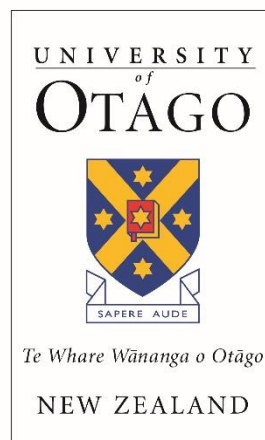


ADHESION BETWEEN YTTRIUM STABILISED ZIRCONIA CERAMIC AND INDIRECT COMPOSITE RESIN



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Abstract:

Purpose:

The purpose of this study was to determine the bond energy of three indirect restorative composite veneering materials to Yttrium stabilised zirconia (YZr) by using the strain energy release rate testing method.

Materials and methods:

Three indirect composite veneering materials (Ceramage – Shofu Inc; Signum - Heraeus Kulzer GmbH; Sinfony- 3M ESPE) were bonded to YZr plates with and without sandblasting and manufacturer's recommended bonding agents. Utilising the method described by Cheng *et al.* (1999), a 12mm composite rod was bonded to a YZr plate with two opaque layers at the bond surface interface then, brought to failure using a universal testing machine. G-values were calculated. One-way ANOVA and Dunnetts's tests ($P = 95\%$) were performed. Homogeneity of the variables was confirmed with Bartlett's test.

Results:

No significant difference in G-values was observed between the control groups of Ceramage, Signum and Sinfony. Within the Ceramage group, there was no significant difference between the surface treatments. In the Signum group no significant difference was observed between the control and sandblasted groups as well as between the sandblasted surfaces in combination with the bonding agent group, but no significant difference between the control and bonding agent alone was observed. In the Sinfony group, no significant difference was observed between the control and sandblasted

groups, but a significant difference was observed between the control and sandblasted with bonding agent groups.

Conclusion:

The application of acidic functional phosphate monomer MDP or silicatising the YZr surfaces before veneering with indirect composite veneering material, resulted in higher bond energy results. Sandblasting the YZr surfaces with 120grit AlO_2 only, did not increase the bond energy. The elastic modulus of the composite material influenced the bond energy required for detachment from to the YZr substructure.

Keywords: Fracture mechanics; Zirconia; Composites; Primers and coupling agents; Interfacial bond energy.

Publications and presentations:

Poster presentation:

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List of acronyms and abbreviations:

| | |
|------------------|-----------------------------------------------------|
| 6-MHPA | 6-methacryloxyhexyl phosphonoacetate. |
| a | crack length |
| ac | critical crack length |
| AlO ₂ | aluminium oxide |
| bis-GMA | 2,2'-bis-[4-(methacryloxypropoxy)-phenyl]-propane) |
| °C | degrees celsius |
| c | critical |
| C&B | crown and bridge |
| CAD/CAM | computer aided design/ computer aided manufacturing |
| CER | ceramage |
| D | diameter of the composite cylinder |
| E | elastic modulus |
| FEA | finite element analysis |
| F | maximum load at failure |
| G | fracture energy |
| G _c | critical energy release rate |
| G _{Ic} | strain energy release rate |
| HfO ₂ | hafnium oxide |

| | |
|------------------|--------------------------------------|
| I | mode 1 (opening mode) |
| ISO | international standards organisation |
| J/m ² | joules per square metre |
| K | stress intensity factor |
| K _{IC} | fracture toughness |
| KN | kilo newton |
| L | distance to loading point (mm) |
| MDP | phosphate monomer |
| MMA | methyl methacrylate |
| Mpa | mega pascal |
| MPS | 3-methacryloxypropyltrimethoxysilane |
| PFM | porcelain fused to metal |
| PJC | porcelain jacket crown |
| PVC | polyvinyl chloride |
| SEM | scanning electron microscopy |
| Si | silicon |
| SIG | signum |
| SIN | sinfony |
| SiO ₂ | silicon oxide |
| TEGDMA | tri (ethylene glycol) dimethacrylate |

| | |
|-------------------------------|----------------------------------|
| TiO ₂ | titanium oxide |
| TZP | tetragonal zirconia poly-crystal |
| UDMA | urethane di-methacrylate |
| Y ₂ O ₃ | yttrium oxide |
| YZr | yttrium stabilised zirconia |
| ZrO ₂ | zirconium oxide |
| Δa | change in crack length |

Chapter 1: Introduction.

Yttrium-stabilised Zirconia Ceramic (YZr) has been developed as a framework material for tooth-supported or implant-supported all-ceramic restorations and implant abutments. This is due to its biocompatibility, low bacterial adhesion, high strength and natural aesthetic properties (Piconi and Maccaoro, 1999; Vult Von Steyern, 2005; Raigrodski, et al. 2006; Göstemeyer et al. 2012).

Failures, with and without exposing the underlying framework, in the form of chipping within the veneering porcelain have been reported in the literature (Anusavice, et al. 2007; Fischer, 2007; Guess, et al. 2008; Fischer, 2008; Komine, et al 2009; Al-Amleh, et al. 2010; Göstemeyer, et al. 2012; Raigrodski, et al. 2012). As an alternative to porcelain, Komine *et al.* (2013) reported on the use of composite resin as a viable veneer system. Composite veneering materials are relatively easy to work with, with the added benefit of very little shrinkage during the curing process. An additional advantage of using composite resin is the energy absorption of composite resulting in a preferable tactile response in natural teeth opposing an implant (Hammerle, 1995; Komine, et al. 2009).

However, due to the chemical inertness of YZr, bonding remains problematic (Kern and Wagner, 1998; Lüthy, et al. 2006; Yang, et al. 2007; Fischer, 2008; Kitayama, et al. 2010; Piascik, et al. 2011; Thompson, et al. 2011; Ural, et al. 2011; Komine, 2012; Liu, et al. 2014). Limited research is available on the bond strength between indirect composite materials and YZr. Published results from which were predominantly obtained by using the shear bond test (Komine, et al. 2012; Komine, et al. 2013) while no reports have been found on the use of the strain energy release rate approach as a

method of testing adhesion energy. The validity of using the strain energy release rate as a method of measuring adhesion of bilayers has been reported by Sun *et al* (2000).

The purpose of this study was to determine the bond energy between YZr and three indirect restorative composite veneering materials using the strain energy release approach.

Chapter 2: Literature review

2.1 Introduction

Prosthodontic treatment involves the restoration or replacement of a compromised dentition. In recent decades the development of restorative dental materials has developed exponentially and became the cornerstone of everyday dental treatment. Modern materials, such as high strength ceramics, more specifically, Yttrium stabilised zirconia (YZr) has gained popularity in the field of fixed prosthodontic treatment, especially in the field of dental implantology (Bressa, et al. 2011). However, attaining predictable results when veneering YZr abutments with ceramic still remains a challenge. Consequently alternative veneering materials such as indirect veneering composites are explored.

The purpose of this literature review is to provide brief overviews of:

- a) Dental implant abutment materials.
- b) Yttrium-stabilised Zirconia in dentistry.
- c) Indirect veneering composite as a restorative material
- d) Bond energy release fracture mechanics
- e) Failure analysis using microscopy.

2.2 Dental implant abutment materials

Traditionally, gold was the material of choice to manufacture custom abutments and restorative super-structures. With the global increase in gold prices and the development of CAD/CAM technology, more cost effective restorative materials like titanium and high strength ceramics gained popularity and further development (Sailer, et al. 2009).

Abrahamsson (1998) investigated abutments made of titanium, gold and ceramic to determine the influence of the type of material on the quality of the mucosal barrier that formed after placement. It was suggested that the surface layers of gold alloys are not as chemically stable as those of titanium and ceramics. An important observation was that the gold alloy abutments were seemingly unable to promote mucosal healing that includes a zone of connective tissue attachment.

Titanium offers material stability and is very resistant to distortion. However, there are disadvantages associated with titanium abutments which include the colour of the alloy itself, which often results in a greyish discolouration of the peri-implant mucosa, especially where the mucosa is thin, impairing the aesthetic result of implant restoration (Zembic, et al. 2009). In cases where veneering ceramic directly onto the abutment is required, the volatility of oxidation of titanium at high temperatures might result in porcelain-to-metal interface fractures or delamination (Adachi, et al. 1990).

As an alternative, abutments made out of the high-strength ceramics like YZr can be used in the aesthetic zone. Zirconia based ceramics can potentially provide better fracture resistance and long-term viability when compared to other inorganic non-metallic alternatives (Thompson, et al. 2011).

2.3 Yttrium-stabilised Zirconia in Dentistry

Zirconia is a polymorphic material which displays more than one crystal phase, depending on the temperature and pressure conditions (Cavalcanti, et al. 2009). Pure Zirconia can present itself in three temperature dependant phases: monoclinic, which remains stable at room temperature to 1170°C. When temperature increase from 1170°C - 2370°C, the crystal structure changes to tetragonal followed by the cubic phase at 2370°C (This phase is not used in dentistry)(Figure 1).

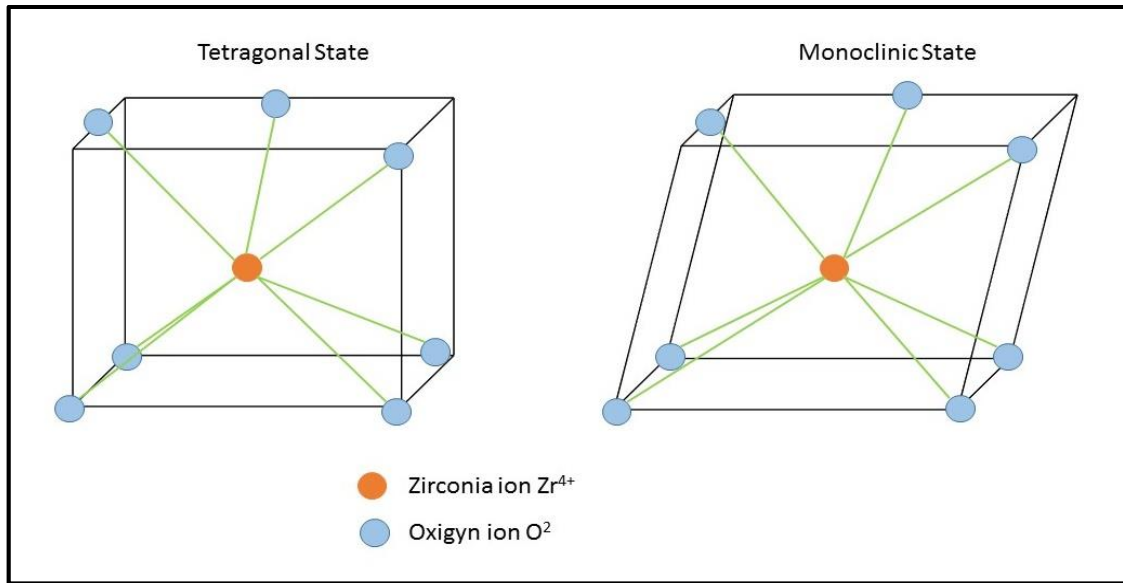


Figure 1. Tetragonal (left) and monoclinic (right) crystallographic phases of zirconia (Vagkopoulou, et al. 2009).

These phase transformations that occur during the cooling stage, are associated with volumetric expansion; which prevents the use of pure zirconia in dentistry. However, the addition of 2 - 3% stabilising oxides such as yttrium, transforms the pure zirconia into a multiphase material. This addition ensures a stabilised tetragonal zirconia polycrystal (TZP) at room temperature. This TZP presents characteristics, such as: high elastic modulus and compressive strength which are advantageous in the medical and dental field (Cavalcanti, et al. 2009; Hisbergues, et al. 2009; Al-Amleh, et al. 2010; Gungor, et al. 2014). One of most important characteristics of TZP is the 4.5% volumetric increase associated with the reversible tetragonal-to-monoclinic phase transformation; this process is known as transformation toughening, which shields crack tips and precludes further crack propagation (Figure 2)(Conrad, et al. 2007; Griggs, 2007).

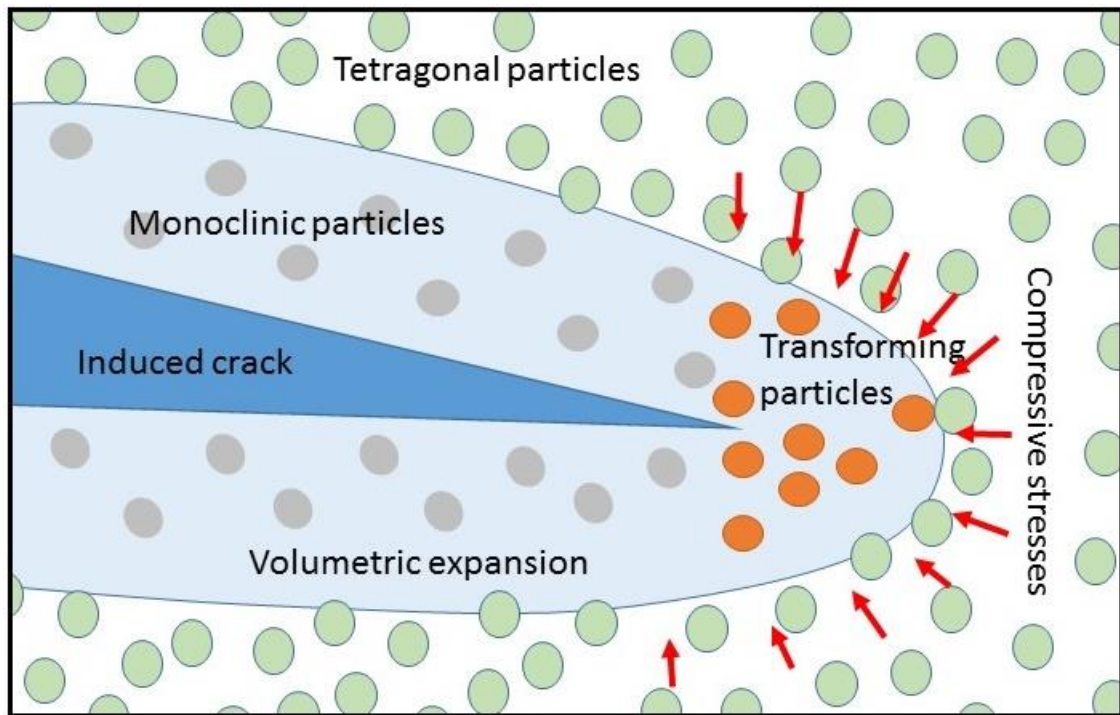


Figure 2. Illustration of YZr transformation toughening occurring in the crack tip (Vagkopoulou, et al. 2009).

