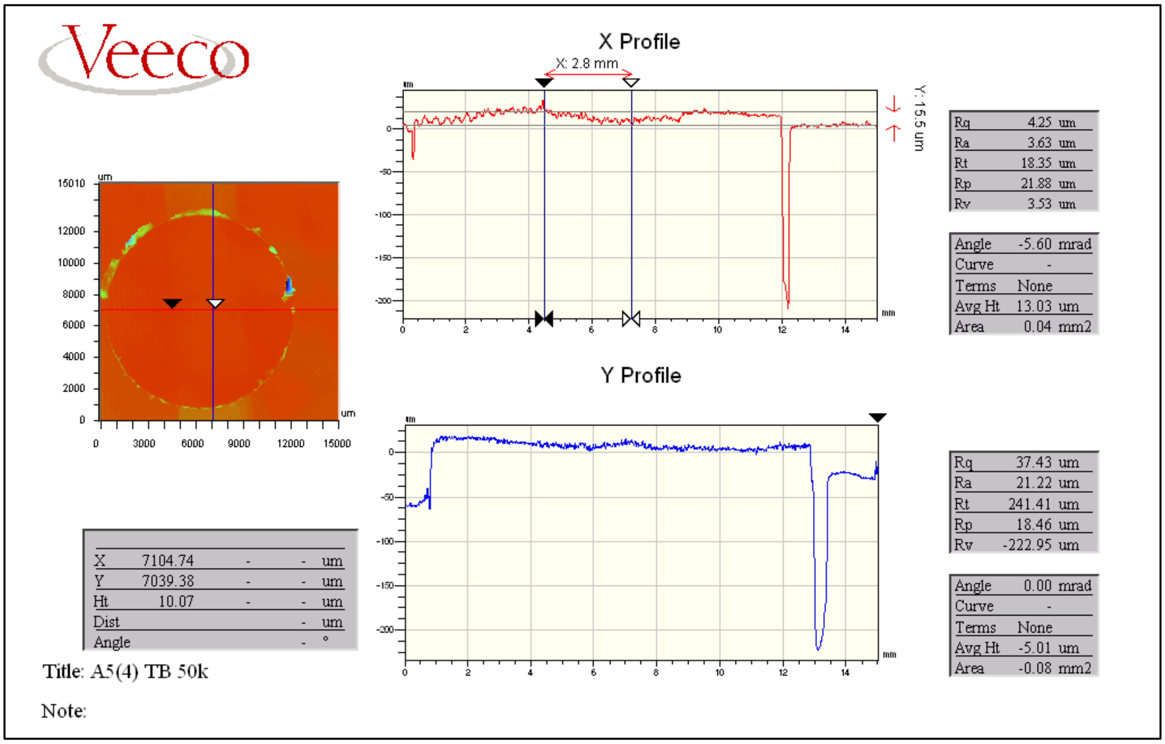
Angle	0.00	mrad
Curve	-	
Terms	None	
Avg Ht	-1.16	um
Area	-0.02	mm2

X	6104.07	-	-	um
Y	6028.03	-	-	um
Ht	9.33	-	-	um
Dist			-	um
Angle			-	°

Title: A5(4) TB 50k

Note:

Figure 30. Second point used in depth determination of Build It after 50,000 TB cycles



Rq	4.25	um
Ra	3.63	um
Rt	18.35	um
Rp	21.88	um
Rv	3.53	um

Angle	-5.60	mrad
Curve	-	
Terms	None	
Avg Ht	13.03	um
Area	0.04	mm2

Rq	37.43	um
Ra	21.22	um
Rt	241.41	um
Rp	18.46	um
Rv	-222.95	um

Angle	0.00	mrad
Curve	-	
Terms	None	
Avg Ht	-5.01	um
Area	-0.08	mm2

X	7104.74	-	-	um
Y	7039.38	-	-	um
Ht	10.07	-	-	um
Dist			-	um
Angle			-	°

Title: A5(4) TB 50k

Note:

Figure 31. Third point used in depth determination of Build It after 50,000 TB cycles

4.3.2 Results

ST compared with Z250 and Build It

a) After 24 hours water storage

Table 5 shows the results of toothbrush testing after 24 hours of water storage, illustrated in Figure 32.

Material	ST	Z250	Build It
N	4	4	4
Mean wear in µm (SD)	55.4 (9.4)	7.1(3.9)	7.1(2.9)

Table 5. Mean Wear Depth after 50,000 TB cycles after 24 hours of water storage.

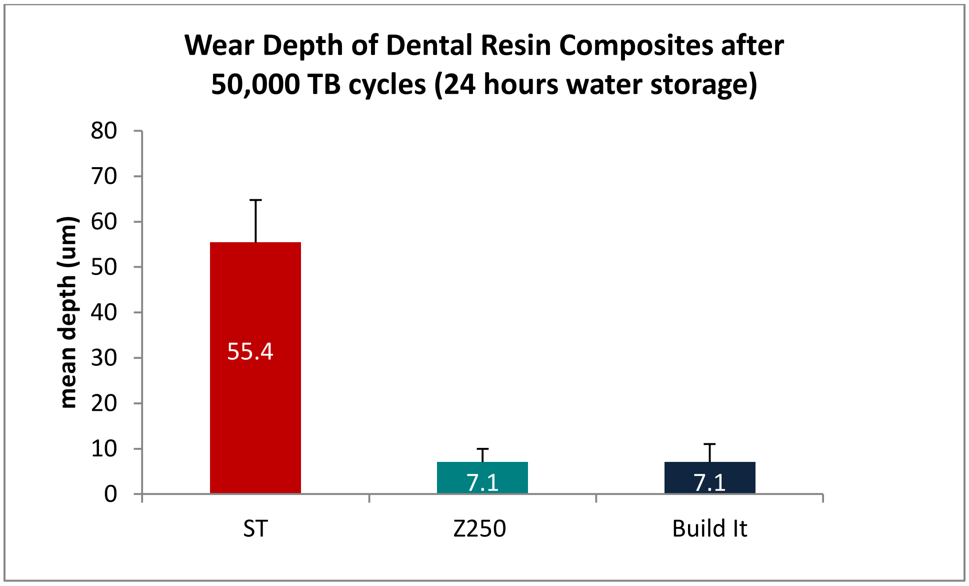


Figure 32. Mean wear depth of ST, Z250 and Build It after 50,000 TB cycles after 24 hours of water storage.

One- way ANOVA showed a significant difference between the three groups tested ($p < 0.05$), with ST having a significantly lower three-body wear resistance compared with Z250 and Build It.after 24 hours water storage.

b) After 1 year water storage

Table 6 shows the mean wear depths and standard deviation of the dental resin composites tested after 50,000 toothbrushing cycles and 1 year water storage, illustrated in Figure 33.

Material	ST	Z250	Build It
n	4	4	4
Mean wear in µm (SD)	54.9 (14.1)	17.3 (4.6)	20.3 (4.7)

Table 6. Mean wear depth (um) after 50,000 TB cycles after 1 year water storage.

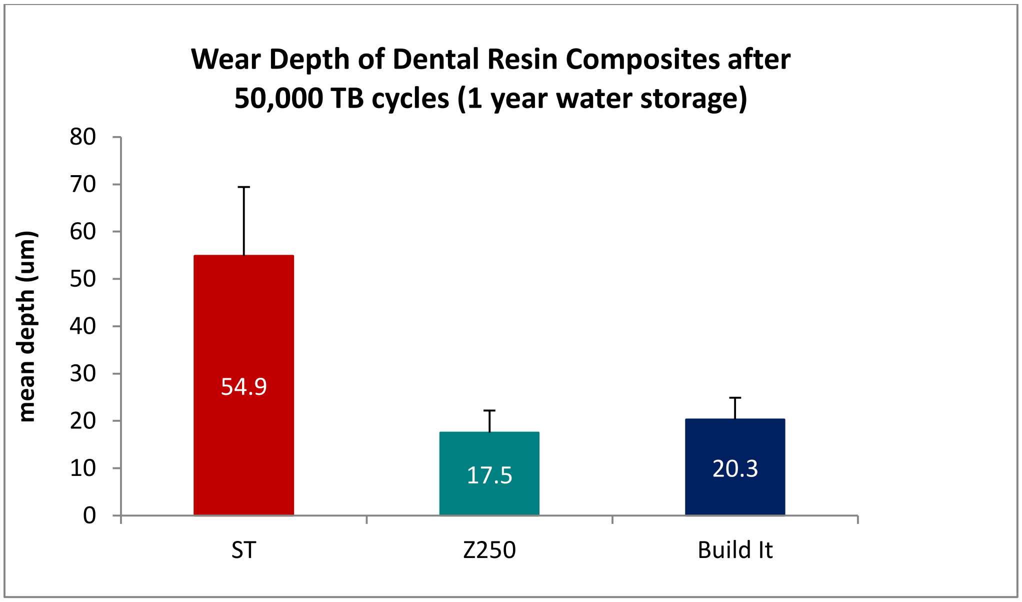


Figure 33. Mean wear depth of ST, Z250 and Build It after 50,000 TB cycles after 1 year of water storage.

One- way ANOVA showed a significant difference between the three groups tested ($p < 0.05$), with ST having a significantly lower three-body wear resistance compared with Z250 and Build It. Two-way ANOVA showed an interaction with water storage as both Z250 and Build It had significantly less three-body wear resistance after 1 year of water storage compared with 24 hours as illustrated in Figure 34.

Material	**ST**	**ST 1 year**	**Z250**	**Z250 1 year**	**Build It**	**Build It 1 year**
n	4	4	4	4	4	4
Mean wear in µm (SD)	54.9 (9.4)	55.4(14.1)	7.1(3.9)	17.3(4.6)	7.1(2.9)	20.3(4.7)

Table 7. Comparison of wear at 24 hours and 1 year after 50,000 TB cycles.

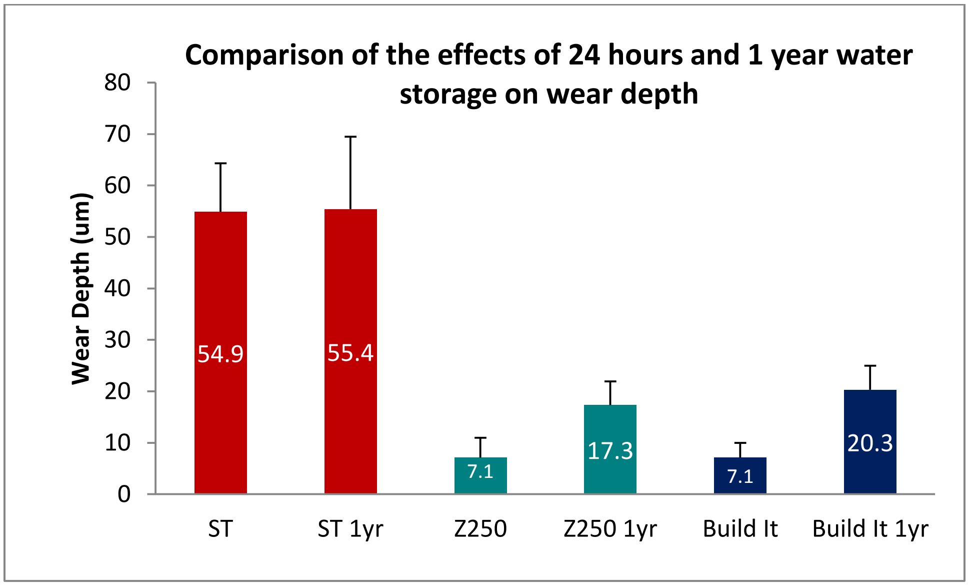
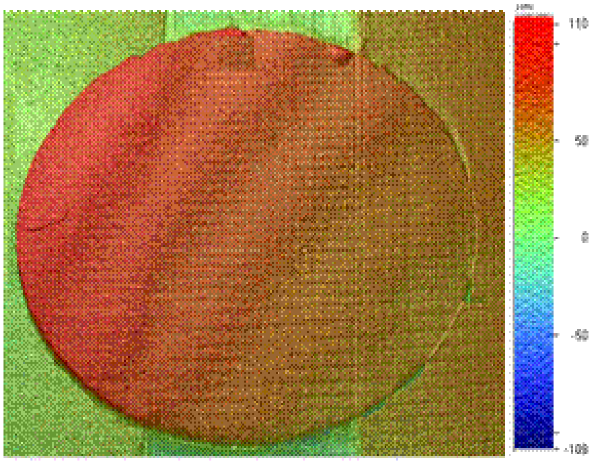


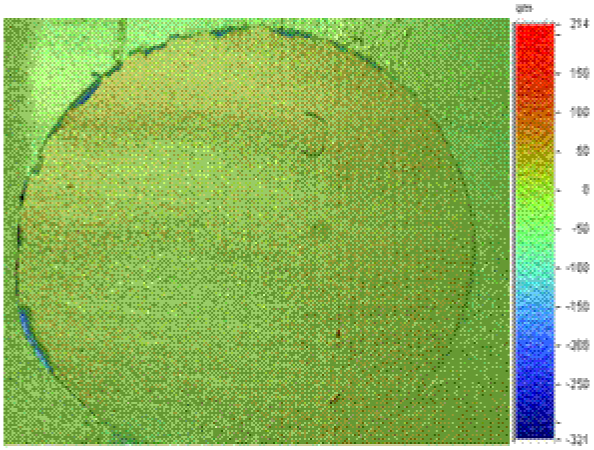
Figure 34. Comparison of the effect of 24 hours and 1 year water storage on wear resistance to 50,000 TB cycles.

- ***Representative Laser Profilometer Scans after 24 hours and 1 year water storage***

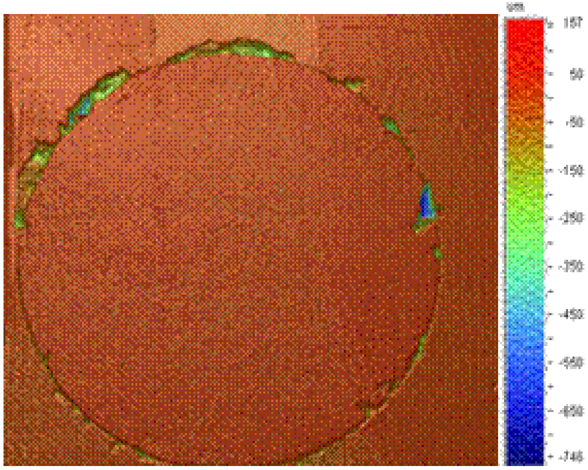
Figure 35 shows representative laser profilometer scans after 24 hours and 1 year water storage. The fibres are clearly visible in the wear track in ST after 24 hours. The track also displays a lack of homogeneity when compared with either Build It or Z250. One year water storage did not have an apparent effect on the wear track in Z250, while both Build It and ST were affected. Build It appears to have preferential wear in certain areas of the specimen and the fibres are less pronounced in ST's wear track.



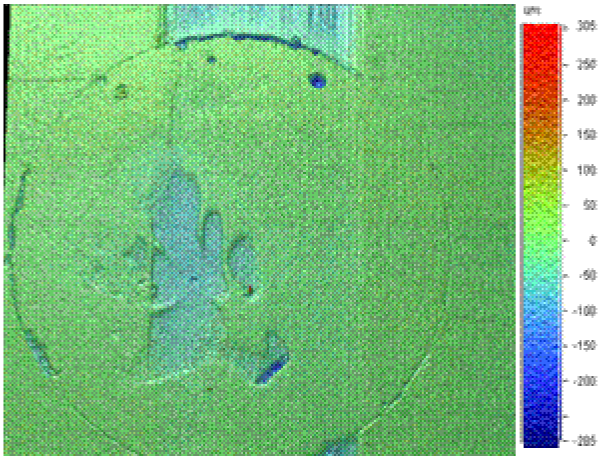
a) Wear track in Z250 after 50,000 TB cycles after 24 hours water storage (max depth 15 µm)



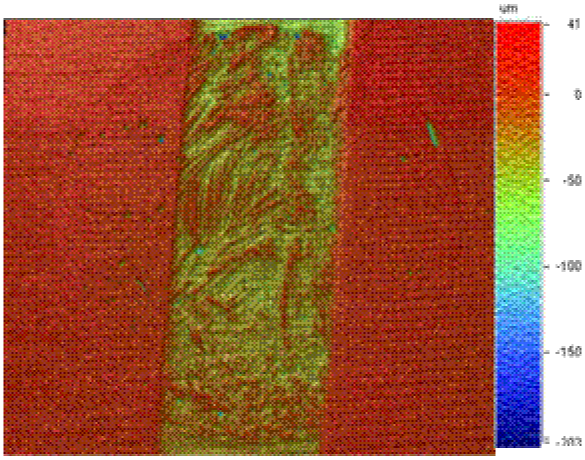
b) Wear track in Z250 after 50,000 TB cycles after1 year water storage (max depth 20 µm)



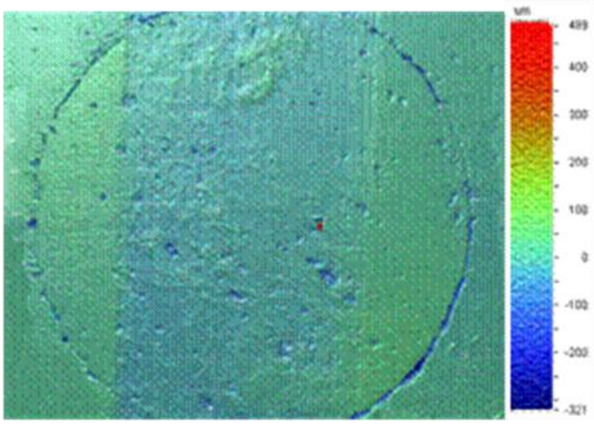
c) Wear track in Build It after 50,000 TB cycles after 24 hours water storage (max depth 15 µm)



d) Wear track in Build It after 50,000 TB cycles after1 year water storage (max depth 50 µm)



e) **Wear track in ST after 50,000 TB cycles after 24 hours water storage(max depth 100 µm**)



f) Wear track in ST after 50,000 TB cycles after 1 year water storage (max depth 200 µm)

Figure 35. Representative laser profilometer scans after 24 hours and 1 year water storage.

- ***SEM image analysis after 24 hours and 1 year water storage***

Figure 36 to Figure 45 represent the SEM images taken of Build It, Z250 and ST 24 hours and 1 year after three body wear testing in the manual toothbrush simulator for 50,000 cycles. It is clear from the lower magnification images that the fibre size in ST is larger in diameter and longer than those used in Build It. The right side of the images is the side which was covered by duct tape, so remains unbrushed while the left side was exposed to the toothpaste slurry. Despite the appearance of a homogeneous surface in Build It after toothbrushing, the SEM revealed some fibre breakdown, especially after 1 year of water storage. Z250 appeared unchanged after 1 year of water storage, while ST showed several signs of surface deterioration.

Figure 36. Build It after 24 hours water storage and 50,000 TB cycles (SEM image x35): (a) is the unbrushed surface, while (b) is the brushed surface.

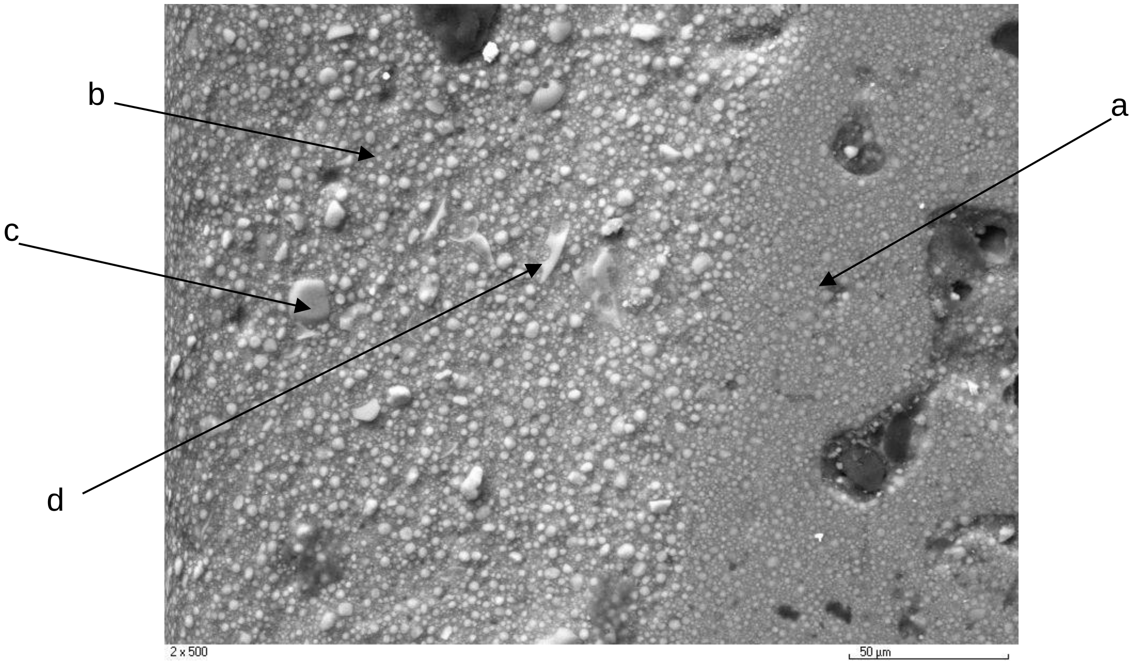


Figure 37. Build It after 24 hours water storage and 50,000 TB cycles (SEM image x 500): (a) is the unbrushed surface and (b) is the brushed surface.
Note the protrusion of (c) particles and (d) fibres as the matrix has been worn away.

Figure 38. Build It after 1 year water storage and 50,000 TB cycles (SEM image x 35): (a) is the unbrushed surface and (b) is the brushed surface.

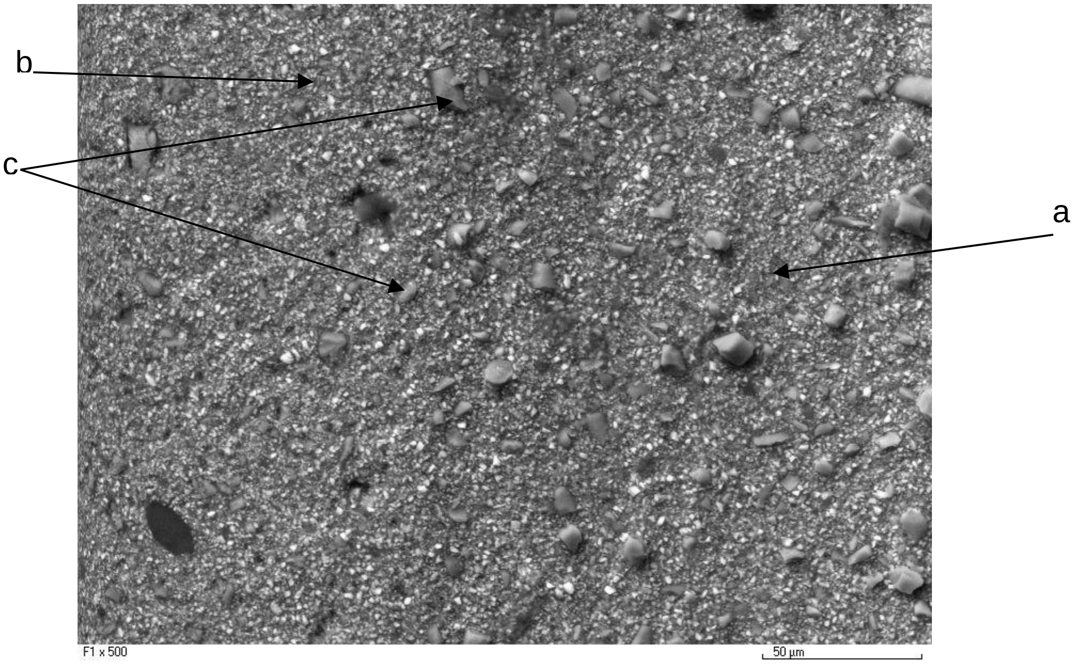


Figure 39. Build It after 1 year water storage and 50,000 TB cycles (SEM image x 500): (a) is the unbrushed surface and (b) is the brushed surface.
note(c) the exposed broken fibres in the brushed surface.

Figure 40. Z250 after 24 hours water storage and 50,000 TB cycles (SEM image x 35): (a) is the unbrushed surface and (b) is the brushed surface.

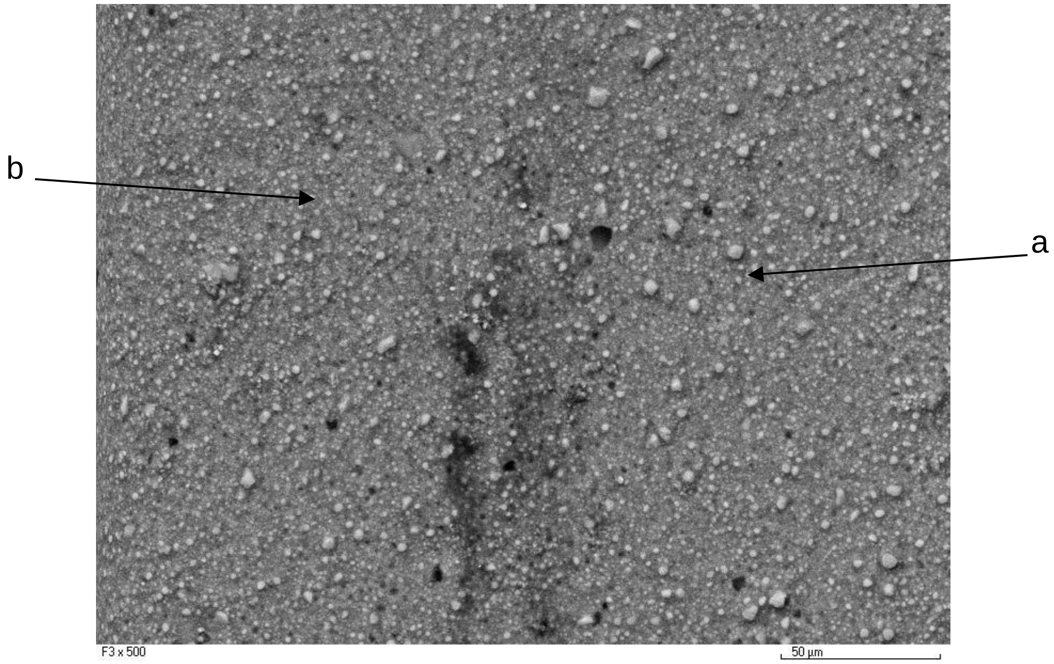


Figure 41. Z250 after 24 hours water storage and 50,000 TB cycles (SEM image x 500): (a) is the unbrushed surface and (b) is the brushed surface.

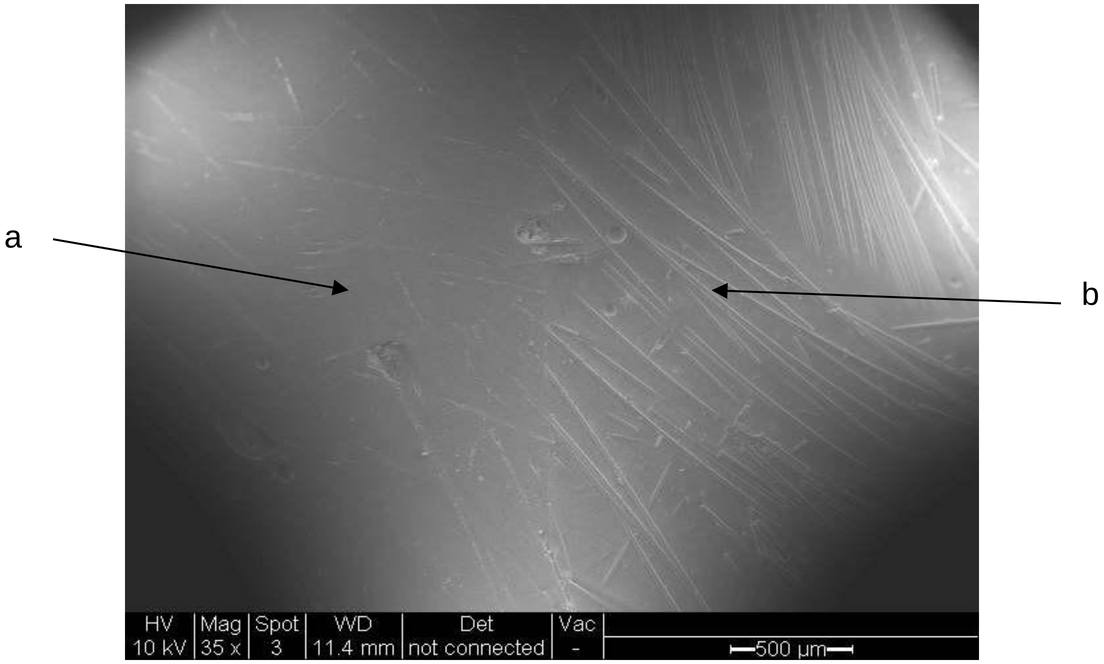


Figure 42. ST after 24 hours water storage and 50,000 TB cycles (SEM image x35): (a) is the unbrushed surface and (b) is the brushed surface.
Note the unequal fibre distribution apparent in the brushed surface.

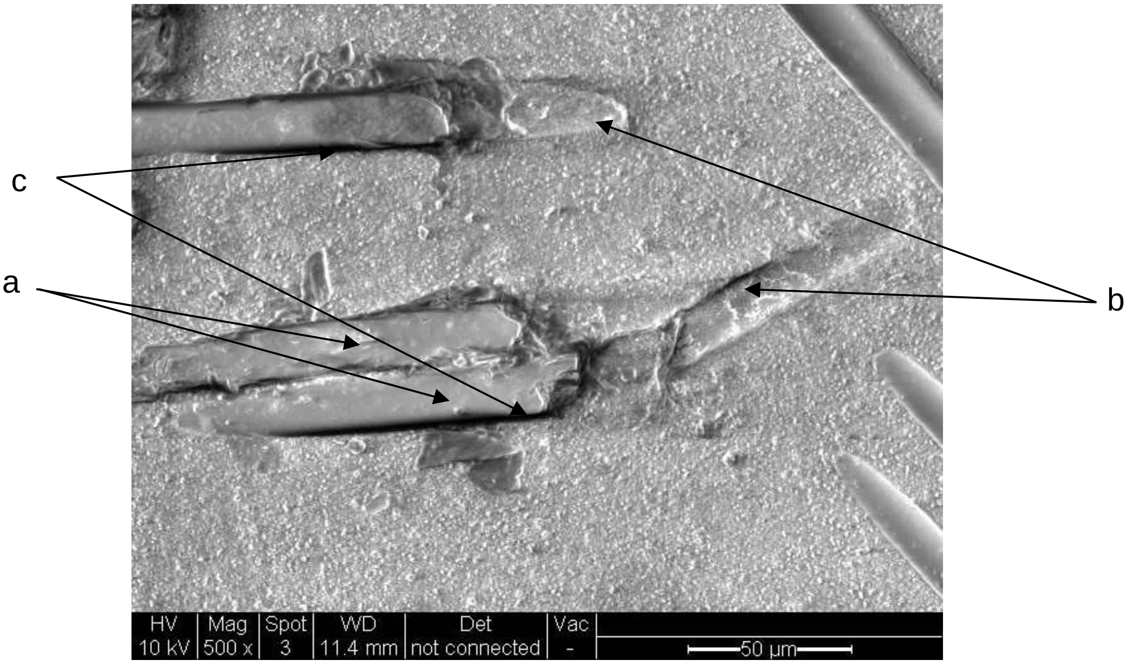


Figure 43. ST after 24 hours water storage and 50,000 TB cycles (SEM image x 500 in the brushed surface): (a) shows crushed fibres, (b) shows areas where fibres have been plucked out and (c) possibly a space between the fibre and the resin matrix.

Figure 44. ST after 1 year water storage and 50,000 TB cycles (SEM image x 35): (a) is the unbrushed surface and (b) is the brushed surface.
Note (c) voids in the brushed surface.

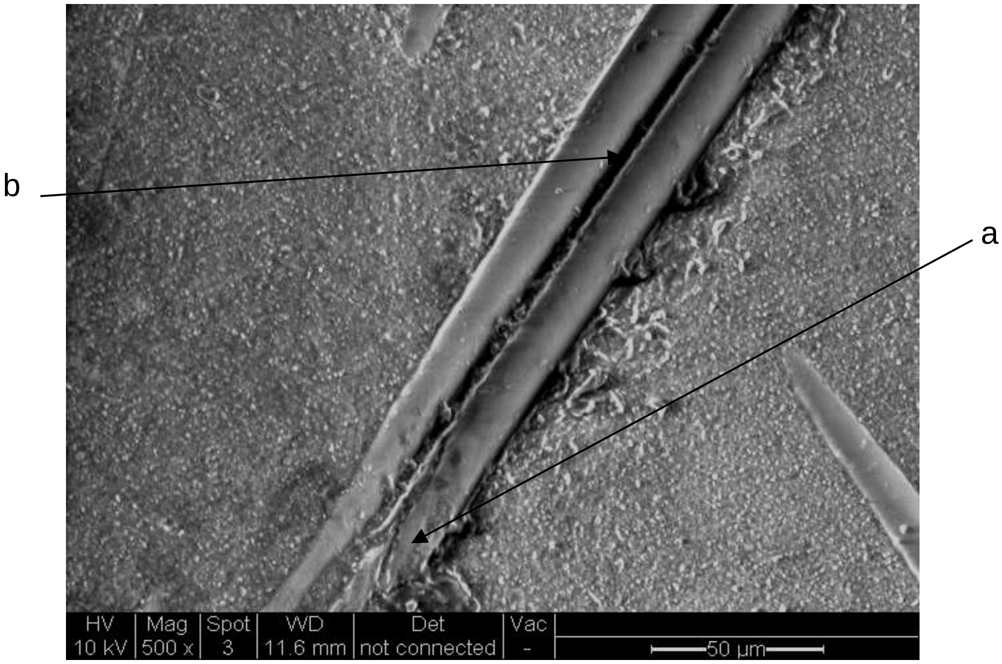


Figure 45. ST after 1 year water storage and 50,000 TB cycles (SEM image x 500 in brushed surface): (a) shows crushed fibre surface.

Different ST formulations

The different formulations of ST were divided into three main groups based on their composition. The three body-wear resistance was then compared within each group. SPSS Statistics 17 was used for the analysis of the data. A Shapiro Wilk test was done to test the normality of the data distribution. As the data were normally distributed, a one-way ANOVA (at a significance level of 0.05) was applied to results of the material and Tukey's post hoc test was used to determine which materials caused a significant difference if found.

Group 1. Different Fibre lengths in 60/40 Bis-GMA/TEGDMA ratio

ST, ST1, and ST2 only differed in the length of fibres used as shown in Table 8. The results of the three-body wear testing are shown in Table 9 and these are illustrated in Figure 46. Error bars represent standard deviation.

Material	Resin (% wt)	Fibre (% wt)	Filler (% wt)	Fibre Length (mm)
ST1	21	19	60	3- 5
ST	21	19	60	8
ST2	21	19	60	25

Table 8. Components of ST, ST1 and ST2.

Material	ST	ST1	ST2
n	4	4	4
Mean wear in µm (SD)	55.4 (9.4)	39.1 (8.6)	45.7 (12.3)

Table 9. Mean Wear depths for Group 1 of ST formuations after 50,000 TB cycles after 24 hours water storage.

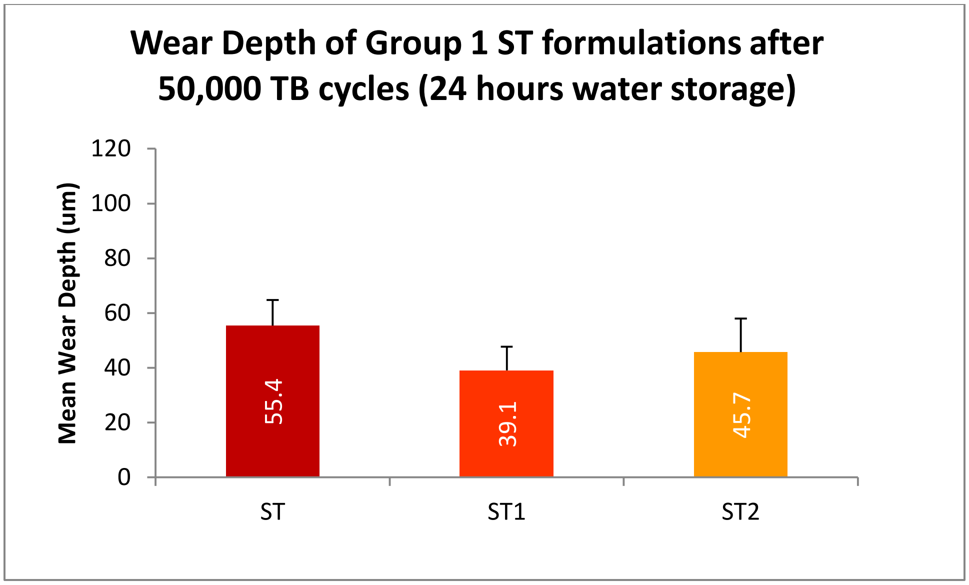


Figure 46. Mean wear depth (µm) of ST, ST1 and ST2 after 50,000 TB cycles after 24 hours of water storage.

One-way ANOVA showed a significant difference between the three groups (p= 0.004). Tukey's test revealed that ST had significantly lower three-body wear resistance compared with ST1 and ST2.

Group 2. Differing Fibre lengths in 70/30 Bis-GMA/TEGDMA ratio

Group 2 has a similar amount of resin, fibres and fillers by weight. They differ in the fibre length used at the time of manufacturing as shown in the Table 10 below. Table 11 shows the results of the mean wear and these are illustrated in Figure 47.

Material	Resin (% wt)	Fibre (% wt)	Filler (% wt)	Fibre Length (mm)
ST3	26	22	52	10
ST4	26	22	52	15
ST5	26	22	52	20

Table 10. Components of ST3, ST4 and ST5.

Material	ST3	ST4	ST5
n	4	4	4
Mean wear in µm (SD)	86.1(25.1)	85.8(17.6)	50.6(14.5)

Table 11. Wear depths for Group 2 of ST formulations after 50,000 TB cycles after 24 hours water storage.

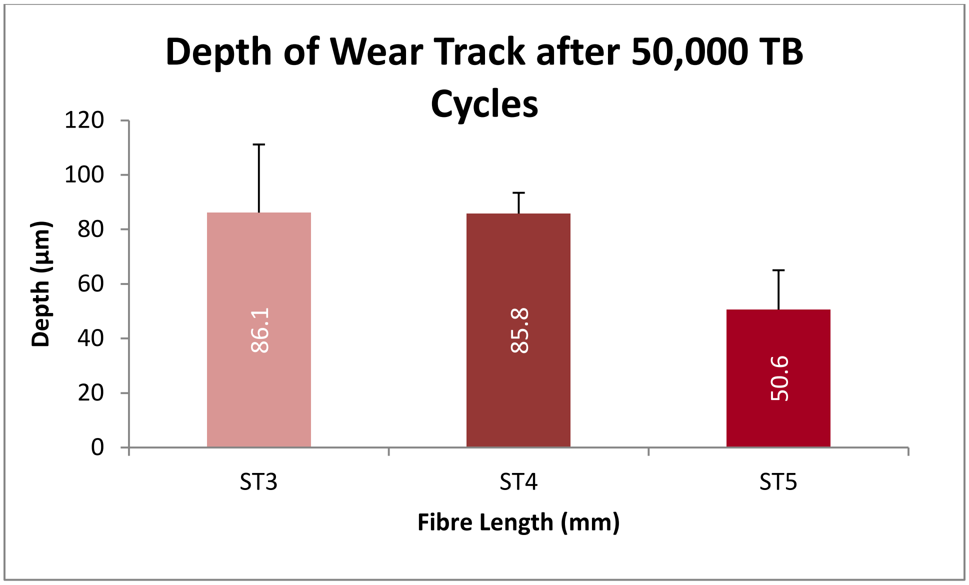


Figure 47. Mean wear depth of ST3, ST4, and ST5 (µm) after 50,000 TB cycles after 24 hours water storage.

One-way ANOVA showed a significant difference between the three groups ($p < 0.05$) Tukey's post hoc test found that ST5 has significantly more wear resistance than either ST3 or ST4.

Group 3. Different Fibre Loading

Group 3 has similar amounts of fibre length 20mm. The main difference was in the percentage of resin and fibres as shown in Table 12. These results are illustrated in Figure 48.

Material Used	**Resin (% wt)**	**Fibre (% wt)**	**Filler (% wt)**	**Fibre length (mm)**
ST5	26	22	52	20
ST6	23.5	21.5	55	20
ST7	19	21	60	20

Table 12. Components of ST5, ST6 and ST7.

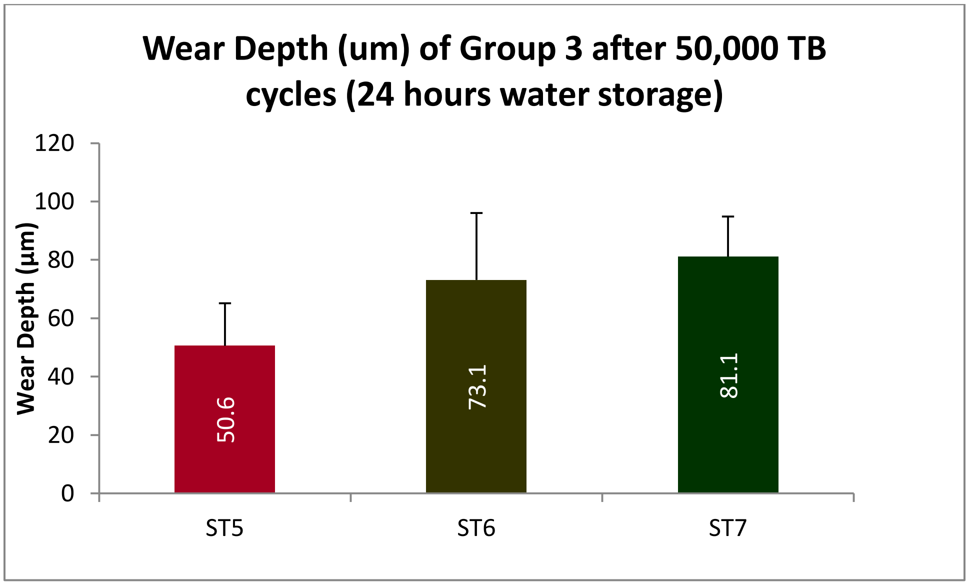


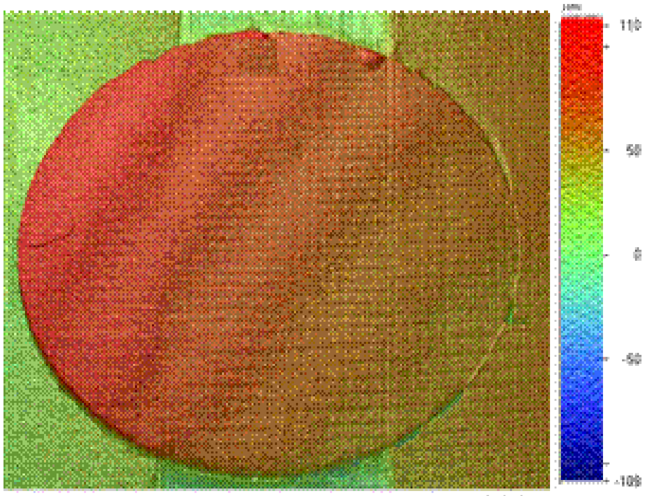
Figure 48. Mean wear depth in ST5, ST6 and ST7 after 50,000 TB cycles after 24 hours water storage.

One-way ANOVA showed a significant difference between the three groups ($p \leq 0.001$). Tukey's post hoc analysis showed that ST5 which had the lowest particulate filler loading and highest resin content had significantly more wear resistance than either ST6 or ST7.

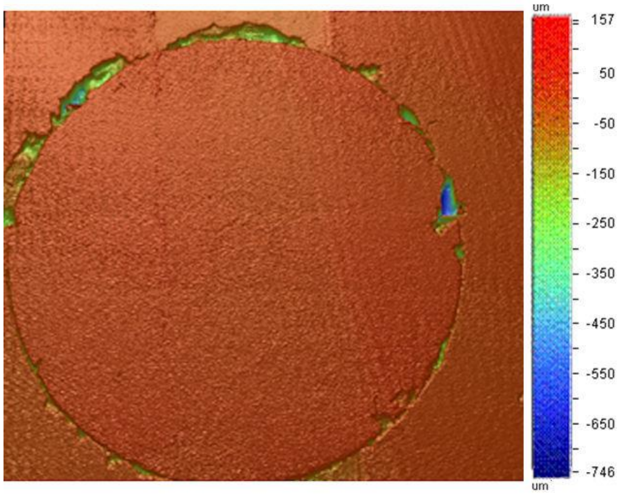
When comparing ST – ST7, one-way ANOVA showed a significant difference between the groups ($p \leq 0.001$). Tukey's post hoc analysis revealed that ST1 and ST2 had the highest wear resistance. When Build It and Z250 were compare with ST1 and ST2, one-way ANOVA showed a significant difference between the groups ($p \leq 0.001$). Tukey's post hoc analysis found that ST1 and ST2 showed significantly less wear resistance than either Build It or Z250.

Representative Laser Profilometer Scans after 24 hours water storage

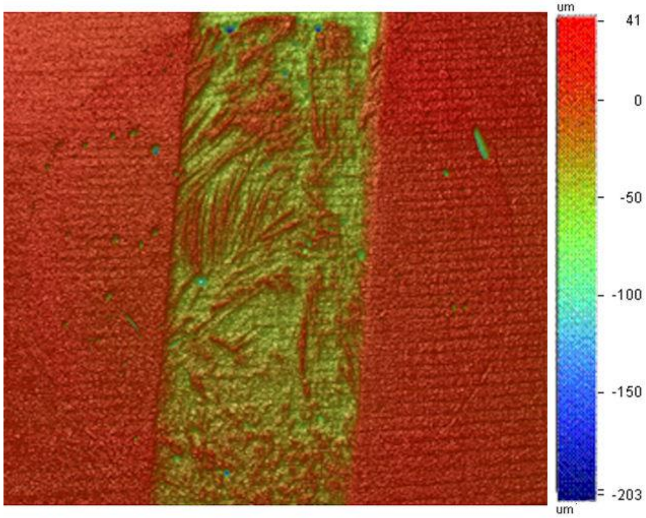
Figure 49 (a-j) shows the profiled three dimensional surfaces of the experimental composites and the comparators after 50,000 cycles of toothbrush testing after 24 hours of water storage. Both Build IT and Z250 show a smooth wear track, while ST and its derivatives showed a much rougher looking track which had unevenly distributed fibres throughout..



