EFFECT OF DIFFERENT SURFACE TREATMENTS OF TITANIUM SURFACES ON THE SHEAR BOND STRENGTH BETWEEN TITANIUM AND ZIRCONIA SURFACES

SUKITA SEEKAEWSIU

A Thesis Submitted to the Graduate School of Naresuan University
in Partial Fulfillment of the Requirements
for the Master of Science in (Master of Sciences in Dentistry (Prosthodontics) - Type A 2)
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Thesis entitled "Effect of Different Surface Treatments of Titanium Surfaces on the Shear Bond Strength between Titanium and Zirconia Surfaces"

By SUKITA SEEKAEWSIU

has been approved by the Graduate School as partial fulfillment of the requirements for the Master of Science in Master of Sciences in Dentistry (Prosthodontics) - Type A 2 of Naresuan University

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Title EFFECT OF DIFFERENT SURFACE TREATMENTS OF TITANIUM SURFACES ON THE SHEAR BOND STRENGTH BETWEEN TITANIUM AND ZIRCONIA SURFACES
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ABSTRACT

The study evaluated the effect of different surface treatments of titanium surfaces on the shear bond strength (SBS) between titanium and zirconia surfaces. This study was separated into 2 parts. In part 1, to evaluate the effect of mechanical surface treatments, 50 titanium disks were divided into 5 groups with different surface treatments (n=10/group): no surface treatment (control group), etched with 37% phosphoric acid (H_3PO_4), etched with 9% hydrofluoric acid (HF), treated with 50% hydrogen peroxide (H_2O_2) and sandblasted with 50 μm aluminum oxide. In part 2, to evaluate the effect of mechanico-chemical surface treatments, 50 titanium disks were divided into 5 groups (n=10/group). The specimens were surface treated with sandblasting combined with 4 different chemical surface treatment methods (applied with V-Primer, Alloy Primer, Clearfil Ceramic Primer and Monobond N) and surface treated with only sandblasting as control group. All titanium specimens were bonded to zirconia disks (treated surface by sandblasting and applied with ceramic primer) with resin cement (Panavia V5). All specimens were stored in water (37°c, 24 hrs). SBS was determined after 5,000 thermocycles. Data were analyzed by one-way ANOVA and Tukey's HSD. In part 1, the result showed that the sandblasted titanium group and treated with 50% H_2O_2 group exhibited significantly higher SBS than the other groups ($P<0.05$). In part 2, the SBS were significant increased in the group of surface treated with Monobond N and the group of surface treated with Clearfil ceramic primer. Within the limit of this study, it indicated that both mechanical and chemical surface treatment on the titanium surfaces had a significant influence on the SBS. The combination of mechanical surface treated by sandblasting and chemical surface treated by applying Monobond N or Clearfil Ceramic Primer were the most effective titanium surface treatment method to improved bonding between titanium and zirconia, that may be recommended for clinical guideline of bonding between the zirconia coping and titanium base abutment. Although sandblasting was widely accepted as the most effective method for titanium surface treatment, but from the result of this study, titanium surface treatment with H_2O_2 might be the promising alternative technique as more simple method with a high shear bond strength value.

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CHAPTER I

Introduction

Rationale of the Study

An implant abutment is a component that is an intermediate between the implant fixture and the restoration and serves to support and/ or retain a prosthesis [1]. The function of an abutment has extended to help support the soft tissue profiles of a dental implant crown and give the base shades at the cervical portion of an implant crown that affect the esthetical prosthetic outcomes [2].

Titanium has been extensively used as the material of implant abutment because it has provided suitable biocompatibility and sufficient mechanical materials [3]. However, applying titanium abutment in patients with thin gingival biotype and high smile line may lead to an unnatural greyish appearance of the surrounding soft tissue [4]. Especially in case of the recessions, peri-implant soft tissue can expose the metal abutment and the compromise esthetic results [5].