Due to these unique material properties and high aesthetics; YZr is considered to be a “Biosmart” material (Badami and Ahuja, 2014) and is used in a wide range of clinical applications. The use of high strength dental ceramics as substructures has become a popular alternative to traditional porcelain fused to metal restorations. As a result, YZr is used in the production of single and multiple unit restorations as well as the production of high strength ceramic custom implant abutments (Gungor, et al. 2014).

Custom implant abutments, are individually shaped according to the anatomical needs of the respective implant site (Zembic, et al. 2009). Often the implant site provides a less than adequate mucosal profile caused by severe alveolar resorption or anatomical anomalies. This profile may result in an unfavourable clinical crown to mucosa ratio (Thompson, et al. 2011; Koizuka, et al. 2013). In order to solve this problem, the technician may elect to shorten the crown length, by veneering the abutment with an

artificial soft tissue profile (Hagiwara, et al. 2007; Jansen van Vuuren, et al. 2007; Peché, et al. 2011).

YZr frameworks can be veneered with ceramics in two ways. Traditionally, ceramic powder is mixed with a liquid to form a ceramic slurry. This is used to incrementally build up the desired profile. Another way is to wax-up the desired restoration profile and follow traditional wax elimination techniques proceeding to hot pressing ceramic into the vacated mould.

2.4 Ceramic as veneering material.

Ceramic materials were first used in dentistry to fabricate porcelain denture teeth in the late 1700s. Almost a decade later Dr. Charles Land produced the first porcelain jacket crown (PJC) (Hopp and Land, 2013). PJCs are manufactured by covering the abutment die with a Platinum foil which acts as support for the brittle ceramic. Ceramic is built-up over the platinum foil and fired. After cooling the foil is removed from the restoration, leaving a metal free ceramic restoration. With the advent of metal-ceramic restorations, leucite containing porcelain was introduced. The increased coefficients of thermal expansion associated with these ceramics permitted bonding to newly formulated gold alloys (Hopp and Land, 2013). These ceramics later evolved to permit veneering to high strength ceramics like alumina and zirconia.

Traditionally, glass ceramic would be the material of choice to veneer YZr frameworks. This might be to construct a simple crown or short span bridge or a more complicated full-arch restoration including artificial soft tissue replacement. However, in the case of long-span restorations some problems are associated with the materials used for the a) implant substructure, b) the surface area to be veneered, as well as, most significantly, c) the veneering material itself.

Veneering ceramics undergo a volumetric shrinkage upon sintering, the amount of which is much more pronounced in larger restorations with multiple units, or when additional sintering firings are required to include additional structures such as interdental papillae reconstructions (Peché, et al. 2011).

In spite of the advantageous material properties, two major drawbacks are associated with YZr restorations when compared to metal ceramic restorations. The first was reported in earlier clinical studies which revealed high fracture rates of porcelain– veneered YZr restorations; these fractures mainly manifested as chipping of the veneering ceramic (Conrad, et al. 2007; Al-Amleh, et al. 2010). These issues however, seem to have been resolved due the adaption to slower heating and cooling rates as shown by the work of by Choi *et al.*(2011) and Benetti *et al.* (2014). The second problem is the phenomenon known as low temperature degradation. This is an accelerated aging process that occur in YZr in the presence of water during which spontaneous phase transformation takes place from tetragonal crystal structure back to the weaker monoclinic state, potentially causing catastrophic failure of the restoration. This can be further aggravated by sandblasting the YZr surface (Agustin-Panadero, et al. 2014; Cavalcanti, et al. 2009). Therefore some clinicians prefer the use of heat-pressed ceramics onto the YZr frameworks.

2.5 Heat-pressed ceramics as a veneering material.

Heat-pressed ceramic can be leucite- or lithium disilicate-based and is a popular choice for manufacturing dental prosthesis, as dental technicians are already familiar with the process involving a lost wax technique. A number of benefits have been reported to lithium disilicate-based heat-pressed ceramics as opposed to the more traditional method of sintering. Fracture toughness and flexural strength values are higher than traditional

feldspathic porcelains (Denry and Holloway, 2010). In addition, pressed ceramics are reported to have excellent marginal fit, as well as better surface contact between the zirconia core and the pressed veneer resulting in higher bond strength between zirconia core and pressed ceramics (Aboushelib, et al. 2005; Lopez-Molla, et al. 2010). However, one of the greatest disadvantages of any ceramic system is the amount of enamel wear caused to the opposing natural dentition. A study done by Sripetchdanond and Leevailoj (2014) showed that glass ceramics caused more enamel wear than monolithic zirconia and composite resin. In addition, enamel, opposed to composite resin before and after testing, indicated no significant difference in surface roughness measurements. Another study by Ramp *et al.* (1997) indicated that lithium silicate- based pressed ceramic resulted in similar enamel wear as glass ceramic. Currently, larger span restorations are challenging to over press, simply because of the muffle size and ingot size limitations.

Taking these factors into account, indirect composite veneering materials offer a promising alternative. However the bond strength between YZr and these materials needs further investigation.

2.6 Indirect Veneering composite as a restorative material.

In 1962, Dr Rafael Bowen developed the first high-molecular weight, di-functional monomer known as *bis*-GMA, also known as Bowen's resin. This material forms a highly durable cross-linked matrix, and organic silane compound (coupling agent) to bind inorganic filler particles to the matrix. Many of today's modern restorative materials still use this technology. Continuous development to improve polishability and appearance lead to the eventual development of micro and nano-filled composites (Rueggeberg, 2002; Anusavice, et al 2013). Modern composite resins have filler distribution of 65% - 77% volume filler content, resulting in a smooth surfaced

restoration with high wear resistance and minimal polymerisation shrinkage (Rawls 2013).

Modern composites also exhibit plastic and viscoelastic properties, which may prove advantageous in high stress bearing areas, such as posterior implant supported prostheses (Hejazi and Watts 1999; Kramer, et al. 2000; Vaidyanathan and Vaidyanathan 2001). Çiftçi and Canay (2000), reported that ceramic and gold alloy implant supported restorations produced a 15% higher stress level in the cortical bone around cervical areas of implants when oblique and horizontal forces were applied, than that of restorations manufactured with reinforced composite materials. Takahashi *et al.* (2002) reported no significant difference between the failure rates of traditional implant supported porcelain fused to metal (PFM) restorations when compared to composite layered implant supported restorations.

Gingiva-coloured composite resins have been successfully used to restore deficient gingival architecture on different alloys for implant frameworks (Hagiwara, et al. 2007; Jansen van Vuuren, et al. 2007; Peché, et al. 2011). By using indirect composite material, the technician has more control over the end result, as there are no further sintering firings being required and a more manageable polymerisation shrinkage, typically between 2% - 3% (Labella, 1999). Aesthetic results are more predictable with composite materials, as the technician is able to monitor and adjust the shade during the build-up process.

The use of indirect veneering composite resin was shown to be a viable alternative to conventional layering and pressed ceramics as a veneering material to YZr by Komine *et al.* (2009) (Komine et al. 2012).

A Pubmed and manual search with the key words “Indirect composite materials AND zirconia” and “Bond strength AND zirconia AND indirect composite” resulted in 14 related publications. The papers are summarised in table 1.

Table 1. Summary of reports on bond strength between indirect composite veneering material and YZr.

| Study | Zirconia material | Layering indirect composite material | Surface treatment of YZr | Mean bond strength values [MPa] | Test method |
|--------------------------------|----------------------------------|---------------------------------------------|--------------------------------------------------------------|----------------------------------------|--------------------|
| Kobayashi <i>et al.</i> (2009) | Katana Zirconia (Noritake) | Estenia C&B (Kuraray Medical) | No treatment | 0.2 | Shear bond test |
| | | | All Bond 2 Primer B (Bisco) | 10.1 | |
| | | | Alloy primer (Kuraray Medical) | 15.6 | |
| | | | Clearfil Ceramic Primer (Kuraray Medical) | 19.8 | |
| | | | Clearfil Photo Bond (Kuraray Medical) | 21.6 | |
| | | | Clearfil Photo Bond + Activator (Kuraray Medical) | 24.2 | |
| | | | Estenia Opaque Primer (Kuraray Medical) | 14.7 | |
| | | | Porcelain Liner M Liquid A (Sun Medical) | 11.9 | |
| | | | V-Primer (Sun Medical) | 0.1 | |
| Komine <i>et al.</i> (2009) | Katana Zirconia (Noritake) | Estenia C&B (Kuraray Medical) | All Bond 2 Primer B (Bisco) (5000 thermocycles) | 4.3 | Shear bond test |
| | | | Alloy primer (Kuraray (5000 thermocycles) | 17.6 | |
| | | | Medical) AZ Primer (Shofu Inc.) (5000 thermocycles) | 17.3 | |
| | | | Estenia Opaque Primer (Kuraray Medical) (5000 thermocycles) | 15.5 | |
| | | | Porcelain Liner M Liquid A (Sun Medical) (5000 thermocycles) | 12.2 | |
| Chihaya <i>et al.</i> (2010) | Procera Zirconia (Nobel Biocare) | Estenia C&B (Kuraray Medical) | Add-on primer + Modeling liquid (Kuraray Medical) | 22 | Tensile bond test |
| Miyaji <i>et al.</i> (2010) | Aadva Zr (GC) | Gradia (GC) | No treatment | 2.3 | Shear bond test |
| | | | Espe Sil (3M ESPE) | 8.9 | |
| | | | Rocatec + Espe Sil (3M ESPE) | 15.7 | |

| <i>Study</i> | <i>Zirconia material</i> | <i>Layering indirect composite material</i> | <i>Surface treatment of YZr</i> | <i>Mean bond strength values [MPa]</i> | <i>Test method</i> |
|------------------------------|----------------------------|---------------------------------------------|-------------------------------------------------------------------------|----------------------------------------|--------------------|
| Hatta <i>et al.</i> (2011) | YTZ (Nikkato) | Estenia C&B (Kuraray Medical) | Zirconia coated with porcelain S3 Bond (Kuraray Medical) | 10.7 | Shear bond test |
| | | | Rocatec + Espe Sil (3M ESPE) | 12.5 | |
| Fushiki <i>et al.</i> (2011) | Katana Zirconia (Noritake) | Estenia C&B (Kuraray Medical) | Zirconia coated with porcelain No treatment | 13.8 | Shear bond test |
| | | | Clearfil Photo Bond (Kuraray Medical) | 14.6 | |
| | | | Clearfil Photo Bond + Activator (Kuraray Medical) | 18.2 | |
| | | | Estenia Opaque Primer (Kuraray Medical) | 14.5 | |
| | | | Porcelain Liner M Liquid B (Sun Medical) | 17.3 | |
| | | | Clearfil Photo Bond (Kuraray Medical) (20,000 thermocycles) | 15.8 | |
| | | | Clearfil Photo Bond + Activator (Kuraray Medical) (20,000 thermocycles) | 23.2 | |
| | | | Estenia Opaque Primer (Kuraray Medical) Porcelain(20,000 thermocycles) | 16.2 | |
| | | | Liner M Liquid B (Sun Medical) (20,000 thermocycles) | 21.0 | |
| Fushiki <i>et al.</i> (2012) | Katana Zirconia (Noritake) | Estenia C&B (Kuraray Medical) | Zirconia sandblasted (untreated) | 0.1 | Shear bond test |
| | | | Cearfil Photo Bonded (Kuraray Medical) | 13.1 | |
| | | | Clearfil Photo Bond + Activator (Kuraray Medical) | 13.3 | |
| | | | Estenia Opaque Primer (Kuraray Medical) | 7.3 | |
| | | | Porcelain Liner M Liquid B (Sun Medical) | 0.2 | |

| <i>Study</i> | <i>Zirconia material</i> | <i>Layering indirect composite material</i> | <i>Surface treatment of YZr</i> | <i>Mean bond strength values [MPa]</i> | <i>Test method</i> |
|-----------------------------|----------------------------|---------------------------------------------|------------------------------------------------------------------|----------------------------------------|--------------------|
| | | | <i>Zirconia coated with porcelain and sandblasted</i> | 3.0 | |
| | | | Cearfil Photo Bonded (Kuraray Medical) | 12.6 | |
| | | | Clearfil Photo Bond + Activator (Kuraray Medical) | 17.9 | |
| | | | Estenia Opaque Primer (Kuraray Medical) | 11.4 | |
| | | | Porcelain Liner M Liquid B (Sun Medical) | 14.5 | |
| | | | <i>Zirconia coated with porcelain and Hydrofluoric acid etch</i> | 3.8 | |
| | | | Cearfil Photo Bonded (Kuraray Medical) | 11.1 | |
| | | | Clearfil Photo Bond + Activator (Kuraray Medical) | 16.2 | |
| | | | Estenia Opaque Primer (Kuraray Medical) | 8.8 | |
| | | | Porcelain Liner M Liquid B (Sun Medical) | 14.0 | |
| | | | | | |
| | | | | | |
| | | | | | |
| | | | | | |
| Komine <i>et al.</i> (2012) | Katana Zirconia (Noritake) | Estenia C&B (Kuraray Medical) | Zirconia as milled (untreated) | 0.4 | Shear bond test |
| | | | Zirconia HF acid etched | 1.0 | |
| | | | Zirconia 600grt sandpaper ground | 5.0 | |
| | | | Zirconia sandblasted at 0.05MPa | 7.3 | |
| | | | Zirconia sandblasted at 0.1MPa | 12.8 | |
| | | | Zirconia sandblasted at 0.2MPa | 13.2 | |
| | | | Zirconia sandblasted at 0.4MPa | 14.2 | |
| | | | Zirconia sandblasted at 0.6MPa | 14.2 | |
| | | | Zirconia as milled (untreated) (20,000 thermocycles) | 0.3 | |