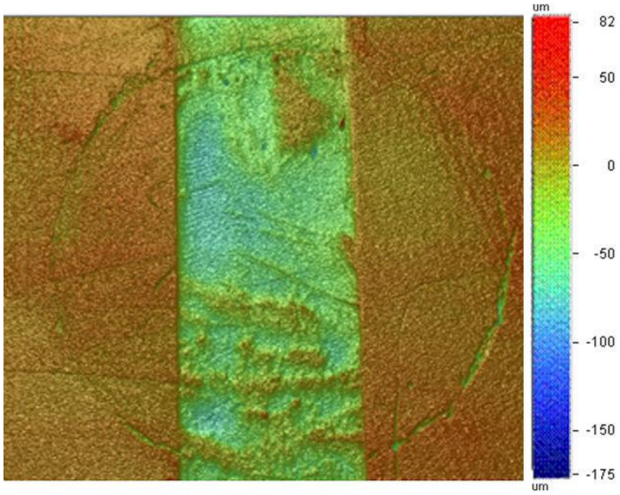
a) Wear track in Z250 after 50,000 TB cycles (max depth 15 µm)



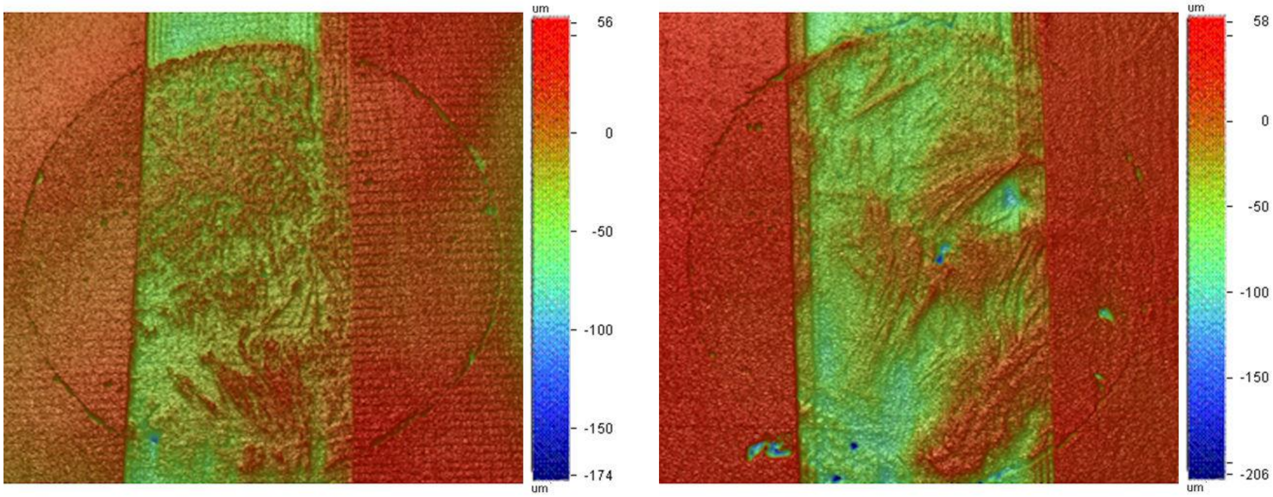
b) Wear track in Build It after 50,000 TB cycles(max depth 15 µm)



c) Wear track in ST after 50,000 TB cycles (max depth 100 µm)

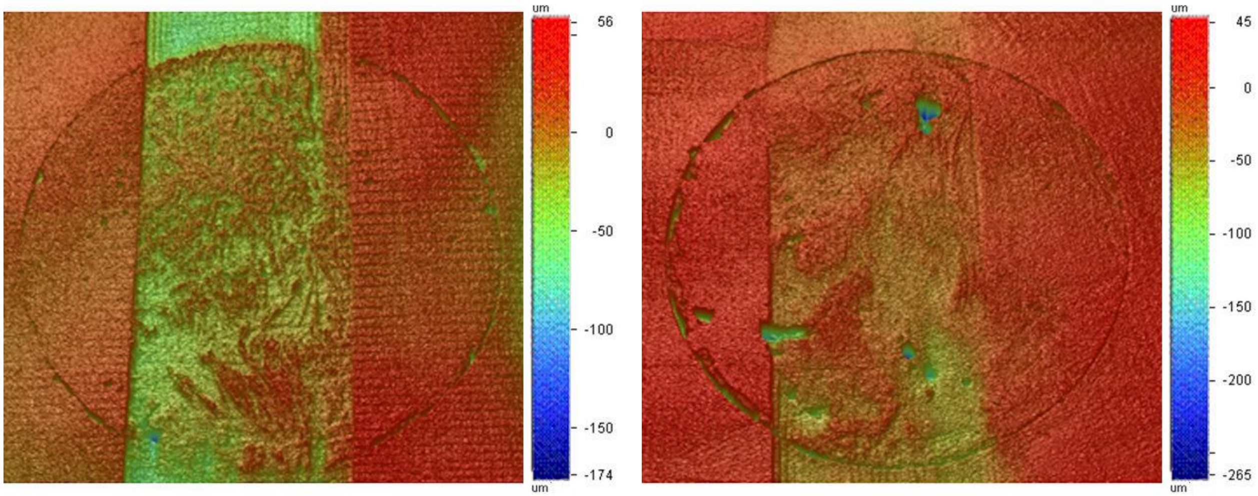


d) Wear track in ST1 after 50,000 TB cycles (max depth 17 µm)



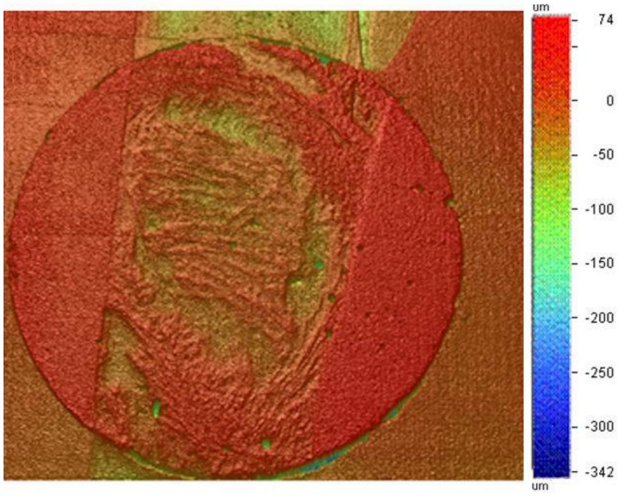
e) **Wear track in ST2 after 50,000 TB cycles (max depth 70 µm)**

f) Wear track in ST3 after 50,000 TB cycles (max depth 20 µm)

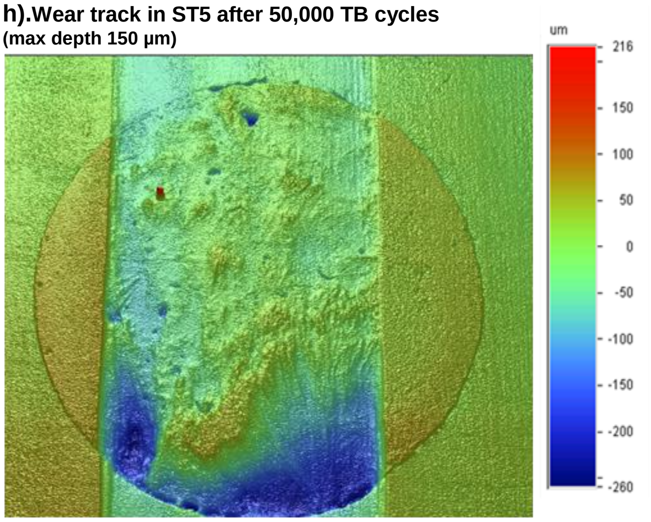


g). Wear track in ST4 after 50,000 TB cycles (max depth 75 µm)

h).Wear track in ST5 after 50,000 TB cycles (max depth 150 µm)



i) Wear track in ST6 after 50,000 TB cycles (max depth 100 µm)



j). Wear track in ST7after 50,000 TB cycles (max depth 260 µm)

Figure 49. Wear tracks in Z250, Build It ST and its derivatives after 24 hours water storage and 50,000 TB cycles.

4.3.3 Conclusions

1. ST shows significantly less wear resistance than either Z250 or Build It after 24 hours water storage.
2. Storage in water for one year had a significant effect on the wear resistance of both Z250 and Build It, but not on ST.
3. Among ST and its derivatives, the highest wear resistance was found in ST1 and ST2.
4. Despite the improvement in ST1 and ST2, ST and its derivatives have significantly less wear resistance than either Z250 or Build It after 24 hours water storage.

Chapter 5. Material Characterisation as a Dentine Replacement

5.1 **Material Characterisation**

This chapter deals with the physical characterisation of ST regarding its polymerisation shrinkage and water sorption. The names and constituents of the materials used are listed in Table 13.

Material	**Manufacturer**	**Lot Number (s)**	**Composition (% by weight)**
ST (An Experimental FRC)	StickTech, Finland	D7.002 D7.003	21% Resin (PMMA + Bis-GMA/TEGDMA =60/40 + initiators) 19% Everstick fibres (8mm) 60% Filler (silica particles) 79% Total inorganic material content (fibres and fillers together)
Z250 (PFC)	Filtek Z250 3M ESPE Dental Products St Paul, MN,USA	9WF 20090327	18 % Resin consisting of BIS-GMA, UDMA, and Bis-EMA 82 % Filler (silica and zirconia particles , with particles ranging from 0.01 to 3.5 µm)
Build It (FRC)	Build IT FR Core material (dual cured) Pentron Clinical, Wallingford, CT, USA	157279	32% Resin (mixture of Bis-GMA, UDMA and HDDMA) 68% Fillers [Mixture of bariumborosilicate, calcium alumino-fluro-silicate, silica and chopped glass fibres (10 – 40 µm in length)]

Table 13. Names, manufacturers and components of materials tested.

Where PMMA = Polymethymetacrylate, Bis-GMA = Bisphenol-A -diglycidyl ether dimethacrylate, TEGDMA = tri[ethylene glycol] dimethacrylate, UDMA = urethane dimethacrylate, Bis- EMA = Bisphenol-A-polyethylene glycol diether dimethacrylate and HDDMA = 1,6-Hexanediol dimethacrylate

5.2 **Polymerisation Shrinkage**

5.2.1 Materials and Methods

The materials used in this study are detailed in Table 13. It is worth noting that ST was supplied as 1-1.5 mm thick sheets in light proof boxes, while Z250 was supplied in composite syringes and Build It was supplied in auto-mix cartridges (see appendix A).

To measure the polymerisation shrinkage, the bonded disc method (Watts *et al.*, 1991) was used. Unset dental composite resin discs measuring approximately 9-10 mm in diameter by 1 mm in depth were produced using a split ring shaped PTFE spacer with an internal diameter of 12 mm. The spacer was made of a 1.0 mm thick rectangular PTFE sheet with a tolerance of -0 to +.15mm (Direct Plastics Online Limited, UK) into which a 12 mm diameter hole had been cut. The spacer was then cut in half to allow its removal before measurement began. The spacer was placed on an optically pure glass slide manufactured to British Standard BS7011 part 2, slides, 19 (Chance Glass Limited, UK) and the uncured composite resin was dispensed into the cut out area of the spacer, leaving a free perimeter of 2- 3 mm. A flexible 0.1 mm cover slip (Chance Glass Limited, UK) was then positioned on top of the slide. Pressure was applied manually using a Perspex block until the uncured material and cover slip were in even contact with the spacer. The set-up is schematically represented in Figure 50.

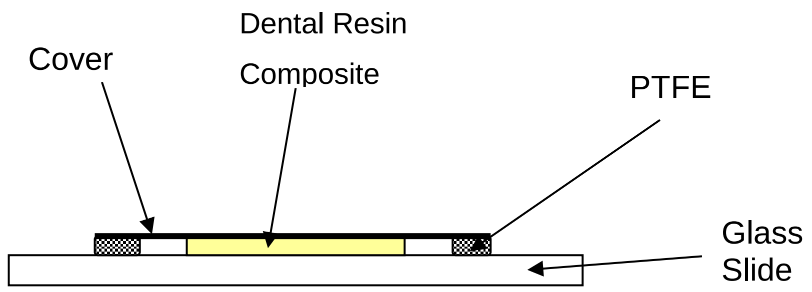


Figure 50. Polymerisation shrinkage sample setup.

The specimen assembly was then secured on a machined brass stand (20 mm high, 24 mm wide, and 100 mm long) using red carding wax on the two edges of the microscope slide, ensuring they did not come into contact with the cover slip. The brass stand had channels 12 mm in diameter to guide the arm of the light cure (Visilux 2 light cure, 3M ESPE Dental Products, USA) into position. To position the fibre optic arm of the light cure, it was guided using the channels in the brass stand until the tip of the light cure came into contact with the lower surface of the microscope slide. A lab clamp was used to secure the light cure, thus ensuring the light cure remained in the same position throughout specimen curing. Once the placement of the setup was complete, the tip of an LVDT transducer core (Sangamo Weston NDI, Sangamo Transducers, UK) was carefully positioned in the centre of the coverslip. The transducer was connected to a signal conditioner (0D3 transducer conditioner, 911040 Schlumberger Industries, tranducer division, UK) which was connected to data-logging software (Instacal Version 1.12, 1998-1999, Computer Boards Inc, USA). The transducer would monitor the movement in the coverslip during polymerisation and for the duration of the experiment. Figure 51and Figure 52 illustrate the set up immediately before light curing took place. To determine the voltage/displacement calibration, the transducer was opposed by a digital micrometer with an accuracy of 1 µm (Mitutoyo, Japan). The micrometer displaced the transducer armature in known increments while monitoring the output recorded in data-logging software. The voltage/displacement calibration factor was then calculated by linear regression.

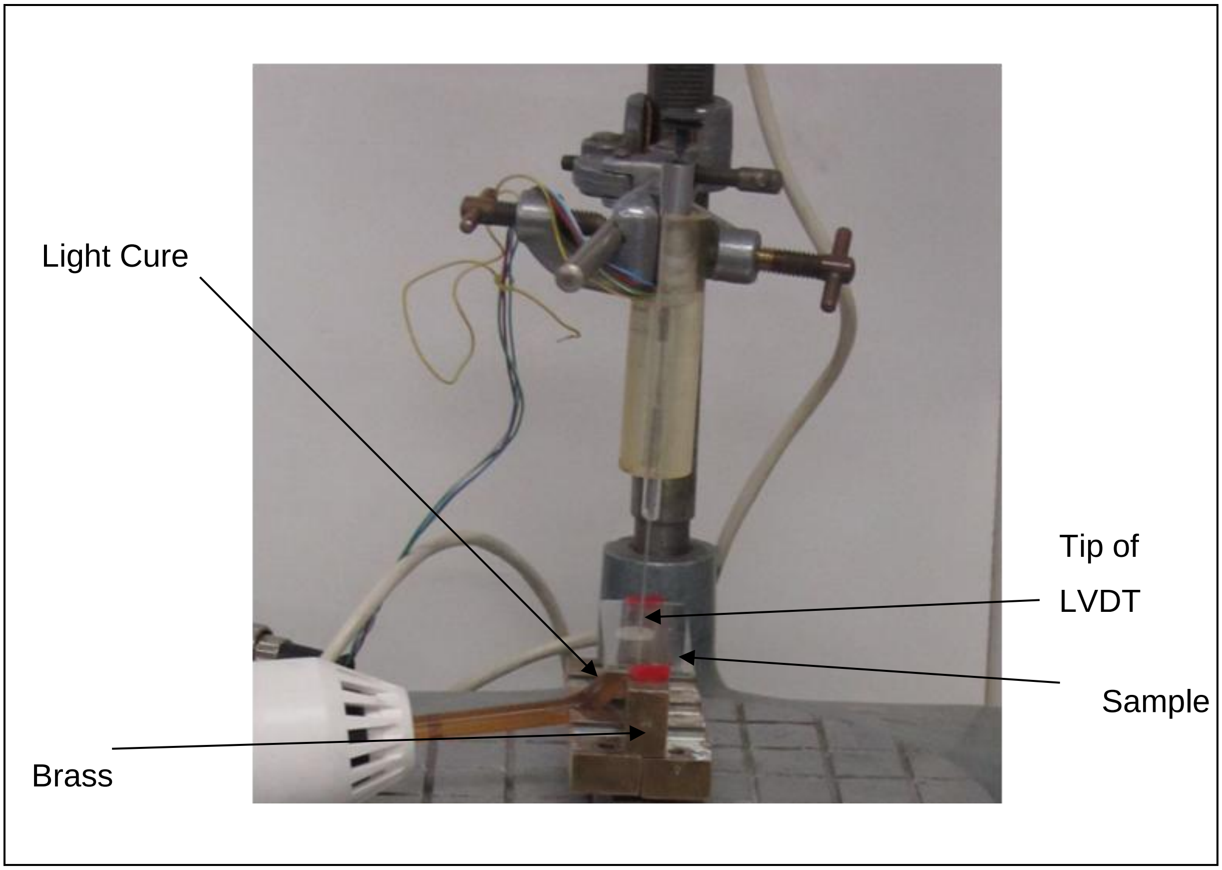


Figure 51. Complete setup of polymerisation shrinkage experiment.

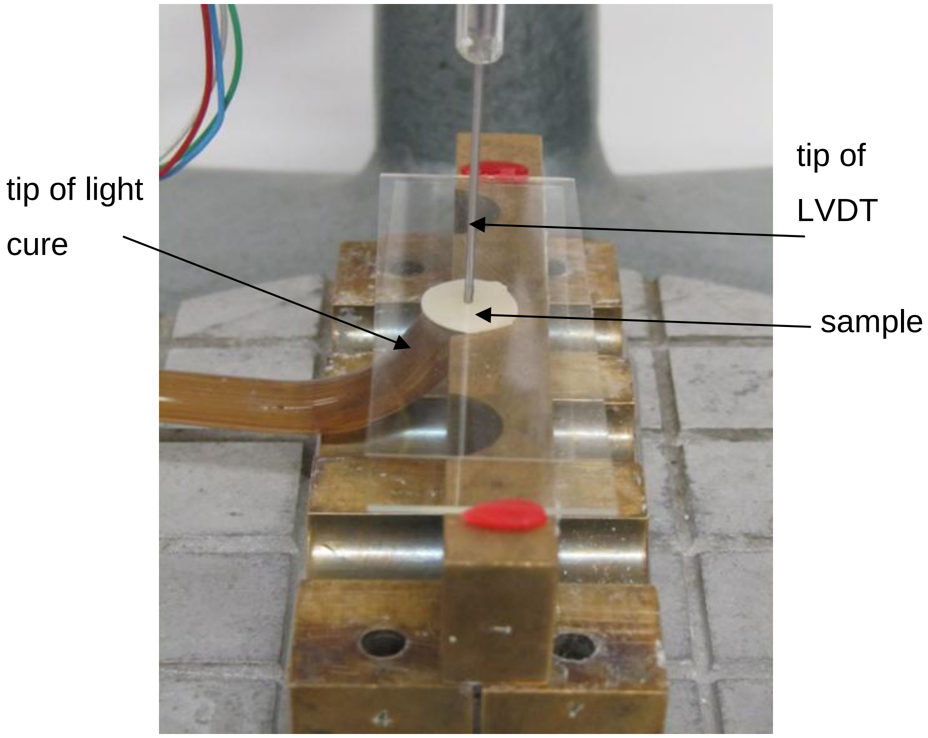


Figure 52. Close up of polymerisation shrinkage experiment setup.

Both ST and Z250 were allowed a five minute temperature equilibration period before testing. This was not possible with Build It as it is a dual cure material, so it was light cured immediately. To begin testing, the specimen was for 40 seconds from directly underneath the dental resin composite. The light intensity used was 500 mw/cm^2 as measured by a Coltolux light meter (Coltene/ Whaledent). The cover slip was pulled axially downwards as shrinkage took place, and the displacement at the centre of the cover slip was monitored over time (1 h) by the LVDT transducer. Data was acquired at 20 seconds before curing, immediately after curing, then at 5, 15 and 60 minutes after curing. The deflection of the cover slip and specimen was determined using the data via the voltage/displacement calibration. $dL = L_0 – L$ where L_0 is the original thickness and L is the final thickness. The percentage shrinkage was calculated immediately after curing, then 5, 15 and 60 minutes after curing to determine the polymerisation shrinkage over time.

Despite the fact that Build It is a dual-cured material, it was light cured while testing its polymerisation shrinkage. This decision was based on studies which observed no significant difference in the polymerisation shrinkage of dual cured materials after one hour whether they were activated by light curing or allowed to chemically cure (Rueggeberg and Caughman ,1993; Feng and Suh, 2006).

SPSS Statistics 17 (released August 2008) was used for the analysis of the data. A Shapiro Wilk test was done to test the normality of the data distribution. As the data was normally distributed, a one-way ANOVA (at a significance level of 0.05) was applied to results of the material. If a significant difference was found, Tukey's post hoc test was then used to determine its cause.

5.2.2 Results

Table 14 shows the mean percentage of polymerisation shrinkage of each material after 0, 5, 15 and 60 minutes (standard deviation). The results are illustrated in Figure 53.

Material	**Z250**	**ST**	**Build It**
Number of Specimens (n) **Time post curing**	5	5	5
0 min (SD)	1.62 (0.33)	1.42 (0.62)	1.83 (0.35)
5 mins (SD)	1.57 (0.41)	1.41 (0.28)	1.83 (0.81)
15 mins (SD)	1.44 (0.27)	1.46 (0.73)	1.57 (0.61)
60 mins (SD)	1.44 (0.27)	1.46 (0.73)	1.57 (0.61)

Table 14. Mean Percentage of Polymerisation Shrinkage Values.

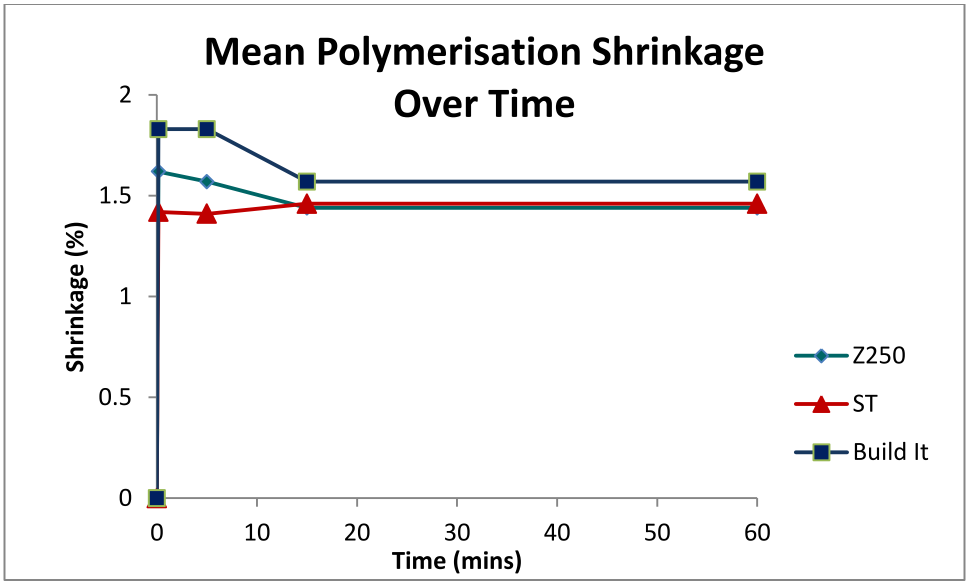


Figure 53. Polymerisation shrinkage Z250, ST and Build It over 1 hour post curing.

Two-way ANOVA showed no significant effect of time (p = 0.903) or material type (p= 0.197) in this experiment.

Figure 54 represents a single run of the polymerisation shrinkage experiment for each of the three materials

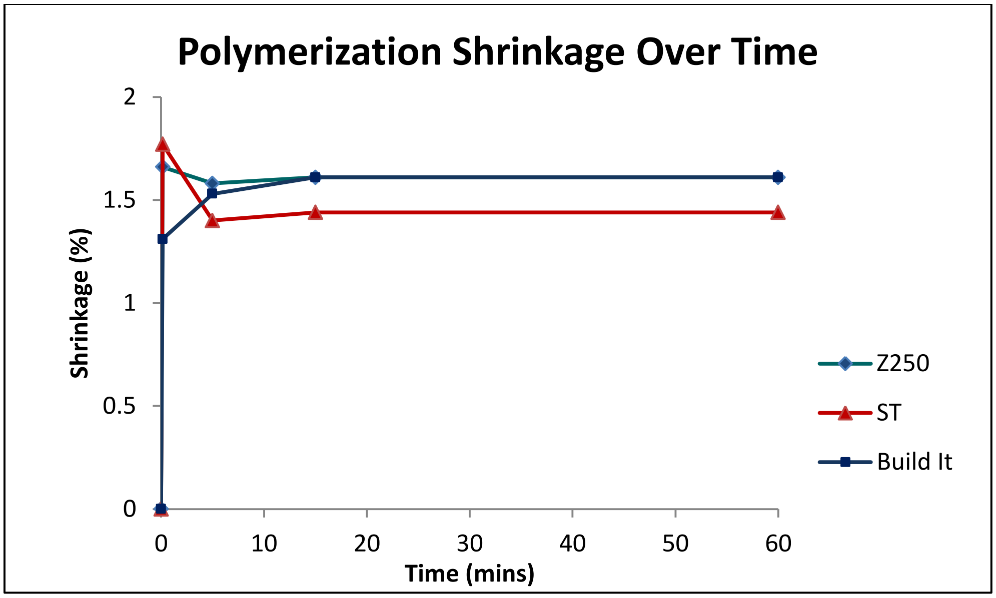


Figure 54. Polymerisaton shrinkage of Z250, ST, and Build It over 1 hour post curing

5.2.3 Conclusions

1. There was no significant difference between the polymerisation shrinkage of any of the materials tested.
2. Time between one minute and one hour did not play a significant role in the amount of polymerisation shrinkage of any of the materials tested.

5.3 **Water Sorption**

5.3.1 Materials and Methods

Table 13 outlines the materials used in this study.

Based on the ISO standard 4049:2000 method for water sorption testing, 10 circular discs (1 mm thick and 10 mm in diameter) of each material (Build It, Z250 and ST) were made by using circular PTFE moulds. The samples were placed in a desiccator with silica gel and then which put into a 37°C oven for 24 hours. The desiccator was then removed from the oven. After maintaining the desiccator at room temperature (23°C) for two hours, the samples were removed and weighed hourly on an electronic scale until a constant weight was obtained for each. A constant weight was achieved when the mass change of each specimen did not exceed 0.1 mg in any 24 hour period. This weight was designated as m_1. Once a constant weight was obtained, the samples were stored in distilled water in a 37°C oven and measured daily until a constant saturated weight was obtained. To weigh each specimen, it was removed from the oven, washed with water, blotted dry until the surface appeared free of visible moisture and air dried for 15 seconds by waving it gently whilst being held by tweezers. The specimen was then immediately weighed (approximately 1 minute after removal from the oven). Once a constant saturated weight was reached, it was designated as m_2. In this work, m_2 was arrived at by the end of two weeks for ST and three weeks for Build It and by the end of the fourth week, m_2 had been achieved for all the specimens. They were then reconditioned to a dry constant mass using a desiccator as described above. The constant mass was designated as m_3.

The volume (V) for each sample was then calculated in cubic mm. The average thickness of each cylindrical sample was determined by measuring the thickness in the centre of each sample as well as 4 equally spaced points around the circumference. The water sorption (W_{sp}) could then be calculated, in μg/mm^3, using the following equation:

Equation 3. Water Sorption (W_{sp})

$$\mathrm{Wsp} = (\mathrm{m2} - \mathrm{m3})/\mathrm{V}$$

SPSS Statistics 17 package was used for the analysis of the data. A Shapiro Wilk test was done to test the normality of the data distribution. As the data was normally distributed, a one-way ANOVA (at a significance level of 0.05) was applied to results of the material. If a significant difference was found, Tukey's post hoc test was used to determine its cause.

5.3.2 Results

Table 15 shows the mean water sorption for each material, illustrated in Figure 55. Table 16 compares the values of m1 and m3 in all three materials.Figure 56 shows the percentage mass change over time for each of the three materials tested..

Material	**Z250**	**ST**	**Build It**
n	10	10	10
Mean Water Sorption (SD)	8.8 (1.2)	20.5 (2.79)	9.3 (2.3)

Table 15. Mean water sorption (µg/mm^3) of Z250, ST and Build It.

Material	**Z250**	**ST**	**Build It**
m$_1$ (SD)	264.76 (24.99)	233.55 (31.90)	283.76 (15.52)
m$_3$ (SD)	265.32 (25.16)	233.08 (32.99)	283.93 (15.67)

Table 16. Comparison of mean m$_1$ and m$_3$ (µg)

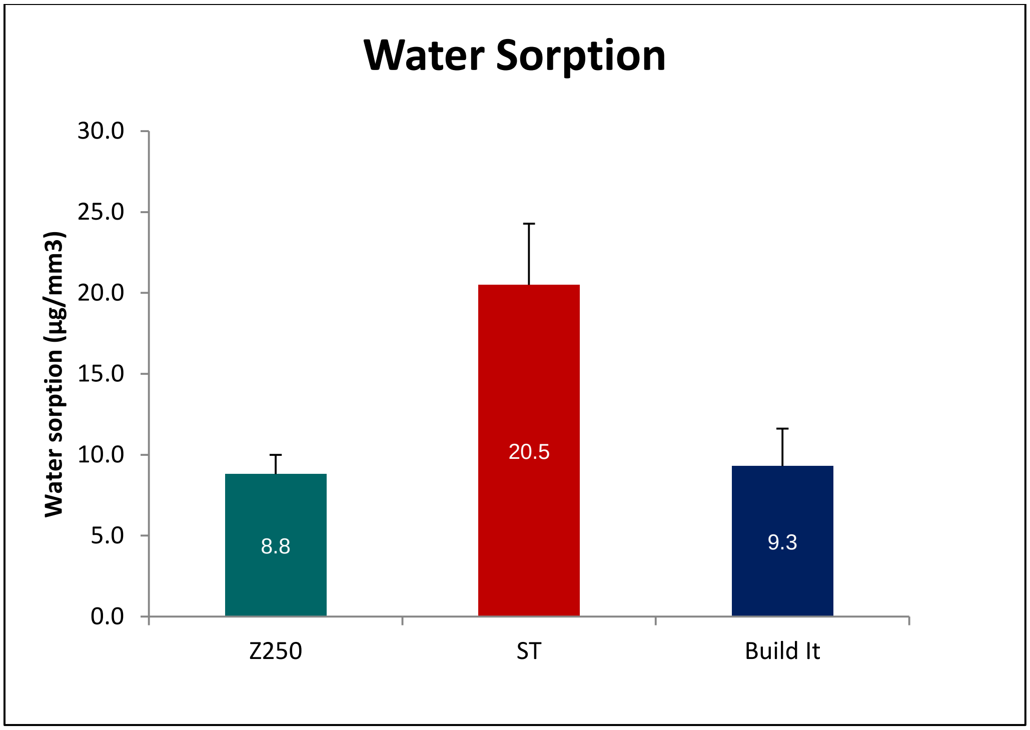


Figure 55. Water Sorption (µg/mm^3) of Build It, ST and Z250 (Error bars show SD).

One-way ANOVA showed a significant difference between the materials tested ($p<0.05$). Tukey's test showed that ST had a significantly higher amount of water sorption after one month compared with Z250 and Build It. Table 17 shows the homogenous subsets resulting from the analysis. Materials in the same column are statistically similar to one another, while a significant difference exists between those in different columns.

Material	**n**	**Subset for Alpha = 0.05**	
		1	2
Z250	10	0.8761	
Build It	10	0.9309	
ST	10		2.946
Significance	__	0.992	1.00

Table 17. Homogenous Subsets in water sorption.

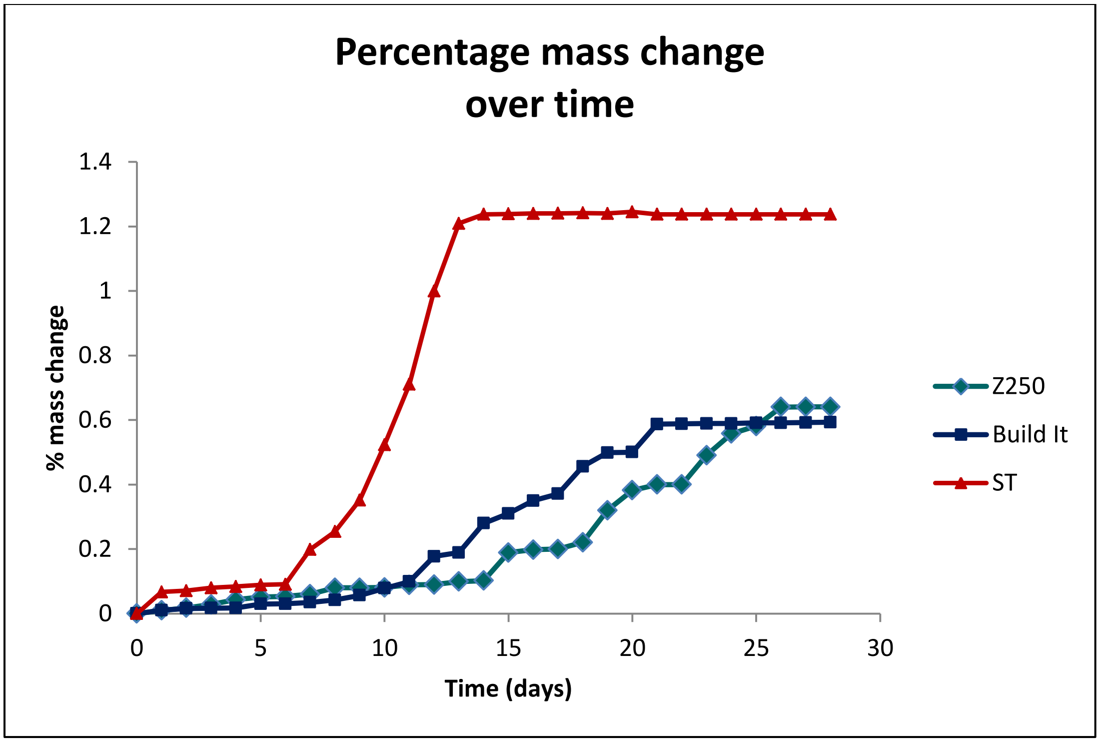


Figure 56. Percentage Mass change over time

5.3.3 Conclusion

The experimental FRC had significantly more water sorption than either of the two materials tested. All the materials tested complied with the first requirement of ISO 5.2.10 as their water sorption was less than 40 µg/mm^3.

Chapter 6. Interfacial Strength

6.1 **Interfacial Strength**

This chapter details the materials, methods and results of the interfacial strength testing to human dentine using an adhesive and testing the interfacial strength between composite increments. The results are discussed in section 7.3.3.

6.2 **Bond Strength to Human Dentine**

6.2.1 Materials and Methods

Along with the materials listed in Table 13, a flowable composite (Stick Flow) was also used. As with ST, Stick Flow is also manufactured by Stick Tech in Finland and is made up of a Bis-GMA/TEGDMA resin with barium glass particles as fillers. The filler loading is 61% by weight.

Stick Flow was included in the testing due to Stick Tech's recommendation that it be used under ST in dental restorations to allow for maximum surface coverage of the cavity floor. It was considered relevant to test the bond strength of Stick Flow as it would be the dental resin composite which is actually bonded to the tooth structure.

This experiment involved testing the shear bond strength of each composite to human dentine. Upper and lower premolars which had been extracted within the last 3 months and stored in a 1% Chloramine T solution were used. 160 caries-free premolars were oriented coronally and potted in self cure resin (Bonda clear casting resin, Bondglass-voss Ltd, UK) to create cylinders 30 mm in diameter and 20 mm high for mounting in the shear bond testing jig. The resin was allowed to set for at least 8 hours. After the resin set, the occlusal side of each specimen was ground using 600 grit silicon carbide paper (Tri-M-ite Wet or Dry paper,3M,St Paul USA) on a lapping machine (Metaserve prerotary grinder, Betchworth, England) until approximately 8 mm of dentine was exposed. Each specimen was then washed to remove any debris before preparing the dentine surface for composite bonding. 600 grit silicon carbide paper was chosen as it corresponds to an extra fine grit diamond bur (Ferracane *et al*., 2009)

Each tooth was then treated with Adper Scotchbond (3M ESPE, USA) as follows. To ensure the standardisation of the size of the dental resin composite samples, a size 5 (4.5 mm diameter) natural gelatine capsule was used as a mould. The capsule was separated into two halves. A 1 mm thick section was cut off one half of the capsule to form a guide on the dentine surface. Within the guide area of 4.5 mm, each tooth was etched using 35% phosphoric acid for 15 seconds which was placed directly onto the dentine surface using the syringe tips provided with the etchant. The etched area was then rinsed for 15 seconds and dried for 5 seconds using a dental 3-way air/water syringe to provide dry, oil free air. A layer of primer was then added using a microbrush and gently air dried after 5 seconds using the 3-way syringe. Finally a layer of adhesive was applied using a new microbrush and light cured for 10 seconds using a halogen light cure unit (Visilux 2 light cure, 3M ESPE Dental Products, USA). The other half of the capsule was filled with composite no longer suitable for clinical use and light cured for 60 seconds, leaving a 2 mm space for the test composite. A fresh increment of the desired test composite was then placed into the 2 mm space. The capsule was then held vertically and placed centrally onto the prepared dentine. Excess material was removed using a clean plastic filling instrument. The test composite in the capsule was subsequently light cured on four sides for 20 seconds a side to maximise curing. Four groups of specimens were prepared (n=40/group). The groups were Z250/dentine, Build It/dentine, ST/dentine and Stick Flow/dentine.

Each group of samples was then split into two subgroups (n=20). One set of four subgroups was stored in distilled, deionised water in a 37˚C oven for 24 hours, while the other was stored for 1 year, with the water being changed weekly.

Once the samples were removed from the oven, they were tested in shear using an ISO standard test (ISO 10477) in an Instron 5567 (Instron Series IX Automated Materials Tester, version 8.15.00, USA) (Figure 57). A 1.0 kN load cell and a cross head speed of 1.0 mm/min were used. Each sample was placed in the shear bond testing jig with a knife edge blade (Figure 58) and mounted on the load frame. A compression force was subsequently applied until the bond between the composite sample and substrate failed and the specimen broke. The jig’s blade was cleaned and visually examined after each specimen was tested. That ensured that excess material was removed before testing a new specimen as well as the integrity of the blade throughout testing. Bluehill 2 material testing software for universal testing systems (version 2.18, 2005 Instron, UK) was used to run the experiment and record the results. The software determined the load at which the specimen failed and converted it to shear bond strength using the following equation

Equation 4. Shear Bond Strength (SBS)

$$\mathrm{SBS} = \mathrm{Load}/\pi \mathrm{r}^2$$

Where SBS is the shear bond strength in MPa

Load is the load at which the specimen failed in Newtons

$\pi = 3.14$

r is the radius of the sample in mm

The type of failure was determined using a stereomicroscope at 40x magnification. Failures were classified as adhesive (located in the adhesive layer between the dental resin composite and the dentine), cohesive (located in dentine or in the resin composite), or mixed (failures which were partially ‘adhesive’ between tooth and composite and partially cohesive).

SPSS Statistics 17 was used for the analysis of the data. A Shapiro Wilk test was done to test the normality of the data distribution. As the data was normally distributed, a one-way ANOVA (at a significance level of $p < 0.05$) was applied to results of the material and Tukey’s post hoc test was used to determine which materials caused a significant difference if found. Two-way ANOVA was used to determine if prolonged water storage had an effect. All pre-test failures were excluded from statistical analysis.

Figure 57. Instron 5567 used for shear bond strength (SBS) testing.

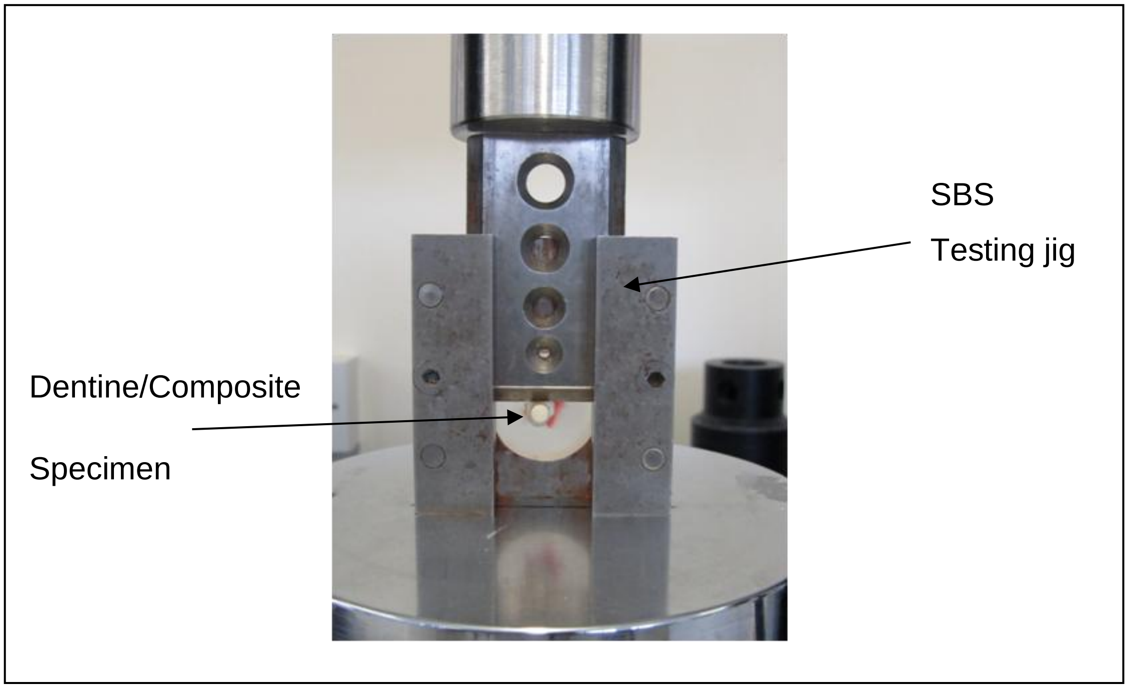


Figure 58. Dentine/Composite Sample on SBS testing jig.

6.2.2 Results

1. *After 24 hours water storage*

Table 18 shows the mean SBS of the human dentine/composite groups after 24 hours water storage in MPa, illustrated in Figure 59. There were no pre-test failures in any of the groups tested, thus n = 20. Typical load displacement curves are presented in appendix B1

Group	**Dentine/Z250**	**Dentine/ST**	**Dentine/ Stick Flow**	**Dentine/Build It**
Type of failure	60% adhesive failure 20% mixed failure 20% cohesive failure(in dentine)	100% adhesive failure	80% adhesive 20% cohesive failure (in dentine)	90% adhesive failure 10% cohesive failure (in dentine)
n	20	20	20	20
Mean SBS (SD)	17.3 (3.5)	10.7 (5.5)	13.5 (3.2)	14.0 (4.4)

Table 18. SBS (MPa) of Dentine/Composite Groups after 24 hours of water storage.

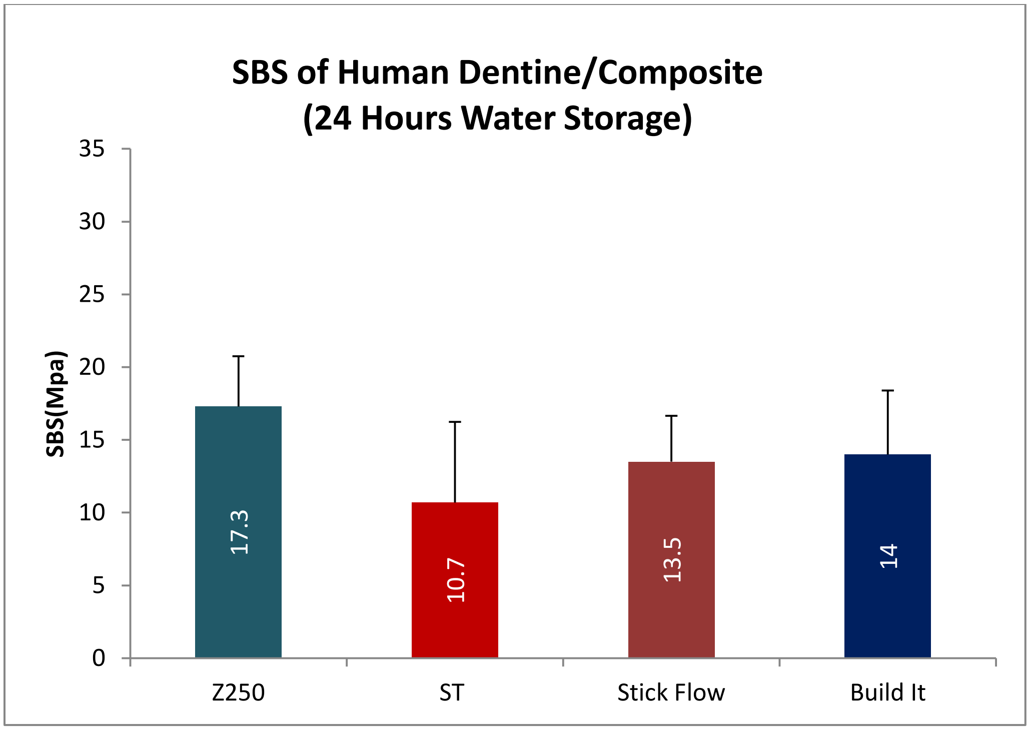


Figure 59. SBS of tested composites to human dentine after 24 hours water storage (error bars represent SD).

A significant difference was found using one-way ANOVA (p=0.035). Tukey's post hoc test showed that Dentine/ST and Dentine/Stick Flow had significantly weaker bond than Dentine/Z250 (see Table 19).

Dentine/Material Group	**Subset for Alpha = 0.05**	
	1	2
Dentine/ST	10.7	
Dentine/Stick Flow	13.5	
Dentine/Build It	14.0	14.0
Dentine/Z250		17.3
Significance	0.077	0.078

Table 19. Homogenous Subsets in Dentine/Composite Groups.

2. *After 1 year water storage*

Table 20 shows the mean shear bond strength of the dentine/composite groups after 1 year of water storage, illustrated in

Figure 60. All pre-test failures were excluded from statistical analysis,thus varying n. Appendix B2 shows typical load displacement curves.

Group	**Dentine/Z250**	**Dentine/ST**	**Dentine/ Stick Flow**	**Dentine/Build It**
Type of Failure	80% adhesive 20% cohesive (in dentine)	100% adhesive	100% adhesive	90% adhesive 10% cohesive (in composite sample)
N	19	17	16	19
Mean SBS (SD)	16.9 (5.7)	9.6 (5.1)	11.6 (4.5)	14.8 (4.3)

Table 20. Mean SBS (MPa) of Dentine/Composite Groups after 1 year water storage.