Several studies attempt to overcome these esthetic problems by using cast gold alloy materials instead of titanium in order to imitate the gingival color. Nevertheless, the opaque of these materials can still limit the translucent of the restoration [6]. Tooth-colored ceramic implant abutments may prevent this incident because the white color shades of the abutments can be matched with distinct tooth hues [7].

Recently, the zirconia implant abutments have received widespread acceptance as a result of their superior esthetic outcomes, fewer bacteria accumulation than titanium [8]. Moreover, abutment made of zirconia exhibits the best mechanical properties among all-ceramic restoration. Therefore, zirconia is generally used for the material of dental implant abutments due to outstanding biocompatibility, esthetic tooth shade and satisfying mechanical stability [9].

Zirconia abutments can be fabricated in two methods. First is the one-piece zirconia abutment which the whole component is made from zirconia. Second is the two-piece zirconia abutment. It consists of a standardized titanium base abutment integrated with a zirconia coping by using a resin-based luting agent [10]. An unfavourable condition of one-piece zirconia abutments is the higher failure rates because of the fractures at implant-abutment connection which may causes by the differences in the surface hardness of titanium and zirconia materials. Foong, et al. [11] evaluated the fracture resistance of one-piece zirconia and titanium abutments. The result showed that one-piece zirconia abutments showed significantly lower the load-bearing capacity than titanium abutments under laboratory conditions. Stimmelmayr, et al. [12] studied the wear of the interface between titanium implant fixtures and one-piece zirconia abutments compare with titanium abutment. The result showed that one-piece zirconia abutments made the surface of the titanium implant fixtures more worn than compared to titanium abutments under cyclic loading conditions. Therefore, the use of one-piece zirconia abutments may affect the long-term stability of the components, owing to this damage to the inner parts of the implant fixtures and may result in abutment screw loosening [13]. On the other hand, the two-piece zirconia abutments or hybrid abutments are applied to combine the advantages of inner titanium with strength and outer zirconia with esthetic. Titanium is made into titanium base abutment and zirconia is made in zirconia coping, both of which are adhered to by resin cement. It can make abutment screw completely seated in by titanium part. The connection between metal and metal interface can protect wearing phenomena and corrosion of the titanium implant [14]. Gehrke, et al. [15] analyzed the maximum load capacity of one- and two-piece zirconia abutments. The result showed that the two-piece zirconia abutments had the highest values of fracture resistance and it displayed a fracture strength similar to that of titanium abutments. Thus, the use of two-piece zirconia abutments is possibly advantaged towards the mechanical stability, lack of wear occurrence and might be clinically beneficial in the high-load area such as premolar and molar single tooth replacements.

However, the connection between zirconia and titanium of two-piece zirconia abutments remains the problem due to the different types of these materials. Zirconia is inert materials so it quite difficult to make chemical bond to titanium. Kim, et al. [16] found that under static loading conditions, the two-piece zirconia abutments displayed separation between the zirconia coping and the titanium base abutment. Especially in cases with limited interocclusal space of posterior teeth when using a short titanium base abutment, which has more chance to adhesively fail between zirconia coping and titanium base abutment [17]. It is quite clear that the bond between zirconia coping and titanium base abutment is the weak point of these abutments [18].

Surface treatment of the materials before adhesive bonding is an important factor in improving the bonded joint's strength and durability [19]. The mechanical surface treatment is the first step for roughing the surface of the titanium to make good adhesion to the resin cement. Several studies have been reported mechanical surface treatment improved titanium bond strength by sandblasting [10, 20, 21], etching with acid [22-24] and treating with H_2O_2 solution [25-27]. However, a clear guideline to bond resin cement to titanium base and a protocol of titanium surface treatment have not been clearly elucidated. It is essential to be clarified to maximize bond strength and anchorage the longevity of prosthodontic restoration. Therefore, in part 1 of this research attempted to find the mechanical surface treatment methods to enhance the bond strength of titanium and zirconia, which is the first important step of titanium surface treatment.