| <i>Study</i> | <i>Zirconia material</i> | <i>Layering indirect composite material</i> | <i>Surface treatment of YZr</i> | <i>Mean bond strength values [MPa]</i> | <i>Test method</i> |
|-----------------------------|--------------------------|---------------------------------------------|----------------------------------------------------------|----------------------------------------|--------------------|
| | | | Zirconia HF acid etched (20,000 thermocycles) | 0.2 | |
| | | | Zirconia 600grt sandpaper ground (20,000 thermocycles) | 6.9 | |
| | | | Zirconia sandblasted at 0.05MPa (20,000 thermocycles) | 9.9 | |
| | | | Zirconia sandblasted at .01MPa (20,000 thermocycles) | 14.3 | |
| | | | Zirconia sandblasted at 0.2MPa (20,000 thermocycles) | 17.4 | |
| | | | Zirconia sandblasted at 0.4MPa (20,000 thermocycles) | 17.6 | |
| | | | Zirconia sandblasted at 0.6MPa (20,000 thermocycles) | 16.7 | |
| Shimoe <i>et al.</i> (2012) | Zircon base (Denseply) | Estenia C&B (Kuraray Medical) | Zirconia (sintered) with MDP primer | 1.1 | Shear bond test |
| | | Gradia (GC Corp.) | Zirconia Sandblasted 10 seconds | 13.7 | |
| | | | Zirconia Sandblasted 20 seconds | 13.6 | |
| | | | Zirconia heat treated at 1200°C | 6.3 | |
| | | Estenia C&B (Kuraray Medical) | Zirconia (sintered) with MDP primer | 18.3 | |
| | | | Zirconia Sandblasted 10 seconds | 24.6 | |
| | | | Zirconia Sandblasted 20 seconds | 23.0 | |
| | | | Zirconia heat treated at 1200°C | 19.7 | |
| | | Gradia (GC Corp.) | Zirconia (sintered) with MDP prime (20,000 thermocycles) | 1.2 | |

| <i>Study</i> | <i>Zirconia material</i> | <i>Layering indirect composite material</i> | <i>Surface treatment of YZr</i> | <i>Mean bond strength values [MPa]</i> | <i>Test method</i> |
|----------------------------|----------------------------|---------------------------------------------|-----------------------------------------------------------|----------------------------------------|--------------------|
| | | Estenia C&B (Kuraray Medical) | Zirconia Sandblasted 10 seconds (20,000 thermocycles) | 12.4 | |
| | | | Zirconia Sandblasted 20 seconds (20,000 thermocycles) | 13.9 | |
| | | | Zirconia heat treated at 1200°C (20,000 thermocycles) | 3.1 | |
| | | | Zirconia (sintered) with MDP primer (20,000 thermocycles) | 1.4) | |
| | | | Zirconia Sandblasted 10 seconds (20,000 thermocycles) | 22.4 | |
| | | | Zirconia Sandblasted 20 seconds (20,000 thermocycles) | 21.5 | |
| | | | Zirconia heat treated at 1200°C (20,000 thermocycles) | 6.9 | |
| Koizuka <i>et al.</i> 2013 | Katana Zirconia (Noritake) | Ceramage Gum (Shofu) | Sintered Zirconia untreated | 0.2 | Shear bond test |
| | | | Alloy Primer (Kuraray Medical) | 8.0 | |
| | | | Estenia Opaque Primer (Kuraray Medical) | 7.0 | |
| | | | Metal Link (Shofu Inc) | 6.2 | |
| | | | V-Primer (Sun Medical) | 4.4 | |
| | | | Sandblasted Zirconia untreated | 7.3 | |
| | | | Alloy Primer (Kuraray Medical) | 14.5 | |
| | | | Estenia Opaque Primer (Kuraray Medical) | 15.1 | |
| | | | Metal Link (Shofu Inc) | 13.9 | |
| | | | V-Primer (Sun Medical) | 11.1 | |

| <i>Study</i> | <i>Zirconia material</i> | <i>Layering indirect composite material</i> | <i>Surface treatment of YZr</i> | <i>Mean bond strength values [MPa]</i> | <i>Test method</i> |
|-----------------------------|----------------------------|---------------------------------------------|-----------------------------------------------------------------------------|----------------------------------------|--------------------|
| Komine <i>et al.</i> 2013 | Katana Zirconia (Noritake) | Estenia C&B (Kuraray Medical) | Alloy Primer (Kuraray Medical) | 15.6 | Shear bond test |
| | | | Cearfil Ceramic Primer (Kuraray Medical) | 19.8 | |
| | | | Clearfil Photo Bond (Kuraray Medical) | 21.6 | |
| | | | Clearfil Photo Bond + Activator (Kuraray Medical) | 24.2 | |
| | | | Estenia Opaque Primer (Kuraray Medical) | 14.7 | |
| | | | Porcelain Liner M Liquid A (Sun Medical) | 11.9 | |
| | | | Alloy Primer (Kuraray Medical) (100,000 thermocycles) | 16.2 | |
| | | | Cearfil Ceramic Primer (Kuraray Medical) (100,000 thermocycles) | 15.9 | |
| | | | Clearfil Photo Bond (Kuraray Medical) (100,000 thermocycles) | 22.7 | |
| | | | Clearfil Photo Bond + Activator (Kuraray Medical) (100,000 thermocycles) | 23.9 | |
| | | | Estenia Opaque Primer (Kuraray Medical) (100,000 thermocycles) | 16.3 | |
| | | | Porcelain Liner M Liquid A (Sun Medical) (100,000 thermocycles) | 9.4 | |
| Komine <i>et al.</i> (2013) | Katana Zirconia (Noritake) | Estenia C&B (Kuraray Medical) | Alloy Primer (Kuraray Medical) | 14.5 | Shear bond |
| | | | Clearfil Photo Bond (Kuraray Medical) | 29.1 | |
| | | | Clearfil Photo Bond + Activator (Kuraray Medical) | 26.5 | |
| | | | Estenia Opaque Primer (Kuraray Medical) | 15.1 | |
| | | | Metal Link (Shofu Inc) | 13.9 | |
| | | | V-Primer (Sun Medical) | 11.1 | |

| <i>Study</i> | <i>Zirconia material</i> | <i>Layering indirect composite material</i> | <i>Surface treatment of YZr</i> | <i>Mean bond strength values [MPa]</i> | <i>Test method</i> |
|-----------------------------|----------------------------|---------------------------------------------|----------------------------------------------------------------------------|----------------------------------------|---------------------|
| | | | Alloy Primer (Kuraray Medical) (20,000 thermocycles) | 5.0 | |
| | | | Clearfil Photo Bond (Kuraray Medical) (20,000 thermocycles) | 11.9 | |
| | | | Clearfil Photo Bond + Activator (Kuraray Medical) (20,000 thermocycles) | 12.1 | |
| | | | Estenia Opaque Primer (Kuraray Medical) (20,000 thermocycles) | 5.2 | |
| | | | Metal Link (Shofu Inc) (20,000 thermocycles) | 4.9 | |
| | | | V-Primer (Sun Medical) (20,000 thermocycles) | 0.2 | |
| Komine <i>et al.</i> (2014) | Katana Zirconia (Noritake) | Estenia C&B (Kuraray Medical) | Clearfil Photo Bond (Kuraray Medical) | 2.72kN | Cyclic loading |
| | | | Estenia Opaque Primer (Kuraray Medical) | 2.43kN | |
| | | | Zirconia without primer | 2.37kN | |
| Taguchi <i>et al.</i> 2014 | Katana Zirconia (Noritake) | Estenia C&B (Kuraray Medical) | Estenia Opaque Primer (Kuraray Medical) | 2.84kN | Fracture resistance |
| | | | Zirconia without primer | 2.5kN | |

(Komine, et al. 2009; Kobayashi, et al. 2011; Komine, et al. 2012; Komine, 2012b, Komine, et al. 2012c; Shimoe, et al. 2012; Koizuka, et al. 2013; Komine, et al. 2013, Komine, et al 2013b; Komine, et al. 2014; Taguchi, et al. 2014)

Of the 14 studies listed in the above table 11 studies have performed shear bond tests; one tensile bond test; one cyclic loading and one fracture resistance. All studies evaluated the bond between zirconia ceramic and indirect veneering composite with either modified surface roughness of the YZr by use of sandblasting; or the application

of priming agents; or a combination of both. Four of the studies also included the use of a porcelain liner prior to the application of the indirect composite veneer. Table 1 will be discussed under four sub-headings: Feldspathic porcelain coated YZr; effect of thermocycling in combination with priming agents; effect of sandblasting on the bond between YZr and indirect composite materials, and the effect of priming agents on the bond of YZr and indirect composite materials.

2.6.1 Feldspathic porcelain coated YZr.

The success of a ceramic restoration is partly credited to effective bonding. This refers to the bond between the veneering material and the substructure, or in the case of all-ceramic restorations, the bond between the restoration and the abutment tooth.

Silica based ceramics have microstructural components (leucite) in the matrix that can be selectively eliminated by acids. This process is known as etching and provides the restoration with micro-mechanical retention for cement infiltration (Kelly and Benetti, 2011). YZr on the other hand, is a bio-inert and non-resorbable metal oxide (Gungor, et al. 2014). Furthermore, acid etching produce no effect on the YZr material, because of the lack of silica in this material; therefore, alternative bonding methods should be approached (Blatz, et al. 2003).

Fushiki *et al.* (2012) evaluated the effect of both feldspathic porcelain coating of zirconia frameworks and priming agents on the shear bond strength of an indirect composite material to zirconia ceramic frameworks and included the effect of artificial aging with thermo-cycling. The results also indicated that the use of a silane coupling agent and opaque material yielded durable bond strength between the indirect composite and porcelain coated zirconia. Although Hatta *et al.* (2011) agreed that the bond between

Zirconia ceramic and indirect veneering composite is greatly improved by a layer of feldspathic porcelain, they found that neither surface treatment nor a silane coupling agent produced a significant improvement in the shear bond strength.

2.6.2 Effect of thermocycling in combination with priming agents.

In studies done by Komine and co-workers, (Komine, 2009; Komine, 2013) the strength of the bond between an indirect composite material and YZr ceramics before and after exposure to thermocycling was measured in combination with priming agents.

Their results indicate that the bond strength was influenced by both the type of priming agent and the application of thermocycling. One study however, showed that thermocycling had no effect on the bond strength, but the application of priming agents had (Komine, et al 2012). In a further study done by Komine *et al.* (2014) on the fracture load of indirect veneered zirconia restorations after thermal cycling and cyclic loading in an artificial oral environment, indicated that the use of different primers for surface treatment of YZr copings did not show a statistically significant improvement in the fracture load values of these restorations.

2.6.3 Effect of Sandblasting on the bond between YZr and indirect composite materials.

Sandblasting is a popular method to increase the surface area and roughness for an improved interfacial bond. However, the surface damage initiated by sandblasting causes the YZr to undergo a phase transformation from tetragonal to a monoclinic crystalline arrangement. This causes localised volumetric expansion of about 4% (Conrad, et al. 2007; Griggs, 2007) and reduction in coefficient of thermal expansion. In order to heal this damage and return to the tetragonal zirconia crystalline arrangement, the material

needs to undergo a firing cycle at 1200°C. However, Shimoe *et al.* (2012) showed that heat treating the zirconia after air-abrasion decreases the bond strength with indirect composite materials.

Komine *et al.* (2012) showed that sandblasting at a pressure 0.1 MPa or higher yields satisfactory initial and durable bond strengths between an indirect composite material and zirconia ceramics. In addition, other studies showed that bond strength was positively influenced by sandblasting in combination with the application of priming agents (Koizuka *et al.* 2013; Komine, *et al.* 2013).

2.6.4 Effect of priming agents on the bond of YZr and indirect composite materials.

Priming agents are developed to enhance or establish a chemical bond between the substrate surface and the veneering material. Because of the quasi-chemical inertness of zirconia ceramic (Inokoshi, *et al.* 2014), the material cannot be etched and chemical bonding is a real challenge. However, the application of an acidic functional monomer containing carboxylic anhydride (4-META), phosphoric acid (6-MHPA), or phosphate monomer (MDP) and saline can yield durable bond strengths between indirect veneering composite and YZr (Komine, *et al.* 2009; Kobayashi, *et al.* 2009; Komine, *et al.* 2012, Komine, *et al.* 2012b; Koizuka, *et al.* 2013; Komine, *et al.* 2013; Komine, *et al.* 2014; Taguchi, *et al.* 2014). Özcan and *et al.*, (2008) explains this as a reaction between hydroxyl groups in the MDP and the YZr ceramic, as the result of bonding of a phosphate ester monomer to metal oxides such as chromium, nickel, aluminum, and zirconium dioxides. Another method to possibly increase the bond strength between YZr and composite resin is to attempt to silicatis the YZr surface. Due to the lack of silica in YZr, silica-coating techniques have been explored to utilize the chemical bonding provided by silanization. The use of a tribochemical silica coating is a common practice

for coating metal alloys and alumina- and zirconia-based dental ceramics (Thompson, et al. 2011). The tribochemical process of silicatising the veneering surface prior to the application of the silane coupling agent, involves a process where silica modified aluminum oxide is used to coat the substrate with a thin layer of SiO₂ via sandblasting (Figure 3 and 4) (Hatta, et al. 2011). The silane molecules react with water to form silanol groups (-Si-OH) from the corresponding methoxy groups (-Si-O-CH₃). The silanol groups then react further to form a siloxane (-Si-O-Si-O-) network with the silica surface, thereby increasing the bond energy (Figure 5) (Sun, et al. 2000; Fischer, 2008; Özcan, et al. 2008).