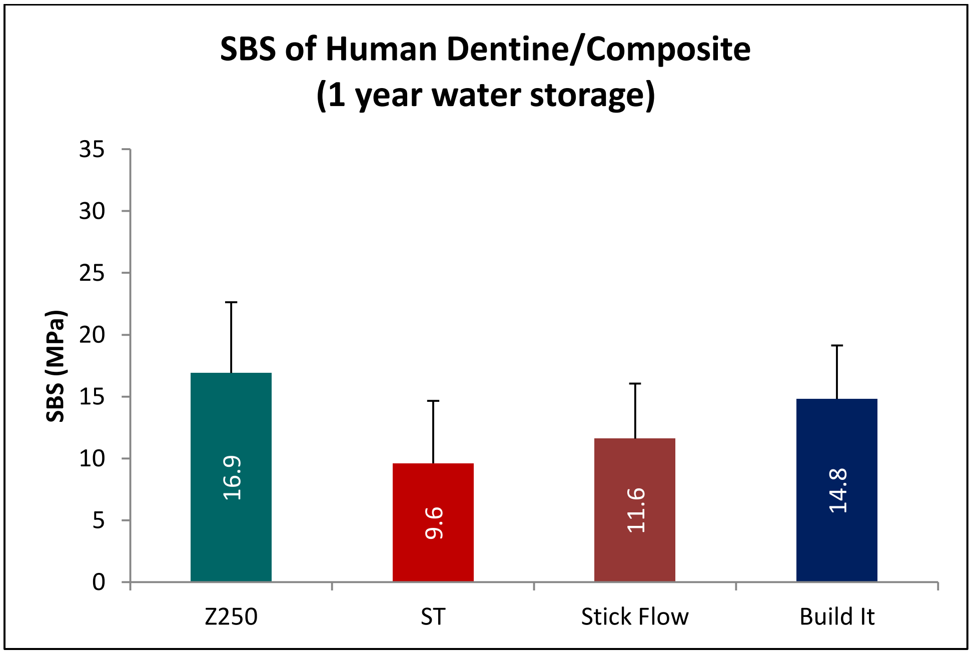


Figure 60. SBS of tested composite groups after 1 year water storage (error bars represent SD).

One-way ANOVA showed a significant difference between groups ($p \leq 0.001$). Tukey's post hoc test showed that Dentine/Z250 and Dentine/Build It had significantly higher bond strength than Dentine/ST (see Table 21).

SBSMat	**Subset for alpha = 0.05**		
	1	**2**	**3**
Dentine/ST	9.6		
Dentine/Stick Flow	11.6	11.6	
Dentine/Build It		14.8	14.8
Dentine/Z250			16.9
Significance	.800	.236	.574

Table 21. Homogenous Subsets of Dentine/Composite Group after 1 year water storage.

A Weibull probability plot was drawn to estimate the characteristic strength and compare the failure probability of the materials (Figure 61 and Figure 62). The characteristic strengths are shown in Table 22.

Dentine/Composite Group	Characteristic Strength after 24 hours (MPa)	5% Failure probability after 24 hours (MPa)	Characteristic Strength after 1 Year (MPa)	5% Failure probability after 1 Year (MPa)
Dentine/Z250	18.58	9.36	18.81	5.26
Dentine/Build It	15.54	6.15	16.32	6.07
Dentine/ST	12.03	1.24	11.38	1.20
Dentine/ Stick Flow	14.63	5.32	13.02	3.53

Table 22. Characteristic Strengths of Human Dentine/Composite Groups.

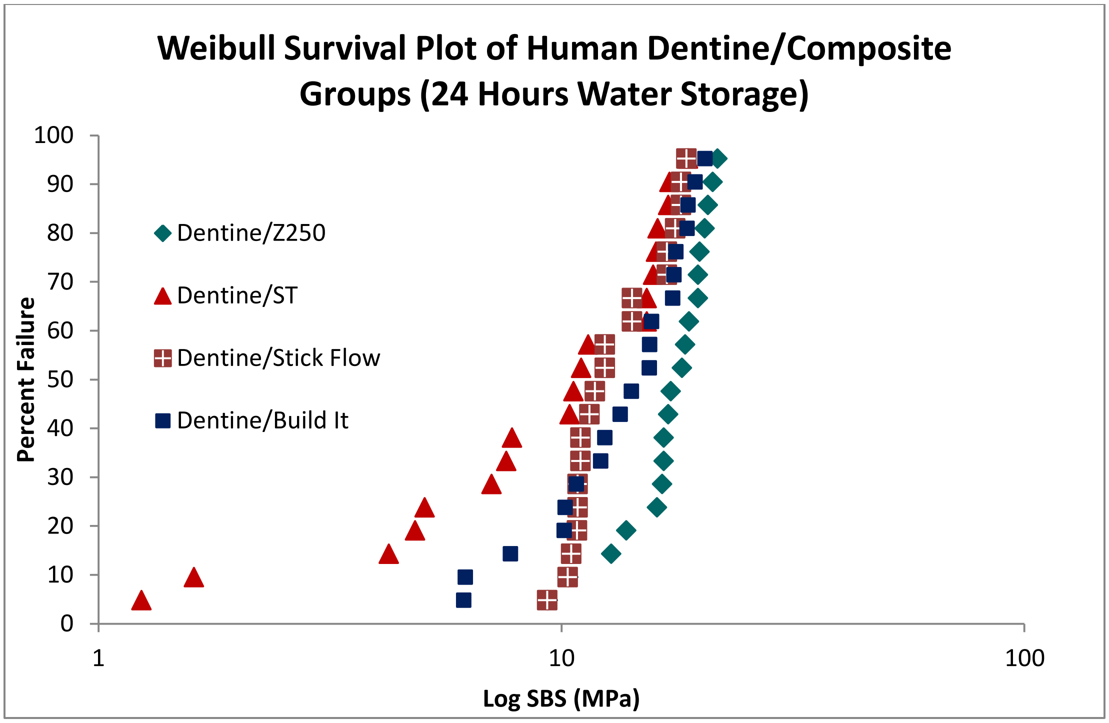


Figure 61. Weibull probability plot of SBS failure of dentine/composite groups after 24 hours water storage.

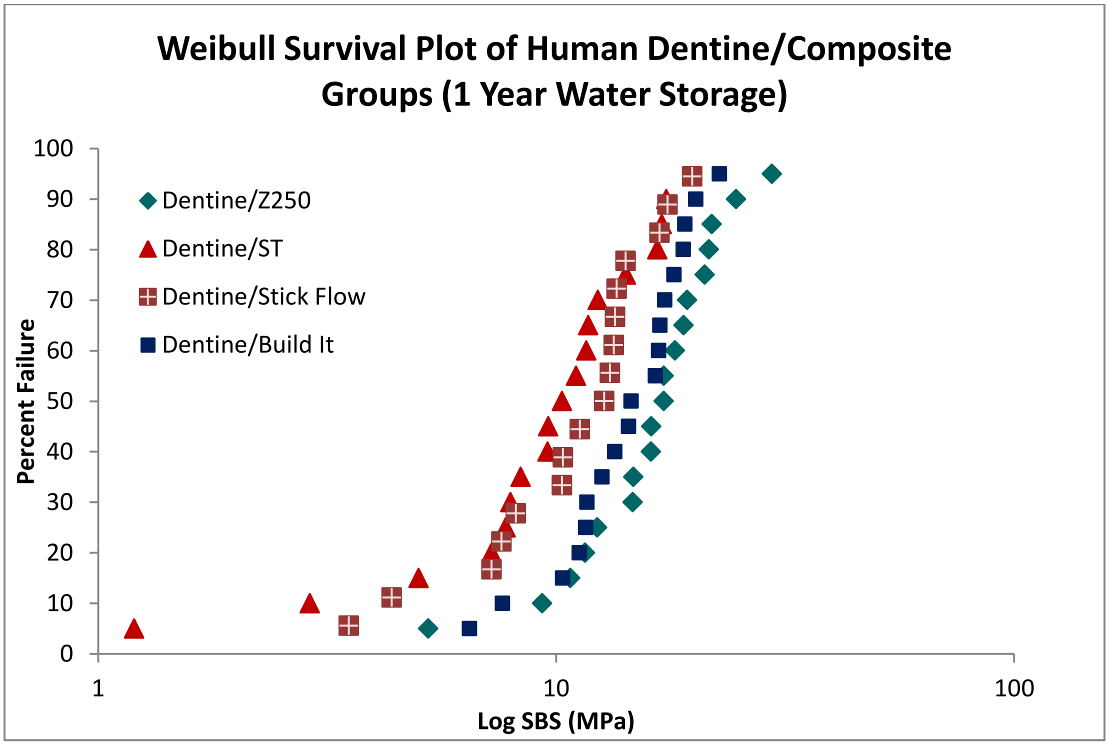


Figure 62. Weibull Probability Plot of SBS failure of dentine/composite groups after 1 year water storage.

6.2.3 Conclusions

1. Dentine/Z250 and Dentine/Build It showed significantly higher bond strengths than Dentine/ST, after 1 year of water storage.
2. The Weibull plots indicated the lowest characteristic strength to dentine was exhibited by the experimental material ST, while Z250 had the highest, irrespective of duration of storage.
3. When comparing the 5% failure probability after 24 hours water storage, Dentine/Z250 required the most force before 5% failure, followed by Dentine/Build It, Dentine/Stick Flow and then Dentine/ST. The order changes after 1 year of water storage to Dentine/Build It, Dentine/Z250, Dentine/Stick Flow and then Dentine/ST, with Dentine/Build It and Dentine/ST showing no change in the amount of force withstood before 5% failure.

6.3 **Bond Strength of Composite to Composite**

6.3.1 Materials and Methods

Table 13 shows the constituents of the materials used in this study according to the manufacturers.

Two groups of samples were prepared and tested as described below;

1. ***Lapped composite group:***

The first series tested the shear bond strength of cured and lapped material to fresh composite. This technique has been used to determine SBS between FRC and PFC materials (Lassila *et al.,* 2007). Discs of impression material (2 mm thick, 10 mm in diameter) were potted in cold cure resin to create cylinders (30 mm in diameter, 15 mm in length) for mounting in the shear bond testing jig. Once the resin was set, the impression material discs were removed to reveal a cavity, which would be filled with the desired dental resin composite and light cured using a halogen light curing unit (Visilux 2 light cure, 3M ESPE Dental Products, USA) for 40 seconds. The composite in the cylinder shall be referred to as the composite substrate in this work. The specimens were then finished on the lapping machine (Metaserve prerotary grinder, Betchworth, England) using 500 through to 600 grit silicon carbide paper (Tri-M-ite Wet or Dry paper,3M,St Paul USA). The specimens were then washed and air dried to remove any debris from the finishing process. To complete the specimen preparation, a fresh increment of composite was cured onto the prepared disc with no intermediary layer. This was done using half a natural gelatine capsule with a 4.5 mm diameter (size 4). Half of the capsule was filled with composite no longer suitable for clinical use and light cured, leaving a 2 mm space for the test composite. A fresh increment of the desired test composite was then placed into the 2 mm space. The capsule was then held vertically and placed centrally onto the composite substrate. Excess material was removed using a clean plastic filling instrument. The test composite in the capsule was subsequently light cured on four sides for 20 seconds a side to ensure a complete cure. A schematic representation is shown in Figure 63.

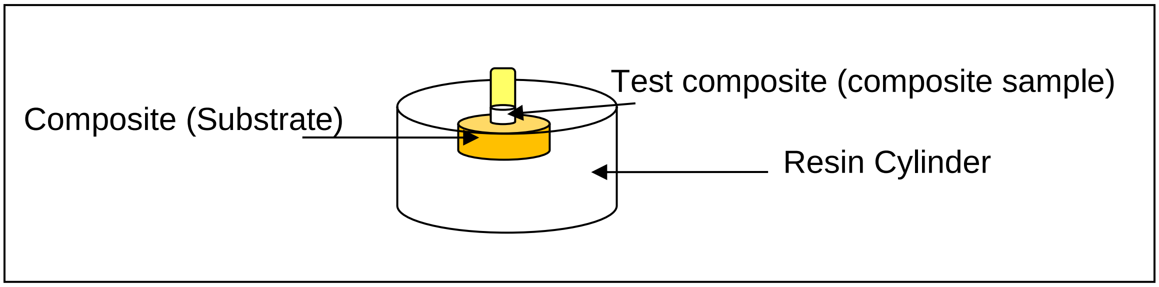


Figure 63. Complete composite sample before testing.

Bonds were formed between Z250/Z250, Build It/Build It, ST/ST, Build It/Z250, ST/Z250 with each group containing 40 specimens. This would test the shear bond strength of each material to itself as well as both the FRCs to a commonly used veneering composite (Z250).

The finished samples from each group were then split into two equal subgroups (n=20):

a. One set of five subgroups was stored in distilled deionised water in a 37°C oven for 24 hours.
b. The other set was stored in distilled deionised water at 37°C for one year. The water was changed weekly.

Once the samples were removed from the oven, they were tested in shear as described in section 6.3.1.Figure 58 shows the completed specimen in the testing jig.

2. Air inhibited group:

While lapped samples have been used to test in vitro SBS of composites due to the reproducibility of the testing parameters, it is not representative of the clinical situation during placement of a composite restoration due to the absence of the oxygen inhibition layer. Thus, the second series examined the shear bond strength of the as-set, air-inhibited surface of a composite to fresh material. This would give an indication of how well the FRC would bond to the PFC veneer materials as well as how well increments within each material would bond to one another in a manner that is more related to the clinical setting. The same five groups (n=20/group) of samples were prepared similarly to those in the previous study. Once again half a size 4 gelatine capsule was filled with composite no longer suitable for clinical use and light cured using a halogen light curing unit (Visilux 2 light cure, 3M ESPE Dental Products, USA), leaving a 2 mm space for the test composite. Once the capsules were prepared, the cavity in resin cylinder had the desired composite substrate placed in it, flattened with a plastic filling instrument and then light cured. A fresh increment of the desired test composite was then placed into the 2 mm space in the gelatine capsule. The capsule was then held vertically and placed centrally onto the freshly cured surface of the substrate. Excess material was removed using a clean plastic filling instrument. The test composite in the capsule was light cured on four sides for 20 seconds a side to ensure a complete cure. The samples were then stored in distilled water in a 37°C oven for 24 hours and tested in shear as described above.

SPSS Statistics 17 was used for the analysis of the data. All pre-test failures were excluded from statistical analysis. A Shapiro-Wilk test was done to test normality of data distribution. As all the data was normally distributed, a one-way ANOVA (at a significance level of 0.05) was then applied and Tukey's post hoc test was used to determine which materials caused a significant difference, if found. Incorporating the SBS results from the previous experiment, two-way ANOVA was used with the factors material and surface preparation (lapped/air inhibited) to determine if there was an interaction.

6.3.2 Results

1. Lapped composite groups

a. After 24 hours

Table 23 shows the mean SBS for the prepared composite groups tested after 24 hours in water storage, illustrated in Figure 64. Pre-test failures were excluded from testing and analysis, thus the difference in 'n' values between groups. Typical load displacement curves are presented in appendix B3.

Materials (specimen/ substrate)	**Z250/Z250**	**Build It/Build It**	**ST/ST**	**Build It/Z250**	**ST/Z250**
Type of Failure	50% Adhesive 50% Mixed	50% Adhesive, 27.8% Cohesive (in specimen) 22.2% Mixed	55% Adhesive, 5% Cohesive (in specimen) 40% Mixed	63% Adhesive 21% Cohesive (in substrate) 16% Mixed	42% Adhesive 10.5% Cohesive (specimen) 47.5% Mixed
n	17	18	19	19	19
Mean SBS (SD)	13.7 (7.0)	14.7 (4.8)	11.0 (7.1)	21.2 (6.07)	14.7 (6.69)

Table 23. SBS (MPa) of Lapped Composite Groups after 24 hours water storage.

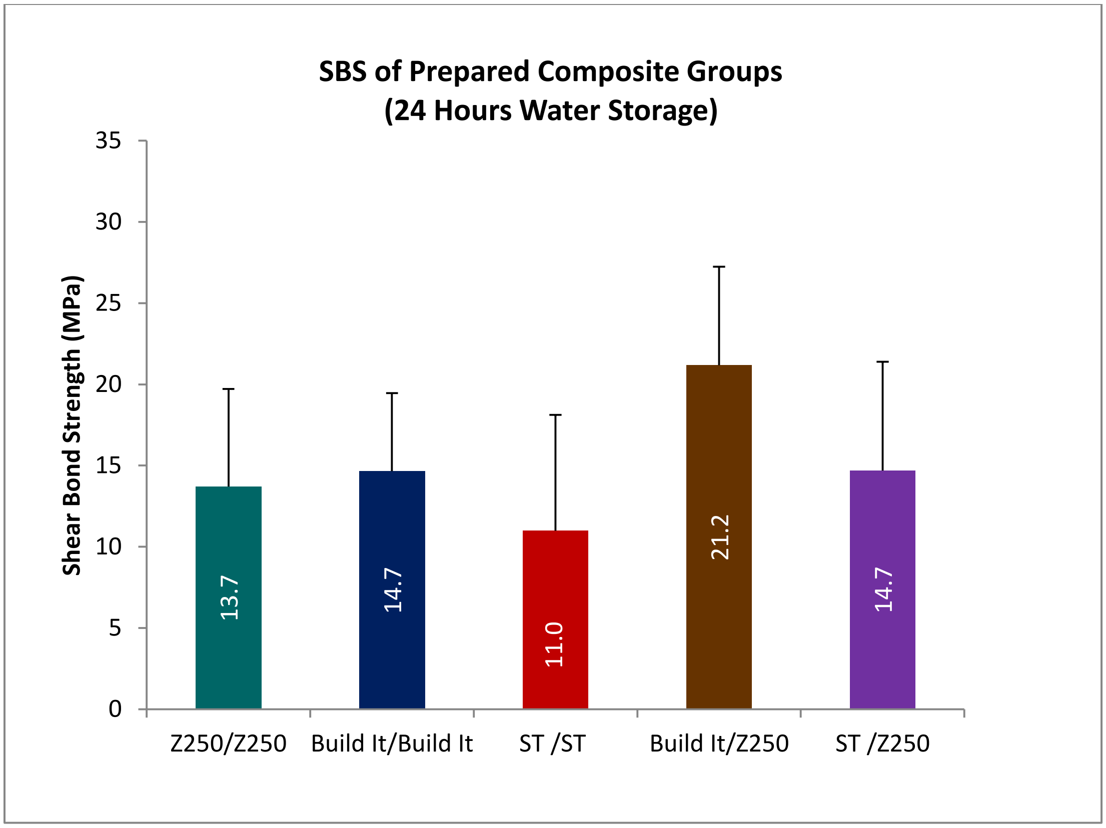


Figure 64. SBS of prepared composite groups after 24 hours water storage.

One-way ANOVA showed a significant difference between the groups (p =0.000). Tukey's post hoc test showed that Build It/Z250 was significantly stronger than any of the other groups (see Table 24).

PrepGrp	n	Subset for alpha = 0.05	
		1	2
ST/ST	19	11.0	
Build It/Build It	18	14.7	
ST/Z250	20	14.7	
Z250/Z250	16	13.7	
Build It/Z250	20		21.2
Significance		.285	1.000

Table 24. Homogenous Subsets in SBS of prepared groups after 24 hours water storage.

b. After 1 year water Storage

Table 25 shows the mean shear bond strengths of the prepared composite groups after 1 year of water storage (rounded to the nearest decimal place), as illustrated in Figure 65. Typical load displacement curves are presented in appendix B4.

Materials (substrate/specimen)	**Z250/Z250**	**Build It/ Build It**	**ST/ST**	**Build It/ Z250**	**ST/Z250**
Type of Failure	95% Adhesive 5% Mixed	45% Adhesive 5%Cohesive 50% Mixed	66.7% Adhesive 11% Cohesive 22.3% Mixed	100% Cohesive	75% Adhesive 25% Mixed
n	20	20	18	20	20
Mean (SD)	10.4(4.42)	12.7 (4.76)	11.0(4.32)	19.0(4.98)	10.0 (4.4)

Table 25. Failure Types and SBS (MPa) of composite/composite groups after 1 year water storage.

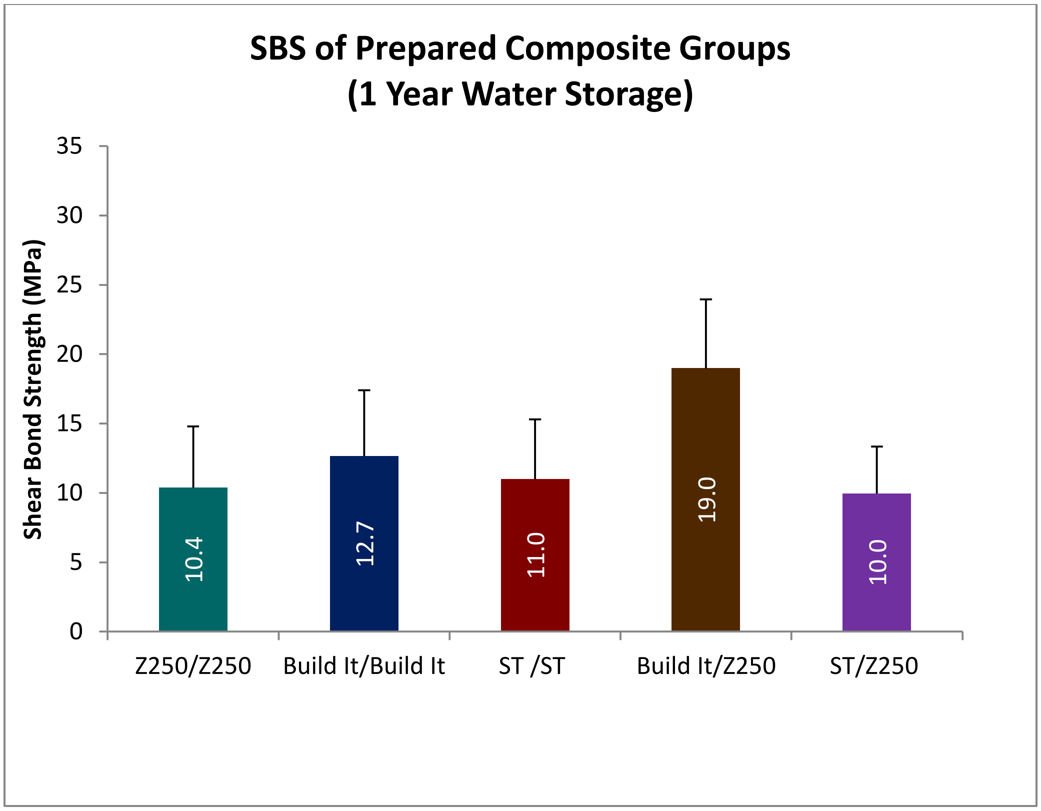


Figure 65. SBS of prepared composite groups after 1 year of water storage (error bars represent SD).

One-way ANOVA showed a significant difference between the materials tested ($p \leq 0.001$). Tukey's post hoc test showed that BuildIt/Z250 had significantly higher shear bond strength than any of the other groups (Table 26). Two way ANOVA showed time had a significant effect on bond strength ($p = 0.016$) with all groups showing a decrease in bond strength after 1 year water storage.

Group	n	Subset for alpha = 0.05		
		1	2	3
ST/Z250	20	10.0		
Z250/Z20	17	10.4		
ST/ST	18	11.0	11.0	
Build It/Build It	19		14.7	
Build It/Z250	20			19.0
Significance		.428	.18	1.00

Table 26. Homogenous Subsets in SBS after 1 year water storage.

Weibull probability plots were drawn to estimate the characteristic strength and compare the failure probability of the materials (Figure 66 and Figure 67). The characteristic strengths are shown in Table 27.

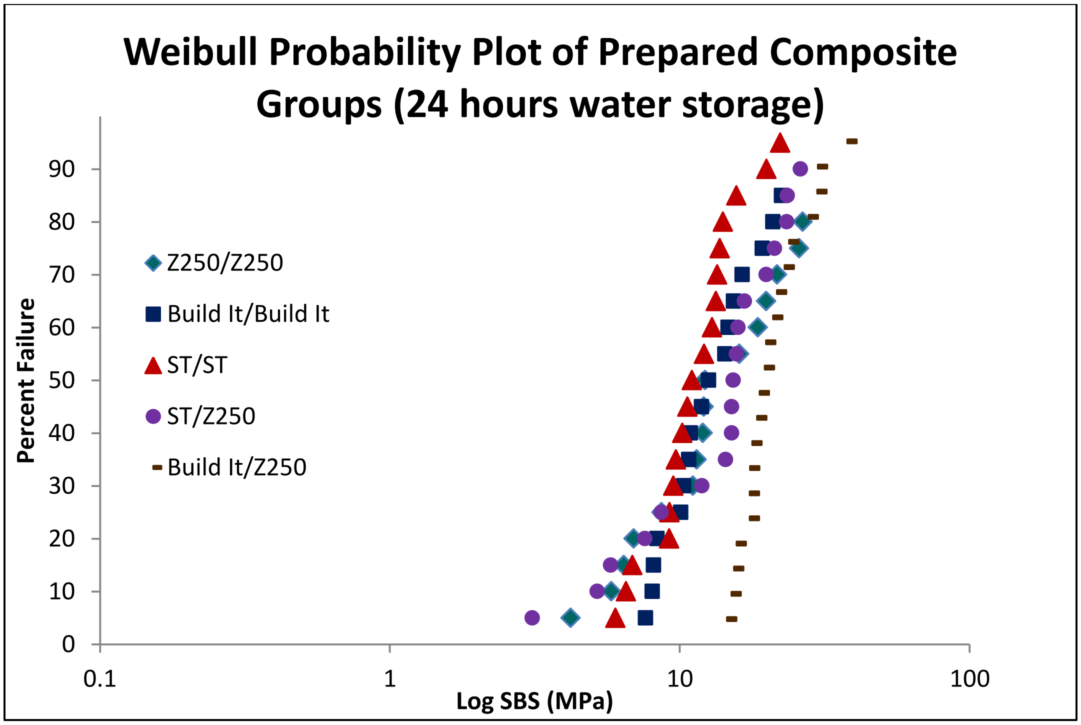


Figure 66. Weibull probability plot of prepared composite groups after 24 hours water storage.

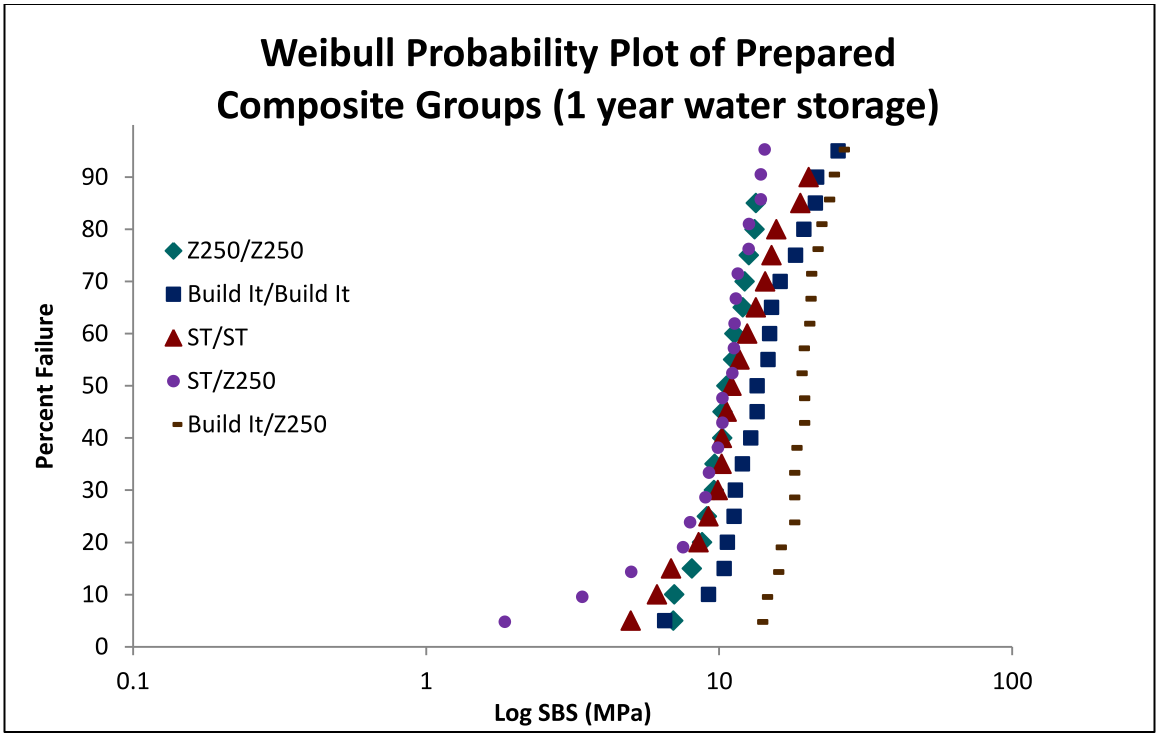


Figure 67. Weibull probability plot of prepared composite groups after 1 year of water storage.

Prepared Mat Group	Characteristic Strength After 24 Hours Water Storage	SBS(MPa) where 5% of samples fail	Characteristic Strength After 1 Year Water Storage	SBS(MPa) where 5% of samples fail
Z250/Z250	15.57	6.98	11.17	4.21
Build It/Build It	14.64	7.63	14.29	6.53
ST /ST	13.34	6.01	13.03	5.03
Build It/Z250	23.42	14.64	20.25	13.06
ST / Z250	16.57	3.10	11.01	1.86

Table 27. Characteristic strengths (MPa) of prepared composite groups.

In the group that was tested after 24 hours of water storage, the lowest Weibull characteristic strength was found in the ST/ST group while Build It/Z250 had the highest. After one year of water storage, the lowest Weibull characteristic strength was noted in the Z250/Z250 group with the highest strength remaining in the Build It/Z250 group.

2. *Air Inhibited Composite Group:*

The mean SBS of the air inhibited groups, rounded to the nearest decimal place, is shown in Table 28 and illustrated in Figure 68. Typical load displacement curves are presented in appendix B5

Composite Group	**Z250/Z250**	**ST/ST**	**Build It/ Build It**	**Build It/Z250**	**ST/Z250**
Type of Failure	58% adhesive 42% mixed	79% adhesive 21% mixed	63% cohesive (substrate) 37% mixed	100% cohesive (substrate)	70% adhesive 30% cohesive (sample)
n	19	19	19	20	20
Mean (SD)	18.4 (6.0)	11.9 (4.5)	18.0 (5.06)	23.3 (5.08)	14.1 (4.43)

Table 28. SBS of Air Inhibited Composite Groups.

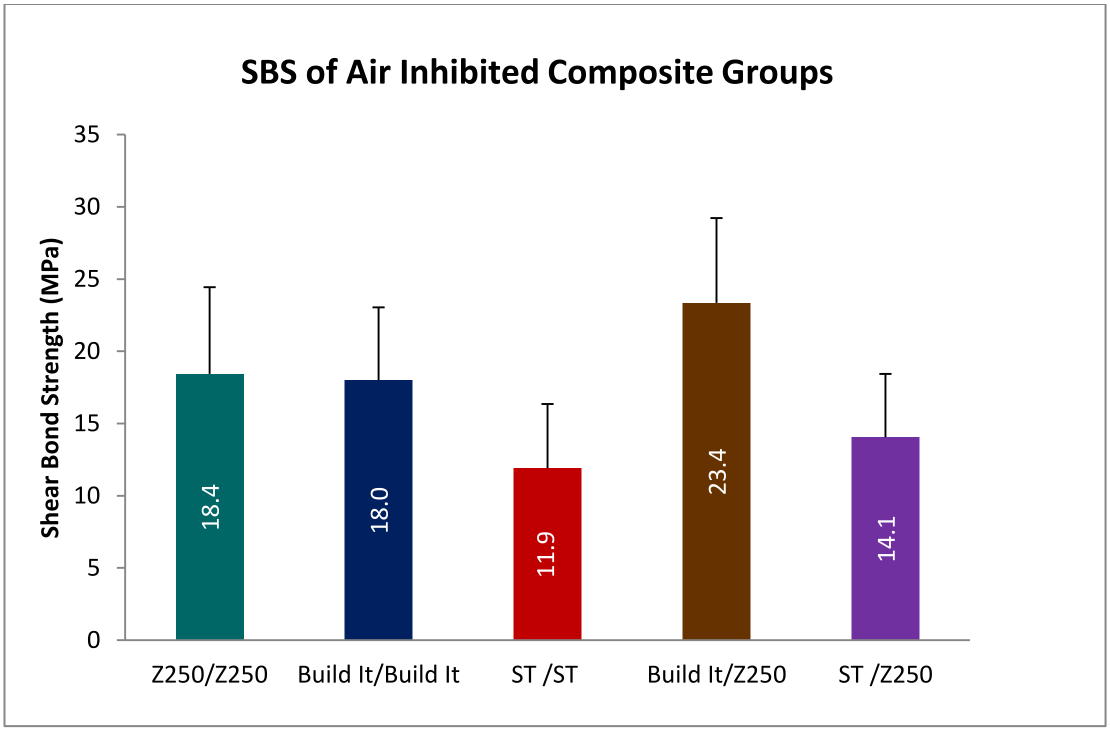


Figure 68. SBS of Air Inhibited Composites.

One-way ANOVA showed a significant difference between the groups (p = 0.00). Tukey's test indicated that ST/ST showed significantly lower bond strength than the remainder of the groups while Build It/Z250 exhibited significantly higher bond strength (see Table 29).

Group	n	Subset for alpha = 0.05		
		1	2	3
ST/ST	19	11.9		
ST/Z250	20		14.1	
Build It/Build It	19		18.0	
Z250/Z250	19		18.4	
Build It/Z250	20			23.3
Sig.		0.664	0.056	1.000

Table 29. Homogenous Subsets in SBS of air inhibited composite groups.

A Weibull probability plot was drawn to estimate the characteristic strength and compare the failure probability of the materials (Figure 69). The characteristic strengths are shown in Table 30.

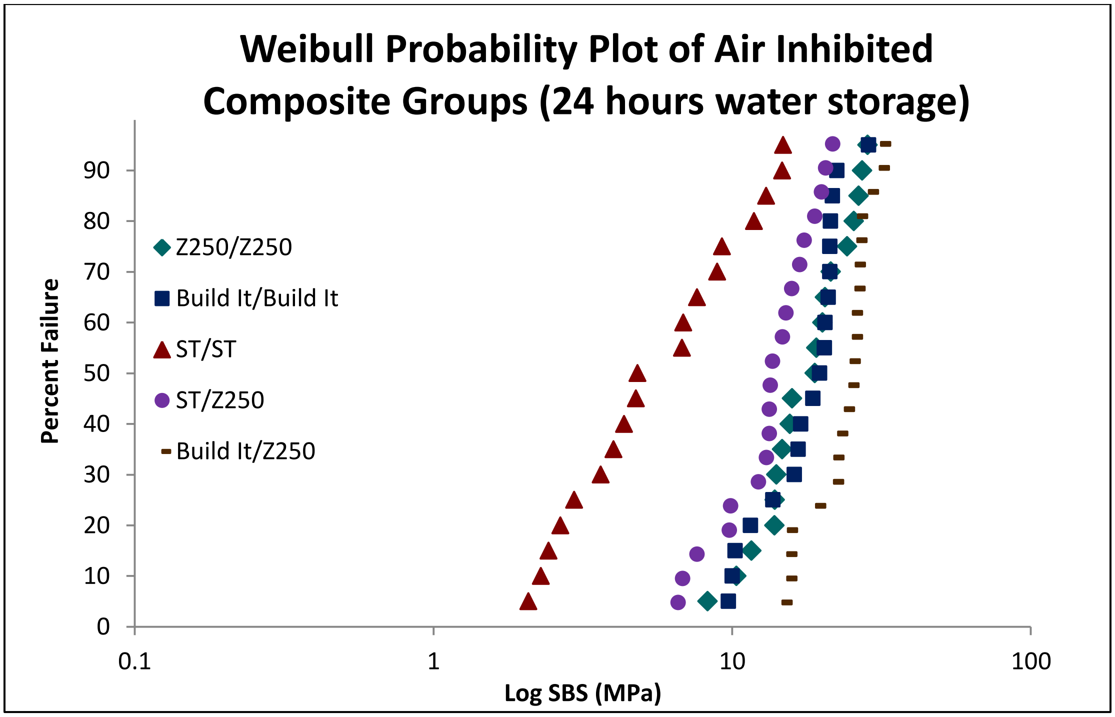


Figure 69. Weibull Probability Plot of Air Inhibited Composite groups.

Air Inhibited Material Group	**Characteristic Strength (MPa)**	**SBS(MPa) where 5% of samples fail**
Z250/Z250	20.54	8.29
Build It/Build It	19.82	9.71
ST /ST	7.60	2.08
Build It/Z250	25.30	14.76
ST / Z250	15.60	6.60

Table 30. Characteristic strengths of air inhibited composite groups.

The prepared groups with 24 hours water storage were compared with the air inhibited groups as shown in Table 31 and illustrated in Figure 70.

Material	**Z250/Z250**	**Build It/Build It**	**ST/ST**	**Build It/Z250**	**ST/Z250**
Mean SBS, lapped (SD)	13.7 (7.0)	14.7 (4.8)	11.0 (7.1)	21.2 (6.07)	14.7 (6.69)
Mean SBS, air inhibited (SD)	18.4 (6.0)	18.0 (5.06)	11.9 (4.5)	23.3 (5.08)	14.1 (4.43)

Table 31. Comparison of Mean SBS of lapped and air inhibited composite groups.

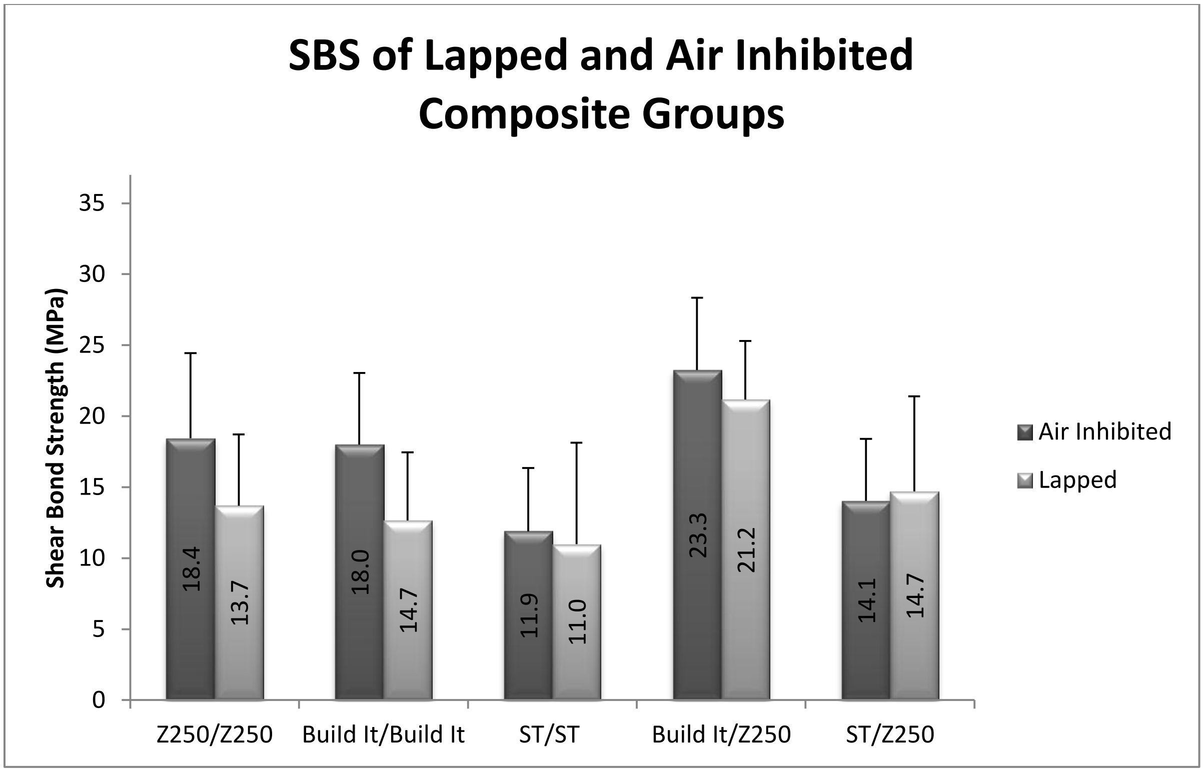


Figure 70. Comparison of SBS of lapped and air inhibited composite groups.

Two-way ANOVA showed a significant difference between the lapped and air inhibited groups ($p \leq 0.001$), with the difference being in the Z250/Z250 and Build It/Build It groups.

6.3.3 Conclusions

1. Build It/Z250 exhibited significantly higher shear bond strength than ST/Z250, irrespective of preparation type or duration of water storage.
2. All lapped groups showed a significant decrease in bond strength after 1 year water storage.
3. The oxygen inhibition layer only had a significant effect on the bond strength of Z250/Z250 and Build It/Build It.

Chapter 7. Discussion

7.1 **Discussion**

This work investigated ST in comparison to two commercial products with regard to its behaviour upon exposure to the oral environment by testing the surface contact fatigue and three body wear. ST derivatives were also tested. However, the poor performance of ST and its derivatives in comparison to the commercially available products ruled out the use of any of the ST formulations in direct contact with the oral environment. Thus, the possibility of using ST was explored by testing its polymerisation shrinkage, water sorption and bond strength to human dentine as well as veneering composites in comparison to the same two commercially available materials. Sections 7.2 and 7.3 will discuss the results of those investigations.

7.2 **Material Testing as a Single Restorative Material**

The demands placed on dental composite materials differ with respect to the cavity type and position in the arch (Beun *et al.*, 2007). Occlusal and proximal restorations require composites with high mechanical properties such as strength, hardness and wear resistance. The success of anterior composite restorations demands excellent aesthetic and mechanical properties. The composite material that fulfils all the criteria has yet to be developed (Beun *et al.*, 2007; Ferracane, 2011).

High wear resistance is an important, almost necessary, property of any dental restorative material directly exposed to the oral environment. While clinical evaluations are the most widely accepted measures of wear resistance (McCabe *et al.*, 2002; Callaghan *et al.*, 2006), it would be ethically unacceptable to test an experimental material such as ST *in vivo* without first assessing its wear characteristics *in vitro.* This is especially true when testing a material such as ST, which was originally manufactured for dentine replacement rather than direct exposure to the oral environment. Thus, *in vitro* testing was carried out to gain a general idea of the ST's wear resistance before any *in vivo* testing was considered. Analysis of the results showed that both the two and three body wear of ST was significantly lower than either one of the comparators.

In an attempt to develop ST as a material that may be directly exposed to the oral environment, fibre lengths and concentrations were changed as was the Bis-GMA/TEGDMA ratio. Small amounts of these materials were made and tested to aid in ST's development. Two main testing regimes were undertaken; surface contact fatigue and three body wear. The objective of the studies was not to simulate the oral environment, but to explore the basic wear mechanisms of these materials under these two specific wear conditions.

7.2.1 Surface Contact Fatigue

Two body abrasive wear, also known as wear due to fatigue, occurs as a result of repeated surface and subsurface stresses by rolling or sliding motions on the restorative material. These stresses lead to crack propagation and loss of material (McCabe *et al.*, 2002). Fatigue testing of dental materials is often carried out using compressive, flexural or tensile testing on bulk specimens (Braem *et al.*, 1995; McCabe *et al.*, 2002; Fujii *et al.*, 2004). While these tests describe the fatigue behaviour of a material up to catastrophic failure, they do not represent the fatigue which contributes to the wear process by increasing the surface breakdown of the material (Braem *et al.*, 1995; Fujii *et al.*, 2004).

In the oral cavity, repetitive cyclic loads onto a restorative material via an opposing tooth or another restorative material may cause surface contact fatigue. The surface of the resin composite is plastically deformed during cyclic loading, generating microcracks that eventually coalesce followed by the subsequent loss of wear particles (Musanje *et al.*, 2006). This can occur during mastication, when opposing teeth come into contact with one another, or during parafunctional movements such as bruxing or grinding. Surface contact fatigue may cause deterioration of the aesthetics of the material, increase roughness, decrease material gloss and contribute to the overall wear process. Thus understanding surface contact fatigue can help determine the longevity of a restoration (Baran *et al.*, 2001; Fujii *et al.*, 2004). This type of behaviour is not predictable using bulk fatigue testing (McCabe *et al*, 2002), so surface contact fatigue rather than bulk fatigue was used to assess ST.

a) Comparing ST to Build It and Z250

ST was compared to both Build It and Z250. Pilot tests showed no measurable surface changes using laser profilometry in any of the three materials until approximately 100,000 rolling ball cycles were completed. So the testing regimen began at 100,000 cycles and continued until 500,000 cycles to allow the estimation of the approximate onset of surface degradation.

ST was able to withstand significantly fewer cycles before showing signs of surface degradation when compared with Z250 and Build It as shown in Table 3. This is most likely due to the fact that ST has E-glass fibres as its reinforcing fibre. E-glass fibres are known to have low resistance to fatigue (Zhang and Matinlinna, 2011). Due to their size, it is probable that the fibres in ST were exposed to the surface of the specimen and thus more prone to fatigue compared with the smaller fibre size found in Build It. The type of glass fibres used in Build It is undisclosed, so it would be difficult to speculate about their inherent fatigue properties. What was noted from results of the experiments presented in this work as well as the SEM image in fig was the relative smoothness of the wear track in Build It.

The images produced by the laser profilometer and the SEM revealed noticeably more voids on the surface of ST than on either one of the comparator materials. These voids may have been introduced during sample preparation as the layers of ST were packed onto one another. As noted in section 4.2.1, ST was supplied in sheets approximately 1-1.5 mm thick which needed to be cut to the required diameter and then placed into the specimen holder in layers to create a 2 mm thick specimen. The production of ST in Stick Tech's laboratory is another area in which voids may be introduced. As noted in section 7.2.1, Stick Tech were aware of the existence of voids in ST during its manufacture and were attempting to address that issue. The location of the voids on the surface of ST leads to the conclusion that they were the result of the manufacturing process rather than the specimen preparation. Defects due to specimen preparation would be at a depth of 0.5 – 1.0 mm from the surface of the sample in the sample rather than on the surface.

The wear track on ST also had a markedly less regular and homogenous appearance after 500,000 cycles. This may be due to higher fibre areas in the material initially preventing surface degradation and forcing a deviation of the circular motion of the ruby ball.

ST, Build It and Z250 were aged for 1 year in distilled deionised water to investigate the effects of water storage on surface contact fatigue. The results showed a significant decrease in the number of cycles required to begin surface degradation in all three materials with ST still being the one with the lowest number of cycles required. A possible explanation of this finding is that water sorption has a limited initial effect and over time contributes to the marked degradation of these materials. This is most likely due to a weakened silane bond between the filler particles and the resin matrix (Al-Turki *et al.*, 2007) resulting in a decrease in the number of cycles until material degradation begins. It has also been found that ageing in water or aqueous fluids decreases the fatigue resistance of polymer-based composites as a result water leaching out filler elements to induce filler failure (Baran *et al.*, 2001). The resin matrix also uptakes water, thus plasticising the matrix and causing hydrolysis of the silane bonding agent (Baran *et al.*, 2001).