In addition to mechanical surface treatments, chemical surface treatments also contain modifying titanium to improve adhesion efficiency. According to the manufacturer, there are many types of activating primers for increasing the bond strength to the metal such as V-Primer [28], Alloy Primer [29], Clearfil Ceramic Primer [30] and Monobond N [31]. But it is still unclear which activating primers would be suitable for titanium surface treatment. Therefore, in part 2 of this research attempted to find the mechanico-chemical surface treatment methods to enhance titanium and zirconia bond strength. It may be useful to develop a clinical guideline of the bonding method between the zirconia coping and titanium base abutment.

Purposes of the Study

1. In part 1, to evaluate the effect of different mechanical surface treatments of titanium surfaces on the shear bond strength between titanium and zirconia surfaces.

2. In part 2, to evaluate the effect of different mechanico-chemical surface treatments of titanium surfaces on the shear bond strength between titanium and zirconia surfaces.

3. To find the efficient surface treatment methods which improve the shear bond strength between titanium and zirconia surfaces.

4. To develop a clinical guideline of effective bonding protocol between the zirconia coping and titanium base abutment.

Scope of the Study

This is a laboratory study conducted at the Faculty of Dentistry, Naresuan University to evaluate the effect of different surface treatments of titanium surfaces on the shear bond strength between titanium and zirconia surfaces from June 2019 Until June 2020

Hypotheses of the Study

Part 1

H_0 = Mechanical surface treatment of titanium surfaces do not affect the shear bond strength between titanium and zirconia surfaces.

Part 2

H_0 = Mechanico-chemical surface treatment of titanium surfaces do not affect the shear bond strength between titanium and zirconia surfaces.

CHAPTER II

Literature Review

Implant abutment

Implant abutment is a part that connects between the implant fixture and the restoration to support the prosthesis. It could be divided into two types based on the retention of the prosthesis to the implant fixture. The screw-retained prosthesis is directly connected between the superstructure and the implant fixture by a retaining screw. The advantages of a screw-retained prosthesis are predictable retention, easily retrievable, lacking residual cement in the sulcus and good soft tissue responses [32]. This type of restorations is very beneficial in many conditions, including a limited interocclusal space, heavy loading force and immediate loading cases. Nonetheless, the manufacture of a screw-retained prosthesis is required a casting process and made from a whole metal. It is time consuming, high cost and compromised esthetic outcome [33]. The cement-retained prosthesis is the implant abutment that connects the implant fixture by the cement. This type of restoration provides better passivity fit, high esthetic outcome, ease of manipulation in the posterior region, reduce the risk of small porcelain fracture due to no screw hole and overcoming angulation problems. However, it is difficult to retrieve without damaging the restoration and may have residual cement after permanent cementation [34].

Implant abutment can generally be classified into two different forms depending upon manufacturing: Standardized abutments and customized abutments.

Standardized abutments are traditionally supported by implant fixture manufacturers that match their specific implant systems. These abutments provide better handling and relatively low cost. However, they have a limitation of the possible individualization [35]. Customized abutments are improved for the personal soft tissue and biomechanical peculiarity of each patient [36]. These abutments are suitable for an individual emergence profile of the renewal directly by the abutment and help to correct improper implant angulations [37].

The most commonly used materials for implant abutment fabrication are two types: Titanium and zirconia.

1. Titanium implant abutment

Commercially pure titanium (CP-Ti) has been extensively used for the material of implant abutment because of its suitable biocompatibility and sufficient mechanical properties. Although in long term clinical studies, these materials have reported desirable outcomes, titanium abutment may appear an unnatural greyish color at the surrounding soft tissue in patients with relatively thin tissues and high smile line that can compromise the esthetic results [38]. Several studies attempt to overcome these esthetic problems by using cast gold alloys and gold-colored titanium abutments. These materials may match the gingival hue, but the opaque of material may limit the translucency of the restoration [39].

