The effect of the oxygen inhibition layer on interfacial bond strengths and stain resistance of dental resin composites

By

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SYNOPSIS

The free-radical polymerisation reactions of photoactive resins used in dentistry are inhibited by oxygen. There is a need to better understand the effects oxygen inhibition on critical properties of dental resins and resin composites which may compromise the success of dental resin composite restorations. This investigation aims to examine the formation of the oxygen inhibition layer (OIL) on experimental and commercial methacrylate and epoxy resin based materials and its effect on incremental bond strengths and stain resistance. Experimental BisGMA and TEGDMA comonomer resin mixtures loaded with either barium- or strontium-silicate glass fillers were fabricated. Commercially available dental resin composite restorative materials, including a novel epoxy-based system were also examined. The OIL of each material type was measured using a novel optical depth of focus technique, the integrity of resin composite layers and stain resistance was assessed by shear bond strength and colorimeter testing, respectively. An OIL was measurable for all materials polymerised in atmospheric air including the epoxy-based system Filtek™ Silorane. Different filler particle types complicate OIL formation for similar BisGMA/TEGDMA comonomer mixtures. The OIL had a detrimental effect on stain resistance, where an increased OIL thickness resulted in increased stain susceptibility. From the present findings it was suggested that incremental bond strength between composite layers is not wholly reliant on surface inhibition.

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1.0 THE DEVELOPMENT OF DENTAL RESIN BASED COMPOSITE MATERIALS

1.1 Historical Perspectives

A composite material can be defined as a "compound of two of more distinctly different materials" with a distinct interface separating the components" (Anusavice, 1996). The resulting properties of the composite material are usually superior to the properties of each of the single constituents. Dental resin based composites (RBCs) can be defined as "complex, tooth-coloured filling materials composed of synthetic polymers, particulate ceramic reinforcing fillers, molecules which promote or modify the polymerization reaction that produces the cross-linked polymer matrix from the dimethacrylate resin monomers, and silane coupling agents which bond the reinforcing fillers to the polymer matrix." (Ferracane, 1995).

RBCs have been in dental use since the mid sixties (Peutzfeldt, 1997), where they provided good aesthetics and acceptable mechanical and physical properties compared to their main alternatives, silicate cements and acrylic resins. Dr Raphael Bowen, whilst employed by the National Bureau of Standards, developed bisphenol A-glycidyl Methacrylate (BisGMA) resin (Figure 1.3a) in 1956 and incorporated its use in a dental RBC restorative together with triethylenglycol dimethacrylate (TEGDMA) (Figure 1.3b). The newly introduced RBC was composed of 75% weight quartz or aluminosilicate glass filler particles dispersed in 25% weight dimethacrylate resin (Bowen, 1962) Methacrylate-based RBC restoratives set world standards in general dental practice especially when combined with Buonocore's recent

innovation in adhesive dentistry, the acid-etch technique, in which the enamel surrounding the cavity to be restored was treated with 85% phosphoric acid to form points for mechanical retention of the RBC (Buonocore, 1955). The combination provided the dental clinician with an aesthetic restoration that performed reliably when placed in anterior cavities. These events signified the start of the popularity of aesthetic RBC restoration, which is continuing to this day further led by patients high aesthetic expectations (Alkhatib et al., 2004) and the current controversy surrounding the clinical safety of amalgam restorations (Jones, 2008) Unfortunately the further development of resins has been very slow and practically non existent. Similar resin chemistry is still being used today, half a century later.

1.2 The Components of Modern Light-Cured RBCs

Most modern RBC materials used in clinical dentistry today are based on a dimethacrylate monomer system which polymerises via a free radical based reaction upon exposure to a high intensity light source with a wavelength range matching that of the photoinitiator system present in the material. This free radical mediated polymerisation reaction may be inhibited by atmospheric oxygen resulting in a surface layer of poorly or unpolymerised monomer.

The components of a typical modern dental light cured RBC are (Anusavice, 1996; Ruyter, 1988)

▪   Organic Resin Matrix: The base matrix component to which all other constituents are added, and most commonly is a blend of two or more dimethacrylate-based resins such as a high molecular weight monomer BisGMA admixed with a low molecular weight diluent monomer such as TEGDMA, and more recently urethane dimethacrylate (UDMA) (Figure

1.3c) and/or bisphenol A hexaethoxylated dimethacrylate (BisEMA) (Figure 1.3d). These resin blends are used in various ratios to impart a range of favourable properties to the final restorative material, namely, a high degree of conversion, decreased polymerisation shrinkage and stress, increased mechanical strength, resistance to hydrolytic and oxidative degradation, and decreased water sorption and appropriate handling characteristics for the dentist.

▪   Inorganic Filler Particles: They provide dimensional stability to the soft resin matrix. Generally, the first generation of RBCs contained mainly quartz particles, the major disadvantage of which is its hardness which far exceeded the hardness of tooth structure. This resulted in opposing tooth wear, as well as difficulties in satisfactory polishing. More recently silica, strontium, and barium glasses, aluminosilicate and yttrium fluoride filler particles have been added to the monomer resin matrix with various sizes, shapes (Lutz and Phillips, 1983) and filler loads. The filler particles are added to the resin matrix to provide the RBC restorative with improved mechanical and physical properties (compressive and tensile strength, hardness, flexural strength and elastic modulus) required to withstand the forces of mastication and the oral environment, to decrease the polymerisation shrinkage and stress of the RBC, and to impart radiopacity to the restorative. Filler particles have also been used to impart various rheological properties to the RBC, i.e. to modify the rheology to the RBC for use in different situations. Flowable RBCs, with a decreased filler load can be fluid-like and are used in situations where cavity access is difficult or as a fissure sealant whereas highly loaded RBCs are used in an effort to simulate or replicate the handling characteristics of amalgam. Condensable 'packable' RBCs usually loaded up to or greater than 80% filler particles (P60, 3M ESPE, Seefeld, Germany). In addition to high filler loading, packable

RBCs may also include irregular shaped filler particles with a wide range of sizes (0.04 – 10μm) (Surefil, Dentsply, Surrey, UK) to impart packable properties.

Various dental RBC classification systems exist based on filler particles, the most common classification is based on filler particle size in which the filler particle sizes are classified into conventional (traditional) (20 - 50μm), macrofilled (1 - 5μm), microfilled (0.05 - 0.1μm), hybrid, (Lutz and Phillips, 1983) and more recently 'nano' sized particles (20 - 75nm). Most of the commercial RBCs currently in the market are hybrid types with a range of macrofilled and microfilled particle sizes, in an attempt to improve both the mechanical and aesthetic properties. The trend has been towards decreasing particle sizes and increasing filler loading. In general, the smaller the particle size and the higher the loading, the better the resulting RBC material properties but there exists a compromise. As filler size decreases, for the same volume percent, surface area increases which limits the maximum volume percent in resin due to surface area to volume effects. Consequently, a distribution of varying particle sizes is used.

- Coupling Agent: Functions primarily to facilitate the bond between the filler particles and the resin matrix and is based on organosilane chemistry. Their bipolar molecule structure allows them to bond to both the organic resin monomer via the methacrylate groups ($-CH_3$) and to the filler particle via silanol groups (Si-OH). The most commonly used silane in dental RBCs is 3-methacryloxypropyl trimethoxysilane (Ferracane, 1995). Following the introduction of a non-methacrylate based restorative material, Filtek™ Silorane an epoxy activated silane coupling agent was developed to be used exclusively with this restorative.

- Photoinitiator System: This component of the RBC is present only in visible light cured RBCs, and most commonly is a diketone such as camphorquinone (CQ) (Figure 1.1)

which absorbs specific and narrow visible (blue) light wavelengths from 400 to 500nm with an optimum peak absorbance of approximately 465nm. The camphorquinone then transfers to an excited triplet state and initiates the polymerisation process in conjunction with a co-initiator (tertiary amine activator) such as dimethylaminoethylmethacrylate (DMAEMA) (Figure 1.2) to generate free radicals which initiate the polymerisation process (Andrzejewska, 2001; Cook, 1992).

▪ Inhibitors and Stabilizers: such as hydroquinone, 4-methoxyphenol (MEHQ) and 2,6-di-tert-butyl-4-methyl phenol or butylated hydroxytoluene (BHT) are added to the RBC to prevent the restorative from premature polymerisation and provides it with increased ambient light stability and improved shelf life.

▪ Optical Modifiers: stains and opacifiers to change and modify the shades of the composite material to better match the tooth colour being restored. Opacity is usually provided by titanium dioxide, whilst magnesium, copper and iron oxides supply a variety of colours and shades.
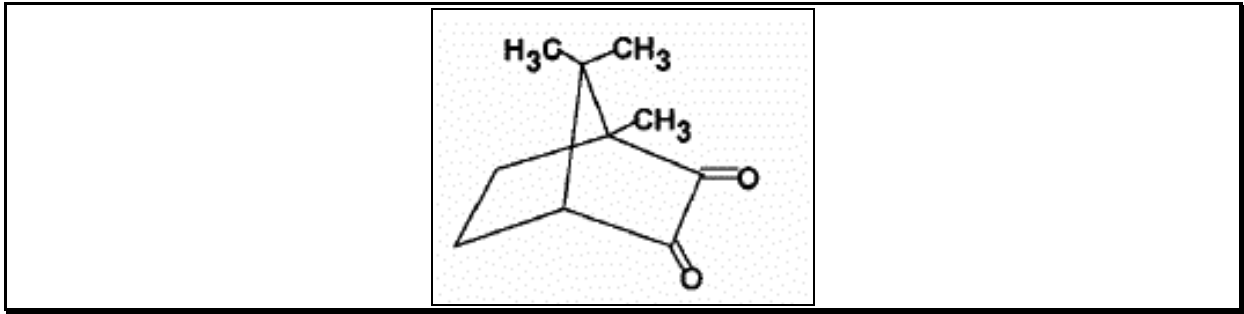
Figure 1.1: Diagram representing the chemical structure of the photoinitiator Camphoroquinone, used in most commercial RBC formulations, including Z100, Filtek™ Z250, and Filtek™ Silorane, and in the experimental resins and RBCs.
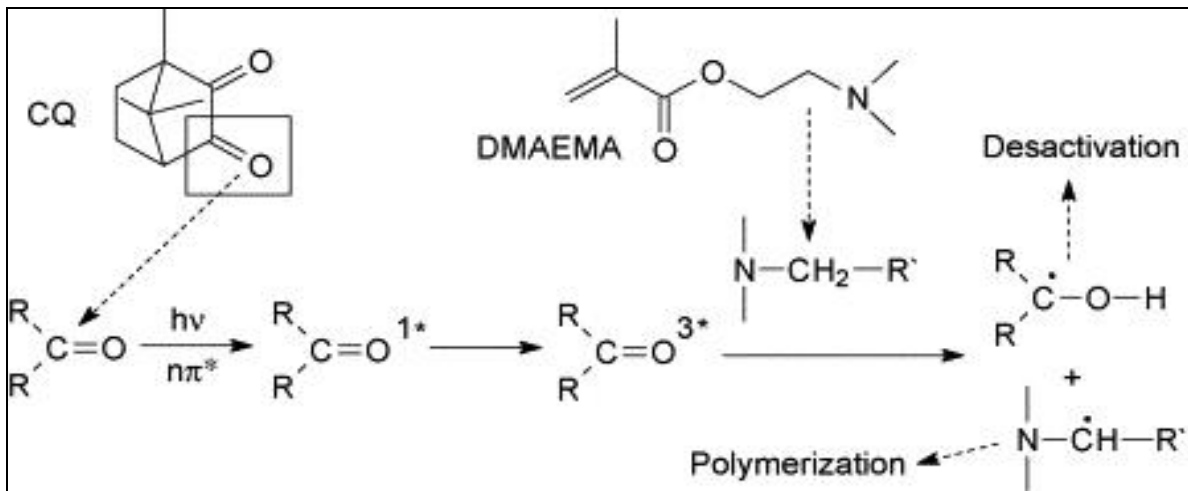
Figure 1.2: Schematic diagram illustrating the roles of CQ and DMAEMA in free radical polymerisation of resin based composite.

1.3 Commonly Used Methacrylate Based Resins in Restorative Dentistry

▪ **BisGMA:** bisphenol A glycidyl methacrylate was the earliest base resin successfully incorporated in an RBC for direct restoration (Bowen, 1962). BisGMA has been a primary component of dental RBCs for more than 50 years and is the main matrix constituent of modern RBCs. This resin was fundamental in the introduction and development of RBCs in aesthetic restorative dentistry. BisGMA is a relatively large methacrylate based molecule with two aromatic carbon rings that add to its molecular weight and stiffness. BisGMA also has two hydroxyl groups which increases its viscosity (Rueggeberg, 2002). When polymerised, BisGMA forms a polymer with high structural rigidity and good mechanical and physical properties. However, the high viscosity of BisGMA (~1,000,000mPa.s) is a disadvantage, since loading the resin to an appropriate mass percentage with reinforcing filler particles required for sufficient mechanical and physical properties is rendered impossible. Therefore, BisGMA it is mixed with lower viscosity dimethacrylate resins which act as a diluent for the matrix system

▪ **TEGDMA:** triethylenglycol dimethacrylate is a smaller molecule than BisGMA with a lower molecular weight and thus less viscosity (~10mPa.s). The mechanical properties of TEGDMA are less than that of BisGMA, mainly as a result of the presence of ether (C-O-C) bonds and the lack of aromatic rings along TEGDMAs structure. TEGDMA's polymerisation shrinkage is also greater, 12.5% compared to BisGMAs 5.2% (Braga et al., 2005), due to its lower molecular weight and therefore, increased concentration of C=C bonds, resulting in a higher degree of conversion (Asmussen, 1982; Munksgaard et al., 1985). Another disadvantage is its low hydrophobicity which may result in increased stain susceptibility and leaching of TEGDMA into the oral environment (Sideridou and Achilias, 2005).

The primary purpose of TEGDMA in a dental RBC is to reduce the viscosity of the restorative to facilitate the addition of greater amounts of inorganic filler which add to the mechanical properties of the final RBC material. Therefore, a compromise must be made between polymerisation shrinkage and mechanical properties as the addition of TEGDMA to an RBC will allow additional loading of filler particles but will also increase the polymerisation shrinkage.

▪ **UDMA:** urethane dimethacrylate (Figure 1.3c) usually replaces or is added in addition to BisGMA in modern composites. UDMA is derived from BisGMA, but differs in the presence of urethane groups which impart strength and toughness to the polymer. It is less viscous than BisGMA (~11,000mPa.s) (Peutzfeldt, 1997), although it has a similar molecular weight. The large difference in viscosity is attributable to UDMA's lack of aromatic groups. A study suggests that the polymerized UDMA resin achieves a higher degree of conversion than BisGMA, i.e. a decrease in unpolymerised residual monomer, and consequently resulting in significantly increased mechanical and physical properties (e.g. less water sorption) (Palin et al., 2003). Greater biocompatibility is another advantage as lower quantities of residual monomer results in a decreased possibility of adverse pulpal reactions (Peutzfeldt, 1997). Furthermore, the presence of urethane groups along UDMA's structure result in lower water sorption, due to their lower bonding ability with water molecules (Peutzfeldt, 1997).

▪ **BisEMA:** bisphenol A hexaethoxylated dimethacrylate (Figure 1.3d) is an ethoxylated version of BisGMA. The hydroxyl groups in BisGMA are replaced by ethoxy groups to form an ethoxylated derivative of BisGMA. The main advantages of BisEMA

when compared to BisGMA is its superior handling properties with a decreased stickiness or tackiness to dental instruments when placed in cavities (Rueggeberg, 2002), as well as less hydrophilicity therefore resulting in less water sorption (Palin et al., 2005b) when compared to BisGMA.

Most of the methacrylate-based resins have been in service in dentistry without any significant modification for over half a century. As such, RBC development has been concentrated on filler particles (size and morphology), bonding systems, polymerisation reactions (chemical, light, or dual cure) and the development of light-curing technology.

(a)

bis-GMA

(b)

TEGDMA

(c)

UDMA

(d)
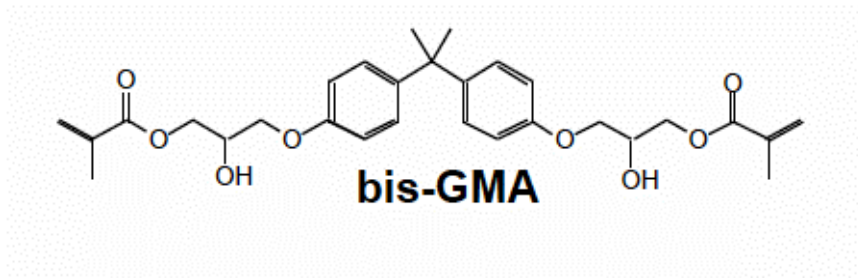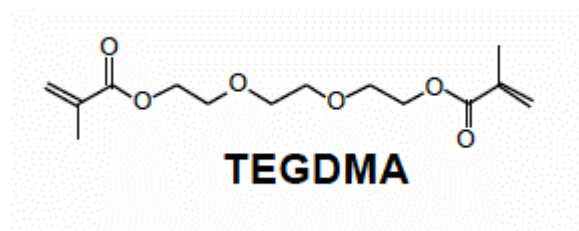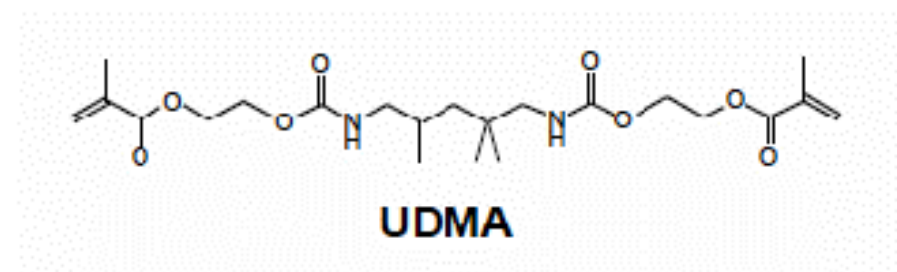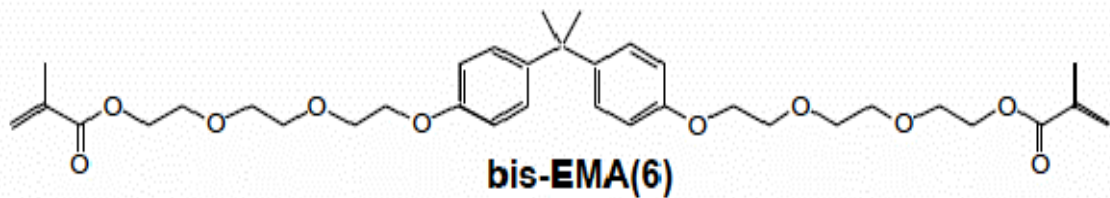
bis-EMA(6)

Figure 1.3 Diagrams representing the chemical structures of dimethacrylate resins utilized in Z100, Monomer blends, and Model RBCs (BisGMA, TEGDMA) and in Filtek™ Z250 (UDMA, BisEMA, BisGMA and TEGDMA).

1.4 Disadvantages of Methacrylate Resin based Composites.

1.4.1 Polymerisation shrinkage and the resulting shrinkage stress.

Polymerisation shrinkage and stress are terms often used in dentistry, these terms may be confusing, and many clinicians may mistakenly believe them to be the same. While polymerisation shrinkage and stress are directly related they are very different. Volumetric shrinkage describes the decrease in volume resulting from the polymerisation of the RBC due to the replacement of the longer intermolecular distances and Van der Waals forces in the unpolymerised material with shorter covalent bonds. Stress, on the other hand is a measure of the forces generated during the shrinkage (contraction) of the RBC as a result of the curing mechanism of modern RBCs. Polymerisation shrinkage and the development of shrinkage stress is a major contributing factor in the marginal microleakage of restorations. Stress forces may result in a variety of damaging consequences on the RBC restoration and the tooth. The RBC restoration is typically micromechanically bonded to the tooth structure. If the adhesive bond to tooth structure fails due to the generation of stress, marginal leakage and therefore discolouration, sensitivity and secondary caries may result (the most important cause of clinical failure of RBCs) (Weinmann et al., 2005). However, if the bond survives resulting in a firmly bonded restoration, stress will build up at the bonding interface and subsequently will transfer to the tooth structure and may result in cuspal deflection (Palin et al., 2005a) and in extreme cases, cracks (Bouillaguet et al., 2006; Weinmann et al., 2005). It has been established that the degree of shrinkage is directly proportional to the degree of conversion of the resin regardless of RBC type or composition (Dewaele et al., 2006). The magnitude of shrinkage stress is a complex phenomenon and dependant on a multitude of factors:

- Viscosity of resin.

- Filler loading.

- The Configuration factor.

- Incremental filling of RBCs.

- Curing protocol (polymerisation).

- Elastic Modulus.

1.4.1.1 Viscosity of resin

The resin viscosity is directly influenced by the molecular weight of the resin. The larger the resin molecule (i.e. higher molecular weight) the less shrinkage will result, thus a monomer molecule such as BisGMA will undergo less shrinkage than a low molecular weight monomer such as TEGDMA. This can be explained by the increased density of double-bonds (C=C) present in any given area of low molecular weight monomers, thus a greater number of covalent bonds are formed during polymerisation, resulting in an increased degree of conversion thus, producing increased shrinkage of the polymer. In higher molecular weight monomers, the methacrylate reactive groups are more spaced apart therefore less covalent bonds form the final polymerised mass under similar curing conditions. The actual polymerisation shrinkage results from the difference between the intermolecular (van der Waals) distances between monomer molecules (0.3-0.4nm) and the length of the covalent bond resulting from the polymerisation reaction (0.15nm), thus a net shrinkage results (Peutzfeldt, 1997; Rueggeberg, 2002). Typically, modern methacrylate-based RBCs shrink approximately 2-5% on polymerisation (Dennison et al., 2000; Watts and Cash, 1991).

1.4.1.2 Filler loading

Filler loading is a major factor affecting polymerisation shrinkage. It is recognized that increasing the filler particle load will decrease polymerisation shrinkage, this effect is due to

the offsetting of resin shrinkage by the relatively inert filler particles (Condon and Ferracane, 2000). However, an increased filler loading also increases the elastic modulus producing a more rigid RBC, which is less able to absorb the shrinkage strain. Condon and Ferracane (2000) reported that increasing filler loading, although decreasing RBC shrinkage, may result in an increased stress generation.