Based on the findings presented in this work, ST exhibited a significantly higher surface contact fatigue than either one of the comparator materials, irrelevant of the duration of the water storage. Thus, improving the wear resistance of ST is a desirable objective. In an attempt to do just that, the ST's formulation was changed. The results of those changes are discussed in the following segment of this work.

d) Different ST formulations

The changes in ST's formulation were in three areas; the fibre lengths, resin concentrations and BisGMA/TEGDMA ratio used. Using one-way ANOVA, no significant difference was found between any of the ST formulations after 100,000 or 500,000 rolling ball cycles. The reason for that may lie in the wide-ranging wear track depths within each sample as shown in Figure 25, leading to a wide variance in the results analysed. Despite the lack of statistically significant difference between the ST variations, the estimated point at which degradation began varied largely, as shown in Table 4.

The first change to ST's composition was in fibre lengths while keeping the resin matrix and filler loading the same. Fibre lengths tested were 8 mm (ST), 3-5 mm (ST1) and 25 mm (ST2). In this group, it was found that ST degraded later than either ST1 or ST2. It is interesting to note that ST with its mid-range fibre length in the group showed the most resistance to surface contact fatigue. It has been reported that the FRCs with longer fibres had better two body wear resistance when compared to materials with shorter fibres (Callaghan *et al.*, 2006; Srinivasan *et al.*, 2010). The reason for that is thought to be that longer fibres are more difficult to pull out. While this may shed light on why ST performed better than ST1, it does not explain ST2's behaviour. The explanation may lie in the voids seen on the surface of ST2 (Figure 25c), despite the best attempts to create a perfectly smooth surface.

When comparing the differing fibre lengths in which the Bis-GMA/TEGDMA ratio was 70/30 rather than 40/60 [ST3 (10 mm), ST4 (15 mm), ST5 (20mm)], the mid-range fibre length ST4 appeared to begin degrading later than either one of the other two materials, thus suggesting a possible optimum fibre length for surface contact fatigue irrespective of the Bis-GMA/TEGDMA ratio. When evaluating ST in relation to ST3, ST4 and ST5, ST has significantly higher wear resistance. Due to the differences in resin formulation and fibre length, it is difficult to isolate a single factor responsible for the higher wear resistance found in ST.

When comparing different resin concentrations/filler loading in the Bis-GMA:TEGDMA group with 70:30 ratio, it was found that ST6 (23.5% resin concentration) began degrading after being exposed to more rolling ball cycles than ST7 (19% resin concentration) which could withstand more rolling ball cycles than ST5 (26% resin concentration). A higher resin concentration translates into a lower filler loading, thus it would be sensible to expect the highest surface contact fatigue resistance to be found in the material with the highest filler loading. However, ST7 withstood fewer cycles before degrading when compared to ST6. In this work, with the lack of homogeneity of the components of the formulation, it is possible that a lower filler loading and higher resin concentration allowed a more homogenous distribution of the fillers within ST6. As the resin concentration was mid-range, it does suggest a filler loading level which optimises the surface contact fatigue.

Despite all the varying formulations tested, no statistical improvement to ST's surface contact fatigue was found in this work. ST still withstood the highest number of cycles before surface degradation began when compared to any of other ST formulations.

7.2.2 Three Body Wear

Abrasive wear of a dental restoration may be classified as two or three body wear depending on the causative factors involved as discussed in section 2.3.7. It has been recommended that two different wear tests be carried out when evaluating the wear behaviour of a restorative material (Heintze *et al.*, 2005; Heintze, 2009). It has also been suggested that three body wear is more clinically important than two body wear as the amount of time that restorative materials contact an opposing tooth or restoration is limited when compared with the amount of contact with a third body such as a bolus of food or toothpaste (McCabe *et al.*, 2002). To assess three-body-wear resistance *in vitro*, a manual toothbrush wear simulator or one of several chewing simulators (Lambrechts *et al.*, 2006; Heintze, 2009) may be used as discussed in section 2.3.7. The effects of mastication are most prominent on the occlusal and incisal surfaces of dental restorations and the force they are subjected to varies from the anterior to posterior regions in the mouth. Toothbrushing affects almost every surface of the restoration and has a more uniform force applied throughout the mouth (Ganss *et al.,* 2009). Consequently, the decision was made to use a manual toothbrush wear simulator to study three body wear in this work. As 10,000 cycles are the equivalent of approximately one year of toothbrushing (Momoi *et al.*, 1997), it would have been ideal to measure the wear track every 10,000 cycles to monitor the wear rate over time. However, no measurable wear was observed after 10,000 or 20,000 cycles on either one of the comparator materials using laser profilometry. The decision was made to subject the samples to 50,000 cycles to assess the materials after the equivalent of 5 years of toothbrushing.

a) Comparing ST to Build It and Z250

When ST was compared with Z250 and Build It after 24 hours water storage, ST had significantly lower wear resistance to three body wear. Despite the Z250 being a PFC and Build It being an FRC, both dental resin composites showed similar wear resistance. One reason may be the presence of microfillers in Build It as reported by the manufacturer and evidenced by the SEM images. Figure 71 and Figure 72 are higher magnification images of Figure 37 and Figure 43 to illustrate the smaller particles in Build It compared with ST.

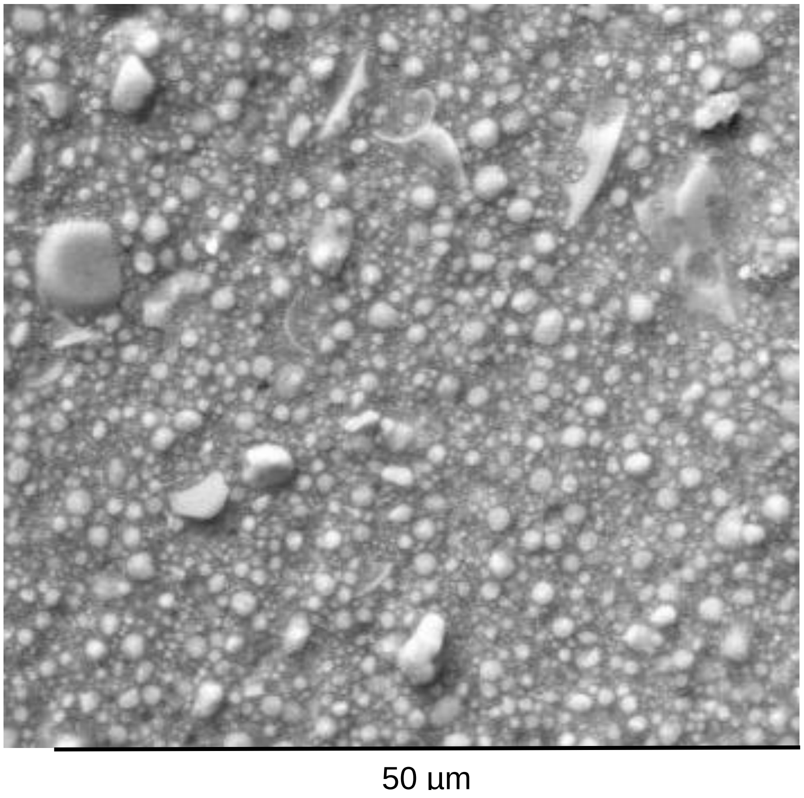


Figure 71. Build It after 24 hours water storage and 50,000 TB cycles in brushed surface (image zoomed 2.5 X from Figure 37).

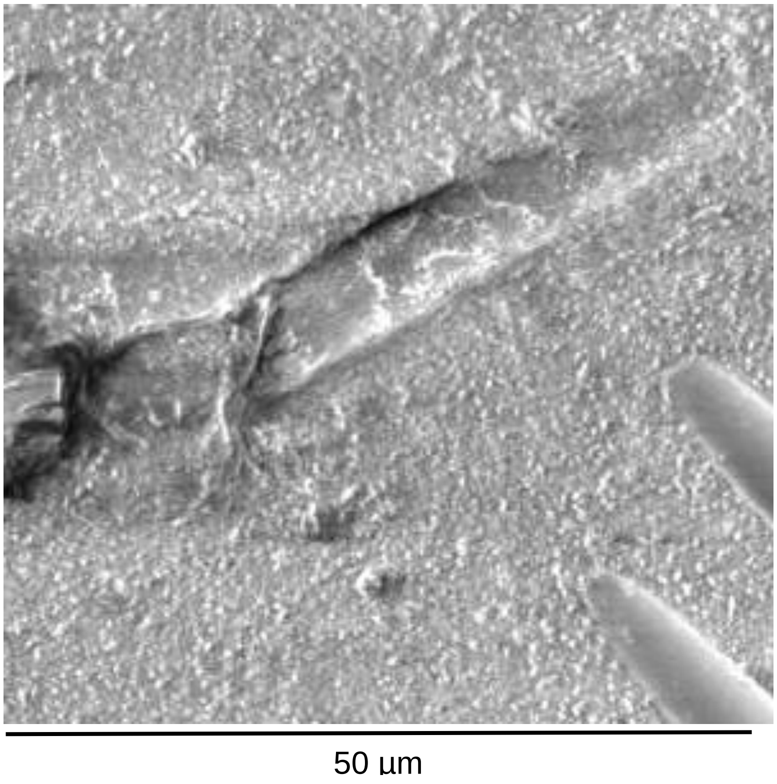


Figure 72. ST after 24 hours water storage and 50,000 TB cycles in brushed surface (image zoomed 2.5 X from Figure 43).

The incorporation of microfillers has been shown to increase wear resistance significantly (Bayne *et al.*, 1992; Lim *et al.*, 2002). This is due to the protection hypothesis put forward by Jorgensen (Jørgensen, 1978; Bayne *et al.*, 1992) and later tested by Bayne *et al.*(1992). The hypothesis states that evenly distributed microfiller particles with inter-particle spaces of 0.1µm would shelter the matrix and prevent wear during the three-body-wear process. As the resin matrix is softer than the filler particles, the wear resistance of the matrix is lower than that of the harder fillers. It follows then that the less matrix exposed to the wear process, the less overall wear there would be. Z250 has filler sizes ranging from 0.01 to 3.5 µm which appear uniformly distributed. Build It also contains microfillers, which are up to 1.3 µm in size. The matrix protection hypothesis would explain their wear resistance. An appearance of uniform filler spacing was noted in the SEM images of both Build It and Z250.

Build It and ST are both FRC, yet their wear resistance varied significantly after 24 hours water storage and 50,000 TB cycles. The explanation is likely to be due to the shorter fibres (10 – 40 µm) in Build It. Three body wear of dental composites has been shown to gradually remove the soft resin matrix between the filler particles which are left unsupported, then easily plucked out (Condon and Ferracane, 1997). The larger ST fibre sizes may facilitate the plucking phenomenon of the fibres, weakening the surrounding matrix and resulting in decreased wear resistance (Manhart *et al.*, 2000a; Yap *et al.*, 2000a). Stress concentrations along the edges of irregular shaped particles also negatively affect the wear resistance (Turssi *et al.*, 2005).

ST also has a higher concentration of fibres when compared with Build It. This increase in fibre concentration may cause clustering and a weaker bond to the surrounding matrix (Callaghan *et al.*, 2006). Figure 43 shows a fibre cluster which does not appear to be fully integrated into the surrounding matrix, supporting that theory. In addition, the fibres in ST are not equally distributed throughout the specimen due to the fact that they are not uniformly distributed throughout the material provided by Stick Tech. This configuration is the most probable cause of the irregular wear pattern seen in the profilometer images of ST as certain areas appeared to be more wear resistant than others within a single specimen (Figure 72). The distribution pattern may have also lead to premature fracture of the fibres during three body wear in areas with a higher fibre concentration. As a result, the fibres no longer reinforce the matrix, which caused the wear resistance to decrease significantly. It is also reasonable to assume that an increase in the size of fillers/fibres would most probably lead to increase in the dimensions of the wear debris. The debris would then become part of the slurry mix and contribute to the three body wear process, resulting in a decrease in wear resistance (Yap *et al.*, 2000a; Heintze, 2007).

The matrix filler interaction is another factor which affects wear resistance, with materials in which the filler is well bonded to the matrix having a higher wear resistance (Manhart *et al.*, 2000a; Manhart *et al.*, 2000b). The fibres in ST may not be as well bonded to the matrix as those in Build It. It is also worth noting that the voids in ST played a role in the poor wear resistance. Voids on the surface of a material accelerate water sorption, which plays a role in the overall degradation of the material.

Another factor which is likely to have contributed to the difference in wear resistance between Build It and ST is the difference in the constituents of their respective resin matrices. Both materials have Bis-GMA in their resin matrices. Build It also has UDMA, which has been found to be harder than Bis-GMA when comparing composites with equivalent filler loading (Sekiya *et al.*, 1993). ST has a semi-IPN structure with both Bis-GMA and PMMA in its resin composition. PMMA is more found more commonly in denture based resins or denture teeth rather than in a dental filling material. Bis-GMA based composite denture teeth are more wear resistant than PMMA based denture teeth, despite the IPN in the PMMA based teeth (Ghazal *et al.*, 2008).

After one year of water storage, the wear resistance of ST was still significantly lower than that of either Z250 or Build It. Despite water storage significantly decreasing the wear resistance of Build It and Z250, ST still exhibited a much lower wear resistance than the comparators. O’Brien and Yee observed five principal wear standards of composite restorations: fracture, loss of particles of filler, wear of the resin matrix, failure of the matrix through cracking, and exposure of air bubbles. (O'Brien and Yee, 1980; Wang *et al.*, 2004). These were all observed in all three materials tested after one year of water storage, as shown by the SEM images in section 6.3.2.

Build It and Z250 both showed a significant decrease in wear resistance after 1 year of storage in distilled water at 37°C. Water sorption is believed to be the main contributing factor which caused that change. This was believed to reduce hoop stresses (which exist due to polymerisation shrinkage of the resin) around filler particles. These hoop stresses increase the frictional forces between the filler and the matrix, thereby increasing the tendency for filler exfoliation or pull out. Water sorption has also been found to contribute to the disintegration of the silane coating at the resin filler interface, thus further facilitating filler pull out (Roulet *et al.*, 1991; Yap *et al.*, 2000b). All those changes would result in the exposure of unprotected resin, and partial debonding of fillers facilitates exfoliation of fillers during wear testing. The outcome is decreased three-body wear resistance, which was found in the present study.

However, ST did not show any change in its wear resistance after one year of water storage. This is in spite of the fact that ST showed significantly higher water sorption when compared with Z250 and Build It. As noted in section 4.3.1, ST reached equilibrium before either Build It or ST in the water sorption experiment. The possibility that ST had already experienced a significant amount of water sorption within the first 24 hours could explain the lack of significant change regarding ST's wear resistance. Once again, the presence of voids in ST would have contributed to this finding.

As with the results of surface contact fatigue testing, the three body wear resistance of ST is significantly lower than either of the comparators. A significant improvement would be required before the material could be deemed fit for direct exposure to the oral cavity. The different ST formulations were also tested. Those results are discussed in the following section.

b) Different ST formulations

The first change was differing fibre lengths while keeping the resin matrix and filler loading the same. Fibre lengths tested were 8 mm (ST), 3-5 mm (ST1) and 25 mm (ST2). It is worth noting at that the fibre lengths in Table 2, quoted by Stick Teck for use in ST and its derivatives are the length of the fibres before the material is produced. During production, the fibre lengths change during both the mixing and the dispensing stages. Once the material was made into a specimen for testing, the fibre size may be changed yet again if the specimen dimensions are smaller than the quoted fibre length. This makes the fibre lengths quoted by Stick Tech different to the final fibre lengths in the samples.

Both ST1 and ST2 showed an improvement in three body wear resistance when compared with ST. The improvement comes with an increase and a decrease in fibre length. An increase in fibre length has been shown to improve the wear resistance in FRCs (Callaghan *et al.*, 2006; Srinivasan *et al.*, 2010). Another reason ST2 may have exhibited improved wear resistance is that it may also be behaving as a continuous FRC rather than a discontinuous FRC, making the fibres more difficult to pluck out. This theory is based on the fact that the diameter of the specimen tested is approximately half the fibre length of ST2, thus making it likely that an uncut fibre runs through the entire specimen. An increased wear resistance has been reported with continuous glass fibre reinforcement in polyurethane composites (Suresha *et al.*, 2007).

Even when the Bis-GMA/TEGDMA ratio in the resin was changed to 70/30, an improved wear resistance was noted when longer fibres were used. ST5, with 20 mm fibres, had significantly more wear resistance compared with ST4 (15mm fibres) and ST3 (10 mm) fibres. Overall however, decreasing the TEGDMA decreased the wear resistance *(Musanje et al., 2006)*. An increase in TEGDMA decreases viscosity and has been reported to increase degree of conversion, which has a positive effect on wear resistance. Bis-GMA/TEGDMA ratios were tested in both 70/30 and 60/40 ratio as unfilled resins and found that the 70/30 ratio had less wear resistance (Kawai et al.(Kawai *et al.*, 1998)).

Using the Bis-GMA/TEGDMA ratio of 70/30, the total filler loading was changed by increasing the amount of fibres in the composite resin. The study presented in this work found that increasing fibre load significantly increased three body wear resistance. ST5 with 22% by weight fibres showed the highest wear resistance when compared with ST6 (21.5% fibres) and ST7 (21% fibres). Based on the matrix protection hypothesis, it is accepted that an increase in filler loading improves wear resistance as it protects the matrix by decreasing the space between the fillers (Jørgensen, 1978; Bayne *et al.*, 1992). It has been reported by several researchers that increasing the concentration of fibres in FRC improved the material's three body wear (Chand *et al.*, 2000; Callaghan *et al*., 2006).

Although wear resistance did show improvement when compared with other materials in the group, these findings are best interpreted with caution. The highest wear resistance found in ST5 formulated with 70/30 BIS-GMA/TEGDMA ratio was still significantly lower than ST1 and ST2 which were formulated with 60/40 Bis-GMA. In industry, it has been found that all fibre reinforcement (short, long, and continuous) in polymers increases the wear resistance and reduces coefficient of friction in the case of sliding wear (Suresha *et al.*, 2007). However, despite the improvement in the three body wear resistance results of ST1 and ST2 when compared with ST, their wear resistance was still significantly lower than either one of the comparator materials and, more importantly, the lack of homogeneity was equally present in ST and all its derivatives (see Figure 49).

Despite the improvement in the three body wear resistance results of ST1 and ST2 when compared with ST, their wear resistance was still significantly lower than either one of the comparator materials and, more importantly, the lack of homogeneity was equally present in ST and all its derivatives (see Figure 49).

7.3 **Material Characterisation**

The polymerisation shrinkage, water sorption and bond strength of a dental restorative material are among its most important properties when attempting to evaluate an experimental dental restorative material. Knowledge of these characteristics will allow an initial assessment of the material's suitability for clinical use.

7.3.1 Polymerisation Shrinkage

The magnitude of polymerisation shrinkage will influence the required bond strength between tooth structure and dental resin composite (Ilie and Hickel, 2006). To measure polymerisation shrinkage, several methods have been employed, from the use of Archimedes principle (Stansbury and Ge, 2003) and dilatometry to the more complex monitoring using sensors during the entire polymerisation process (de Gee *et al.*, 1993; Stansbury and Ge, 2003). Several techniques used to measure polymerisation shrinkage are based on dilatometry (Feilzer *et al.*, 1988; Rees and Jacobsen, 1989; Lai and Johnson, 1993).

Using the bonded disc method gives similar results to dilatometry with the added advantages of being simpler and not as sensitive to temperature changes (Watts and Cash, 1991; Garoushi *et al.*, 2008a). The use of the bonded disc method also allows direct curing of the dental resin composite, without a liquid medium between the light source and material, and there is no potential safety hazard regarding the use of mercury (Watts and Cash, 1991; Stansbury and Ge, 2003). The main limitation of using the bonded disc method in the experiments presented in this work was the possibility of changing the configuration of the fibres in the FRCs tested, thus changing the material's behaviour from isotropic, i.e. shrinking equally in all directions, to anisotropic. However, ST came packaged in 1- 1.5 mm thick sheets so there was no real change to the orientation of the fibres from the original packaging which made the test suitable for the material available. Previous work has also been done using the same technique to measure polymerisation shrinkage of an FRC similar to ST (Garoushi *et al.*, 2008a).

In this work, a dual cure dental resin composite core material, Build It, was compared with two light activated dental resin composites, ST and Z250. No significant difference was found between the three mterials. The decision was made to use a light cure to activate the polymerisation in Build It rather than allow it to chemically cure. This was based on research which showed no significant difference between the polymerisation shrinkage of light activated and chemically activated dual cured dental resin composites after one hour of curing (Rueggeberg *et al.*, 1994; Feng and Suh, 2006). Light curing Build It would also allow standardisation of the testing protocol for all three materials.

Conflicting results have been found in the literature when comparing the polymerisation shrinkage of FRCs to PFCs. Some have reported that FRC exhibited less shrinkage than the PFC Z250 when measured using a strain gauge (Tezvergil *et al.*, 2006) while other researchers (Nagem Filho *et al.*, 2007; Garoushi *et al.*, 2008b) found that the FRCs had significantly higher shrinkage when compared with a commercially available PFC. It is interesting to note the similarity results of the studies which reported a higher shrinkage of FRC despite the difference in methodology used and in the FRCs tested. Nagem Filho *et al.* (2007) weighed their samples while Garoushi *et al.* (2008b) used the bonded disc method.

The experimental dental resin composite tested by Garoushi *et al.* (2008b) was a precursor to ST, thus making their experimental results all the more relevant to this project. Their material was a randomly oriented E-glass FRC with a semi-IPN matrix composed of Bis-GMA/TEGDMA and PMMA. Despite the similarity in materials and measuring techniques used for the FRCs, the results reported in this work were in contrast to those of Garoushi *et al.* (2008b). They noted significantly lower shrinkage of the PFC (2.04 ±0.09) compared with that of their experimental FRC (2.45 ±0.11). The experiments reported in this work found no significant difference between any of the three materials tested. Garoushi *et al.* (2008b) believed that it was highly likely that their findings were due to a change in fibre orientation from randomly oriented, which resulted in an isotropic material, to a more aligned orientation resulting in an anisotropic material, with greater shrinkage being exhibited perpendicular to the direction of the fibres. This was the main reason cited for the significantly higher shrinkage found in their experimental FRC. However, they did not specify how their FRC was presented prior to testing. The contrast between the results of the Garoushi *et al.* (2008b) study and this work is most likely due to the difference in material composition. The experimental FRC used by Garoushi *et al.* (2008b) had 22.5% by weight resin while ST only has 19%, thus predisposing to a lower shrinkage for ST. Resin materials with a higher level of filler fraction have been found to shrink less than those with a lower filler fraction. This is attributed to the fact that an increase in the filler fraction relatively decreases the fraction of monomer in the composite, thus reducing the concentration of carbon double bonds resulting in an overall reduction of shrinkage (Kahler *et al.*, 2008; Goncalves *et al.*, 2010; Goncalves *et al.*, 2011).

Z250 has a higher filler loading (82% by weight) than either ST (79% by weight) or Build It (68% by weight). Based on the filler loadings of the materials tested in this work as supplied by the manufacturers, it would have been reasonable to expect Z250 and ST to exhibit similar shrinkage levels. This assumption was confirmed by the findings reported in this work. Since Build It has the lowest filler loading, it may also have been speculated that it would display the highest amount of shrinkage. However, the experiments presented in this work found no significant difference in the polymerisation shrinkage measured between the three materials immediately after curing or an hour later. Despite what appeared to be a decrease in the shrinkage of Build It (possibly due to the lack of temperature equilibration) and Z250 while ST showed a minor increase, the results of the experiments presented in this work showed no significant differences between the measured shrinkage immediately after curing and that measured after one hour within each material.

As stated earlier, the reason for the similarity between ST and Z250 may lie in the similarity of their filling loading. Build It has a lower filler loading than either ST or Z250, yet there was still no significant difference in the measured shrinkage. The explanation for that is likely to be the fact that Build It is an FRC which has randomly oriented fibres distributed throughout its resin matrix. As the fibres themselves do not shrink, they limit polymerisation shrinkage within the material. This theory is supported by previous findings (Kahler *et al.*, 2008). They reported that fibres had a measurable effect in decreasing polymerisation shrinkage when compared with spherical particles and concluded that the use of disc or fibre shaped particles can be considered to be an effective way to reduce volumetric shrinkage. It is worth noting that the orientation of fibres also plays a role. While the amount of shrinkage along the length of the fibre itself has been found to be minimal, transverse shrinkage was higher (Tezvergil *et al.*, 2006; Anttila *et al.*, 2008). Random orientation ensures that shrinkage along the length of the fibre occurs in all directions, thus limiting shrinkage.

Another possible cause of the similarity in the polymerisation shrinkage measured in this work is that the filler loadings by weight may rank differently to filler loadings by volume in the three materials tested - depending on the relative densities of the composites' fillers. Manufacturers often give values for filler loading by weight but in reality the volume fraction of resin undergoing polymerisation contraction is likely to be more closely related to composite filler volume rather than composite filler weight. Stick Tech only supplied the filler loading for ST by weight, which is why all filler loadings for the materials are quoted in percent weight rather than percent volume. It would be worth exploring this further by systematically measuring filler volume and weight and relating these to the shrinkage of different composite resins. Such a study would be a useful addition to the few papers in the literature which compare the polymerisation shrinkage of FRC with PFC.

Interestingly, the shrinkage percentages reported in this work for Z250 (1.44 % ±0.27) fall within a wide range of percentages reported in the literature. Nagem Filho *et al.* (2007) found that Z250 shrank 1.99% ± 0.037 while Tezvergil *et al*. (2006) found that Z250 exhibited a shrinkage of 0.55% ± 0.05. The reason for the varying shrinkage found is likely to be due to the measuring techniques. Nagem Filho *et al.* (2007) weighed their samples while Tezvergil *et al*. (2006) used a strain gauge. Even when the same technique was employed, discrepancies were noted. For example, both this work and that of Watts and Marouf (2000) used the bonded disc method yet Watts and Marouf (2000) found Z250 shrank 1.618% ± 0.030. The difference may be due to a higher degree of conversion leading to an increase in shrinkage in their work.

In summary, ST showed polymerisation shrinkage similar to both a commercially available PFC and FRC. Within the limitations of this study, ST has been found to have polymerisation shrinkage (1.46%) which falls within the limits reported for commercially available dental resin composites (Ferracane, 2005).

7.3.2 Water Sorption

When a dental resin composite is soaked in water, two processes occur; a rapid elution of unreacted monomer(s) and the absorption of water by the resin. The water sorption measured is actually the net gain in the weight of a specimen as a result of the ingress of water molecules and egress of monomers and other small molecules (Chai *et al.*, 2004; Sideridou *et al.*, 2007). Water absorbs into the FRC polymeric materials by diffusion, which is a time-dependent process. The ingress of water into the resin composite is slower than the elution of unreacted monomer (Ortengren *et al.*, 2001; Chai *et al.*, 2004; Sideridou *et al.*, 2007). Water occupies the spaces left by the eluting monomer(s) as well as any spaces between polymer chains (Hashimoto *et al.*, 2000; Costella *et al.*, 2010). The water absorbed can reduce the frictional forces between the polymer chains, which can in turn negatively affect the mechanical properties of the resin as well as swelling the polymer. This process is referred to as plasticization of the resin (De Munck *et al.*, 2005; Sideridou *et al.*, 2007). A more positively perceived effect of water sorption is its ability to counterbalance some of the polymerisation shrinkage of a dental resin composite (Bowen *et al.*, 1982; Feilzer *et al.*, 1990; Sideridou *et al.*, 2003).

Based on ISO 4049, discs of each dental resin composite material were made and stored in water. The advantage of the disc size recommended by ISO is their large surface area to volume ratio which would allow rapid saturation and representative measurements after just 1 week. However, ISO 4049 has a note to indicate that dental resin composites may take up to six weeks to achieve a constant mass. The ISO recommendation is to test 5 discs per material, yet due to the lack of homogeneity seen in ST, 10 discs were made to ensure representation of both the fibre rich and less fibrous sections of the material.

All of the tested materials had water sorption levels which complied with ISO 4049. However, ST was found to have significantly higher levels of water sorption compared with Build It and Z250 after one month of water storage. The main reason for this difference lies in the formulation of the materials tested. While they all have Bis-GMA based resin matrices, only ST has TEGDMA as the copolymer. Z250 uses UDMA and Bis-EMA while Build It uses UDMA and HDDMA. Gradual replacement of TEGDMA with UDMA and Bis-EMA in copolymerisation with Bis-GMA has been found to result in resins with lower water sorption (Sideridou *et al.*, 2003). Another difference in formulation lies in ST's semi-IPN matrix. ST is the only one of the three tested materials which has a semi-IPN resin with PMMA as one of its constituents. PMMA-based composites have been found to accommodate additional water at the interface between filler particles and the matrix (Kalachandra, 1989).

The results reported in this work are supported by previous findings regarding the water sorption of FRCs (Lassila *et al.*, 2005; Schulein, 2005). Both studies found that an experimental FRC with a semi-IPN matrix made up of BisGMA/TEGDMA and PMMA had significantly more water sorption than a commercially produced dental resin composite. One of the studies (Garoushi *et al.*, 2007e) used a PFC (Z250) as its comparator material while the other (Lassila *et al.*, 2005) used an FRC (BR-100 from Kuraray Medical Group, Japan).

In FRCs with different fibre lengths, the FRC with the longer fibres in higher concentrations has been found to exhibit less water sorption(Polat *et al.*, 2003). Unexpectedly, the results of the experiments described in this work show that ST had significantly higher water sorption despite its higher fibre content and longer fibres when compared to Build It. ST exhibited over twice the measured water sorption seen in Build It. Along with the difference in resin formulations, another likely reason for such a finding is the likelihood of the presence of voids within ST. The inclusion of 1% voids has been found to double the amount of sorption in a resin composite (Thomason, 1995). Voids within ST may have been introduced during specimen production or may be present within the material itself. Due to the manner in which ST was packaged (sheets), specimens were prepared by layering the material into the moulds. Voids may have been formed between the layers. However, the moulds used for specimen preparation were only 1 mm thick and ST was supplied in sheets 1- 1.5 mm thick. So, only one layer of ST was required in each mould, thus eliminating the chance of void introduction during specimen fabrication. This suggested the possibility of voids in ST during manufacturing. Poor impregnation of the fibres into the resin matrix would create microvoids, which would be the ideal channels for water uptake in the dental resin composite (Lassila *et al.*, 2002). Stick Tech confirmed the existence of voids within the material due to their mixing process (personal communication, 2009). That shed light on the most likely reason for the significantly higher water sorption exhibited by ST. It would be interesting to examine the difference in water sorption of ST once the microvoids had been eliminated according to the manufacturer.

When comparing the original with the reconstituted mass of the three materials (m1 with m3 respectively), ST's results were once again different to that of Build It and Z250. ST was the only material which exhibited a lower m3. The elution of monomers and other small molecules during the specimens' immersion in water is a likely reason for the lowering of the specimens weight after reversibly extracting the water. However, despite identical experimental conditions with ST, both Z250 and Build It exhibited a slight increase in the weight of m3. Among the possible explanations for this dissimilarity is that some of the water absorbed by Z250 and Build It became bound within the resin matrix and could not be reversibly extracted. The voids present in ST may have contributed to the complete extraction of absorbed water. Another possible justification for the higher m3 in Z250 and Build It is that they exhibited less elution than ST. That may be due to differences in the materials' degrees of conversion as a higher degree of conversion has been associated with less elution (Ferracane, 1994). This work did not examine degree of conversion thus making it difficult to speculate on which of the materials exhibited higher or lower conversion. Such testing would be useful in further understanding the behaviour of ST

In summary, despite the voids present in ST, all three materials tested exhibited water sorption levels within the limit recommended by ISO.

7.3.3 Bond Strength

i) To Human Dentine

The bond strength of a dental resin composite to tooth structure is an important factor in ensuring the longevity of the restoration. It is worth mentioning that dental resin composite materials do not inherently bond to tooth structure, an adhesive is necessary. Thus, when discussing the bond strength of a particular resin composite to tooth structure in the experiments presented in this work, the results are specific to both the type of dental resin composite used in conjunction with the particular adhesive and the specific tooth structure bonded. The use of a different adhesive may change the result. The adhesive used in this work was based on Stick Tech's recommendation (personal communication, 2009). Adper Scotchbond Multipurpose was used, which is classified as an 'etch and rinse' or 'three step' adhesive.

As discussed in section 2.3.4, there are several ways to test the bond strength of a dental restorative material, each with its own advantages and disadvantages. The ability to use one tooth for several specimens also helped increase the popularity of micro-testing. One of the most popular micro-methods used is microtensile bond strength testing. Among its main perceived advantages is to lower the coefficient of variation of bond strengths recorded. This is due to the smaller bonding surface area and lower number of possible strength limiting flaws (Sano *et al.*, 1994; Pashley *et al.*, 1999). Yet, when both microtensile and macrotensile adhesive tests were compared, there was no difference in the coefficient of variation for most of the adhesives reported in the literature (Scherrer *et al.*, 2010). Interestingly, intra-tooth variability has also been found to be higher than inter-tooth variability (Loguercio *et al.*, 2005). Some have even found that microtensile testing had a higher coefficient of variance when compared with macroshear testing, further questioning the lower coefficient of variation when micro-testing methods (Braga *et al.*, 2005). Variables such as specimen shape (hourglass, dumbbell or stick), flaws in the adhesive (such as air bubbles), or flaws created during specimen preparation all contributed to the high coefficient of variation.

Due to the non-homogenous distribution of the fibres in ST, using a micro-testing technique to test ST's bond strength to human dentine had one obvious disadvantage; the potential to create samples with unequal fibre distribution. With a bonded area smaller than 3 mm^2, it was very likely that the resulting samples would have major variations in fibre content. Using macro-testing techniques with a bonded area larger than 3 mm^2 would allow a more even distribution of the fibres in the specimens. As ST was intended for use as a core build up/dentine replacement, testing a larger bonded area would also be more representative of its intended clinical usage. It has also been noted that the strength values and pre-test failures were lower with macro-testing than with micro-testing (Loguercio *et al.*, 2005; Scherrer *et al.*, 2010). For the purposes of the bond strength studies presented in this work, it was decided that underestimating the bond strength of a material would be more advantageous than overestimating it.

A commonly used method for testing bond strength to do so is in shear. This is in spite of the known limitations of variable stress distribution along the sample interface and the lack of 'true shear' stresses until the specimen fails. The simplicity of specimen preparation and fewer pre-test failure contribute to shear bond strength's popularity (Placido *et al.*, 2007; Salz and Bock, 2010; Scherrer *et al.*, 2010). An often cited limitation of using macro-shear bond strength testing is the frequency of cohesive failures within the substrate. The theory that cohesive data reflects a mixture of material properties rather than simply the durability of the bond between the structures being tested is considered a key reason that many researchers have turned to micro-tensile or micro-shear bond strength testing, with some authors even suggesting rejecting samples which failed cohesively (Braga *et al.*, 2010; Scherrer *et al.*, 2010). Placing an FRC at the adhesive interface resulted in a lack of cohesive failures in the substrate which was attributed to a change in the path of crack propagation at the interface and result in no cohesive failures in the substrate (Tezvergil *et al.*, 2005). To further examine that theory, the experiments presented in this work used macroshear bond strength testing.

In this work, the shear bond strength of the dental resin composites to human dentine using Adper Scotchbond Multipurpose adhesive was investigated. Once the samples were made, half were tested after 24 hours in distilled deionised water at 37°C. This gave initial bond strength values of the materials tested. The remaining 50% of samples were aged for 1 year. Methods of ageing vary in the storage medium used for the samples. Distilled water is among the most common media used (De Munck *et al.*, 2005). To prevent bacterial growth during the storage period, investigators have changed the water weekly, added chloramine T (Armstrong *et al.*, 2003; De Munck *et al.*, 2003), or even antibiotics. The use of artificial saliva solutions has also been advocated, but pure water degradation was found to produce the same changes in bond strength (Kitasako *et al.*, 2000; De Munck *et al.*, 2005).

Thermocycling is another common feature of the ageing regime. Several studies found no significant effect when thermocycling was used to age specimens for bond strength testing (Leloup *et al.*, 2001; Ferracane *et al.*, 2009; Korkmaz *et al.*, 2010) after up to four years of storage in water. Based on those findings, the samples were aged in distilled deionised water without thermocycling for 1 year to determine what, if any effects, water storage would have on bond strength. The water was changed weekly to prevent bacterial growth.

When comparing the results of bond strength studies, it is tempting to compare the shear bond strengths, reported in MPa, of materials from different studies. However, the reported shear bond strengths depend on the dimensions of the specimens tested along with the speed at which the force was loaded onto the jig and have been calculated from the force at which failure occurred (Van Meerbeek *et al.*, 2010). This means that each set of results is unique to the testing environment and thus the shear bond strengths resulting from different studies are not directly comparable. A more meaningful comparison would be that of the rankings of materials in different studies.

When testing the bond strength of dental resin composite to human dentine after 24 hours in this work, it was found that the bond strength of the ST was significantly lower than either one of the comparator materials or of the flowable resin composite used. No published work in the literature appears to have compared an FRC bonded to dentine with a PFC bonded to dentine. There has been work comparing PFC bonded to dentine with a reinforced PFC (by the addition a layer of FRC at the adhesive interface) bonded to dentine. Conflicting results have been reported when such a comparison was made. Some authors found no significant difference between the reinforced and unreinforced PFC materials (Tezvergil *et al.*, 2003; Tezvergil *et al.*, 2005; Tezvergil-Mutluay *et al.*, 2008), while others found that placing a layer of FRC served to decrease the bond strength to flat dentinal surfaces (Belli *et al.*, 2006).

The findings presented in this project are different for each FRC tested. ST was found to have a significantly lower bond strength compared to Build It. This result was supported by previous findings of FRC having significantly lower bond strength to dentine than a PFC (Belli *et al.*, 2006), while contrasting others who found no difference (Tezvergil *et al.*, 2003; Tezvergil *et al.*, 2005; Tezvergil-Mutluay *et al.*, 2008). Build It's results were in support of the work done by Tezvergil *et al.* (Tezvergil *et al.*, 2003; Tezvergil *et al.*, 2005) and Tezvergil-Mutluay (2008) while contrasting the findings of Belli *et al.* (2006).

The results reported by Tezvergil *et al.* (Tezvergil *et al.*, 2003; Tezvergil *et al.*, 2005) are of particular interest in this project due to the fact that the FRC tested was a precursor to ST (personal communication, 2008). The difference in the findings is most likely due to the methodology used. Tezvergil *et al.* (Tezvergil *et al.*, 2003; Tezvergil *et al.*, 2005) placed the FRC as a single layer underneath an increment of particulate composite resins, thus essentially testing the bond strength of PFC reinforced with an FRC to dentine. In the experimental work presented in this thesis, the FRC's own bond strength to dentine was tested without the addition of a PFC. Another potential reason for the conflicting results may be a difference in the fibre loading of ST compared with the FRC used in the Tezvergil *et al.* (2005) study. ST's fibre content is approximately 19%. The fibre content used in the randomly oriented FRC in the Tezvergil study was low according to the authors. Unfortunately, they did not state its percentage, thus preventing an accurate comparison between the two materials.

Build It, on the other hand, exhibited results which are supported by the findings of Tezvergil *et al.* and Tezvergil-Mutluay *et al*. (Tezvergil *et al.*, 2003; Tezvergil *et al.*, 2005; Tezvergil-Mutluay *et al.*, 2008). There were no significant differences found between the shear bond strength of Build It and Z250 after 24 hours water storage. The difference in the bond strengths demonstrated by ST and Build It is likely to be due the differences in resin formulation. ST's lower bond strength is likely to be due to its higher fibre loading. The higher the fibre volume, the more the damage to those fibres would influence the entire composite structure. Resin composites with a high volume fraction of fibres show a more pronounced response to stress (Lee and Simunovic, 2000). Another reason may lie in the adhesion between the fibres and the matrix. Incomplete adhesion between the fibres and the matrix may lead to the fibres protruding during placement on dentine, possibly creating microvoids at the interface as well as reducing the amount of resin matrix in contact with the dentine, which would decrease the amount of resin available to infiltrate the collagen network and create the hybrid layer, thus leading to lower bond strength.

The difference in the handling of the two materials, while a subjective parameter, may be another factor which contributes to the contrasting results between ST and Build It. ST has fibres 8 mm in length while Build It's fibres are only 10- 40 µm in length. While Build It is a homogenous, injectable material, ST has to be cut to size from a sheet and is difficult to handle. Anecdotally, from this researcher's experience, once ST was cut to size, fibres were noted extruding from the cut surface of the material. When placing each material into the end of a gelatin capsule and then onto dentine, this contrast in handling could have played a role in how well each material adhered to the dentine with ST possibly not adapting as well to the dentine surface as Build It in spite of equal pressure being applied to the gelatine capsule by the operator.

The literature showed more harmonious results when reporting the mode of failure of FRCs. Tezvergil *et al.* (Tezvergil *et al.*, 2003; Tezvergil *et al.*, 2005; Tezvergil-Mutluay *et al.*, 2008) and Fennis *et al.*(2005) all reported no cohesive failures in tooth structure when an FRC was used. Thus, it was theorised that FRCs provide a change in the mode of fracture from cohesive within the tooth structure to adhesive or cohesive within the fibres, which the authors all interpreted to be beneficial in preventing catastrophic tooth failures.

Once believed to be solely an indication of strong bonding, cohesive failure has been explained by the mechanics of the test and the brittleness of the materials involved as well (Armstrong *et al.*, 2010). Finite element analysis (FEA) has shown that the cohesive failure in dentine or the substrate is due to the uneven distribution of forces created during a macroshear bond strength test (Armstrong *et al.*, 2010). In the shear test, tensile stress concentration in dentine near the crack tip causes the failure to propagate into the substrate. Researchers studied the tendency for dentine failure both experimentally and using a failure accumulation computer model. They found a tendency for dentine failure increased at lower crosshead speeds (0.5 mm), thicker adhesive layers and moving the point of load application away from the bonded interface. Shear stresses start to prevail over tension at 0.3mm from the load application area (Versluis *et al.*, 1997).

Once again, the two FRCs tested in this work exhibited different behaviour. ST had no cohesive failures in dentine after 24 hours of water storage, while Build It had approximately 10 % cohesive failure in the dentine. Although that is much less than the 20% cohesive failures in dentine found when using Z250 or Stick Flow specimens, it did not completely eliminate such failures. As with the bond strength results, the size and volume of fibres in ST are believed to be a reason behind the difference in failure modes of Build It and Z250. ST's fibres are 8 mm in length and 15 – 20 µm in diameter while Build It's fibres are 10 – 40 µm in length. The increase in length and width of ST's fibres may cause the fibre to carry more stresses along their axes, deflecting the stress from dentine and cause a failure in the adhesive layer or within ST itself failure rather than within the tooth structure. The fibres transferred the stress away from tooth structure and thus any failure within the tooth was avoided. Build It has fibres 10 – 40 µm in length which may be too short to effectively transfer stress.

Despite the possibility of uneven stress distributions during testing, ST still had no cohesive failures in any of the specimens tested after 24 hours water storage. This would appear to indicate that ST had a potentially positive effect on the stress distribution at the adhesive interface and supports previous research regarding the effect of an FRC of mode of failure (Tezvergil *et al.*, 2003; Tezvergil *et al.*, 2005).

However, this interpretation must be looked at cautiously as the reality may be that the failure stresses were insufficiently high to damage the dentine. ST's mean shear bond strength was 10.7 MPa and was the only one of the tested materials with no SBS values approaching or higher than 20 MPa (the threshold above which cohesive failure was observed in this work). The study presented in this work appears to be the first one which evaluated an FRC material without the addition of PFC. Further work would facilitate a deeper understanding of the effect of directly adhering an FRC material to tooth structure rather than using it in combination with a PFC at the adhesive interface.

It is worth noting the fibre length attributed to ST is that used by the manufacturer during the initial production of the material. This length may be changed during mixing as the glass fibres break and changed again during specimen production based on the dimensions of the cavity. As the sample bonded to dentine was 4.5 mm in diameter and 2 mm in depth, the effective fibre length of ST was definitely changed from the original 8 mm quoted by Stick Tech. However, the diameter and concentration of the fibres should remain constant.

While knowledge of the existence of significantly higher or lower bond strengths is helpful, due to the high coefficient of variance in these studies, a more clinically relevant marker may be obtained by using a failure probability curve (McCabe and Carrick, 1986; Armstrong *et al.*, 2003). A Weibull probability distribution allows the calculation of not only a Weibull modulus and characteristic strength, but also the failure stress at a specified probability of failure (in this case, 5%). To estimate the force required for a given probability of failure, the Weibull probability plots were used to extrapolate the SBS data to the 5% level. The force (N) has been rounded to the nearest whole number. Table 32 shows the estimated force required for the failure of the tested materials in descending order.

Material	**SBS (MPa) for 5% probability of failure**	**Force (N) for 5 % probability of failure**
Z250	9.36	149
Build It	6.15	98
Stick Flow	5.32	85
ST	1.24	20

Table 32. SBS and Force for 5 % probability of failure after 24 hours water storage.

If this information is correlated with the measured magnitude of force produced during mastication, it may give an indication of how the material may perform in the oral cavity. The magnitude of the biting force was measured to be 10 – 20 N at the incisors during the initial biting phase. At the end of the chewing cycle, the force was 25- 45 N at the incisors and 100- 140 N at the molars (Kohyama *et al.*, 2004; Heintze, 2009). The occlusal force at each posterior tooth during the chewing cycle was also measured (Kon *et al.*, 2006). They found that the force ranged from 17.9- 32.4 N for the first premolar, 31.1-51.8 N for the second premolar, 83.7- 163.6 N at the first molar and 155.1- 296.0 N at the second molar (Kon *et al.*, 2006). While the ranges are useful indicators, the type of food also has an effect. It has been reported that the chewing force for rice cracker was around 100 N while a piece of bread or fresh carrot would generate 80N and chewing a piece of minced fish gel gave a range of 30 to 40 N (Kohyama *et al.*, 2001a; Kohyama *et al.*, 2001b; Kon *et al.*, 2006).

Consequently, for the present data and assuming the masticatory forces are allowed to act purely in shear at a flat interface, all 3 materials have a 5% probability of failure during chewing on the first and second molars. ST would be the material most likely to debond, followed by Stick Flow, then Build It and then Z250. Analysing the material in this way has allowed them to be ranked individually rather than simply to find the one in the group which is significantly lower or higher (Armstrong *et al.*, 2003).

After 1 year water storage, the bond strength between dentine and Z250 was still significantly higher than that between dentine and ST. Although bond strength did appear to decrease after water storage, this was not significant. This may be due to the use of whole teeth as specimens rather than splitting a single tooth into micro specimens before storage, which some have suggested would accelerate the effect of aging (Armstrong *et al.*, 2001; Hashimoto *et al.*, 2002).