1.1 Properties of titanium

Titanium has been used as the material of choice in implant dentistry because of good mechanical stability, suitable biocompatibility, superior corrosion resistance, low density and high strength to weight ratio [40]. Titanium exists in two distinct forms. CP-Ti has a hexagonal closed packed crystal structure (HCP) or alpha atomic structure. At high temperature above 883 ℃, titanium transforms to the body-centered cubic structure (BCC) or beta atomic structure, but it can be alloyed with other metals such as molybdenum or vanadium to stabilize its structure room temperature [41].

CP-Ti (Grade 1-4) has greatly high reactivity. It immediately oxidizes if contact with air, resulting in an oxide layer to protect the surface from corrosion when it exposes to air, water or any electrolyte. However, oxygen and nitrogen content have influenced on the strength of CP-Ti. It exhibits higher corrosion resistance, higher biocompatible but lower strength than the titanium alloys [42].

Beta titanium is titanium alloys which has the highest strength values. It can be heat treated to gain higher strengths. However, beta titanium is less biocompatible and arranges fewer oxides than Alpha-beta alloy. Ti-6Al-4V (Grade 5), contains 6% aluminum and 4% vanadium, which has found for the manufacture of implants and abutments. It has higher yield strength than CP-Ti, but it is less biocompatible and difficult to improve the surface properties [43].

Dental implant and abutment are usually made from grade four CP-Ti because it has higher flexural strength than other grades (550 MPa) and high biocompatibility [44]

Figure 1 Titanium implant abutment

Source: https://images.app.goo.gl/d8syHEJW2h6RyNeZA

2. Zirconia implant abutment

Nowadays, the zirconia implant abutments became the most generally used in the esthetic zone due to their superior esthetic outcomes, fewer bacteria accumulation than titanium and better fracture resistance compared to alumina. Several in vitro studies have exhibited that the fracture resistance of zirconia implant abutments range from 200 N to 831 N under static loading and from 104 N to 567 N after dynamic loading. Even though this fracture load exceeds the maximal reported incisal force (89 to 111 N) [45], zirconia abutment found problems such as fretting wear, fracture at the apical part and unpredictably of its long term efficiency [46].

2.1 Properties of zirconia

Zirconia or zirconium oxide (ZrO2) has received popular in dentistry due to its superior physical properties (high flexural strength 800-1000 MPa), esthetic (white shade) and biocompatibility [47]. Zirconia is a polycrystalline structure that occurs in 3 phases depending on the temperature; monoclinic (room temperature to 1170 ℃), tetragonal (1170 ℃ to 2370 ℃) and cubic phase (2370 ℃ to melting point) [48]. In the cooling temperature, the tetragonal phase transforms into the monoclinic phase that can induce internal stress, which is a cause of the fracture. Yttrium oxide (Y_2O_3) as a phase stabilizer is added to maintain the metastable tetragonal phase at room temperature and become Yttria-stabilized tetragonal zirconia polycrystalline (Y-TZP) ceramics as a type used in dentistry [49]. External stress may induce a crack in the ceramic composition and change the partially stabilized tetragonal particle into a monoclinic structure. The gained monoclinic structure has an enlarged volume (approximately 3%-5%), producing internal compressive stresses and puts the crack into compression. This mechanism is also called transformation toughening which can prevent crack growth [50].

2.2 Types of zirconia abutment

Zirconia abutments can be fabricated in two separate ways. First is the one-piece zirconia abutment which is made from zirconia. Second is the two-piece zirconia abutment. It consists of a standardized titanium base abutment integrated with a zirconia coping by using a resin-based luting agent. Two-piece zirconia abutments are used to combine the advantage of titanium-to-titanium connection and an esthetic abutment. It provides a more precise fit with the implant fixture, more support to zirconia abutment that is brittle ceramic and enhances the fracture resistance of the abutment due to maximum load capacity of these abutments may be comparable with titanium abutment [51].