1.4.1.3 The Configuration factor

The Configuration factor (C-factor) is defined as the ratio of unbonded surfaces to bonded surfaces. Therefore a C-factor value of 5 (typical of class I cavities) is more confined than a C-factor value of 0.5 (as present in class IV cavities). There has been debate in the literature regarding the influence of the C-factor on the generation of shrinkage stress (Alster et al., 1997; Lu et al., 2004; Miguel and de la Macorra, 2001; Watts et al., 2003). In a low C-factor configuration, the decrease in shrinkage stress results from the lack of impediments to volumetric shrinkage of the RBC material. Cavity design and incremental filling techniques may reduce shrinkage stress but not necessarily reduce shrinkage by reducing the C-factor (Feilzer et al., 1987). A previous study reported an increase in stress generation when the bonded surfaces in relation to unbonded surfaces increased, i.e. a decrease in C-factor values, when using a rigid (non-compliant) testing apparatus (Section 1.4.1.6) (Feilzer et al., 1987). However, other authors (Braga et al., 2006; Miguel and de la Macorra, 2001; Watts and Cash, 1991) reported that compliance of the stress testing apparatus may not be indicative of the compliance of tooth structure. In a recent study, Braga et al. (2006) reported that for a given restoration, stress generation was more influenced by cavity depth and diameter, where increasing depth and/or diameter caused an increased stress production, regardless of C-factor values. Furthermore, the authors concluded that the C-factor may only be useful to compare stress generation where similar volumes of restorative material are tested. Therefore the Configuration factor as a significant issue in stress generation in RBC restorations will

continue to be debated in the dental literature, where the shrinkage stress values from different studies cannot be directly compared due to differences in test system compliances, stress monitoring procedures, RBC material specimen geometry, and direction of photo-polymerisation. Shrinkage stress studies are also very rarely correlated with microleakage and clinical studies which further increases the difficulties in interpreting their clinical relevance

1.4.1.4 Incremental filling of RBCs

The primary clinical use of the incremental filling technique of RBC restoratives is to overcome the limited depth of cure of the material (Section 1.4.3). The incremental technique has also been associated with the reduction of shrinkage stress of RBC restoratives. As each RBC increment is light-cured it undergoes shrinkage. However as the restoration is placed in increments, when the cavity is fully packed the total shrinkage volume of the last increment is significantly less than shrinkage volume of the bulk filled restoration (Koenigsberg et al., 1989) Concerns have been raised about the validity of this widely-practiced technique, as the RBC material does not polymerise completely at the time of placement, therefore the RBC does not fully shrink (only 70-85% shrinkage at placement) (Sakaguchi et al., 1992) consequently, when the subsequent increment is placed it may not fully compensate the shrinkage of the underlying layer (Loguercio et al., 2004). It has also been suggested that the main advantage of using an incremental technique to reduce shrinkage stress lies in the reduction of the C-factor, which consequently reduces the interface stress developed by the RBC (Carvalho RM, 1996; Davidson and Feilzer, 1997) and although Braga et al. (2006) recently suggested that the volume of the restoration was more relevant than the C-factor in the reduction of shrinkage stress, an incremental placement technique also decreases the volume of the restoration by reducing depth and/or diameter of the cavity.

1.4.1.5 Curing protocol (polymerisation)

When a RBC material polymerises it goes through various stages of polymerisation, the most important stage regarding stress formation is when the material begins to solidify; this point is referred to as the gel point. Shrinkage stresses are developed post-gelation of the resin at which the material can no longer flow sufficiently to absorb the contraction caused by polymerisation (Stansbury et al., 2005). Before gelation of the monomer there is adequate monomer flow to overcome the stress developed (Davidson & Feilzer, 1997). Therefore, any forces developed before the gel point contribute minimally to the overall stress of the polymer, thus a major area of interest is to delay the onset of the gel point by different curing regimes.

Different techniques of photo-polymerising resins have been developed. In the ramped technique, the operator begins the polymerization process with a low intensity light gradually increasing to a higher intensity. The rationale behind this technique is that the low intensity at the start of curing delays the materials gel point, thus allowing the resin to flow and maintain adaptation to the cavity surfaces consequently decreasing and relaxing the residual stresses developed. Various researchers have reported different results regarding the efficiency of this technique. Some studies (Charton et al., 2007; Cunha et al., 2006; Yoshikawa et al., 2001) report a significant reduction in polymerisation shrinkage stress following a ramped compared with a standard curing regime. Uno, (1991) also reported an increase in marginal adaptation. However, Christensen, (1999) suggested that different curing techniques resulted in no significant differences in reduction of stress. Other techniques such as soft-start, two-step and pulse delay have also been used to try to decrease stress development (Stansbury et al., 2005), although much controversy exists as to whether any significant reduction in stress can be achieved.

1.4.1.6 Elastic Modulus

The elastic modulus is a measurement of a materials stiffness or rigidity, the lower the modulus the more elastic the material. The most rigid RBCs may generate the highest stress whereas low viscosity resins are generally more flexible and thus have a low elastic modulus which purportedly enables the material to absorb the stresses generated by shrinkage (Condon and Ferracane, 2000). Polymerisation shrinkage stress may be either relieved internally by the rearrangement of the internal polymer structure of the RBC material prior to gelation, or it may be relieved externally by surrounding cavity wall compliance, i.e. the ability of the cavity walls to yield and conform to the stresses produced (Alster et al., 1997). Consequently, if the cavity walls are lined by a low elastic modulus material, increased compliance might be artificially induced, thus shrinkage stresses can be cushioned and their effects on the tooth structure reduced (Labella et al., 1999). Currently some authors advocate the lining of cavities with an unfilled or a lightly filled resin to allow improved adaptation of the RBC to the cavity walls, to increase the compliance of the cavity, and therefore reduce the shrinkage stress (Cunha et al., 2006; Unterbrink and Liebenberg, 1999) thus reducing the incidence of microleakage (Davidson and Feilzer, 1997; Kemp-Scholte and Davidson, 1990) Flowable RBCs are most suited for this application, due to their decreased filler load. However, Braga et al. (2003) reported that flowable RBCs developed shrinkage stress values similar to highly loaded RBCs, regardless of their low elastic moduli. This may have been caused by the lower filler loading of flowable RBCs resulted in up to 6% volumetric shrinkage (Labella et al., 1999). Furthermore, other researchers (Leevailoj et al., 2001; Wibowo and Stockton, 2001) have reported that the use of a low-elastic modulus flowable RBC as a stress relieving layer did not significantly affect stress reduction, as measured indirectly by *in vitro* microleakage studies.

1.4.3 Limited depth of cure

When modern light-cured dental methacrylate-based RBCs are subjected to high intensity visible light, the polymerisation reaction of the RBC is fastest towards the surface of the restoration and decreases through bulk as the curing light is attenuated (with the exception of inhibitory effects from oxygen at the surface). The limited curing depth is also due to the mobility of the reactive species (radicals) within the resin. The rapid onset of vitrification from the monomer paste limits diffusion of radicals and polymerization reactions are terminated. The depth of cure is also dependent upon filler morphology where particles may reflect, refract, scatter or absorb the light thus permitting only a fraction of the total emitted light to reach the depth of the material. Light scattering was suggested to be the main factor influencing the depth of cure. Ruyter and Oysaed, (1982) postulated that maximum light scattering results when the filler particle size equals half the wavelength of the emitted polymerisation light. Shortall et al. (2008) also reported that a reactive index mismatch between the filler and resin affected cure depth significantly.

The clinically advised maximum thickness of RBC material during clinical placement is ~2 – 4mm (dependent on material and curing light properties). If the RBC is layered any thicker it may not polymerise adequately in the deeper segments of the cavity, resulting in poorly polymerised material which may adversely affect the longevity and overall mechanical, physical and biological properties of the restoration.

1.4.4 Limited degree of conversion

Degree of conversion (DC) is a measure of the amount of methacrylate carbon double bonds (C=C) which have reacted to form covalent bonds with adjacent methacrylate groups. The majority of resin monomers in use in dentistry are bifunctional, i.e. they have two reactive

methacrylate groups per monomer, thus two carbon to carbon double bonds which have the capability to react and produce a polymer. The DC in a methacrylate based resin is in the range of 50-70%, therefore 30-50% of the remaining double bonds may have not reacted and of that percentage only 10% of monomers may have both unreacted double bonds (Rueggeberg, 2002), resulting in an unattached monomer molecule which may also leach out to cause pulpal damage, discolouration of the tooth (Peutzfeldt, 1997) or cytotoxicity (Brackett et al., 2007).

A low degree of monomer conversion of the RBC material usually results in lower mechanical properties although simultaneously produces less polymerisation shrinkage. Therefore a balance between acceptable mechanical properties and decreased polymerisation shrinkage is required. Research is still underway for a compromise between the two conflicting properties (Visvanathan et al., 2007).

The oxygen inhibited layer (OIL) can be defined as a layer of inhibited or retarded monomer present on the surface layer of resins cured in the presence of oxygen. This inhibition forms as a result of the increased affinity of the free radicals towards oxygen, which is greater than their attraction towards the methacrylate carbon-carbon double bonds thus retarding the formation of a polymer (Dall'Oca, 2007; Eliades and Caputo, 1989) This layer has been reported to range in thickness from 4µm (Finger et al., 1996) to 37 ± 16µm (Rueggeberg and Margeson, 1990). Currently, opinion is still divided on whether the inhibition layer is detrimental (Rueggeberg and Margeson, 1990; Eliades and Caputo, 1989) or beneficial (Kim et al., 2006; Truffier-Boutry et al., 2003) to interfacial resin-to-resin bonding (Section 1.6).

1.5 Recent Developments in Dental RBCs.

The majority of RBCs presently used in dentistry are based almost exclusively on methacrylate chemistry. BisGMA has been and still is the predominant constituent in the majority of commercial RBCs. Although it provides a relatively fast polymerization rate and results in a polymer with high mechanical properties, methacrylate-based resins suffer from various disadvantages such as polymerisation shrinkage, limited degree of conversion and hydrolytic instability. Therefore attempts have been made to develop BisGMA substitutes or analogues or even alternative chemistries which attempt to overcome or improve the properties of conventional resin types.

- **Oxirane:** Although there have been no significant changes in commercial resin chemistry, there has been much research into different resin systems. Epoxy-based resin based dental materials were studied for dental restorative use before methacrylate based resins (Bowen, 1956) but their clinical viability was dismissed mainly because of the excessively long setting times (Palin et al., 2005b; Peutzfeldt, 1997 ; Rueggeberg, 2002) and their tendency to discolour rapidly in the oral environment (Phillips, 1973). However, there has been a renewed interest in epoxy resins, leading to research into materials such as Oxirane (Figure 1.4) which polymerises with minimum shrinkage due to a double ring opening reaction based on cationic and not free-radical polymerisation associated with methacrylate-based monomers (Rueggeberg, 2002). Other favourable properties of the material include OIL elimination, decreased polymerization shrinkage, adequate hardness and excellent mechanical strength (Tilbrook et al., 2000) However, a limited depth of cure of 1mm and slow development of flexural strength together with excessively long setting times

were reported (Palin et al., 2005) and precluded their clinical use as dental restorative materials.
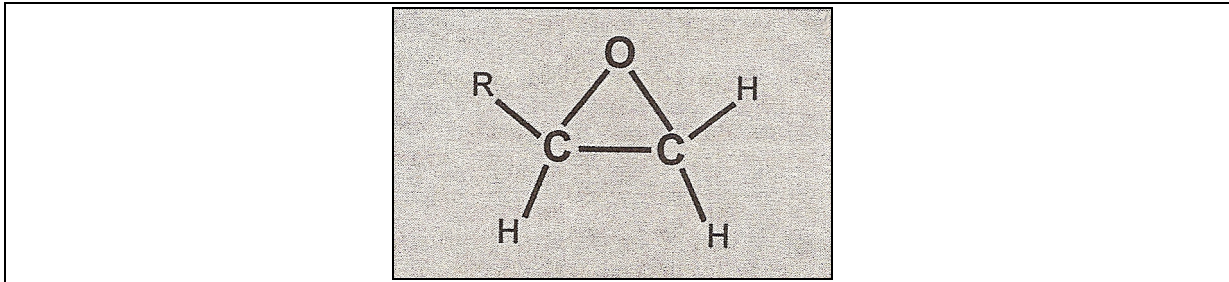
Figure 1.4: The chemical structure of the three-membered, oxygen-containing Oxirane ring present in the functional group of epoxy resins.

▪ **Spiro-orthocarbonates:** (SOC) (Figure 1.5) is a cyclic monomer based on an ester of orthocarboxylic acid with four oxygen atoms bound to a single carbon atom, the "spiro" part of the name signifies that this carbon atom is shared by two adjacent rings. SOC polymerises via a cationic double ring opening reaction which is reported to yield an overall expansion (Endo and Bailey., 1975). However clinical SOC formulations mostly result in a slight shrinkage (Palin et al., 2003; Rueggeberg, 2002). This effect has been suggested to be due to incomplete ring opening of the SOC molecule during light curing (Eick et al., 2007) and the polymerization of SOC via alternative non-ring opening pathways (Moszner and Salz, 2001). Admixing SOC with BisGMA or other dimethacrylate based monomers resulted in negligible non-shrinking effects with a significant decrease in the restoratives mechanical properties (Peutzfeldt, 1997; Palin et al., 2003). Various SOC based materials have also been admixed with Silorane in an attempt to produce formulations with reduced stress generation (An addition of 1% SOC to a Silorane resulted in a 70% stress reduction) although mechanical properties and depth of cure were significantly decreased when SOC concentrations exceeded

5% (Eick et al., 2007). Eick et al. (2007) also proposed that the stress reducing properties of SOC may be related to factors such as low elastic modulus, slower polymerization rates and lower glass transition temperatures and not to the double ring opening mechanism.

▪ **Ormocers:** an acronym for Organically Modified Ceramics can be defined as '3 dimensionally cross-linked copolymers synthesized from a sol-gel process from multifunctional urethane and trioether (meth)acrylate alkoxysilanes.' (Ajlouni, 2005). Ormocer monomer is based on dimethacrylate chemistry that polymerises with a free radical reaction, and is reported to cure without leaving a residual monomer, thus increasing biocompatibility. However, the commercial product is usually admixed with TEGDMA as a diluent to reduce the viscosity of Ormocers therefore the disadvantages of TEGDMA are incorporated into the final Ormocer restorative material. (Moszner & Salz, 2001). Two products are currently on the market, Admira released by Voco (Cuxhaven, Germany) and Definite by Dentsply (Konstanz, Germany) neither of which improved on either the mechanical or physical properties of dimethacrylate RBCs (Bottenberg et al., 2007; Rosin et al., 2003).

▪ **Liquid crystalline monomers:** (LCM) are a more recent development in dental restoratives; they have a relatively low viscosity enabling addition of fillers. More importantly they also have high monomer conversion rates and low polymerization shrinkage levels. However, to achieve maximal benefit from the low levels of polymerization shrinkage, the LCM material has to result in an amphorous polymer network rather than an organized crystalline structure on polymerization. That occurs in high temperatures (≈80 ℃) that are clinically unrealistic to attain. Structural changes (varying spacer length and changing

mesogenic groups) of these LCMs were attempted, and resulted in an ambient-temperature LCM which displayed a melting point at room temperature (Ritter H et al., 2000). However, liquid crystalline monomers are still prohibitively expensive to manufacture and suffer from excessive flexibility which may decrease its mechanical properties (Moszner & Salz, 2001).

This led to the development of highly branched non-liquid crystalline monomers, like their predecessors these also exhibited low viscosity and low levels of polymerization shrinkage, however the low flexural strength and modulus of elasticity of these materials precluded them from being used clinically. Research is currently ongoing in a bid to improve the mechanical properties of these materials (Moszner & Salz, 2001).

- **Silorane:** 3,4-epoxycyclohexylcyclopolymethylsiloxane (Figure 1.6) is an epoxy-based RBC developed from the aforementioned oxirane-based materials recently developed and marketed by 3M ESPE Dental Products (Seefeld, Germany). Filtek™ Silorane is synthesized from oxirane and siloxane moieties resulting in a polymer with similar mechanical and physical properties compared to methacrylate based RBCs whilst imparting several favourable properties to the final material, including increased hydrophobicity (Palin et al., 2005), decreased cytotoxicity (Schweikl et al., 2004), increased ambient light stability (Weinmann et al., 2005) and decreased polymerisation shrinkage and stress (Ernst et al., 2004; Weinmann et al., 2005). The initiating system is based on a three component cationic system composed of camphorquinone, an iodonium salt and an electron donor. The electron donor decomposes the iodonium salt to form the cation and thus initiate polymerization (Weinmann et al., 2005) (Figure 4.1). Weinmann et al. (2005) reported that the ring opening cationic polymerization reaction resulted in less than 1% shrinkage which is a significant improvement over traditional methacrylate-based RBCs. However, the mechanical properties

(depth of cure, flexural modulus, hardness) of Filtek™ Silorane are comparable to methacrylate based RBCs (Ilie and Hickel, 2006). Also, it has been recently reported that since Filtek™ Silorane is polymerized primarily via a cationic reaction, the influence of atmospheric oxygen on the dynamics of the reaction are greatly reduced which may suggest that the formation of an oxygen inhibited layer is eliminated.
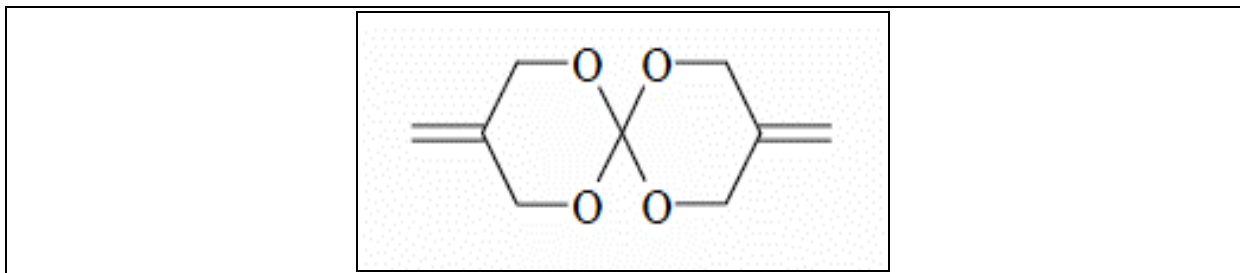
Figure 1.5: A diagram illustrating the chemical structure of a cationically-cured Spiro-orthocarbonate (SOC), which results in (Volume) expansion during polymerisation due to the presence of cyclic ring opening
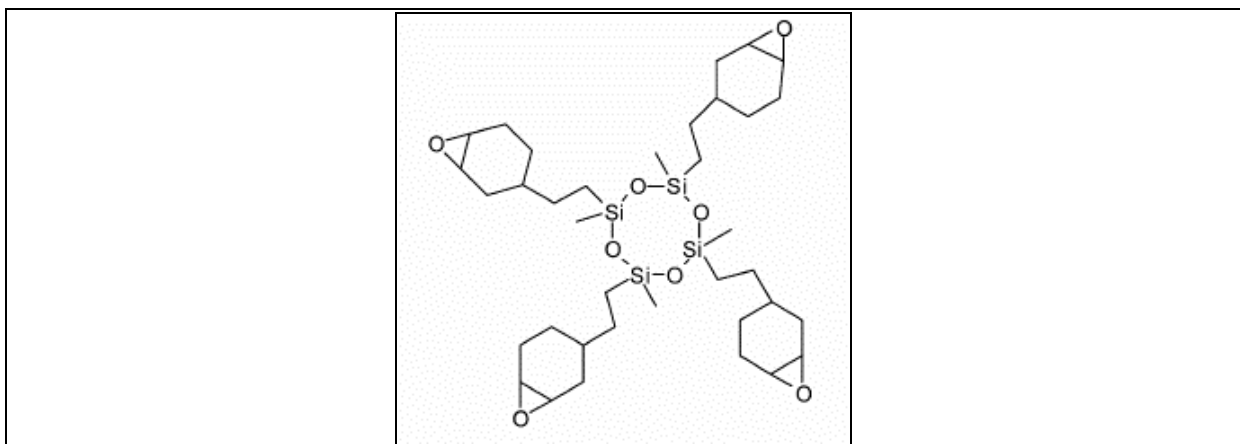
Figure 1.6: A diagram illustrating the chemical structure of a cationically-cured Silorane (3,4-epoxycyclohexylcyclopolymethylsiloxane), which results in a decreased shrinkage during polymerisation due to the cyclic ring opening reaction.

1.6 Oxygen Inhibition of Methacrylate Resin based Restorative Materials

1.6.1 The oxygen inhibition layer

The oxygen inhibition layer (OIL) that forms on the surface of methacrylate based resins cured in the presence of oxygen has received much attention in the literature, both positive (Kim et al., 2006; Truffier-Boutry et al., 2003) and negative (Eliades and Caputo, 1989; Rueggeberg and Margeson, 1990; von Beetzen et al., 1996). The OIL forms as a result of the increased affinity of the free radicals towards oxygen, which is greater than their attraction towards the methacrylate carbon-carbon double bonds thus retarding the formation of a polymer (Dall'Oca, 2007; Eliades and Caputo, 1989), thus the OIL can be defined as a layer of inhibited or retarded monomer present on the surface layer of methacrylate resins cured in the presence of oxygen. The OIL is purported to have a similar composition to the uncured resin although with partially consumed photoinitiators and co-initiators (Rueggeberg and Margeson, 1990). However, the OIL still has the capability to undergo polymerisation due to the diffusion of free radicals from the overlying uncured RBC utilized in the layering technique in the placement of RBC restorations in order to overcome curing depth limitations (Section 1.4.1.4). However, this diffusion has been purported to be inadequate for satisfactory bonding (Rueggeberg and Margeson, 1990).

Experimental techniques in measuring the OIL thickness has varied between researchers and has been reported to range from 4μm (Finger et al., 1996) to 84μm (Ruyter, 1981). The former measurement was achieved by a 'depth of focus technique', the latter measurement was taken using a glass slide method, in which a drop of resin was placed between a glass microscopic slide and a coverslip, and the resin was allowed to flow. The resin was

subsequently cured and the oxygen inhibition layer thickness was measured under magnification in five positions. Both of the above mentioned studies used unfilled resins and in the case of Ruyter (1981) the quoted measurement was observed in a 7.7% (by weight) filled resin so one may reasonably expect lower OIL thickness values in a filled RBC, especially in modern highly filled RBC restoratives where it is common to have +70% fillers (by volume). Furthermore, as the surface layer is partially taken up by the filler particles less resin is exposed to atmospheric oxygen and thus the depth of inhibition may decrease. Gauthier et al. (2005) reported that filler loads greater than 40% decrease oxygen inhibition.

It has also been reported that the uppermost surface layer of RBCs had a lower degree of conversion than that was normally observed in its counterpart unfilled bisphenol A-glycidyl methacrylate/ triethyleneglycol dimethacrylate (BisGMA/TEGDMA) mix which amounted to $25 \pm 5\%$ (Gauthier et al., 2005). This decrease in degree of conversion may be explained by the diffusion of oxygen into the resin mass and retarding the polymerization reaction. As the OIL is an inhibited, poorly or unpolymerized monomer with a decreased degree of conversion, one could reasonably expect reduced RBC mechanical and physical properties (Palin et al., 2003; Peutzfeldt and Asmussen, 2000).

1.6.2 Factors influencing oxygen inhibition of resin based composites

The degree and depth of oxygen inhibition at the surface of a methacrylate RBC may be influenced by various factors.

1.6.2.1 Resin viscosity

Finger et al. (1996) performed a study in which different percentages of BisGMA were admixed with hydroxyethylmethacrylate (HEMA) (specifically 100:0, 80:20, 60:40, 50:50, and 40:60 BisGMA:HEMA ratios), in which the authors reported that a 100% BisGMA resin developed an oxygen inhibition layer thickness of 4μm which increased significantly to 14μm for the 40:60 mix. These results demonstrate that the oxygen inhibition layer increased with increasing HEMA content, a low viscosity methacrylate monomer, which is also in agreement with the study by Gauthier et al. (2005) showing that the OIL increases with decreasing resin viscosity.