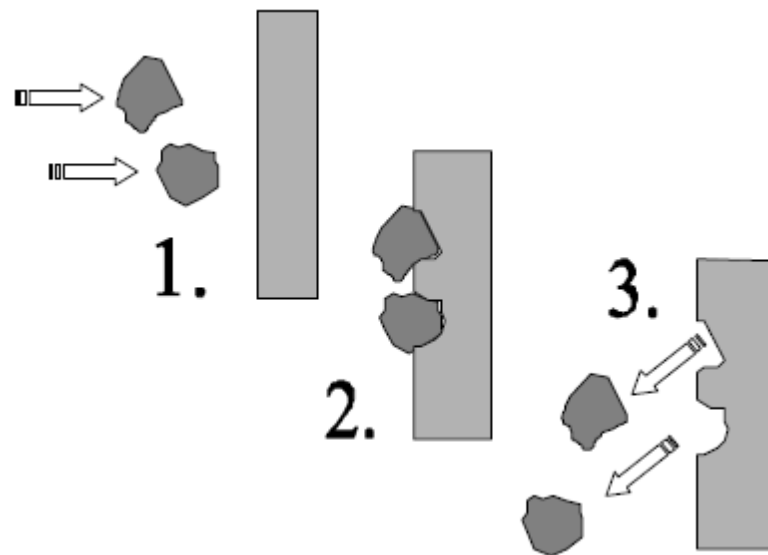


Figure 3. Micro blasting with Rocatec Pre: 1. 110 Micron AlO₂ sand is used to clean the veneering surface. 2. Micro retention is achieved. 3. A clean activated surface is created. ("Rocatec bonding: scientific profile" published Scientific affairs in 2001)

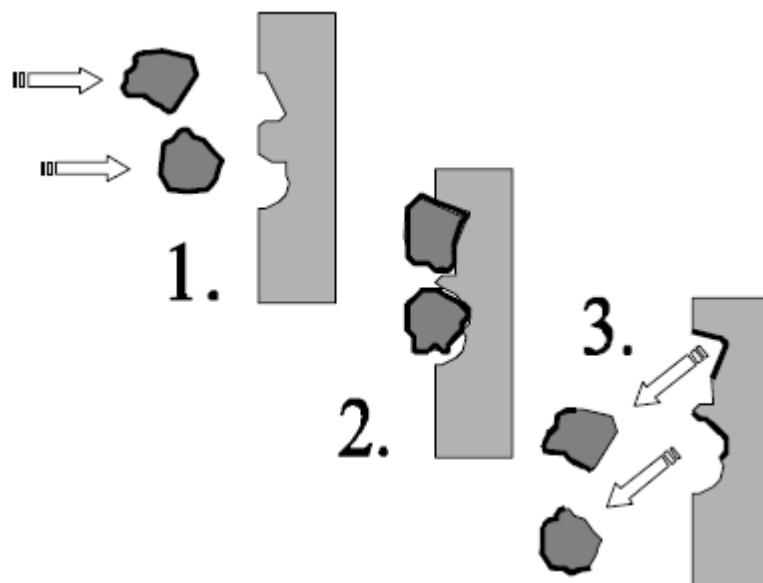


Figure 4. Ceramisation with Rocatec. 1. 110 Micron Si coated AlO_2 is blasted onto the clean surface. 2. A triboplasma is created in the microscopic ranges. 3. Partially coated AlO_2 leaves the surface. ("Rocatec bonding: scientific profile" published Scientific affairs in 2001)

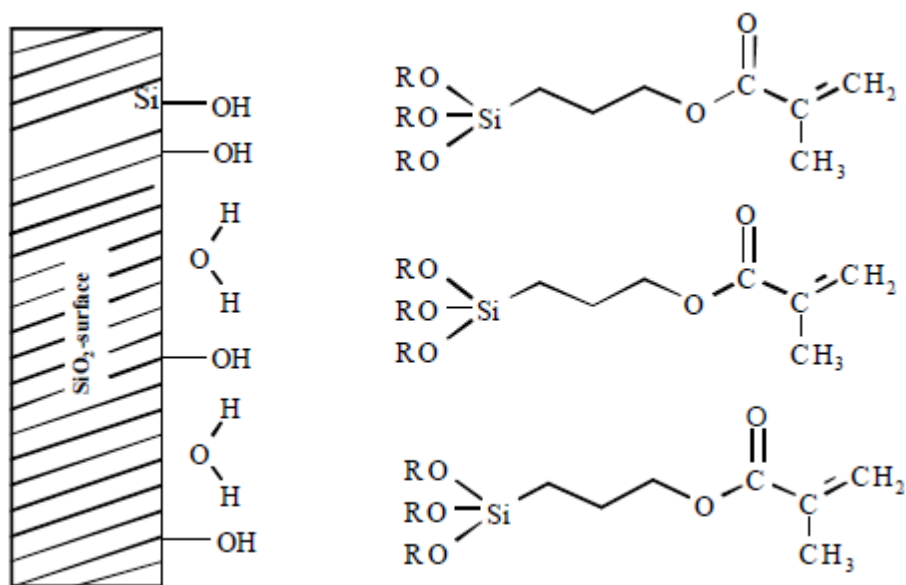


Figure 5. The silane molecules approach the inorganic surface which is covered in hydroxide groups and water molecules. ("Rocatec bonding: scientific profile" published Scientific affairs in 2001)

Various authors have reported on the effect of silanization to the bond strength between YZr and composite resin materials. In studies done by Kern and Wagner (1998) and Özcan *et al.* (2008), no significant improvement in bond was recorded. This is mainly attributed to the hardness of the zirconia and the inability of the AlO_2 to penetrate the YZr surface to a satisfactory depth to deposit the Si particles. In Contrast to this, a review by Thompson *et al.* (2011) reported other studies that stated different combinations of tribochemical silanization increase the bond between YZr and composite resin (Thompson, et al. 2011). Although the science and technology applied to adhesion and/or bonding issues with YZr have improved, there is still much to be learned to make the behaviour predictable in clinical use.

2.7 Shear bond testing method.

Most of the above mentioned studies have performed a shear bond strength test. In a shear bond test, two materials are connected via an adhesive agent and loaded in shear until failure occurs. The nominal bond strength is calculated by dividing the maximum applied force by the bonded cross-sectional area (Van Noort, et al. 1989; De Hoff, 1995; Della Bona and van Noort 1995). The ISO (International standards organisation) standard for shear bond strength test methods was established in 1994, and has not been given much credit (Versluis, et al 1997).

As evident in the above literature, most of the research on the bond between indirect veneering composite resin and YZr attempts to assess the integrity and strength of the interfacial bond. Experimental approaches for measurement of adhesive bond strengths in dentistry to date have consisted primarily of tensile or shear bond strength tests (Tam and Pilliar 1993). The shear bond test method played a leading role in the rapid development of bonding agents as a feedback tool for product quality control.

Unfortunately the rate of development of these products often leads to insufficient time for clinical trials to be performed (Davidson, et al. 1993). As a result, the shear bond test is frequently used in marketing strategies to compare products (Versluis, et al. 1997). However, data from these measurements, using the concept of nominal stress, are inconsistent and contain large deviation in test results between laboratories (Van Noort, et al. 1989; Della Bona and van Noort, 1995; Cheng, et al. 1999; Scherrer, et al. 2010). In fact, the mechanics of the nominal shear bond test, draws more criticism than approval. This however does little to discourage the use of this test method because of the relative simplicity of the test. De Hoff *et al.* (1995) highlighted the difficulty in correctly interpreting the test data generated by a shear bond test because of the lack of information regarding the stress distribution as well as the type of stresses generated within each specimen. Some studies employed Finite Element Analysis (FEA) to study the sensitivity of bond strengths to specimen design and changes in testing conditions (Van Noort, et al. 1989; De Hoff, 1995; Della Bona and van Noort, 1995; Versluis, et al. 1997; Tantbirojn, et al 2000; Scherrer, et al. 2010). FEA is a computerised method based on mathematical models to predict how a material would react when forces are applied to it. These studies demonstrated that tensile and shear bond strength measurements were highly dependent on the geometry of the test arrangement; the nature of the load applied; film thickness of the adhesive; Young's modulus of the materials involved and the presence or absence of adhesive flash. The authors reported that non- uniform stresses acted upon the bonded interface and therefore questioned the concept of "average stress" for the measurement of bond strength. The formation of a bonded interface is suitable to produce microscopic flaws which could act as critical stress risers leading to non-uniform stresses generated within the reaction zone, which can have a significant effect on the mode of failure (Scherrer, et al. 2010) (Figure 6). Shear bond testing between composite

resin and dentine revealed that the failure mode is often recorded as cohesive within the ceramic base rather than at the adhesive interface, on the basis of which it has been suggested that the bond strength exceeds the cohesive strength of the ceramic (Tam and Pilliar, 1993; Della Bona and van Noort, 1995, Scherrer, et al. 2010).

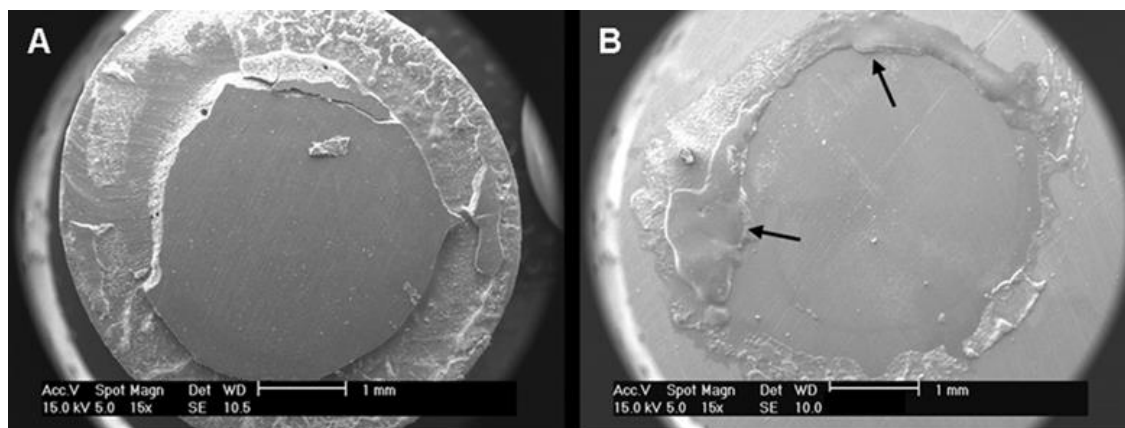


Figure 6 (a & b) De-bonded surfaces after Shear bond strength test of an endodontic sealer to Dentine. The arrows indicates fractured cement. (Teixeira, 2009)

Scherrer *et al.* (2010) states that shear bond strength test results including cohesive failures reflect a mixture of mechanical properties of both the dentine and resin, rather than the performance of the adhesive tested.

The science of fracture mechanics has evolved to such an extent that the conditions under which cracks will initiate and propagate in an unstable manner in materials can be predicted (Tam and Pilliar, 1993; Cheng, et al. 1999). These studies show that there is a need for a more critical approach to the design of appropriate tests for evaluating the bond strength of resin composite to ceramic if the desire for a standardised test procedure is to be achieved. For this objective to be accomplished, a careful examination of bond strength tests is mandatory for correct interpretation of the bond strength data (Van Noort, et al. 1989; De Hoff, 1995; Della Bona and van Noort, 1995; Versluis, et al. 1997; Tantbirojn, et al. 2000; Scherrer, et al. 2010).

However, the question arises whether another testing approach would describe the bond strength between two materials more accurately. It has been shown by Sherrer *et al.* (2010) that it is possible by using the fracture mechanics approach which determines the potential power of stable crack propagation within an interface, to deliver a better picture

of what is happening at the bond interface. This can be achieved using either K_{Ic} (fracture toughness) which is a material's resistance to crack propagation, or G_{Ic} (strain energy release rate) which is the amount of energy required to separate two bonded materials (Scherrer, et al. 2010).

2.8 Bond energy release fracture mechanics approach

Most bond strength tests are associated with stress gradients along the bond interface of the adhesive components as well as the effect of stress concentration points or flaws within the material (Chung, et al. 1997; Anusavice, et al. 2007). The stress condition within the loaded adhesive joint is complex and is further complicated by the mechanical properties of the different adhesive components, including the Young's modulus, shear modulus, Poisson's ratio and yield strength (Soderholm, 2010).

Factors such as G (fracture energy or strain energy release rate) and K (stress intensity factor) are often determined and presented in fracture mechanics studies. When the crack propagation criterion is based on the stress state of the crack tip, it is characterised by the stress intensity factor (K) and referred to as "local" because the attention is focused at the small material volume at the crack tip (Anderson, 2005). Because the K_{Ic} is a mechanical property of a monolithic material, it is more suitable to employ an energy concept to describe the interfacial properties of bond strength.

Griffith (1921) explained that the presence of existing cracks are very important and that crack extension takes place when sufficient energy is available to overcome the resistance of the material and generate new crack surfaces. The critical crack length (a_c) is an absolute number and is not dependent on the size of the structure that contains it. When the crack is propagated by small increments (Δa) additional strain energy is released from

the newly unloaded material near the crack (Figure 7) (Roylance, 2001). The energy release rate is an essential measurement in energy balance criteria and dependant on the material type. The energy release rate, is defined as the rate of change in potential energy with the crack area for a linear elastic material. At the moment of fracture $G = G_c$, the critical energy release rate, which is a measure of fracture toughness, or the energy per unit area required to form a new crack surface (Anderson, 2005). In this case, the resulting crack propagation criterion is referred to as “global” because a large volume of material is considered.

Cheng *et al.* (1999) suggested a new bond test method, based on the chevron geometry, to determine adhesion by measuring the bond energy between adhesive components (Cheng, et al. 1999). The loading configuration (Figure 8) causes a crack to initiate at a chevron tip in an opening mode. The steady-state crack is thus independent of any fatigue pre-cracking procedure (Barker, 1977; Cheng, et al.1999).

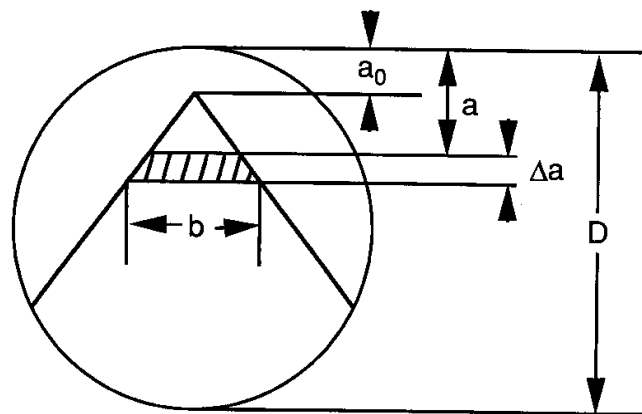


Figure 7. Adhesive surface geometry of proposed test specimen.

a_0 Is the distance from the top of the specimen to the vertex of the adhesive layer; a is the distance from the top of the sample to the crack-front; Δa is an infinitesimal increment of crack-front; b is the width of the crack; and D is the diameter of the cylindrical specimen (material B) (Cheng, et al. 1999).