2.2.1 One-piece zirconia abutment

One-piece zirconia abutment is made from the entire zirconia. When it connects with the titanium implant fixture, it will cause a fracture of the implant-abutment connection because of the differences in the surface hardness of titanium and zirconia materials. It also makes titanium implant easily wear, resulting in the abutment screw loosening. Therefore, the use of one-piece zirconia abutments may be harmful to the long-term stability of the components [13].

2.2.2 Two-piece zirconia abutment

Several in vitro studies demonstrated that zirconia abutments with titanium bases had higher fracture resistance [52]. The two-piece zirconia abutments have two designs. First, Hybrid-abutment-crown is a one piece that will be attached to titanium base and then screwed to the implant fixture. Second, Hybrid-abutment with a separate crown is the abutment which is bonded to titanium base first, then screwed to the implant fixture followed by a crown on top with cement. Hybrid-abutments have been designed to correct the inappropriate angulation of implants. Nogueira and colleagues found that the hybrid-abutment design has lower failure due to the existence of many interfaces (crown/abutment and abutment/titanium base) that may allow better force distribution [53]. However, the failure of the two-piece zirconia abutment is the separation between the zirconia coping and the titanium base abutment.

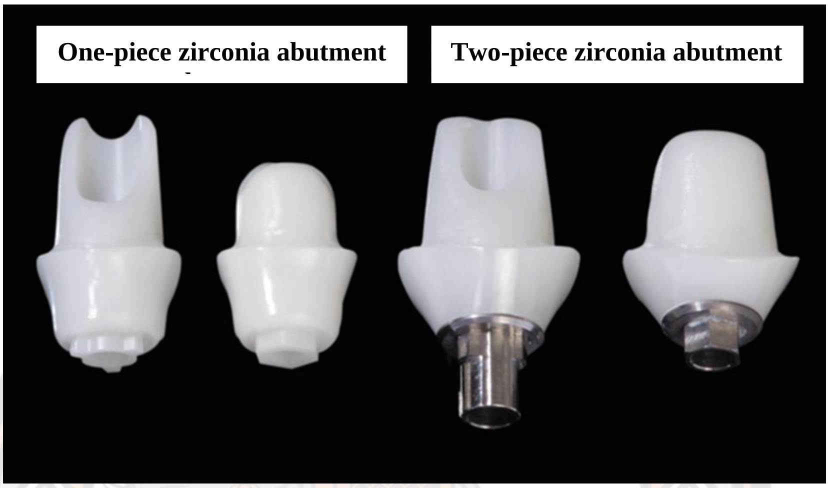

Figure 2 Zirconia implant abutment

Source: https://www.bmbdentalclinic.com.au/services/dental-implant/

Factors affecting the adhesion of zirconia and titanium

The failure of the two-piece zirconia abutment is the separation between the zirconia coping and the titanium base abutment. There are few investigations have shown that the retention force between the zirconia coping and the titanium base abutment is influenced by the surface conditioning methods and the type of cement [18].

1. Surface treatment of titanium

Metal surface treatments can increase retentive strength with resin cement by mechanical surface treatment and chemical surface treatment. The promoter of mechanical surface treatment is micromechanical retention, air-abrasion with aluminum oxide particle (Al_20_3) is most widely used. This procedure creates defects on the metal surface, resulting in increased surface roughness and surface area [54]. Moreover, it also creates a highly activated surface and supports the wettability of the substrate by the material applied subsequently [55]. Other surface treatments such as grinding with a diamond bur, etching with acid [22-24] and treating with a H_2O_2 solution have been shown to increase surface bond strength possibly [25, 26, 56, 57]. Apart from mechanical surface treatments, chemical surface treatments also contain modifying titanium. According to the manufacturer, there are many types of activating primers for increasing the bond strength to the metal such as V-Primer [28], Alloy Primer [29], Clearfil Ceramic Primer [30], and Monobond N [31]. Chemical bonding can be accomplished with metal primers and silanes. Metal primers contain active monomers react chemically with the oxides on the metal surface [58]. Silane can establish a chemical bond between the resin cement and the metal surface with silica coating due to its bifunctional properties. So it can improve a durable bond strength of resin cement to metal [59] [60].