1.6.2.2 Filler load

Gauthier et al. (2005) reported that a filler load greater than 40% caused a decrease in the amount of oxygen inhibition into the RBC material. However, in the same study, filler concentrations of 30% did not significantly reduce inhibition for the same resin material (BisGMA:TEGDMA ratios). This was explained by the authors as resulting from the increased diffusivity of atmospheric oxygen in the interface between the resin and filler particles, which was not offset by the increased viscosity that the increased filler density provides. Consequently, the degree of filler load may also have the potential to affect the degree of oxygen inhibition by affecting the routes of atmospheric oxygen diffusion into the RBC.

1.6.2.3 Temperature

Temperature has also been reported to influence the degree of oxygen inhibition, whereby, an increase in temperature decreases oxygen inhibition. Temperatures above ~110°C have

shown to eliminate oxygen inhibition completely (Andrzejewska, 2001; Gauthier et al., 2005). However a recent study reported an opposite trend, in which high temperatures caused an increase in oxygen inhibition (Studer et al., 2003b). The authors suggested that the increase in temperature caused a decrease in the viscosity of the resin, which consequently resulted in increased diffusion of atmospheric oxygen into the resin matrix thus resulting in increased oxygen inhibition. However, it should be noted that the study was performed with acrylate resin based monomers polymerized with UV light, which although they have similar polymerisation kinetics to methacrylate resins, are much more sensitive to the inhibitory effects of oxygen.

1.6.3 Clinical Significance

Clinically, the presence of an oxygen inhibition layer is of significance, since dental practitioners are required to place large RBC restorations in increments to overcome curing depth limitations, where the surface of each increment will be exposed to atmospheric oxygen. Clinicians are generally advised to place 2 - 4mm thick increments (dependant on RBC material and curing unit light intensity) and commence curing with visible light for 20 - 40s (Boyer et al., 1984; Truffier-Boutry et al., 2003). Therefore, the interfacial RBC-to-RBC bond between the pre-existing RBC and the newly placed RBC increment may be critical in determining sufficient mechanical properties through the bulk of large multi-increment RBC restorations.

Most modern bond strength tests measure either shear, tensile or microtensile strengths and based on these results determine whether an oxygen inhibited surface layer is in fact detrimental or advantageous to bond strengths. There have been several studies regarding this topic and the results are contradictory. Truffier-Boutry et al. (2003) reported a positive effect

of oxygen inhibition on bond strengths, in which an oxygen inhibited surface more than doubled shear bond strengths from 21.6MPa to 44.9MPa whereas a negative effect on bond strengths was reported by Eliades and Caputo (1989). Rueggeberg and Margeson (1990) also reported a negative effect, in which the shear bond strengths of resin cured in atmospheric air was 5.3 ± 2.0MPa, and when cured in an argon atmosphere significantly increased to 8.9 ± 1.5MPa. On the other hand, no significant differences were found by Dall'Oca et al. (2007) where the microtensile bond strengths were 29.4 ± 9.8MPa and 28.5 ± 7.8MPa as measured on specimens with and without an OIL, respectively. No significant differences in shear bond strengths were also found by Kupiec and Barkmeier, (1996), although the highest bond strength value was recorded when bonding to an air inhibited surface using a bonding agent (24.1 ± 3.1MPa) and the lowest value was observed when the composite surface was smoothed to a 600-grit surface thus reflecting the importance of surface roughness in bond values. The results reported by various researchers differ significantly and an explanation must be determined as to why these variations occur. A simple explanation is proposed by Truffier-Boutry et al. (2003) regarding the surface area of the samples, as the oxygen deprived sample is usually cured under a glass cover or a Mylar™ strip thus resulting in a smooth surface almost devoid of any mechanical irregularities while the oxygen inhibited sample has many surface irregularities which increase mechanical retention when the second layer of RBC is applied. Another study suggested that the unpolymerised inhibited surface layer intermingled, and was displaced into the newly applied RBC, forming a hybrid layer with the bulk RBC material, which resulted in an increase in mechanical retention (Rueggeberg and Margeson, 1990). However, the previous study by Dall'Oca et al. (2007) reported no significant differences in bond strengths between atmospheric air or nitrogen polymerised specimens. The specimens were identically prepared resulting in no major differences in surface morphology. Although, curing of the oxygen deprived specimens was

through a glass chamber which may have affected the quality of curing as the light intensity and exposure time would not have been equal between atmospheric air and nitrogen polymerised specimens, even though exposure time for the nitrogen polymerised specimens was also increased from 20s to 40s and further cured outside the glass chamber for a further 20s, the curing procedure lacked sufficient standardization.

Von Beetzen et al. (1996) reported that when curing RBC species in a nitrogen atmosphere, an increase in bond strength in two of the three RBCs tested was observed. P50 (3M, St Paul, Minn., USA) and Heliomolar (Vivadent, FL-9494 Schaan, Liechtenstein) showed increased shear bond strengths whereas Herculite XR (Sybron/Kerr, Romulus, Mich., USA) displayed no difference which highlights the effect of RBC material constituents on the magnitude of O_2 inhibition. The authors postulated that free radicals may have longer half-lives in nitrogen than in atmospheric air which may lead to the formation of more covalent bonds. One shortfall of this study was the substantial differences in temperature (24 ± 4ºC) in the nitrogen chamber compared with atmospheric air during polymerisation, which may have adversely affected the results.

Another report (Eliades and Caputo, 1989) suggested that wiping the oxygen inhibition layer with acetone effectively increased interfacial RBC-to-RBC bond strengths (28.94 ± 7.54MPa). However, the authors also reported no significant differences between specimens cured with an OIL (19.28 ± 4.70MPa), specimens prepared with a polymerised interfacial unfilled resin (18.95 ± 5.14MPa), specimens with an uncured unfilled resin interfacial layer (22.46 ± 4.65MPa) and specimens in which the interfacial surface was ground down (17.61 ± 4.23MPa). These results are taken from tests conducted on a representative RBC (Estilux Posterior, Kulzer & Co GmbH, Hamburg, Germany) (Eliades and Caputo, 1989).

In industry, several techniques have been used to successfully block or decrease oxygen inhibition, ranging from high intensity light irradiation, where specimens are polymerised with a high intensity light source to increase the initiation rate so that it overcomes the effect of oxygen inhibition (Kim et al., 2006; Studer et al., 2003a), to barrier techniques, where oxygen is physically prevented from reacting with the material (Studer et al., 2003a). A further method is the addition of amines or thiols (Allison K. O'Brien, 2006) to the resin to overcome the inhibitory effects of oxygen. Whilst these techniques may be unfeasible for everyday dental use in all clinical situations for practical reasons, many have been incorporated in one form or another into clinical practice in many situations. High intensity light irradiation of dental RBCs has increased in popularity in recent years albeit not because of overcoming the effects of oxygen inhibition, but rather of an increased desire for clinicians to speed up the restorative process. Matrix bands and Mylar® strips have been used to ease placement and contouring of the restoration, but also have the added benefit of blocking atmospheric oxygen from the surface of the restoration. Clinically, The OIL has properties which can either be detrimental (poor stain resistance) or allegedly beneficial (increased bond strength) to the overall longevity of the RBC restoration. However, routine removal of the OIL cannot be advocated in every clinical situation. It would be prudent to remove the OIL where it is present on atmospheric air exposed surfaces of the restoration, but where the OIL is present on a surface that will be subsequently covered with another layer of material then there is no conclusive evidence supporting either removal or retention of the OIL.

1.7 Colour Stability of Methacrylate Resin based Restorative Materials

Tooth coloured (aesthetic) restorations have revolutionised restorative dentistry. For the first time clinicians had the ability to restore tooth aesthetics as well as form and function. Early tooth-coloured restorative materials, such as acrylic resin and silicate although exhibited satisfactory aesthetics when first placed, rapid bulk discoloration of the restorative often occurred (Rueggeberg, 2002). Various other clinical shortcomings, such as high levels of volumetric shrinkage during polymerization, poor adherence to tooth structure, and large differences between the thermal coefficient of the material and the tooth structure often resulted in a high incidence of secondary caries and marginal staining of the material, giving rise to many replacements and repairs. Modern RBCs can reproduce tooth colour accurately, replicating various hues, tints, translucencies and opacities giving a natural appearance, as evidenced by the proliferation of numerous shades of commercial RBCs. It is undeniable that dental aesthetics has now become a major concern for patients. A recent study reported that 17.9-21.3% of UK patients were dissatisfied with the colour of their teeth (Alkhatib et al., 2005).

The ability of RBCs to resist discolouration in the oral environment is of the utmost importance, as a key advantage of these materials is the aesthetic resemblance to tooth structure.

1.7.1 Factors affecting colour change in RBCs

Many factors have been purported to affect colour changes in RBCs among these are:

1.7.1.1 Incomplete polymerisation

It is desirable for a dental RBC restorative to achieve complete polymerisation of its monomer components to achieve maximum physical properties. However it is presently acknowledged that methacrylate based RBCs only reach approximately 50 - 70% conversion of carbon-carbon double bonds (degree of polymerisation) (Asmussen, 1982; Ferracane and Greener, 1984). Decreased or incomplete polymerisation of methacrylate-based RBCs has been proposed to cause an increased susceptibility to discolouration. De Gee et al. (1984) performed a study in which he demonstrated the specific selectively of Astra blue dye to poorly polymerised methacrylate RBCs, especially on the deeper portions of the material, and around voids and pores in the material, indicating the effects of depth of cure and oxygen inhibition, respectively. A previous study by Ferracane et al. (1992), in which the authors used a silver nitrate staining agent also postulated that differences in the degree of cure between different RBC materials may cause differences in stain diffusion. The authors suggested that a higher degree of cure may result in RBCs that were more resistant to the diffusion of the staining material through the resin matrix.

1.7.1.2. The oxygen inhibition layer

When a dental RBC material is cured against a matrix (Mylar™) strip or a glass cover, a resin rich layer forms on the upper surface of the RBC. The resin rich layer forms during placement of the matrix strip which flattens the surface of the RBC and therefore forces the filler particles further from the surface. This has been suggested to result in decreased filler

loading in the uppermost layer of the RBC (Hachiya et al., 1984) which is more susceptible to discolouration (Patel et al., 2004). This increased staining susceptibility in the resin-rich layer can be tentatively explained by a decreased level of polymerization resulting from trapped oxygen between the surface of the RBC and the matrix strip thus resulting in increased discolouration (Patel et al., 2004). This increase can also be explained by the hypothesis that the resin component is the key factor affecting staining susceptibility (Patel et al., 2004; Reis et al., 2003), thus the resin rich layer although resulting in a very smooth, uniform surface will be more susceptible to staining.

Although there have been few studies that specifically examine the effect of the oxygen inhibition layer on RBC discolouration, it is generally recognized that incompletely polymerised RBCs and residual monomers are most susceptible to staining (Patel et al., 2004; Reis et al., 2003). Consequently the formation of an OIL, which is comprised of unpolymerized or poorly polymerized resin monomers, may also be highly susceptible to staining. A previous study by Park et al. (2004) compared the staining susceptibility of three microhybrid RBCs that were cured in either a nitrogen environment or in normal atmospheric air. During curing all specimens were covered by a celluloid strip therefore minimizing OIL formation. Although the OIL was minimized, compared with RBC specimens cured with no celluloid strip in atmospheric air, the entrapment of oxygen between the surface of the RBC and the celluloid strip was unavoidable. The authors attributed the increased discolouration of RBCs due to the decreased conversion of the resin in the uppermost layers of the RBC (Park et al., 2004).

1.7.1.3 Surface roughness and wear

Increased surface roughness of the RBC has been proposed to increase the staining potential due to the presence of surface defects which may result in greater stain incorporation (Ferracane et al., 1992). Conversely various studies have shown although surface roughness is a factor, resin chemistry and filler particles play much more important roles (Reis et al., 2003). Increased surface roughness of RBC restoratives in service may also result in increased susceptibility to bacterial adhesion and plaque deposition (Carlen et al., 2001; Kawai et al., 2000) subsequently resulting in an increased bacterial acid production which may cause softening of the resin matrix of the RBC facilitating colourant diffusion and increased staining (Asmussen and Hansen, 1986).

Surface wear may also affect stain uptake of RBCs. A previous study reported a significant decrease in staining of an RBC (Estelite Σ, Tokuyama Dental Corp, Tsukuba, Japan) following wear testing (Lee et al., 2007). The decreased colour change of the worn surfaces compared to the unworn surfaces was thought to be due to the removal of the weak, surface resin rich layer.

Thermocycling may facilitate the diffusion of the colourant into the RBCs resin matrix thus increasing RBC discolouration. Furthermore, thermal shocks may induce internal stresses resulting in the formation of microcracks and defects in the RBC surface which may also decrease stain resistance (Dietschi et al., 1994).

1.7.1.4 Surface defects

Microcracks and subsurface defects may be incorporated onto the restorative as a result of various dental RBC restorative finishing procedures. These defects may cause the increased

incorporation of stains and dyes onto the restorative surface. A study by Mair, (1991) demonstrated by using a silver nitrate based staining reagent that there was an increased deposition of subsurface stain in areas that have been subjected to attrition and surface defects. However, Ferracane et al. (1992) performed a related study, in which the effects of surface defects were found not to significantly result in the increased diffusion of silver nitrate into the RBC. These differing results may be attributed to the inherent differences in the materials tested, such as the degree of conversion and filler particle size.

1.7.1.5 Resin and filler chemistry

The chemical properties of the constituents used in dental RBC materials may also be a major factor in the colour stability of these materials. In general, it is recognized that methacrylate monomers such as BisGMA and TEGDMA are hydrophilic by virtue of their ether chemical groups, whereas BisEMA and UDMA are less hydrophilic due to their ethoxy and urethane groups respectively. The relative hydrophilicity of the RBCs monomer system may be a vital factor in the colour stability of the RBC material, directly affecting the water sorption properties of the RBC material. A previous study, (Iazzetti, 2001) concluded that the hydrophobic materials showed greater colour stability and stain resistance than their hydrophilic counterparts, and in a study performed by Douglas and Craig, (1982), a similar conclusion was presented after various RBC materials were stained by Methylene blue. In addition to resin hydrophilicity and water sorption potential, filler particle chemistry has also been proposed to affect the staining susceptibility of RBCs. Iazzetti et al. (2000) and Reis et al. (2003) proposed that porosity of glass filler particles may cause patterns of discolouration that cannot be explained sufficiently by resin constituents. Ferracane et al. (1992) also proposed that the density and distribution of filler particles near the surface of the RBC may

influence the volume of the resin at the surface and thus affect the diffusion of the stain into the RBC material.

1.7.1.6 Oral hygiene, diet and smoking habits

The effect of diet on the staining of resin based composite restoratives is well documented in the literature. Food with an increased tannic acid content such as red wine, tea and coffee have been implicated in the discolouration of RBCs in the oral cavity (Satou et al., 1989; Um and Ruyter, 1991). Another study has implicated the nicotine content in cigarettes as a likely cause of RBC discolouration (Raptis et al., 1982). Poor oral hygiene also plays a role in the stain susceptibility of RBCs, as a result of bacterial byproducts and organic acids which soften the resin matrix allowing the diffusion of staining compounds into the restoration, this was demonstrated by the storage of methacrylate-based materials in either water or propionic acid, where the colour changes (ΔE) were up to 50 units, compared with 10 units for materials stored in water (Asmussen and Hansen, 1986).

1.7.4 Measurement of colour change of RBCs

The human perception of colour is not static; it varies with differences in illuminant, background colour, positioning of object relative to illuminant and observer, translucency of material, and eye fatigue (Dagg et al., 2004; Joiner, 2004; van der Burgt et al., 1990). The matching of dental restorative materials to teeth is further complicated by moisture, skin tone, cosmetics and the surface characteristics (gloss, matt, roughness) of the restoration and the tooth (Johnston and Kao, 1989). The ability of RBCs to match natural tooth colour may be its greatest advantage over non-aesthetic metallic restorations, therefore a standardized method

of quantifying and measuring changes in colour is important to determine if a restoration is clinically acceptable from an aesthetic point of view.

The main methods of colour measurement in dentistry are either by visual observation or instrumental assessment (Cho et al., 2007; Johnston and Kao, 1989; Seghi et al., 1989).

1.7.4.1 Visual Observation

Colour assessment and determination is accomplished by comparison of a patients tooth with a colour standard (tooth shade guide) and is the most common method used in clinical dentistry (Van Der Burgt et al., 1990). It is generally regarded as a subjective assessment and unreliable since the perception of colour varies from person to person (Ragain Jr and Johnston, 2000). The same person may even visualize the same colour differently at different times (Culpepper, 1970; Okubo et al., 1998). The colour of the tooth is matched with the restorative material by comparing the colours visually with a commercial tooth shade guide constructed by either the manufacturer of the RBC material, or more commonly by Vident with their VITA® Classical Shade Guide (which have been in use for over fifty years). The shade match may be repeated under different lighting conditions (daylight, incandescent or fluorescent), to try to decrease the effects of metamerism[1], as a result, the matching procedure is time consuming and difficult. However, the primary limitation for visual matching with tooth shade guides is that they do not fully represent the whole range of teeth colour; therefore, the volume of colour space is not fully covered, with duplication of certain shades and omissions of others, together with a lack of organization and logical distribution between tooth shade tabs (Sproull, 2001). A further disadvantage of visual matching is that the tooth shade guide rarely matches the RBC used for the restoration (Yap et al., 1997). In

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[1]Metamerism can be defined as the change in colour matching between two material specimens when viewed under a different light source, resulting from the differences in the spectral output of the individual light sources.

addition, many shade guides are constructed from porcelain. The differences in colour parameters and properties that exist between RBCs and porcelain (Kim et al., 2006) may result in a colour mismatch clinically. Additionally many of the porcelain shade guide teeth are cervically stained and/or have an incisal edge translucency in an effort to make them more life-like, but further complicate the matching process. Some clinicians have been known to remove the stained areas and use only the body of the tooth for shade matching, whereas other clinicians cure a small piece of the RBC and use it for shade matching (Yap et al., 1999). However, despite of all the inherent disadvantages with visual assessment, it is still the most common method of determining tooth colour and shade matching, due to its low cost, where dental instrumental colour measurement devices may be prohibitively expensive (Brewer et al., 2004). Furthermore, with training and experience, a clinician can become very proficient (Joiner, 2006).

1.7.4.2 Instrumental Assessment

Colour, opacity and translucency are usually measured by either a colorimeter or a spectrophotometer. Light is irradiated onto the test which is transmitted, reflected, refracted, diffused or absorbed by the test material (Van Der Burgt et al., 1990). The light reflected from the material under examination is measured by the colorimeter. The resultant reflectance pattern (fingerprint) is different for each colour, and can therefore be quantified numerically. Instrumental assessment of colour is more accurate, consistent and reliable than visual assessment but it is also subject to errors, mainly resulting from the translucent nature of tooth structure and the occurrence of edge loss, in which the tooth structure may be affected by the background colour (Bolt et al., 1994; Brewer et al., 2004; Seghi, 1990). A further shortcoming of instrumental assessment of colour is poor inter-instrumental agreement. However, intra-instrumental reliability is high (Douglas, 1997). Different

illuminants are used in dental material colour measurement, the most common are standard illuminant D65 which corresponds to average daylight illumination conditions and standard illuminant A which represents typical, domestic, tungsten-filament (incandescent) lighting. Spectrophotometers were generally considered more accurate in colour measurement than colorimeters (Seghi, 1990). However, due to improved accuracy of modern colorimeters, difference in reliability compared with spectrophotometers are negligible and are more than sufficient to meet the requirements for the measurement of dental restorative materials (Seghi, 1990).

When using a colorimeter/spectrophotometer to assess colour changes, a light source, corresponding to a standard illuminant, is irradiated onto the test material with a specific orientation. In dental material colour measurement, the orientation of the light is usually at a 45º angle to the specimen surface, or irradiated in a diffuse manner, to provide uniform surface illumination. The reflected light is then captured and analyzed by sensors in the mechanism of the instrument, orientated at either 0º or 45º to the test surface. The spectrum of reflected light indicates the test material colour. Different illuminating/viewing orientations may be used for the assessment of colour change of dental restorative materials. The Commission Internationale de l'Eclairage (CIE) recommended four illuminating/viewing configurations to be used for materials with diffuse reflecting surfaces, such as dental RBC materials (Seghi, 1990) (Figure 1.7)
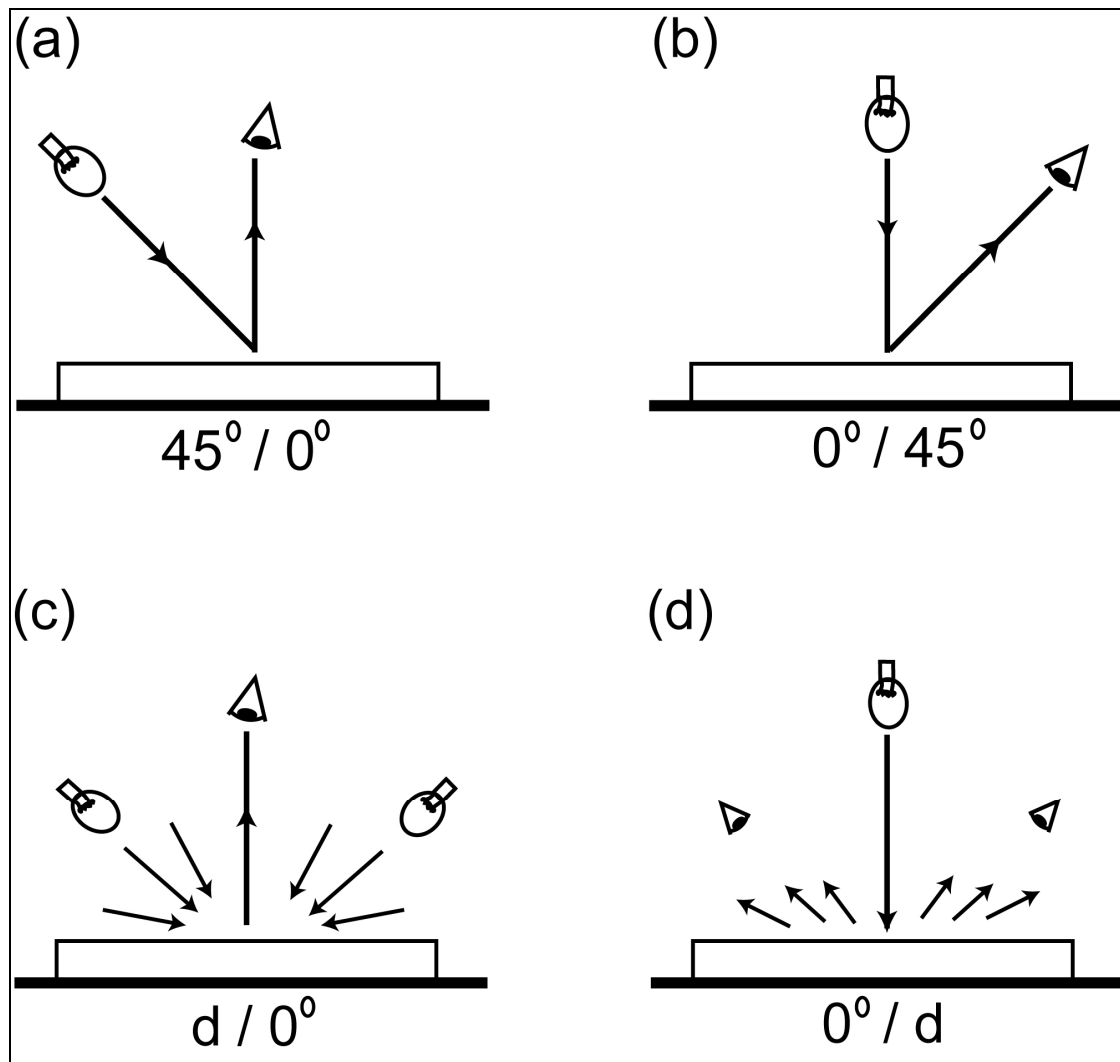
Figure 1.7 A diagram illustrating the four CIE recommended illuminating/viewing configurations to be used for materials with diffuse reflecting surfaces. (Illustration adapted from Seghi, 1990)

In 1931, the CIE introduced standards by which the human perception of colour could be quantified numerically. The most frequently used to assess the colour and opacity of materials (RBCs, Ceramics, and natural tooth structure) in dental materials is the CIE L*a*b* (CIELAB) measuring system (Guler et al., 2005b; Lee and Powers, 2005; Stober et al., 2001) in which three variables are measured.