Baker *et al.* (1977) has shown that the crack growth in a chevron-notch specimen is stable in a range of $a < a_c$, (Figure 7) where critical crack length a_c depends on the given specimen geometry and loading configuration. When crack length a equals a_c , the crack propagation becomes unstable and increases rapidly until failure (Cheng, et al. 1999).

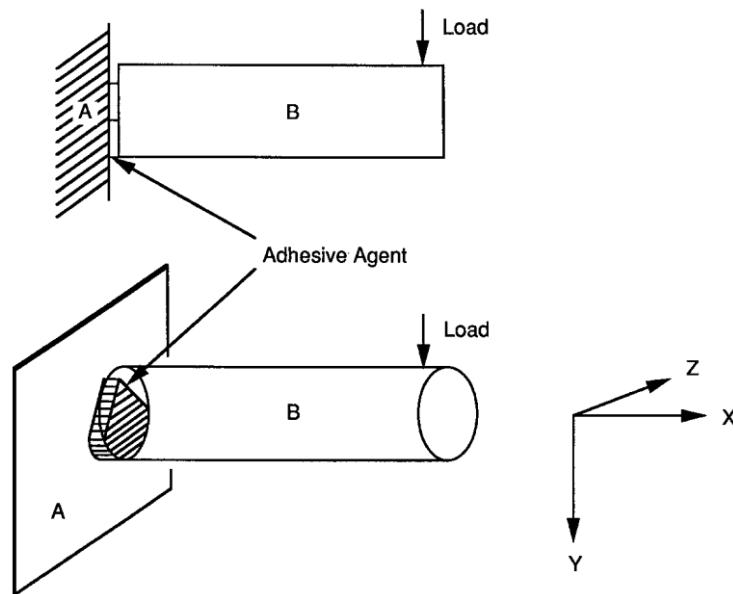


Figure 8. Schematic representation of the proposed bond strength test method. (Cheng, et al. 1999)

The relatively simple experimental configuration and specimen geometry adds to the advantages of this method. As the identification of crack initiation and stable crack propagation is very important in fractography, this adhesive surface geometry enables the researcher to easily analyse the fractured surfaces.

2.9 Fracture analysis using Scanning Electron Microscopy (SEM)

Fractured surfaces of specimens should be observed in order to perform fracture analysis which includes the inspection of the fractured surfaces to determine any obvious complications that might exclude specimens from the test sample. The next step is to use

a stereomicroscope for imaging details of fractured surfaces as well as identify candidate specimens for SEM. SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. Secondary or backscattered electron signals are detected and renders a detailed high resolution; high magnification image of the specimen. By using SEM, the observer can detect the origin of fractures with great accuracy as well as determine the mode of failure.

2.10 Summary

YZr is a modern high strength ceramic material used in restorative dentistry. However some issues exist regarding the bond reliability between YZr frameworks and traditional veneering ceramics as well as pressed ceramics. Alternative veneering materials are utilised and developed to simplify the complicated YZR/ceramic veneered working protocol. The chemical inertness of the YZr provides a challenge in attaining a reliable bond between the YZr and composite resin. All of the studies cited in this work, have tried a different combination of chemical primers, bonding agents or mechanical or chemical surface roughening in order to promote a better bond between these materials. Although most of the studies followed the recognised ISO standard for shear bond testing, this doesn't provide information on the energy needed to de-bond the two surfaces, but rather focus on the flaws within the materials involved. Therefore, the purpose of this study was to use the strain energy release approach to determine the bond energy between YZr with different surface preparations and three indirect restorative composite veneering materials.

Chapter 3: Materials and method

3.1 Introduction

The purpose of this study was to determine the amount of energy required to break the bond between indirect veneering composite resin and Yttrium stabilised Zirconia Oxide ceramic (YZr). Three popular composite resins were chosen, each with their own recommended zirconia bonding agent. In the case of the Sinfony composite resin, the “bonding agent” can be better described as a “bonding treatment”, however for consistency with regards to the term used in the tables and figures, the term “bonding agent” was used for all three resin materials. It should also be noted that the second test group for all resins consisted of the resin bonded to a smooth YZr plate. This means the YZr plate was hand polished under irrigation with abrasive paper, prior to sintering.

3.2 Materials and Method:

Three indirect composite veneering materials were bonded to zirconia plates using the manufacturer’s recommended bonding agents (Table 1) and preparation techniques (Table 2). 132 YZr rectangular plates were sectioned from milling blocks, using a diamond grit blade on a low speed cutting machine (DTQ-5, Laizhou Huayin Testing Instrument Co., Ltd., Shangdong, China) under water irrigation. Prior to sintering the plates were hand polished using 400 grit silicon carbide abrasive paper (Struers, Denmark) to ensure a flat veneering surface

Table 2 List of materials used by material type/trade name, lot number, elastic, constituents and name of manufacturer

| Material/ Trade name | Lot | Constituents | Reference for constituents | Manufacturer |
|--------------------------------------------------|--------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------|-------------------------------------|
| <i>YZr Ceramic</i> | | | | |
| Vita In-Ceram YZ for inLab (E-modulus 210Gpa) | 35760 | 91% Zirconium oxide (ZrO ₂), 5% yttrium oxide (Y ₂ O ₃), 3% hafnium oxide (HfO ₂), small amounts (,1%) of aluminum oxide (Al ₂ O ₃) and silicon oxide (SiO ₂) | Bottino et al. (2014) (Bottino, Bergoli et al. 2014) | VITA Zahnfabrik, Germany |
| <i>Indirect Composite Materials</i> | | | | |
| Ceramage Dentine (E-modulus 10.7Gpa) | 041024 | UDMA (Urethane dimethacrylate) | Soancă et al. (2012) | Shofu Inc, Kyoto, Japan |
| Ceramage Opaque | 100906 | UDMA, aluminum silicate, 2-HEMA, glass, pigment, others | Muratomi et al. (2013) | Shofu Inc, Kyoto, Japan |
| Signum Dentine (E-modulus 3.5 Gpa) | 01300 | Bis-GMA(2,2'-bis-[4-(methacryloxypropoxy)-phenyl]-propane) and TEGDMA (Tri (ethylene glycol) dimethacrylate) - SiO ₂ , Ba-Al-Si (1,0 µm) | Jada et al. (2007) Alves et al. (2013) | Heraeus Kulzer GmbH, Hanau, Germany |
| Signum Opaque F | 010209 | Multifunctional dimethacrylates; Pyrogenic SiO ₂ Photoinitiator Camphorquinone; TiO ₂ , iron oxides | Jada et al. (2007) | Heraeus Kulzer GmbH, Hanau, Germany |
| Sinfony Dentine (E-modulus 3.1 Gpa) | 449469 | Micro-hybrid composite containing: strontium aluminium borosilicate glass, pyrogenic silica, glass ionomer, a mixture of aliphatic and cycloaliphatic monomers | Alves et al. (2013) Özcan and Kumbuloglu (2009) | 3M ESPE, Minnesota, USA |
| Sinfony Opaque Powder | 445066 | 3-(trimethoxysilyl)propyl, titaniumdioxide, calciumfluoride, dilauroylperoxide, 1,1,1-trimethyl-N-(trimethylsilyl), silaneamine, hydrolyzation products with silica, iron oxide | Özcan and Kumbuloglu (2009) | 3M ESPE, Minnesota, USA |

| Material/ Trade name | Lot | Constituents | Reference for constituents | Manufacturer |
|-----------------------|--------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------|-------------------------------------|
| Sinfony Opaque Liquid | 518929 | bis(methylene)diacrylate, MMA, vinylchloride–vinylacetate copolymer, trimethylbenzoyl-diphenylposphone oxide | Özcan and Kumbuloglu. (2009) | 3M ESPE, Minnesota, USA |
| <i>Bonding Agents</i> | | | | |
| AZ Primer (Ceramage) | 071213 | 6-MHPA(6-methacryloxyhexyl phosphonoacetate.), acetone, others | Kitayama <i>et al.</i> (2010) | Shofu Inc, Kyoto, Japan |
| Rocatec | - | Silicatized aluminum oxide particles | Bottino <i>et al.</i> (2014) Özcan and Kumbuloglu (2009) | 3M ESPE, Minnesota, USA |
| ESPE Sil | 495219 | 3-methacryloxypropyltrimethoxysilane(MPS) in ethanol | Özcan and Kumbuloglu (2009) | 3M ESPE, Minnesota, USA |
| Zirconia Bond I + II | 010021 | Bond I: Acetone, 10-MDP (10-methacryloyloxy-decyl-dihydrogenphosphate), acetic acid 010106 Bond II: Methyl methacrylate, diphenyl(2,4,6- trimethylbenzoyl) phosphinoxide | Ural <i>et al.</i> (2011) | Heraeus Kulzer GmbH, Hanau, Germany |

Table 3 YZr specimen preparation prior to veneering with indirect composite resin. For each test group (n=12)

| Material | Sandblasted with 120µm grit AlO ₂ , 2 bar pressure. | Bonding agent |
|-----------------|----------------------------------------------------------------------|----------------------------------------------------|
| <i>Ceramage</i> | | |
| CER 1 (Control) | NO | NO |
| CER 2 | NO | AZ Primer |
| CER 3 | YES | NO |
| CER 4 | YES | AZ Primer |
| <i>Signum</i> | | |
| SIG 1(Control) | NO | NO |
| SIG 2 | NO | Zirconia Bond 1&2 |
| SIG 3 | YES | NO |
| SIG 4 | YES | Zirconia Bond 1&2 |
| <i>Sinfony</i> | | |
| SIN 1(Control) | NO | NO |
| SIN 2 * | N/A | N/A |
| SIN 3 | YES | NO |
| SIN 4 | YES | Sandblasted again with Rocatec and ESPESil applied |

* Sinfony incorporates the use of Rocatec (3M ESPE, USA) sandblasting as part of the bonding system. This process is reflected in group Sin4 and therefore no specimens were prepared for this surface treatment option as per Cer2 and Sig2

All the plates were veneered according to each individual manufacturer's instructions with a composite rod as described by Cheng *et al.* (1999) consisting of two opaque layers at the bond surface interface and a 12mm dentine rod. The geometry of the chevron shaped bond interface was adapted from Tantbirojn *et al.* (2000) (Figure 9). The chevron shaped bonding surface was created by using a custom-made cut-out sticker made of ± 50 micron non-stick polymeric transparent PVC film (Grafiprint; Houthalen, Belgium), after which the YZr plate was opaqued (Figure 10 a). A precision glass tube, inside

diameter of 4mm, lined with a thin film of petroleum jelly to prevent adhesion, was positioned over the chevron-shaped bonding area and incrementally filled with indirect composite resin. The specimens were polymerised according to the manufacturer's instructions (Table 3). After polymerization, the glass tube was removed (Figure 11a-c).

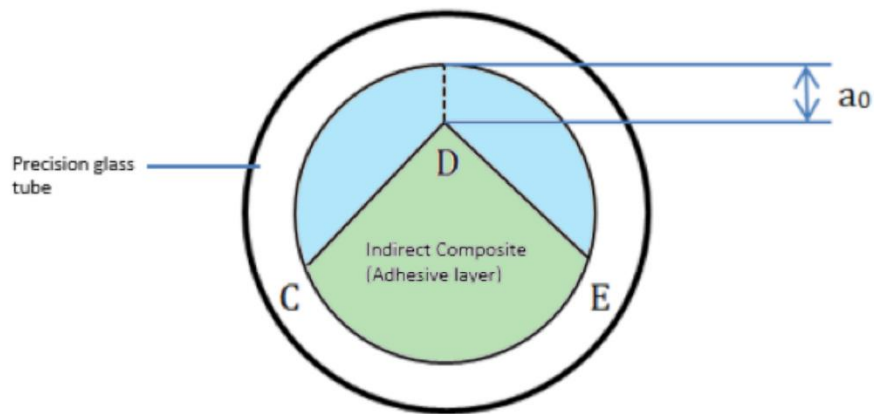


Figure 9. Geometry of the chevron shaped bond interface (green) as adapted from Tantbironj, et al. (2000). The blue represents the un-bonded surface area created by the non-stick polymeric transparent PVC film. Diameter 4mm; CDE angle = 90°; $a_0 = 0.6\text{mm}$.

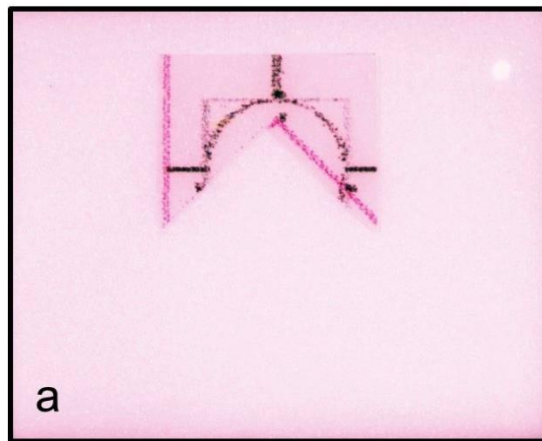


Figure 10. (a) YZr plate prepared with a chevron cut sticker ready for composite veneering.

