# THE EFFECT OF NON-THERMAL PLASMA ON THE ADHESION OF RESIN CEMENT TO ZIRCONIA CERAMIC

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# ABSTRACT

**Aim**: The aim of this in vitro study was to investigate the effect of non-thermal plasma on zirconia towards resin-zirconia bond strength and its durability using three different systems of adhesive resin cement.

**Methodology**: Sixty zirconia (Y-TZP) discs were divided into six groups with twenty specimens each (n=20/group) and were subjected to two different surface treatments: 1) Control group: Sandblast and primer (SB); 2) Test group: Sandblast, non-thermal plasma for 60 seconds and then primer (SB+NTP). Resin cylinders were then bonded on the discs using three different adhesive resin cements; Panavia™V5, Multilink®Automix, and RelyX™Ultimate utilizing its recommended primer. Half of the specimens from each group were tested after 24 hours polymerisation, and the other half were tested after aging process with water storage (48 hours, 37ºC) and thermocycling (5000 cycles) using microshear bond test. Data were analysed with Linear Mixed Model and Šídák's test for multiple comparisons ($\alpha = 0.05$) and failed specimens were examined for failure mode under a Tandom Scanning Microscope.

**Results**: Multiple comparison with Šídák's test revealed no statistically significant difference between test (SB+NTP) groups and control groups (SB) ($p<0.05$). However, a statistically significant difference was found between Multilink SB and Rely X SB groups, as well as between short-term (ST) and long-term (LT) groups ($p<0.05$). Predominant failure modes were found to be cohesive.

**Conclusion**: Non-thermal plasma application as added surface modification to current technique had no significant effect on the resin-zirconia bond strength or its durability. Aging process with water storage and thermocycling played an important role in resin-zirconia bonds degradation.

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# DEDICATION

To my dearest wife, Zeety, and my little one, Uzayr, for their love, support, and company throughout this project.

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# INTRODUCTION

## 1.1 YTTRIUM-STABILIZED ZIRCONIA (3Y-TZP)

The use of zirconia in dentistry is mainly due to its superior mechanical properties compared to alumina and silica based ceramics. Its fracture strength can exceed 1000 MPa (Ashizuka et al. 1988). Clinical applications of zirconia include but are not limited to; single crowns, fixed dental prostheses, implants, orthodontic brackets, endodontic posts/dowels, and abutments.

Three phases of the crystal structure of zirconia are known, depending on the temperature. The crystal structure is monoclinic below 1170°C, tetragonal between 1170°C and 2370°C; and cubic above 2370°C up to the melting point (Denry and Kelly 2008). Upon cooling, the crystal structure transforms from tetragonal to monoclinic and is accompanied by a substantial increase in the volume of about 4.5%. This volume expansion induces stress and creates micro fractures which could lead to catastrophic failure of the material (Denry and Kelly 2008, Souza et al. 2013).

To overcome this problem, stabilizing oxides such as magnesium oxide, calcium oxide, yttrium oxide and cesium oxide are used (Souza et al. 2013). The addition of small amounts of these oxides to pure zirconia allows the high-temperature tetragonal phase to be retained at room temperature (Guazzato et al. 2004, Denry and Kelly 2008). 3mol% of yttria as stabilizer has been proven to produce a material known as 3Y-TZP with white and translucent appearance, biocompatible and possess excellent mechanical properties. Hence, zirconia in 3Y-TZP form is widely used in biomedical implants and dentistry (Camposilvan et al. 2015).

The retained tetragonal structure in 3Y-TZP is in a metastable state. It can transform from tetragonal to monoclinic under stress. For example, high stresses at a crack initiation site under loading will induce tetragonal to monoclinic

transformation around the growing crack. As mentioned earlier, tetragonal to monoclinic transformation is accompanied by a 4.5% increase in volume. Thus, it generates compressive stresses around the growing crack and limiting its propagation. This increase the fracture toughness. The phenomenon is called transformation toughening and is the mechanism behind the mechanical behaviour of 3Y-TZP (Guazzato et al. 2004, Camposilvan et al. 2015).

## 1.2 BONDING TO ZIRCONIA

Various clinical studies have documented the long-term success of bonding silica-based ceramic material restoration using resin cements (Blatz et al. 2003). The efficiency of the bonding most often relies on the adhesive technique, which is the combination of micromechanical retention and chemical functionalisation (Valverde et al. 2013). Despite favourable mechanical properties of zirconia as a dental restorative material, obtaining adequate bonding to it with resin has been proven very difficult (Piascik et al. 2009). Micromechanical retention on silica-based ceramic restoration is achieved by etching with hydrofluoric acid which improves the wettability and increases the surface area available for mechanical interlocking (Thompson et al. 2011). The use of hydrofluoric acid on silica-based ceramic prior to bonding is well-documented. Unlike traditional silica-based ceramic, conventional etching technique on zirconia has no positive effect in producing surface roughness for micromechanical retention as it is acid resistant.

Air particle abrasion, also known as sandblasting using aluminium oxide particles is the most commonly used method for this purpose instead. Air particle abrasion has been proposed to be used on different materials such as metals, ceramics and dental hard tissues to increase micromechanical retention as well as surface area (Tzanakakis et al. 2016). The bond strength of resin cements to zirconia were found to be increased by surface treatment of zirconia with air particle abrasion (Blatz et al. 2010).

This method, however, could create micro cracks and surface flaws which then act

as crack initiation sites and can potentially decrease fracture toughness of zirconia (Thompson et al. 2011, Zhang et al. 2004, Kumbuloglu et al. 2006). Numerous in vitro studies were done to investigate and minimize this effect, comparing different particle composition, sizes and pressure during air abrasion. Aluminium oxide particles ranging from 50 to 250 μm in size is recommended by several studies (Derand and Derand 2000, Wegner et al. 2000, Thompson et al. 2011) but a systematic review by Kern (2015) and Tzanakakis et al. (2016) suggested air abrasion with 50μm alumina particles at 0.1 to 0.25 MPa for optimum bonding.

On the other hand, apart from work by Guazzato et al. (2004) and Kosmač et al. (1999), many other studies also showed that sandblasting was able to induce tetragonal to monoclinic transformation at low temperature effectively with minimal surface damage which could counteract the flaw-induced reduction in strength by transformation toughening mechanism. Kern (2005) studied the long-term survival of In-Ceram Alumina and Zirconia resin bonded fixed partial denture, and found that fractures occurred on connector sites without air abrasion but never on the ones which were air abraded before bonding. This suggested the positive effect of air particle abrasion in clinical practice.

A systematic review by Kern (2015) revealed that there is strong clinical evidence that air particle abrasion at a moderate pressure combined with the use of phosphate monomer containing primers and resin cements could provide long term durable bonding to zirconia ceramic in the oral conditions. Kern and Wegner (1998) were the first to report the long-term bond strength potential when phosphate monomer, 10-methacryloyloxydecyl dihydrogen phosphate (MDP)-containing resin cements were bonded to zirconia. Their work also proposed that the functional phosphate ester group in MDP could form a water-resistant or hydrolytically stable chemical bond with zirconia. Based on their results, MDP-containing resin cements were recommended for bonding zirconia in clinical practice. Thompson et al. (2011) also pointed out that the use of MDP or primers with phosphate monomer could produce silane-like adhesion through a similar type of hydroxylation-driven

chemistry between resin cements and zirconia. Chemical reactions are believed to be formed between hydroxyl groups in the MDP monomer and hydroxyl groups on the zirconia ceramic surface. A number of in vitro studies (Ikemura et al. 2011a, b, c; Yoshida et al. 2006, Cavalcanti et al. 2009, Ozcan et al. 2008, Tsuo et al. 2006) investigated different chemical compounds; either phosphate-containing or non-phosphate primers to improve bond strength between adhesive cements and zirconia ceramics but neither have proven to provide a long-term superior bond compared to MDP.

## 1.3 ALTERNATIVE SURFACE TREATMENTS METHODS TO ZIRCONIA

Alternative methods to improve resin bonding to zirconia are still being explored. This is because there is still no universally accepted protocol for long-lasting and biologically safe zirconia cementing (Tzanakakis et al. 2016). Tribochemical silica coating is one popular alternative technique which uses alumina particles that have been coated with nano-silica (with either Cojet or Rocatec systems (3M ESPE, Seefeld, Germany)) to embed silica particles onto the zirconia surface. It is originally designed for surface treatment of soft metals. The idea is to convert silica-free to silica-rich zirconia surface and utilize the proven chemical bonding provided by silanation (siloxane bonds). However, according to Chen and Suh (2012), previous studies showed that this technique has no significant benefit and only provide similar effect of surface roughness as air particle abrasion with aluminium oxide. It was also reported that it did not produce stable resin-zirconia bond strength and susceptible to hydrolytic degradation (Kern and Wegner 1998, Matinlinna et al. 2006). Other similar treatments utilizing silica-coating onto zirconia surface include 'silicoating', which uses flame treatment with tetraethoxy silane-containing butane as fuel gas, glazing zirconia surface with silica, internal coating technique, gas-phase chloro-silane pre-treatment and sol-gel process silica coating (Chen and Suh 2012).

Laser treatment is another interesting concept tried to produce surface irregularities on zirconia to improve adhesion. Ablation is the process to remove particles by micro-explosions and vaporization induced by the laser. Among the types of laser tested were the erbium: yttrium-aluminum-garnet (Er: YAG), neodymium: yttrium-aluminum-garnet (Nd: YAG) and $CO_2$ laser (Aranha et al. 2005). It was found that the results from laser treatments were contradictory. Some studies showed that erbium: Er: YAG and Nd: YAG laser significantly increased bond strength of zirconia, whereas $CO_2$ laser treatment was less effective for improving zirconia bonding (Akin et al. 2011, 2012; Paranhos et al. 2011). A study by Foxton et al. (2011) concluded that Er: YAG laser treatment of zirconia surface did not result in durable resin-ceramic bond. The micro-shear bond strength was dropped significantly after six months of water storage.

A novel surface roughening method for zirconia called selective infiltration etching has been explored by Aboushelib and colleagues (Aboushelib et al. 2007). Selective infiltration etching used the principle of heat-induced maturation and grain boundary diffusion to create a retentive surface on zirconia. The process involved pre-stressing surface grain boundaries by controlled heating and allowing selective infiltration of specially formulated molten glass into the surface structure. The glass is then etched out using hydrofluoric acid, creating a surface with three-dimensional network of inter-granular porosity that allows nano-mechanical interlocking of resin cement.

## 1.4 NON-THERMAL PLASMA

In the recent years, there is a growing interest among researchers on the use of atmospheric-pressure low-temperature plasma or non-thermal plasma in the dental industry particularly as a surface treatment, aimed to improve the bond strength of adhesives. Non-thermal plasma is an established method for fine cleaning and activating surfaces by increasing the surface energy (Liebermann & Lichtenberg 2005, Silva et al. 2011).

An early study on non-thermal plasma as a bond enhancer in dentistry was done on elastomeric impression material in 1993 by Vassilakos and colleagues who found promising results. Surface treatment with non-thermal plasma was found to improve the wettability of elastomeric impression material and produced void-free die stone casts. More recent studies by Valverde et al. (2013) and Silva et al. (2011) suggested that non-thermal plasma has the potential to enhance bonding performance of resin cement to zirconia. Ito et al. (2016) also concluded that non-thermal plasma treatment improved the bond strength of adhesive resin cement to zirconia.

However, contradicting findings were observed by Vechiato et al. (2017), Balkenhol et al. (2017) and Kong (2016) which showed inconsistent results and no significant difference in the resin-zirconia bond strength when non-thermal plasma treatment was used. Plasma treatment was also tried to improve the bond strength of Cobalt-chromium alloy to self-cured, as well as heat-cured to self-cured acrylic resins but only to find inconsistent results (Nishigawa et al. 2003, Maruo et al. 2004).
Work by Moon et al. (2014) found that plasma treatment on leucite-reinforced ceramics did not produce a significant difference in early bond strength compared to standard hydrofluoric acid treatment. Therefore, more investigations of the effects of non-thermal plasma treatment are needed before it can be applied in clinical practice.

## 1.5 ARTIFICIAL AGING AND DURABILITY TESTING

Simulation of the aggressive and aqueous oral environment is important in in vitro studies to allow researchers to draw conclusions on the long-term durability of a specific bonding procedure and also to identify superior materials and techniques. The widely accepted methods to artificially aging and applying stress to the bonding interface is by long-term water storage and thermocycling of the bonded specimens. Some studies on bond strength used one month to six months water storage (Aboushelib et al. 2007, Foxton el al. 2011); thermocycling without water

storage (Everson et al. 2012, Guess et al. 2008, Vechiato et al. 2017); or water storage combined with thermocycling (Hallmann et al. 2016) for artificial aging process. Most studies which applied the aging process found significant differences in bond strength values before and after the procedure. Beside artificial aging, the application of mechanical cyclic loading or fatigue load could also be used to test for the bond durability. These methods have also been shown to cause significant reduction of bond strengths (Blatz et al. 2003).

Water is the most common solution used for artificial aging due to its simplicity and low cost but the use of other solutions like artificial saliva and sodium hypochlorite has also been reported. Kitasako et al. (2000) reported a study on effects of different storage solution and condition on the bond durability over the period of one year and found different storage condition could affect the results. Microbial inhibitors or preservatives sometimes were added to prevent changes of the storage solution; however, this act could affect the bond strength measurements and invalidate the results.