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}$$

<div align="right">Equation 1.1</div>

where ΔE is the measure of difference in colour prior to and following the testing regime, L* refers to white (L=100) or black (L=0), the a* measures the green (-ve), red (+ve) spectrum, on the other hand b* signifies the difference between blue (+ve) and yellow (-ve) according to CIE (1976)

Many different opinions exist on the acceptability of differences in colour in RBC materials (Guler et al., 2005b; Johnston and Kao, 1989; Lee and Powers, 2005). A colour difference of 1 unit (ΔE=1) using the CIELAB scale was found to be visually perceptible to 50% of observers (Johnston & Kao, 1989). However, the clinical acceptability of such a colour change is significantly higher. Lee & Powers (2005) suggested that a ΔE of 3.3 is the upper limit of clinical acceptability, while Johnston & Kao (1989) proposed an even higher value of 3.7 units. It is interesting to note that the acceptable differences in colour for car varnishes according to the DIN 6175 standard in Germany is only 0.3-0.9 units (Ruyter et al., 1987). Ruyter et al. (1987) also suggested that a colour difference of 3.3 units between tooth and restoration was not clinically acceptable.

Although RBC colour matching is much more complicated than simple matching of numerical values as many factors can affect the appearance of the material, a standardized method of quantifying colour and measuring colour change is important to determine if a restoration is clinically acceptable from an aesthetic point of view.

1.8 Aims of the Present Investigation

Methacrylate based resins are the predominant resins in use in modern dental RBC restoratives. However, many different resin systems are being developed and tested often from technologies 'borrowed' from other industries. Research has been mostly directed towards improving the resin systems, as the shortcomings of methacrylate monomers are evident. In addition to polymerisation shrinkage and the resulting stress, another primary disadvantage of methacrylate based RBCs is the formation of an oxygen inhibition layer, and its subsequent discolouration, which is especially relevant in anterior high-visibility areas of the oral cavity. Aesthetic requirements are the primary reason RBCs continue to be used clinically and worsening aesthetics are also one of the most important causes of RBC failure and subsequent replacement.

The oxygen inhibition layer is inevitable at the surface of methacrylate-based resins cured in atmospheric air. It remains unclear whether the OIL serves a beneficial purpose in interfacial RBC bond strengths, as past studies have been contradictory and inconclusive. Therefore, further elucidation of the effect of this inhibition on bond strengths is required.

Thus the present study aims to:

1. Assess the effect of resin chemistry on the oxygen inhibition layer thicknesses of experimental and commercial resins and resin composite systems which contain conventional methacrylate and silorane-based chemistries.

2. Investigate whether an oxygen inhibition layer plays a significant role in improving the bond strength between increments of resin composite layers.

3. Quantify the effect of different oxygen inhibition layer thicknesses on the stain susceptibility of methacrylate and silorane-based resins.

2.0 EXPERIMENTAL PROCEDURES

2.1. Materials

2.1.1 Experimental resin monomers and filled composites

Resin monomer formulations of 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl]propane (bisphenol A glycol dimethacrylate; BisGMA) (Figure 1.3a) and triethyleneglycol dimethacrylate (TEGDMA) (Figure 1.3b) at ratios of 85/15, 70/30, 41/59, 10/90 by mass were supplied by Ivoclar Vivadent (Schaan, Liechtenstein), resulting in four monomer blends with decreasing viscosity (Table 2.1). Silane coated barium or strontium glass fillers (Ivoclar Vivadent, Schaan, Liechtenstein) with an average particle size of 1µm were loaded into the monomer formulations (70% by wt), resulting in eight experimental RBCs (Table 2.2). The photoinitiator system consisted of Camphoroquinone (CQ) (0.3wt%) (Figure 1.1) and dimethylamino-ethylmethacrylate (DMAEMA) (0.6% by wt) (Figure 1.2).

CODE	Ratio by mass
M1	85/15 BisGMA/TEGDMA
M2	70/30 BisGMA/TEGDMA
M3	41/59 BisGMA/TEGDMA
M4	10/90 BisGMA/TEGDMA

Table 2.1: Experimental resin blends with increasing TEGDMA concentrations (M1<M2<M3<M4), subsequently utilized as the resin base for experimental barium and strontium-glass filled RBCs.

CODE	Monomer by mass%	Filler particle type
BaC1	85/15 BisGMA/TEGDMA	1 µm barium glass
BaC2	70/30 BisGMA/TEGDMA	1 µm barium glass
BaC3	41/59 BisGMA/TEGDMA	1 µm barium glass
BaC4	10/90 BisGMA/TEGDMA	1 µm barium glass
SrC1	85/15 BisGMA/TEGDMA	1 µm strontium glass
SrC2	70/30 BisGMA/TEGDMA	1 µm strontium glass
SrC3	41/59 BisGMA/TEGDMA	1 µm strontium glass
SrC4	10/90 BisGMA/TEGDMA	1 µm strontium glass

Table 2.2: Experimental RBCs, loaded with 70% mass, with either barium (BaC1-BaC4) and strontium-glass (SrC1-SrC4) filled RBCs, and with an increasing TEGDMA concentration C1<C2<C3<C4.

2.1.2 Commercial resin based composites

Two commercially available methacrylate based RBCs (Filtek™ Z250 and Z100, 3M ESPE, Seefeld, Germany) and one silorane based RBC (Filtek™ Silorane, 3M ESPE) were tested in the current investigation (Table 2.3). Filtek™ Z250 and Z100 both contain silane coated zirconia/silica (ZrO_2-SiO_2) fillers with a particle size ranging from 3.5 to 0.01µm with an average size of 0.6µm. Filler loading was 60% and 66% by volume for Filtek™ Z250 and Z100 respectively. The resin matrix of Z100 consisted of BisGMA and TEGDMA. However in Filtek™ Z250, the majority of TEGDMA was replaced by 2,2-bis[4-(2methacrylyloxyethoxy)phenyl] propane (bisphenol A hexaethoxylated dimethacrylate; BisEMA) (Figure 1.3d) and 1,6-bis(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane (urethane dimeth-acrylate; UDMA) (Figure 1.3c). CQ and a co-initiator DMAEMA were added to enable light initiation and polymerisation of Z100 whereas in Filtek™ Z250 an iodonuim salt was added in addition to CQ and DMAEMA. The third RBC was based on a epoxy resin based Silorane (3,4-epoxycyclohexylcyclopolymethylsiloxane) (Figure 1.6) monomer system loaded with silane treated yttrium fluoride and quartz particles

with a particle size ranging from 0.1-2µm with an average size of 0.47µm. The photoinitiator

system consisted of an iodonuim salt, CQ and a co-initiator (ethyl 4-dimethylaminobenzoate)

(Filtek™ Silorane Low Shrink Posterior Restorative Technical Data Sheet, 3M ESPE,

Seefeld, Germany).

CODE	Material	Resin Constituents	Filler type and volume	Filler size(µm)	Lot number	Shade
Z2	Filtek™ Z250	BisGMA,TEGDMA, BisEMA, UDMA	Silica/Zirconia,60%	0.01-3.5	20070531	A3
Z1	Z100	BisGMA,TEGDMA	Silica/Zirconia,66%	0.01-3.5	20070312	A3
SI	Filtek™ Silorane	Silorane	Quartz/Yttrium fluoride 55%	0.1-2	20071018	A3

Table 2.3: Lot numbers, shade, resin and filler constituents of both dimethacrylate-based commercial RBCs, Filtek™ Z250 and Z100, and epoxy-based Filtek™ Silorane, (BisGMA: bisphenol-A glycol dimethacrylate; **TEGDMA:** triethylene glycol dimethacrylate; **BisEMA:** bisphenol-A hexaethoxylated dimethacrylate; **UDMA:** urethane dimethacrylate; **Silorane:** 3,4-epoxycyclohexylcyclopolymethylsiloxane.**)**

2.2 Oxygen inhibition thickness measurement procedure

2.2.1 Specimen preparation

The specimens prepared for oxygen inhibition layer (OIL) thickness measurements were nominally identical. Each model resin, resin composite and commercial RBC were prepared in a 4mm diameter and 3mm thick (n=5) black nylotron cylindrical mould. The RBC specimens were cured in either air or a nitrogen atmosphere 1mm from the upper surface using a light emitting diode (LED) curing unit (Bluephase, Ivoclar Vivadent, Schaan, Liechtenstein) for 30s. The average irradiance throughout the study was measured as 1200 ± 4.6mW/cm^2 and was verified with a handheld radiometer (Coltolux light meter, Coltene/Whaledent, NJ, USA). For high viscosity RBCs, each material was packed into the mould (which was positioned on a glass slide placed on a white PTFE base) using a dental condenser. The upper surface was smoothed flat using a PTFE roller (CompoRoller, KerrHawe, Bioggio, Switzerland) to ensure nominally identical surface morphology for all specimens. The LED curing light was concentrically positioned over each specimen using a cylindrical alignment jig to ensure uniform irradiation. For the monomer resin specimens, smoothing of the surface with the CompoRoller was not necessary as the natural flow of the resins resulted in a smooth surface; otherwise the curing procedure was identical. Avoidance of bubble incorporation into the upper surface of the specimens was avoided by careful mixing of the model composites and manually eliminating any bubbles which formed near the surface of the specimen.

For the specimens cured in a nitrogen atmosphere, the RBCs, Nylotron mould, filling instruments, and curing light were all placed in a glove box (Erlab, North Andover, MA, US) (Figure 2.1) that was directly attached to a compressed nitrogen cylinder. The bag was

completely deflated prior to filling with nitrogen to minimize the amount of atmospheric air present. A 4 mm diameter connector hose from the gas inlet was positioned 10 mm above the specimen to allow for a free flow of nitrogen over the specimen surface throughout light irradiation. The glove bag was then inflated and subsequently purged with nitrogen at least three times to eliminate oxygen within the chamber; the elimination of oxygen was further confirmed with an oxygen meter which recorded an oxygen concentration to be approximately 3%. The number of specimens and the curing procedure was identical to the specimens cured in atmospheric air.
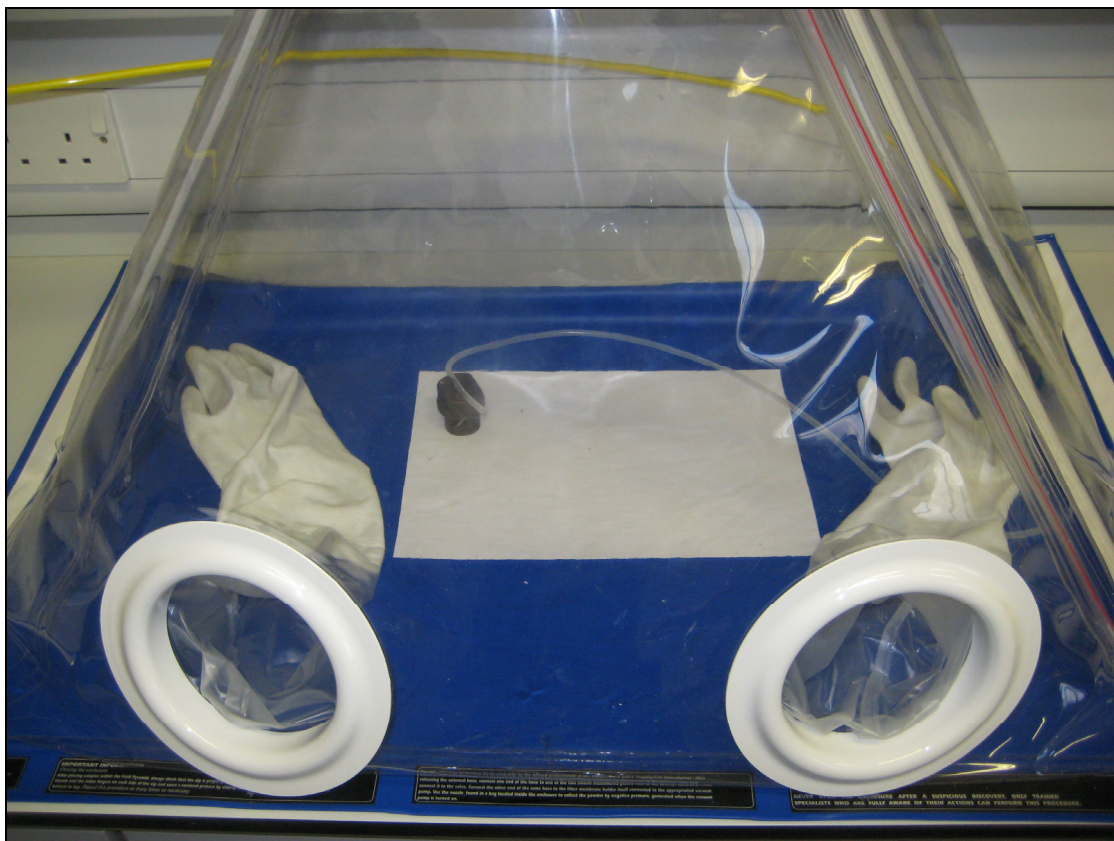
Figure 2.1: Photograph illustrating the apparatus used to ensure an air-tight inert atmosphere for the nitrogen cured specimens

Each specimen was stored dry for 24h in a lightproof container at 37ºC to standardise the degree of cure. The specimens were then placed in a 0.2% Fuschin solution[*] for 1h. This staining procedure allowed the inhibited layer to be visualized, as the fuschin diffuses through the unpolymerized layer as determined by a pilot study in which fuschin did not cause staining of RBCs cured under a Mylar strip or cured in a nitrogen environment. Following staining, the specimens were gently rinsed in distilled water and allowed to dry.

2.2.2 Microscopic depth of focus technique

In an attempt to assess the effects of the oxygen inhibition layer (OIL) thickness on various physical and mechanical properties of RBCs, the OIL thickness was measured for all experimental resins, resin composites and commercial RBCs.

The OIL thickness for each material was determined using a modified depth of focus technique adapted from Finger et al. (1996). The OIL thickness measurements were recorded using a 40X microscope to focus on the surface of the RBC at five predetermined X and Y coordinates spaced 0.5mm apart and at least 1mm from the outer edges of the specimen. The Z axis was attached to a brushless motorized vertical translating stage accurate to 20nm (Bipolar Stepper Mike™, Oriel Instruments, Stratford, CT, US) which was programmed to travel in 240nm increments using a motor controller (DMC-18x2, Galil Motion Control, California, USA) (Figure 2.2). Immediately following recording the baseline focal distance to the surface of the specimen, the stained layer was gently brushed away using a toothbrush soaked in 70% ethanol. The brushing continued until removal of the stained layer was

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[*] Astra Blue (AB) in Methanol 0.2% also resulted in demarcation of the OIL in methacrylate based RBCs but was less successful in identifying the OIL in low viscosity resins (all resins). Of interest, the first batch of Silorane received from 3M ESPE was resistant to staining with AB (used in pilot study) but the subsequent batch (commercially available restorative) readily stained with AB.

accomplished and visually verified, this took approximately 20s. The motorized stage was then repositioned towards the microscope lens in 240nm increments until the specimen surface was refocused at the same X-Y coordinates. The focal distance was recalculated to obtain the oxygen inhibition layer thickness accurate to 0.24μm.
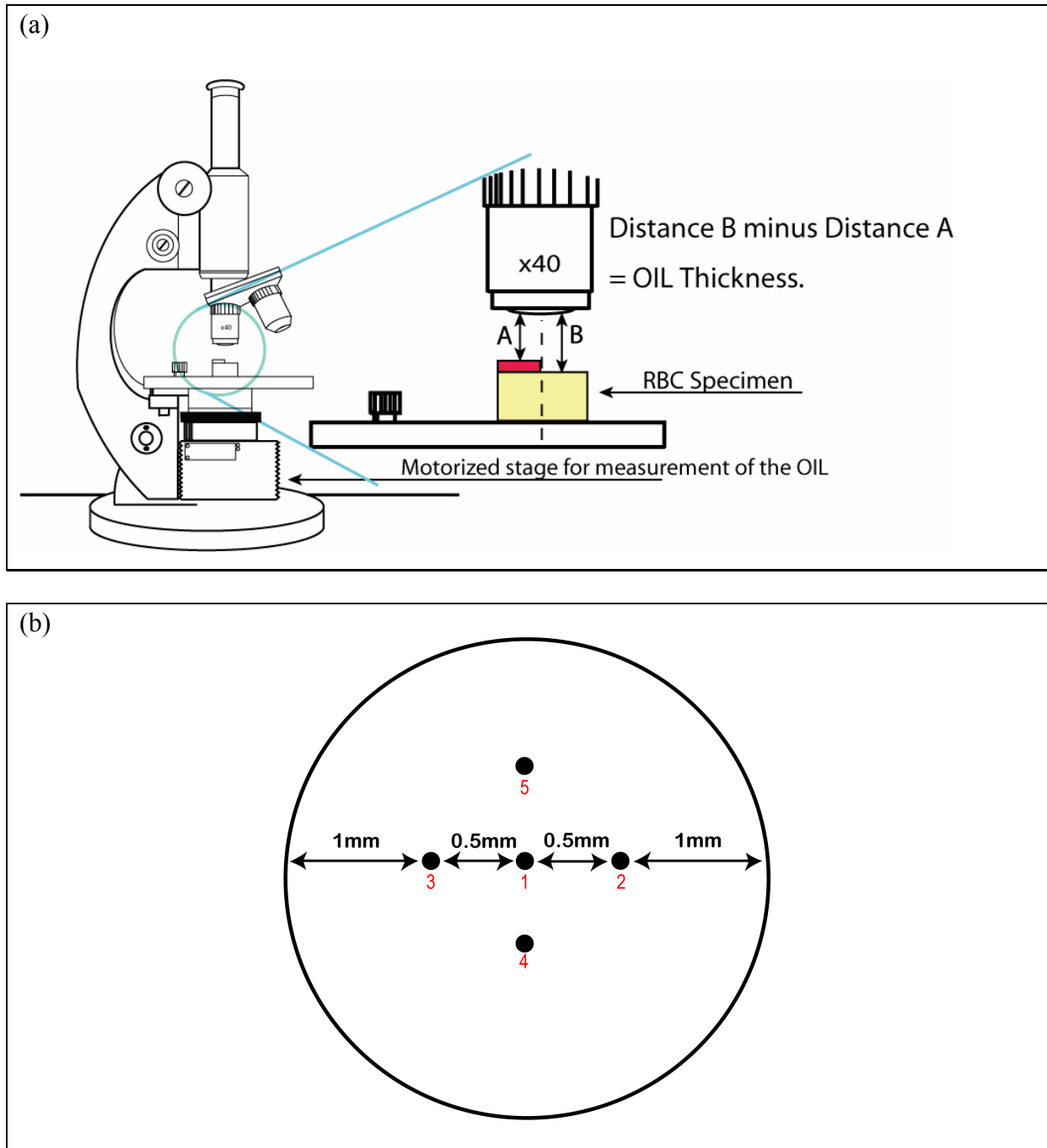
Figure 2.2: (a) A schematic diagram illustrating the method employed for oxygen inhibition thickness measurements, and (b) a diagram representing the surface of the specimen illustrating the sequence of OIL measurements (red) and the distances between measurement points and the outer edge of the specimen.

2.3 Interfacial shear bond strength determination

2.3.1 Specimen preparation.

In an attempt to evaluate the relationship between the OIL thickness and RBC to RBC bond strengths, five disc-shaped specimens of Z100, Filtek™ Z250, Filtek™ Silorane and model resin composites containing barium-glass filler particles (BaC1-BaC4) were fabricated either in air or a nitrogen atmosphere.

The specimens were fabricated in a two stage procedure. Firstly, 8mm diameter, 1.5mm thick disc specimens were fabricated using a white polyester plastic mould. Specimen preparation and curing regime was identical to the previous specimens made for OIL thickness determination and colour stability (sections 2.2.1 and 2.3.1). The disc shaped specimens (n=5) were either immediately bonded with the subsequent RBC increment or stored 'wet' for 7 or 30d in a lightproof container at 37 ± 1ºC. Following the various storage regimes, the cured surface of the disc was placed within a plastic alignment mould containing a hollow cylinder (4mm diameter, 3mm thick) where cylindrical stubs of RBCs of the same material type were applied directly to the uppermost surface of the disc specimen. Each 3mm diameter, 4mm long RBC cylindrical stub was condensed directly onto the surface of the disc shaped specimen. RBC material was packed directly into the hollow cylinder onto the surface of the first specimen with a small sized dental condenser. The stub was identically cured, resulting in mushroom-shaped test specimens (Figure 2.3). All specimens were stored dry for 24h before bond strength testing to standardize the degree of cure. Any specimens identified with significant flash or an excess of material in the bonding region were immediately discarded.