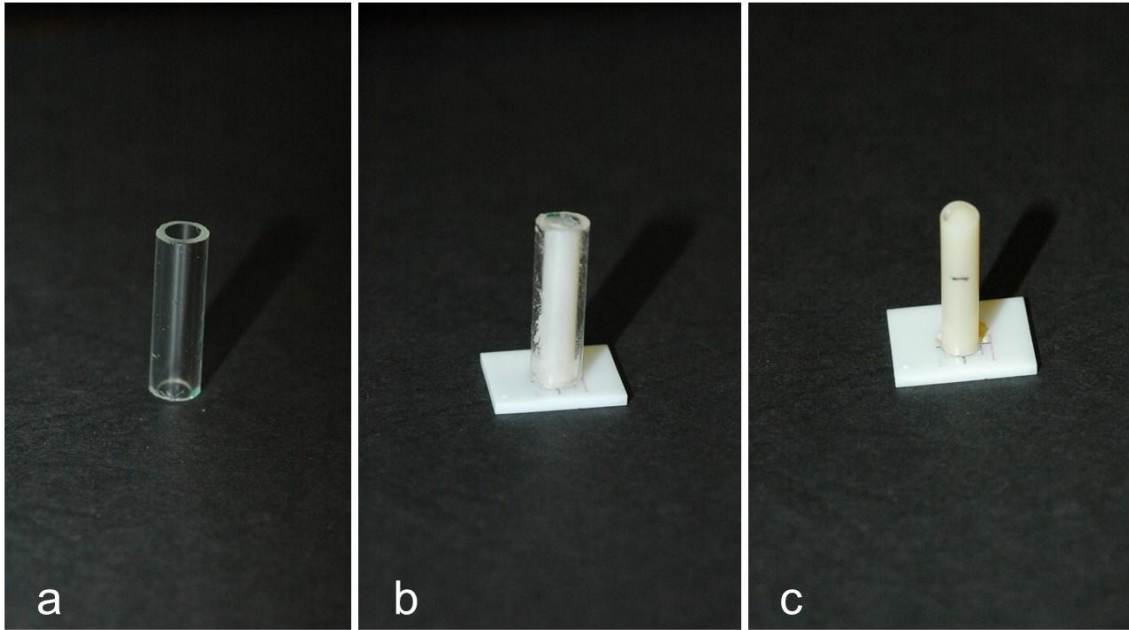


Figure 11. Preparation of the composite rod. (a) Precision glass rod was sectioned and squared. b) The glass rod was positioned according to the chevron sticker on the opaqued YZr plate and filled with composite material and d) glass tube was removed and a loading distance of 10mm mark on the composite rod.

Table 4 Sequence in which materials were polymerised using the manufacturer's prescribed light curing units, light source and exposure time

| Composite material | Polymerizing Units | Light source | Exposure time |
|-----------------------------|---------------------------|-------------------------------------------|----------------------|
| Signum Opaque | UniXS II | Xenon Stroboscopic tube 100Wx2, 350-520nm | 1.5min |
| Signum Dentine | UniXS II | Xenon Stroboscopic tube 100Wx2, 350-520nm | 1.5min |
| Signum Final Cure | UniXS II | Xenon Stroboscopic tube 100Wx2, 350-520nm | 3min |
| Ceramage opaque | Solidilite | Halogen lamps 4x150w, 400-550nm | 3min |
| Ceramage dentine (pre-cure) | Solidilite | Halogen lamps | 1min |
| | Sub-Light | 1x150w, 400-550nm | |
| Ceramage final cure | Solidilite | Halogen lamps 4x150w, 400-550nm | 5min |
| Sinfony Opaque | Visio-Alfa | Halogen lamp 100W x1, 400-550nm | 10sec |
| Sinfony Dentine (pre-cure) | Visio-Alfa | Halogen lamp 100W x1, 400-550nm | 10sec |
| Sinfony dentine Final cure | Visio-Beta | Fluorescent tubes | 15min |
| | Vario | 250Wx2, 400-550nm | |

The specimens were loaded 10mm from the bonded interface (Figures 12) at a cross-head speed of 0.5mm/min in a universal testing machine (Instron, model 3369, Instron

Corp. Canton, MA, USA). The load at failure (F_{\max}) was recorded using a 1KN load cell and Istron Bluehill 3 software (Instron Corp. Canton, MA, USA).

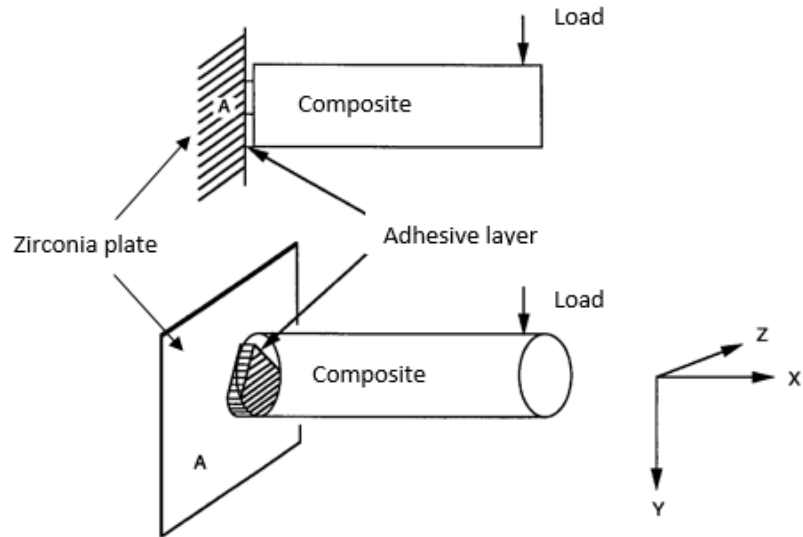


Figure 12. Schematic diagram of the bond strength measurement test method (adapted from Cheng, et. al. 1999)

The Zirconia plate was fixed in a custom made jig while the composite cylindrical specimen was loaded in such a way that a crack initiated at the vertex of the chevron, and propagated through the adhesive layer during the adhesive bond test (Figure 13).

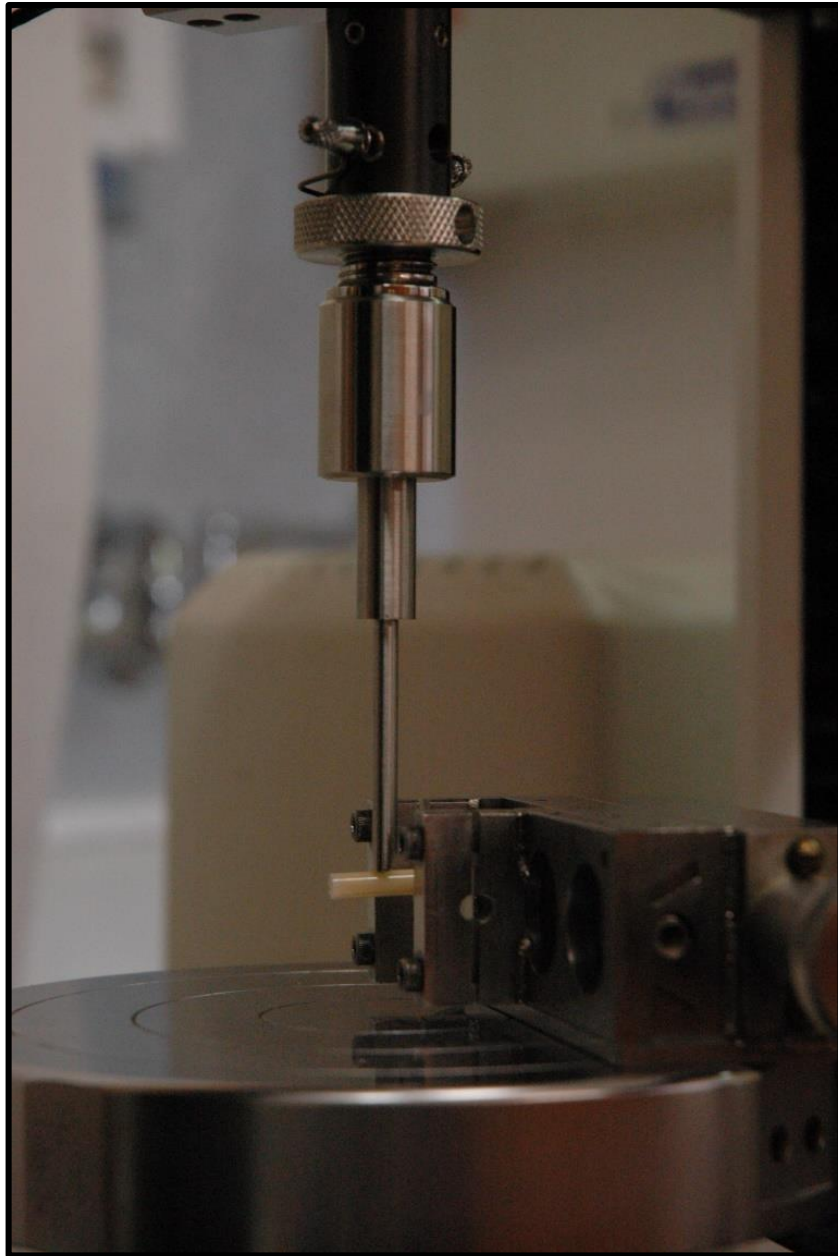


Figure 13. Test set-up of the Composite resin tube bonded to the YZr plate. A custom made jig was used to minimise compliance during the testing process.

Strain energy release rates were calculated using the formula by Cheng *et al.* (1999).

$$G_{Ic} (J/m^2) = \frac{104.5 (F_{max})^2 L^2}{ED^6}$$

Where:

F_{max} = Load at failure (N)

L = Distance to loading point (mm)

E = Elastic modulus of the composite cylinder

D = Diameter of the composite cylinder (4mm)

Statistical analysis was done using STATA software (StatCorp LP, Texas, USA). The data was log transformed for better distribution. One-way ANOVA (P = 95%) was performed to determine significant differences between the G-values of the test groups for each material type. Homogeneity of the variables was confirmed with Bartlett's test. Dunnett's test was performed to determine statistical difference (P = 95%) to the control within the material groups.

3.3 Microscopy analysis

After de-bonding, the percentage surface area and mode of failure (adhesive, cohesive and mixed mode) was established using a stereoscopic zoom microscope (SMZ800, Nikon Corporation, Tokyo, Japan). Selected specimens, highest and lowest G values, were qualitatively analysed with SEM (JSM 6700 FESEM, JEOL, Japan) to confirm the mode of failure identified with the light microscope and illustrate the differences in surface treatments prior to bonding.

Chapter 4: Results

4.1 Introduction:

Statistical analysis of the raw data was performed with STATA software (StatCorp LP, Texas, USA). The data was log transformed for better distribution. One-way ANOVA ($P = 95\%$) was performed to determine significant differences between the G-values of the test groups for each material type. Homogeneity of the variables was confirmed with Bartlett's test. Dunnett's test was performed to determine statistical difference ($P = 95\%$) to the control within the material groups. These tables can be found in Appendix 1.

4.2 Bond strength test:

The data for the strain energy release rate in mode opening mode (G_{Ic}), values, illustrated with the box and whisker plots shown in Figure 14, indicate that the median values are very different for the three materials. The box includes 50% of the data and shows the median (line) and the upper and lower quartile. The statistical comparison for the Ceramage group showed that there was an overall difference among the groups ($p < 0.001$). However only the sandblasted/bonding agent group was different from the control group. The overall difference was also significant for the Signum groups ($p < 0.001$). In this case the differences between both the bonding agent group and sandblasted/bonding agent group and the control were significant. The overall test for differences among the groups was significant ($p < 0.001$) for Sinfony as was Dunnett's test for the comparison between sandblasted/bonded agent and the control.

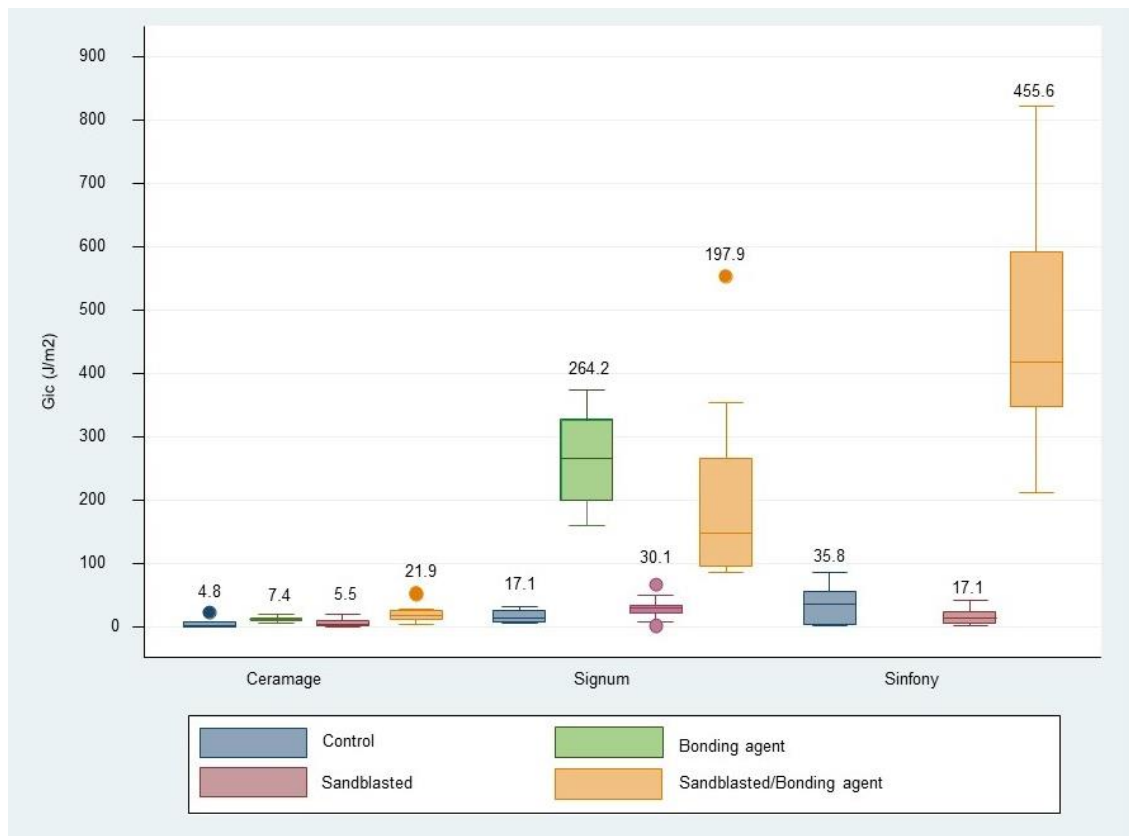


Figure 14. Mean bond strength (strain energy release rate - G_{Ic}) according to material type, sandblasting, bonding agent and combination of sandblasting with bonding agent.