There is a much published work in the literature which reported significant decreases in bond strengths, even after relatively short water storage periods (Armstrong *et al.*, 2001; Meiers and Young, 2001; Armstrong *et al.*, 2003; De Munck *et al.*, 2003). However, several of those studies used microspecimens (Armstrong *et al.*, 2001; Armstrong *et al.*, 2003; De Munck *et al.*, 2003), which has been considered to accelerate the effect of ageing (Armstrong *et al.*, 2001). Others used single bottle adhesives (Meiers and Young, 2001). When single bottle adhesives were compared with three step etch and rinse, the three step etch and rinse adhesives had no significant change in bond strength while the single bottle adhesives did (Blunck and Roulet, 2002; Shirai *et al.*, 2005).

Examining the 5 % probability of failure of the samples after 1 year water storage revealed that Build It was the material which could withstand the highest force, followed by Z250, Stick Flow and then ST as shown in Table 33. It is interesting to note that while all the materials showed some decrease in the bond strength required for 5% failure probability of samples, the FRCs showed the smallest changes as shown in Table 34.

Material	SBS at 5% probability rate	Force (N)
Build It	6.07	96
Z250	5.26	84
Stick Flow	3.53	56
ST	1.24	20

Table 33. SBS and Force for 5 % probability of failure after 1 year water storage.

Material	Force (N) for 5% failure probability after 24 hours water storage	Force (N) for 5% failure probability after 1 year water storage
Z250	149	84
Build It	98	96
Stick Flow	85	56
ST	20	20

Table 34. Comparison of forces required for 5% failure probability after 24 hours and 1 year water storage.

After 1 year water storage, the failure modes for ST remained constant, with no cohesive failures at all. However, Build It’s failure modes changed, with none of the samples showing cohesive failures in dentine. Thus, it can be deduced that if either ST or Build It debond from the tooth structure after a year of service, the tooth surface may very well remain intact. Nevertheless, the relatively low forces required to debond ST from human dentine might predispose to partial debonding of the core resulting in secondary caries. Further testing would need to be carried out before the use of ST in clinical trials is recommended.

ii) To dental resin composites

While determining ST's bond strength to dentine is necessary, assessing the bond strength of composite/composite association is equally important. In the case of an experimental material such as ST, knowledge of the bond strength of composite to itself when placing it incrementally in a cavity is as important as the approximation of the bond strength between the core composite to a veneering layer. While the results of *in vitro* testing are not necessarily reproducible in the oral cavity, they do give an idea of how a material may behave when it is subjected to particular stresses (Van Meerbeek *et al.*, 2010).

Previously published data regarding incremental bond strength is scarce (Truffier-Boutry *et al.*, 2003; Ribeiro *et al.*, 2008). To test the bond strength of an FRC to itself and to a veneering PFC, the composite sample was finished and polished before curing the new increment of composite onto it in keeping with previously published protocols (Keski-Nikkola *et al.*, 2004; Lassila *et al.*, 2007). This method is reproducible *in vitro* and ensures that there is no mechanical component affecting the results when bonding dental resin composites. This method was also used in the experiments presented in this work to test composite/composite bond strengths after 24 hours and 1 year of water storage.

While the technique of lapping specimens is reproducible *in vitro*, it removes the oxygen-inhibited layer found when methacrylate material polymerise with a free surface. Lapping specimens before adding a new increment of composite reflects the clinical situation of a dental practitioner placing a veneering layer over a core composite after preparing the core with a bur. However, lapping the specimens does not reflect the clinical situation where the veneering layer is placed immediately onto the oxygen-inhibited surface layer. Both the clinical situations (i.e. bonding to a prepared/lapped surface and bonding to an oxygen inhibited surface) merit assessment in this researcher's opinion, so they were both tested in this work after 24 hours water storage.

To determine whether shear bond strength was affected by bonding identical or dissimilar materials, this work assessed each of the materials (Z250, Build It and ST) by making both the composite sample and substrate of the same material as well as bonding Z250 to each of the FRCs to assess the bond strength between the fibre reinforced dental composite resin and the veneering particulate filled composite resin. As in the previous section, the testing regime chosen was macroshear bond strength testing. This was due to the size of the fibres in ST and would allow comparison between the results of both studies. It would also allow further investigation into what, if any, effect ST had on the mode of failure.

After 24 hours of water storage, in the lapped composite groups, Build It/Z250 had significantly higher shear bond strength than any of the other groups. This may be due to the similarity of the resin matrices of both Build It and Z250. It has been found that conversion of C=C bonds in a light-cured composite continues for at least 24 h after exposure to light (Keski-Nikkola *et al.*, 2004 ; Boyer *et al.*,1984 ; Leung *et al.*, 1983). As Build It has the lowest filler loading of the three materials tested, it has the highest resin content, thus assumed to have more sites available for another dental resin composite to bond to. Thus it may be a logical to assume that there were a higher number of un-reacted double bonds on the surface of cured Build It when compared to ST. These un-reacted double bonds could allow formation of covalent bonds between Z250 and Build It (Polacek and Jancar, 2008). It has also been suggested that the oxygen-inhibited layer is contains unreacted acrylate groups able to improve the adhesion strength between the substrate and the second layer by the formation of covalent bonds within an interpenetrating network (Truffier-Boutry *et al.*, 2003; Ghivari *et al.*, 2010).

The findings regarding Build It/Z50, Z250/Z250, Build It/Build It and ST/ST are supported by the work of Ribiero *et al.* (2008). They found that different resin composites had higher bond strengths than those of identical resin associations in microhybrid dental resin composites.

The Weibull probability plot allows insight into the force required for a given probability of failure. To estimate the force required for a given probability of failure, Table 35, the Weibull probability plots were used to extrapolate the SBS data to the 5% level. The composite/composite groups are presented in descending order of force required for 5% probability of failure.

Composite/Composite Group	SBS (MPa) for 5 % probability of failure	Force (N) for 5% probability of failure
Build It/Z250	14.64	288
Build It/Build It	7.63	150
Z250/Z250	6.98	137
ST/ST	6.01	118
ST/Z250	3.10	60

Table 35. SBS and Force for 5% probability of failure after 24 hours water storage.

Table 35 clearly demonstrates that Build IT/Z250 required the highest force for 5% probability of failure while ST/Z250 required the lowest. The reason behind the poor performance of the ST/Z250 group may be due to a change in the fibre orientation of ST during specimen preparation. As mentioned previously in section 7.2.1, ST was provided in sheets approximately 1-1.5 mm thick. When preparing the 2 mm thick composite samples, the 1.5 mm sheet was cut to size, and then placed in the cavity. To overfill the cavity, the remaining 0.5 -1 mm was filled by adding another increment of ST and flattening it using a plastic filling instrument. The entire sample then had a 1 kg weight placed over a Mylar strip and Perspex sheet to completely flatten the sample before curing. This may have caused the fibres to align in a single direction, which is perpendicular to the direction of the force application during shear bond strength testing. Lasilla *et al.* (2007) found that the lowest bond strength of unidirectional FRC to be when the fibres were in a transverse direction to the force applied. On the other hand, Build It had much shorter fibres (10 – 40 µm) and could be placed as a single increment without being compacted until the entire 2 mm was filled. That may explain why the fibre orientation in Build It did not exhibit the same behaviour.

After 1 year of water storage of the lapped specimens, one-way ANOVA revealed that Build It/Z250 continued to exhibit the highest bond strength. Two-way ANOVA showed the duration of water storage did play a significant role, with shear bond strength decreasing for all the groups with the exception of ST/ST. This is agreement with the general consensus that water storage degrades several properties of dental resin composites. This has been attributed to the swelling and plasticisation of the polymer as well as the hydrolysis of the silane bond between the fillers and the resin matrix. Those changes have been found to cause a reduction in modulus and strength (Sideridou *et al.*, 2007).

ST/ST did not show a significant difference when its 24 hour shear bond strength was compared with its 1 year shear bond strength. This may appear unexpected especially when the water sorption experiment discussed in section 7.1.2 clearly illustrated that ST had the highest water sorption of all three materials tested. When taking those results into account, it may be reasonable to believe that ST would show a decrease in bond strength after one year of water storage. The fact that ST/ST did not appear to exhibit a significant difference may be due to the high standard deviation in both the 24 hour and 1 year groups, which would have influenced the results of the statistical tests. When comparing the 5% probability of failure for the samples using the Weibull probability plots, it was found that all the groups tested exhibited a decrease in bond strength within 1-2 MPas as shown in Table 36.

Composite Group	**SBS (MPa) at 5% probability of failure after 24 hours water storage**	**SBS (MPa) at 5% probability of failure after 1 year water storage**
Build It/Z250	14.64	13.06
Build It/Build It	7.63	6.53
ST/ST	6.01	5.23
Z250/Z250	6.98	4.21
ST/Z250	3.10	1.86

Table 36. SBS (MPa) at 5 % probability of failure after 24 hours and 1 year water storage.

As shown in Table 36 , the percentages of force required for 5% probability of failure after 1 year water storage are varied. Build It/Z250 continued to exhibit higher bond strength than any of the other groups, with its SBS at 5% probability of failure decreasing by 11% after 1 year of water storage, while Build It/Build It decreased by 15% and 13% respectively. However, both Z250/Z250 and ST/Z250 exhibited approximately 40% decrease in SBS after 1 year water storage. These results indicate that the bonds within Z250/Z250 and ST/Z250 degraded more than those within Build It/Z250, Build It/Build It or ST/ST.

At both time intervals, the lapped specimens of ST/Z250 exhibited no cohesive failures in the composite substrate. 21% of the Build It/Z250 specimens failed cohesively in the composite substrate at 24 hours water storage and 100% of the samples failed cohesively in the substrate after 1 year of water storage. Based on these results, it is speculated that there is a higher likelihood of delamination of the veneering Z250 when ST is a core material or dentine replacement. That would result in ST being directly exposed to the oral environment. Thus, it would be worthwhile to investigate some surface characteristics of ST. The two and three body wear behaviour of ST and the comparator materials were investigated and the results of those investigations are discussed in section 7.3.

When looking at the results of the bond strengths of composite/composite groups in the presence of an oxygen inhibition layer, one-way ANOVA showed a significant difference between the groups ($p = 0.00$). Tukey's test indicated that ST/ST had a significantly lower bond strength than the remainder of the groups while Build It/Z250 exhibited a significantly higher bond strength. These results, with the exception of ST/ST, are consistent with those of the lapped composite groups. When comparing the air inhibited and lapped groups, no significant difference was found in the either of the FRCs bonded to Z250, while Z250/Z250 and Build It/Build It showed significantly stronger shear bond strengths in the presence of an oxygen inhibition layer.

When assessing the bond strengths between dental resin composites, there has been no clear consensus reached regarding the effect of the oxygen-inhibited layer in the literature. While some reported an improvement in bond strength between composite increments (Truffier-Boutry *et al.*, 2003; Kim *et al.*, 2006; Shawkat *et al.*, 2009), others found no difference (Rueggeberg and Margeson, 1990; Suh, 2004; Dall'Oca *et al.*, 2007; Shawkat *et al.*, 2009). However, as an oxygen inhibition layer is present when composite restorations are layered in a cavity and when a tooth is built up using different dental resin composites, investigating the effect of such a layer is an important part of attempting to understand how a material will behave in a clinical setting.

The theory that the presence of an oxygen-inhibited layer increases incremental composite bond strength is based on the principle of molecular interaction. The soft, liquid-like consistency of the oxygen inhibition layer is believed to improve interfacial bonding between two contacting polymers due to an increase in the contacting area. The oxygen-inhibited layer would also allow the polymers on both sides to blend together to form an ‘‘intermixed’’ or ‘‘interdiffused’’ zone characterised by the formation of chemical bonds due to copolymerisation (Truffier-Boutry *et al.*, 2003; Dall'Oca *et al.*, 2007). For curing systems sensitive to oxygen, it might be reasonable to expect that a resin-rich surface would provide improved integrity between incremental layers compared with a surface with no oxygen inhibition layer since chemical bonds within interpenetrating networks would form more readily. However, the oxygen inhibited layer also has the same composition as the uncured resin, with the exception that the photoinitiator system has been consumed or decomposed. That led to the oxygen inhibited layer interfering with the formation of an adequate bond with the overlying resin composite (Eliades and Caputo, 1989; Suh, 2004).

When comparing the air inhibited and lapped groups, no significant difference was found in the either of the FRCs bonded to Z250. This was in support of previous work (Rueggeberg and Margeson, 1990; Suh, 2004; Shawkat *et al.*, 2009). Dall’Oca *et al*. (2007) also found that the presence of an oxygen-inhibited layer does not significantly affect the composite-to-composite bond strength if bonding is performed within 14 days.

Both Z250/Z250 and Build It/Build It showed significantly stronger shear bond strengths in the presence of an oxygen inhibition layer in this study. This is in agreement with the studies which suggested that an oxygen inhibited surface layer is required to increase bond strengths between dental resin composite increments(Truffier-Boutry *et al.*, 2003; Kim *et al.*, 2006; Shawkat *et al.*, 2009). Ribeiro *et al.* (2008) found the strongest associated between Z250/Z250 in the presence of an oxygen inhibition layer when testing several composite/composite associations. However, there was no comparator group without an oxygen inhibition layer tested in their study (Ribeiro *et al.*, 2008).

When comparing the 5% failures of the oxygen inhibited versus the lapped composite groups, it is interesting to note that all groups show improved bond strength of ≥1 MPa with the exception of ST/ST and Build It/Z250 as shown in Table 37. The presence of an oxygen inhibition layer resulted in Build It/Build It withstanding 30 % more force at 5% probability of failure compared with the lapped group. Z250/Z250 withstood 20% more force while ST/Z250 withstood approximately 100% more. However, ST/ST showed a decrease of approximately 60% in the force it could tolerate.

Mat Group	**SBS (MPa) at 5% probability failure (Lapped, 24 hours water storage**	**SBS (MPa) at 5% probability failure (air inhibited, 24 hours water storage)**
Build It/Z250	14.64	14.76
Build It/Build It	7.63	9.71
Z250/Z250	6.98	8.29
ST /ST	6.01	2.08
ST / Z250	3.10	6.6

Table 37. Comparison of SBS at 5% probability failure for lapped and air inhibited samples.

ST/ST failed at 2.08 MPa in the presence of the oxygen inhibition layer compared with 6.01 MPa in the lapped composite group. This may be due to the viscosity and lack of homogeneity of ST. When bonding ST to ST during oxygen inhibited specimen preparation, the material may lack the fluidity necessary to permeate into any irregularities on the surface of the composite substrate. Build It/Z250 remained largely unchanged.

The failure modes of the oxygen inhibited samples once again demonstrated that ST/Z250 had no cohesive failures in the composite substrate while Build It/Z250 had

50% cohesive failures in the composite substrate. This series of tests show that, within the limitations of this study and despite the known limitations of the testing methodology employed, ST has displayed mainly adhesive failure whether bonded to human dentine or to a veneering dental resin composite. When bonded to a veneering composite, there does appear to be a risk of delamination at a significantly lower force than that if the veneering composite was bonded to Build It. As both resin composites carry the risk of delamination, it is worthwhile to examine their wear resistance in the laboratory. The results of those investigations are discussed in the following section.

Chapter 8. Conclusion

8.1 **Conclusions and Recommendations for Future Work**

The studies presented allowed a better understanding of the behaviour of two FRC regarding several material properties. Based on the results found and within the limitations of the studies presented in this work, the following conclusions and recommendations are made:

1. This work tested two FRC materials which exhibited contrasting results in some cases and that is due to the differences in their overall formulations. Thus, the conclusion is drawn that behaviour of an FRC, similar to a PFC, is dependant on its overall formulation.
2. Based on the results of the wear resistance testing, the recommendation would be to ensure that ST is not directly exposed to the oral environment in its current formulation.
3. Changing the fibre lengths in the current formulation of ST had a significant positive impact on three body wear resistance. However, it negatively affected surface contact fatigue. As the change was from 8 mm to 25mm or 3-5mm, a fibre length between those ranges may give a more acceptable result in both two and three-body wear tests. It would be beneficial to test narrow ranges of fibre lengths to determine the optimum length, if one exists.
4. Regarding ST, while it exhibited water sorption which was deemed acceptable by ISO standards as well as similar polymerisation shrinkage to the comparator materials, both its bond strength to human dentine and wear resistance were significantly lower. ST’s bond strength to the veneering composite used in this work was also significantly lower than that of the comparable FRC (Build It).
5. ST did not appear to be affected by the presence of the oxygen inhibition layer during its bond strength testing, unlike Build It which exhibited an increase in bond strength in the presence of the oxygen inhibition layer.
6. Based on the results of the interfacial bond strength testing between the composites in the presence and absence of an oxygen inhibition layer after 24 hours water storage, it recommended to repeat the experiment after ageing both

the oxygen inhibited samples as well as the lapped samples. This will give a more comprehensive view on the effect of the oxygen inhibition layer.

7. Further development of ST is required before the material may be deemed suitable for use as a single restorative material. Its surface contact fatigue and three body wear was significantly lower than either of the comparator materials and it exhibited a definite lack of homogeneity and smoothness after wear testing.
8. The suggested development of ST would be in two main areas:
    a. The mixing of ST. This development would occur by ensuring a void free, uniform mixture of ST with a homogenous fibre content throughout the material. This would create a material with more consistent behaviour, especially during wear testing.
    b. A more gradual change in fibre lengths when testing new materials. This would allow the possibility of finding the optimal length with more precision.
9. An interesting finding of this work was the high bond strength exhibited between Build It and Z250, both with and without an oxygen inhibition layer. Despite the significant decrease shown after ageing for 1 year, the force at which 5% of its samples failed was higher than that exhibited by any other group after only 24 hours. This finding is an area for further research as it could impact on the usage of Build It in the clinical setting.

References

References

Al-Turki LI, Drummond JL, Agojci M, Gosz M, Tyrus JM, Lin L (2007). Contact versus flexure fatigue of a fiber-filled composite. *Dent Mater* 23:648-653.

Alomari QD, Reinhardt JW, Boyer DB (2001). Effect of liners on cusp deflection and gap formation in composite restorations. *Oper Dent* 26:406-411.

Alvim HH, Alecio AC, Vasconcellos WA, Furlan M, de Oliveira JE, Saad JR (2007). Analysis of camphorquinone in composite resins as a function of shade. *Dent Mater* 23:1245-1249.

Amirouche-Korichi A, Mouzali M, Watts DC (2009). Effects of monomer ratios and highly radiopaque fillers on degree of conversion and shrinkage-strain of dental resin composites. *Dent Mater* 25:1411-1418.

Angker L, Swain MV, Kilpatrick N (2005). Characterising the micro-mechanical behaviour of the carious dentine of primary teeth using nano-indentation. *J Biomech* 38:1535-1542.

Angker L, Swain MV (2006). Nanoindentation: Application to dental hard tissue investigations. *J. Mater. Res* 21:1893-1905.

Anttila EJ, Krintila OH, Laurila TK, Lassila LV, Vallittu PK, Hernberg RG (2008). Evaluation of polymerization shrinkage and hydroscopic expansion of fiber-reinforced biocomposites using optical fiber Bragg grating sensors. *Dent Mater* 24:1720-1727.

Anusavice K (1996). Challenges to the development of esthetic alternatives to dental amalgam in adacemic research center. *Transactions of the Academy of Dental Materials* 9:25-50.

Anusavice KJ (2003). Structure of Matter and Principles of Adhesion. In: Phillips' Science of Dental Materials. Rudolph editor: Saunders, pp. 21- 40.

Armstrong SR, Keller JC, Boyer DB (2001). Mode of failure in the dentin-adhesive resin-resin composite bonded joint as determined by strength-based (muTBS) and fracture-based (CNSB) mechanical testing. *Dent Mater* 17:201-210.

Armstrong SR, Vargas MA, Fang Q, Laffoon JE (2003). Microtensile bond strength of a total-etch 3-step, total-etch 2-step, self-etch 2-step, and a self-etch 1-step dentin bonding system through 15-month water storage. *J Adhes Dent* 5:47-56.

Armstrong S, Geraldeli S, Maia R, Raposo LH, Soares CJ, Yamagawa J (2010). Adhesion to tooth structure: a critical review of "micro" bond strength test methods. *Dent Mater* 26:e50-62.

Asmussen E, Peutzfeldt A, Heitmann T (1999). Stiffness, elastic limit, and strength of newer types of endodontic posts. *Journal of Dentistry* 27:275-278.

Asmussen E, Peutzfeldt A (2001). Influence of selected components on crosslink density in polymer structures. *Eur J Oral Sci* 109:282-285.

Atai M, Watts DC (2006). A new kinetic model for the photopolymerization shrinkage-strain of dental composites and resin-monomers. *Dent Mater* 22:785-791.

Baidya KP, Ramakrishna S, Rahman M, Ritchie A (2001). Quantitative radiographic analysis of fiber reinforced polymer composites. *J Biomater Appl* 15:279-289.

Baran G, Boberick K, McCool J (2001). Fatigue of restorative materials. *Crit Rev Oral Biol Med* 12:350-360.

Baroudi K, Saleh AM, Silikas N, Watts DC (2007). Shrinkage behaviour of flowable resin-composites related to conversion and filler-fraction. *J Dent* 35:651-655.

Barucci-Pfister N, Gohring TN (2009). Subjective and objective perceptions of specular gloss and surface roughness of esthetic resin composites before and after artificial aging. *Am J Dent* 22:102-110.

Bayne SC, Taylor DF, Heymann HO (1992). Protection hypothesis for composite wear. *Dent Mater* 8:305-309.

Bednarek S, Absil G, Vandoorne C, Lachaussee S, Vanmeerbeek M (2009). [Neglected children: birth, life and survival]. *Presse Med* 38:377-383.

Belli S, Donmez N, Eskitascioglu G (2006). The effect of c-factor and flowable resin or fiber use at the interface on microtensile bond strength to dentin. *J Adhes Dent* 8:247-253.

Beun S, Glorieux T, Devaux J, Vreven J, Leloup G (2007). Characterisation of nanofilled compared to universal and microfilled composites. *Dental Materials* 23:51-59.

Black J, Hastings GW, Knovel (Firm) (1998). Handbook of biomaterial properties London ; New York: Chapman & Hall.

Blunck U, Roulet J (2002). Effect of one-year water storage on the effectiveness of dentin adhesives in class V composite resin restorations (abstract). *J Dent Res* 81:946.

Boccaccini AR (2005). Continuous Fibre Reinforced Glass and Glass-Ceramic Matrix Composites. In: Handbook of Ceramic Composites. Springer US, pp. 461- 484.

Bolotin VV, Bolotin VVe (1999). Mechanics of fatigue: CRC Press.

Bouschlicher MR, Rueggeberg FA, Boyer DB (2000). Effect of stepped light intensity on polymerization force and conversion in a photoactivated composite. *J Esthet Dent* 12:23-32.

Bowen RL (1963). Properties of a silica-reinforced polymer for dental restorations. *J Am Dent Assoc* 66:57-64.

Bowen RL, Rapson JE, Dickson G (1982). Hardening shrinkage and hydroscopic expansion of composite resins. *J Dent Res* 61:654–658.

Bowen RL, Marjenhoff WA (1992). Dental composites/glass ionomers: the materials. *Adv Dent Res* 6:44-49.

Boyer DB, Chan KC, Reinhardt JW (1984). Built-up and repair of light-cured composites: bond strength. *J Dent Res* 63:1241–1244

Braem MJ, Lambrechts P, Gladys S, Vanherle G (1995). In vitro fatigue behavior of restorative composites and glass ionomers. *Dent Mater* 11:137-141.

Braga RR, Ferracane JL (2002). Contraction stress related to degree of conversion and reaction kinetics. *J Dent Res* 81:114-118.

Braga RR, Ballester RY, Ferracane JL (2005). Factors involved in the development of polymerization shrinkage stress in resin-composites: a systematic review. *Dent Mater* 21:962-970.

Braga RR, Meira JB, Boaro LC, Xavier TA (2010). Adhesion to tooth structure: a critical review of "macro" test methods. *Dent Mater* 26:e38-49.

Breschi L, Mazzoni A, Ruggeri A, Cadenaro M, Di Lenarda R, De Stefano Dorigo E (2008). Dental adhesion review: aging and stability of the bonded interface. *Dent Mater* 24:90-101.

Breschi L, Mazzoni A, De Stefano Dorigo E, Ferrari M (2009). Adhesion to Intraradicular Dentin; A review. *Journal of Adhesion Science and Technology* 23:1053 - 1083.

Brown D (1997). The status of restorative dental materials. *Dent Update* 24:402-406.

Bryant R, Mahler D (2007). Volumetric contraction in some tooth-coloured restorative materials *Australian Dental Journal* 52:112-117.

Bryant RW (1990). Comparison of three standards for quantifying occlusal loss of composite restorations. *Dent Mater* 6:60-62.

Buonocore MG (1955). A simple method of increasing the adhesion of acrylic filling materials to enamel surfaces. *J Dent Res* 34:849-853.

Burette P, Vanmeerbeek M, Bouuaert C, Giet D (2006). [Family practitioner and carbon monoxide poisoning]. *Rev Med Liege* 61:285-290.

Burette P, Bouuaert C, Vanmeerbeek M, Giet D (2008). [Four years of application of the law that decriminalizes euthanasia in Belgium]. *Presse Med* 37:1281-1288.

Burke FJ, Hussain A, Nolan L, Fleming GJ (2008). Methods used in dentine bonding tests: an analysis of 102 investigations on bond strength. *Eur J Prosthodont Restor Dent* 16:158-165.

Burrow M, Thomas D, Swain M, Tyas M (2004). Analysis of tensile bond strengths using Weibull statistics. *Biomaterials* 25:5031-5035.

Cadenaro M, Antoniolli F, Sauro S, Tay FR, Di Lenarda R, Prati C*, et al.* (2005). Degree of conversion and permeability of dental adhesives. *Eur J Oral Sci* 113:525-530.

Caldas DB, de Almeida JB, Correr-Sobrinho L, Sinhoreti MA, Consani S (2003). Influence of curing tip distance on resin composite Knoop hardness number, using three different light curing units. *Oper Dent* 28:315-320.

Callaghan DJ, Vaziri A, Nayeb-Hashemi H (2006). Effect of fiber volume fraction and length on the wear characteristics of glass fiber-reinforced dental composites. *Dent Mater* 22:84-93.

Callister WD (2007). Materials science and engineering : an introduction. 7th ed. New York: John Wiley & Sons.

Carmichael AJ, Gibson JJ, Walls AW (1997). Allergic contact dermatitis to bisphenol-A-glycidyldimethacrylate (BIS-GMA) dental resin associated with sensitivity to epoxy resin. *Br Dent J* 183:297-298.

Carrilho MR, Carvalho RM, de Goes MF, di Hipolito V, Geraldeli S, Tay FR*, et al.* (2007). Chlorhexidine preserves dentin bond in vitro. *J Dent Res* 86:90-94.

Chadwick RG, McCabe JF, Walls AW, Storer R (1990). The effect of storage media upon the surface microhardness and abrasion resistance of three composites. *Dent Mater* 6:123-128.

Chai J, Takahashi Y, Hisama K, Shimizu H (2004). Water sorption and dimensional stability of three glass fiber-reinforced composites. *Int J Prosthodont* 17:195-199.

Chan KHS, Mai Y, Kim H, Tong KCT, Ng D, Hsiao JCM (2010). Review: Resin Composite Filling. *Materials* 3:1228-1243.

Chand N, Nayak A, Neogi S (2000). Three-Body Abrasive Wear of Short Glass Fiber Polyester Composite. *Wear* 242:32–46.

Chand S (2000). Carbon fibers for composites. *Journal of Materials Science* 35:1303-1313.

Chen MH (2010). Update on dental nanocomposites. *J Dent Res* 89:549-560.

Chen YC, Ferracane JL, Prahl SA (2005). A pilot study of a simple photon migration model for predicting depth of cure in dental composite. *Dent Mater* 21:1075-1086.

Choi KK, Ferracane JL, Hilton TJ, Charlton D (2000). Properties of packable dental composites. *J Esthet Dent* 12:216-226.

Combe EC, Burke FJ (2000). Contemporary resin-based composite materials for direct placement restorations: packables, flowables and others. *Dent Update* 27:326-332, 334-326.

Condon JR, Ferracane JL (1996). Evaluation of composite wear with a new multi-mode oral wear simulator. *Dent Mater* 12:218-226.

Condon JR, Ferracane JL (1997). In vitro wear of composite with varied cure, filler level, and filler treatment. *J Dent Res* 76:1405-1411.

Cook W (1992). Photopolymerization kinetics of dimethacrylates using the camphorquinone/amine initiator system. *Polymer* 33:600-609.

Cook WD, Forrest M, Goodwin AA (1999). A simple method for the measurement of polymerization shrinkage in dental composites. *Dent Mater* 15:447-449.

Costella AM, Trochmann JL, Oliveira WS (2010). Water sorption and diffusion coefficient through an experimental dental resin. *Journal of Materials Science-Materials in Medicine* 21:67-72.

Cramer NB, Stansbury JW, Bowman CN (2011). Recent advances and developments in composite dental restorative materials. *J Dent Res* 90:402-416.

Cvar JF, Ryge G (2005). Reprint of Criteria for the clinical evaluation of dental restorative materials (Reprinted from US Department of Health, Education, and Welfare, US Public Health Service 790244, San Francisco Printing Office 1971 : 1-42). *Clinical Oral Investigations* 9:215-232.

Dall'Oca S, Papacchini F, Goracci C, Cury AH, Suh BI, Tay FR*, et al.* (2007). Effect of oxygen inhibition on composite repair strength over time. *J Biomed Mater Res B Appl Biomater* 81:493-498.

Davidsen C, Andre JF, Giet D, Vanmeerbeek M (2011). [Patient-physician electronic communication]. *Rev Med Liege* 66:417-423.

de Gee AF, Feilzer AJ, Davidson CL (1993). True linear polymerization shrinkage of unfilled resins and composites determined with a linometer. *Dent Mater* 9:11-14.

de Gee AJ, ten Harkel-Hagenaar HC, Davidson CL (1985). Structural and physical factors affecting the brush wear of dental composites. *J Dent* 13:60-70.

de Gee AJ, Pallav P (1994). Occlusal wear simulation with the ACTA wear machine. *J Dent* 22 Suppl 1:S21-27.

De Munck J, Van Meerbeek B, Yoshida Y, Inoue S, Vargas M, Suzuki K*, et al.* (2003). Four-year water degradation of total-etch adhesives bonded to dentin. *J Dent Res* 82:136-140.

De Munck J, Van Landuyt K, Peumans M, Poitevin A, Lambrechts P, Braem M*, et al.* (2005). A critical review of the durability of adhesion to tooth tissue: methods and results. *J Dent Res* 84:118-132.

DeLong R, Douglas WH (1983). Development of an artificial oral environment for the testing of dental restoratives: bi-axial force and movement control. *J Dent Res* 62:32-36.

Dewaele M, Truffier-Boutry D, Devaux J, Leloup G (2006). Volume contraction in photocured dental resins: the shrinkage-conversion relationship revisited. *Dent Mater* 22:359-365.

Draughn RA (1979). Compressive fatigue limits of composite restorative materials. *J Dent Res* 58:1093-1096.

Drummond JL (1989). Cyclic fatigue of composite restorative materials. *J Oral Rehabil* 16:509-520.

Drummond JL (2008). Degradation, fatigue, and failure of resin dental composite materials. *J Dent Res* 87:710-719.

Duncan JP, Freilich MA, Latvis CJ (2000). Fiber-reinforced composite framework for implant-supported overdentures. *J Prosthet Dent* 84:200-204.

Dyer SR, Lassila LV, Jokinen M, Vallittu PK (2004). Effect of fiber position and orientation on fracture load of fiber-reinforced composite. *Dent Mater* 20:947-955.

Eick JD, Kotha SP, Chappelow CC, Kilway KV, Giese GJ, Glaros AG*, et al.* (2007). Properties of silorane-based dental resins and composites containing a stress-reducing monomer. *Dent Mater* 23:1011-1017.

Eliades GC, Caputo AA (1989). The strength of layering technique in visible light-cured composites. *Journal of Prosthetic Dentistry* 61:31-38.

Ellakwa A, Cho N, Lee IB (2007). The effect of resin matrix composition on the polymerization shrinkage and rheological properties of experimental dental composites. *Dent Mater* 23:1229-1235.

Emami N, Soderholm K (2009). Young's Modulus and Degree of Conversion of Different Combination of Light-Cure Dental Resins. *Open Dent J* 3:202-207.

Fano V, Ortalli I, Pizzi S, Bonanini M (1997). Polymerization shrinkage of microfilled composites determined by laser beam scanning. *Biomaterials* 18:467-470.

Feilzer AJ, De Gee AJ, Davidson CL (1988). Curing contraction of composites and glass-ionomer cements. *J Prosthet Dent* 59:297-300.

Feilzer AJ, De Gee AJ, Davidson CL (1989). Increased wall-to-wall curing contraction in thin bonded resin layers. *J Dent Res* 68:48-50.

Feilzer AJ, de Gee AJ, Davidson CL (1990). Relaxation of polymerization contraction shear stress by hygroscopic expansion. *J Dent Res* 69:36-39.

Feilzer AJ, Dauvillier BS (2003). Effect of TEGDMA/BisGMA ratio on stress development and viscoelastic properties of experimental two-paste composites. *J Dent Res* 82:824-828.

Feng L, Suh BI (2006). The effect of curing modes on polymerization contraction stress of a dual cured composite. *J Biomed Mater Res B Appl Biomater* 76:196-202.

Fennis WM, Tezvergil A, Kuijs RH, Lassila LV, Kreulen CM, Creugers NH*, et al.* (2005). In vitro fracture resistance of fiber reinforced cusp-replacing composite restorations. *Dent Mater* 21:565-572.

Ferracane JL, Greener EH (1986). The effect of resin formulation on the degree of conversion and mechanical properties of dental restorative resins. *J Biomed Mater Res* 20:121-131.

Ferracane JL (1994). Elution of leachable components from composites. *Journal of Oral Rehabilitation* 21: 441-452

Ferracane JL (1995). Current trends in dental composites. *Crit Rev Oral Biol Med* 6:302-318.

Ferracane JL (1997). Water sorption and solubility of experimental dental composites. *Polymer Preprints* 38:116–117.

Ferracane JL, Berge HX, Condon JR (1998). In vitro aging of dental composites in water--effect of degree of conversion, filler volume, and filler/matrix coupling. *J Biomed Mater Res* 42:465-472.

Ferracane JL (2005). Developing a more complete understanding of stresses produced in dental composites during polymerization. *Dent Mater* 21:36-42.

Ferracane JL (2006). Hygroscopic and hydrolytic effects in dental polymer networks. *Dent Mater* 22:211-222.

Ferracane JL, Dossett JM, Pelogia F, Macedo MRP, Hilton T (2009). Navigating the Dentin Bond Strength Testing Highway: Lessons and Recommendations. *Journal of Adhesion Science and Technology* 23:1007-1022.

Ferracane JL (2011). Resin composite--state of the art. *Dent Mater* 27:29-38.

Ferrari M, Cardoso PEC (2002). SEM evaluation of microtensile sample integrity before being tested. *J Dent Res* 81:A139-A139.

Field JS, Swain MV (1993). A simple predictive model for spherical indenter. *J. Mater. Res.* 8:297-306.

Floyd CJ, Dickens SH (2006). Network structure of Bis-GMA- and UDMA-based resin systems. *Dent Mater* 22:1143-1149.

Folwaczny M, Mehl A, Kunzelmann KH, Hickel R (2000). Determination of changes on tooth-colored cervical restorations in vivo using a three-dimensional laser scanning device. *Eur J Oral Sci* 108:233-238.

Freilech (2000). Fiber-Reinforced Composites in Clinical Dentistry.

Freilich MA, Meiers JC, Duncan JP (2000). Chairside Applications of FRC In: Fiber-Reinforced Composites in Clinical Dentistry. MA Freilich, JC Meiers, JP Duncan and AJ Goldberg editors. Univ. of Connecticut, Farmington: Quintessence Pub Co, pp. 49-70.

Fu SY, Lauke B (1996). Effects of fibre length and fibre orientation distributions on the tensile strength of short-fibre-reinforced polymers. *Composites Science and Technology* 56:1179-1190.

Fujibayashi K, Ishimaru K, Takahashi N, Kihno A (1998). Newly developed curing unit using blue light-emitting diodes,. *Dent. Jpn* 34:49–53.

Fujihara K, Huang ZM, Ramakrishna S, Satknanantham K, Hamada H (2004). Feasibility of knitted carbon/PEEK composites for orthopedic bone plates. *Biomaterials* 25:3877-3885.

Fujii K, Carrick TE, Bicker R, McCabe JF (2004). Effect of the applied load on surface contact fatigue of dental filling materials. *Dent Mater* 20:931-938.

Galvão MR, Costaa SXS, Victorinoa KR, Ribeirob AA, Menezesc FCH, Rastellia ANS*, et al.* (2010). Influence of Light Guide Tip Used in the PhotoActivation on Degree of Conversion and Hardness of One Nanofilled Dental Composite. *Laser Physics* 20:2050-2055.

Gao X, Jensen RE, Li W, Deitzel J, McKnight SH, J.W. Gillespie J (2008). Effect of Fiber Surface Texture Created from Silane Blends on the Strength and Energy Absorption of the Glass Fiber/Epoxy Interphase. *Journal of Composite Materials* 42:513-534.

Garoushi S (2006). Bilayered Dental Composite Resin Load Bearing Capacity of Combinations of Fibre-Reinforced and Particulate-Filler Composite. Turku, Turku.

Garoushi S, Lassila LV, Tezvergil A, Vallittu PK (2006a). Load bearing capacity of fibre-reinforced and particulate filler composite resin combination. *J Dent* 34:179-184.

Garoushi S, Lassila LV, Tezvergil A, Vallittu PK (2007a). Static and fatigue compression test for particulate filler composite resin with fiber-reinforced composite substructure. *Dent Mater* 23:17-23.

Garoushi S, Vallittu PK, Lassila LV (2007b). Direct restoration of severely damaged incisors using short fiber-reinforced composite resin. *J Dent* 35:731-736.

Garoushi S, Vallittu PK, Lassila LV (2007c). Fracture resistance of short, randomly oriented, glass fiber-reinforced composite premolar crowns. *Acta Biomater* 3:779-784.

Garoushi S, Vallittu PK, Lassila LV (2007d). Use of short fiber-reinforced composite with semi-interpenetrating polymer network matrix in fixed partial dentures. *J Dent* 35:403-408.

Garoushi S, Vallittu PK, Lassila LV (2007e). Short glass fiber reinforced restorative composite resin with semi-inter penetrating polymer network matrix. *Dent Mater* 23:1356-1362.

Garoushi S, Vallittu PK, Watts DC, Lassila LV (2008a). Effect of nanofiller fractions and temperature on polymerization shrinkage on glass fiber reinforced filling material. *Dent Mater* 24:606-610.

Garoushi S, Vallittu PK, Watts DC, Lassila LV (2008b). Polymerization shrinkage of experimental short glass fiber-reinforced composite with semi-inter penetrating polymer network matrix. *Dent Mater* 24:211-215.

Garoushi SK, Ballo AM, Lassila LV, Vallittu PK (2006b). Fracture resistance of fragmented incisal edges restored with fiber-reinforced composite. *J Adhes Dent* 8:91-95.

Garoushi SK, Lassila LV, Tezvergil A, Vallittu PK (2006c). Fiber-reinforced composite substructure: load-bearing capacity of an onlay restoration and flexural properties of the material. *J Contemp Dent Pract* 7:1-8.

Garoushi SK, Lassila LV, Vallittu PK (2006d). Fiber-reinforced composite substructure: load-bearing capacity of an onlay restoration. *Acta Odontol Scand* 64:281-285.

Garoushi SK, Lassila LV, Vallittu PK (2006e). Short fiber reinforced composite: the effect of fiber length and volume fraction. *J Contemp Dent Pract* 7:10-17.

Garoushi SK, Lassila LV, Vallittu PK (2007e). Direct composite resin restoration of an anterior tooth: effect of fiber-reinforced composite substructure. *Eur J Prosthodont Restor Dent* 15:61-66.

Garoushi SK, Lassila LV, Vallittu PK (2007f). Fatigue strength of fragmented incisal edges restored with a fiber reinforced restorative material. *J Contemp Dent Pract* 8:9-16.

Gatti AM (2004). Biocompatibility of micro- and nano-particles in the colon. Part II. *Biomaterials* 25:385-392.

Ghazal M, Hedderich J, Kern M (2008). Wear of feldspathic ceramic, nano-filled composite resin and acrylic resin artificial teeth when opposed to different antagonists. *European Journal of Oral Sciences* 116:585–592.

Ghivari S, Chandak M, Manvar N (2010). Role of oxygen inhibited layer on shear bond strength of composites. *J Conserv Dent* 13:39-41.

Goldberg AJ, Rydinge E, Santucci EA, Racz WB (1984). Clinical evaluation methods for posterior composite restorations. *J Dent Res* 63:1387-1391.

Goldstein GR, Lerner T (1991). The effect of toothbrushing on a hybrid composite resin. *J Prosthet Dent* 66:498-500.

Goncalves F, Kawano Y, Braga RR (2010). Contraction stress related to composite inorganic content. *Dent Mater* 26:704-709.

Goncalves F, Azevedo CL, Ferracane JL, Braga RR (2011). BisGMA/TEGDMA ratio and filler content effects on shrinkage stress. *Dent Mater* 27:520-526.

Guggenberger R, Weinmann W (2000). Exploring beyond methacrylates. *Am J Dent* 13:82D-84D.

Hahnel S, Schultz S, Trempler C, Ach B, Handel G, Rosentritt M (2011). Two-body wear of dental restorative materials. *J Mech Behav Biomed Mater* 4:237-244.

Halvorson RH, Erickson RL, Davidson CL (2003). The effect of filler and silane content on conversion of resin-based composite. *Dent Mater* 19:327-333.

Hannig M, Friedrichs C (2001). Comparative in vivo and in vitro investigation of interfacial bond variability. *Oper Dent* 26:3-11.

Hansel C, Leyhausen G, and UEM, Geurtsen W (1998). Effects of various resin composite (co) monomers and extracts on two caries-associated micro-organisms in vitro. *J Dent Res* 1:7-60.

Hashimoto M, Ohno H, Endo K, Kaga M, Sano H, Oguchi H (2000). The effect of hybrid layer thickness on bond strength: demineralized dentin zone of the hybrid layer. *Dent Mater* 16:406-411.

Hashimoto M, Ohno H, Sano H, Tay FR, Kaga M, Kudou Y*, et al.* (2002). Micromorphological changes in resin-dentin bonds after 1 year of water storage. *J Biomed Mater Res* 63:306-311.

Hebling J, Pashley DH, Tjaderhane L, Tay FR (2005). Chlorhexidine arrests subclinical degradation of dentin hybrid layers in vivo. *J Dent Res* 84:741-746.

Heintze SD, Zappini G, Rousson V (2005). Wear of ten dental restorative materials in five wear simulators--results of a round robin test. *Dent Mater* 21:304-317.

Heintze SD (2007). Systematic reviews: I. The correlation between laboratory tests on marginal quality and bond strength. II. The correlation between marginal quality and clinical outcome. *J Adhes Dent* 9 Suppl 1:77-106.

Heintze SD (2009). Predictability of Clinical Wear by Laboratory Wear Methods for the Evaluation of Dental Restorative Materials. Groningen, The Netherlands, University of Groningen.

Heintze SD, Blunck U, Gohring TN, Rousson V (2009). Marginal adaptation in vitro and clinical outcome of Class V restorations. *Dent Mater* 25:605-620.

Heintze SD, Zimmerli B (2011). Relevance of In-vitro Tests of Adhesive and Composite Dental Materials. A Review in 3 Parts. Part 2: Non-standardized tests of composite materials. *Schweiz Monatsschr Zahnmed* 121:916-923.

Hickel R, Peschke A, Tyas M, Mjor I, Bayne S, Peters M*, et al.* (2010). FDI World Dental Federation: clinical criteria for the evaluation of direct and indirect restorations-update and clinical examples. *Clin Oral Investig* 14:349-366.

Hirschfeld T, Chase B (1986). Ft-Raman Spectroscopy - Development and Justification. *Applied Spectroscopy* 40:133-137.

Horst JJ, Spoormaker JL (1997). Fatigue fracture mechanisms and fractography of short-glass fibre-reinforced polyamide 6. *Journal of Materials Science* 32,:3641-3651,.

Hu X, Harrington E, Marquis PM, Shortall AC (1999a). The influence of cyclic loading on the wear of a dental composite. *Biomaterials* 20:907-912.

Hu X, Marquis PM, Shortall AC (2003). Influence of filler loading on the two-body wear of a dental composite. *J Oral Rehabil* 30:729-737.

Hu XQ, Marquis PM, Shortall AC (1999b). Two-body in vitro wear study of some current dental composites and amalgams. *Journal of Prosthetic Dentistry* 82:214-220.

Ilie N, Hickel R (2006). Silorane-based dental composite: behavior and abilities. *Dent Mater J* 25:445-454.

Ilie N, Hickel R (2011). Resin composite restorative materials. *Aust Dent J* 56 Suppl 1:59-66.

International Organization for Standaridization (ISO) (2000). Dentistry-Polymer-based filling, restorative and luting materials. Switzerland: ISO 4049-4. 2003: 2.

International Organization for Standaridization (ISO) (2000). Dentistry-Polymer-based filling, restorative and luting materials. Switzerland: ISO 4049-7.12. 2003: 18-21.

Imazato S, Tarumi H, Kato S, Ebi N, Ehara A, Ebisu S (1999). Water Sorption, Degree of Conversion, and Hydrophobicity of Resins containing Bis-GMA and TEGDMA. *Dent Mater J* 18:124-132.

Imazato S, McCabe JF, Tarumi H, Ehara A, Ebisu S (2001). Degree of conversion of composites measured by DTA and FTIR. *Dent Mater* 17:178-183.

Jakubiak J, Sionkowska A, Linde´n L, Rabek J (2001). Isothermal photo differential scanning calorimetry. Crosslinking polymerization of multifunctional monomers in presence of visible light photoinitiators. *J Therm Anal Calorim* 65:435-443.

Jakubiak J, Allonas X, Fouassier J, Sionkowska A, Andrzejewska E, Linden L*, et al.* (2003). Camphorquinone—amines photoinitating systems for the initiation of free radical polymerization. *Polymer* 44.

Jancar J, DiBenedeto A (1993). Thermoplastic fibre-reinforced composites for dentistry *Journal of Materials Science: Materials in Medicine* 4 562-568.

Jørgensen KD (1978). Occlusal abrasion of a composite resin with ultra-fine filler - an initial study. *Quintessence International* 6:73–78.

Kahler B, Kotousov A, Swain MV (2008). On the design of dental resin-based composites: a micromechanical approach. *Acta Biomater* 4:165-172.