2.3.2 Shear bond strength testing.

Following each storage regime, the specimens were firmly attached with cyanoacrylate glue to dental stone contained within stainless steel specimen holders. The specimens were then placed in a Bencor Multi-T shear assembly (Danville Engineering Inc., San Ramon, CA) with a chisel shaped shearing rod centrally positioned on the specimen, parallel to the interface between the specimens (Figure 2.4). The specimens were then tightened securely and fixed to an Instron 5540 universal testing machine (Instron 5540, High Wycombe, Bucks UK). Load at failure was determined at a crosshead speed of 0.75mm/min to determine the shear bond strengths of the specimens. Load at failure (N) were then divided by the specimen cross-sectional surface area as measured with a micrometer (Moore and Wright, Sheffield, England) and the cross-sectional area calculated (mm^2) to give the results as MPa (Equation 2.2).

$$Mpa = \frac{N}{mm^2}$$ Equation 2.2

where N is the load at failure in Newtons, mm^2 is the specimen cross-sectional surface area and MPa is the load at shear failure in Megapascals. After testing, the mode of failure was visually identified and recorded as either cohesive, adhesive or a mixed pattern of failure.
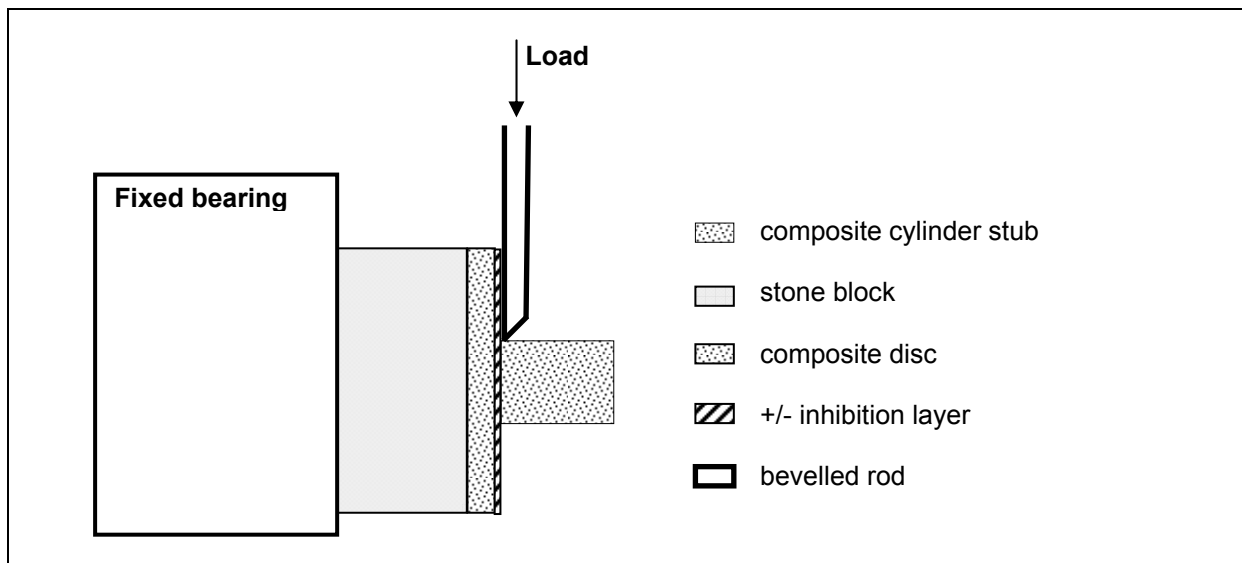
Figure 2.3: A schematic drawing of the shear bond strength test apparatus. The chisel-shaped shearing rod is placed as close as possible to the bonding interface.
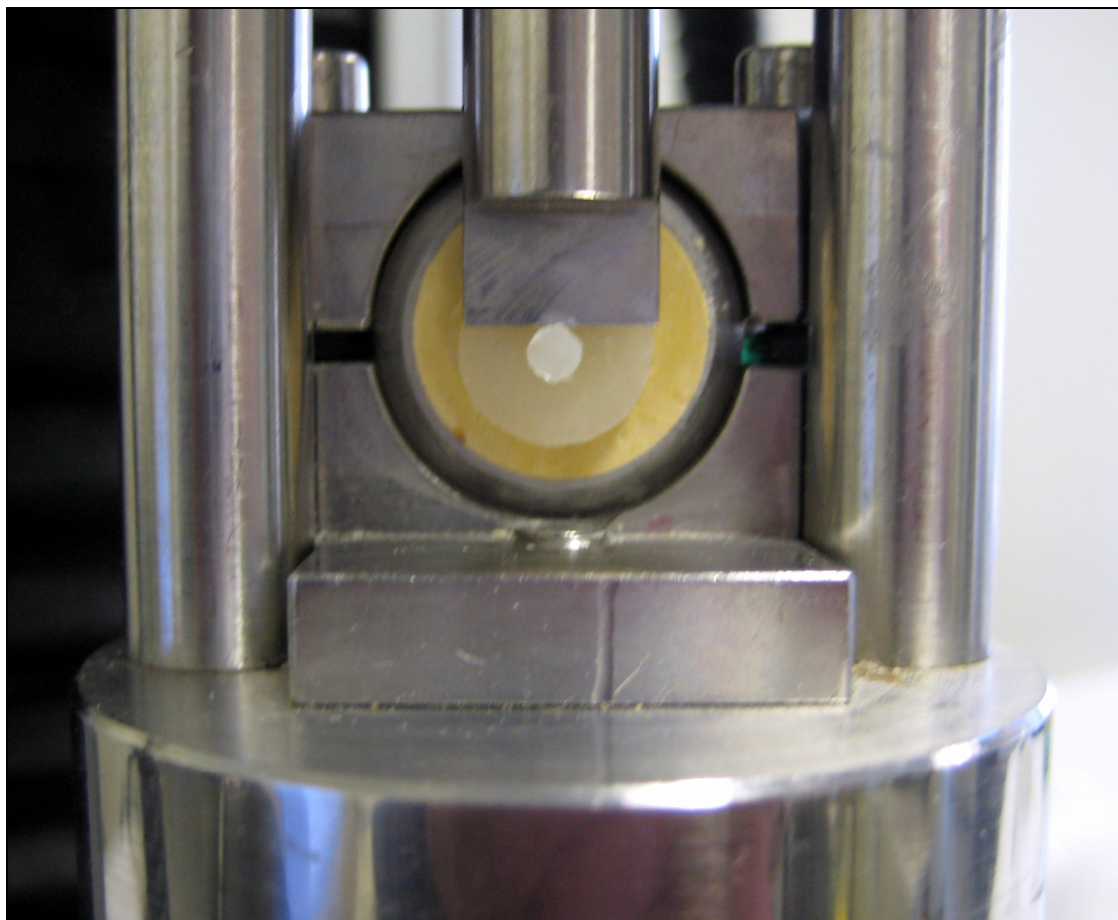
Figure 2.4: Photograph of a specimen placed in the Bencor Multi-T shear assembly.

2.4 Staining susceptibility measurements

2.4.1 Specimen preparation

In an attempt to evaluate the relationship between OIL thickness and staining susceptibility of model resins, resin composites and commercial RBCs, each material was cured in either air (Group 1) or a nitrogen atmosphere (Group 2). A white Delrin cylindrical mould, 8mm inner diameter, 2mm thick and with a 24mm outer diameter was used to produce disc shaped specimens. Each RBC was packed into the mould using a dental condenser; the top surface was smoothed using the PTFE roller. The LED curing light was concentrically positioned over the specimen using a cylindrical alignment jig to assure uniform irradiation. For the monomer resin specimens, smoothing of the surface with the PTFE roller was not necessary; otherwise the curing procedure was identical.

For the specimens cured in nitrogen, the resin-based materials, Delrin mould, filling instruments, and curing light were all placed in the glove bag that was directly attached to a compressed nitrogen cylinder. The bag was completely deflated prior to filling with nitrogen. The bag was then inflated and subsequently purged with nitrogen at least three times to ensure the elimination of oxygen. The curing regime was identical across all specimens and identical to the specimens made for OIL thickness determination

Immediately following curing, ten specimens for each experimental material were stored in distilled water at a temperature of 37 ± 1ºC for 24h.

2.4.2 Stain measurement experimental procedure

Following each storage regime the baseline surface colour of each specimen was measured using a colorimeter (CR-321, Minolta Co., Ltd., Osaka, Japan) with an aperture size of 3mm. Illuminating and viewing angles were according to Commission internationale de l'éclairage (CIE) 45º/0º, respectively. The CIE $L^*a^*b^*$ colour space was measured relative to a CIE Standard Illuminant D65 (D65 corresponds to average midday light in the northern hemisphere). The measurements were repeated three times for each specimen and the mean value calculated. A white background was used for all colour measurements.

Immediately after baseline measurements, specimens of each RBC were placed in air tight containers filled with 50ml of 0.5% methylene blue (BDH Ltd., Poole, UK). A further subgroup acted as a control where the specimens were stored 'dry' for the duration of the experiment.

The containers were sealed and submerged in a water bath at 37 ± 1ºC for 7d. Following staining, samples were rinsed thoroughly with distilled water and blotted dry with tissue paper. The difference between the baseline colour and the colour at the end of each staining regime was measured with the colorimeter and calculated by Equation 2.3

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \qquad \text{Equation 2.3}$$

where ΔE signifies the difference in colour between specimens, the L^* corresponds to white (L=100) or black (L=0), the a^* measures the green (-ve) red (+ve) spectrum, and b^* signifies the difference between blue (+ve) and yellow (-ve) values (the subscript 1 refers to the colour of the specimen prestaining and 2 refers to the colour after the staining regime).

3.0 RESULTS

3.1 Oxygen inhibition layer thickness determination

3.1.1 Experimental resins and filled resin composites

For specimens cured in air, the mean oxygen inhibition layer thicknesses (OIL) for the dimethacrylate resin monomer formulations (M1-M4) were $12.8 \pm 4.5\mu m$, $19.2 \pm 6.5\mu m$, $24.4 \pm 4.2\mu m$ and $34 \pm 8.4\mu m$ for BisGMA/TEGDMA monomer blends of 85:15, 70:30, 41:59, and 10:90 mass percent, respectively (Figure 3.1, Table 3.1). The data for OIL thickness measurements did not follow a normal distribution; therefore non-parametric statistical methods were performed. A Kruskal-Wallis and Mann-Whitney tests revealed significant increases in OIL thickness for increasing TEGDMA content of each unfilled resin mixture where OIL thickness of M1<M2<M3<M4 ($P<0.001$). When barium-glass fillers were loaded into the resin blends, the OIL was measured as $20.4 \pm 6.3\mu m$, $27.2 \pm 3.8\mu m$, $26.4 \pm 3.8\mu m$, and $33.2 \pm 3.1\mu m$, respectively (Figure 3.1, Table 3.1), in order of increasing TEGDMA concentration (BaC1-BaC4). Kruskal-Wallis and Mann-Whitney tests revealed a significantly reduced OIL thickness for BaC1 compared with each other barium-glass filled composite ($P<0.005$). The OIL thickness of BaC2 and BaC3 were statistically similar ($P=0.5274$) and BaC3 less than that of BaC4 ($P=0.0001$). For strontium-glass filled materials, the OIL was measured to be $26.4 \pm 3\mu m$, $22 \pm 8.4\mu m$, $38 \pm 5.9\mu m$, and $47.6 \pm 7\mu m$, respectively (Figure 3.1, Table 3.1) in order of increasing TEGDMA concentration (SrC1-SrC4). The OIL thickness of SrC1 was significantly reduced compared with SrC3 and SrC4 ($P<0.001$), but similar to SrC2 ($P=0.1700$) and SrC2<SrC3<SrC4 ($P<0.05$).

For the least viscous resin composite types with decreased TEGDMA content, the barium-glass filled materials, BaC3 and BaC4 exhibited a significantly reduced OIL thickness compared with the strontium-filled materials, SrC3 and SrC4, respectively (P<0.001)

Generally, comparisons of unfilled resin formulations with their corresponding filled counterparts (M1 with BaC1, M3 with SrC3, etc) showed a decreased OIL thickness for each unfilled resin mixture (P<0.05). However, for the least viscous barium-glass filled materials, BaC3 and BaC4 exhibited no significant difference in OIL thickness compared with M3 and M4 (P=0.1929 and 0.3557, respectively). All experimental resins and RBCs did not develop an OIL when polymerised in the nitrogen atmosphere.

3.1.2 Commercial resin based composites

For the commercial RBC specimens, the OIL thicknesses were measured to be 19.2 ± 6.3 and 13.8 ± 5.3 μm for Filtek™ Z250 and Z100, respectively and 9.0 ± 6.6 μm for Filtek™ Silorane (Figure 3.2, Table 3.2). All commercial RBCs developed no OIL layer when polymerised in the nitrogen atmosphere. Kruskal-Wallace and Mann-Whitney tests revealed a significantly lower OIL thickness for Filtek™ Silorane compared with both Filtek™ Z250 and Z100 (P=0.0001 and 0.0079, respectively). The OIL thickness of Filtek™ Z250 was significantly increased compared with Z100 (P=0.0317).
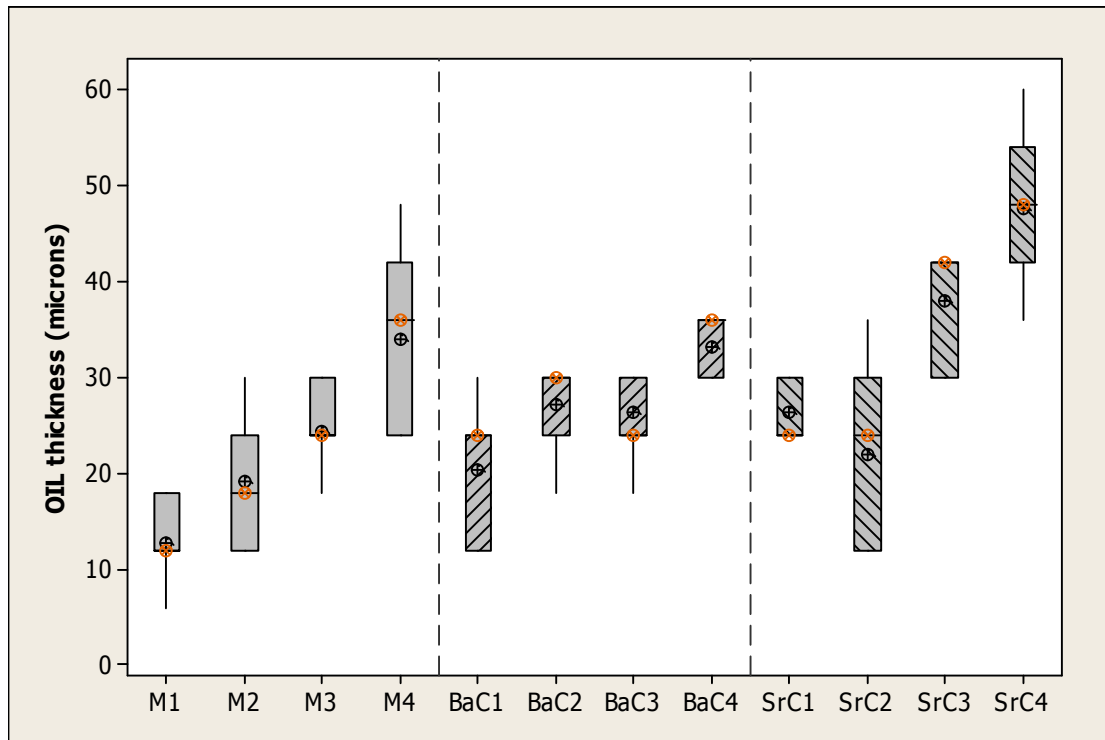
Figure 3.1: Box and whisker plots of the oxygen inhibition layer thickness of each unfilled resin (M1-M4) and corresponding barium-glass (BaC1-BaC4) and strontium-glass (SrC1-SrC4) filled resin composites. The boxes represent the inter quartile range which contains 50% of the thickness values, the whiskers represent the highest and lowest thicknesses and ⊕ and ⊗ within the box indicates the mean and median, respectively.

Specimens		OIL Thickness (µm)
Resins	M1	12.8 (4.5)
	M2	19.2 (6.5)
	M3	24.4 (4.2)
	M4	34.0 (8.4)
Barium-glass RBCs	BaC1	20.4 (6.3)
	BaC2	27.2 (3.8)
	BaC3	26.4 (3.8)
	BaC4	33.2 (3.1)
Strontium-glass RBCs	SrC1	26.4 (3.0)
	SrC2	22.0 (8.4)
	SrC3	38.0 (5.9)
	SrC4	47.6 (6.9)

Table 3.1: The oxygen inhibition layer thicknesses of experimental resins, barium and strontium-glass filled RBCs, as measured by the depth of focus technique.
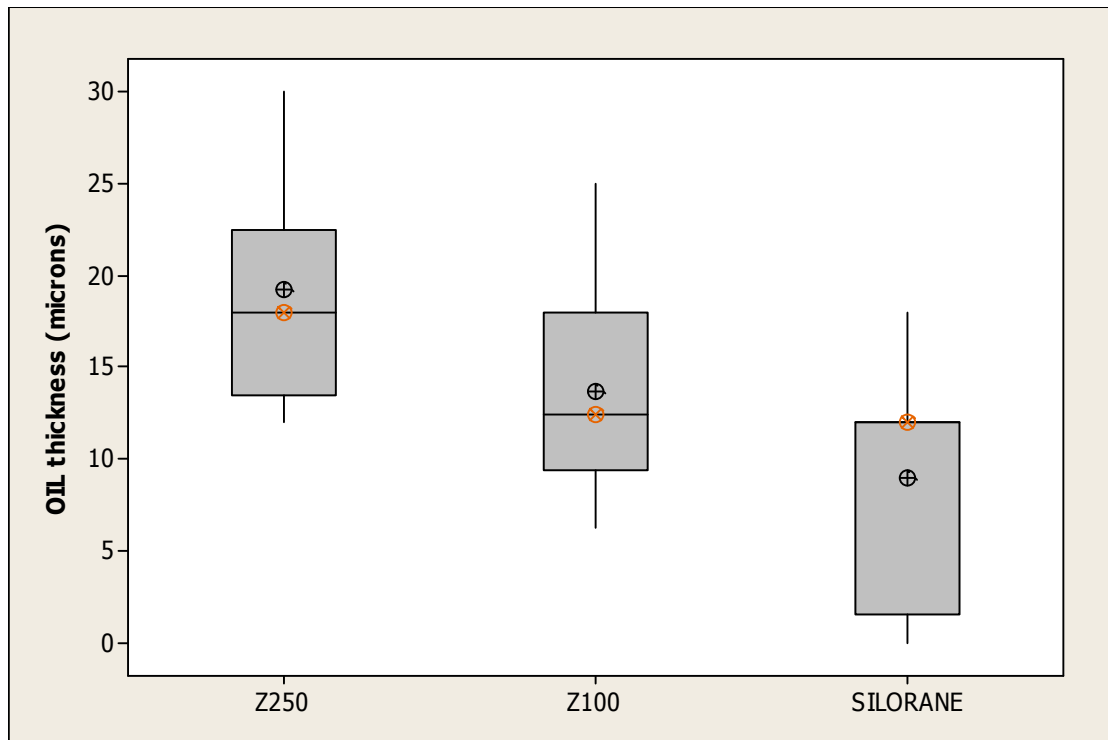
Figure 3.2: Box and whisker plots of the oxygen inhibition layer thickness of each commercial resin-based composite. The boxes represent the inter quartile range which contains 50% of the thickness values, the whiskers represent the highest and lowest thicknesses and $\oplus$ and $\otimes$ within the box indicates the mean and median, respectively.

Specimens	OIL Thickness (microns)
Z250	19.2(6.3)
Z100	13.7(5.4)
Silorane	9.0(6.6)

Table 3.2: Table highlighting the differences in the oxygen inhibition layer thickness between Filtek™ Z250, Z100 and Filtek™ Silorane, using the depth of focus technique.

3.3 Interfacial shear bond strength measurements

3.3.1 Effect of the oxygen inhibition layer thickness on shear bond strengths

The mean shear bond strengths of the dimethacrylate-based barium-glass filled RBCs, BaC1-BaC4 are presented in Figure 3.3 and Table 3.4. A two-way ANOVA revealed that experimental RBC type with varying viscosity had a significant effect on shear bond strength between incremental layers (P=0.037; Table 3.3). However, no significant differences in shear bond strength was identified for RBC increments cured in either air or the nitrogen atmosphere (P=0.954) although a significant interaction between material type and curing atmosphere existed (P=0.022). For samples cured in air, a one-way ANOVA revealed no significant differences between material types, BaC1-BaC4 (P=0.163). For samples cured in the nitrogen atmosphere the shear bond strength of BaC4 was significantly reduced compared with all other experimental RBC types (P<0.05).

Source	DF	Seq SS	Adj MS	F	P
Experimental RBC	3	187.87	62.6225	3.19	*0.037
Curing atmosphere	1	0.07	0.0655	0.00	0.954
Interaction	3	216.32	72.1063	3.67	*0.022
Error	32	627.88	19.6213		
Total	39	1032.13			

Table 3.3: A two-way ANOVA highlighting any significant differences in shear bond strengths between incremental layers of experimental RBCs with varying viscosities cured in either air or the nitrogen atmosphere (P=0.05).
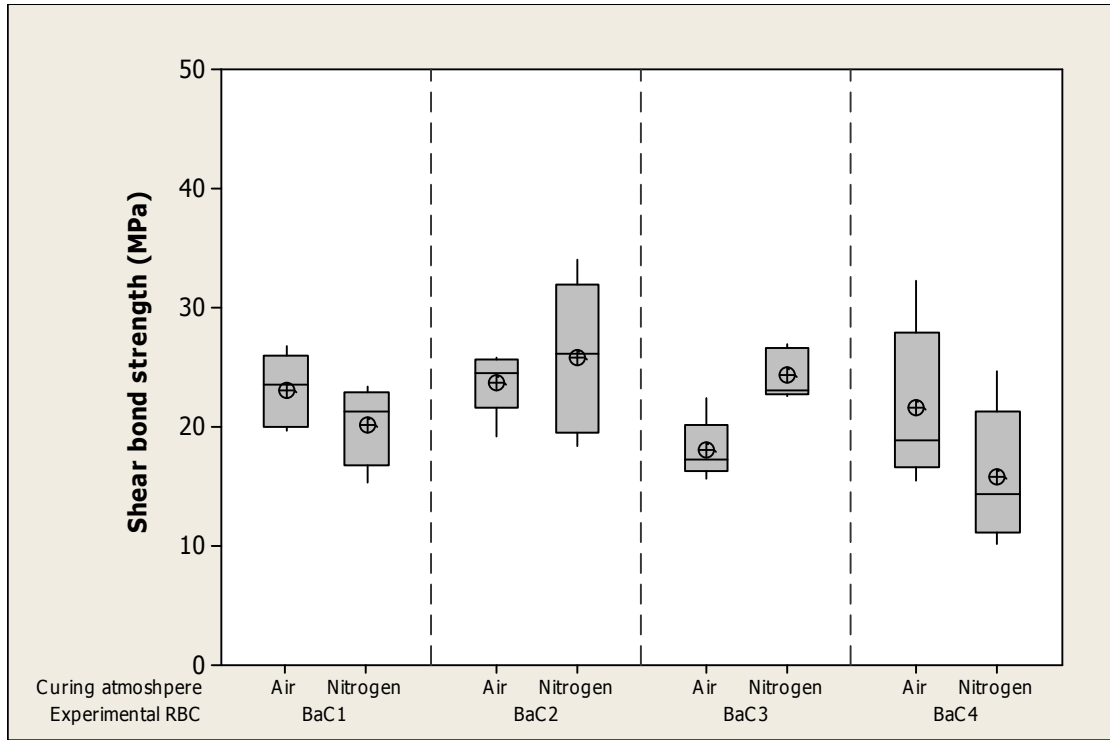
Figure 3.3: A box and whisker plot demonstrating the shear bond strength values (MPa) of barium-glass filled RBCs (BaC1-BaC4) following polymerisation in either air or a nitrogen atmosphere. The boxes represent the inter quartile range which contains 50% of the bond strength values. The crosshair and line within the box indicates the mean and median, respectively.