4.3 Microscopy analysis.

Adhesive failure occurred when the failure occurred at the interface between the composite system and the YZr surface. Cohesive failure occurred within the composite system. The high strength properties of the YZr prevented any cohesive failure within itself. Mixed mode failure was a combination of adhesive and cohesive. The modes of failure was recorded and represented in figure 15.

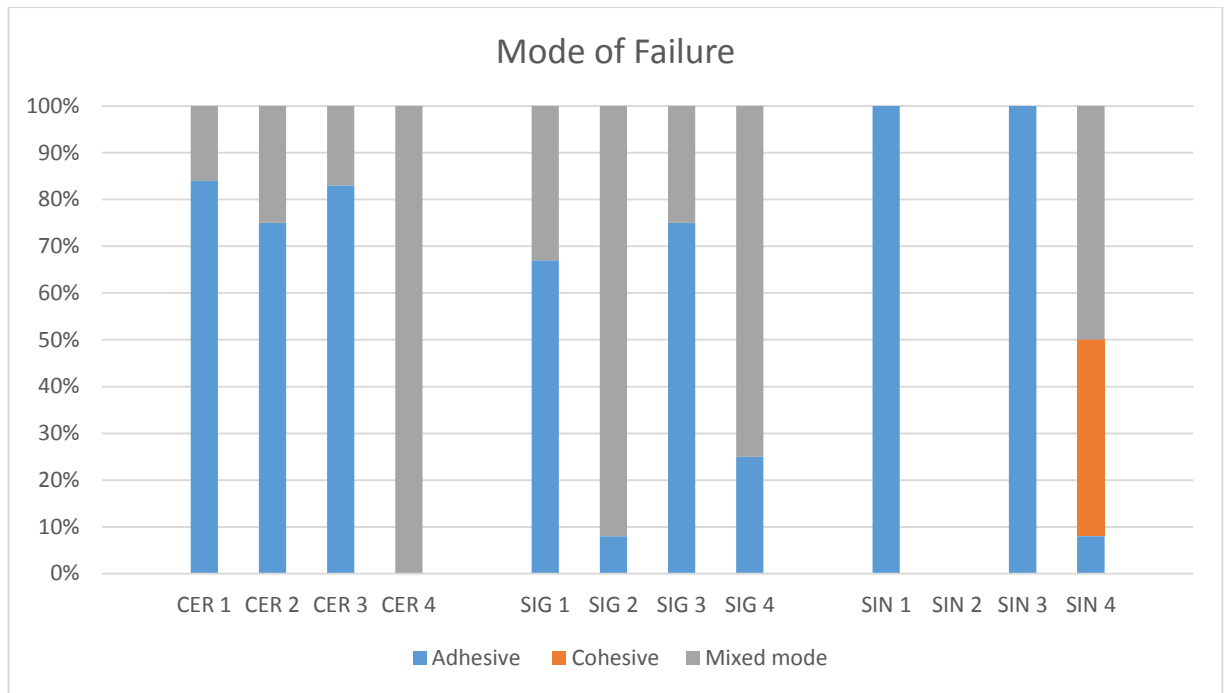


Figure 15. Mode of failure between of indirect composite and Zirconia plates.

4.4 SEM analysis

SEM analysis confirmed the mode of failure images obtained from the light microscope (Figure 16). SEM images of the YZr surface treatment options prior to composite resin application are shown in Figure 17.

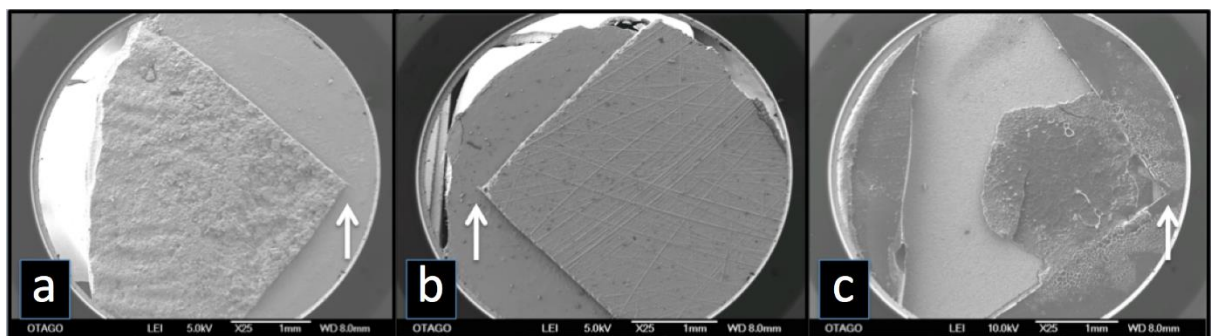


Figure 16. . Shows SEM images of typical mode of failure for the various treatment options. The arrows indicate the tip of the chevron notch from where crack propagation initiated. (a) Cohesive failure within the composite material from the specimen group SIN4. (b) Adhesive failure between the composite and zirconia plate taken from specimen group SIN1. (c) mixed-mode failure between the composite and zirconia plate taken from specimen group CER4.

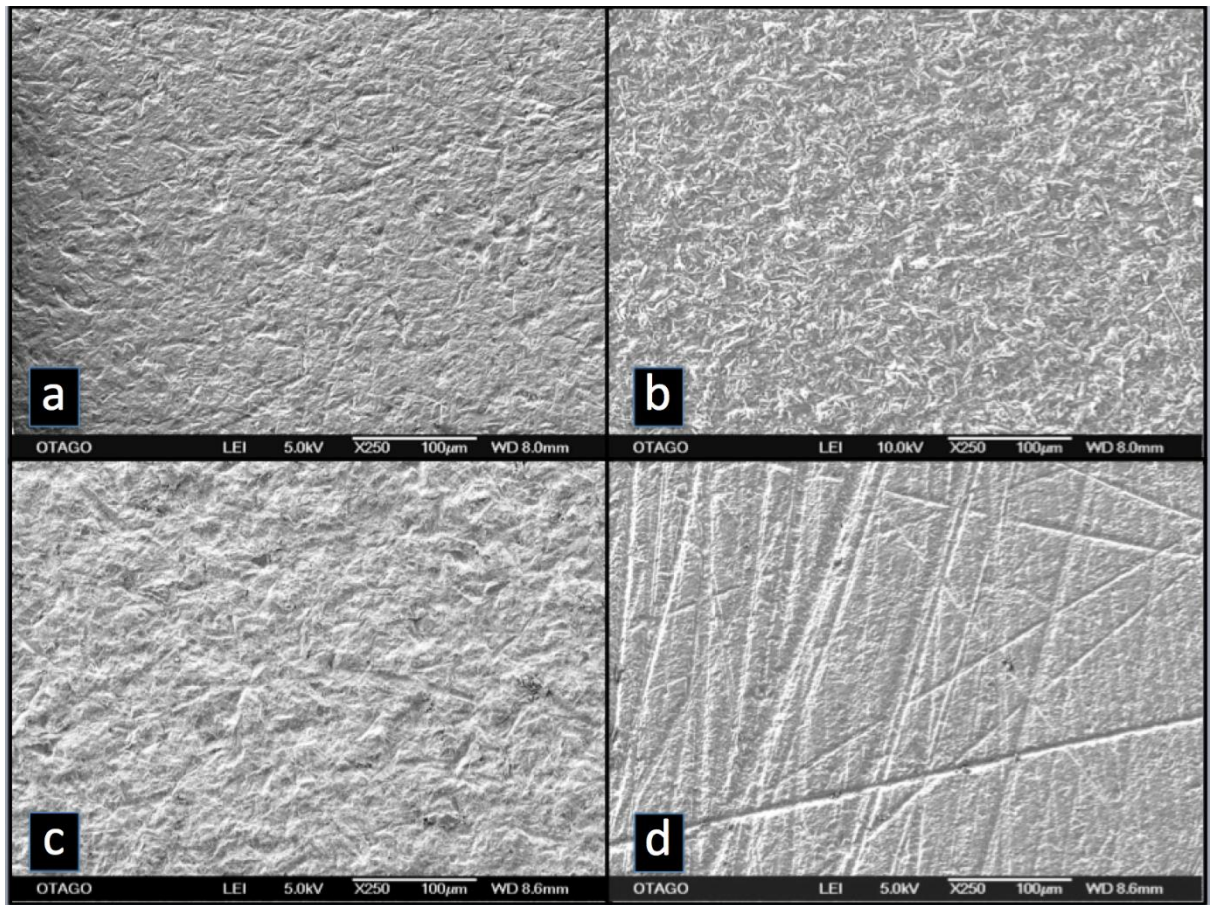


Figure 17. Shows SEM images (x250) of the YZr surface treatment options prior to composite resin application. 4a, sandblasted YZr treated with zirconia-bond 1&2; 4b, sandblasted YZr treated with AZ Primer; 4c, sandblasted YZr treated with Rocatec and ESPE-Sil; 4d, YZr Hand polished with 400 grit Silicon Carbide abrasive paper and sintered.

Chapter 5: Discussion

5.1 Introduction:

In this study, a fracture mechanics approach was utilised to determine the the bond energy release rate between indirect veneering composite materials and YZr with and without sandblasting and bonding agents. The results show that the bond energy release rates between indirect composite materials and YZr surfaces were influenced by the application of different bonding agents and surface treatments.

5.2 The relationship between the G-value and types of bonding agents.

A relationship was observed between the G-value and the types of bonding agent. The low G-values recorded in all the control groups, where the composites were bonded to the YZr plates without sandblasting or bonding agents, was expected based on the reports by Komine *et al.* (2012). A mixed result was recorded in the second treatment option where only the bonding agent was applied to the YZr surfaces (SIN2 was not included as sandblasting is part of the bonding agent's protocol. Table 2). CER2 recorded a low mean G-value ($7.4 \text{ G}_{\text{IC}} / \text{Jm}^2$), whereas SIG2 recorded a significantly higher mean G-value ($264.2 \text{ G}_{\text{IC}} / \text{Jm}^2$). According to previous studies the application of acidic functional monomer containing carboxylic anhydride (4-META) in combination with phosphoric acid (6-MHPA) (Komine, et al. 2009; Komine, et al. 2012; Komine, et al. 2013), or phosphate monomer (MDP) and MDP and silane (Kobayashi, et al. 2009) can yield durable bond strength between indirect veneering composite and YZr. This corresponded with the SIG2 results where Zirconia Bond I + II, which is a functional Phosphate monomer (MDP), was used. This indicates that the application of an MDP primer (10-

methacryloyloxy-decyl-dihydrogenphosphate) containing resin improved the bond between the indirect composite resin and YZr. Thompson *et al.*, (2008) explains this as a reaction between hydroxyl groups in the MDP and the zirconia ceramic, being the result of bonding of a phosphate ester monomer to metal oxides such as chromium, nickel, aluminum, and zirconium dioxides. A possible explanation of the low CER2 results is the absence of the carboxylic acid component (4-META) in combination with an acidic functional monomer containing phosphoric acid (6-MHPA) in the AZ Primer (Table 2).

5.3 The relationship between the G-value and sandblasting the YZr surface.

Sandblasting is a popular method to increase the surface area and roughness for improved interfacial bond. However, sandblasting the YZr bonding surfaces prior to veneering (CER3, SIG3 and SIN3) with composite resin and without the use of a bonding agent, showed no significant increase in the G-values compared to the controls despite the larger surface area available for bonding. This is in contradiction to a study by Komine *et al.* (2012) who reported that sandblasting at 0.1 MPa pressure or higher, yields satisfactory initial and durable bond strengths between an indirect composite material and zirconia ceramics. The reason for this difference could be explained by the shear bond test method used by Komine which has been shown to produce highly variable results. By sandblasting a surface, the surface morphology will change from smooth to roughened which present more surfaces perpendicular to the direction of shear loading. This results in more shear resistance as well as increasing the available surface area. In contrast, the opening mode of the fracture energy release rate approach does not encounter perpendicular resistance, only increased area available for adhesive bonding.

5.4 Relationship between G-value and a combination of sandblasting and bonding agent.

In the fourth treatment option (CER4, SIG4 and SIN4) where the specimens were sandblasted prior to application of the bonding agent, SIG4 and SIN4 showed a significant increase in bond energy compared to their controls and SIN4 was significantly higher than the rest of the groups. This may be due to the increased surface area available for bonding in combination with the efficacy of the bonding agent applied. The reason for the additional increase of the SIN4 can be explained by the tribochemical process of silicatising the surfaces prior to the application of the silane coupling agent. This involves a process where silica-modified aluminum oxide is used to coat the substrate with a thin layer of SiO₂ via sandblasting. The silane molecules react with water to form silanol groups (-Si-OH) from the corresponding methoxy groups (-Si-O-CH₃). The silanol groups then react further to form a siloxane (-Si-O-Si-O-) network with the silica surface, thereby increasing the bond energy (Sun, et al. 2000; Fischer, et al. 2008; Özcan, et al. 2008).

5.5 Relationship between G-value and elastic modulus of the composite resins.

A relationship was also observed between the elastic modulus of the composite resins (Table 2) and the mean G-values. The two materials with the lower elastic moduli (Signum, E-modulus 3.5 GPa; Sinfony, E-modulus 3.1 GPa), recorded higher G-Values, suggesting that the elastic energy build-up in these materials prior to crack initiation was higher than that of the Ceramage composite (E-modulus 10.7GPa). This suggests that the lower elastic modulus might result in the material behaving in an elastic manner, where more energy is absorbed and requiring a larger energy build-up to initiate failure. The cantilever beam of the specimen underwent deflection as the load was applied. This

deflection was caused by the incremental crack growth in the adhesive area between the zirconia plate and the composite cantilever beam (Cheng, et al. 1999). In the case of the Ceramage, the higher elastic modulus makes this material more brittle and thus have a lower yielding tolerance than the other two composite materials. Sinfony recorded the highest G-values, suggesting that these specimens have greater stored elastic energy that can be converted to specimen surface energy, thereby creating more cracks and rougher surfaces as observed in Figure 16a (Quinn and Quinn 2010).