## 1.6 MICRO-SHEAR BOND STRENGTH TEST

Bond strength tests have been the most commonly reported means of evaluating the adhesion of adhesive restorative materials. This includes tensile, shear, microtensile and microshear protocols (Meerbeek et al. 2010). The variety of methods used in in-vitro tests has made comparison among studies difficult due to limited standardisation.

Shimada et al. (2002) stated that when the size of the cross-sectional bond area tested is less than $3mm^2$, it is classified as the micro-bond strength test. A review by Scherrer et al. (2010) revealed that micro-tests generally delivered higher strength values due to smaller specimen size which was associated with a low probability of encountering strength-limiting flaws. Since its introduction by Sano et al. (1994), the microtensile bond strength test has been a popular method for

testing the bonding efficacy of adhesives as it was found to have better stress distribution (Armstrong et al. 2010). Generally, smaller-sized test specimens are preferred due to the lower probability of defects on the specimens which could lead to a higher incidence of cohesive failures as observed in the "macro" tests. This makes the micro-bond tests, that is microshear bond test and microtensile bond test a more reliable method.

The most frequently cited protocol for microshear bond test was described by Shimada et al. (2002). The microshear bond strength test has some advantages compared to the microtensile bond test. The microshear bond test would allow for regional mapping or depth profiling of the substrates. Also, sample preparation is less complicated than microtensile bond test thus preserving the integrity of the specimens and would yield more reliable results (Armstrong et al. 2010, Shimaoka et al. 2011). Despite the advantages, preparing samples for microshear bond strength test can be challenging. Shimaoka et al. (2011) reported on the importance of restricting the adhesive area on the sample to that which is actually being tested. Most of the earlier in vitro studies applied the adhesive on the whole substrate prior to the construction of the resin cylinder to be tested. This could potentially lead to an overestimation of the actual bonding performance of the adhesives being tested. This was due to the influence of the adhesive area exceeding the limits of the specimen actually being tested. Shimaoka et al. (2011) in their conclusion suggested that area delimitation technique as an important step to obtain more reliable results.

## 1.7 RESIN-BASED ADHESIVE CEMENTS

Resin-based adhesive cements have compositions and characteristics similar to conventional restorative composites. They can be classified based on their initiation mode as chemically-activated, photo-activated or dual-activated materials. In general, chemically-activated resin cements are indicated for bonding metal-based or opaque high-strength ceramic restorations due to their higher degree of

polymerisation. This potentially allows for a superior hardness of the material. On the other hand, dual-activated resin cements would allow for an extended working time and controlled polymerisation (Kramer et al. 2000).

Filler contents in the resin cements affect the characteristics and mechanical properties of the cements. For example, highly-filled resin cements showed an increase in bond strength and abrasion resistance, reduced polymerisation shrinkage and micro leakage (Kramer et al. 2000, Hahn et al. 2001). Resin cements with a reduced filler contents have an increased surface-wettability and offer better flowability, thus allowing for optimal positioning of the restoration (Kramer et al. 2000). Various viscosities of the cements have different clinical implications. For low viscosity cements, it may be difficult to remove the excess cement from the margins of the restorations, whereas with higher viscosity cements, it may cause debonding of the restorations during dental procedures such as ultrasonic scaling (Kramer et al. 2000).

As mentioned earlier, MDP was found to be the primer effective for a stronger adhesion of resin cements to zirconia. Traditional resin cements normally contain no adhesive functional monomer and require a separate ceramic primer. Examples of adhesive systems which need a separate primer are like Panavia™ V5, Multilink® Automix, and RelyX™ Ultimate. These systems are dual-cured adhesive resin cement and come with a separate ceramic primer which contain MDP or phosphate-based functional monomer as the main component. These are relatively new systems and not many studies have been done to test their bond strength. However, earlier range of Panavia systems which also contain MDP in the primer have been used multiple times and demonstrated high and durable bond strength when compared to other systems without MDP.

Manufacturers also have developed self-adhesive resin cements for simplicity and to allow for easier clinical applications. Examples of self-adhesive resin cements include BisCem (Bisco), G-Cem (GC), Clearfil SA Cement (Kuraray), RelyX

Unicem (3M ESPE) and MaxCem (Kerr). However, studies revealed self-adhesive resin cements had poor self-cure ability (Vrochari et al. 2009), weaker physical properties and more hydrophilic, which led to faster hydrolytic degradation compared to traditional resin cements (Blatz et al. 2010, Kumbuloglu et al. 2005, Cavalcanti et al. 2009 and Ozcan et al. 2008).

## 1.8 MICRO-RAMAN SPECTROSCOPY

The Raman effect, which was discovered by C.V. Raman in 1928 is a phenomenon of inelastic scattering of the light. This is due to a shift in the wavelength of radiation scattered by the molecular vibrations. This important discovery led to the development of the Raman spectroscopy, which was a technique to measure the fundamental molecular vibrations. Micro-Raman could produce better analysis of biomolecular information compared to the standard spectroscopic techniques using fluorescence and immunoassay (Pappas et al. 2000).

In dentistry, Raman spectroscopy is a popular tool to investigate changes of structure and phase composition of zirconia surfaces as the Raman shift is different for the monoclinic and tetragonal phase in zirconia crystal structure (Paul et al. 2011). The application allowed for the possibilities of study of the material's crystal structure, the phase transformation peculiarities, the quantum size effect, compositional effects and the material evolution with treatment (Naumenko et al. 2008). This method of analysis non-destructive and requires no special preparation or manipulation of the sample. It is a rapid method compared to techniques such as X-ray diffraction (XRD) and can be used to obtain both qualitative and quantitative data (Paul et al. 2011). Inokoshi et al. (2016) made a structural and chemical analysis at zirconia-veneering ceramic interphase using micro Raman and found tetragonal to monoclinic phase transformation as well as residual compressive stress at the sandblasted zirconia surface.

## 1.9 FAILURE ANALYSIS

According to the Glossary of Prosthodontic Terms (GPT 2005), the definition of adhesion is "the property of remaining in close proximity, as that resulting from the physical attraction of molecules to a substance or molecular attraction existing between the surfaces of bodies in contact" whereas cohesion is "the force whereby molecules of matter adhere to one another; the attraction of aggregation". In light of this, the bond formed at the resin-zirconia interphase is referred to as adhesion and the bond existed within the resin cement were cohesion. The combination of adhesion and cohesion determines the overall bonding effectiveness of an adhesive and a substrate. When carrying out an in vitro study on adhesive material, it is important to analyse the failure modes of the specimens. Failure patterns give information on stress distribution during the test and the weakest area in the complex adhesive-substrate interface as mentioned by Pocius (1997). He defined the mode of failure as 'the locus in the adhesive bond through which failure propagates'.

Failure modes were usually recorded as adhesive (failures at adhesive interface), cohesive (failures in resin or substrate) or mixed (combination of adhesive and cohesive) failures although there was no consensus in the literature regarding the classification of failure modes (Scherrer et al. 2010). It is important to interpret the modes of failure with caution as it can be an indication of the reliability of a bond strength test. If the predominant failures were found to be cohesive or mixed, the overall bond strength results could potentially become rather unreliable. This is because they represent breaking stresses that result from different materials with varying mechanical properties and thus no longer a representative of adhesive bond strength values. Interestingly, a critical review by Scherrer et al. (2010) revealed a high degree of cohesive failure with shear bond strength tests. A considerable amount of cohesive failures was also found from the microtensile bond strength test. Micro-bond strength tests were thought to be less prone to produce cohesive failures in the samples due to the smaller bonding surface area.

Some studies then showed that the introduction of micro cracks and defects in the specimens during sample preparation could initiate cohesive failures in microshear and microtensile bond strength tests (Sadek et al. 2005).

Armstrong et al. (1998) suggested that although cohesive failures can be evaluated with a stereomicroscope at low magnification, the adhesive failure modes can only be properly made using a Scanning Electron Microscope at high magnification with a classical fractography techniques. This also allows identification of the fracture initiation site and extension of the crack in relation to the interface.

## 1.10 SUMMARY OF THE LITERATURE REVIEW

Despite the increase in the clinical use of zirconia ceramics, the bonding performance of zirconia restorations is still a concern. The current knowledge recommends air particle abrasion with aluminium oxide and use of MDP or phosphate-containing primer as the surface treatment on zirconia before cementing with resin cement. Evidence to date showed that this is the most reliable method for bonding zirconia restorations. However, a systematic review of the clinical success by Larsson and Wennerberg (2014) pointed out that one of the most common reasons for failure in tooth-supported zirconia-based crowns is the loss of retention. Thus, researchers are still looking for techniques to improve the bond strength as well as the durability of the bond and provide evidence to establish a more reliable method to bond zirconia restorations. Research in this field is not an easy task, as various parameters could affect bond strength values (and durability) to be considered and studied. In one area, the study of the effects of non-thermal plasma on bonding at resin-zirconia interface is still limited and remains unclear. Therefore, this study is exploring the use of non-thermal plasma in bonding resin to zirconia and the purpose as well as objectives are explained in more details under section 2.1; Aims of the study.

# AIMS AND OBJECTIVES

## 2.1 AIMS OF THE STUDY

The primary aim of this in vitro study is to investigate whether non-thermal plasma treatment on zirconia as added surface modification can enhance the bond strength of resin-zirconia interface compared to current recommended technique with just air-particle abrasion and phosphate-containing primer. The secondary aim is to evaluate the durability of the resin-zirconia bond and the influence of non-thermal plasma after aging process by water storage and thermocycling between three resin cements; Panavia™ V5, Multilink® Automix, and RelyX™ Ultimate.

## 2.2 RESEARCH QUESTIONS

1) Will added surface modification on zirconia with non-thermal plasma increase the bond strength of resin cements to zirconia compared to current recommended technique?
2) What is the effect of water storage and thermocycling on the bond strength of resin cements to zirconia?
3) Is there any difference on the resin-zirconia bond strength between the three resin cements; Panavia™ V5, Multilink® Automix, and RelyX™ Ultimate with and without non-thermal plasma treatment?

## 2.3 NULL HYPOTHESES

1) Non-thermal plasma treatment as added surface modification does not improve bond strength of resin cements to zirconia compared to current recommended technique with air-particle abrasion and phosphate-containing primer.
2) 48-hour water storage combined with 5000 cycles of thermocycling have no effects on bond strength of resin cements to zirconia.
3) There is no difference on resin to zirconia bond strength between the three resin cements; Panavia™ V5, Multilink® Automix, and RelyX™ Ultimate.

# MATERIALS AND METHOD

This study is an extension of previous in vitro study by Kong in 2016. Part II of this study was carried out by Han (2017). The difference is in the sequence of surface treatment, that is the non-thermal plasma, either before or after primer application. This study investigates the effect of non-thermal plasma treatment on zirconia prior to applying the primer.

## 3.1 FLOW CHART OF METHODOLOGY

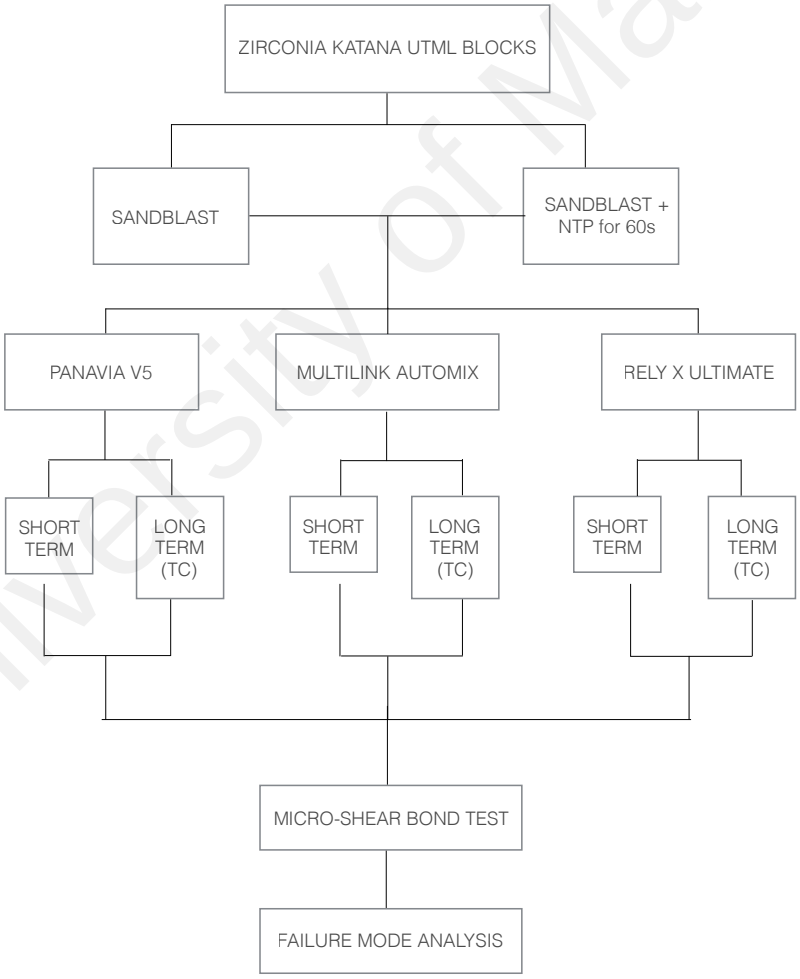


Figure 1: Simplified flow chart of the methodology and protocols used in this study.