	24h 'dry' Shear Bond Strength (MPa)	
	N_2	Air
BaC1	20.5(3.1)	23.1(3.1)
BaC2	25.8(6.4)	23.8(2.7)
BaC3	24.4(2.1)	18.8(2.9)
BaC4	15.8(5.7)	20.7(6.4)

Table 3.4: The mean shear bond strengths (MPa) of M1B-M4B RBCs polymerised in either air or nitrogen, after 24h 'dry' storage at $23 \pm 1°C$.

The shear bond strengths of commercial RBCs, Filtek™ Z250, Z100 are presented in Figure 3.4 and Table 3.6. A two-way ANOVA revealed that the commercial RBC type had a significant effect on shear bond strength between incremental layers (P<0.001; Table 3.5). However, no significant difference in shear bond strength was identified for RBC increments cured in either air or the nitrogen (P=0.483) although a significant interaction between material type and curing atmosphere existed (P=0.006). For samples cured in air, a one-way ANOVA revealed no significant differences in incremental shear bond strength regardless of commercial material type (P=0.400). For samples cured in the nitrogen atmosphere the shear bond strength of Filtek™ Silorane was significantly reduced (P<0.001) compared with Filtek™ Z250 and Z100, which exhibited statistically similar results (P>0.05).

Source	DF	Seq SS	Adj MS	F	P
Commercial RBC	2	496.23	248.116	11.80	*0.000
Curing atmosphere	1	10.69	10.692	0.51	0.483
Interaction	2	272.99	136.493	6.49	*0.006
Error	24	504.62	21.026		
Total	29	1284.53			

Table 3.5: A two-way ANOVA highlighting any significant differences in shear bond strengths between incremental layers of commercial RBCs cured in either air or the nitrogen atmosphere (P=0.05).
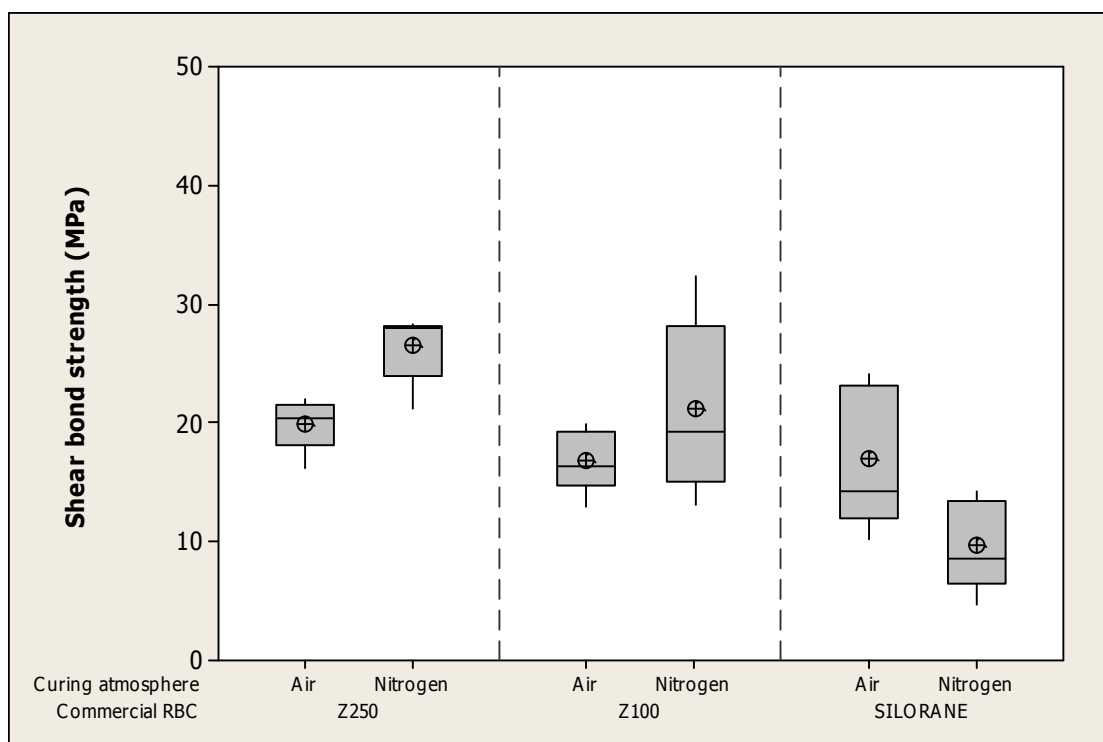
Figure 3.4: A box and whisker plot demonstrating the shear bond strength values (MPa) of each commercial resin-based composite, following polymerisation in either air or a nitrogen atmosphere. The boxes represent the inter quartile range which contains 50% of the bond strength values. The crosshair and line within the box indicates the mean and median, respectively.

24h 'dry' Shear Bond Strength (MPa)		
Specimens	N_2	Air
Z250	23.9(5.1)	20.9(3.5)
Z100	21.2(6.2)	22.4(5.8)
Silorane	9.7(3.8)	16.1(5.5)

Table 3.6: The mean shear bond strengths (MPa) of Filtek™ Z250, Z100, and Filtek™ Silorane polymerised in either atmospheric air or nitrogen, after 24h dry storage at 23 ± 1ºC.

3.3.2 Effect of post-irradiation time on interfacial bond strength

The interfacial shear bond strengths of each experimental barium-glass RBC sample groups following 'fresh' (0h), 7d and 30d storage in distilled water are presented in Figure 3.5 and Table 3.8,. A three-way multifactorial ANOVA (Table 3.7) revealed that post-cure time prior to increment placement and experimental RBC type had a significant influence on incremental shear bond strength (P<0.001). One-way ANOVAs demonstrated that for RBC types BaC1 and BaC2, the shear bond strength of increments placed following 30d were significantly reduced compared with those placed 'fresh' (P=0.009 and 0.028, respectively). Conversely, RBC types BaC3 and BaC4 exhibited no significant difference in bond strength regardless of post-cure placement time (P=0.562 and 0.141, respectively)

Source	DF	Seq SS	Adj MS	F	P
Post-cure time	2	593.05	296.53	12.96	*0.000
Curing atmosphere	1	9.06	9.06	0.40	0.530
Experimental RBC	3	1217.60	405.87	17.74	*0.000
Error	129	2951.38	22.88		
Total	135	4771.10			

Table 3.7: A three-way ANOVA highlighting significant differences in shear bond strengths between incremental layers of experimental RBCs with varying viscosities, cured in either air or the nitrogen atmosphere following 'fresh' placement or 7 and 30 days post-cure (P=0.05).
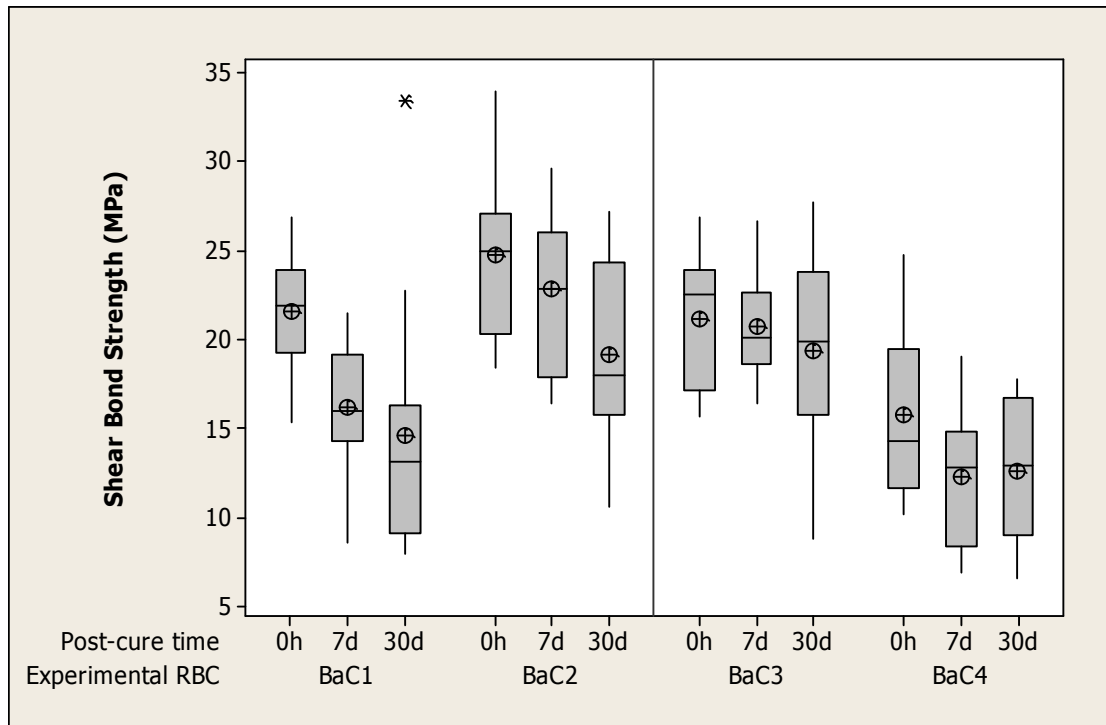
Figure 3.5: A box and whisker plot demonstrating the shear bond strength values (MPa) of each barium-glass RBC and increment placement following various post-cure times. The boxes represent the inter quartile range which contains 50% of the bond strength values. The crosshair and line within the box indicates the mean and median, respectively and the asterix indicates an outlying result

	Shear Bond Strength (MPa)		
	'Fresh'	7 days	30 days
BaC1	21.6 (3.4)	16.1 (3.4)	14.6 (7.3)
BaC2	24.8 (4.8)	22.8 (4.5)	19.2 (5.0)
BaC3	21.2 (4.0)	20.7 (3.0)	19.3 (5.2)
BaC4	15.8 (5.4)	12.3 (3.7)	12.6 (4.0)

Table 3.8: The shear bond strengths (MPa) of nitrogen and atmospheric air cured specimens of Barium glass filled experimental RBCs after 7 and 30d storage in distilled water in a lightproof container at $23 \pm 1^{\circ}C$

Materials		Failure Modes (%)	
		Adhesive	Cohesive
C1	Nitrogen	10.4	89.6
	Air	10.4	89.6
C2	Nitrogen	4	96
	Air	3.8	96.2
C3	Nitrogen	7	93
	Air	0	100
C4	Nitrogen	27.6	72.4
	Air	20	80

Table 3.9: The failure modes (cohesive or adhesive) of nitrogen and atmospheric air cured specimens of barium-glass filled composites after fresh, 7 and 30d storage in distilled water in a lightproof container. The results are collated throughout all three time periods.

The mean incremental shear bond strengths of the commercial RBCs following 0h, 7d and 30d are presented in Figure 3.6 and Table 3.11. A three-way multifactorial ANOVA (Table 3.10) revealed that post-cure time prior to increment placement and commercial RBC type had a significant influence on incremental shear bond strength ($P<0.001$). For all commercial materials, a one-way ANOVA and Tukey post-hoc comparisons revealed a significant decrease in shear bond strength following 30d compared with 0h and 7d ($P<0.01$). Filtek™ Z250 specimens exhibited significantly greater bond strengths than Z100 following 30d ($P<0.05$). Following 7 and 30d, the bond strengths of both Filtek™ Z250 and Z100 were significantly greater than that of Silorane ($P<0.05$).

Source	DF	Seq SS	Adj MS	F	P
Post-cure time	2	1614.09	807.05	39.42	*0.000
Curing atmosphere	1	13.46	13.46	0.66	0.420
Commercial RBC	2	1537.32	768.66	37.54	*0.000
Error	84	1719.78	20.47		
Total	89	4884.65			

Table 3.10: A three-way ANOVA highlighting significant differences in shear bond strengths between incremental layers of commercial RBCs with varying viscosities, cured in either air or the nitrogen atmosphere following 'fresh' placement or 7 and 30 days post-cure (P=0.05).
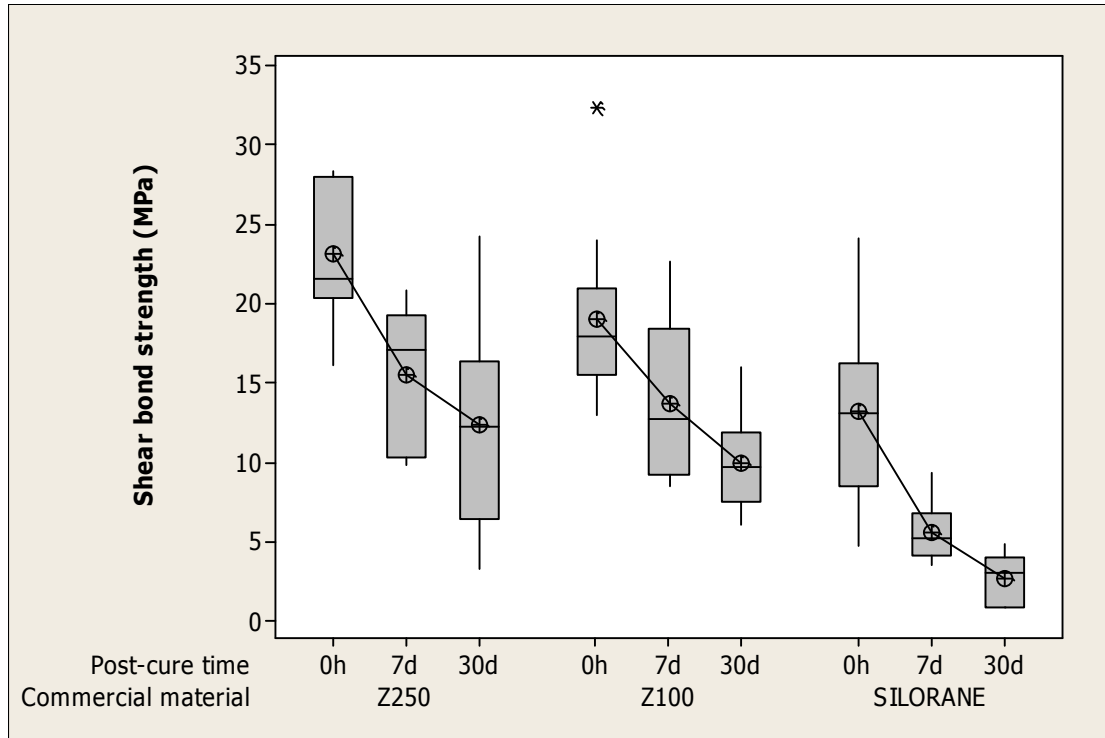
Figure 3.6: A box and whisker plot demonstrating the shear bond strength values (MPa) of Filtek™ Z250, Z100, and Filtek™ Silorane and increment placement following various post-cure times. The boxes represent the inter quartile range which contains 50% of the bond strength values. The crosshair and line within the box indicates the mean and median, respectively and the asterix indicates an outlying result

	Shear Bond Strength (MPa)		
	'Fresh'	7 days	30 days
Z250	21.6 (3.4)	15.5 (4.3)	12.4 (6.7)
Z100	24.8 (4.8)	13.7 (5.0)	9.9 (2.9)
Silorane	21.2 (4.0)	5.6 (1.8)	2.7 (1.5)

Table 3.11; The shear bond strengths (Mpa) of nitrogen and atmospheric air cured specimens of Filtek™ Z250, Z100, and Filtek™ Silorane after 7 and 30d storage in distilled water in a lightproof container at 23 ± 1ºC

Materials		Failure Modes (%)	
		Adhesive	Cohesive
Z250	Nitrogen	32.2	67.8
	Air	41	59
Z100	Nitrogen	25	75
	Air	26	74
Silorane	Nitrogen	100	0
	Air	87.5	12.5

Table 3.12: The failure modes (cohesive or adhesive) of nitrogen and atmospheric air cured specimens of Filtek™ Z250, Z100, and Filtek™ Silorane after fresh, 7 and 30d storage in distilled water in a lightproof container at 23 ± 1ºC. The results are collated throughout all three time periods.

3.4 Determination of staining susceptibility

3.4.1 Experimental resins and filled resin composites

The results of staining susceptibility for experimental resins and resin composites are displayed in Figures 3.7 and Table 3.13. For unfilled resin mixtures (M1-M4) a two-way ANOVA revealed that both curing atmosphere and resin type were significant factors in colour change ($P<0.001$ and 0.024, respectively) following 7 days immersion in methylene blue solution. One-way ANOVAs revealed that resins cured in air stained more readily than those cured in a nitrogen atmosphere ($P<0.001$) although no significant difference in colour change between each resin cured in air was observed ($P=0.408$). For specimens cured in the nitrogen atmosphere, the change in colour for M1 was significantly greater than that for resins M2-M4 ($P<0.05$) and M4 exhibited the smallest colour change ($P>0.05$; Figure 3.7a). Generally, unfilled resins were less susceptible to staining compared with their filled counterparts (Figure 3.7b and c).

For both barium and strontium-based RBCs, the staining susceptibility of specimens cured in air was either greater than or equal to that of specimens cured in nitrogen. The barium-based RBC, BaC4 showed higher staining susceptibility compared with BaC1-BaC3 ($P<0.01$) and the lower TEGDMA content samples BaC1 and BaC2 were similar ($P>0.05$) but exhibited less staining than BaC3 ($P<0.05$) in both air and nitrogen (Figure 3.7b). For strontium-based RBCs, a similar trend was observed although SrC3 specimens exhibited significantly less staining than SrC1, SrC2 and SrC4 in both air and nitrogen ($P<0.05$).The trend in staining susceptibility of the experimental composites varied with filler type. Staining of BaC1 and BaC2 was significantly less compared with SrC1 and SrC2, however, for the least viscous RBC types, BaC3 and BaC4 exhibited significantly greater colour change than SrC3 and SrC4 in both air and nitrogen, respectively ($P<0.05$; Figure 3.7c).

(a)

(b)

(c)
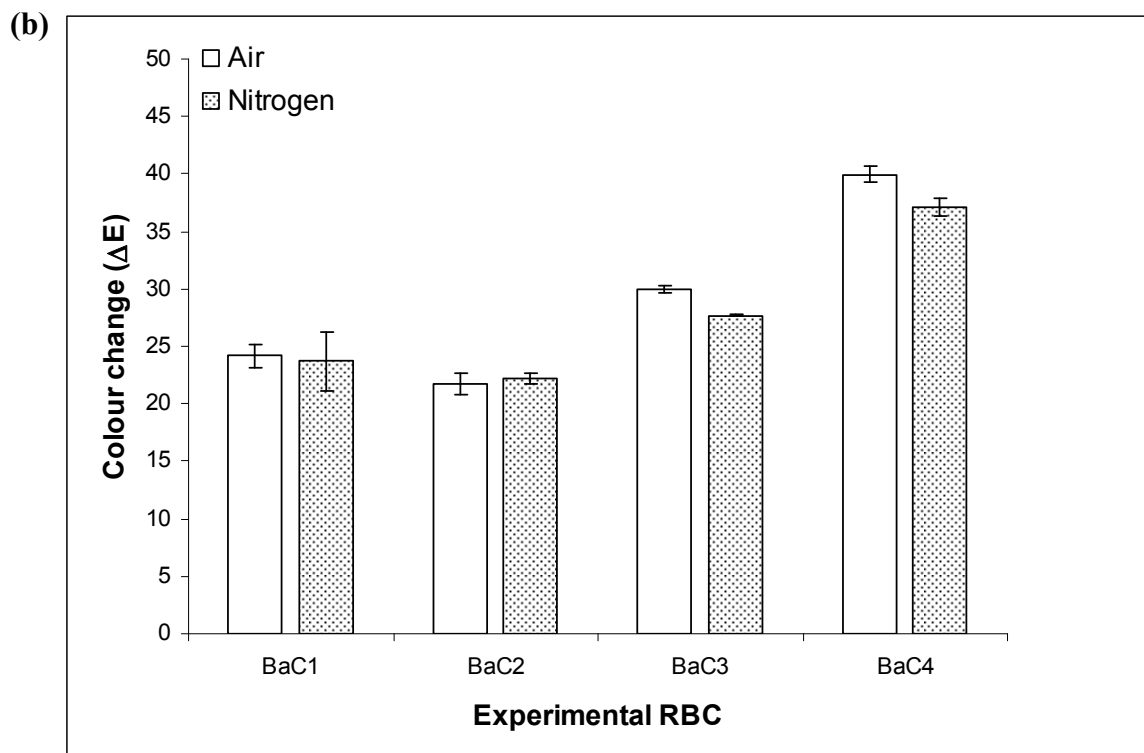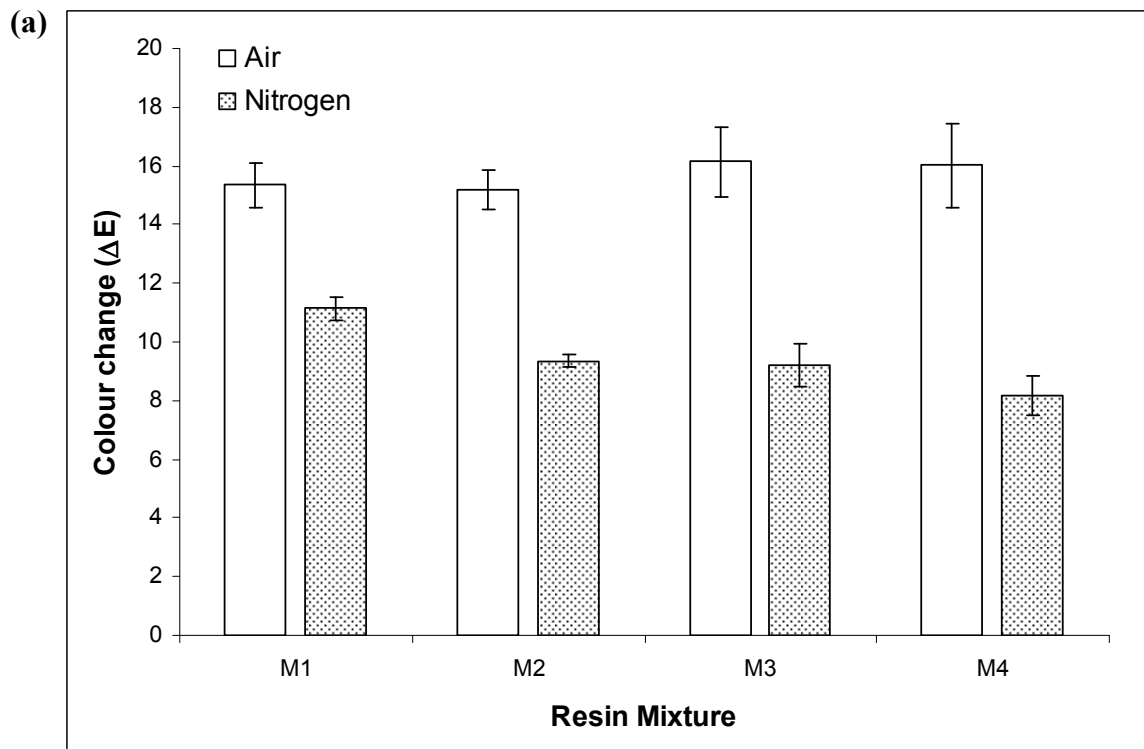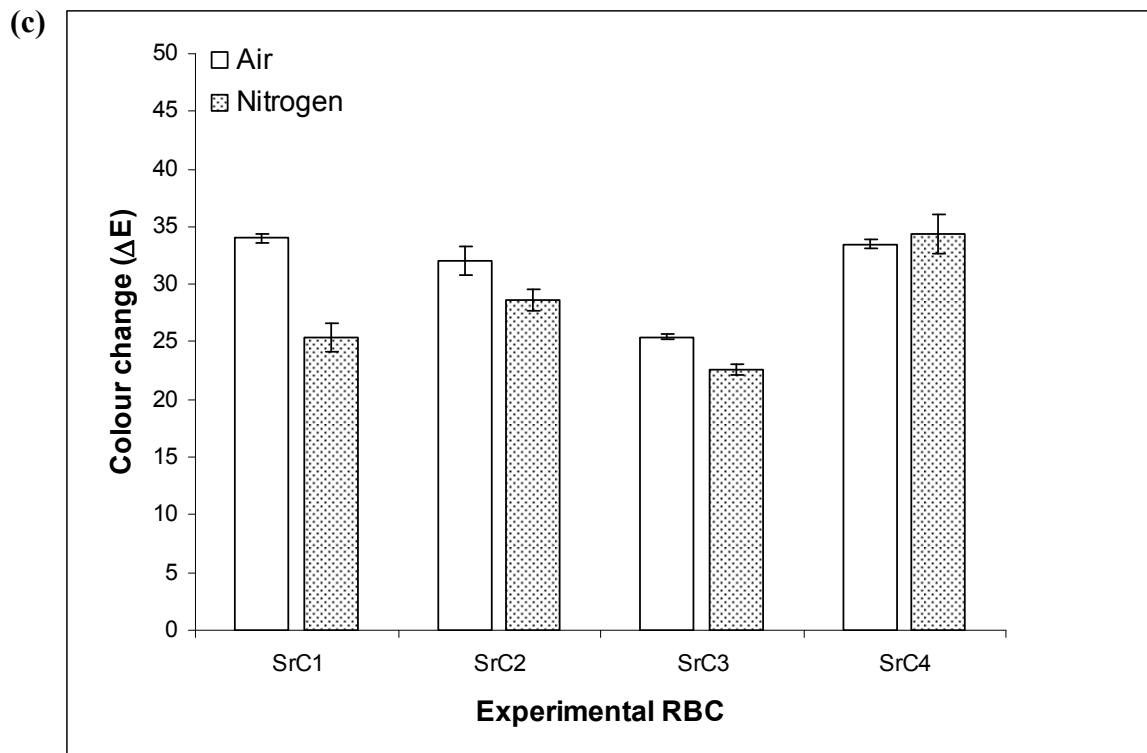
Figure 3.7: Staining susceptibility (∆E) of (a) unfilled resins M1-M4 and corresponding (b) barium or (c) strontium-glass filled composites after immersion in 0.5% Methylene Blue solution at 37ºC ± 1ºC for 7d, demonstrating the increase in staining with an increasing oxygen inhibition layer thickness for the unfilled resin materials (a), and demonstrating the complicated effects of different filler particle types on staining susceptibility (b and c).