Kaidonis JA, Richards LC, Townsend GC, Tansley GD (1998). Wear of human enamel: a quantitative in vitro assessment. *J Dent Res* 77:1983-1990.

Kalachandra S, Turner DT (1987). Water sorption of polymethacrylate networks: bis-GMA/TEGDM copolymers. *J Biomed Mater Res* 21:329-338.

Kalachandra S (1989). Influence of fillers on the water sorption of composites. *Dent Mater* 5:283-288.

Kanca J, 3rd, Suh BI (1999). Pulse activation: reducing resin-based composite contraction stresses at the enamel cavosurface margins. *Am J Dent* 12:107-112.

Kang JD, Ososkov Y, Embury JD, Wilkinson DS (2007). Digital image correlation studies for microscopic strain distribution and damage in dual phase steels. *Scripta Materialia* 56:999–1002.

Kawai K, Leinfelder KF (1995). In vitro evaluation of OCA wear resistance of posterior composites. *Dent Mater* 11:246-251.

Kawai K, Iwami Y, Ebisu S (1998). Effect of resin monomer composition on toothbrush wear resistance. *J Oral Rehabil* 25:264-268.

Keski-Nikkola MS, Alander PM, Lassila LV, Vallittu PK (2004). Bond strength of Gradia veneering composite to fibre-reinforced composite. *J Oral Rehabil* 31:1178-1183.

Kessler A, Bledzki A (2000). Correlation between interphase-relevant tests and the impact-damage resistance of glass/epoxy laminates with different fibre surface treatments *Composites Science and Technology*

60:125-130

Keusch S, Haessler R (1999). Influence of surface treatment of glass fibres on the dynamic mechanical properties of epoxy resin composites. *Composites Part A: Applied Science and Manufacturing* 30:997 - 1002.

Khanna SK, Winter RM, Ranganathan P, Yedla SB, Kalukanimuttam M, Paruchuri K (2003). Sample preparation techniques for nano-mechanical characterization of glass fiber reinforced polyester matrix composites. *Composites Part A: Applied Science and Manufacturing* 34:53-65.

Kim JS, Choi YH, Cho BH, Son HH, Lee IB, Um CM*, et al.* (2006). Effect of light-cure time of adhesive resin on the thickness of the oxygen-inhibited layer and the microtensile bond strength to dentin. *J Biomed Mater Res B Appl Biomater* 78:115-123.

Kinomoto Y, Torii M, Takeshige F, Ebisu S (2000). Polymerization contraction stress of resin composite restorations in a model Class I cavity configuration using photoelastic analysis. *J Esthet Dent* 12:309-319.

Kitasako Y, Burrow MF, Nikaido T, Tagami J (2000). The influence of storage solution on dentin bond durability of resin cement. *Dent Mater* 16:1-6.

Kohyama K, Sakai T, Azuma T (2001a). Patterns observed in the first chew of foods with various textures. *Food Sci Technol Res* 7.

Kohyama K, Sakai T, Azuma T, Mizuguchi T, Kimura I (2001b). Pressure distribution measurement in biting surimi gels with molars using a multiple-point sheet sensor. *Bioscience, Biotechnology and Biochemistry* 56.

Kohyama K, Hatakeyama E, Sasaki T, Dan H, Azuma T, Karita K (2004). Effects of sample hardness on human chewing force: a model study using silicone rubber. *Arch Oral Biol* 49:805-816.

Kon M, Kakuta K, Ogura H (2006). Effects of occlusal and brushing forces on wear of composite resins. *Dent Mater J* 25:183-194.

Koran P, Kurschner R (1998). Effect of sequential versus continuous irradiation of a light-cured resin composite on shrinkage, viscosity, adhesion, and degree of polymerization. *Am J Dent* 11:17-22.

Korkmaz Y, Gurgan S, Firat E, Nathanson D (2010). Effect of adhesives and thermocycling on the shear bond strength of a nano-composite to coronal and root dentin. *Oper Dent* 35:522-529.

Kreulen CM, van Amerongen WE (1991). Wear measurements in clinical studies of composite resin restorations in the posterior region: a review. *ASDC J Dent Child* 58:109-123.

Kurachi C, Tuboy AM, Magalhaes DV, Bagnato VS (2001). Hardness evaluation of a dental composite polymerized with experimental LED-based devices. *Dent Mater* 17:309-315.

Labella R, Braden M, Deb S (1994). Novel hydroxyapatite-based dental composites. *Biomaterials* 15:1197-1200.

Labella R, Lambrechts P, Van Meerbeek B, Vanherle G (1999). Polymerization shrinkage and elasticity of flowable composites and filled adhesives. *Dent Mater* 15:128-137.

Ladizesky NH, Cheng YY, Chow TW, Ward IM (1993). Acrylic resin reinforced with chopped high performance polyethylene fiber--properties and denture construction. *Dent Mater* 9:128-135.

Lai JH, Johnson AE (1993). Measuring polymerization shrinkage of photo-activated restorative materials by a water-filled dilatometer. *Dent Mater* 9:139-143.

Lambrechts P, Debels E, Landuyt KV, Peumans M, Meerbeek BV (2006). How to simulate wear? Overview of existing methods *Dental Materials* 2:693-701.

Lassila LV, Nohrstrom T, Vallittu PK (2002). The influence of short-term water storage on the flexural properties of unidirectional glass fiber-reinforced composites. *Biomaterials* 23:2221-2229.

Lassila LV, Tezvergil A, Lahdenperä M, Alander P, Shinya A, Shinya A*, et al.* (2005). Evaluation of some properties of two fiber-reinforced composite materials. *Acta Odontologica Scandinavica* 63:196-204.

Lassila LV, Tezvergil A, Dyer SR, Vallittu PK (2007). The bond strength of particulate-filler composite to differently oriented fiber-reinforced composite substrate. *J Prosthodont* 16:10-17.

Lastumaki TM, Lassila LV, Vallittu PK (2003). The semi-interpenetrating polymer network matrix of fiber-reinforced composite and its effect on the surface adhesive properties. *J Mater Sci Mater Med* 14:803-809.

Lee A, He LH, Lyons K, Swain MV (2011). Tooth wear and wear investigations in dentistry. *J Oral Rehabil*.

Lee HK, Simunovic S (2000). Modeling of progressive damage in aligned and randomly oriented discontinuous fiber polymer matrix composites. *Composites Part B-Engineering* 31:77-86.

Lee IB, Son HH, Um CM (2003). Rheologic properties of flowable, conventional hybrid, and condensable composite resins. *Dent Mater* 19:298-307.

Lee IB, Cho BH, Son HH, Um CM (2005). A new method to measure the polymerization shrinkage kinetics of light cured composites. *J Oral Rehabil* 32:304-314.

Lee IB, An W, Chang J, Um CM (2008). Influence of ceramic thickness and curing mode on the polymerization shrinkage kinetics of dual-cured resin cements. *Dent Mater* 24:1141-1147.

Lee JH, Um CM, Lee IB (2006). Rheological properties of resin composites according to variations in monomer and filler composition. *Dent Mater* 22:515-526.

Leinfelder KF (1987). Wear patterns and rates of posterior composite resins. *Int Dent J* 37:152-157.

Leinfelder KF (1988). Current developments in posterior composite resins. *Adv Dent Res* 2:115-121.

Leloup G, D'Hoore W, Bouter D, Degrange M, Vreven J (2001). Meta-analytical review of factors involved in dentin adherence. *J Dent Res* 80:1605-1614.

Leung RL, Fan PL, Johanston WM(1983). Post-irration polymerization of visible Light-activated Composite Resin. *J Dent Res* 62:363–365.

Li J, Fok AS, Satterthwaite J, Watts DC (2009). Measurement of the full-field polymerization shrinkage and depth of cure of dental composites using digital image correlation. *Dent Mater* 25:582-588.

Li Y, Swartz ML, Phillips RW, Moore BK, Roberts TA (1985). Effect of filler content and size on properties of composites. *J Dent Res* 64:1396-1401.

Lim BS, Ferracane JL, Condon JR, Adey JD (2002). Effect of filler fraction and filler surface treatment on wear of microfilled composites. *Dent Mater* 18:1-11.

Lin CT, Lee SY, Keh ES, Dong DR, Huang HM, Shih YH (2000). Influence of silanization and filler fraction on aged dental composites. *J Oral Rehabil* 27:919-926.

Loguercio AD, Barroso LP, Grande RH, Reis A (2005). Comparison of intra- and intertooth resin-dentin bond strength variability. *J Adhes Dent* 7:151-158.

Lohbauer U, Frankenberger R, Kramer N, Petschelt A (2003). Time-dependent strength and fatigue resistance of dental direct restorative materials. *J Mater Sci Mater Med* 14:1047-1053.

Lohbauer U, Frankenberger R, Kramer N, Petschelt A (2006). Strength and fatigue performance versus filler fraction of different types of direct dental restoratives. *J Biomed Mater Res B Appl Biomater* 76:114-120.

Lopes MB, Moraes RR, Gonini-Junior A, Piva E (2009). Impact of curing protocol on the selected properties of a model bis-GMA/TEGDMA dental resin composite. *Biomed Mater* 4:025014.

Lovell LG, Stansbury JW, Syrpes DC, Bowman CN (1999). Effects of composition and reactivity on the reaction kinetics of dimethacrylate/dimethacrylate copolymerizations. *Macromolecules* 32:3913–3921.

Lu H, Stansbury JW, Bowman CN (2005). Impact of curing protocol on conversion and shrinkage stress. *J Dent Res* 84:822-826.

Lührs AK, Geurtsen W (2009). The Application of Silicon and Silicates in Dentistry: A Review In: Biosilica in Evolution, Morphogenesis, and Nanobiotechnology. EG Werner, A Müller Mikhael and Grachev editors: Springer Berlin Heidelberg.

Mair LH, Stolarski TA, Vowles RW, Lloyd CH (1996). Wear: mechanisms, manifestations and measurement. Report of a workshop. *J Dent* 24:141-148.

Mallick P (2008). Fiber-reinforced composites: materials, manufacturing, and design 3rd edition Boca Raton, FL: Taylor & Francis Group.

Manhart J, Kunzelmann KH, Chen HY, Hickel R (2000a). Mechanical properties and wear behavior of light-cured packable composite resins. *Dent Mater* 16:33-40.

Manhart J, Kunzelmann KH, Chen HY, Hickel R (2000b). Mechanical properties of new composite restorative materials. *J Biomed Mater Res* 53:353-361.

Manhart J, Chen HY, Hickel R (2001). The suitability of packable resin-based composites for posterior restorations. *J Am Dent Assoc* 132:639-645.

Manhart J, Chen H, Hamm G, Hickel R (2004). Buonocore Memorial Lecture. Review of the clinical survival of direct and indirect restorations in posterior teeth of the permanent dentition. *Oper Dent* 29:481-508.

McCabe J, Abu Kasim N, Cleary S (1997). A rolling-ball device for producing surface fatigue and its application to dental materials. *J Mater Sci: Mater Med* 32:283–287.

McCabe J, Wang Y, Braem M (2000). Surface contact fatigue and flexural fatigue of dental restorative materials. *J Biomed Mater Res* 50:375-380.

McCabe J, Walls A (2008). Applied Dental Materials Oxford: Blackwell.

McCabe JF (1985). Cure performance of light-activated composites by differential thermal analysis (DTA). *Dent Mater* 1:231-234.

McCabe JF, Carrick TE (1986). A statistical approach to the mechanical testing of dental materials. *Dent Mater* 2:139-142.

McCabe JF, Molyvda S, Rolland SL, Rusby S, Carrick TE (2002). Two- and three-body wear of dental restorative materials. *International Dental Journal* 52:406-416.

McCabe JF, Rusby S (2004). Water absorption, dimensional change and radial pressure in resin matrix dental restorative materials. *Biomaterials* 25:4001-4007.

Mehl A, Gloger W, Kunzelmann KH, Hickel R (1997). A new optical 3-D device for the detection of wear. *J Dent Res* 76:1799-1807.

Meiers JC, Young D (2001). Two-year composite/dentin bond stability. *Am J Dent* 14:141-144.

Mendes LC, Tedesco AD, Miranda MS (2005a). Determination of degree of conversion as function of depth of a photo-initiated dental restoration composite. *Polym. Test.* 24:418–422.

Mendes LC, Tedesco AD, Miranda MS, Benzi MR, Chagas BS (2005b). Determination of degree of conversion as a function of depth of a photo-initiated dental restoration composite-II application to commercial SureFil™,. *Polym. Test.* 24:942–946.

Miettinen VM, Narva KK, Vallittu PK (1999). Water sorption, solubility and effect of post-curing of glass fibre reinforced polymers. *Biomaterials* 20:1187-1194.

Migliaresi C, Alexander H (2004). Composites. In: Biomaterials science 2nd edn. R BD, H AS, S FJ and L JE editors. San Diego: Academic Press, pp. 181–197

Minguez N, Ellacuria J, Soler JI, Triana R, Ibaseta G (2003). Advances in the history of composite resins. *J Hist Dent* 51:103-105.

Minus M, Kumar S (2005). The processing, properties, and structure of carbon fibers. *Journal of the minerals, metals and materials society* 57:52-58.

Moin JC, Nomura Y, Urabe H, Okazaki M, Shintani H (2001). The relationship between leachability of polymerization initiator and degree of conversion of visible light-cured resin. . *J Biomed Mater Res* 58:42-46.

Momoi Y, Hirosaki K, Kohno A, McCabe JF (1997). In vitro toothbrush-dentifrice abrasion of resin-modified glass ionomers. *Dent Mater* 13:82-88.

Moszner N, Völkel T, Fischer UK, Klester A, V. Rheinberger (1999). Synthesis and polymerisation of new multifunctional urethane methacrylates. *Angew Makromol Chem* 265 31–35.

Moszner N, Salz U (2001). New developments of polymer dental composites. *Progress in Polymer Science* 26:535-576.

Moszner N, Fischer UK, Angermann J, Rheinberger V (2008). A partially aromatic urethane dimethacrylate as a new substitute for Bis-GMA in restorative composites. *Dent Mater* 24:694-699.

Murphy J (1998). The Reinforced Plastics Handbook 2nd edition New York, NY: Elsevier Science.

Musanje L, Shu M, Darvell BW (2001). Water sorption and mechanical behaviour of cosmetic direct restorative materials in artificial saliva. *Dent Mater* 17:394-401.

Musanje L, Ferracane JL, Ferracane LL (2006). Effects of Resin Formulation and Nanofiller Surface Treatment on In Vitro Wear of Experimental Hybrid Resin Composite *J Biomed Mater Res Part B: Appl Biomater* 77B:120-125.

Nagem Filho H, Nagem HD, Francisconi PA, Franco EB, Mondelli RF, Coutinho KQ (2007). Volumetric polymerization shrinkage of contemporary composite resins. *J Appl Oral Sci* 15:448-452.

Nakabayashi N, Kojima K, Masuhara E (1982a). The promotion of adhesion by the infiltration of monomers into tooth substances. *J Biomed Mater Res* 16:265-273.

Nakabayashi N, Takeyama M, Kojima K, Masuhara E (1982b). [Studies on dental self-curing resins (20) - adhesion mechanism of 4-META/MMA-TBB resin to dentine (author's transl)]. *Shika Rikogaku Zasshi* 23:34-39.

Nakajima M, Sano H, Burrow MF, Tagami J, Yoshiyama M, Ebisu S*, et al.* (1995). Tensile bond strength and SEM evaluation of caries-affected dentin using dentin adhesives. *J Dent Res* 74:1679-1688.

Nomoto R (1997). Effect of light wavelength on polymerization of light-cured resins. *Dent Mater J* 16:60-73.

O'Brien WJ, Yee J, Jr. (1980). Microstructure of posterior restorations of composite resin after clinical wear. *Oper Dent* 5:90-94.

Obici AC, Sinhoreti MA, de Goes MF, Consani S, Sobrinho LC (2002). Effect of the photo-activation method on polymerization shrinkage of restorative composites. *Oper Dent* 27:192-198.

Obici AC, Sinhoreti MAC, Frollini E, Sobrinho LC, Consani S (2004). Degree of Conversion of Z250 Composite Determined by Fourier Transform Infrared Spectroscopy: Comparison of Techniques, Storage Periods and Photo-activation Methods. . *Materials Research* 7:605-610.

Obici AC, Sinhoreti MAC, Frollini E, Sobrinho LC-, Goes MFd, Henriques. GEP (2006). Monomer conversion at different dental composite depths using six light-curing methods. *Polymer Testing* 25:282-288.

Ortengren U, Wellendorf H, Karlsson S, Ruyter IE (2001). Water sorption and solubility of dental composites and identification of monomers released in an aqueous environment. *J Oral Rehabil* 28:1106-1115.

Osborne JW, Gale EN, Ferguson GW (1973). One-yer and two-year clinical evaluation of a composite resin vs. amalgam. *J Prosthet Dent* 30:795-800.

Padipatvuthikul P, Jarad FD, Mair L (2010). Determination of surface and subsurface fatigue damage in dental composites. *Wear* 268:1483-1489.

Pandey M, Patel S, Gabriel A (2004). Insights into the role of an active site aspartate in Ty1 reverse transcriptase polymerization. *J Biol Chem* 279:47840-47848.

Papadogiannis Y, Lakes RS, Palaghias G, Helvatjoglu-Antoniades M, Papadogiannis D (2007). Fatigue of packable dental composites. *Dent Mater* 23:235-242.

Parry J, Harrington E, Rees GD, McNab R, Smith AJ (2008). Control of brushing variables for the in vitro assessment of toothpaste abrasivity using a novel laboratory model. *J Dent* 36:117-124.

Pashley DH, Carvalho RM, Sano H, Nakajima M, Yoshiyama M, Shono Y*, et al.* (1999). The microtensile bond test: a review. *J Adhes Dent* 1:299-309.

Pastila P, Lassila LV, Jokinen M, Vuorinen J, Vallittu PK, Mantyla T (2007). Effect of short-term water storage on the elastic properties of some dental restorative materials--A resonant ultrasound spectroscopy study. *Dent Mater* 23:878-884.

Patel MP, Braden M, Davy KW (1987). Polymerization shrinkage of methacrylate esters. *Biomaterials* 8:53-56.

Patel MP, Braden M (1989). Cross-linking and ring opening during polymerization of heterocyclic methacrylates and acrylates. *Biomaterials* 10:277-280.

Patel PH, Jacobo-Molina A, Ding J, Tantillo C, Clark AD, Jr., Raag R*, et al.* (1995). Insights into DNA polymerization mechanisms from structure and function analysis of HIV-1 reverse transcriptase. *Biochemistry* 34:5351-5363.

Perry R, Kugel G, Kunzelmann KH, Flessa HP, Estafan D (2000). Composite restoration wear analysis: conventional methods vs. three-dimensional laser digitizer. *J Am Dent Assoc* 131:1472-1477.

Petersen RC (2005). Discontinuous fiber-reinforced composites above critical length. *J Dent Res* 84:365-370.

Peutzfeldt A, Asmussen E (1989). Hardness of restorative resins: effect of camphorquinone, amine, and inhibitor. *Acta Odontol Scand* 47:229-231.

Peutzfeldt A (1997). Resin composites in dentistry: the monomer systems. *Eur J Oral Sci* 105:97-116.

Peutzfeldt A, Sahafi A, Asmussen E (2000). Characterization of resin composites polymerized with plasma arc curing units. *Dent Mater* 16:330-336.

Placido E, Meira JB, Lima RG, Muench A, de Souza RM, Ballester RY (2007). Shear versus micro-shear bond strength test: a finite element stress analysis. *Dent Mater* 23:1086-1092.

Polacek P, Jancar J (2008). Effect of filler content on the adhesion strength between UD fiber reinforced and particulate filled composites *Composites Science and Technology* 68:251-259.

Polat TN, Karacaer O, Tezvergil A, Lassila LV, Vallittu PK (2003). Water sorption, solubility and dimensional changes of denture base polymers reinforced with short glass fibers. *J Biomater Appl* 17:321-335.

Puckett AD, Smith R (1992). Method to measure the polymerization shrinkage of light-cured composites. *J Prosthet Dent* 68:56-58.

Puckett AD, Fitchie JG, Kirk PC, Gamblin J (2007). Direct composite restorative materials. *Dent Clin North Am* 51:659-675.

Raabe D, Alemzadeh K, Harrison AL, Ireland AJ (2009). The chewing robot: a new biologically-inspired way to evaluate dental restorative materials. *Conf Proc IEEE Eng Med Biol Soc* 2009:6050-6053.

Raabe D, Harrison A, Alemzadeh K, Ireland A, Sandy J (2011). Capturing motions and forces of the human masticatory system to replicate chewing and to perform dental wear experiments. *2011 24th International Symposium on Computer-Based Medical Systems (Cbms)*.

Ravindra R, McIlroy PJ, Patel SA (1997). Drugs that influence tubulin polymerization modulate thyrotropin-releasing hormone receptor number in AtT-20 cells. *Pharmacol Toxicol* 80:24-29.

Rees JS, Jacobsen PH (1989). The polymerization shrinkage of composite resins. *Dent Mater* 5:41-44.

Ribeiro JC, Gomes PN, Moyses MR, Dias SC, Pereira LJ, Ribeiro JG (2008). Shear strength evaluation of composite-composite resin associations. *J Dent* 36:326-330.

Roberson T, Heymann H, Swift E (2006). Sturdevant's Art and Science of Operative Dentistry

Mosby Elsevier.

Roether JA, Boccaccini AR (2005). Dispersion-reinforced glass and glass-ceramic matrix composites. In: Handbook of ceramic composites. NP Bansal editor. Kluwer: Dordrecht.

Roulet JF, Salchow B, Wald M (1991). Margin analysis of posterior composites in vivo. *Dent Mater* 7:44-49.

Rueggeberg F, K. Tamareselvy (1995). Resin cure determination by polymerization shrinkage. *Dental Materials; Official Publication of the Academy of Dental Materials* 11:265-268.

Rueggeberg FA, Margeson DH (1990). The effect of oxygen inhibition on an unfilled/filled composite system. *J Dent Res* 69:1652-1658.

Rueggeberg FA, Caughman WF, Curtis JW, Jr. (1994). Effect of light intensity and exposure duration on cure of resin composite. *Oper Dent* 19:26-32.

Rueggeberg FA, Ergle JW, Lockwood PE (1997). Effect of photoinitiator level on properties of a light-cured and post-cure heated model resin system. *Dent Mater* 13:360-364.

Rueggeberg FA (2002). From vulcanite to vinyl, a history of resins in restorative dentistry. *J Prosthet Dent* 87:364-379.

Rueggeberg FA (2011). State-of-the-art: dental photocuring--a review. *Dent Mater* 27:39-52.

Ruttermann S, Dluzhevskaya I, Grosssteinbeck C, Raab WH, Janda R (2010). Impact of replacing Bis-GMA and TEGDMA by other commercially available monomers on the properties of resin-based composites. *Dent Mater* 26:353-359.

Sadek FT, Monticelli F, Muench A, Ferrari M, Cardoso PE (2006). A novel method to obtain microtensile specimens minimizing cut flaws. *J Biomed Mater Res B Appl Biomater* 78:7-14.

Sakaguchi RL, Berge HX (1998). Reduced light energy density decreases post-gel contraction while maintaining degree of conversion in composites. *J. Dent.* 26:695–700.

Salz U, Bock T (2010). Testing adhesion of direct restoratives to dental hard tissue - a review. *J Adhes Dent* 12:343-371.

Sano H, Shono T, Sonoda H, Takatsu T, Ciucchi B, Carvalho R*, et al.* (1994). Relationship between surface area for adhesion and tensile bond strength—evaluation of a micro-tensile bond test. *Dental Materials* 10.

Sano H, Yoshikawa T, Pereira PN, Kanemura N, Morigami M, Tagami J*, et al.* (1999). Long-term durability of dentin bonds made with a self-etching primer, in vivo. *J Dent Res* 78:906-911.

Santerre JP, Shajii L, Leung BW (2001). Relation of dental composite formulations to their degradation and the release of hydrolyzed polymeric-resin-derived products. *Crit Rev Oral Biol Med* 12:136-151.

Santos C, Clarke RL, Braden M, Guitian F, Davy KW (2002). Water absorption characteristics of dental composites incorporating hydroxyapatite filler. *Biomaterials* 23:1897-1904.

Sarac D, Sarac YS, Kulunk S, Ural C, Kulunk T (2006). The effect of polishing techniques on the surface roughness and color change of composite resins. *J Prosthet Dent* 96:33-40.

Sarkar NK (2000). Internal corrosion in dental composite wear. *J Biomed Mater Res* 53:371-380.

Sarrett DC, Soderholm KJ, Batich CD (1991). Water and abrasive effects on three-body wear of composites. *J Dent Res* 70:1074-1081.

Sato T, Miyazaki M, Rikuta A (2004a). Real-time dimensional change in light-cured composites at various depths using laser speckle contrast analysis. *European Journal of Oral Sciences* 112:538-554.

Sato T, Miyazaki M, Rikuta A, Kobayashi K (2004b). Application of the laser speckle-correlation method for determining the shrinkage vector of a light-cured resin. *Dental Materials Journal* 23:284-290.

Scherrer SS, Cesar PF, Swain MV (2010). Direct comparison of the bond strength results of the different test methods: a critical literature review. *Dent Mater* 26:e78-93.

Schneider LF, Pfeifer CS, Consani S, Prahl SA, Ferracane JL (2008). Influence of photoinitiator type on the rate of polymerization, degree of conversion, hardness and yellowing of dental resin composites. *Dent Mater* 24:1169-1177.

Schneider LF, Cavalcante LM, Silikas N (2010). Shrinkage Stresses Generated during Resin-Composite Applications: A Review. *J Dent Biomech* 2010.

Schroeder WF, Vallo CI (2007). Effect of different photoinitiator systems on conversion profiles of a model unfilled light-cured resin. *Dent Mater* 23:1313-1321.

Schulein TM (2005). Significant events in the history of operative dentistry. *J Hist Dent* 53:63-72.

Senawongse P, Pongprueksa P (2007). Surface roughness of nanofill and nanohybrid resin composites after polishing and brushing. *J Esthet Restor Dent* 19:265-273; discussion 274-265.

Sepulchre C, Bouniton M, Collette G, Vanmeerbeek M, Giet D (2006). [Some Websites frequently used in general practice]. *Rev Med Liege* 61:520-537.

Sharp LJ, Choi IB, Lee TE, Sy A, Suh BI (2003). Volumetric shrinkage of composites using video-imaging. *J Dent* 31:97-103.

Shawkat ES, Shortall AC, Addison O, Palin WM (2009). Oxygen inhibition and incremental layer bond strengths of resin composites. *Dent Mater* 25:1338-1346.

Shin WS, Li XF, Schwartz B, Wunder SL, Baran GR (1993). Determination of the Degree of Cure of Dental Resins Using Raman and Ft-Raman Spectroscopy. *Dental Materials* 9:317-324.

Shintani H, Inoue T, Yamaki M (1985). Analysis of camphorquinone in visible light-cured composite resins. *Dent Mater* 1:124-126.

Shirai K, De Munck J, Yoshida Y, Inoue S, Lambrechts P, Suzuki K*, et al.* (2005). Effect of cavity configuration and ageing on the bonding effectiveness of six adhesives to dentin. *Dent Mater.* 21:110-124.

Sideridou I, Tserki V, Papanastasiou G (2002). Effect of chemical structure on degree of conversion in light-cured dimethacrylate-based dental resins. *Biomaterials* 23:1819-1829.

Sideridou I, Tserki V, Papanastasiou G (2003). Study of water sorption, solubility and modulus of elasticity of light-cured dimethacrylate-based dental resins. *Biomaterials* 24:655-665.

Sideridou ID, Karabela MM, Bikiaris DN (2007). Aging studies of light cured dimethacrylate-based dental resins and a resin composite in water or ethanol/water. *Dent Mater* 23:1142-1149.

Silikas N, Eliades G, Watts DC (2000). Light intensity effects on resin-composite degree of conversion and shrinkage strain. *Dent Mater* 16:292-296.

Silva FF, Mendes LC, Ferreira M, Benzi MR (2007). Degree of conversion versus the depth of polymerization of an organically modified ceramic dental restoration composite by Fourier transform infrared spectroscopy, . *Journal of Applied Polymer Science* 104:325-330.

Soderholm KJ (1984). Influence of silane treatment and filler fraction on thermal expansion of composite resins. *J Dent Res* 63:1321-1326.

Soderholm KJ, Zigan M, Ragan M, Fischlschweiger W, Bergman M (1984). Hydrolytic degradation of dental composites. *J Dent Res* 63:1248-1254.

Soderholm KJ, Roberts MJ (1990). Influence of water exposure on the tensile strength of composites. *J Dent Res* 69:1812-1816.

Soderholm KJ (2007). Dental adhesives .... how it all started and later evolved. *J Adhes Dent* 9 Suppl 2:227-230.

Spencer P, Swafford JR (1999). Unprotected protein at the dentin-adhesive interface. *Quintessence Int* 30:501-507.

Spencer P, Wang Y, Bohaty B (2006). Interfacial chemistry of moisture-aged class II composite restorations. *J Biomed Mater Res B Appl Biomater* 77:234-240.

Spencer P, Ye Q, Park J, Topp EM, Misra A, Marangos O*, et al.* (2010). Adhesive/Dentin interface: the weak link in the composite restoration. *Ann Biomed Eng* 38:1989-2003.

Sperling LH (1994). Interpenetrating polymer networks: an overview. Interpenetrating polymer networks ACS Series. Washington DC: American Chemical Society, pp. 3–38

Srinivasan V, Karthikeyan R, Ganesan G, Asaithambi B (2010). Comparative study on the wear behavior of long and short glass fiber reinforced plastics. *Metals and Materials International* 16:205-212.

Stansbury J, Ge J (2003). Photopolymerization Shrinkage and Stress in Resins and Composites By. *RADTECH REPORT*:56-62.

Stansbury JW (2000a). Curing dental resins and composites by photopolymerization. *J Esthet Dent* 12:300-308.

Stansbury JW (2000b). Curing Dental Resins and Composites by Photopolymerization. *Journal of Esthetic and Restorative Dentistry* 12:300-308.

Stansbury JW, Dickens SH (2001). Determination of double bond conversion in dental resins by near infrared spectroscopy. *Dent Mater* 17:71-79.

Stein PS, Sullivan J, Haubenreich JE, Osborne PB (2005). Composite resin in medicine and dentistry. *J Long Term Eff Med Implants* 15:641-654.

Stipho HD (1998). Repair of acrylic resin denture base reinforced with glass fiber. *J Prosthet Dent* 80:546-550.

Sturdevant C (2006). The art and science of operative dentistry St Louis: Mosby.

Suh BI (2004). Oxygen-inhibited layer in adhesion dentistry. *J Esthet Restor Dent* 16:316-323.

Sun J, Lin-Gibson S (2008). X-ray microcomputed tomography for measuring polymerization shrinkage of polymeric dental composites. *Dent Mater* 24:228-234.

Suresha B, Chandramohan G, Jawali ND (2007). Effect of Short Glass Fiber Content on Three-Body Abrasive Wear Behaviour of Polyurethane Composites. *Journal of Composite Materials* 41:2701-2713.

Suzuki S, Leinfelder KF, Kawai K, Tsuchitani Y (1995). Effect of particle variation on wear rates of posterior composites. *Am J Dent* 8:173-178.

Tarle Z, Knezevic A, Demoli N, Meniga A, Sutaloa J, Unterbrink G*, et al.* (2006). Comparison of composite curing parameters: effects of light source and curing mode on conversion, temperature rise and polymerization shrinkage. *Oper Dent* 31:219-226.

Tay FR, Kwong SM, Itthagarun A, King NM, Yip HK, Moulding KM*, et al.* (2000). Bonding of a self-etching primer to non-carious cervical sclerotic dentin: interfacial ultrastructure and microtensile bond strength evaluation. *J Adhes Dent* 2:9-28.

Teixeira EC, Thompson JL, Piascik JR, Thompson JY (2005). In vitro toothbrush-dentifrice abrasion of two restorative composites. *Journal of Esthetics and Restorative Dentistry* 17:172-180; discussion 181-172.

Tezvergil-Mutluay A, Lassila LV, Vallittu PK (2008). Microtensile bond strength of fiber-reinforced composite with semi-interpenetrating polymer matrix to dentin using various bonding systems. *Dent Mater J* 27:821-826.

Tezvergil A, Lassila LV, Vallittu PK (2003). Strength of adhesive-bonded fiber-reinforced composites to enamel and dentin substrates. *J Adhes Dent* 5:301-311.

Tezvergil A, Lassila LV, Vallittu PK (2005). The shear bond strength of bidirectional and random-oriented fibre-reinforced composite to tooth structure. *J Dent* 33:509-516.

Tezvergil A, Lassila LV, Vallittu PK (2006). The effect of fiber orientation on the polymerization shrinkage strain of fiber-reinforced composites. *Dent Mater* 22:610-616.

Thalacker C, Heumann A, Weinmann W, Guggenberger R, Luchterhandt T, Syrek A (2004). Marginal integrity of class V silorane and methacrylate composite restorations. *J Dent Res* 83 (SI-A).

Thalacker C, Heumann A, Hampe R, Weinmann W, Guggenberger R, Syrek A (2005). Marginal integrity of silorane and methacrylate restorations after load cycle,. *J Dent Res* 84 (SI-A).

Thomason JL (1995). The interface region in glass fibre-reinforced epoxy resin composites: 2. Water absorption, voids and the interface *Composites* 26:477-485.

Toledano M, Osorio R, Osorio E, Fuentes V, Prati C, Garcia-Godoy F (2003). Sorption and solubility of resin-based restorative dental materials. *J Dent* 31:43-50.

Truffier-Boutry D, Place E, Devaux J, Leloup G (2003). Interfacial layer characterization in dental composite. *J Oral Rehabil* 30:74-77.

Turssi CP, de Magalhaes CS, Serra MC, Rodrigues Junior AL (2001). Surface roughness assessment of resin-based materials during brushing preceded by pH-cycling simulations. *Oper Dent* 26:576-584.

Turssi CP, De Moraes Purquerio B, Serra MC (2003). Wear of dental resin composites: insights into underlying processes and assessment methods--a review. *J Biomed Mater Res B Appl Biomater* 65:280-285.

Turssi CP, Ferracane JL, Vogel K (2005). Filler features and their effects on wear and degree of conversion of particulate dental resin composites. *Biomaterials* 26:4932-4937.

Turssi CP, Ferracane JL, Ferracane LL (2006). Wear and fatigue behavior of nano-structured dental resin composites. *J Biomed Mater Res B Appl Biomater* 78:196-203.

Uhl A, Mills RW, Vowles RW, Jandt KD (2002). Knoop hardness depth profiles and compressive strength of selected dental composites polymerized with halogen and LED light curing technologies. *J Biomed Mater Res* 63:729-738.

Vallittu P (2009). Interpenetrating Polymer Networks (IPNs) in Dental Polymers and Composites. *Journal of Adhesion Science and Technology* 23:961-972.

Vallittu PK, Lassila VP, Lappalainen R (1994). Transverse strength and fatigue of denture acrylic-glass fiber composite. *Dent Mater* 10:116-121.

Vallittu PK (1995). The effect of void space and polymerization time on transverse strength of acrylic-glass fibre composite. *J Oral Rehabil* 22:257-261.

Vallittu PK (1996). A review of fiber-reinforced denture base resins. *J Prosthodont* 5:270-276.

van Dijken JW (2000). Direct resin composite inlays/onlays: an 11 year follow-up. *J Dent* 28:299-306.

Van Ende A, De Munck J, Mine A, Lambrechts P, Van Meerbeek B (2010). Does a low-shrinking composite induce less stress at the adhesive interface? *Dent Mater* 26:215-222.

Van Landuyt KL, Snauwaert J, De Munck J, Peumans M, Yoshida Y, Poitevin A*, et al.* (2007). Systematic review of the chemical composition of contemporary dental adhesives. *Biomaterials* 28:3757-3785.

Van Meerbeek B, De Munck J, Yoshida Y, Inoue S, Vargas M, Vijay P*, et al.* (2003). Buonocore Memorial Lecture - Adhesion to enamel and dentin: Current status and future challenges. *Oper Dent* 28:215-235.

Van Meerbeek B, Van Landuyt KL, De Munck J, Inoue Y, Perdigao J, Lambrechts P*, et al.* (2006). Fundamentals of Operative Dentistry: Quintessence Books.

Van Meerbeek B, Peumans M, Poitevin A, Mine A, Van Ende A, Neves A*, et al.* (2010). Relationship between bond-strength tests and clinical outcomes. *Dent Mater* 26:e100-121.

Vandewalle KS, Ferracane JL, Hilton TJ, Erickson RL, Sakaguchi RL (2004). Effect of energy density on properties and marginal integrity of posterior resin composite restorations. *Dent Mater* 20:96-106.

Vanmeerbeek M, Louis E (2006). [PPI very long-term treatment: is the problem only economic?]. *Rev Med Liege* 61:483-487.

Vasudeva G (2009). Monomer systems for dental composites and their future: a review. *J Calif Dent Assoc* 37:389-398.

Venhoven BA, de Gee AJ, Davidson CL (1993). Polymerization contraction and conversion of light-curing BisGMA-based methacrylate resins. *Biomaterials* 14:871-875.

Venhoven BA, de Gee AJ, Werner A, Davidson CL (1996). Influence of filler parameters on the mechanical coherence of dental restorative resin composites. *Biomaterials* 17:735-740.

Venz S, Dickens B (1991). NIR-spectroscopic investigation of water sorption characteristics of dental resins and composites. *J Biomed Mater Res* 25:1231-1248.

Versluis A, Tantbirojn D, Douglas WH (1997). Why Do Shear Bond Tests Pull Out Dentin. *Journal of Dental Research* 76:1298-1307.

Versluis A, Tantbirojn D, Douglas WH (2004). Distribution of transient properties during polymerization of a light-initiated restorative composite. *Dent Mater* 20:543-553.

Walls AW, McCabe JF, Murray JJ (1988). The polymerization contraction of visible-light activated composite resins. *J Dent* 16:177-181.

Walls AW, Lee J, McCabe JF (2001). The bonding of composite resin to moist enamel. *Br Dent J* 191:148-150.

Wang L, Garcia FC, Amarante de Araujo P, Franco EB, Mondelli RF (2004). Wear resistance of packable resin composites after simulated toothbrushing test. *J Esthet Restor Dent* 16:303-314; discussion 314-305.

Wang Y, Spencer P, Yao X, Brenda B (2007). Effect of solvent content on resin hybridization in wet dentin bonding. *J Biomed Mater Res A* 82:975-983.

Wassell RW, McCabe JF, Walls AW (1992). Subsurface deformation associated with hardness measurements of composites. *Dent Mater* 8:218-223.

Wassell RW (1992). Composites for Making Dental Inlays. Newcastle Upon Tyne, Newcastle

Wassell RW, McCabe JF, Walls AW (1994). A two-body frictional wear test. *J Dent Res* 73:1546-1553.

Watts DC, Cash AJ (1991). Determination of polymerization shrinkage kinetics in visible-light-cured materials: methods development. *Dent Mater* 7:281-287.

Watts DC, Marouf AS (2000). Optimal specimen geometry in bonded-disk shrinkage-strain measurements on light-cured biomaterials. *Dent Mater* 16:447-451.

Weinmann W, Thalacker C, Guggenberger R (2005). Siloranes in dental composites. *Dent Mater* 21:68-74.

Wening JV, Katzer A, Nicolas V, Hahn M, Jungbluth KH, Kratzer A (1994). [Imaging of alloplastic ligament implant. An in vivo and in vitro study exemplified by Kevlar]. *Unfallchirurgie* 20:61-65.

Willems G, Celis JP, Lambrechts P, Braem M, Roos JR, Vanherle G (1992a). In vitro vibrational wear under small displacements of dental materials opposed to annealed chromium-steel counterbodies. *Dent Mater* 8:338-344.

Willems G, Lambrechts P, Braem M, Celis JP, Vanherle G (1992b). A classification of dental composites according to their morphological and mechanical characteristics. *Dent Mater* 8:310-319.

Xu HH, Quinn JB, Giuseppetti AA, Eichmiller FC, Parry EE, Schumacher GE (2004). Three-body wear of dental resin composites reinforced with silica-fused whiskers. *Dent Mater* 20:220-227.

Yap AU, Low JS, Ong LF (2000a). Effect of food-simulating liquids on surface characteristics of composite and polyacid-modified composite restoratives. *Oper Dent* 25:170-176.

Yap AU, Teoh SH, Tan KB (2000b). Influence of water exposure on three-body wear of composite restoratives. *J Biomed Mater Res* 53:547-553.

Yankell SL, Shi X, Emling RC, Nelson BJ, Triol CW (1998). Laboratory evaluations of three dentifrices with polishing or brushing. *J Clin Dent* 9:61-63.

Yap AU, Tan CH, Chung SM (2004). Wear behavior of new composite restoratives. *Oper Dent* 29:269-274.

Ye Q, Spencer P, Wang Y, Misra A (2007). Relationship of solvent to the photopolymerization process, properties, and structure in model dentin adhesives. *J Biomed Mater Res A* 80:342-350.

Ye Q, Park J, Topp E, Spencer P (2009). Effect of photoinitiators on the in vitro performance of a dentin adhesive exposed to simulated oral environment. *Dent Mater* 25:452-458.

Yearn JA (1985). Factors affecting cure of visible light activated composites. *Int Dent J* 35:218-225.

Yesil ZD, Alapati S, Johnston W, Seghi RR (2008). Evaluation of the wear resistance of new nanocomposite resin restorative materials. *J Prosthet Dent* 99:435-443.

Yoshida K, Greener EH (1994). Effect of photoinitiator on degree of conversion of unfilled light-cured resin. *J Dent* 22:296-299.

Yoshida K, Condon JR, Atsuta M, Ferracane JL (2003). Flexural fatigue strength of CAD/CAM composite material and dual-cured resin luting cements. *Am J Dent* 16:177-180.

Zhang M, Matinlinna JP (2011). E-Glass Fiber Reinforced Composites in Dental Applications. *Silicon*:1 - 6.

Zhou J, Tan J, Chen L, Li D, Tan Y (2009). The incorporation of chlorhexidine in a two-step self-etching adhesive preserves dentin bond in vitro. *J Dent* 37:807-812.