## 3.2 SUMMARY OF PROTOCOL

Sixty Y-TZP discs (Katana, Kuraray, Noritake Dental Inc, Tokyo, Japan) measuring 15mm in diameter and 1mm thickness were obtained from the manufacturer. They were randomly divided into six groups of twenty specimens each (n=20/group) and were subjected to two different surface treatments: 1); sandblast and primer (SB) as control group or 2); sandblast and 60s of non-thermal plasma prior to primer application (SB+NTP). Three types of resin cement: Panavia™ V5, Multilink® Automix, and RelyX™ Ultimate used to bond resin cylinders on the treated zirconia surface. One specimen from each group were tested after 24 hours polymerisation as short-term storage (ST), and the other one tested after aging process or long-term storage (LT) in distilled water (48 hours at 37ºC) and 5000 cycles of thermocycling using microshear bond strength test. Ultimately, six groups with the total of 120 specimens (n=120) were made and labelled as below:

1. Panavia SB
2. Panavia SB+NTP
3. Multilink SB
4. Multilink SB+NTP
5. Rely X SB
6. Rely X SB+NTP

## 3.3 MATERIALS USED IN THE STUDY

The resin cements used in this study were dual-cured adhesive resin cement systems; Panavia™ V5, Multilink® Automix, and RelyX™ Ultimate. The product identifier, composition as well as other materials used in this study were as attached in appendix I, II, III and IV.

## 3.4 PILOT TEST

A pilot test was carried out prior to performing this study. Materials from the previous study by Kong (2016) were used for this purpose. The main reason for a pilot test in this study was for training in preparing the specimens as it was relatively technique sensitive thus aiming to reduce pre-test failures during the preparation of the specimens. Microshear bond strength tests were also carried out at this stage to pre-stress the wire loop.

## 3.5 PREPARATION OF THE TEST SPECIMENS

Each zirconia discs were first sandblasted at two points or areas with 50µm aluminium oxide particles (Danville, San Ramon, California) at 0.2MPa pressure using intraoral sandblaster (MicroEtcher™, Danville, San Ramon, California) for 10 seconds from a distance of 10mm perpendicular to the zirconia surfaces (adherend surface).

Figure 2: Nozzle of sandblaster (MicroEtcher™, Danville, San Ramon, California) was fixed at a distance of 10mm from the adherend surface of zirconia.

Figure 3: Non-thermal plasma device (Piezo Brush®PZ2 Handheld Device, Relyon Plasma, Regensburg, Germany) was fixed at a distance of 5mm from the adherend surface of zirconia.

Sandblasted discs were then cleaned in an ultrasonic cleaning machine (Fisherbrand® 15060) with an isopropanol solution (Acros Organics™, Extra Pure 99.5%) for 2 minutes and dried according to the manufacturer's recommendation.

The cleaned discs were then randomly divided into six groups where two specimens will be made on each disc (n=20/groups). Each type of resin cement had a control and a test group. The test groups received 60 seconds of non-thermal plasma surface treatment using the non-thermal plasma device (Piezo Brush®PZ2 Handheld Device, Relyon Plasma, Regensburg, Germany). The device was a hand-held unit that generated a plume of plasma jet at atmospheric pressure. The nozzle of the non-thermal plasma device was fixed at a distance of 5mm from the zirconia discs. For the control groups, only this step was omitted.

A double-faced adhesive tape (Sellotape, UK) was cut to the size of approximately 3mm x 3mm and perforated at the centre to allow for a delimitation area of 0.8mm in diameter. The tape was then positioned carefully onto the zirconia disc to expose the sandblasted areas through the perforation.

Ceramic/zirconia primer (Clearfil™ Ceramic Primer Plus, Kuraray Noritake Dental / Monobond® Plus, Ivoclar Vivadent / Scotchbond™ Universal, 3M ESPE) was then applied to the exposed surface of sandblasted zirconia with a disposable brush tip according to the resin cement system to be used. The primer was then dried by blowing with oil-free air (according to manufacturer's instructions).

The other side of the tape was then peeled off, a slice of micro bore Tygon tubing (Fischer Scientific UK Ltd., Loughborough) with an internal diameter of approximately 0.8mm and height of 1mm were positioned over the uncovered tape, ensuring that their lumen coincide with the circular zirconia areas exposed.

Resin cement (according to the primer used, Panavia™ V5, Kuraray Noritake Dental / Multilink® Automix, Ivoclar Vivadent / RelyX™ Ultimate, 3M ESPE) was freshly mixed and carefully filled into the lumen to avoid air-bubbles. The oxygen barrier gel was applied and the resin cement was light-cured with an LED curing light (Elipar™ Deep Cure-S LED Curing Light, 3M-ESPE, Seefeld, Germany) for 20 seconds as manufacturer's recommendation. Constant output of 1470mW/cm$^2$ was verified with light meter. In this manner, resin cement cylinders of approximately 0.8mm in diameter and 1mm in height were bonded at two locations on the zirconia surface.


Figure 4: Primer (Clearfil™ Ceramic Primer Plus) and the resin cement for Panavia™ V5 system.


Figure 5: Primer (Monobond® Plus) and the resin cement for Multilink® Automix system.


Figure 6: Primer (Scotchbond™ Universal) and the resin cement for RelyX™ Ultimate system.

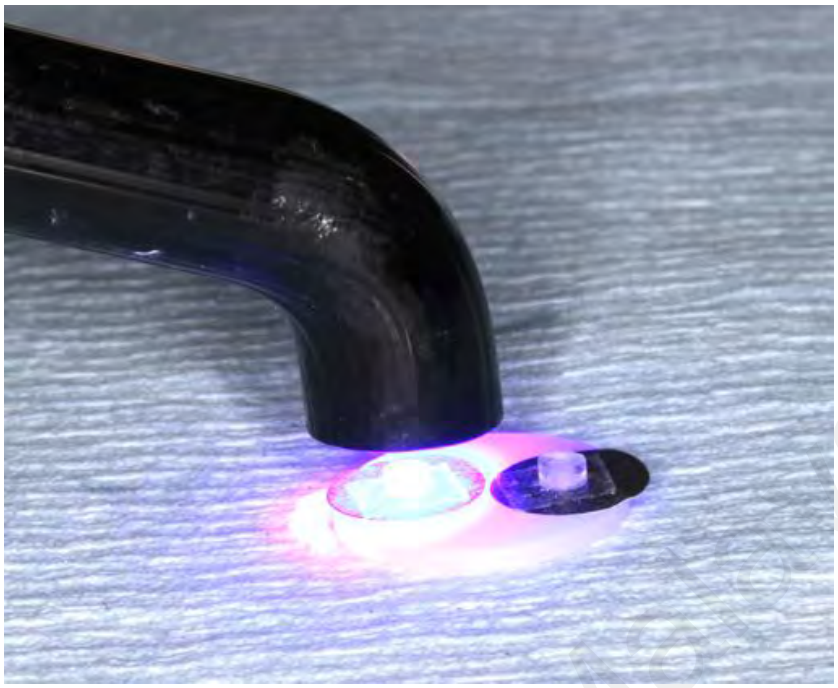

Figure 7: Resin cement moulded by Tygon tubing was cured as per manufacturer's recommendation.

Figure 8: Resin cylinders bonded on zirconia surface after removal of Tygon tubing. Excess cement around the base of resin cylinders was then removed using a scalpel blade.

The cured resin cement was then left to completely polymerize for 24 hours at room temperature (23ºC) prior to removal of Tygon tubing. Tygon tubing and the tape were gently removed by cutting with a scalpel blade to expose the bonded resin cylinder specimens. Any excess resin cement on the zirconia surfaces around the resin cylinders was carefully removed with a scalpel blade. Short term groups were tested immediately after removal of Tygon tubing. Long term groups were stored in distilled water at 37$^{o}$C for 48 hours in an incubator (Sanyo Electric Company Ltd., Osaka, Japan) and subjected to 5000 cycles of thermoycling. The thermoycling regime used an in-house constructed robot arm (AX-12A Dynamixel robot actuators, Robotis) to provide automated alternate periods of 30 seconds of immersion in a Grant water bath (Grant Instruments Ltd., Barrington, Cambridge) at 55$^{o}$C and 30 seconds of immersion in a Jencons Julabo F10 circulating water bath (Jencons Scientific Ltd., Bedfordshire, England) at 5$^{o}$C.

## 3.6 MICRO-RAMAN SPECTROSCOPY

The zirconia surfaces were examined under inVia™ microRaman microscope (Renishaw plc, Wotton-under-Edge UK) with a x20 /0.45 NA lens before and after non-thermal plasma treatment for surface chemistry changes. Three-point scan was made on each zirconia discs with exposure time of 10 seconds.

## 3.7 SPECIMEN TESTING

After the artificial aging process, each zirconia disc with the resin cylinders was adhered with a cyanoacrylate adhesive (Everbuild Stick 2 Superglue Gel) on a microshear custom jig mounted onto the testing device; LAL300 linear actuator (SMAC Europe Ltd, Horsham UK) with a stroke length of 50 mm with a peak force of 250 N and a resolution of 0.5 microns. Control code for the actuator was transmitted by use of a LAC1 controller unit (SMAC UK) and tests were recorded to a workstation. Prior to that, each group with different protocols were labelled accordingly for identification in the failure modes analysis later on. A thin pre-stressed stainless-steel round wire (0.2mm in diameter) was looped around the base of the resin cylinders at the resin-zirconia interface to contact half its circumference, and was held on the other end against the fixed metal turret on the jig. The assembly was aligned carefully to ensure the microshear test force is applied at the resin-zirconia interface. Shear load was then applied onto the specimens at a crosshead speed of 1.0 mm/min until failure (debonding) occurred. The highest force value (in internal units) culminating in failure of the bond (failure load) was extracted from the computer-generated data files. The force was then converted to microshear bond strength in MPa units using the following formula:

Microshear bond strength (MPa) = $\frac{Fmax}{A} = \frac{\text{Force (internal units) x 0.3667}}{\text{Surface area}}$

(Average diameter of resin composite turrets = 0.8mm)

Surface area = $\pi r^2 = 3.142 \times (0.4)^2$

Surface area = A = 0.5

∴ Microshear bond strength (MPa) = $\frac{\text{Force x 0.3667}}{0.5}$

Figure 9: Specimens assembled and mounted onto a microshear bond strength test machine, ready to be tested.

## 3.8 DATA ANALYSIS

The converted data in MPa (mean and standard deviation) were then sent to a statistician and statistically analysed using Linear Mixed Models which are analogous to ANOVA. Multiple pairwise comparisons were accomplished using the Šídák's test. Statistical analysis was carried out in Stata 14.2, StataCorp. 2015 with a statistical significance level defined as $p<0.05$.

## 3.9 FAILURE MODE ANALYSIS

Following microshear bond test, failure modes analysis was carried out using a x5 / 0.1 NA lens under a Tandom Scanning Microscope (TSM) (Noran Instruments, Middleton, WI, USA) equipped with a motorized lab jack (MLJ050/M, Thorlabs, LTD; Ely, United Kingdom). Images of the failed interfaces were captured using an iXon 885 EM-CCD (Andor Technology; Northern Ireland, UK), using Micromanager Image capture software, (Open Imaging; Inc. San Francisco, CA, USA). Failure was defined as adhesive if more than 75% of the zirconia surface within delimitation area was visible. A cohesive fracture showed more than 75% of the surface covered with resin cement. All other cases were classified as mixed failure (Behr et al. 2011).

# RESULTS

## 4.1 PRE-TEST FAILURES

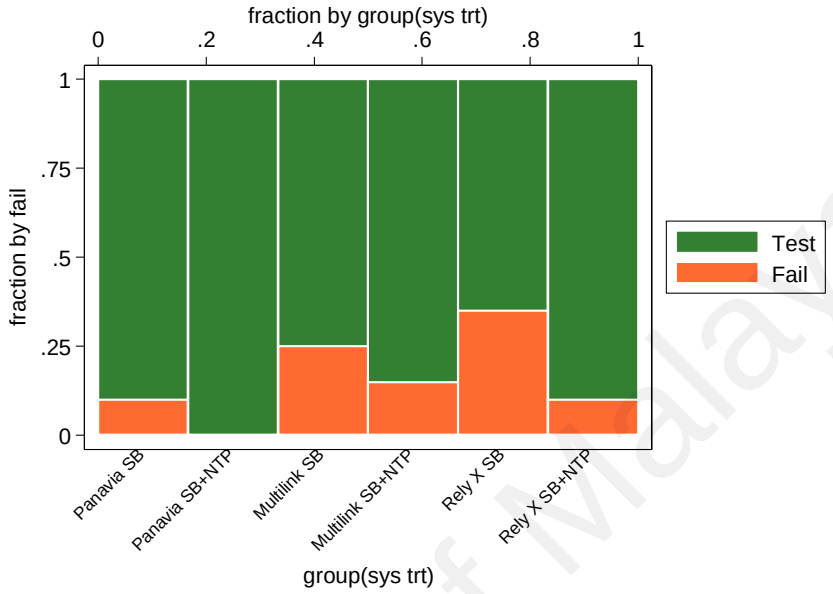


Figure 10: Spine plot showing distribution of pre-test failures of specimens for each group.

Out of 120 specimens available for testing, 19 specimens however fractured during removal of Tygon tubing prior to testing. No specimens failed after water storage and thermocycling. Figure 10 presents the fraction of failed specimens according to the types of cement and their protocols. It was observed that the groups treated with non-thermal plasma had lower pre-test failures than those without non-thermal plasma treatment. Panavia SB+NTP group was the only group without pre-test failures, while Rely X SB group had the highest pre-test failures. These pre-test failures were included in the statistical analysis with the value of microshear bond strength recorded as 0MPa.