Atmosphere	Material	Colour change (ΔE)
Air	M1	15.4 (0.8)
	M2	15.2 (0.7)
	M3	16.1 (1.2)
	M4	16.0 (1.4)
Nitrogen	M1	11.1 (0.4)
	M2	9.4 (0.2)
	M3	9.2 (0.7)
	M4	8.2 (0.7)
Air	BaC1	24.2 (1.0)
	BaC2	21.7 (1.0)
	BaC3	30.0 (0.3)
	BaC4	40.0 (0.7)
Nitrogen	BaC1	23.7 (2.6)
	BaC2	22.3 (0.5)
	BaC3	27.7 (0.0)
	BaC4	37.2 (1.7)
Nitrogen	SrC1	34.0 (0.4)
	SrC2	32.2 (1.2)
	SrC3	25.4 (0.2)
	SrC4	33.5 (0.4)
Air	SrC1	25.4 (1.2)
	SrC2	28.6 (1.0)
	SrC3	22.6 (0.4)
	SrC4	34.3 (1.7)

Table 3.13: Staining susceptibility (ΔE) of unfilled resins M1-M4 and corresponding strontium or barium-glass filled composites after immersion in 0.5% Methylene Blue solution at 37ºC $\pm$ 1ºC for 7d, illustrating the general increase in staining with an increasing oxygen inhibition layer thickness

3.4.2 Commercial resin based composites

The results of staining susceptibility for the commercial resin composites are displayed in Figure 3.8 and Table 3.12. All commercial RBC types exhibited a decreased staining susceptibility cured in the nitrogen atmosphere compared with air ($P<0.05$; Figure 3.8). Two and one-way ANOVAs revealed a significant increase in colour change of Filtek™ Z250 compared with Z100 specimens cured in nitrogen, although an opposite significant trend occurred for specimens cured in air ($P<0.001$). Filtek™ Silorane exhibited a significantly reduced change in colour compared with Filtek™ Z250 and Z100 in both nitrogen and air ($P<0.001$).
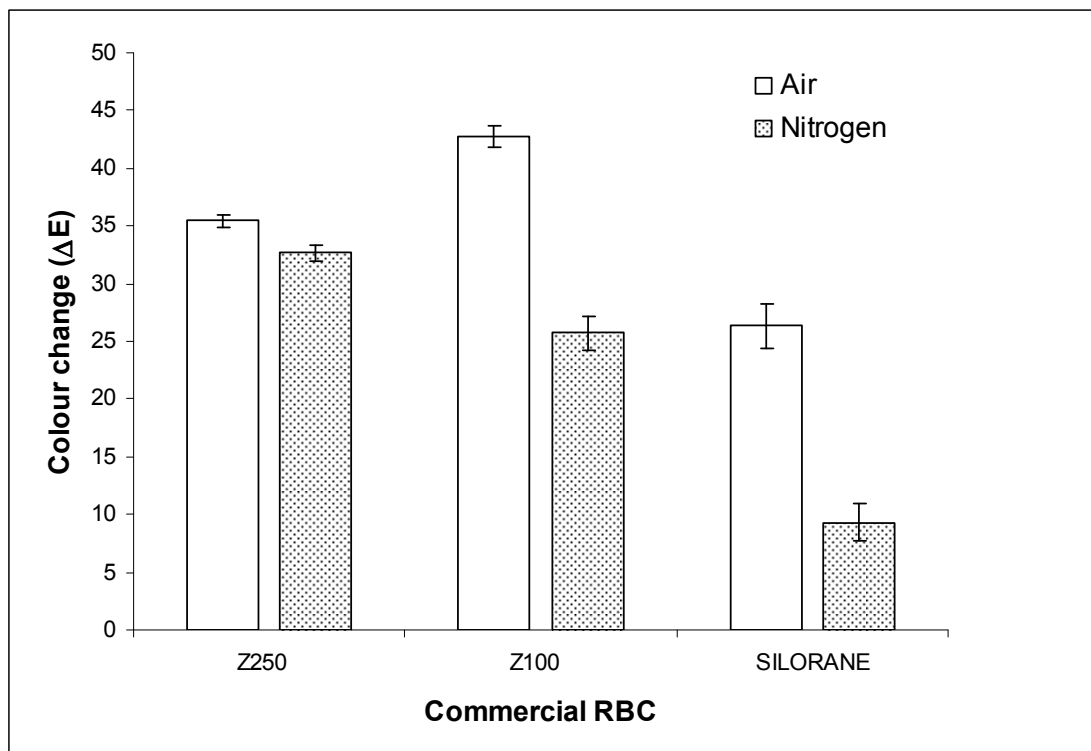
Figure: 3.8: Staining susceptibility (ΔE) of commercial composites, Filtek™ Z250, Z100 and Filtek™ Silorane after immersion in 0.5% Methylene Blue solution at 37ºC ± 1ºC for 7d, illustrating the general decrease in staining in Filtek™ Silorane compared with conventional dimethacrylate-based Filtek™ Z250 and Z100 and demonstrating the decreased staining in nitrogen-cured specimens compared with air-cured specimens.

Atmosphere	Material	Colour change (ΔE)
Air	Z250	35.5 (0.6)
	Z100	42.7 (0.9)
	Silorane	26.3 (1.9)
Nitrogen	Z250	32.7 (0.7)
	Z100	25.7 (1.5)
	Silorane	9.3 (1.6)

Table 3.14: Staining susceptibility (ΔE) of commercial composites, Filtek™ Z250, Z100 and Filtek™ Silorane after immersion in 0.5% Methylene Blue solution at 37ºC ± 1ºC for 7d, illustrating the general decrease in staining in Filtek™ Silorane compared with conventional dimethacrylate-based Filtek™ Z250 and Z100 and demonstrating the decreased staining in nitrogen-cured specimens compared with air-cured specimens.

4.0 DISCUSSION

4.1 Oxygen inhibition layer thickness

There have been a multitude of different methods of measuring the oxygen inhibition layer (OIL) thickness of dental resins and RBCs, ranging from techniques whereby the OIL is optically identified and measured using a light microscope (Finger et al., 1996; Rueggeberg and Margeson, 1990), to more elaborate methods using magnetic resonance imaging (MRI) (Guillot et al., 2004) and Fourier transform near infra-red spectroscopy (FT-NIRS) (Kim et al., 2006) and Raman spectroscopy (Gauthier et al., 2005). In the current investigation, the OIL thickness was measured with an optical method adapted from an earlier technique (Finger et al., 1996). Many factors can affect oxygen inhibition of methacrylate resin based materials, including atmospheric oxygen concentration, specimen temperature and thickness, monomer chemical structure and viscosity, filler particle types, photoinitiator type and concentration, and polymerisation light intensity (Andrzejewska, 2001; Burtscher, 1993; Gauthier et al., 2005; Studer et al., 2003a; b). The current experimental method was designed to appropriately isolate the factors under investigation, namely, atmospheric oxygen, material viscosity, monomer chemistry and the effects of different filler particles.

The majority of research conducted on the OIL is in agreement that increasing resin viscosity decreases the OIL thickness. The results from this study are generally in line with earlier research (Finger et al., 1996; Gauthier et al., 2005; Studer et al., 2003b). However, the presence of filler particles further complicates the relationship between resin viscosity and OIL thickness.

4.1.1 The effect of viscosity on oxygen inhibition

BisGMA, a large molecular weight methacrylate resin is commonly used as the main constituent of dental RBCs. However, BisGMAs chemical structure, specifically its large molecular weight and presence of aromatic rings (Figure 1.3a) results in steric hindrance and a degree of inflexibility of the resin mass during polymerisation (Elliott et al., 2001), thus decreasing mobility of the polymer chains, therefore resulting in a relatively low degree of conversion with a less densely packed polymer network (Darvell, 2000). Therefore, BisGMA is usually admixed with a low molecular weight monomer with a higher degree of mobility in an attempt to decrease the materials viscosity such as TEGDMA. However, the addition of TEGDMA while decreasing the viscosity of the material, it also increases the diffusion of atmospheric oxygen into the upper surface of the material, thus exacerbating the inhibitory effects of oxygen. The incorporation of TEGDMA as a diluent into dental RBCs has been shown to be a key factor in the diffusion of atmospheric oxygen into the polymerised material. It is also well documented in the literature that a decrease in resin viscosity will result in an increased diffusion of oxygen, therefore increasing the inhibitory effects of oxygen (Finger et al., 1996; Gauthier et al., 2005; Studer et al., 2003b). As the resins used in this study were BisGMA/TEGDMA blends with ratios of 85/15, 70/30, 41/59, 10/90 by mass resulting in four resin mixtures with decreasing viscosity (M4>M3>M2>M1), it was assumed that increasing the concentration of TEGDMA will exacerbate the inhibitory effects of atmospheric oxygen on the specimen. As all the experimental monomer blends and experimental RBCs were polymerised under nominally identical conditions in both nitrogen and atmospheric air, the results can be directly comparable. There was no determinable OIL when the resin specimens were cured in nitrogen. However, when the specimens were cured in atmospheric air there was a significant increase in OIL thickness as viscosity decreased by

increasing TEGDMA content which is in agreement with the findings of the previous studies (Finger et al., 1996; Gauthier et al., 2005; Studer et al., 2003b).

4.1.2 The effect of fillers on oxygen inhibition

The experimental resins were loaded with either barium or strontium-glass filler particles to result in eight RBCs with different monomer concentrations and filler type combinations (Figure 2.2). The inclusion of filler particles within the resin further complicates the relationship between resin viscosity and OIL thickness. For the least viscous barium-glass filled RBCs (BaC3-BaC4) the OIL thickness was significantly decreased when compared with strontium-glass filled RBCs (SrC3-SrC4), in spite of identical loading of 70% (by weight) and nominally identical 1μm particle sizes (Table 2.2). Therefore, it can be postulated that the decrease in OIL thicknesses may be due to the chemical composition of the filler particles, where different filler chemical compositions and resin-filler interactions may result in different rates of oxygen diffusion into the resin matrix, by either directly adsorbing oxygen onto the filler surface or by facilitating the diffusion of oxygen between the filler particle/resin matrix interface. The effect of oxygen adsorption of fillers and inhibition thickness within resin composite formulations is poorly understood and only one previous study has focused on such phenomena (Gauthier et al., 2005). In that study, an inhibitory effect was not present when the filler particles load reached 40% compared with the present investigation wherein an inhibition layer was measured with all resin composite formulations loaded to 70 wt%. This discrepancy might be associated with differences in filler type, size and resin-filler interaction. In the study of Gauthier et al. (2005), unsilanised silica particles ranging from 0.5-10μm diameter were investigated. The increase in average filler size compared with 1μm diameter filler particles used in the current investigation will inevitably result in significantly decreased resin-filler surface area exposed to atmospheric oxygen and

may reduce the inhibitory effect compared with the 1μm particle size used in this investigation. This suggests that differences in filler type, size and resin-filler interaction may significantly affect oxygen inhibition and warrants further investigation. Interestingly, the OIL thicknesses for the most viscous RBCs (BaC1, BaC2, SrC1 and SrC2) were significantly increased compared with their corresponding unfilled experimental resins. This was unexpected since filler particles would increase viscosity and are known to act as obstacles to oxygen diffusion (Odrobina et al., 2001), and may be explained by deeper diffusion of atmospheric oxygen into the resin matrix due to resin-filler interactions and/or increased porosity of the viscous mixes which are mixed by hand, and thus increases the likelihood of oxygen diffusion resulting in an increased OIL thickness. Another explanation may be that different filler particle materials may affect the rates of free radical decomposition in the RBC. A study by Burtscher (1993) demonstrated different rates of free radical decomposition, where fumed silica particles caused a significant decrease in free radical stability when compared with ytterbium trifluoride and barium-glass particles. However, the fumed silica particles were 0.04μm on average compared with 0.2μm and 9μm for ytterbium trifluoride and barium-glass particles, respectively, which may also influence the stability of the radicals. A previous study (Ruyter, 1981) also reported an increase in OIL thickness of an unfilled resin (Concise Enamel Bond; 3M, St Paul, Minnesota, USA) when compared to its filled counterpart (7.7wt%; Concise White Sealant; 3M, St Paul, Minnesota, USA).

4.1.3 The oxygen inhibition layer thickness of commercial RBCs

The filler particle size and content of dimethacrylate based RBCs, Filtek™ Z250 and Z100 are nominally identical (Filtek™ Z250 Technical Product Profile, 3M ESPE, Seefeld, Germany), thus it can be expected that the filler constituents of both materials do not contribute to any differences in OIL thickness. However, the resin constituents of Filtek™

Z250 and Z100 were considerably different. In Filtek™ Z250, the majority of the low molecular weight monomer, TEGDMA was replaced by the higher molecular weight monomers, UDMA and BisEMA (Table 2.3), thus any differences in OIL thickness are most likely attributed to the differences in resin formulation. In the present study, it was difficult to fully explain the small but significant differences OIL thickness between Filtek™ Z250 and Z100 (Figure 3.2) even though filler particle size and content are nominally identical. However, Z100 contains 6% more filler particles than Filtek™ Z250 which may act in combination with a higher degree of monomer cross-linking to provide a thinner OIL layer compared with Filtek™ Z250. The significant decrease in OIL thickness of Z100 may also be attributed to the presence of TEGDMA, which may increase the diffusion of oxygen into the resin matrix of the material due to its low viscosity, thus resulting in an overall increase in oxygen inhibition. However, TEGDMA is also a highly flexible and mobile monomer, as a result of its low molecular weight and lack of aromatic rings. TEGDMA low molecular weight also results in an increased cross-link density, therefore is highly reactive compared to BisGMA, thus resulting in a more integral polymer structure at the surface of the material which may prevent oxygen diffusion to a greater extent than BisGMA or UDMA, the predominant resin constituents of Filtek™ Z250. These properties may counteract some of the deleterious effects of TEGDMAs low viscosity (Studer et al., 2003a). Furthermore, Filtek™ Z100 is known to be a fast setting material compared with other light-activated RBCs [3M ESPE internal], which may be attributed to differences in the resin matrix and initiator chemistry, which may result in a increased initiation rate of polymerisation that decreases the potential of oxygen inhibition

In Contrast, Filtek™ Silorane, which contains a significantly different monomer and photoinitiation chemistry. The epoxy groups within Silorane undergo cationic ring-opening

polymerisation reactions and as such are insensitive to oxygen. Filtek™ Silorane is reported to polymerise without a surface OIL as reported by Tezvergil-Mutluay et al. (2008), in which the authors tested incremental bond strengths of Silorane-Silorane specimens, which is contradictory to the findings of the present investigation since an OIL for Filtek™ Silorane was observed (Figure 3.2). However, in order for Filtek™ Silorane to be a viable photo-cured dental material it must have the ability to be cured by conventional light curing units, This is achieved using an electron-transfer photosensitisation process, whereby light absorption of the photosensitiser Camphorquinone (CQ) and the co-initiator, dimethylaminoethylmethacrylate (DMAEMA) (Figure 1.1), result in an excited state complex (exciplex), which is formed as an intermediate between the iodonium salt and photosensitiser (Crivello JV, 2008). A redox reaction occurs, resulting in an electron transfer between the two species yielding a radical and a cation-radical, which generate the cationic initiating species (Odian, 2004), which are subsequently utilized in the cationic polymerisation stages of Filtek™ Silorane (Weinmann et al., 2005). Thus the polymerisation of Filtek™ Silorane is mediated by two separate processes, an initial free-radical stage and a subsequent cationic stage (Figure 4.1). The generation of radicals are a consequence of the need for curing regimes in the visible light spectrum and presumably to achieve suitable adhesion to the bonding layer. Consequently, oxygen may react with these radicals and result in an inhibited layer observed in this study, albeit at a significantly reduced thickness compared with the dimethacrylate-based RBCs where radical concentration is most likely to be greater. Therefore, Filtek™ Silorane also has the potential to be inhibited by atmospheric oxygen.
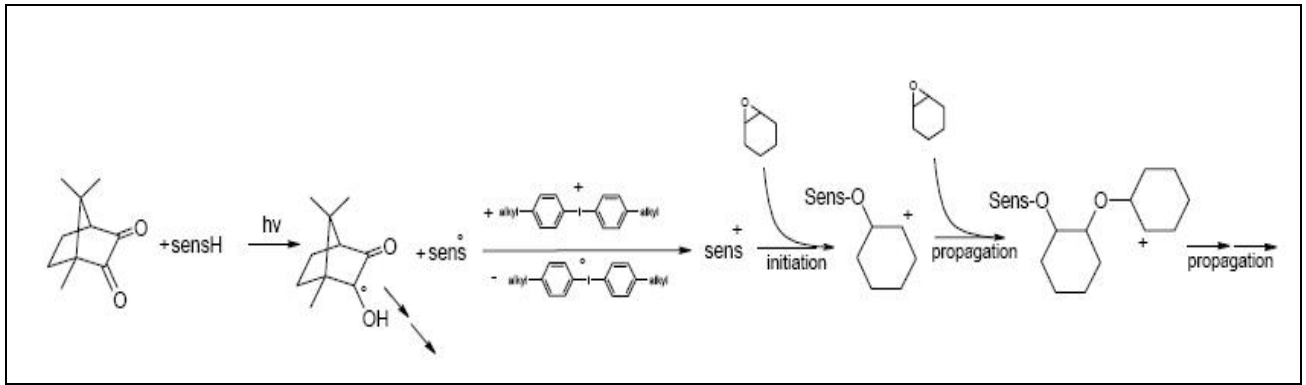
Figure 4.1: A schematic diagram demonstrating the utilization of Camphorquinone (CQ), dimethylaminoethylmethacrylate (DMAEMA) and free radicals in the initiation stage of the polymerisation reaction of Filtek™ Silorane. The propagation phase of the polymerisation is mediated cationically without free radical involvement (personal communication, 3M ESPE, Seefeld Germany).

4.2. Shear bond strength determination

4.2.1 The effect of the oxygen inhibition layer on shear bond strengths

Complete removal of defective RBC restorations can often be avoided by relatively simple RBC repair or refurbishment procedures. Repair of RBC restorations can be performed either immediately after insertion, such as in cases of inadequate contact points or presence of voids; or may be necessary after some time due to failure of the restoration, in both cases it is increasingly important to investigate and understand the factors that influence the success or failure of such procedures. Interfacial bond strengths between RBC layers can potentially be affected by several factors, such as surface roughness, monomer reactivity, material viscosity, intermediary bonding materials, time of repair, and the oxygen inhibition layer (OIL) (Azarbal et al., 1986; Eick et al., 2006; Li, 1997; Papacchini et al., 2007). The current study evaluated the effects of the OIL on composite-to composite shear bond strengths to freshly prepared and older specimens, as previous investigators have often reported conflicting results (Eliades and Caputo, 1989; Papacchini et al., 2007; Truffier-Boutry et al., 2003).

Previous investigations have either used a glass slide or a Mylar strip to block O_2 from the surface of the tested specimen (Li, 1997) which results in disparate surface roughnesses between nitrogen cured and air cured specimens in which surfaces were left uncovered and exposed to the atmosphere. Numerous studies have found that Mylar-covered RBCs result in smoother surfaces compared with other finishing techniques (Pratten and Johnson, 1988; Stoddard and Johnson, 1991). This smooth surface may reduce interfacial bond strengths due to the lack of micromechanical interlocking (Truffier-Boutry et al., 2003) in addition to not

completely eliminating atmospheric O_2 from the surface of the RBC, although it will decrease or block the continued diffusion of atmospheric O_2 into the RBC.

In the current study the oxygen-deprived specimens were polymerised in a glove box, which was subsequently inflated with N_2. Analysis of the atmospheric content of the glove box was then undertaken where the oxygen concentration was found to be approximately 3%. This low concentration may have been insufficient to affect the formation of an OIL layer. In addition, as the N_2 nozzle was approximately placed at a distance of only 2cm from the RBC specimen undergoing polymerisation it may be that the N_2 concentration was higher in the immediate vicinity of specimen. This method of blocking oxygen from the surface of the specimen ensured that the surface properties of different specimens were nominally identical.