2. Surface treatment of zirconia

Zirconia is an inert material, no glass composition and un-etchable. So, it has limited adhesive luting potential [61]. Different mechanical and chemical surface treatments have been reported to enhance the potential of the bonding between resin cement and zirconia.

Air-abrasion with Al_20_3 size of 50-110 µm under pressure 2.5 bars provided more zirconia surface roughness to improve retention of resin cement. In additional to enhance surface area, increased surface energy and wettability made resin cement flow to zirconia surface [62]. Air-abrasion can eliminate organic contaminants from the zirconia surface. However, inappropriate air-abrasion may increase subsurface damage and fracture of zirconia [63]. Therefore, the effect of air-abrasion on the mechanical strength of zirconia seems controversial with some studies showing a strengthening effect. Ban, et al. [64] analyzed the pressure used for air-abrasion, which had been tested for pressure 2, 4 and 6 bar. They concluded that increasing air pressure resulted in increase the surface roughness of zirconia but decrease flexural strength. So Kern, et al. [65] recommended to use 50 µm Al_20_3 with a pressure of 2.5 bars or less to decrease surface damage of zirconia and to be effective to the strength of zirconia restoration on a clinically relevant level.

Many studies have found that pretreatment zirconia surface by air-abrasion with Al_20_3 combined with the use of a primer containing an adhesive phosphate monomer (MPD) can achieve superior long-term tensile and shear bond strength between zirconia and resin cement [62] [66]. Kern, et al. [67] compared Clearfil Ceramic Primer and Alloy Primer with aspect to adhesion with zirconia. They concluded that Clearfil Ceramic Primer accomplished the best adhesion to zirconia. According to Kern et al, zirconia surface treatment with aluminum oxide sandblasting followed MDP containing resin cement can improved tensile bond strength between zirconia and resin cements. Since the zirconia surface is high hardness, only blasting with aluminum oxide is may not as effective. The combination of mechanical and chemical preconditioning provides the durability of the bond of resin cement to zirconia ceramics [68].

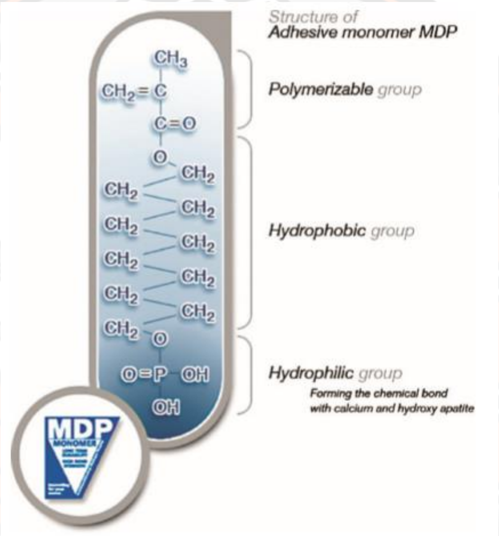

Figure 3 Structure of MDP functional monomer

Source: https://kuraraydental.com/clearfil/key-technologies/mdp-monomer/

Chemical agents

Chemical bonding of titanium can be performed with metal primers and silanes. Metal primers contain active monomers such as 10-methacryloyloxydecyl dihydrogen phosphate (MDP), 6-(4-vinylbenzyl-n-propyl) amino-1,3,5-triazine-2,4-dithione (VBATDT) and 4-methacryloxyethyltrimellitate anhydride (4META) that react chemically with the oxides on the metal surface [58]. Silane can establish a chemical bond between the resin cement and the metal surface due to its bifunctional properties [60].