## 4.2 UNIVARIATE SUMMARY STATISTICS

Table 1 shows the mean and standard deviation of the microshear bond strength of all groups according to their protocols. Except for short-term Multilink SB+NTP, all test groups which were treated with non-thermal plasma prior to bonding to zirconia showed increased bond strength compared to control groups. However, this increase was not statistically significant as revealed by the statistical analysis (Table 2).

| Testing time | Group (Control or Test) | Resin cement system, Surface treatment | Microshear bond strength (Mean MPa and s.d) |
|---|---|---|---|
| **Short-Term (ST)** | Control | Panavia SB | 40.92 (16.34) |
| | Test | Panavia SB+NTP | 42.39 (14.58) |
| | Control | Multilink SB | 70.19 (18.39) |
| | Test | Multilink SB+NTP | 54.71 (12.28) |
| | Control | Rely X SB | 30.29 (23.85) |
| | Test | Rely X SB+NTP | 42.98 (16.21) |
| | | | |
| **Long-Term (LT)** | Control | Panavia SB | 32.64 (20.05) |
| | Test | Panavia SB+NTP | 34.32 (11.58) |
| | Control | Multilink SB | 17.38 (21.39) |
| | Test | Multilink SB+NTP | 20.24 (15.95) |
| | Control | Rely X SB | 20.76 (21.81) |
| | Test | Rely X SB+NTP | 25.08 (10.68) |

Table 1: Mean and standard deviation of the microshear bond strength (MPa) of all groups dictated by the factors.

Deviation plot in Figure 11 shows data deviations from the mean of microshear bond strength in increasing order. It also clearly shows the downward trend of the microshear bond strength of all the groups when comparing between ST (24-hour polymerisation) and LT (after artificial aging) groups.

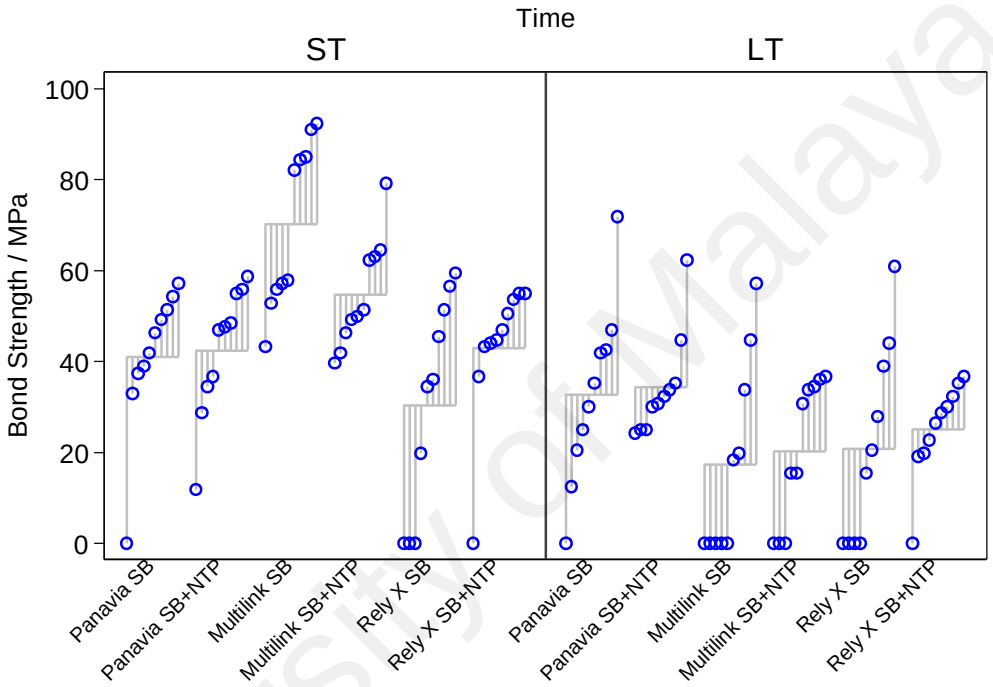


Figure 11: Deviation plot shows mean microshear bond strength and the deviations (MPa) of all groups.

Design plot (Figure 12) represents as a visual summary of the mean microshear bond strength of the control and test groups, and the influence of aging process (ST and LT group plots).

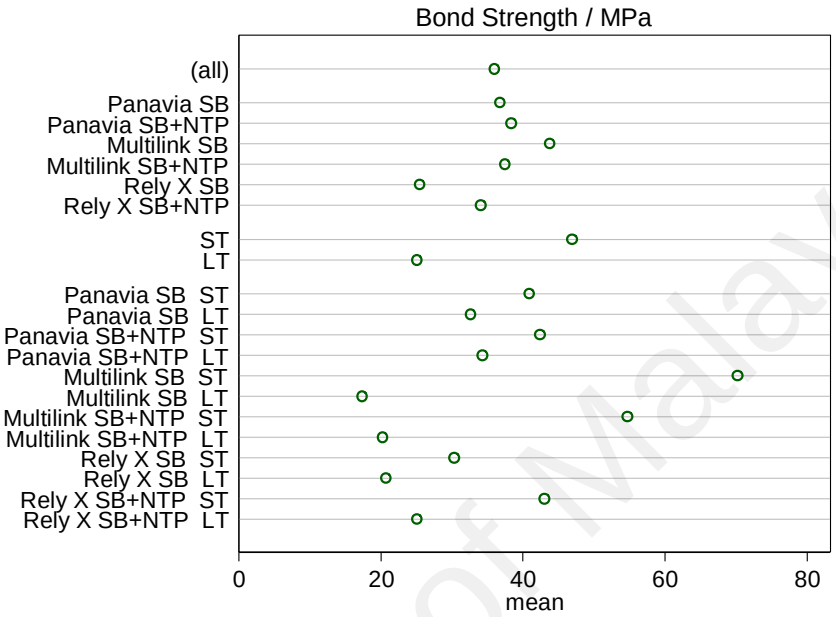


Figure 12: Design plot summarizing the mean bond strength (MPa) of control and test groups and influence of aging process (ST and LT).

From the design plot, all three systems of resin cement demonstrated decreased microshear bond strength after long term protocol (water storage and thermocycling). This was found to be statistically significant (Table 2). Multilink® Automix resin cement was the most affected by water storage and thermocycling. Both control (Multilink SB) and test groups (Multilink SB+NTP) in Multilink® Automix resin cement showed obvious reduction compared to the other resin cement systems. Panavia™ V5 showed the least bond strength reduction in both non-thermal plasma treated and the control group after aging process.

## 4.3 STATISTICAL ANALYSIS

| System | Margin | Standard Error | Sidak Groups |
|---|---|---|---|
| **Panavia SB** | 36.78 | 3.69 | AB |
| **Panavia SB+NTP** | 38.36 | 3.69 | AB |
| **Multilink SB** | 43.78 | 3.69 | B |
| **Multilink SB+NTP** | 37.48 | 3.69 | AB |
| **Rely X SB** | 25.52 | 3.69 | A |
| **Rely X SB+NTP** | 34.03 | 3.69 | AB |
| **Time** | | | |
| **ST** | 46.91 | 2.13 | |
| **LT** | 25.07 | 2.13 | |

Table 2: Statistical analysis using Šidák's method for multiple comparison to test for statistical significance. Groups with statistically significant difference were highlighted. Margins sharing a letter in the group label were not significantly different at the 5% level. ST and LT had no 'letter' associated with them, indicating that the difference of microshear bond strength between short-term and long-term groups was statistically significant ($p<0.05$).

The data was analysed using linear mixed models (LMM) which are analogous to ANOVA. For all hypothesis tests, significance level was pre-determined at α = 0.05. Šídák's multiple comparison were used to compare levels of the factors as there were more than two variables observed in this study. Table 2 presents statistical analysis using Šidák's method for multiple comparison which revealed:

1) No significant difference in the microshear bond strength between control and test groups (SB and SB+NTP).
2) Significant difference ($p<0.05$) in the microshear bond strength between Multilink® Automix and Rely X™ Ultimate control groups (Multilink SB and Rely X SB).
3) Significant difference ($p<0.05$) in the microshear bond strength before and after water storage/thermocycling (ST and LT)

The interactions of the variables were summarised as margins plots in Figure 13.

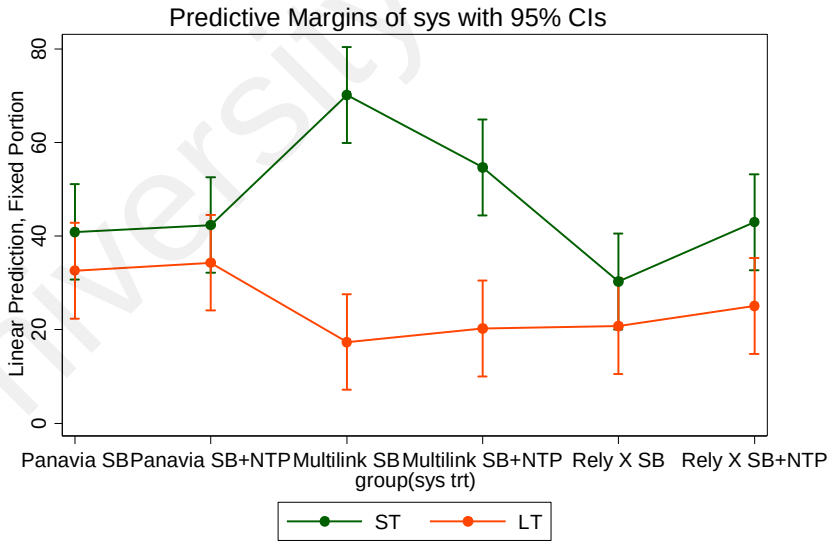


Figure 13: Margins plots summarising the interactions between the groups.

## 4.5 MICRO-RAMAN SPECTROSCOPY

The Raman spectroscopy was undertaken to detect any material composition, properties, and chemical changes of the surface of the zirconia after sandblasting and non-thermal plasma treatment. The results showed the spectra of sandblasted and non-thermal plasma-treated zirconia surfaces appeared to be the same as the baseline which was the untreated zirconia (Figure 14 to 16). They were also found to be uniform and consistent for all specimens.

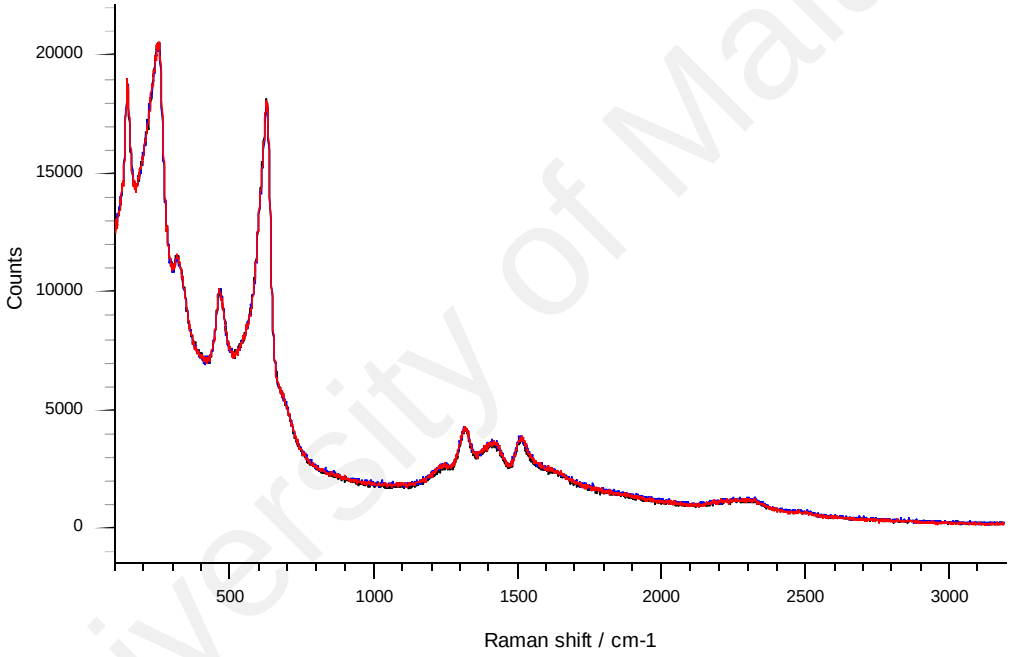


Figure 14: Spectra of untreated zirconia surface (baseline).

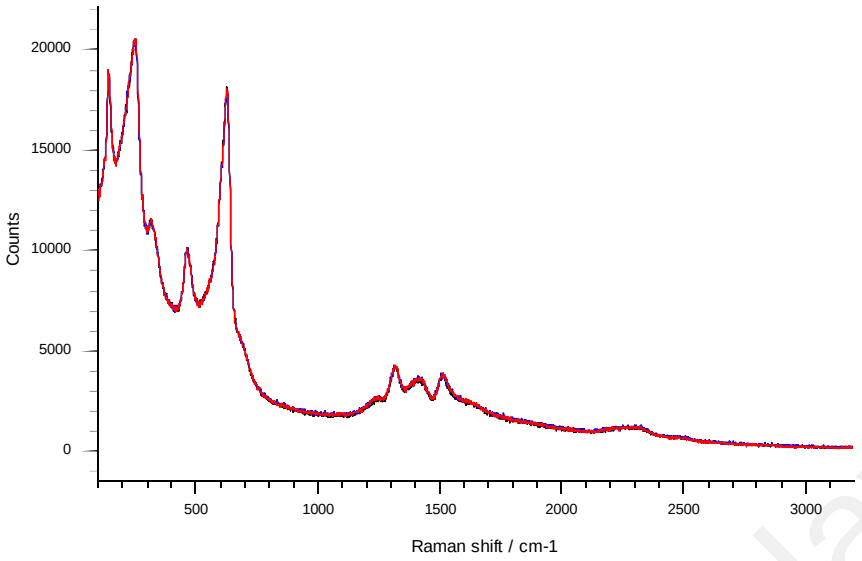


Figure 15: Spectra of sandblasted zirconia surface, without non-thermal plasma treatment.