In a previous study undertaken by Dall'Oca (2007), specimens were polymerised in an N_2 environment to homogenize the surface roughness of specimens. However, curing of the N_2 specimens was undertaken through the glass wall of the nitrogen container, thus resulting in a non-standardized radiant exposure between atmosphere and nitrogen cured specimens (Dall'Oca, 2007). The resulting differences in the degree of cure may affect OIL thicknesses. In the present study, all the curing apparatus was placed in the glove box prior to N_2 purging, therefore ensuring all specimens were irradiated identically. In another investigation, the curing unit was placed in a nitrogen box together with the specimens (von Beetzen et al., 1996) but as the nitrogen box was relatively small sized, there was a highly significant increase in temperature within the box (24±4ºC) compared to the ambient temperature, which may have affected the viscosity and the degree of conversion of the specimens, to avoid this complication, in the present study, a thermometer was inserted into the glove bag and the

temperature was determined to have been maintained at 23±1ºC inside and outside the glove bag throughout curing.

4.2.1.1 Experimental RBCs and commercial RBCs

Previous studies have found that the use of unfilled low-viscosity dimethacrylate-based intermediate resins can improve bonding strength (Azarbal et al., 1986; Kallio et al., 2001; Saunders, 1990) due to the penetration of the low viscosity resin into surface microdefects present on the first increment of RBC resulting in micromechanical retention. A similar method of action, where the liquid, sticky OIL diffuses and interlocks with the substrate thus increasing the bonding surface area has been proposed for the effect of the OIL in increasing bond strengths (Eliades and Caputo, 1989; Rueggeberg and Margeson, 1990). It therefore follows that the least viscous material should be expected to have superior bond strength values. In the current investigation, the low viscosity experimental RBCs bond strengths, were also found to be superior to higher viscosity materials (Table 3.3) which is in agreement with the previous studies. This may be due to the mechanical interlocking of the low viscosity OIL onto the subsequently placed substrate material. However, there were no statistically significant differences in shear bond strengths between experimental RBCs cured in either nitrogen or atmospheric air (Table 3.4). Therefore, it can be assumed that incremental composite-to-composite bond strength is not wholly reliant on surface oxygen inhibition. For specimens cured in the nitrogen atmosphere, BaC1, BaC2 and BaC3 exhibited significantly increased incremental bond strengths compared with the lower viscosity BaC4. The increased amounts of BisGMA in the BisGMA/ TEGDMA mixtures are known to affect reaction speed, where R_p max is reached more quickly due to the rapid onset of auto-acceleration and a dramatic increase in free radical concentration (Shortall et al., 2008; Zhu S et al., 1990). It was therefore suggested that increased curing rate and radical concentration of resin mixtures

containing higher quantities of BisGMA improved adhesion between increments due to the formation of more covalent bonds which counteracted any detrimental effect on bond strength due to lower or no OIL thickness and increased viscosity.

When comparing commercial RBCs, the shear bond strengths of methacrylate based RBCs cured in either nitrogen or atmospheric air were statistically similar (Table 3.6). For specimens cured in air, there were no significant differences in incremental shear bond strength regardless of commercial material type and OIL thickness. Therefore, it can be assumed that incremental composite-to-composite bond strength is not wholly reliant on surface oxygen inhibition. However, there was a marked decrease in Filtek™ Siloranes shear bond strength when cured in a nitrogen atmosphere. This decrease in bond strength can be explained by the large decrease in the concentration of free-radicals present within Filtek™ Silorane as it is cationically cured. As Filtek™ Silorane was observed to be markedly more viscous than both Z100 and Filtek™ Z250 it may be that the increased viscosity may result in the poor adaptation of Filtek™ Silorane into the micro-surface defects of the substrate RBC which may also partially explain the decreased shear bond strengths.

4.2.2 The effect of time on shear bond strengths

4.2.2.1 Experimental RBCs

Bonding between the aged composite resin and added fresh composite resin is affected by various factors, namely, surface roughness, intermediary material used, repair material used, and time after repair. (Shahdad and Kennedy, 1998) In the current study, the surface roughness was nominally identical and no intermediary material was used, as each RBC material was directly bonded to the same RBC. In the current investigation, the specimens were stored in distilled water at 37 ± 1℃. Although pellicle formation did not occur as the specimens were stored in distilled water, it seems prudent from a clinical aspect to thoroughly clean any surface exposed to the oral environment with water at the very minimum before bonding, and when an RBC restoration undergoes repair in the oral cavity, it is most likely that the restoration would have been exposed to the wet oral environment. This will result in water sorption into the material and hydrolytic degradation of the matrix with decreased free radical activity. (Ferracane and Marker, 1992) Although there is no single regime to replicate the effects of the oral cavity on restorative materials, this study has used a simple protocol of storing the materials in 37 ± 1℃ distilled water without agitation of the specimen to preserve the OIL.

In the current investigation, the curing atmosphere was not a significant factor affecting the shear bond strengths. It has been previously reported that a gradual decay in free radical activity occurs over time (Burtscher, 1993) which may directly affect the subsequent composite-to-composite bond strengths. In the current study there was a significant decrease in shear bond strengths over 30d for BaC1 and BaC2, whereas BaC3 and BaC4 shear bond strengths were not significantly reduced. This may be explained by the higher concentration

of TEGDMA in BaC3 and BaC4 (59% and 90% respectively) compared with BaC2 and BaC1 (30% and 15% TEGDMA respectively) which has been reported to decrease the final degree of conversion of the material (Lovell et al., 1999). Furthermore, the increased TEGDMA content and lower viscosity of BaC3 and BaC4 may result in cyclisation of the monomer, (Elliott et al., 2001) where TEGDMA double bonds react to form primary cycles due to the increased flexibility of TEGDMA, therefore decreasing the cross-linking density of the material and resulting in a low degree of cure. This consequently may result in an increased number of unreacted double-bonds and an increased concentration of free radicals which subsequently may increase the bonding capability of the material over a longer period of time than BaC1 and BaC2, which are BisGMA rich.

4.2.2.2 Commercial RBCs

In agreement with numerous studies (Brendeke and Ozcan, 2007; Karl-Johan M. Soderholm, 1991; Padipatvuthikul and Mair, 2007) the bond strengths of all commercial RBCs decreased significantly over time. It has been reported that the half-life of free radicals in methacrylate resins is 53h at 37°C (Burtscher, 1993), which may explain the general deterioration of bond strengths for all commercial RBCs following 7 and 30d post-cure due to radical decay. The percentage decrease in bond strength for Filtek™ Silorane increments cured in air following 30d post-cure was greater than Z100 and Filtek™ Z250, which may be a consequence of decreased radical concentration associated with the cationic polymerisation mechanism. This effect is decreased in the nitrogen atmosphere (Figure 3.6) since radicals are known to possess longer half-lives in nitrogen than air (von Beetzen et al., 1996). In clinical situations, for large restorations requiring multiple increments which are placed on fresh material, the bond strength between layers of Filtek™ Silorane should be no different to conventional methacrylate materials as immediate curing of Filtek™ Silorane in the presence of oxygen

may not exhibit inferior incremental bond strengths (Figure 3.6) compared with methacrylate resins due to the combined effect of radical concentration and the presence of an OIL, which provide a significant interactive effect on bond strength. Therefore, for large restorations requiring multiple increments which are placed on fresh material, the bond strength between layers of Filtek™ Silorane should be no different to conventional methacrylate materials, although repair and bonding to aged Filtek™ Silorane restorations may exhibit inferior incremental bond strengths. Of interest, a previous study (Tezvergil-Mutluay et al., 2008) measured Silorane-to-Silorane bond strengths after immediate bonding, bonding after 20 seconds, and 5 minutes. The shear bond strengths decreased from 26.7MPa to 22.4MPa within 5m which also suggests a potential of even greater deterioration of bond strengths after a longer period of storage. Furthermore, there was also a higher percentage of adhesive failures for Filtek™ Silorane (100% and 87.5% in Nitrogen and Air respectively) compared with both Z100 (25% and 26% in Nitrogen and Air respectively) and Filtek™ Z250 (32.2% and 41% in Nitrogen and Air respectively) (Figure 3.12)

4.3 Staining susceptibility measurements

Aesthetic RBCs are gradually replacing amalgam as the predominant restorative material due to various reasons, including alleged amalgam toxicity, environmental concerns and aesthetics (Alkhatib et al., 2005; Mjor et al., 1999). RBCs are capable of restoring all classes of cavities whether anterior or posterior. However they are mostly used in anterior cavities where aesthetics are of the utmost importance, thus the ability of RBCs to resist discolouration in the oral cavity is vital in ensuring the acceptability and longevity of the restoration. Most RBC materials used clinically are based on a dimethacrylate monomer system which polymerises via a free radical based reaction upon exposure to a high intensity light source with a wavelength range matching that of the photoinitiator system present in the material. This free radical mediated polymerisation reaction may be inhibited by atmospheric oxygen resulting in a surface layer of unpolymerized monomer. Although the oxygen inhibition layer (OIL) is widely reported in dental literature (Eliades and Caputo, 1989; Rueggeberg and Margeson, 1990; Gauthier et al. 2005; Dall'Oca et al., 2007), most studies have focused on the effects of the OIL on composite to enamel/dentin bond strengths during placement of the resin based bonding agent and relatively few have examined the OIL effects on staining.

Anecdotal reports from dental clinicians suggest that this remaining OIL becomes stained relatively quickly resulting in worsening aesthetics. Patients often complain of the resultant stain, especially in anterior class IV restorations which are usually highly visible. Studies have also reported that RBC staining susceptibility decreases when oxygen was removed from the RBC storage environment (Asmussen, 1983; Bowen and Argentar, 1967), thus underlying the importance of the effects of oxygen on the colour stability of RBCs. Degree of

conversion (DOC), which is a measure of polymerisation of the RBC is also postulated to be of significant importance in stain resistance as demonstrated by a previous study (de Gee et al., 1984) in which incompletely polymerised methacrylate resin was readily stained.

Removal of the OIL is possible via various methods, ranging from exposure to an air/water syringe spray, manual application of wet/dry cotton rolls to cleaning with a pumice/water slurry. However, in all methods the OIL was incompletely removed and thus the potential for staining remained (Rueggeberg et al., 1999). Although the OIL can be present on any RBC surface exposed to atmospheric air during polymerisation, pit and fissure sealant materials have more potential of forming an oxygen inhibited layer, as they are generally cured without a Mylar strip, thus resulting in an incompletely cured layer on the outer surface. (Komurcuoglu et al., 2005)

Different dyes, stains and colourants have been used to measure RBC colour stability and susceptibility to staining, including, red wine, coffee, tea, chlorohexidine, turmeric and methylene blue (Guler et al., 2005b; Lee and Powers, 2005; Lee and Powers, 2007; Stober et al., 2001). Most of these colourants have been observed *in vivo* to discolour teeth (Prayitno et al., 1979; Prayitno and Addy, 1979) and thus assessment of their ability to stain aesthetic restorations is an important consideration in the future development of tooth coloured dental restorative materials. In the current investigation 0.5% methylene blue was used to measure the staining potential of the different RBC systems as it is an aggressive staining agent and therefore is able to measure subtle differences in staining susceptibility between various RBC materials. Consequently, the clinical acceptability for colour change was not assessed as all colour changes resulting from the storage regimes were not clinically acceptable according to both Lee & Powers (2005) ($\Delta E = 3.3$ units) and Johnston & Kao (1989) ($\Delta E = 3.7$ units).

4.3.1 The effect of viscosity and fillers on staining susceptibility

The resins used in this study were BisGMA/TEGDMA blends with ratios of 85/15, 70/30, 41/59, 10/90 by mass resulting in four resin mixtures with decreasing viscosity (M4>M3>M2>M1) (Table 2.1). The experimental resins (M1-M4) were then loaded with either barium (BaC3-BaC4) or strontium-glass (SrC3-SrC4) filler particles to result in eight RBCs with different monomer concentrations and filler type combinations (Table 2.2). In the current investigation, the upper surfaces of all specimens were smoothed flat using a PTFE roller (CompoRoller, KerrHawe, Bioggio, Switzerland) to ensure nominally identical surface morphology, as variations in surface morphology was previously shown to affect stain uptake (Guler et al., 2005a; Hachiya et al., 1984; Reis et al., 2003; Sarac et al., 2006), In the present investigation, the experimental resins and experimental RBCs (both barium and strontium-glass RBCs) cured in air stained more readily than those cured in a nitrogen atmosphere, therefore we can assume that the presence of an OIL on the upper surface of the specimen may increase the staining susceptibility of the material. It was expected that the increased diffusion of oxygen into the poorly polymerised surface material will result in increased stain susceptibility, as previous studies reported that oxygen inhibited methacrylate resin may be more susceptible to stain uptake (de Gee et al., 1984; Park et al., 2004). However, no significant differences in colour change between each resin cured in air was observed (Figure 3.7a). As all the unfilled resins had a surface layer of OIL ranging from 11μm to 34μm, it may be that the minimum thickness of OIL was sufficient to result in a high levels of discolouration. It should be noted that M1 resin when cured in a nitrogen atmosphere exhibited a significantly higher discolouration than M2-M4; this may be due to the manual mixing of the material where due to its high viscosity may increase porosity and therefore increase the likelihood of oxygen diffusion thus resulting in localized areas of poorly

polymerised material which may stain excessively, resulting in a generalized higher reading from the colorimeter. Generally, unfilled resins were less susceptible to staining compared with their filled counterparts, which may be due to the chemical composition of the filler particles, where different filler chemical compositions and resin-filler interactions may result in different rates of oxygen diffusion into the resin matrix, by either directly adsorbing oxygen onto the filler surface or by facilitating the diffusion of oxygen between the filler particle/resin matrix interface thus indirectly affecting the level of stain incorporation into the resin matrix and filler interface. The effect of oxygen adsorption of fillers and inhibition thickness within resin composite formulations is poorly understood and only one previous study has focused on such phenomena (Gauthier et al., 2005). When the experimental resins (M1-M4) were loaded with barium glass particles, the greatest colour change was exhibited by BaC4 followed by BaC3, which both stained more than both BaC2=BaC1 (Figure 3.7b), this staining pattern was evident in both oxygen and nitrogen polymerised specimens, and was attributed to the decreasing concentration of TEGDMA, in those resin mixtures (BaC4>BaC3>BaC2>BaC1). The incorporation of TEGDMA which is of lower molecular weight and therefore lower viscosity and higher mobility as a diluent into dental RBCs has been shown to be a key factor in the diffusion of atmospheric oxygen into the polymerised material thus exacerbating the inhibitory effects of atmospheric oxygen on the specimen (Finger et al., 1996; Gauthier et al., 2005; Studer et al., 2003b) resulting in a thicker inhibition layer on the surface of the specimen. Numerous studies have reported that colour stability of the RBC system is directly related to the concentration of hydrophilic resins present in the RBC, where an increased concentration of a hydrophilic monomer, such as TEGDMA, may increase staining susceptibility. (Dietschi et al., 1994; Douglas and Craig, 1982; Iazzetti, 2001; Reis et al., 2003; Satou et al., 1989). The current investigation was in agreement with the previous studies in this respect.

The strontium-glass particle filled RBCs exhibited a pattern of discolouration similar to their barium-glass filled counterparts, (SrC4>SrC2>SrC1) which can also be explained by the increasing TEGDMA concentration. However SrC3 exhibited a significantly lower colour change compared with SrC1, SrC2 and SrC4 in both air and nitrogen, this phenomenon could be explained by the relative reactivity of the resin-filler combination of SrC3, where a resin-filler refractive index mismatch may result in higher reaction rates and a higher degree of cure (DOC) due to the deeper penetration of the curing light into the material, thus affecting the staining susceptibility of the material. Of interest, SrC3 also had the lowest OIL thickness compared with strontium-glass filled RBCs (Figure 3.1). Furthermore, BaC1 and BaC2 were significantly less susceptible to staining when compared to SrC1 and SrC2. Interestingly, for the least viscous RBC types, BaC3 and BaC4 exhibited significantly greater colour change than SrC3 and SrC4 in both air and nitrogen, respectively, which share the same resin constituents (Figure 3.7b, c). This may imply that specific filler type/resin combinations may affect the stain resistance of RBCs. A previous study reported that porosity of glass filler particles increased staining susceptibility of an RBC (Iazzetti, 2001), although the barium and strontium glass filler particles were different than those used in the authors study, similar processes may be responsible. In another study, the authors reported an RBC with high colour instability, which was unexpected as it was a based on a hydrophobic resin with low water sorption values. (Dietschi et al., 1994). The authors attributed the increased stain susceptibility to the filler phase of the RBC which was composed of quartz, yttrium fluoride and pyrolytic silica particles. However, the exact mechanisms of filler type/resin interactions and their effect on staining susceptibility in the current investigation should be further studied and clarified.

4.3.2 The staining susceptibility of commercial composites

A previous report suggested that most water sorption of RBC specimens occurred during the first week of storage in water, as water sorption may be partially responsible for staining susceptibility, it follows that most of staining may also occur during the first week (Dietschi et al., 1994), therefore in the current investigation, a storage period of 7 days was selected.

In the present investigation, similarly to the experimental resins and RBCs, all commercial RBCs that were cured in nitrogen were more stain resistant than those cured in an atmospheric air (Figure 3.8); we can therefore assume that the presence of an OIL on the upper surface of the specimens may increase the staining susceptibility of the material as the increased diffusion of oxygen into the poorly polymerised surface material will result in increased stain susceptibility, as previous studies reported that oxygen inhibited methacrylate resin may be more susceptible to stain uptake (de Gee et al., 1984; Park et al., 2004). Numerous studies have reported that hydrophilic monomers are more susceptible to water sorption than hydrophilic monomers (Dietschi et al., 1994; Douglas and Craig, 1982; Iazzetti, 2001; Reis et al., 2003; Satou et al., 1989), it has also been reported that stain susceptibility is directly influenced by the resin systems ability to uptake water. This was in agreement with the current investigation where Filtek™ Z250 was significantly more stain resistant than Z100. As differences in the filler component of both Filtek™ Z250 and Z100 are negligible, the main difference lies in the substitution of the majority of TEGDMA in Z100 with BisEMA and UDMA in Filtek™ Z250, both of which are more hydrophilic than TEGDMA, thus the increased staining of Z100 in air compared with Filtek™ Z250 can be explained by the increased water sorption of high TEGDMA content present within the unreacted OIL of Z100 compared to Filtek™ Z250. Interestingly, when Filtek™ Z250 and Z100 are cured in nitrogen an opposite significant trend occurs, where Filtek™ Z250 is more stain susceptible. This may be attributed to the increased TEGDMA content in Z100 which because of its low

molecular weight and flexibility provides an increased cross-linked structure in surface layers where no atmospheric oxygen is present, thus no OIL is formed (Elliott et al., 2001; Floyd and Dickens, 2006).

A significantly reduced staining susceptibility on the surfaces of Filtek™ Silorane compared with that of Filtek™ Z250 and Z100 was observed in the current study when polymerised in both atmospheric air and nitrogen. This reduction can be attributed to the cationic ring-opening polymerisation associated with the oxirane groups within Filtek™ Silorane which are insensitive to oxygen resulting in a low OIL at the surface of the specimen, which may be a factor in the high stain resistance of Filtek™ Silorane. Furthermore, differences in monomer chemistry of Filtek™ Silorane compared with Filtek™ Z250 and Z100, where the hydrophobicity of the siloxane groups improves stability in biological fluids (Eick et al., 2006) and significantly reduces water uptake compared with conventional material types (Palin et al., 2005) thus reduces stain uptake.

5.0 CONCLUSIONS AND FURTHER WORK

5.1 Conclusions

Within the limitations of the current investigation, a number of conclusions can be proposed:

No oxygen inhibition layer (OIL) was measurable on any test material when specimens were polymerised in a nitrogen atmosphere. The oxygen inhibition layer thickness was measurable on specimens polymerised in atmospheric air where the OIL increased with decreasing viscosity, mainly as a result of increasing TEGDMA content.

The addition of filler particles to a resin system complicates the effects of resin viscosity and oxygen diffusion. The interactions between the resin and different filler particle size and material warrant further investigation to elucidate the relationship.

Filtek™ Silorane exhibited an oxygen inhibition layer, which is contrary to expectations. However, this layer was significantly less than that of the methacrylate-based materials. Thus we can conclude that inhibition thickness varies with monomer chemistries.

Furthermore, we can conclude that:

Incremental bond strength is not dependant on surface inhibition since no differences in bond strength were observed between air and nitrogen atmosphere for any experimental or commercial material following immediate placement. Therefore, for restorations requiring

multiple increments which are placed on fresh material, the bond strengths between layers of Filtek™ Silorane should be no different to conventional methacrylate restoratives.

Interfacial bond strengths decreased over time, presumably as a result of free-radical decay. However, interfacial bond strengths between Filtek™ Silorane specimens decreased more rapidly than that of the methacrylate based materials, with a higher percentage of adhesive failures. This finding has implications in clinical repair of Filtek™ Silorane restorations. However, in clinical situations, the restorative surface will most likely be roughened with a bur prior to undergoing repair and the use of an adhesive agent will be mandatory, thus further research into Filtek™ Silorane bonding agents will be required to further explore this issue.

In addition it may be concluded from the findings of the current work that:

Test materials that were polymerised in a nitrogen atmosphere without the presence of a surface oxygen inhibition layer were significantly more stain resistant than their atmospheric air polymerised counterparts.

In general, increased levels of TEGDMA within the material significantly increased the staining susceptibility. However, the presence of filler particles complicated the relationship. This suggests that differences in filler type, size and resin-filler interactions may significantly affect staining susceptibility and thus warrants further investigation

Filtek™ Silorane was significantly more stain resistant than both commercial methacrylate based materials (Z100 and Filtek™ Z250). This phenomenon was explained by the relative

hydrophobicity of Filtek™ Silorane which imparted favourable water sorption properties that helped lessen the amount of stain uptake.

Therefore, it can be concluded that the presence of the oxygen inhibition layer on the surface layer of methacrylate based materials significantly increases the stain susceptibility of the material. From a clinical standpoint, the utmost effort should be done to remove the unreacted layer from the surface of restorations by physical removal with finishing burs and points, especially in aesthetically visible areas of the mouth,.

5.2 Further Work

Determination of Filtek™ Siloranes oxygen inhibition layer thickness by non-optical methods such as FTIR, or MRI to confirm the findings of this work, as one concern of the present investigation is that a non-optical method may overly rely on the subjective measurement of the observer.

Further testing of the Silorane to Silorane shear and micro-tensile bond strengths with and without the addition of an intermediary bonding agent is also an area of research which should be developed further as little is currently known about Filtek™ Siloranes proprietary bonding agent developed for exclusive use by Filtek™ Silorane. Additional research is required to determine Filtek™ Siloranes bond strength to conventional methacrylate based materials in an effort to establish compatibility for repair procedures.

Although Filtek™ Silorane has been shown to be exceptionally stain resistant when compared to commercially available RBC restorative, this study has also shown that similar

levels of stain resistance can be achieved with conventional methacrylate based resins, further research is require to determine the optimum relationship between different filler particle materials and sizes and different resin mixtures to result in a material with excellent stain resistance without sacrificing the mechanical properties of the resulting RBC restorative .

Investigation and elucidation of the factors that affect the particle-resin interface in RBC materials and its effects on RBC properties such as water sorption, stain resistance, and bonding is also an area which is severely lacking in quality research.

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