Appendices

Appendix A. Presentation of materials used in this work

Figure 73. Presentation of the materials used in this work

Figure 74. ST in its original packaging

Figure 75. A section of the sheet of ST

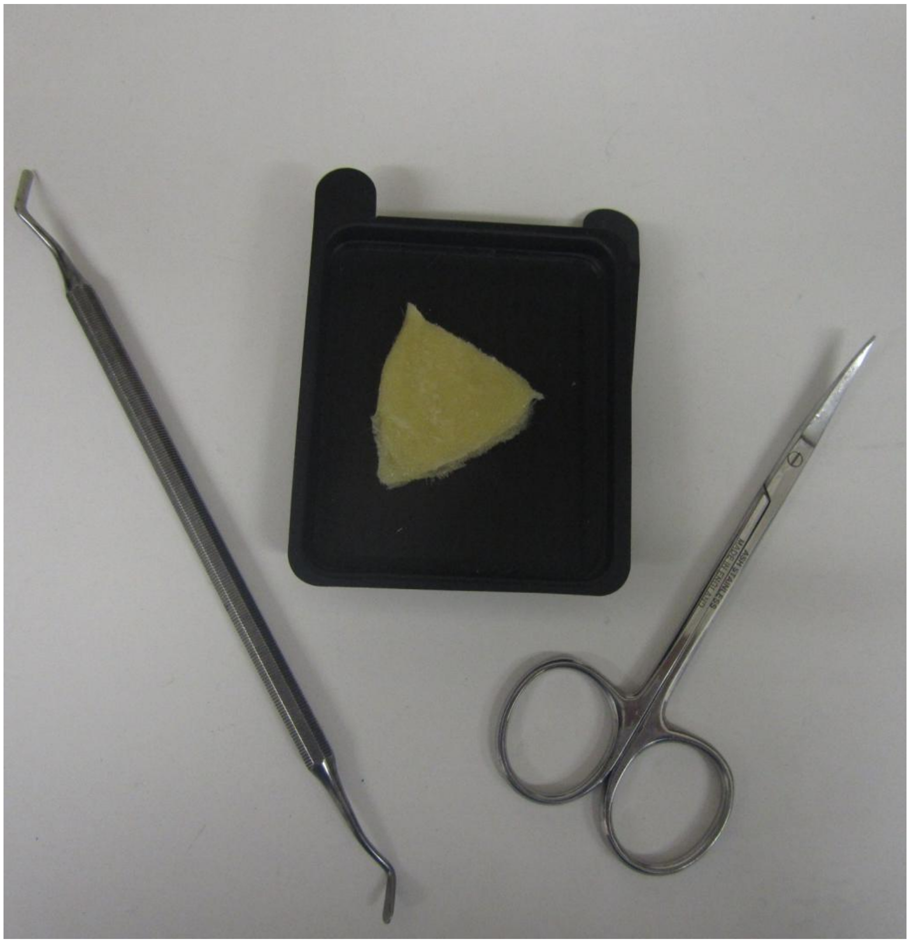


Figure 76. Instruments used for ST placement

Appendix B . Load displacement curves for bond strength experiments

1. Typical load displacement curves of composites bonded to human dentine after 24 hours water storage

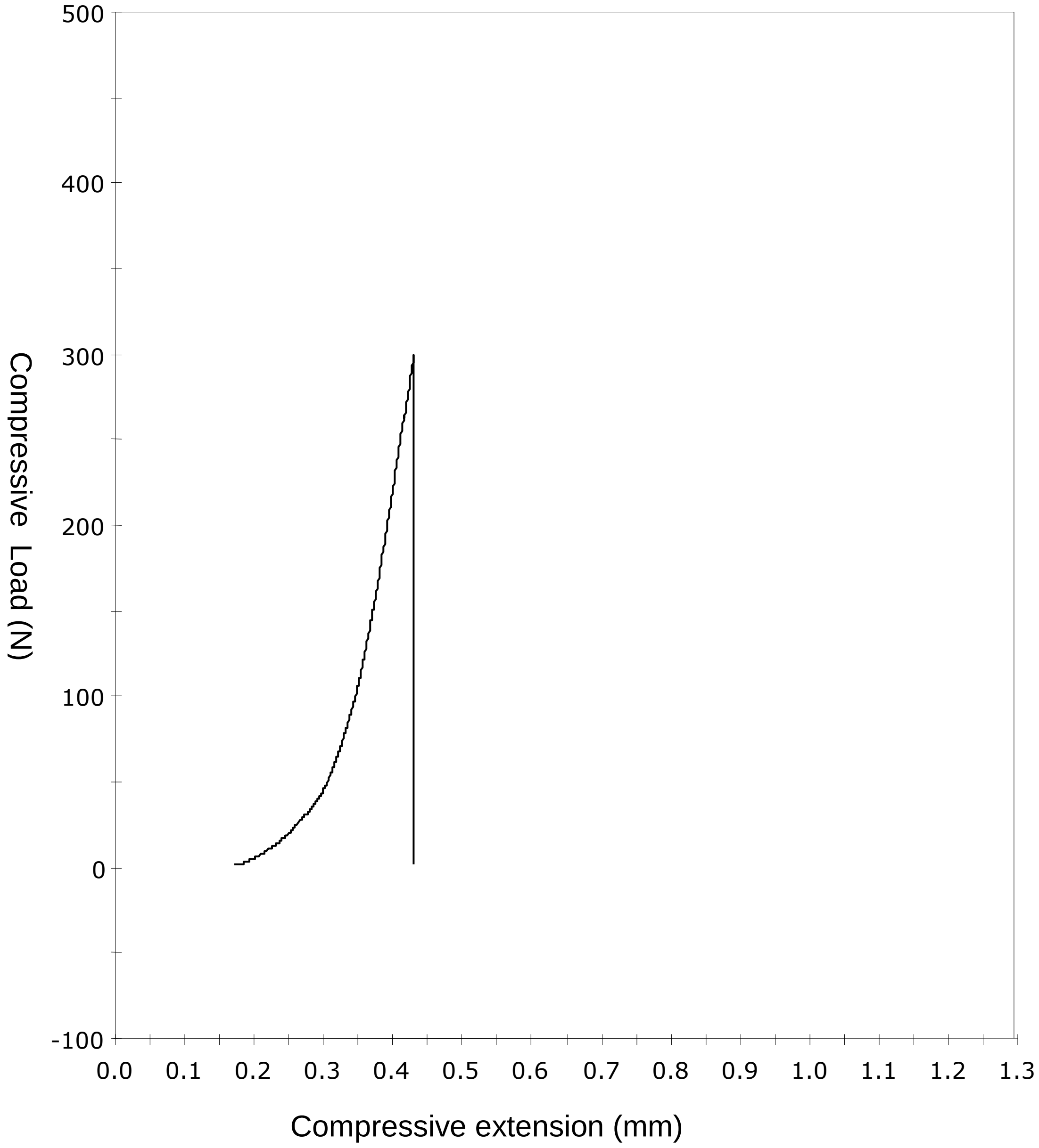


Figure 77. Typical load displacement curve for dentine/Z250 samples after 24 hours water storage

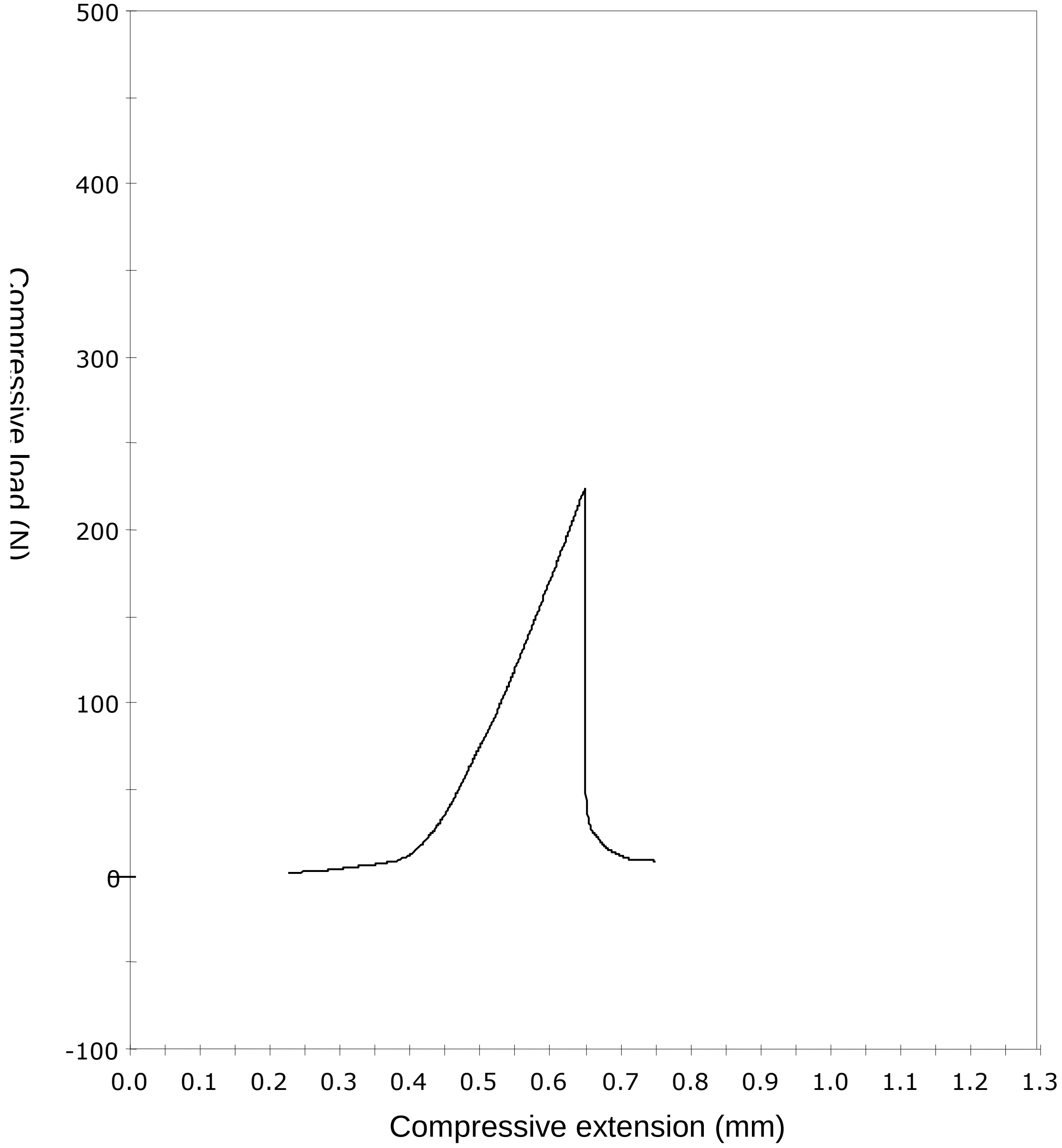


Figure 78. Typical load displacement curve for Dentine/ST samples after 24 hours water storage

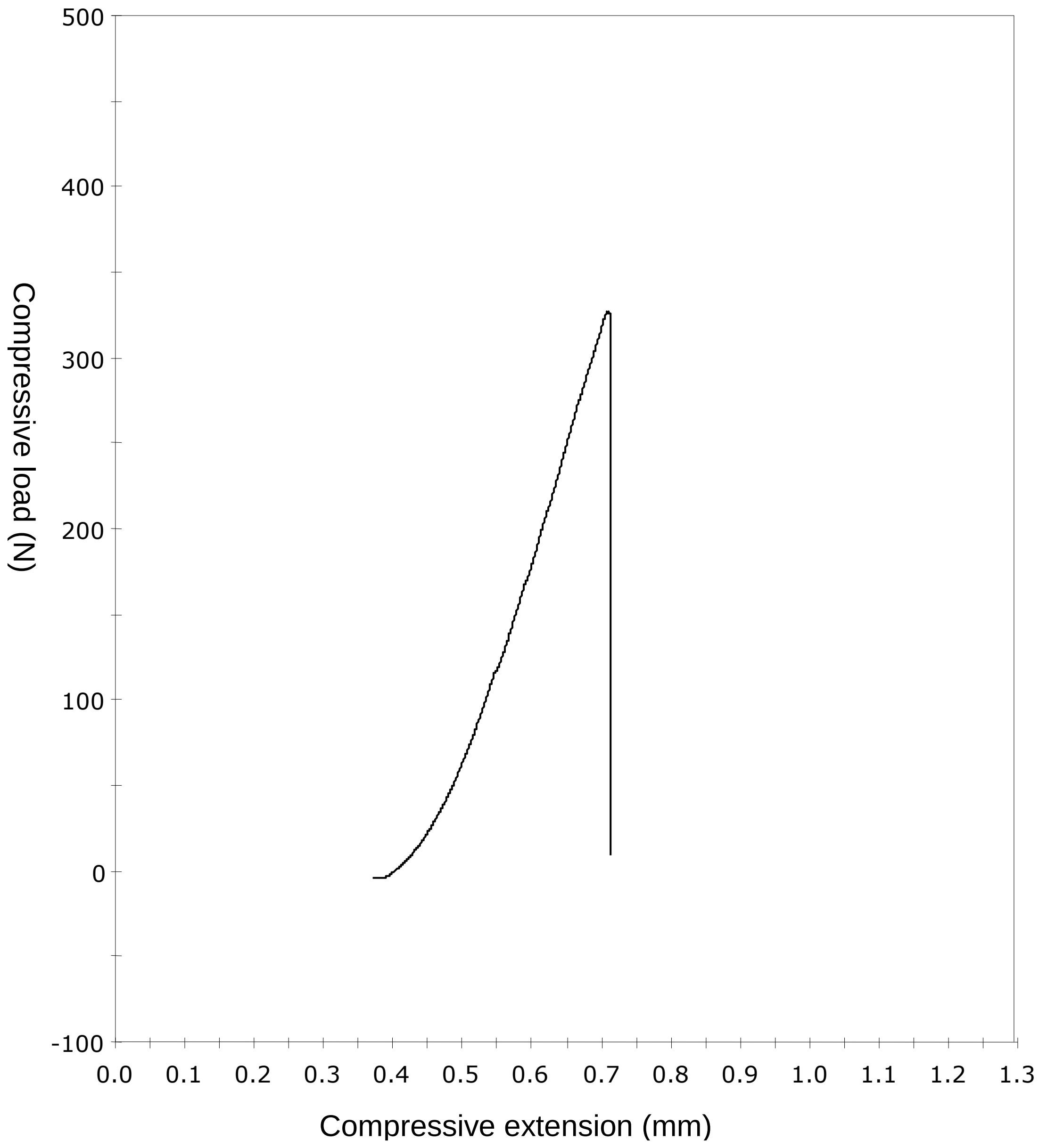


Figure 79. Typical load displacement curve for Dentine/Stick Flow samples after 24 hours water storage

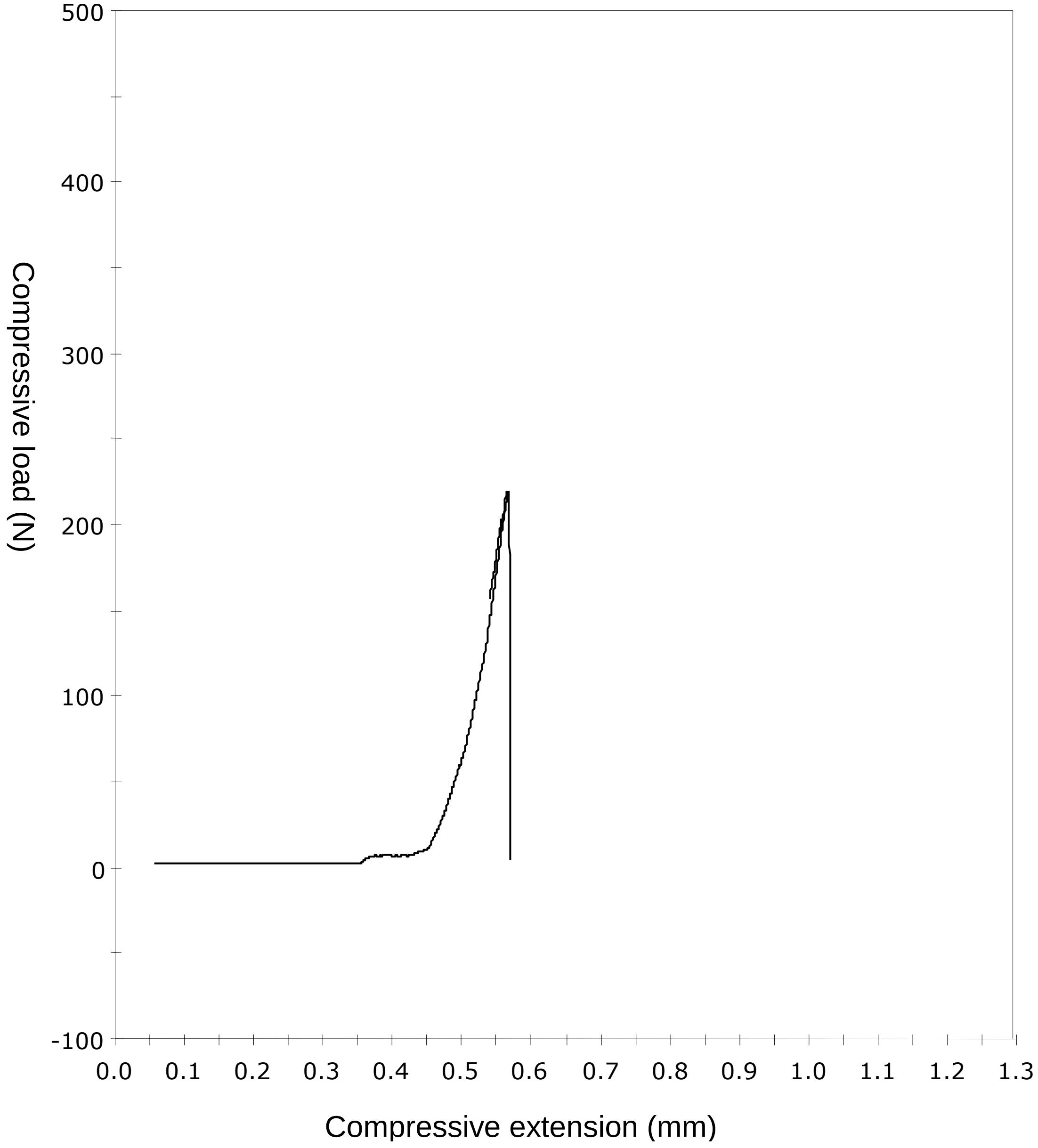


Figure 80. Typical load displacement curve for Dentine/Build It samples after 24 hours water storage

2. Typical load displacement curves of composites bonded to human dentine after 1 year water storage

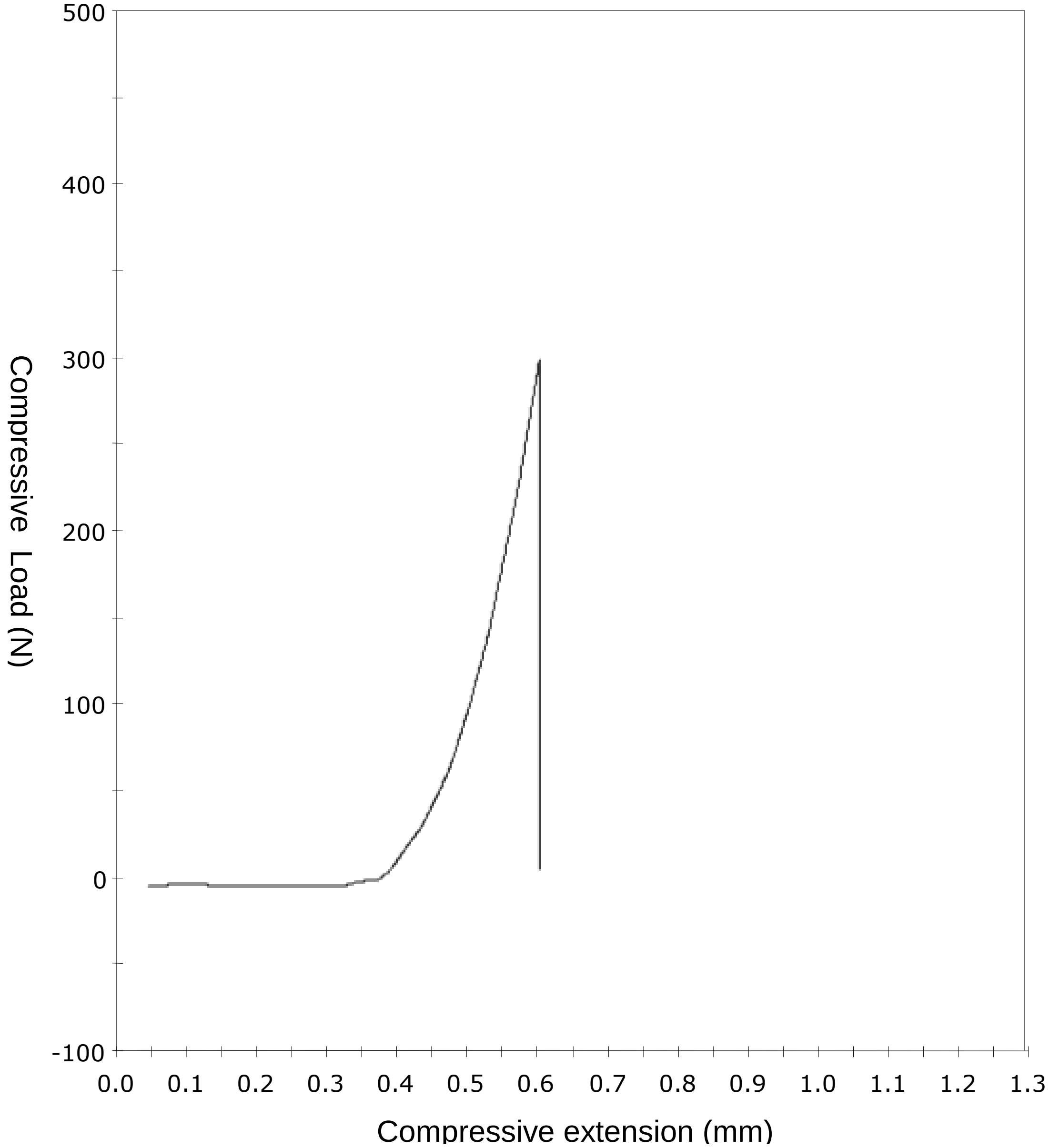


Figure 81. Typical load displacement curve for Dentine/Z250 samples after 1 year water storage

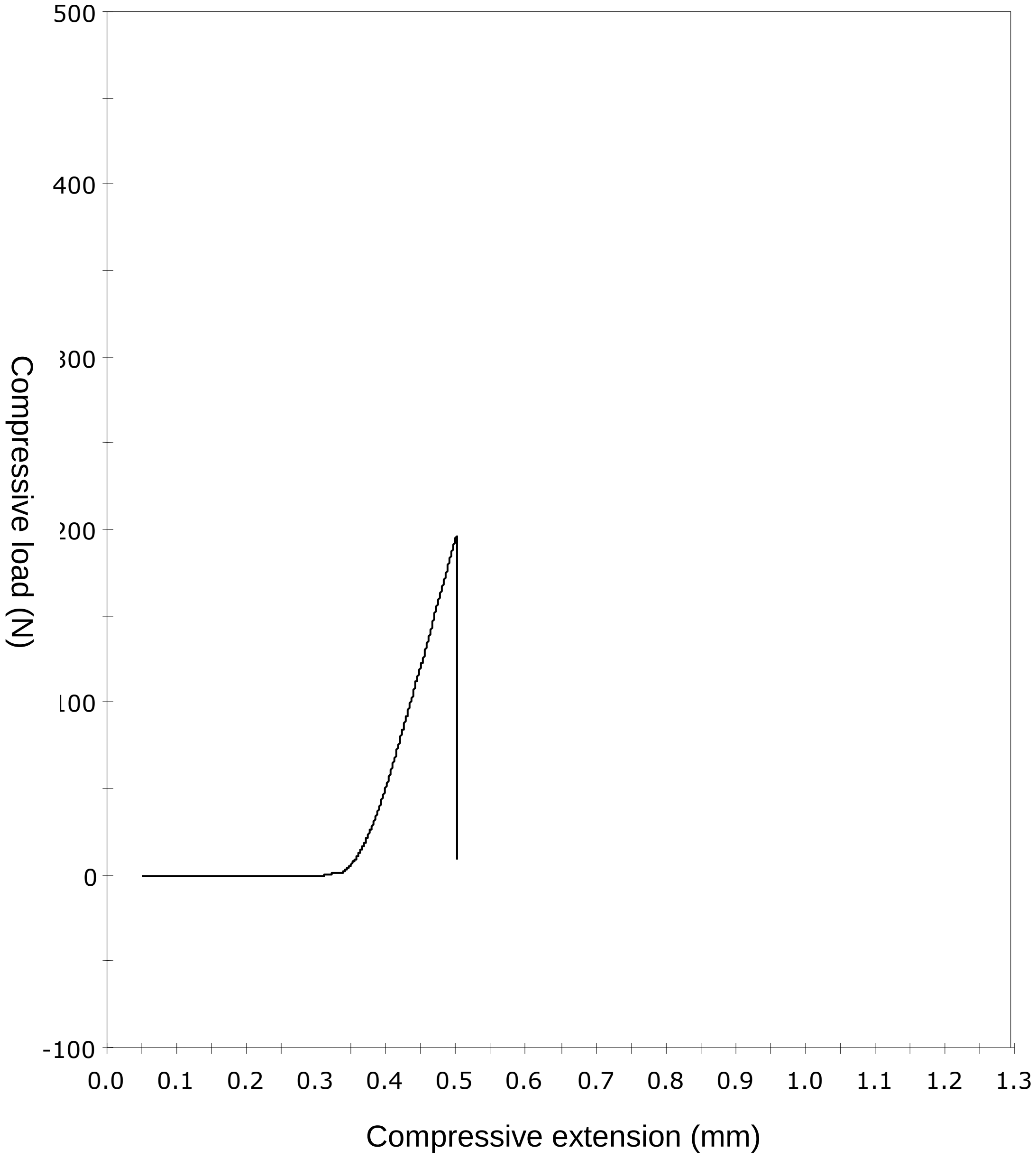


Figure 82. Typical load displacement curve for Dentine/ST samples after 1 year water storage

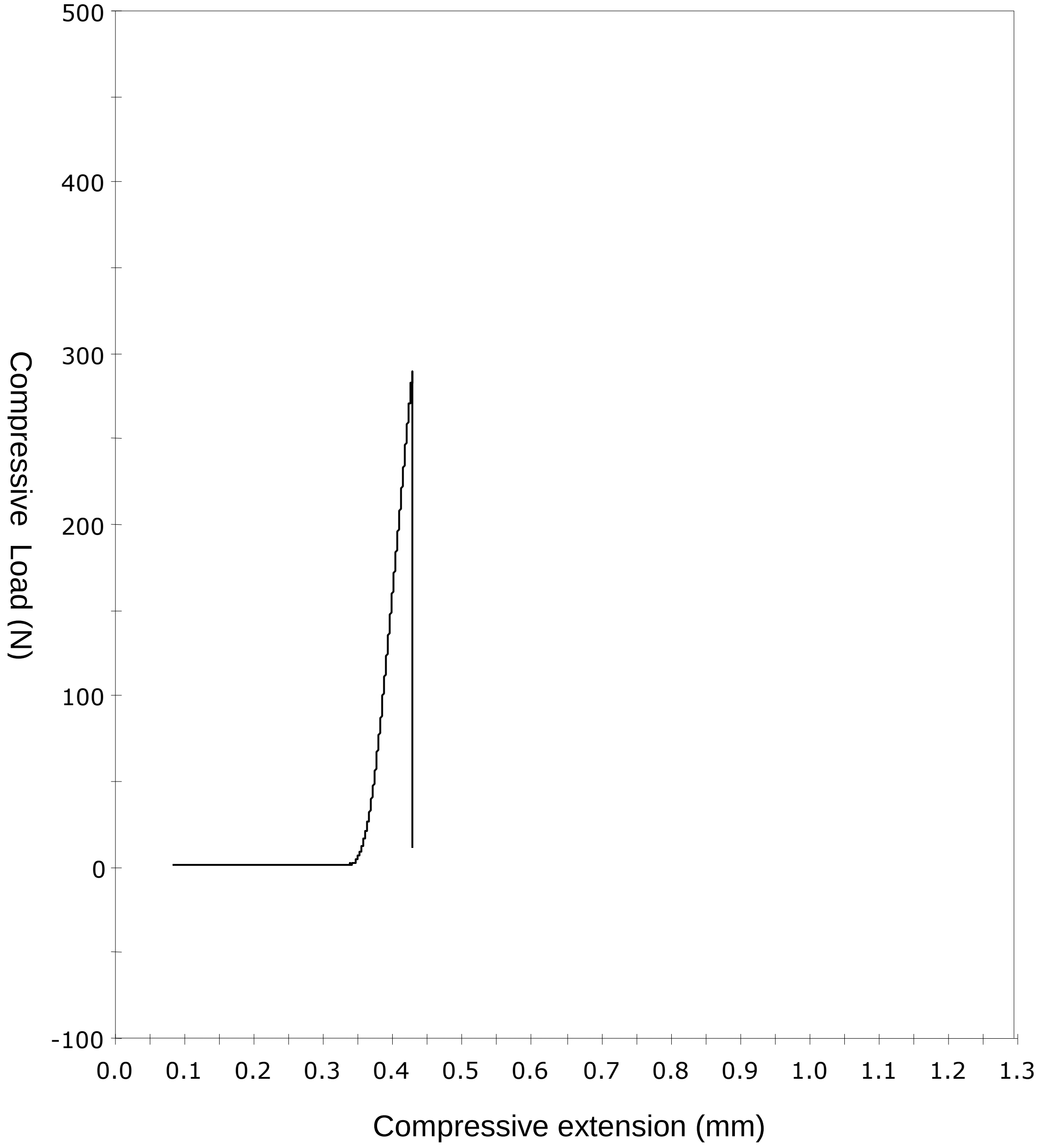


Figure 83. Typical load displacement curve for Dentine/Build It samples after 1 year water storage

3.Typical load displacement curves of lapped composite groups after 24 hours water storage

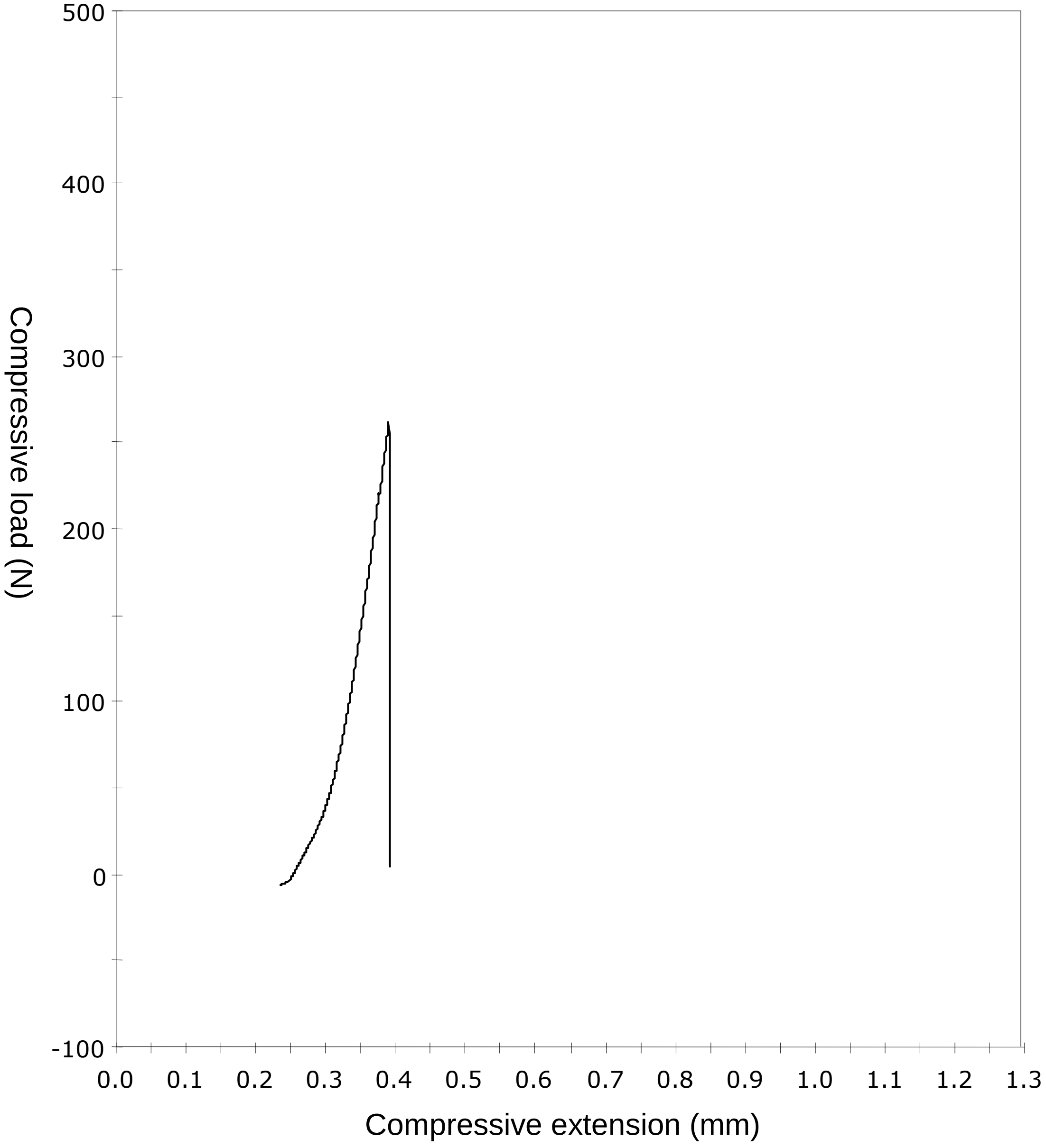


Figure 84. Typical load displacement curve for lapped Z250/Z250 group after 24 hours water storage

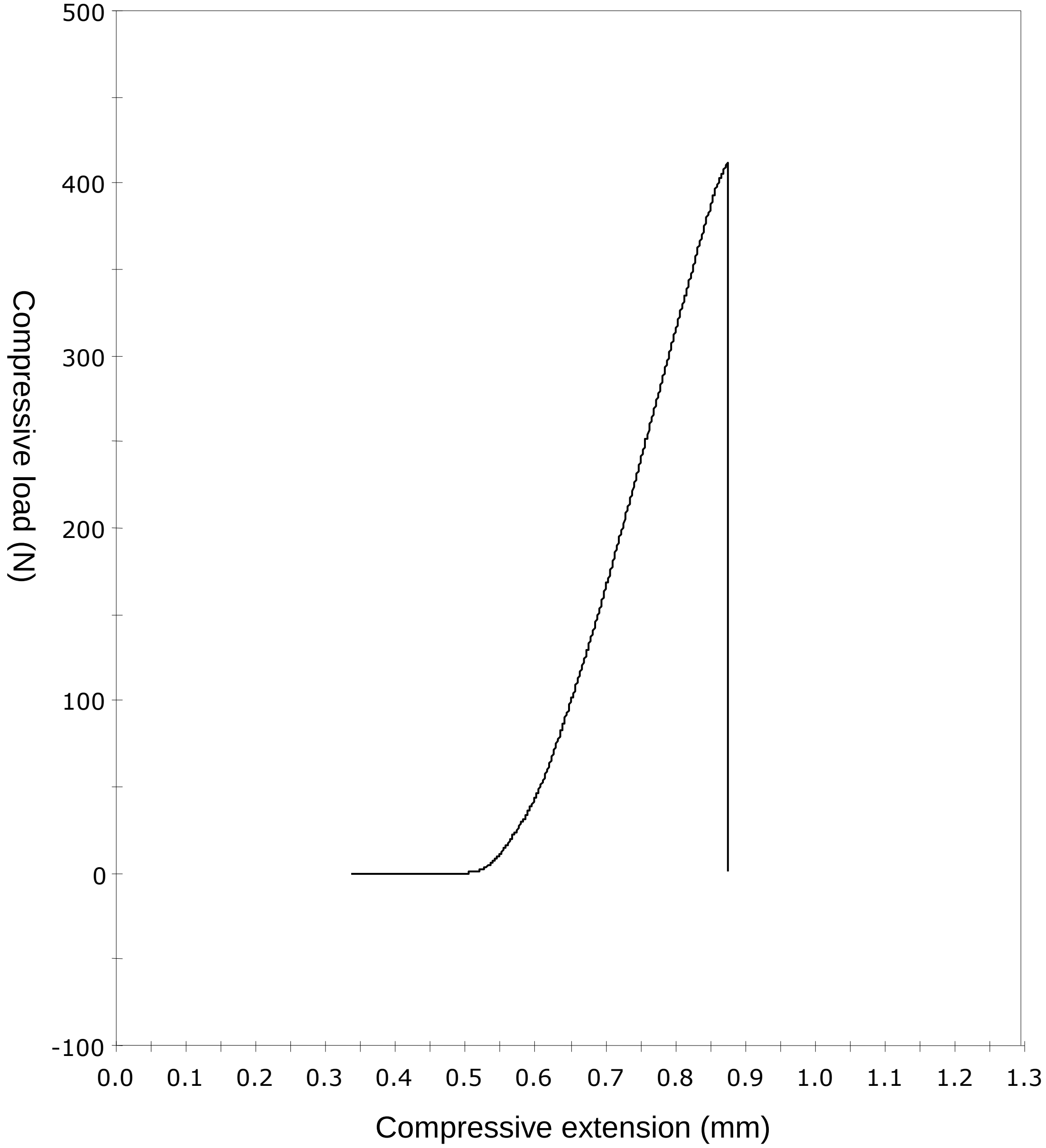


Figure 85. Typical load displacement curves of lapped Build It/Build It groups after 24 hours water storage

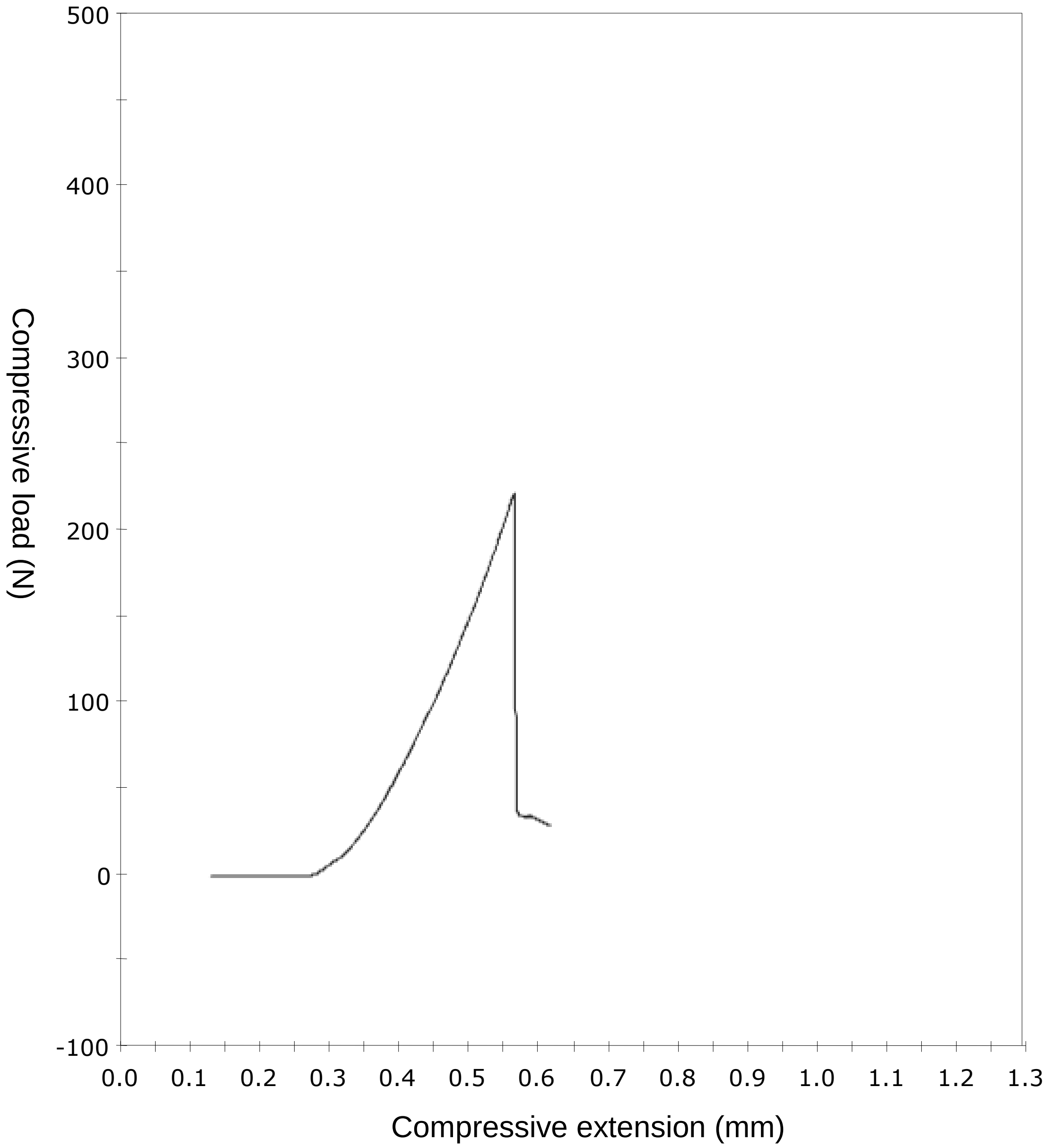


Figure 86.Typical load displacement curves of lapped ST/ST group after 24 hours water storage

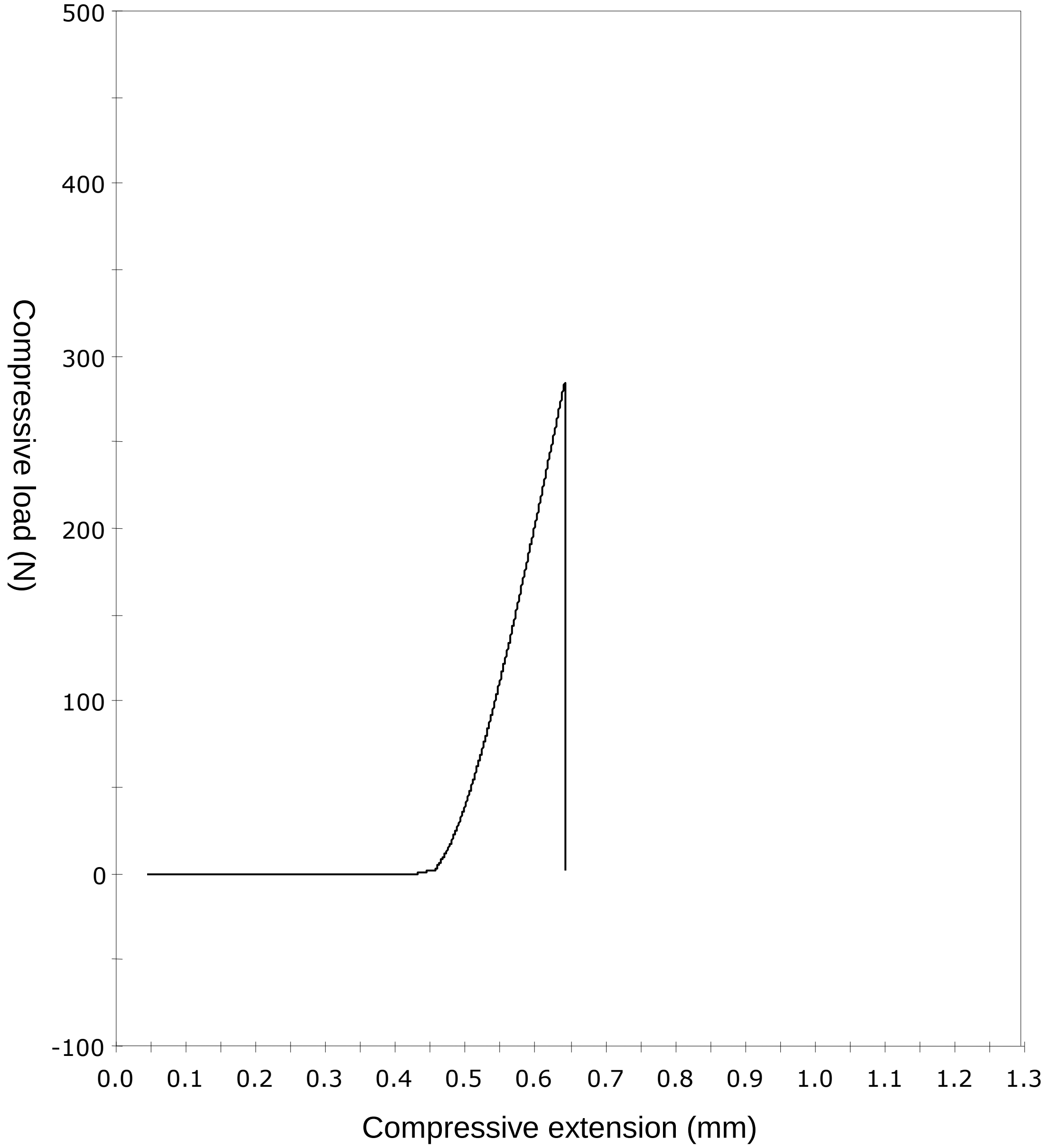


Figure 87. Typical load displacement curves of lapped ST/Z250 group after 24 hours water storage

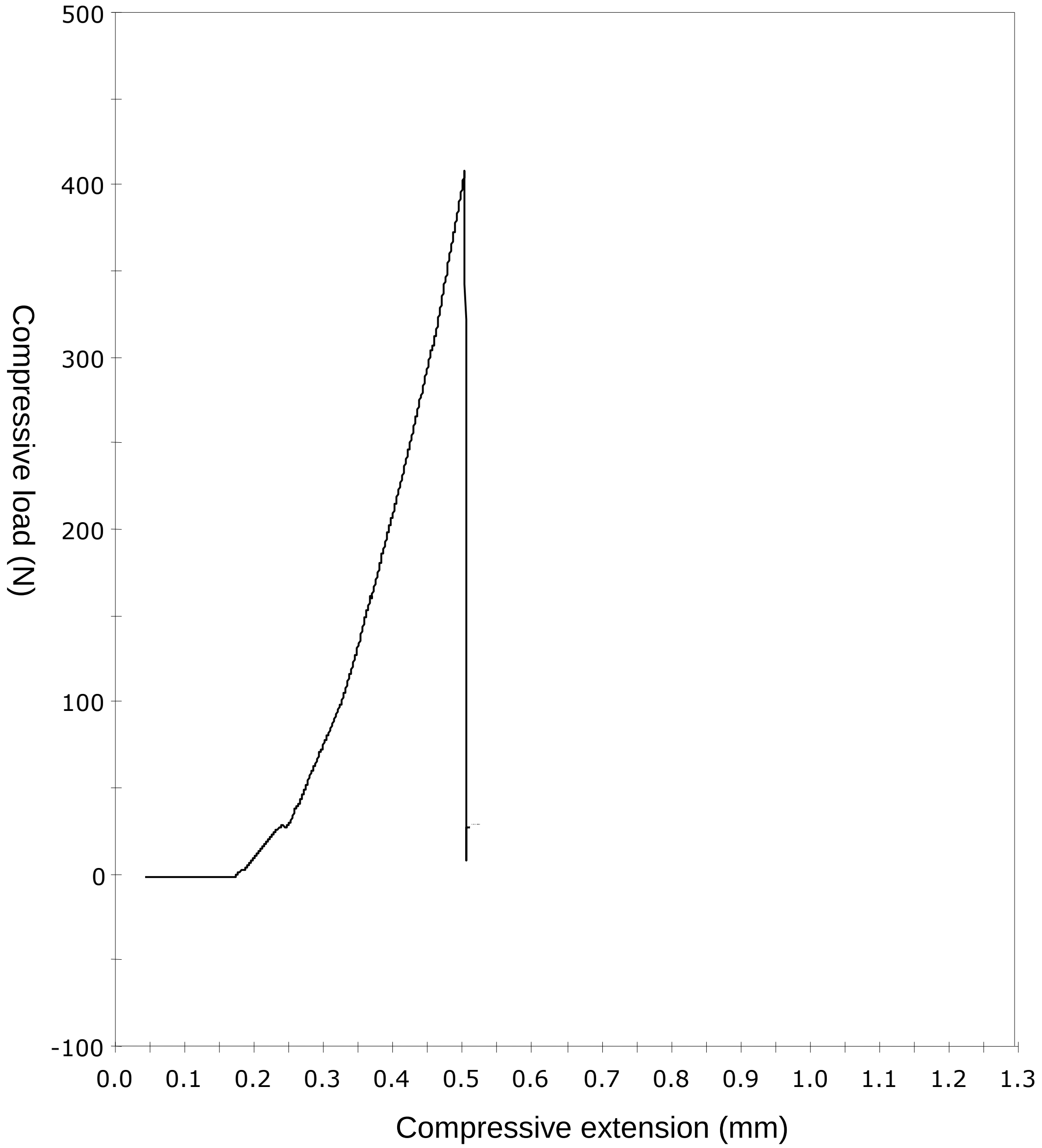


Figure 88. Typical load displacement curves of lapped Build It/Z250 group after 24 hours water storage

4. Typical load displacement curves of lapped composite groups after 1 year of water storage

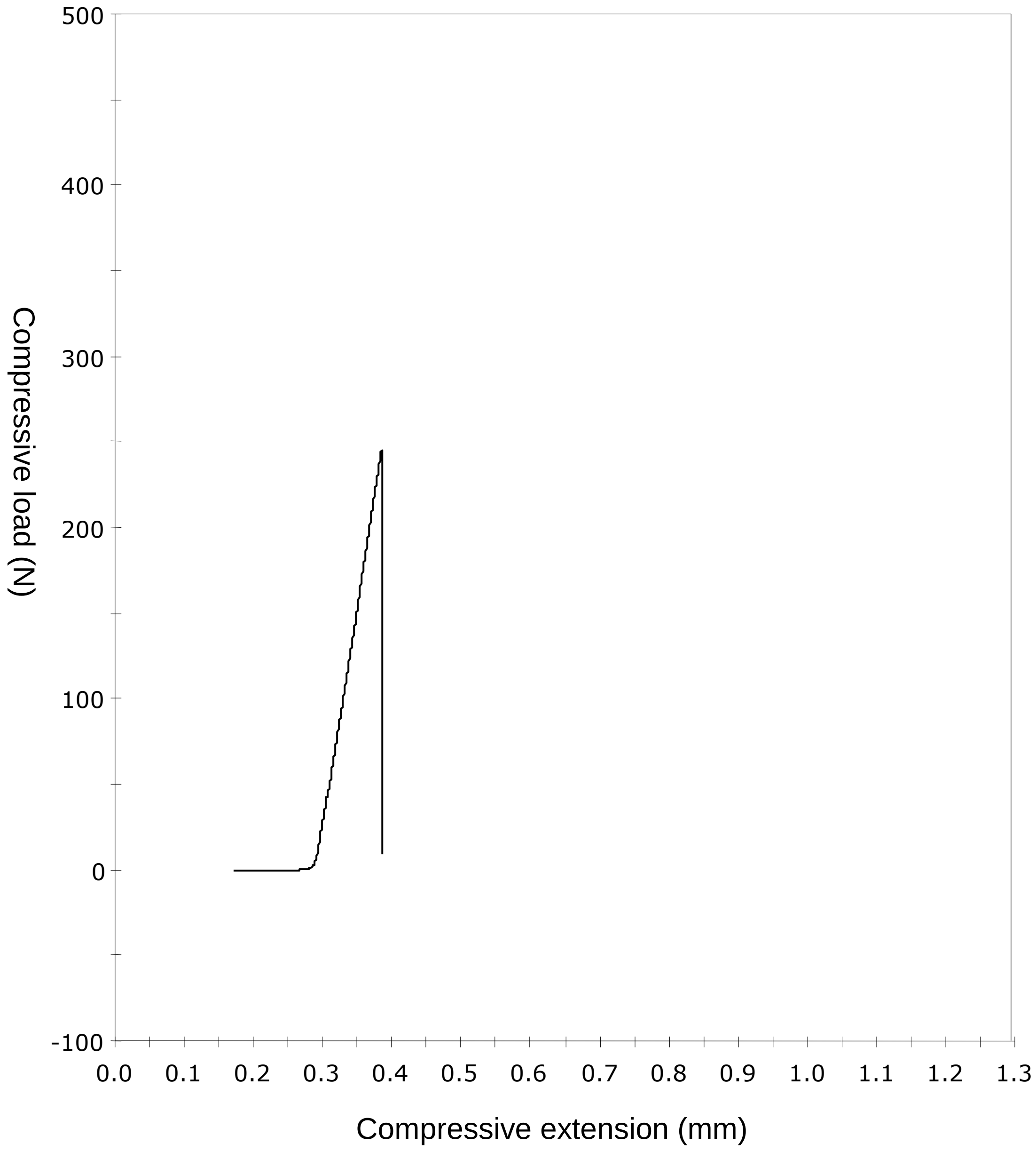


Figure 89. Typical load displacement curves of lapped Z250/Z250 group after 1 year of water storage