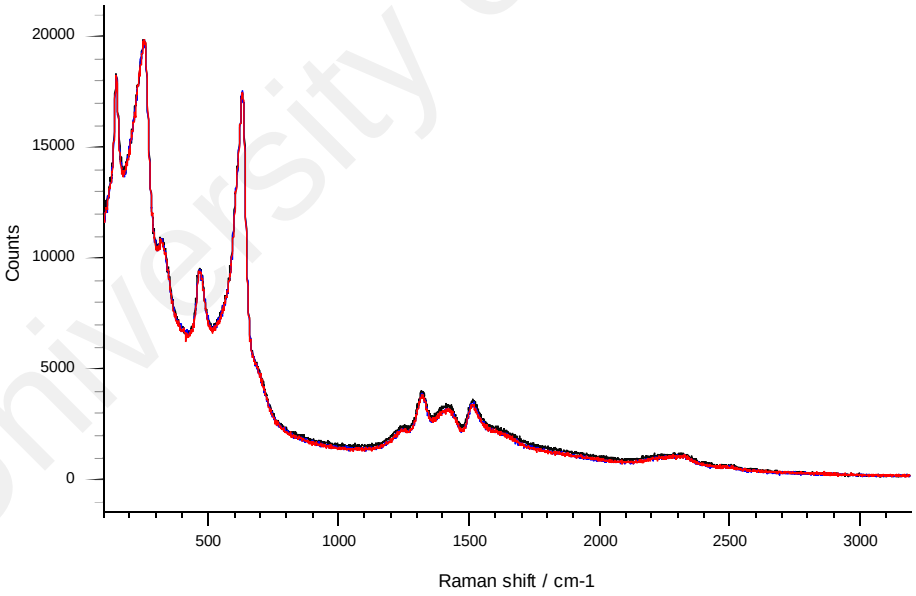


Figure 16: Spectra of sandblasted and non-thermal plasma treated zirconia surface.

## 4.6 MICROSCOPIC ANALYSIS OF FAILED TEST SPECIMENS

Figures 17, 18, and 19 show representative examples of the locus of failures (adhesive, cohesive and mixed failures) on the adherend surface of the zirconia ceramics, as observed under the Tandom Scanning Microscope (TSM) (Noran Instruments, Middleton, WI, USA).

Figure 17: Adhesive failure. More than 75% of the zirconia surface was visible on the adherend surface.

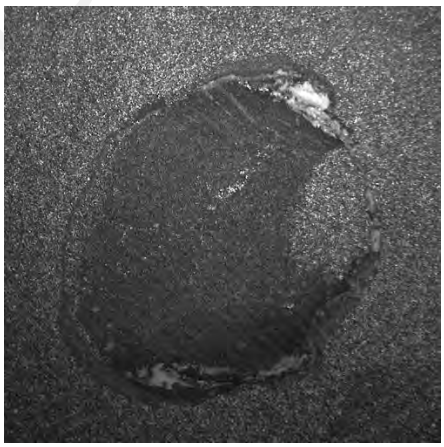

Figure 18: Cohesive failure, more than 75% of the resin cement present on the adherend surface.

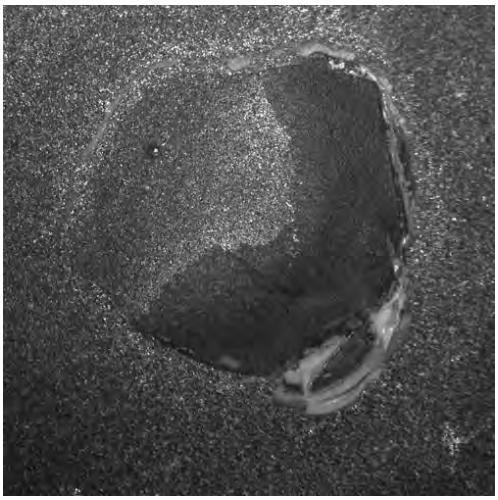

Figure 19: Mixed failure, characterised by partial presence of thin layer of cement and partial loss of the cement on the adherend surface.

## 4.7 FAILURE MODE ANALYSIS

The majority of the specimens failed cohesively in both control (50%) and test groups (40%). Overall, 45% of cohesive failures observed at the resin-zirconia interphase in all groups regardless of the surface treatment. This was followed by mixed failures (33.3%) and adhesive failures were the least at 21.7%.
Table 3 shows the frequency and percentage of each locus of failure recorded after microshear bond strength testing for all groups.

| Group | Surface Treatment methods | Time | Adhesive Failure | Cohesive Failure | Mixed Failure |
|---|---|---|---|---|---|
| **Control (Sandblast only)** | Panavia SB | ST | 0 | 8 | 2 |
| | Panavia SB | LT | 3 | 5 | 2 |
| | Multilink SB | ST | 0 | 10 | 0 |
| | Multilink SB | LT | 0 | 4 | 6 |
| | Rely X SB | ST | 3 | 1 | 6 |
| | Rely X SB | LT | 7 | 2 | 1 |
| **Total failures (n=60, %)** | | | **13(21.7%)** | **30(50%)** | **17(28.3%)** |
| **Test (NTP treated)** | Panavia SB+NTP | ST | 2 | 3 | 5 |
| | Panavia SB+NTP | LT | 1 | 5 | 4 |
| | Multilink SB+NTP | ST | 1 | 6 | 3 |
| | Multilink SB+NTP | LT | 4 | 3 | 3 |
| | Rely X SB+NTP | ST | 4 | 2 | 4 |
| | Rely X SB+NTP | LT | 1 | 5 | 4 |
| **Total failures (n=60, %)** | | | **13(21.7%)** | **24(40%)** | **23(38.3%)** |
| **Total failures (n=120, %)** | | | **26(21.7%)** | **54(45%)** | **40(33.3%)** |

Table 3: Frequency and percentage of failure modes after microshear bond strength test, comparing the control (SB) and test groups (SB+NTP).

# DISCUSSION

## 5.1 STUDY METHOD

In the literature, previous studies on the bond strength of dental adhesives were predominantly in vitro. An advantage of in vitro studies is that they allow for isolation of specific variables thus could aid for a better understanding of different factors that have an influence on the efficacy of dental materials.

Very few clinical trials on bonding to zirconia are available at present (Kern 2015) although it is the gold standard in research and potentially could generate more reliable results. Perhaps the most obvious reason for this is in vitro studies are relatively easier to be performed and are less time-consuming. One of the limitations of this study is that it did not replicate clinical applications. The specimens had only one adhesive interface (resin-zirconia) to be tested, whereas clinically, two interfaces are present, which is the resin-tooth interface being the other one. This difference could affect the stress pattern in the bond test and would not represent the actual value clinically. However, most of the previous adhesive studies tested the interface between adhesive materials and tooth.

Another vital aspect of this study was the preparation of the specimens. The preparation of resin cylinders using Tygon tubing was employed by Shimada et al. (2002) in an in vitro adhesive study. This method, however, was rather technique sensitive and required operator experience to perform. The resin cylinders needed to be uniform and homogeneously distributed on the minuscule bonded area. If defects such as an interfacial gap, air bubbles, excess resin flash or mismatch between resin cylinders and their delimited bonding area were present, the microshear bond strength value could be affected (Armstrong et al. 2010). Therefore, ideally, the samples needed to be assessed under the microscope to detect such defects and be excluded from the study. However, due to time constraints, all specimens in this study were assumed defect less. Nonetheless, a pilot test was carried out as training for sample preparation. Precautions were

taken by ensuring all steps were done precisely preparing the specimens. One critical step was area delimitation before bonding with resin cement. A double-sided adhesive tape was used for this according to the recommendation by Shimaoka et al. (2011).

The microshear bond strength test has been used by many similar studies on the bond strength of adhesive dental materials. Although researchers have used a variety of bond strength test methods, shear testing has become a popular way over tensile as shear stresses are believed to be the principal stresses involved in in-vivo bonding failures of restorative materials. The microtensile bond strength test is another favoured bond test in many other studies as the stress distribution is found to be more uniform. However, the microtensile test was relatively harder to conduct and more time-consuming. Preparing the specimens for microtensile bond test often needs trimming of the bonded sample. This step led to high pre-test failures, yielding dubious results (Cavalcanti et al. 2009). There is no ideal in vitro bond strength test. While the tests were not perfect, it has enabled the development of improved bonding systems and techniques. Apparently, different methods of load application would lead to different stress distributions, and investigators must expect and acknowledge that the bond strengths reported are nominal values and need cautious interpretation (Shimada et al. 2002a).

## 5.2 NON-THERMAL PLASMA

In recent years, non-thermal plasma or atmospheric plasma has been a subject of interest in biomedical and biomaterials application, especially for surface modification and functionalization of biomaterials. Non-thermal plasma is partially ionized gases containing a mixture of electrons, ions, and free radicals in a background of neutrals, while the gas phase remains near room temperature. These highly reactive plasma species were found to be able to react with, clean and etch surface materials, bond to various substrates, or modify the surface characteristics of plastic, metal or ceramic materials (Chen et al. 2014, Ritts et al.

2010). Non-thermal plasma was explored for enhancing bonding performance of zirconia restorations because of its known adhesion potentials, simplicity, feasibility, economically viable as well as it is environmental-friendly. However, studies on its efficacy to improve the bond strength of resin to zirconia are still limited and rather inconsistent.

It has been suggested that non-thermal plasma can be utilised to optimise the surface chemistry of zirconia for bonding or cementation procedures. Silva et al. (2011) showed that wettability of MDP primer on zirconia surface increased significantly after non-thermal plasma application and that the high polarity obtained on zirconia surface after non-thermal plasma treatment appeared promising to enhance bonds. Work by Valverde et al. (2013) found that non-thermal plasma application significantly increased microtensile bond strength at the resin-zirconia interface when used alone or combined with Clearfil ceramic primer. Both studies employed comprehensive methodologies to investigate surface roughness, surface energy, surface characterization and contact angle reading for plasma-treated zirconia surfaces. Vechiato-Filho et al. (2017), found non-thermal plasma significantly improved the bond strength between Rely X U200 and zirconia.

In contrast, Balkenhol et al. (2017) found inconsistent results on the resin-zirconia bond strength after plasma treatment. They had found that plasma treatment had no significant effect on resin-zirconia bond strength when MDP-containing primer was used. However, two other groups in the study which had no MDP in the primer were significantly affected by plasma treatment whereby plasma treatment significantly reduced the resin-zirconia microshear bond strength. The study used Variolink®II which is a dual-cured resin cement. Kong (2016) who did a similar study using Panavia™ V5 found no statistical difference in microshear bond strength of resin to zirconia with or without non-thermal plasma surface treatment. Another study on plasma by Moon et al. (2014) also found that plasma treatment on leucite-reinforced ceramics did not produce a significant difference in early bond

strength compared to standard hydrofluoric acid treatment.

This study is in agreement with the latter studies described. There was no significant statistical difference found in the microshear bond strength between the control (SB) and test groups (SB+NTP). Ito et al. (2016) demonstrated the same result when comparing non-thermal plasma-treated group to sandblasted group, as no significant difference was found in the bond strength values. This finding suggested that non-thermal plasma did not provide additional benefit when used as an extra step for surface treatment. Therefore, this study failed to reject the first null hypothesis.

Micro-Raman spectroscopy from this study also revealed no obvious findings in the spectra. There were no apparent peak shifts noted between non-thermal plasma treated zirconia surface and pure zirconia or sandblasted-only zirconia surface, suggesting no obvious chemical or physical changes at the molecular level on non-thermal plasma-treated zirconia surface. This finding was in line with work by Khan (2016).

Nevertheless, the large variabilities and lack of standardisation in the methodology among existing studies have made comparison challenging. For example, there are numerous parameters from the non-thermal plasma device alone like power, pressure, gas composition and flow rate as well as treatment duration. Thus, the results of this study need to be interpreted with caution due to time constraints and other limitations as discussed earlier.

## 5.3 DURABILITY TESTING AND FAILURE MODES

Durability testing with water storage and thermocycling have been described as one of the most important factors in an in vitro studies of adhesive restorative materials. The test simulates the humid intraoral conditions and accelerates the hydrolytic degradation of the adhesive interface which aimed to provide clinically

relevant information (Soderholm 1991).

This study found that water storage and thermocycling significantly affected the bond strength regardless of the protocols. Multiple comparison by Šídák's test revealed a statistically significant difference between the mean bond strength of ST groups (46.91 MPa) groups compared to LT groups (25.07 MPa) groups. Therefore, the second null hypothesis for this study was rejected.

This finding is consistent with numerous previous in vitro adhesive studies which have demonstrated significant reduction in bond strength after artificial aging process either with long term water storage, thermocycling or combination of both (Kitasako et al. 2000, Blatz et al. 2004, Luthy et al. 2006, Ozcan et al. 2008, Aguiar et al. 2009, Oyagüe et al. 2009, D'Amario et al. 2010, Heikkinen et al. 2013). Fatigue at the resin-zirconia interphase caused by repeated thermal expansion and contraction of the resin cement as well as hydrolytic degradation of the material itself might explain this phenomenon (Heikkinen et al. 2013). This information is critical in clinical practice as reduced bonding values by time could cause loosening or debonding of the zirconia restoration.