When one compares the range of G-values for the composite to YZr bond from this study to those reported for conventional porcelain fused to YZr bonding, in a study by Choi *et al.* (2011) who reported values ranging between 17.1 Jm^2 and 26.7 Jm^2 , while Li *et al.* (2013) reported values ranging between 10.16 Jm^2 and 18.67 Jm^2 . This would indicate that with the appropriate combination of sandblasting and use of a bonding agent with carboxylic acid component (4-META) in combination with an acidic functional monomer containing phosphoric acid (6-MHPA), or alternatively silicatising the YZr surfaces prior to veneering, will produce high strength bonding that exceeds the clinically acceptable bond strength produced in the porcelain fused to YZr systems. As a cautionary note to this, although most of the studies done on the bond between YZr and indirect composite resin have reported a reliable bond between the two materials, several disadvantages of composite materials have been reported in the literature, including insufficient wear resistance, increased plaque accumulation, and surface degradation over time (Komine, et al. 2012).

The small sample size and lack of Weibull analysis is recognised as limitations of this study, thus further research with a larger sample size and Weibull analysis is recommended.

Chapter 6: Conclusion

Within the limitations of this study, it was found that:

- The application of acidic functional phosphate monomer MDP or silicatising the YZr surfaces before veneering with indirect composite veneering material produced higher bond energy.
- Sandblasting the YZr surfaces with 120grit AlO₂ only, did not increase the bond energy.
- The elastic modulus of the composite material can potentially influence the bond energy to the YZr substructure.

Both the clinician and technician should take these findings into consideration when selecting YZr veneering materials. The relatively easy repair ability and serviceability of composite materials in general makes it an ideal material for artificial gingival reconstruction in implant abutments and bridges. However, as these results do not represent longevity of the bond further research, which includes thermocycling, is recommended.

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Appendix:

- a) Log transformed statistical analysis: $\text{Log } G_{ic} \text{ Jm}^2$ (materials)
- b) Geometric statistical analysis: $G_{ic} \text{ Jm}^2$ (materials)

A.) Log Transformed data analysis

One-way Log Gic (Jm²) order if material=="Ceramage"

One-way ANOVA (P>0.005)

| <i>Order</i> | <i>Mean</i> | <i>Std. Dev</i> | <i>Freq.</i> |
|------------------------------------------------------|------------------|------------------|--------------|
| <i>Control</i> | .85195683 | 1.2827045 | 12 |
| <i>Bonding Agent only</i> | 1.5125176 | 1.1352831 | 12 |
| <i>Sandblasted only</i> | 1.4548395 | .8012786 | 12 |
| <i>Combination of sandblasting and bonding agent</i> | 2.8694972 | .70881282 | 12 |
| Total | 1.6722028 | 1.2292018 | 48 |

Analysis of Variance

| <i>Source</i> | <i>SS</i> | <i>df</i> | <i>MS</i> | <i>F</i> | <i>Prob > F</i> |
|-----------------------|------------------|-----------|-----------------|----------|--------------------|
| <i>Between groups</i> | 26.1487623 | 3 | 8.7162541 | 8.55 | 0.0001 |
| <i>Within groups</i> | 44.8652767 | 44 | 1.01966538 | | |
| Total | 71.014039 | 47 | 1.510937 | | |

Bartlett's test for equal variances: $\chi^2(3) = 4.8500$ Prob> $\chi^2 = 0.183$

Dunnett Test: Log Gic (Jm²) Ceramage, control (1)

| <i>Order</i> | <i>Mean</i> | <i>Diff</i> | <i>[2-Sided 95% SCI]</i> | | <i>abs(Diff)</i> | <i>Different from control?</i> |
|------------------------------------------------------|-------------|-------------|----------------------------|----------|------------------|--------------------------------|
| <i>Control</i> | .8519568 | --- | --- | --- | --- | --- |
| <i>Bonding Agent only</i> | 1.512518 | .6605608 | -.345312 | 1.666434 | .6605608 | No |
| <i>Sandblasted only</i> | 1.454839 | .6028826 | -.402990 | 1.608755 | 3.6028826 | No |
| <i>Combination of sandblasting and bonding agent</i> | 2.869497 | 2.01754 | 1.011668 | 3.023413 | 2.01754 | Yes |

Diff = mean(order)-mean(control)

Different from mean(control) if abs(Diff) > 1.00587

One-way Log Gic (Jm²) order if material=="Signum"

One-way ANOVA (P>0.005)

| <i>Order</i> | <i>Mean</i> | <i>Std. Dev</i> | <i>Freq.</i> |
|----------------------------------------------------------|------------------|------------------|--------------|
| <i>Control</i> | 2.6918694 | .58049576 | 12 |
| <i>Bonding Agent only</i> | 5.5441124 | .27010013 | 12 |
| <i>Sandblasted only</i> | 3.1490486 | .91092326 | 12 |
| <i>Combination of sandblasting and bonding agent</i> | 5.1015194 | .60795933 | 12 |
| Total | 4.1216375 | 1.3790824 | 48 |

Analysis of Variance

| <i>Source</i> | <i>SS</i> | <i>df</i> | <i>MS</i> | <i>F</i> | <i>Prob > F</i> |
|-----------------------|-------------------|-----------|-------------------|----------|--------------------|
| <i>Between groups</i> | 71.6852346 | 3 | 23.8950782 | 59.39 | 0.0000 |
| <i>Within groups</i> | 17.7025766 | 44 | .402331285 | | |
| Total | 89.3878111 | 47 | 1.90186832 | | |

Bartlett's test for equal variances: $\chi^2(3) = 13.2020$ Prob> $\chi^2 = 0.004$

Dunnett Log Gic (Jm²) order if material=="Signum", control (1)

| Order | Mean | Diff | [2-Sided 95% SCI] | | abs(Diff) | Different from control? |
|------------------------------------------------------|-------------|-------------|----------------------------|----------|------------------|--------------------------------|
| <i>Control</i> | 2.691869 | --- | --- | --- | --- | --- |
| <i>Bonding Agent only</i> | 5.544112 | 2.852243 | 2.220404 | 3.484082 | 2.852243 | Yes |
| <i>Sandblasted only</i> | 3.149049 | .4571791 | -.1746594 | 1.089018 | .4571791 | No |
| <i>Combination of sandblasting and bonding agent</i> | 5.101519 | 2.40965 | 1.777811 | 3.041489 | 2.40965 | Yes |

Diff = mean(order)-mean(control)

Different from mean(control) if abs(Diff) > .631839

One-way Log Gic (Jm²) order if material=="Sinfony"

One-way ANOVA (P>0.005)

| <i>Order</i> | <i>Mean</i> | <i>Std. Dev</i> | <i>Freq.</i> |
|----------------------------------------------------------|-----------------|------------------|--------------|
| <i>Control</i> | 3.0010047 | 1.3520976 | 12 |
| <i>Bonding Agent only</i> | --- | --- | --- |
| <i>Sandblasted only</i> | 2.489058 | .95340094 | 12 |
| <i>Combination of sandblasting and bonding agent</i> | 6.0574382 | .37797973 | 12 |
| Total | 3.849167 | 1.8595618 | 36 |

Analysis of Variance

| <i>Source</i> | <i>SS</i> | <i>df</i> | <i>MS</i> | <i>F</i> | <i>Prob > F</i> |
|-----------------------|-------------------|-----------|-------------------|----------|--------------------|
| <i>Between groups</i> | 89.3488486 | 2 | 44.6744243 | 46.54 | 0.0000 |
| <i>Within groups</i> | 31.6801092 | 33 | .96000331 | | |
| Total | 121.028958 | 35 | 3.45797022 | | |

Bartlett's test for equal variances: $\chi^2 (2) = 13.9085$ Prob> $\chi^2 = 0.001$

Dunnett Log Gic (Jm²) order if material=="Sinfony", control (1)

| Order | Mean | Diff | [2-Sided 95% SCI] | | abs(Diff) | Different from control? |
|------------------------------------------------------|-------------|-------------|----------------------------|----------|------------------|--------------------------------|
| <i>Control</i> | 3.001005 | --- | --- | --- | --- | --- |
| <i>Bonding Agent only</i> | --- | --- | --- | --- | --- | --- |
| <i>Sandblasted only</i> | 2.489058 | -.5119468 | -1.439948 | .4160548 | .5119468 | No |
| <i>Combination of sandblasting and bonding agent</i> | 6.057438 | 3.056433 | 2.128432 | 3.984435 | 3.056433 | Yes |

Diff = mean(order)-mean(control)

Different from mean(control) if abs(Diff) > .928002

B) Geometric statistical analysis: G_{ic} Jm² (materials)

One-way ANOVA G_{ic} (Jm²) order if material=="Ceramage"

| Order | Mean | Std. Dev | Freq. |
|--------------------------------------------------|-----------------|------------------|--------------|
| Control | 4.846817 | 6.4612133 | 12 |
| Bonding Agent only | 7.3917437 | 6.8779506 | 12 |
| Sandblasted only | 5.5306757 | 3.8794339 | 12 |
| Combination of sandblasting and bonding agent | 21.974828 | 15.615732 | 12 |
| Total | 9.936016 | 11.474356 | 48 |

Analysis of Variance

| Source | SS | df | MS | F | Prob > F |
|-------------------|------------------|-----------|-------------------|----------|--------------------|
| Between groups | 2360.55934 | 3 | 786.853115 | 9.05 | 0.0001 |
| Within groups | 3827.50026 | 44 | 86.9886423 | | |
| Total | 6188.0596 | 47 | 131.660843 | | |

Bartlett's test for equal variances: $\chi^2(3) = 21.9061$ Prob> $\chi^2 = 0.000$

Dunnett G_{ic} (Jm^2) order if material=="Ceramage", control (1)

| Order | Mean | Diff | [2-Sided 95% SCI] | | abs(Diff) | Different from control? |
|-----------------------------------------------|-------------|-------------|----------------------------|----------|------------------|--------------------------------|
| Control | 4.846817 | --- | --- | --- | --- | --- |
| Bonding Agent only | 7.391744 | 2.544927 | -6.74571 | 11.83556 | 2.544927 | No |
| Sandblasted only | 5.530676 | .6838587 | -8.606778 | 9.974495 | .6838587 | No |
| Combination of sandblasting and bonding agent | 21.97483 | 17.12801 | 7.837374 | 26.41865 | 17.12801 | Yes |

Diff = mean(order)-mean(control)

Different from mean(control) if abs(Diff) > 9.29064

One-way ANOVA G_{ic} (Jm^2) order if material=="Signum"

| Order | Mean | Std. Dev | Freq. |
|----------------------------------------------------------|------------------|------------------|--------------|
| <i>Control</i> | 17.166095 | 9.6703422 | 12 |
| <i>Bonding Agent only</i> | 264.17823 | 68.602498 | 12 |
| <i>Sandblasted only</i> | 30.062874 | 17.309055 | 12 |
| <i>Combination of sandblasting and bonding agent</i> | 197.88352 | 140.84387 | 12 |
| Total | 127.32268 | 131.91932 | 48 |

Analysis of Variance

| Source | SS | df | MS | F | Prob > F |
|-----------------------|------------------|-----------|-------------------|----------|--------------------|
| <i>Between groups</i> | 543626.599 | 3 | 181208.866 | 29.07 | 0.0000 |
| <i>Within groups</i> | 274300.587 | 44 | 6234.10426 | | |
| Total | 6188.0596 | 47 | 131.660843 | | |

Bartlett's test for equal variances: $\chi^2(3) = 67.3920$, $Prob > \chi^2 = 0.000$

Dunnett G_{ic} (Jm²) order if material== "Signum", control (1)

| <i>Order</i> | <i>Mean</i> | <i>Diff</i> | <i>[2-Sided 95% SCI]</i> | | <i>abs(Diff)</i> | <i>Different from control?</i> |
|------------------------------------------------------|-------------|-------------|----------------------------|----------|------------------|--------------------------------|
| <i>Control</i> | 17.1661 | --- | --- | --- | --- | --- |
| <i>Bonding Agent only</i> | 264.1782 | 247.0121 | 168.3617 | 325.6626 | 247.0121 | Yes |
| <i>Sandblasted only</i> | 30.06287 | 12.89678 | -65.75367 | 91.54723 | 12.89678 | No |
| <i>Combination of sandblasting and bonding agent</i> | 197.8835 | 180.7174 | 102.067 | 259.3679 | 180.7174 | Yes |

Diff = mean(order)-mean(control)

Different from mean(control) if abs(Diff) > 78.6505

One-way ANOVA G_{ic} (Jm^2) order if material== "Sinfony"

| Order | Mean | Std. Dev | Freq. |
|--------------------------------------------------|------------------|------------------|--------------|
| Control | 35.839062 | 28.804807 | 12 |
| Bonding Agent only | --- | --- | --- |
| Sandblasted only | 17.040126 | 13.136091 | 12 |
| Combination of sandblasting and bonding agent | 455.6483 | 170.89071 | 12 |
| Total | 169.50916 | 227.29127 | 36 |

Analysis of Variance

| Source | SS | df | MS | F | Prob > F |
|-------------------|-------------------|-----------|-------------------|----------|--------------------|
| Between groups | 1475881.29 | 2 | 737940.646 | 73.29 | 0.0000 |
| Within groups | 332264.999 | 33 | 10068.6363 | | |
| Total | 1808146.29 | 35 | 131.660843 | | |

Bartlett's test for equal variances: $\chi^2(2) = 58.1260$, $Prob > \chi^2 = 0.000$

Dunnett G_{ic} (Jm²) order if material== "Sinfony", control (1)

| Order | Mean | Diff | [2-Sided 95% SCI] | | abs(Diff) | Different from control? |
|------------------------------------------------------|-------------|-------------|----------------------------|----------|------------------|--------------------------------|
| <i>Control</i> | 35.83906 | --- | --- | --- | --- | --- |
| <i>Bonding Agent only</i> | --- | --- | --- | --- | --- | --- |
| <i>Sandblasted only</i> | 17.04013 | -18.79894 | -113.837 | 76.23915 | 18.79894 | No |
| <i>Combination of sandblasting and bonding agent</i> | 455.6483 | 419.8092 | 514.8473 | 259.3679 | 419.8092 | Yes |

Diff = mean(order)-mean(control)

Different from mean(control) if abs(Diff) > 95.0381