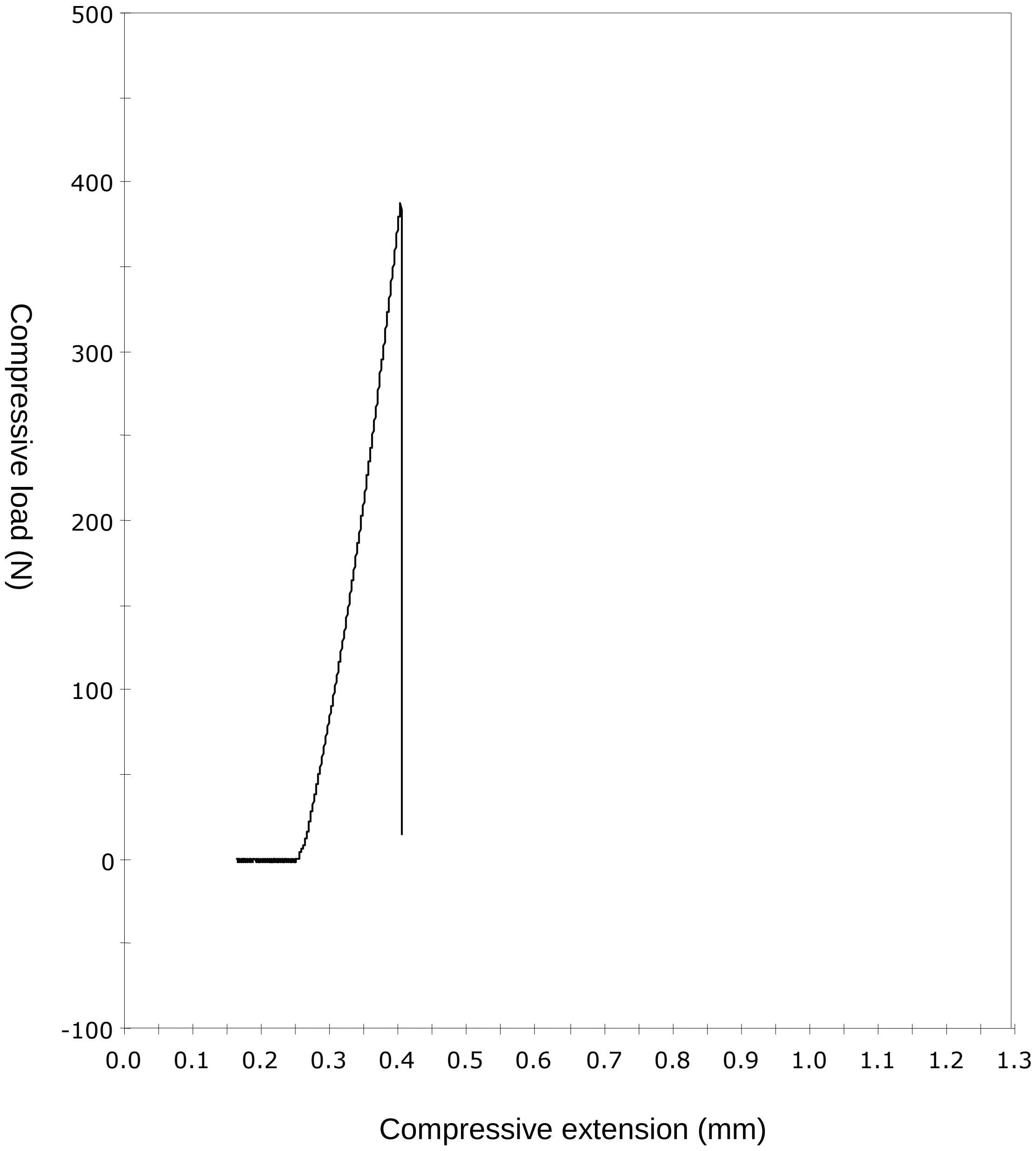


Figure 90. . Typical load displacement curves of lapped Build It/Build It group after 1 year of water storage

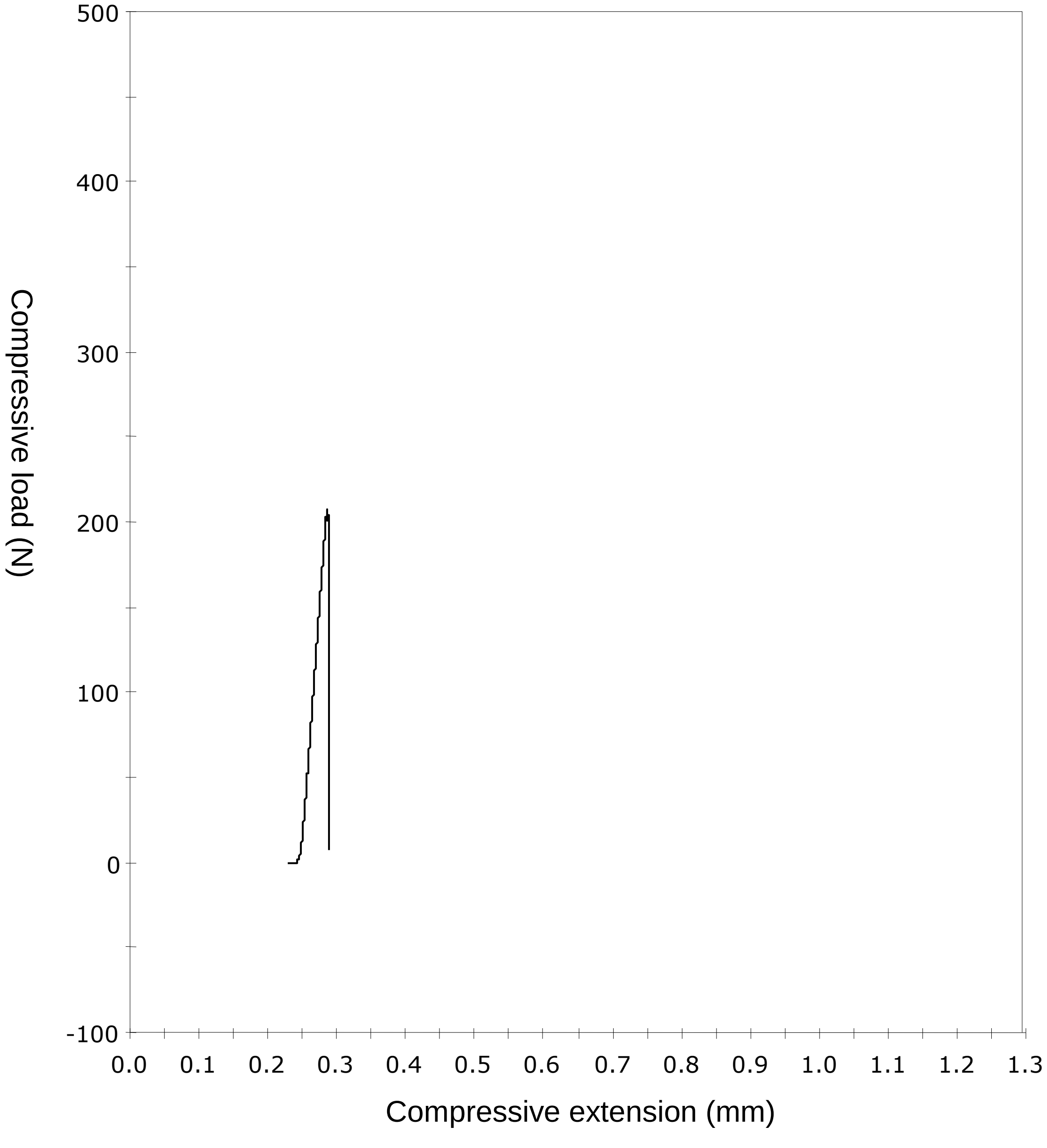


Figure 91. . Typical load displacement curves of lapped ST/ST group after 1 year of water storage

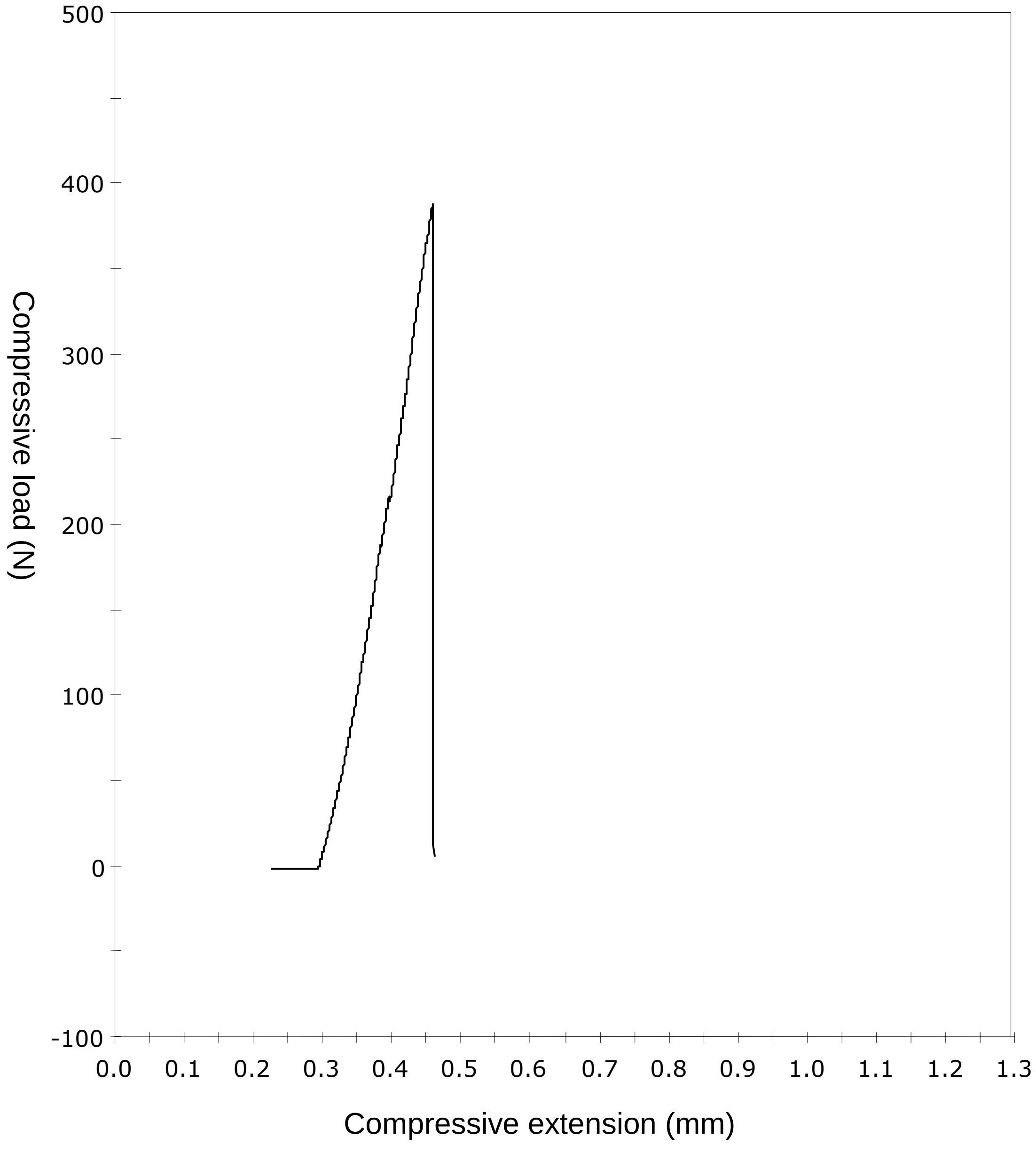


Figure 92. . Typical load displacement curves of lapped Build It/Z250 group after 1 year of water storage

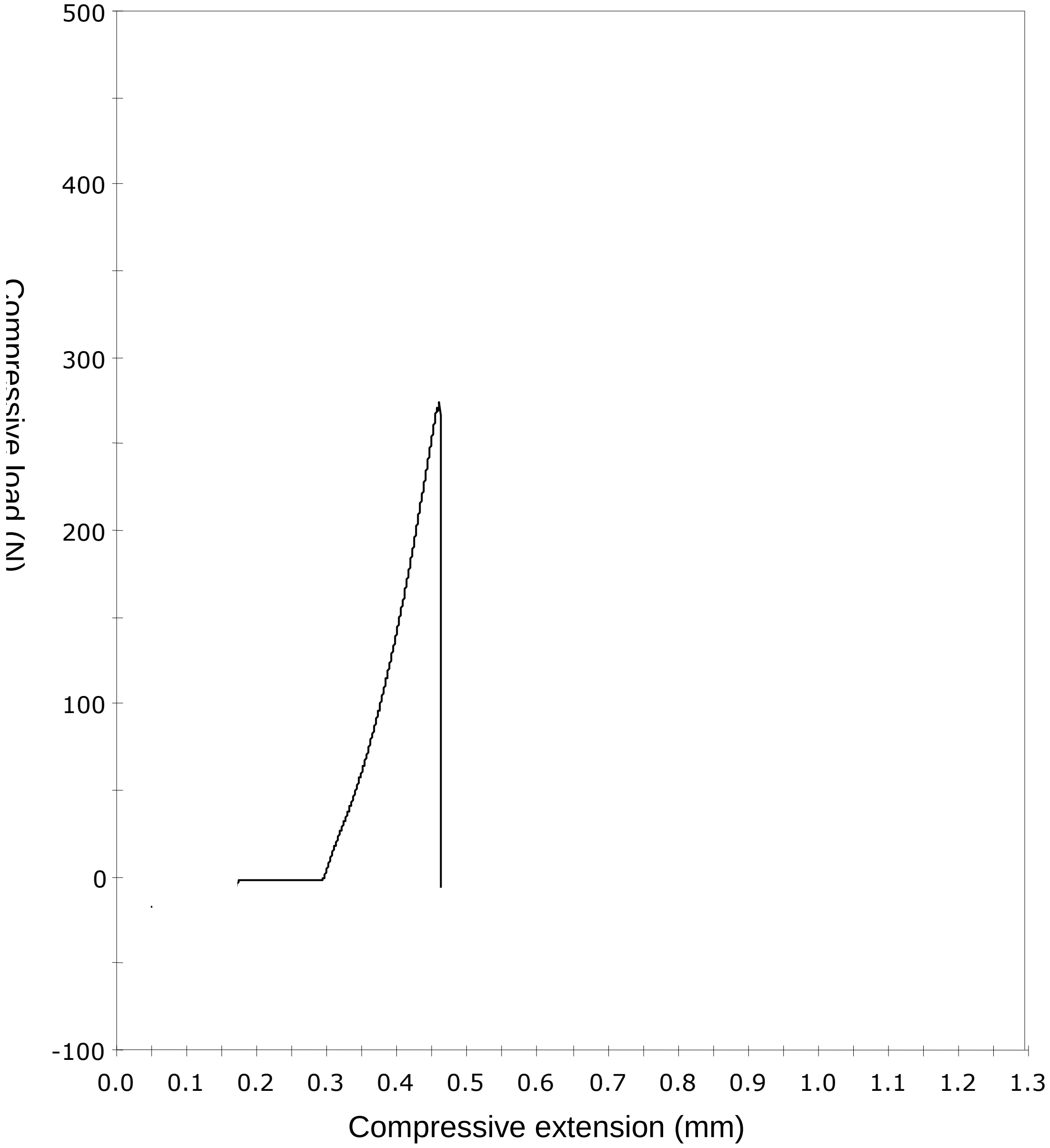


Figure 93. . Typical load displacement curves of lapped ST/Z250 group after 1 year of water storage

5. Typical load displacement curves of oxygen-inhibited composite groups after 24 hours water storage

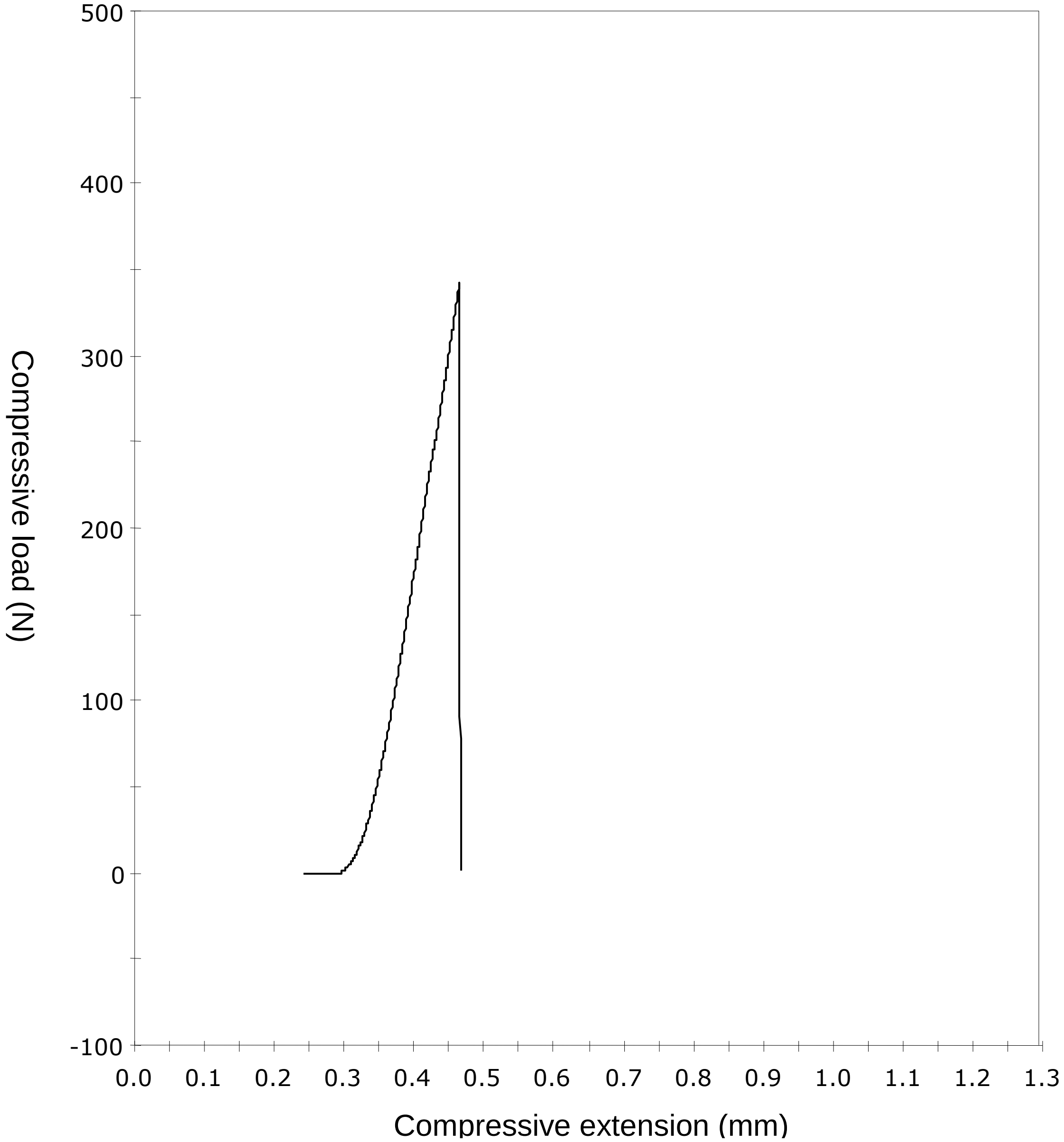


Figure 94. Typical load displacement curve of oxygen-inhibited Z250/Z250 group after 24 hours water storage

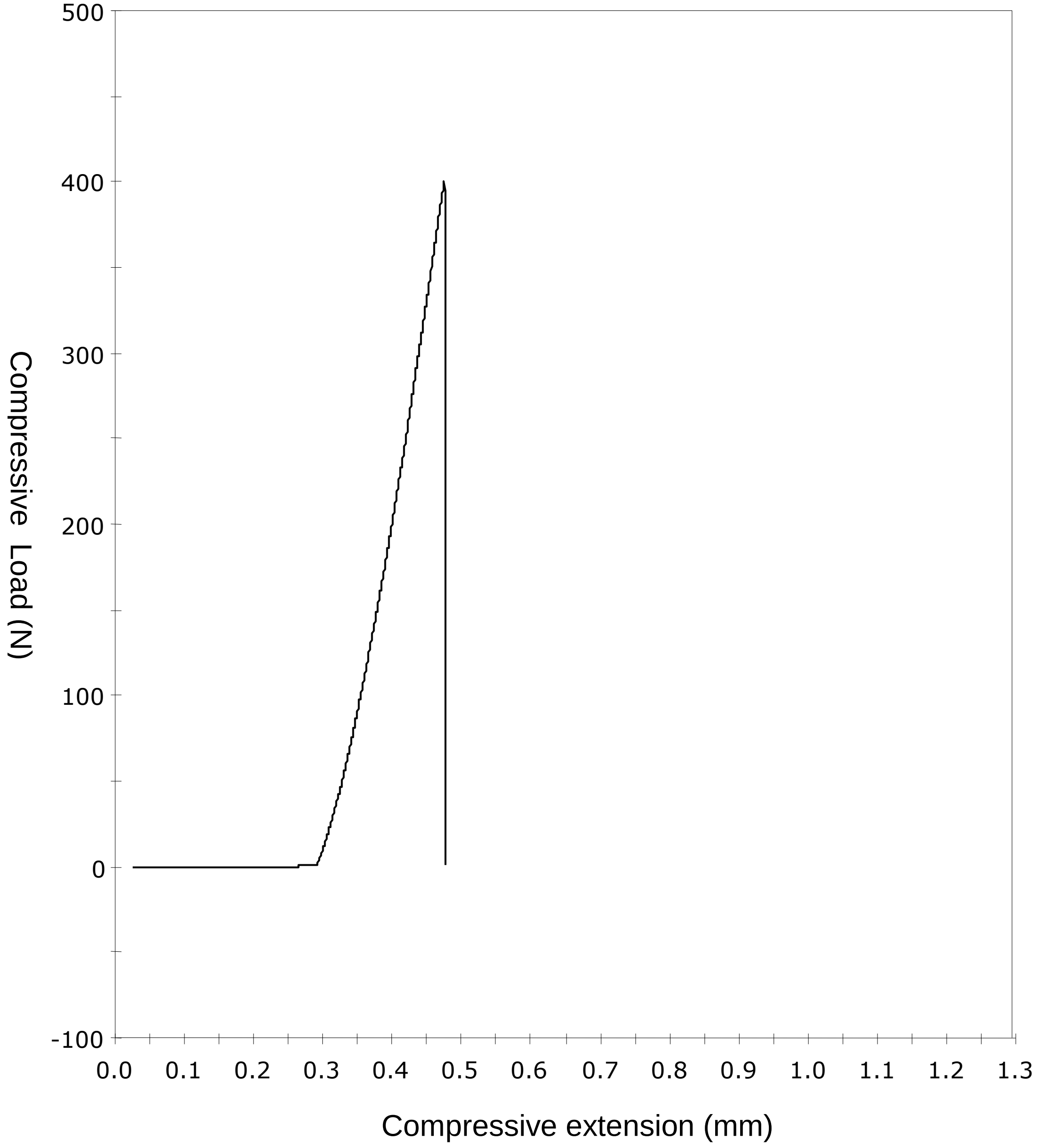


Figure 95. Typical load displacement curve of oxygen-inhibited Build It/Build It group after 24 hours water storage

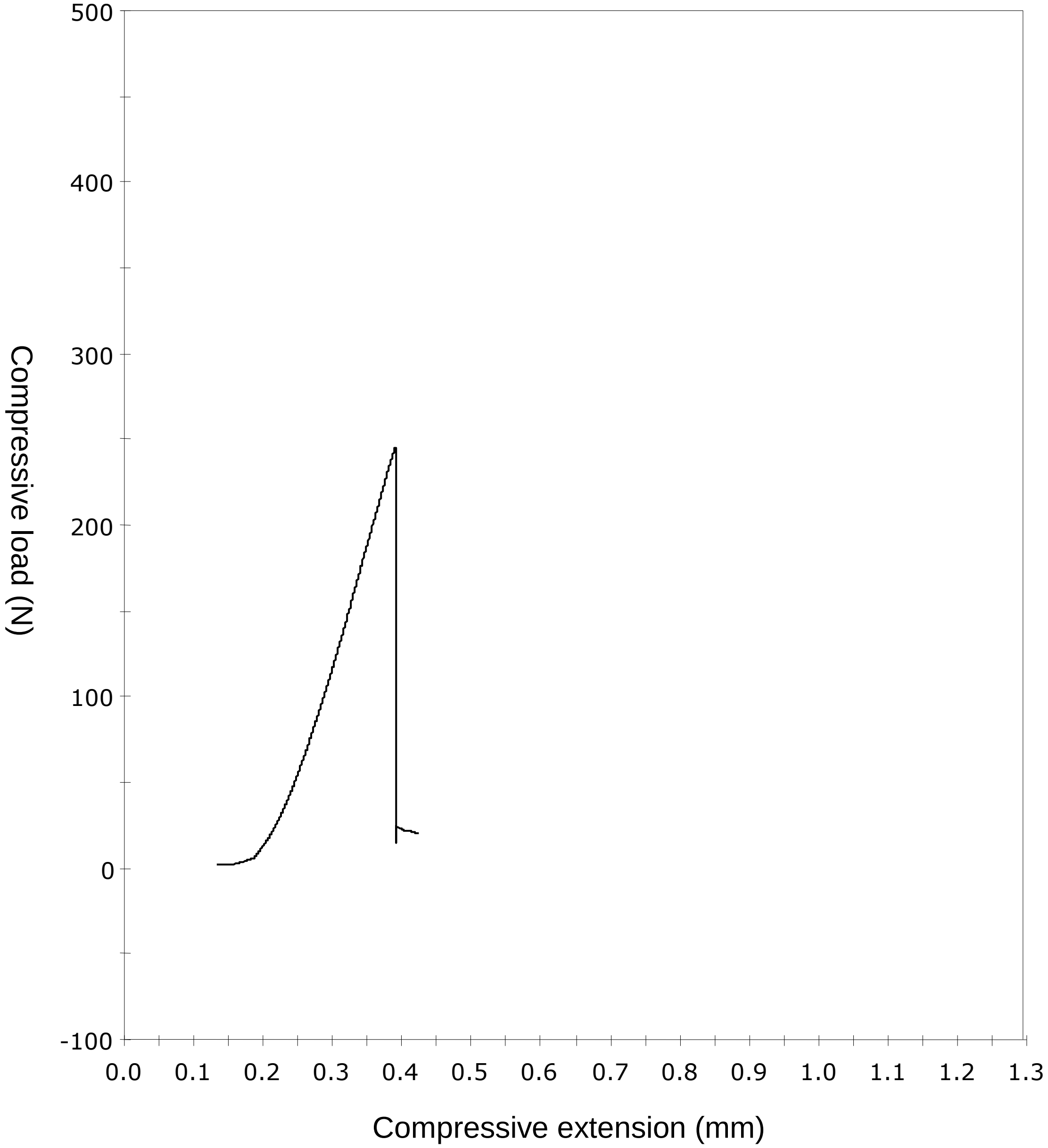


Figure 96. Typical load displacement curve of air-inhibited ST/ST group after 24 hours water storage

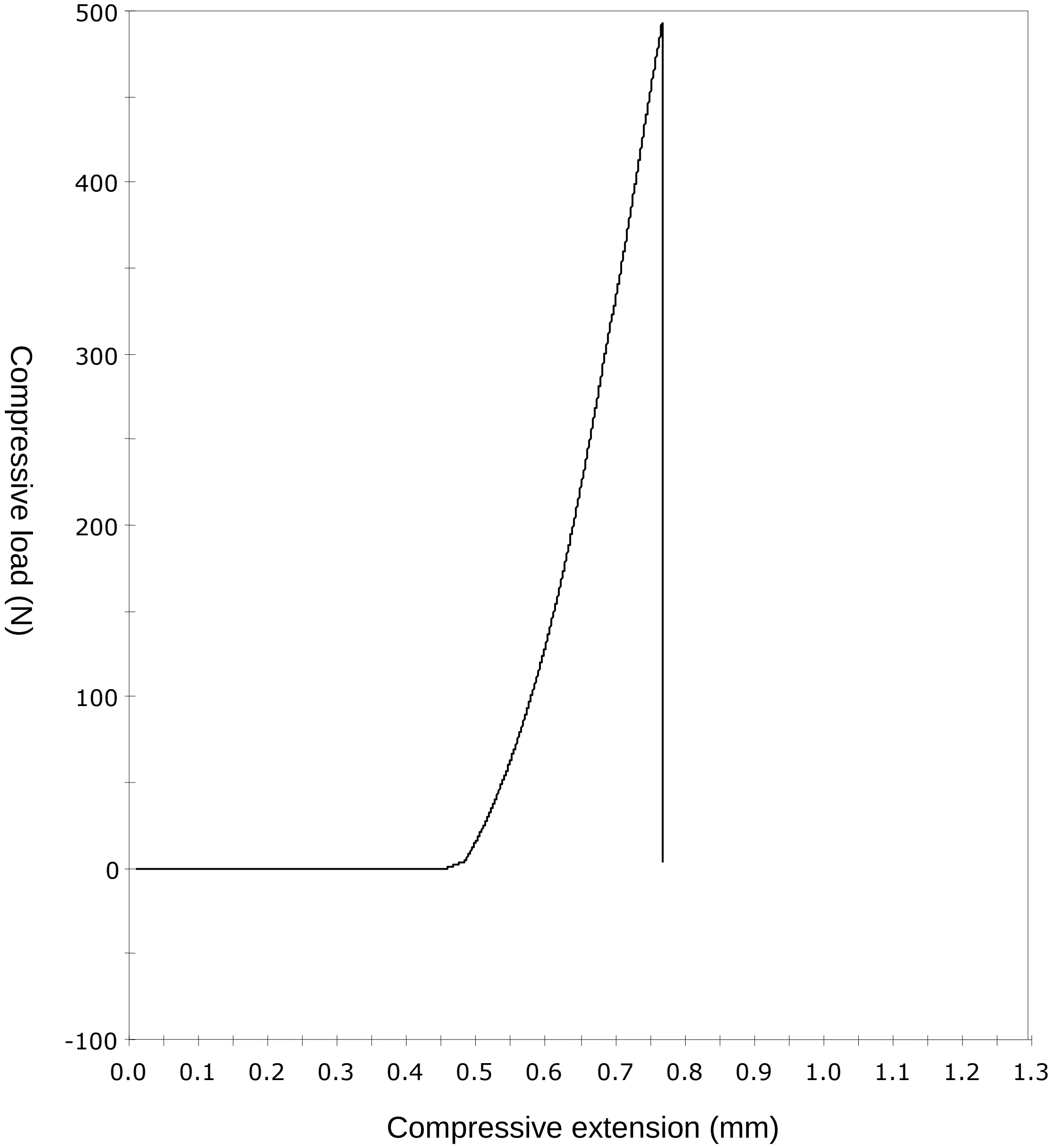


Figure 97. Typical load displacement curve of air-inhibited Build It/Z250 group after 24 hours water storage

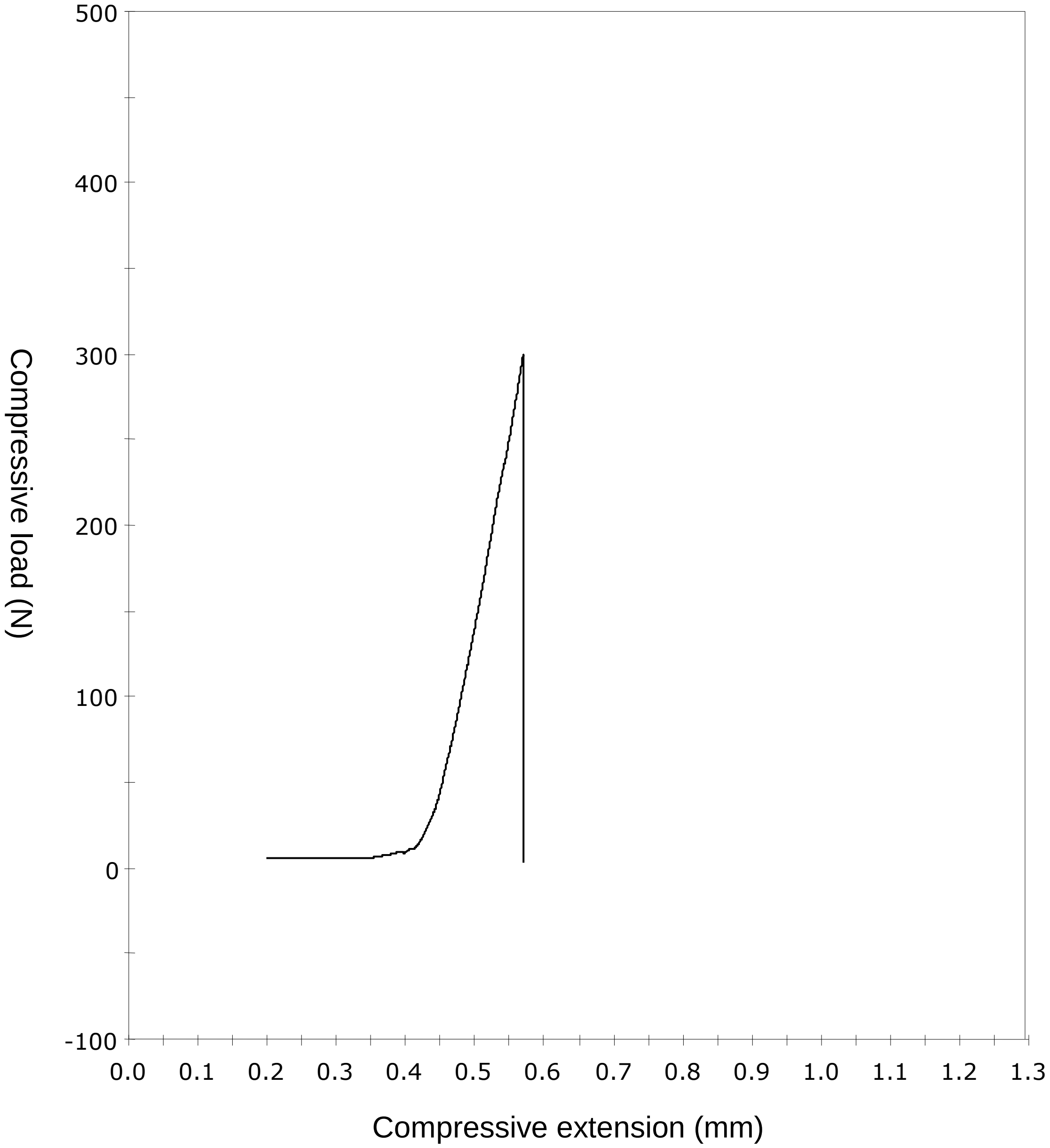
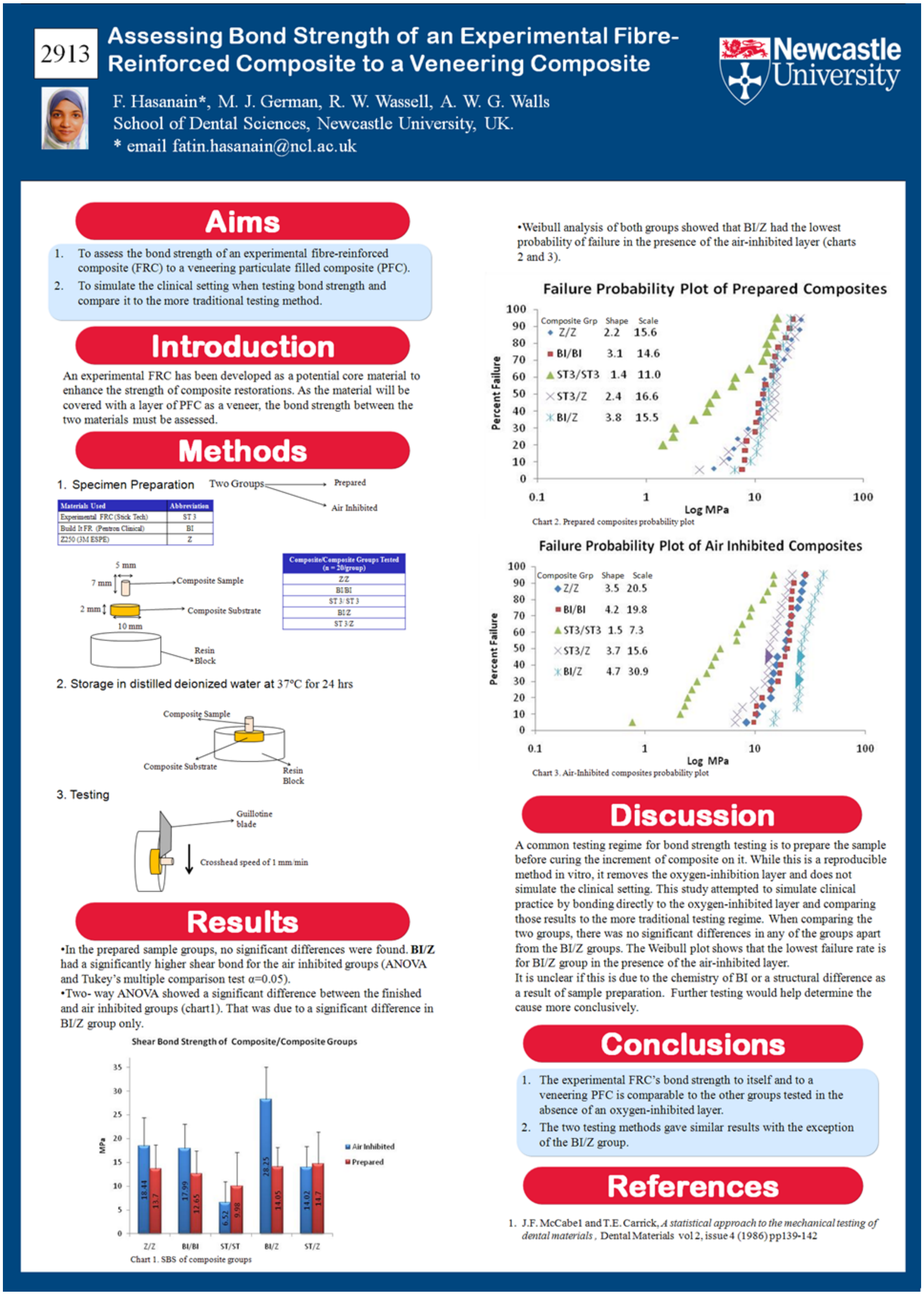


Figure 98. Typical load displacement curve of air-inhibited ST/Z250 group after 24 hours water storage

Appendix C . PhD related scientific presentations



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Assessing Bond Strength of an Experimental Fibre-Reinforced Composite to a Veneering Composite

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Aims

1. To assess the bond strength of an experimental fibre-reinforced composite (FRC) to a veneering particulate filled composite (PFC).
2. To simulate the clinical setting when testing bond strength and compare it to the more traditional testing method.

Introduction

An experimental FRC has been developed as a potential core material to enhance the strength of composite restorations. As the material will be covered with a layer of PFC as a veneer, the bond strength between the two materials must be assessed.

Methods

1. Specimen Preparation

Two Groups → Prepared
→ Air Inhibited

Materials Used	Abbreviation
Experimental FRC (Stick Tech)	ST 3
Build It FR (Pentron Clinical)	BI
Z250 (3M ESPE)	Z

Composite/Composite Groups Tested (n = 20/group)
Z/Z
BI/BI
ST 3/ ST 3
BI/Z
ST 3/Z

2. Storage in distilled deionized water at 37°C for 24 hrs

3. Testing

Results

- In the prepared sample groups, no significant differences were found. **BI/Z** had a significantly higher shear bond for the air inhibited groups (ANOVA and Tukey's multiple comparison test α=0.05).
- Two- way ANOVA showed a significant difference between the finished and air inhibited groups (chart1). That was due to a significant difference in BI/Z group only.

Shear Bond Strength of Composite/Composite Groups

Chart 1. SBS of composite groups

- Weibull analysis of both groups showed that BI/Z had the lowest probability of failure in the presence of the air-inhibited layer (charts 2 and 3).

Failure Probability Plot of Prepared Composites

Chart 2. Prepared composites probability plot

Failure Probability Plot of Air Inhibited Composites

Chart 3. Air-Inhibited composites probability plot

Discussion

A common testing regime for bond strength testing is to prepare the sample before curing the increment of composite on it. While this is a reproducible method in vitro, it removes the oxygen-inhibition layer and does not simulate the clinical setting. This study attempted to simulate clinical practice by bonding directly to the oxygen-inhibited layer and comparing those results to the more traditional testing regime. When comparing the two groups, there was no significant differences in any of the groups apart from the BI/Z groups. The Weibull plot shows that the lowest failure rate is for BI/Z group in the presence of the air-inhibited layer.

It is unclear if this is due to the chemistry of BI or a structural difference as a result of sample preparation. Further testing would help determine the cause more conclusively.

Conclusions

1. The experimental FRC's bond strength to itself and to a veneering PFC is comparable to the other groups tested in the absence of an oxygen-inhibited layer.
2. The two testing methods gave similar results with the exception of the BI/Z group.

References

1. J.F. McCabe1 and T.E. Carrick, *A statistical approach to the mechanical testing of dental materials* , Dental Materials vol 2, issue 4 (1986) pp139-142

#95

Assessing Resistance of an Experimental Fibre-Reinforced Composite to Toothbrush Wear

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Aim

To assess the resistance of an experimental fibre-reinforced composite (FRC) to manual toothbrush wear

Introduction

More patients are requesting composite restorations , even as an alternative to crowns.

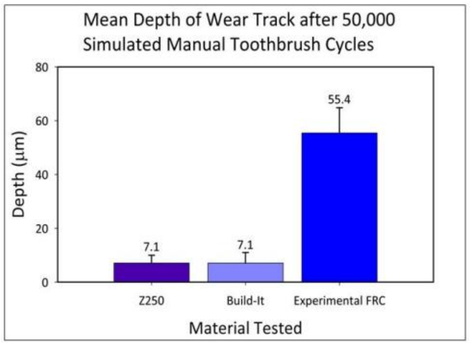
A Finnish company (Stick Tech) has developed an experimental fibre reinforced composite (FRC) as a potential core material to enhance the strength of composite restorations. Normally, the core would be covered by a veneering composite. The abrasion resistance must be evaluated in case the core inadvertently becomes exposed to the mouth.

Methods

1. 4 specimens were prepared from each of the experimental FRC (Stick Tech), a conventional particulate composite resin (*Z250 (3M ESPE)*) and a commercially available FRC (*Build It FR (Pentron Clinical)*).
2. Samples of composite resins 12 mm in diameter and 2 mm deep were prepared in rectangular Perspex blocks. After finishing, polishing and water storage for at least 24 hours, each specimen was subject to 50000 brushing cycles in an ISO conforming toothbrushing simulator with a water/dentifrice slurry (1).
3. Each sample was assessed using a laser profilometer and the maximum depth of the wear track used as a measure of total wear. SEM images were taken as well.
4. Differences between specimens were assessed using ANOVA and Tukey's test.

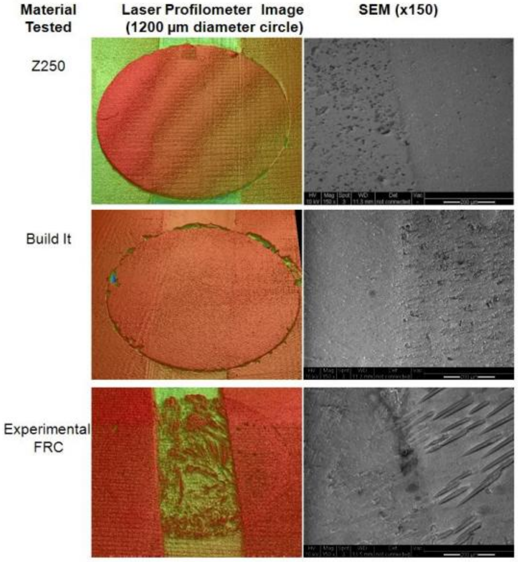
Results

The results shown below clearly indicate that the experimental FRC is more susceptible to wear than either the PFC or the commercially available FRC. ANOVA showed a significant difference (P<0.05), with Tukey's test showing that the experimental FRC was significantly different from both the comparator materials.



Results

Laser profilometer and SEM images show an irregular wear track surface for the experimental FRC compared with Z250 and Build It. Representative examples are shown below.



Discussion

In this study, the experimental FRC's larger, more regular filler size may explain the decrease in wear resistance.

For dental resin composites, the wear process is controlled mainly by filler properties, i.e. the size, shape and concentration of fillers, and the interfacial bonding strength. Turssi found that the magnitude of material loss may be reduced by decreasing the filler particles size and that irregularly shaped fillers wear less than spherical ones of similar size (2).

Conclusion

The experimental FRC wears significantly more than the controls. Thus, it is important that restorations made with the experimental FRC are designed to ensure the core is properly covered by the veneering material

References

1. B.S 5136/1974
2. C.P. Turssi, J.L. Ferracane, K. Vogel, *Filler features and their effects on wear and degree of conversion of particulate dental resin composites*, Biomaterials 26 (2005) 4932–4937.