Nevertheless, it is interesting to note that all three systems of resin cement have demonstrated a relatively high bond strength even after the aging process which was ranging from 17.38MPa in Multilink SB group to 34.32MPa showed by Panavia SB+NTP group. Behr et al. (2011) suggested that bond strength higher than 10MPa as being clinically sufficient. Hence, this might suggest that Panavia™ V5, Multilink® Automix, and RelyX™ Ultimate could produce a sufficiently durable resin-zirconia bond. Longer aging time will plausibly reduce the bond strength further, although, work by Kern and Wegner (1998) found no significant difference even after 150 days of water storage and 37500 cycles of thermocycling when using MDP-containing resin cement bonded to zirconia. They also concluded that using an MDP-containing resin cement can form a durable resin-zirconia bond.

Analysis of failure modes was carried out for all specimens, including the pre-test failures. Regarding evaluating the effectiveness of an adhesive material in in vitro studies, ideally adhesive failures are desired as they represent the materials' performance in adhesion. Data from this study revealed, regardless of protocol, there was no distinct difference in the type of failure for both groups, as indicated by the descriptive analysis in Table 3. However, cohesive failures were found to be slightly higher in both control and test groups than mixed failures, followed by adhesive failures. Kern and Wegner (1998) found entirely cohesive failure in their resin-ceramic adhesive study with MDP using tensile bond strength test. They have suggested that hydrolytic degradation within the resin material itself played a significant role in reducing the mechanical properties of the resin which ultimately led to cohesive failures. They also speculated that that MDP promoted a water-resistant chemical bond. Scherrer et al. (2010) pointed out that errors in sample preparation such as the introduction of air bubbles and defects could also lead to cohesive failures. From a clinical point of view, cohesive and mixed failure patterns are preferable to total adhesive type of failure as the latter is usually associated with low bond strength values (Oyagüe et al. 2009).

## 5.4 RESIN CEMENTS

At present, the use of phosphate-containing primer and resin cement for adhesive bonding of zirconia restorations has been advocated by numerous studies (Kern and Wegner 1998, Blatz et al. 2007, Kern 2015). Compared to glass ionomer cement, resin cement exhibited greater protection to occlusal loading. Dual-cure resin cement is favoured over auto-cure as they allow for controlled polymerization and have extended working time.

The resin cement used in this study were Panavia™ V5, Multilink® Automix, and RelyX™ Ultimate. It was found that non-thermal plasma treatment had no influence on the resin-zirconia microshear bond strength between the three resin cement.

However, all the three resin cement used exhibited high initial microshear bond strength in both control and test groups. The mean values of the initial bond strength in both groups were ranging from 30.29MPa (RelyX SB) to 70.19MPa (Multilink SB) which are comparable to the bond strength of the amelodentinal junction which is about 50MPa.

Previous studies suggested that bond strength higher than 10MPa as being clinically sufficient (Behr et al. 2011, Kim et al. 2011). Interestingly, the mean of the microshear bond strength of all three systems of the resin cement used in this study surpassed 10MPa even after water storage and thermocycling, with least bond strength showed by Multilink SB group in the long-term protocol (17.38MPa). This finding is in agreement with numerous previous studies which found that zirconia bonded with resin cement using a phosphate-containing primer like MDP produced a higher and more durable bond strength compared to non-resin systems (Kern and Wegner 1998, Blatz et al. 2003, Blatz et al. 2004, Foxton et al. 2011). Studies have shown that the hydroxyl groups in MDP and phosphate-containing primer react to the hydroxyl groups on zirconia to form a chemical bond which when combined with the micromechanical retention formed by the air particle abrasion, produce a robust and durable bond at the resin-zirconia interface (Thompson et al. 2011).

Statistically significant differences in the bond strength between group Multilink SB (43.78MPa) and Rely X SB (25.52MPa) found in this study might suggest that Multilink® Automix resin cement can produce higher initial resin-zirconia bond strength. However, this is relatively clinically irrelevant as the durability testing with water storage and thermocycling revealed the bond strength of all the three systems were significantly affected and in fact, Multilink® Automix exhibited the highest reduction in the microshear bond strength compared to Panavia™ V5 and RelyX™ Ultimate. The margins plot showed this interaction in Figure 13.

One possible explanation for this is in the composition of the primers. Multilink®

Automix resin cement system comes with Monobond™ Plus as the primer which contains phosphonic acid methacrylate as the adhesive monomer. Panavia™ V5 and RelyX™ Ultimate systems, however, used MDP as the adhesive monomer. A study by Ahn et al. (2014) looked at the effects of different phosphate-containing primers on the shear bond strength at resin-zirconia interface. They have found that after water storage and thermocycling, MDP-based product (Z- PRIME Plus) had a significantly higher bond strength than did the phosphonic acid-based Metal/Zirconia Primer. Therefore, the third null hypothesis in this study was rejected as we found Multilink® Automix resin cement had significantly higher initial bond strength, but the bond was not as durable as Panavia™ V5 and RelyX™ Ultimate.

# CONCLUSION

Within the limitations of this in vitro study, the following conclusions were drawn:

1. Non-thermal plasma treatment on zirconia as added surface modification to current technique had no significant effect on resin-zirconia bond strength and its durability.
2. Aging process with water storage and thermocycling played an important role in resin-zirconia bonds degradation.
3. All three systems of resin cement; Panavia™ V5, Multilink® Automix, and RelyX™ Ultimate demonstrated high initial bond strength, but Multilink® Automix could produce higher initial bond strength compared to RelyX™ Ultimate.

This study suggested that non-thermal plasma use for modification of zirconia surface did not yield significant additional benefit to current technique, i.e., treatment with air particle abrasion and phosphate-containing primer. However, it contradicted with previous studies which showed promising results when non-thermal plasma was used as surface treatment. Thus, further investigations on non-thermal plasma use on zirconia are recommended. More work on a water-resistant or hydrophobic bond between resin cement and zirconia by manufacturers are also advocated to improve the durability of the bond over time. For the meantime, use of air particle abrasion and MDP or phosphate-containing primer as zirconia surface treatment remains standard technique in bonding resin cement to zirconia.

# BIBLIOGRAPHY

Aboushelib, M. N., C. J. Kleverlaan and A. J. Feilzer., 2007. Selective infiltration-etching technique for a strong and durable bond of resin cements to zirconia-based materials. *The Journal of Prosthetic Dentistry* 98(5): 379-388.

Aguiar, T. R., Cavalcanti, A. N., Fontes, C. M., Marchi, G. M., Muniz, L., and Mathias, P., 2009. 24 Hours and 3-Months Bond Strength Between Dual-Cured Resin Cements and Simplified Adhesive Systems. *ActaOdontologica Latinoamericana : AOL*, 22 (3), 171–176.

Ahn, J.S., Yi, Y.A., Lee, Y. and Seo, D.G., 2015. Shear bond strength of MDP-containing self-adhesive resin cement and Y-TZP ceramics: effect of phosphate monomer-containing primers. *BioMed Research International*, *2015*.

Akın, H., Ozkurt, Z., Kırmalı, O., Kazazoglu, E. and Ozdemir, A.K., 2011. Shear bond strength of resin cement to zirconia ceramic after aluminum oxide sandblasting and various laser treatments. *Photomedicine and Laser Surgery*, *29*(12), pp.797-802.

Akin, H., Tugut, F., Akin, G.E., Guney, U. and Mutaf, B., 2012. Effect of Er: YAG laser application on the shear bond strength and micro leakage between resin cements and Y-TZP ceramics. *Lasers in Medical Science*, *27*(2), pp.333-338.

Aranha, A.C.C., Turbino, M.L., Powell, G.L. and Eduardo, C.D.P., 2005. Assessing micro leakage of class V resin composite restorations after Er:YAG laser and bur preparation. Lasers in surgery and medicine, 37(2), pp.172-177.

Armstrong, S., Geraldeli, S., Maia, R., Raposo, L.H.A., Soares, C.J. and Yamagawa, J., 2010. Adhesion to tooth structure: a critical review of “micro” bond strength test methods. *Dental Materials*, *26*(2), pp.e50-e62.

Armstrong, S.R., Boyer, D.B. and Keller, J.C., 1998. Microtensile bond strength

testing and failure analysis of two dentin adhesives. *Dental Materials*, *14*(1), pp.44-50.

Ashizuka, M., Kiyohara, H., Okuno, T. and Kubota, Y., 1988. Fatigue Behavior of Tetragonal Zirconia Polycrystals (Y-TZP) Containing 2 and 4mol% Y2O3 (Part 2). *Journal of the Ceramic Society of Japan*, *96*(1115), pp.749-754.

Balkenhol, M., Nothdurft, F.P., Hannig, M., Schindler, A., Lehmann, A., Arnold, T., Knauber, A. and Rupf, S., 2017. Bonding to zirconia ceramic: The effect of cold plasma treatment and 4-META. *Clinical Plasma Medicine*, *5*, pp.8-13.

Blatz, M.B., Sadan, A. and Kern, M., 2003. Resin-ceramic bonding: A review of the literature. *The Journal of Prosthetic Dentistry*, 89(3), pp.268-274.

Blatz, M.B., Sadan, A., Martin, J. and Lang, B., 2004. In vitro evaluation of shear bond strengths of resin to densely-sintered high-purity zirconium-oxide ceramic after long-term storage and thermal cycling. *The Journal of Prosthetic Dentistry*, 91(4), pp.356-362.

Blatz, M.B., Phark, J.H., Ozer, F., Mante, F.K., Saleh, N., Bergler, M. and Sadan, A., 2010. In vitro comparative bond strength of contemporary self-adhesive resin cements to zirconium oxide ceramic with and without air-particle abrasion. *Clinical Oral Investigations*, 14(2), pp.187-192.

Camposilvan, E., Marro, F.G., Mestra, A. and Anglada, M., 2015. Enhanced reliability of yttria-stabilized zirconia for dental applications. *Acta Biomaterialia*, *17*, pp.36-46.

Cavalcanti, A.N., Foxton, R.M., Watson, T.F., Oliveira, M.T., Giannini, M. and Marchi, G.M., 2009. Bond strength of resin cements to a zirconia ceramic with different surface treatments. *Operative Dentistry*, *34*(3), pp.280-287.

Chen, L. and Suh, B.I., 2012. Bonding of resin materials to all-ceramics: a review. *Curr Res Dent*, *3*(1), pp.7-17.

D'Amario, M., Campidoglio, M., Morresi, A.L., Luciani, L., Marchetti, E. and Baldi, M., 2010. Effect of thermocycling on the bond strength between dual-cured resin cements and zirconium-oxide ceramics. *Journal of Oral Science*, *52*(3), pp.425-430.

Denry, I. and Kelly, J.R., 2008. State of the art of zirconia for dental applications. *Dental materials*, *24*(3), pp.299-307.

Dérand, P. and Dérand, T., 2000. Bond strength of luting cements to zirconium oxide ceramics. *International Journal of Prosthodontics*, *13*(2).

Everson, P., Addison, O., Palin, W.M. and Burke, F.T., 2012. Improved bonding of zirconia substructures to resin using a “glaze-on” technique .*Journal of Dentistry*, 40(4), pp.347-351.

Foxton, R.M., Cavalcanti, A.N., Nakajima, M., Pilecki, P., Sherriff, M., Melo, L. and Watson, T.F., 2011. Durability of resin cement bond to aluminium oxide and zirconia ceramics after air abrasion and laser treatment. *Journal of Prosthodontics*, 20(2), pp.84-92.

GPT (2005). The Glossary of Prosthodontic Terms. *The Journal of Prosthetic Dentistry* **94**(1): 10-92.

Guazzato, M., Albakry, M., Ringer, S.P. and Swain, M.V., 2004. Strength, fracture toughness and microstructure of a selection of all-ceramic materials. Part II. Zirconia-based dental ceramics. *Dental materials,* 20(5), pp.449-456.

Guess, P.C., Kuliš, A., Witkowski, S., Wolkewitz, M., Zhang, Y. and Strub, J.R.,

2008. Shear bond strengths between different zirconia cores and veneering ceramics and their susceptibility to thermocycling. *Dental materials*, *24*(11), pp.1556-1567.

Hahn, P., Attin, T., Gröfke, M. and Hellwig, E., 2001. Influence of resin cement viscosity on micro leakage of ceramic inlays. *Dental Materials*, *17*(3), pp.191-196.

Han, S.S., 2017. The effect of non-thermal plasma on the bonding of resin cements to zirconia. [Dissertation]. London: King's College School of Medicine and Dentistry.

Heikkinen, T.T., Matinlinna, J.P., Vallittu, P.K. and Lassila, L.V.J., 2013. Long term water storage deteriorates bonding of composite resin to alumina and zirconia short communication. *The Open Dentistry Journal*, *7*, p.123.

Ikemura, K., Tanaka, H., Fujii, T., Deguchi, M., Endo, T. and Kadoma, Y., 2011a. Development of a new single-bottle multi-purpose primer for bonding to dental porcelain, alumina, zirconia, and dental gold alloy. *Dental Materials Journal*, 30(4), pp.478-484.

Ikemura, K., Jogetsu, Y., Shinno, K., Nakatsuka, T., Endo, T. and Kadoma, Y., 2011b. Effects of a newly designed HEMA-free, multi-purpose, single-bottle, self-etching adhesive on bonding to dental hard tissues, zirconia-based ceramics, and gold alloy. *Dental Materials Journal*, 30(5), pp.616-625.

Ikemura, K., Tanaka, H., Fujii, T., Deguchi, M., Negoro, N., Endo, T. and Kadoma, Y., 2011c. Design of a new, multi-purpose, light-curing adhesive comprising a silane coupling agent, acidic adhesive monomers and dithiooctanoate monomers for bonding to varied metal and dental ceramic materials. *Dental Materials Journal*, 30(4), pp.493-500.

Inokoshi M, Yoshihara K, Nagaoka N, et al. 2016. Structural and chemical analysis

of the zirconia–veneering ceramic interface. *J Dent Res*. 95(1):102–109.

Ito, Y., Okawa, T., Fukumoto, T., Tsurumi, A., Tatsuta, M., Fujii, T., Tanaka, J. and Tanaka, M., 2016. Influence of atmospheric pressure low-temperature plasma treatment on the shear bond strength between zirconia and resin cement. *Journal of Prosthodontic Research*, *60*(4), pp.289-293.

Kern, M. and Wegner, S.M., 1998. Bonding to zirconia ceramic: adhesion methods and their durability. *Dental Materials*, 14(1), pp.64-71.

Kern, M., 2005. Clinical long-term survival of two-retainer and single-retainer all-ceramic resin-bonded fixed partial dentures. *Quintessence International*, *36*(2).

Kern, M. 2015. "Bonding to oxide ceramics-laboratory testing versus clinical outcome." *Dental Materials,* 31(1): 8-14.

Khan, N. 2016. Investigation into effect of plasma on resin cement application to zirconia using Micro Raman Spectroscopy and Micro Shear Bond Strength Testing. [Dissertation]. London: King's College School of Medicine and Dentistry.

Kitasako, Y., Burrow, M.F., Nikaido, T. and Tagami, J., 2000. The influence of storage solution on dentin bond durability of resin cement. *Dental Materials*, *16*(1), pp.1-6.

Kong, L.L., 2016. Plasma-modified surface bonding to Y-TZP. [Dissertation]. London: King's College School of Medicine and Dentistry.

Kosmač, T., Oblak, C., Jevnikar, P., Funduk, N. and Marion, L., 1999. The effect of surface grinding and sandblasting on flexural strength and reliability of Y-TZP zirconia ceramic. *Dental Materials*, 15(6), pp.426-433.

Krämer, N., Lohbauer, U. and Frankenberger, R., 2000. Adhesive luting of indirect

restorations. *American Journal of Dentistry*, *13*(Spec No), pp.60D-76D.

Kumbuloglu, O., Lassila, L.V.J., User, A., Toksavul, S. and Vallittu, P.K., 2005. Shear bond strength of composite resin cements to lithium disilicate ceramics. *Journal of Oral Rehabilitation*, 32(2), pp.128-133.

Kumbuloglu, O., Lassila, L.V.J., User, A. and Vallittu, P.K., 2006. Bonding of resin composite luting cements to zirconium oxide by two air-particle abrasion methods. *Operative Dentistry*, *31*(2), pp.248-255.

Larsson, C. and Wennerberg, A., 2014. The clinical success of zirconia-based crowns: a systematic review. *International Journal of Prosthodontics*, *27*(1).

Lieberman, M.A. and Lichtenberg, A.J., 2005. Principles of plasma discharges and materials processing. John Wiley & Sons.

Maruo, Y., Nishigawa, G., Oka, M., Minagi, S., Suzuki, K. and Irie, M., 2004. Does plasma irradiation improve shear bond strength of acrylic resin to cobalt–chromium alloy? *Dental Materials*, *20*(5), pp.509-512.

Matinlinna, J.P., Heikkinen, T., Özcan, M., Lassila, L.V. and Vallittu, P.K., 2006. Evaluation of resin adhesion to zirconia ceramic using some organosilanes. *Dental Materials*, *22*(9), pp.824-831.

Naumenko, A.P., Berezovska, N.I., Biliy, M.M. and Shevchenko, O.V., 2008. Vibrational analysis and Raman spectra of tetragonal Zirconia. *Phys. Chem. Solid State*, *9*(1), pp.121-125.

Nishigawa, G., Maruo, Y., Oka, M., Oki, K., Minagi, S. and Okamoto, M., 2003. Plasma treatment increased shear bond strength between heat cured acrylic resin and self-curing acrylic resin. *Journal of Oral Rehabilitation*, *30*(11), pp.1081-1084.

Oyagüe, R.C., Monticelli, F., Toledano, M., Osorio, E., Ferrari, M. and Osorio, R.,

2009. Effect of water aging on microtensile bond strength of dual-cured resin cements to pre-treated sintered zirconium-oxide ceramics. *Dental Materials*, *25*(3), pp.392-399.

Özcan, M., Nijhuis, H. and Valandro, L.F., 2008. Effect of various surface conditioning methods on the adhesion of dual-cure resin cement with MDP functional monomer to zirconia after thermal aging. *Dental Materials Journal*,27(1), pp.99-104.

Pappas, D., Smith, B.W. and Winefordner, J.D., 2000. Raman spectroscopy in bioanalysis. *Talanta*, *51*(1), pp.131-144.

Paranhos, M.P.G., Burnett Jr, L.H. and Magne, P., 2011. Effect of Nd: YAG laser and CO 2 laser treatment on the resin bond strength to zirconia ceramic. *Quintessence international*, *42*(1).

Paul, A., Vaidhyanathan, B. and Binner, J., 2011. Micro- Raman spectroscopy of indentation induced phase transformation in nanozirconia ceramics. *Advances in Applied Ceramics*, 110 (2), pp. 114-119.

Piascik, J.R., Swift, E.J., Thompson, J.Y., Grego, S. and Stoner, B.R., 2009. Surface modification for enhanced silanation of zirconia ceramics. *Dental Materials*, *25*(9), pp.1116-1121.

Ritts, A.C., Li, H., Yu, Q., Xu, C., Yao, X., Hong, L. and Wang, Y., 2010. Dentin surface treatment using a non-thermal argon plasma brush for interfacial bonding improvement in composite restoration. *European journal of oral sciences*, *118*(5), pp.510-516.

Sadek, F.T., Cury, Á.H., Monticelli, F., Ferrari, M. and Cardoso, P.E.C., 2005. The influence of the cutting speed on bond strength and integrity of microtensile

specimens. *Dental Materials*, *21*(12), pp.1144-1149.

Sano, H., Shono, T., Sonoda, H., Takatsu, T., Ciucchi, B., Carvalho, R. and Pashley, D.H., 1994. Relationship between surface area for adhesion and tensile bond strength—evaluation of a micro-tensile bond test. *Dental Materials*, *10*(4), pp.236-240.

Scherrer, S.S., Cesar, P.F. and Swain, M.V., 2010. Direct comparison of the bond strength results of the different test methods: A critical literature review. *Dental Materials*, *26*(2), pp. e78-e93.

Shimada, Y., Senawongse, P., Harnirattisai, C., Burrow, M.F., Nakaoki, Y. and Tagami, J., 2002b. Bond strength of two adhesive systems to primary and permanent enamel. *Operative dentistry,* 27(4), pp.403-409.

Shimada, Y., Yamaguchi, S. and Tagami, J., 2002a. Micro-shear bond strength of dual-cured resin cement to glass ceramics. *Dental Materials,* 18(5), pp.380-388.

Shimaoka, A.M., de Andrade, A.P., Cardoso, M.V. and de Carvalho, R.C., 2011. The importance of adhesive area delimitation in a microshear bond strength experimental design. *Journal of Adhesive Dentistry*, 13(4).

Silva, N.R., Coelho, P.G., Valverde, G.B., Becker, K., Ihrke, R., Quade, A. and Thompson, V.P., 2011. Surface characterization of Ti and Y-TZP following non-thermal plasma exposure. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, *99*(1), pp.199-206.

Souza, R.O., Valandro, L.F., Melo, R.M., Machado, J.P., Bottino, M.A. and Özcan, M., 2013. Air–particle abrasion on zirconia ceramic using different protocols: Effects on biaxial flexural strength after cyclic loading, phase transformation and surface topography. *Journal of the Mechanical Behavior of Biomedical Materials*, *26*, pp.155-163.

Srikanth, R., Kosmac, T., Della Bona, A., Yin, L. and Zhang, Y., 2015. Effects of cementation surface modifications on fracture resistance of zirconia. *Dental Materials*, *31*(4), pp.435-442.

Thompson, J.Y., Stoner, B.R., Piascik, J.R. and Smith, R., 2011. Adhesion/cementation to zirconia and other non-silicate ceramics: where are we now?.*Dental Materials*, *27*(1), pp.71-82.

Tsuo, Y., Yoshida, K. and Atsuta, M., 2006. Effects of alumina-blasting and adhesive primers on bonding between resin luting agent and zirconia ceramics. *Dental materials journal,* 25(4), pp.669-674.

Tzanakakis, E.G.C., Tzoutzas, I.G. and Koidis, P.T., 2016. Is there a potential for durable adhesion to zirconia restorations? A systematic review. *The Journal of prosthetic dentistry*, *115*(1), pp.9-19.

Valverde, G.B., Coelho, P.G., Janal, M.N., Lorenzoni, F.C., Carvalho, R.M., Thompson, V.P., Weltemann, K.D. and Silva, N.R., 2013. Surface characterisation and bonding of Y-TZP following non-thermal plasma treatment. *Journal of Dentistry*, *41*(1), pp.51-59.

Van Meerbeek, B., Peumans, M., Poitevin, A., Mine, A., Van Ende, A., Neves, A. and De Munck, J., 2010. Relationship between bond-strength tests and clinical outcomes. *Dental Materials*, *26*(2), pp. e100-e121.

Van Noort, R., Noroozi, S., Howard, I.C. and Cardew, G., 1989. A critique of bond strength measurements. *Journal of dentistry*, *17*(2), pp.61-67.

Vassilakos, N. and Nilner, K., 1993. Effect of plasma treatment on the wettability of elastomeric impression materials. *The Journal of Prosthetic Dentistry*, *70*(2), pp.165-171.

Vechiato-Filho, A.J., Matos, A.O., Landers, R., Goiato, M.C., Rangel, E.C., De

Souza, G.M., Barão, V.A.R. and dos Santos, D.M., 2017. Surface analysis and shear bond strength of zirconia on resin cements after non-thermal plasma treatment and/or primer application for metallic alloys. *Materials Science and Engineering: C*, *72*, pp.284-292.

Vrochari, A.D., Eliades, G., Hellwig, E. and Wrbas, K.T., 2009. Curing efficiency of four self- etching, self-adhesive resin cements. *Dental Materials,*25(9), pp.1104-1108.

Wegner, S.M. and Kern, M., 2000. Long-term resin bond strength to zirconia ceramic. *Journal of Adhesive Dentistry*, *2*(2).

Yoshida, K., Tsuo, Y. and Atsuta, M., 2006. Bonding of dual-cured resin cement to zirconia ceramic using phosphate acid ester monomer and zirconate coupler. *Journal of Biomedical Materials Research Part B: Applied Biomaterials,* 77(1), pp.28-33.

Zhang, Y., Lawn, B.R., Rekow, E.D. and Thompson, V.P., 2004. Effect of sandblasting on the long-term performance of dental ceramics. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, *71*(2), pp.381-386.

# APPENDICES

## APPENDIX I: MATERIALS AND EQUIPMENTS USED IN THE STUDY

| MATERIAL/ EQUIPMENT | TRADE NAME | MANUFACTURER | PRODUCT IDENTIFIER | EXPIRY DATE |
|---|---|---|---|---|
| Zirconia Disc | Katana UTML | Kuraray, Noritake Dental Inc, Tokyo, Japan | 60W15106 | - |
| Sandblaster | MicroEtcher™ | Danville Materials, San Ramon, California USA | 22005-01 | - |
| Aluminium Oxide Particles | Aluminum Oxide 50 micron white | Danville Materials, San Ramon, California USA | Lot 22668 | - |
| Tygon Tubing | Flexible Plastic Tubing E-3603 | Saint-Gobain Performance Plastics France | 1681448 | |
| Plasma Device (non-thermal) | Piezo Brush®PZ2 Handheld Device | Relyon Plasma, Regensburg, Germany | PG-41-103672-14201 | - |
| Dual-cured adhesive resin cement (1) | Panavia™V5 | Kuraray, Noritake Dental Inc., Okayama, Japan | Lot 8P0038 | 05/2019 |
| Dual-cured adhesive resin cement (2) | Multilink® Automix | Ivoclar Vivadent | Lot V25890 | 12/2017 |
| Dual-cured adhesive resin cement (3) | RelyX™ Ultimate | 3M Deutschland GmbH, Neuss, Germany | Lot 645839 | 04/2018 |
| Phosphate Containing Primer (1) | Clearfil™ Ceramic Primer Plus | Kuraray, Noritake Dental Inc., Okayama, Japan | Lot 8W0019 | 05/2019 |
| Phosphate Containing Primer (2) | Monobond™ Plus | Ivoclar Vivadent | Lot V12120 | 03/2018 |
| Phosphate Containing Primer (3) | Scotchbond™ Universal | 3M Deutschland GmbH, Neuss, Germany | Lot 642275 | 09/2018 |
| Curing Light | Elipar™ Deep Cure-S LED Curing Light | 3M ESPE, Seefeld, Germany | 933123001489 | - |

| | | | | |
|---|---|---|---|---|
| Incubator | Sanyo Heated-Only Incubator | Sanyo Electric Company Ltd., Osaka, Japan | MIR 262 08010003 | - |
| Thermocycling machine | AX-12A Dynamixel robot actuators, Robotis/ Grant water bath/Jencons Julabo F10 circulating water bath | Grant Instruments Ltd, Barrington, Cambridge/Jencons Scientific Ltd., Bedfordshire, England | - | - |
| Micro-Raman Spectroscope | inVia™ MicroRaman microscope | Renishaw plc, Wotton-under-Edge UK | | - |
| Microshear Bond Strength testing machine | SMAC Moving Coil Actuators | SMAC Europe, Horsham, Sussex | R4708 | - |
| Cyanoacrylate Adhesive | Everbuild Stick 2 Superglue Gel | Everbuild Building Products Ltd, Leeds, England | 40915 | 03/2019 |
| Wire Loop | Stainless Steel Europa™ Form 1 Upper .020" | Forestadent® German Precision in Orthodontics, Milten Keynes, Buckinghamshire, UK | 201965 | - |
| Microscope For Failure Mode Analysis | Tandom Scanning Microscope (TSM) | Noran Instruments, Middleton, WI, USA | - | - |

## APPENDIX II: COMPOSITION OF PANAVIA™ V5 AND CLEARFIL™ CERAMIC PRIMER PLUS.

| Material | Composition |
|---|---|
| **Panavia™V5** | **Paste A (Catalyst Paste)**<br>• Bisphenol A diglycidylmethacrylate (Bis-GMA)<br>• Triethyleneglycoldimethacrylate (TEGDMA)<br>• Hydrophobic aromatic dimethacrylate<br>• Hydrophilic aliphatic dimethacrylate<br>• Initiators<br>• Accelerators<br>• Silanated barium glass filler<br>• Silanatedfluoroaluminosilicate glass filler<br>• colloidol silica<br><br>**Paste B (Base Paste)**<br>• Bisphenol A diglycidylmethacrylate (Bis-GMA)<br>• Hydrophobic aromatic dimethacrylate<br>• Hydrophilic aliphatic dimethacrylate<br>• Silanated barium glass filler<br>• Silanated aluminium oxide filler<br>• Accelerators<br>• dl-Camphorquinone<br>• Pigments |
| **Clearfil™ Ceramic Primer Plus** | • 3-Methacryloxypropyl trimethoxysilane<br>• 10-Methacryloyloxydecyl dihydrogen phosphate (MDP)<br>• Ethanol |

## APPENDIX III: COMPOSITION OF RELYX™ ULTIMATE AND SCOTCHBOND™ UNIVERSAL ADHESIVE.

| Material | Composition |
|---|---|
| **Scotchbond™ Universal Adhesive** | • MDP Phosphate Monomer<br>• Dimethacrylate Resins<br>• HEMA<br>• Vitrebond™ Copolymer<br>• Filler<br>• Ethanol<br>• Water<br>• Initiators<br>• Silane |
| **RelyX™ Ultimate Adhesive Resin Cement** | Resin cement: Base and Catalyst<br><br>**Base Paste**<br>• Methacrylate Monomers<br>• Radiopaque silanated fillers<br>• Initiator components<br>• Stabilisers<br>• Rheological additives<br>**Catalyst Paste**<br>• Methacrylate Monomers<br>• Radiopaque alkaline fillers<br>• Initiator components<br>• Stabilisers<br>• Pigments<br>• Rheological additives<br>• Fluorescence dye<br>• Dark cure activator for Scotchbond™ Universal Adhesive |

## APPENDIX IV: COMPOSITION OF MULTILINK® AUTOMIX AND MONOBOND PLUS

| **Multilink Automix** | Base | Catalyst |
|---|---|---|
| Dimethacrylates and HEMA | 33.1 | 32.4 |
| Barium glass filler, Ba-Al-Fluoro-Silicate glass | 37.4 | 37.4 |
| Ytterbium trifluoride | 23.0 | 23.0 |
| Highly dispersed silica | 5.4 | 5.4 |
| Catalysts and Stabiliser | 1.0 | 1.8 |
| Pigments | < 0.03 | - |

| **Multilink Primer A** | |
|---|---|
| Water | 85.7 |
| Initiators | 14.3 |

| **Multilink Primer B** | |
|---|---|
| Phosphonic acid acrylate | 48.1 |
| Hydroxyethyl methacrylate, Methacrylate mod. Polyacrylic acid | 51.9 |
| Stabiliser | < 0.02 |

| **Monobond™ Plus** | |
|---|---|
| **COMPOSITION** | **PERCENTAGE** |
| ETHANOL | 50-100% |
| 3-trimethoxysilylpropyl methacrylate | ≤2.5% |
| Methacrylated phosphoric acid ester | ≤2.5% |

# APPENDIX V: MICROSHEAR BOND STRENGTH VALUES (RAW DATA)

| Group | Specimen | Aging Time (ST/LT) | Force (S50 Internal Units) | Microshear Bond Strength (MPa) | Mean MPa | s.d | Failure Mode |
|---|---|---|---|---|---|---|---|
| **Panavia™V5 +SB** | 1 | ST | 53 | 38.8702 | 40.92372 | 16.3365204398543 | cohesive |
| | 2 | | 45 | 33.003 | | | cohesive |
| | 3 | | 57 | 41.8038 | | | cohesive |
| | 4 | | 51 | 37.4034 | | | cohesive |
| | 5 | | 63 | 46.2042 | | | mix |
| | 6 | | 74 | 54.2716 | | | cohesive |
| | 7 | | 78 | 57.2052 | | | cohesive |
| | 8 | | 70 | 51.338 | | | cohesive |
| | 9 | | 67 | 49.1378 | | | mix |
| | 10 | | 0 | 0 | | | cohesive |
| | | | | | | | |
| **Panavia™V5 +SB+NTP** | 1 | ST | 66 | 48.4044 | 42.39052 | 14.5772667043814 | cohesive |
| | 2 | | 75 | 55.005 | | | mix |
| | 3 | | 47 | 34.4698 | | | cohesive |
| | 4 | | 64 | 46.9376 | | | adhesive |
| | 5 | | 16 | 11.7344 | | | mix |
| | 6 | | 80 | 58.672 | | | mix |
| | 7 | | 50 | 36.67 | | | mix |
| | 8 | | 39 | 28.6026 | | | mix |
| | 9 | | 76 | 55.7384 | | | cohesive |
| | 10 | | 65 | 47.671 | | | adhesive |
| | | | | | | | |
| **Panavia™V5 +SB** | 1 | LT | 98 | 71.8732 | 32.6363 | 20.0470119780147 | cohesive |
| | 2 | | 57 | 41.8038 | | | cohesive |
| | 3 | | 28 | 20.5352 | | | mix |
| | 4 | | 17 | 12.4678 | | | adhesive |
| | 5 | | 58 | 42.5372 | | | mix |
| | 6 | | 64 | 46.9376 | | | cohesive |
| | 7 | | 48 | 35.2032 | | | cohesive |
| | 8 | | 34 | 24.9356 | | | cohesive |
| | 9 | | 41 | 30.0694 | | | adhesive |
| | 10 | | 0 | 0 | | | adhesive |
| | | | | | | | |
| **Panavia™V5 +SB+NTP** | 1 | LT | 85 | 62.339 | 34.32312 | 11.584728249515 | mix |
| | 2 | | 61 | 44.7374 | | | cohesive |
| | 3 | | 48 | 35.2032 | | | cohesive |
| | 4 | | 33 | 24.2022 | | | mix |
| | 5 | | 34 | 24.9356 | | | mix |
| | 6 | | 34 | 24.9356 | | | adhesive |
| | 7 | | 42 | 30.8028 | | | cohesive |
| | 8 | | 46 | 33.7364 | | | cohesive |
| | 9 | | 41 | 30.0694 | | | cohesive |
| | 10 | | 44 | 32.2696 | | | mix |
| | | | | | | | |
| **Multilink ® Automix+SB** | 1 | ST | 78 | 57.2052 | 70.18638 | 18.3888665170472 | cohesive |
| | 2 | | 115 | 84.341 | | | cohesive |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | 3 | | 79 | 57.9386 | | | cohesive |
| | 4 | | 116 | 85.0744 | | | cohesive |
| | 5 | | 112 | 82.1408 | | | cohesive |
| | 6 | | 72 | 52.8048 | | | cohesive |
| | 7 | | 126 | 92.4084 | | | cohesive |
| | 8 | | 59 | 43.2706 | | | cohesive |
| | 9 | | 76 | 55.7384 | | | cohesive |
| | 10 | | 124 | 90.9416 | | | cohesive |
| | | | | | | | |
| **Multilink ® Automix+SB +NTP** | 1 | ST | 63 | 46.2042 | 54.71164 | 12.282838360285 | cohesive |
| | 2 | | 67 | 49.1378 | | | cohesive |
| | 3 | | 86 | 63.0724 | | | mix |
| | 4 | | 85 | 62.339 | | | cohesive |
| | 5 | | 54 | 39.6036 | | | mix |
| | 6 | | 57 | 41.8038 | | | cohesive |
| | 7 | | 70 | 51.338 | | | mix |
| | 8 | | 68 | 49.8712 | | | adhesive |
| | 9 | | 88 | 64.5392 | | | cohesive |
| | 10 | | 108 | 79.2072 | | | cohesive |
| | | | | | | | |
| **Multilink ® Automix+SB** | 1 | LT | 25 | 18.335 | 17.38158 | 21.3934175391404 | cohesive |
| | 2 | | 78 | 57.2052 | | | cohesive |
| | 3 | | 46 | 33.7364 | | | mix |
| | 4 | | 61 | 44.7374 | | | mix |
| | 5 | | 27 | 19.8018 | | | cohesive |
| | 6 | | 0 | 0 | | | mix |
| | 7 | | 0 | 0 | | | mix |
| | 8 | | 0 | 0 | | | cohesive |
| | 9 | | 0 | 0 | | | mix |
| | 10 | | 0 | 0 | | | mix |
| | | | | | | | |
| **Multilink ® Automix+SB +NTP** | 1 | LT | 50 | 36.67 | 20.24184 | 15.9455245635605 | mix |
| | 2 | | 21 | 15.4014 | | | mix |
| | 3 | | 47 | 34.4698 | | | cohesive |
| | 4 | | 46 | 33.7364 | | | cohesive |
| | 5 | | 42 | 30.8028 | | | mix |
| | 6 | | 21 | 15.4014 | | | adhesive |
| | 7 | | 49 | 35.9366 | | | adhesive |
| | 8 | | 0 | 0 | | | cohesive |
| | 9 | | 0 | 0 | | | adhesive |
| | 10 | | 0 | 0 | | | adhesive |
| | | | | | | | |
| **RelyX™ Ultimate+SB** | 1 | ST | 70 | 51.338 | 30.28942 | 23.8478455037021 | mix |
| | 2 | | 27 | 19.8018 | | | mix |
| | 3 | | 47 | 34.4698 | | | mix |
| | 4 | | 62 | 45.4708 | | | mix |
| | 5 | | 81 | 59.4054 | | | cohesive |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | 6 | | 49 | 35.9366 | | | mix |
| | 7 | | 77 | 56.4718 | | | adhesive |
| | 8 | | 0 | 0 | | | adhesive |
| | 9 | | 0 | 0 | | | adhesive |
| | 10 | | 0 | 0 | | | mix |
| | | | | | | | |
| **RelyX™ Ultimate+SB +NTP** | 1 | ST | 73 | 53.5382 | 42.97724 | 16.2131354946263 | adhesive |
| | 2 | | 61 | 44.7374 | | | adhesive |
| | 3 | | 64 | 46.9376 | | | mix |
| | 4 | | 59 | 43.2706 | | | mix |
| | 5 | | 60 | 44.004 | | | adhesive |
| | 6 | | 75 | 55.005 | | | mix |
| | 7 | | 50 | 36.67 | | | adhesive |
| | 8 | | 75 | 55.005 | | | mix |
| | 9 | | 69 | 50.6046 | | | cohesive |
| | 10 | | 0 | 0 | | | cohesive |
| | | | | | | | |
| **RelyX™ Ultimate+SB** | 1 | LT | 53 | 38.8702 | 20.75522 | 21.8084272550162 | adhesive |
| | 2 | | 28 | 20.5352 | | | adhesive |
| | 3 | | 60 | 44.004 | | | mix |
| | 4 | | 21 | 15.4014 | | | adhesive |
| | 5 | | 83 | 60.8722 | | | cohesive |
| | 6 | | 38 | 27.8692 | | | adhesive |
| | 7 | | 0 | 0 | | | adhesive |
| | 8 | | 0 | 0 | | | adhesive |
| | 9 | | 0 | 0 | | | adhesive |
| | 10 | | 0 | 0 | | | cohesive |
| | | | | | | | |
| **RelyX™ Ultimate+SB +NTP** | 1 | LT | 41 | 30.0694 | 25.08228 | 10.6773457909518 | cohesive |
| | 2 | | 50 | 36.67 | | | cohesive |
| | 3 | | 36 | 26.4024 | | | cohesive |
| | 4 | | 0 | 0 | | | cohesive |
| | 5 | | 31 | 22.7354 | | | cohesive |
| | 6 | | 48 | 35.2032 | | | mix |
| | 7 | | 39 | 28.6026 | | | mix |
| | 8 | | 27 | 19.8018 | | | mix |
| | 9 | | 26 | 19.0684 | | | mix |
| | 10 | | 44 | 32.2696 | | | adhesive |