Chemical agents with the MDP monomer contain a phosphate ester group and a methacrylate group can promote chemical bonds to zirconia through the chemical interaction between phosphate ester group of MDP and hydroxyl groups in the zirconia surface. The chemical bond between MDP and Bis-GMA composite resin is accomplished through the methacrylate group of MDP and the composite resin matrix of the luting cement. The MDP monomer can promote the long term durable bond strength of zirconia under clinical conditions [69].

V-Primer is an acetone solution with adhesive monomer VBATDT that contains thiol group. Thiol group of VBATDT has sulfur to react chemically with the oxides on the metal surface. It used to enhance the bond durability to precious metals (including Au/Ag/Pd alloys) [70].

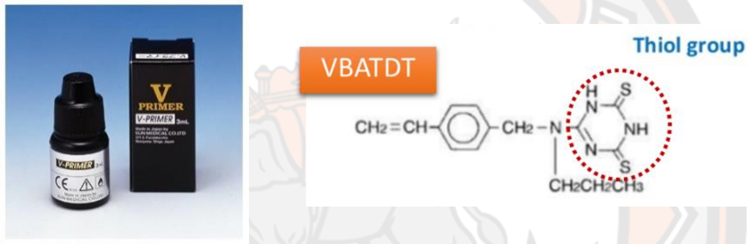

Figure 4 V-Primer and structural formula of VBATDT

Source: http://www.generiqueinternational.com/produit-V-Primer-Collage-40-0.html

Alloy Primer is a metal primer used to increase the bond strength between dental metal and resin base materials. It consists of acetone, MDP and VBATDT. Alloy Primer is a pretreatment agent for conditioning metal and is used to secure the adhesive capability of resins and acrylic ester to gold, titanium and other dental alloys [30].

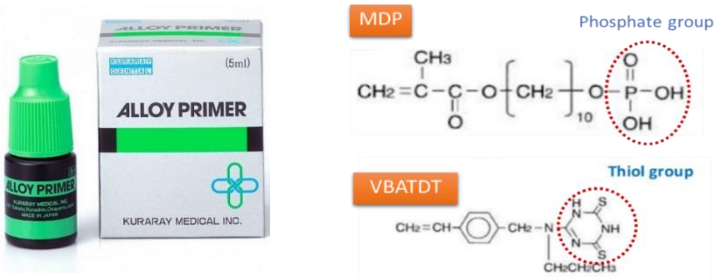

Figure 5 Alloy Primer and structural formula of MDP & VBATDT

Source: https://www.aosmedical.com/alloy-primer.html

Clearfil Ceramic Primer is a single-component adhesive primer used to enhance the bond strength between resin-based materials and ceramic materials. This primer contains the 3-methacryloxypropyl trimethoxy silane, MDP and ethanol. It is indicated for the surface treatments of lithium disilicate ceramics, zirconia ceramics, hybrid ceramics, composite resins and metal surfaces [31].

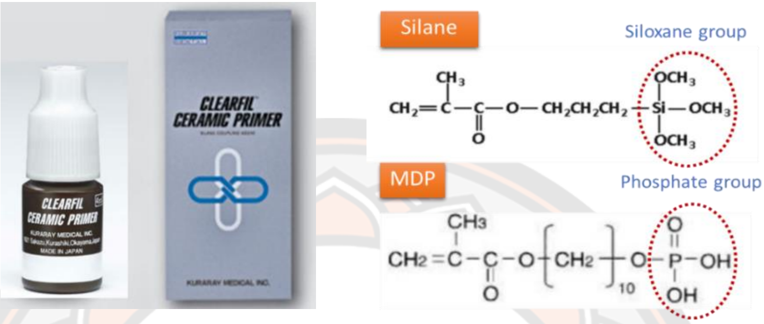

Figure 6 Clearfil Ceramic Primer and structural formula of Silane & MDP

Source: http://www.isoteeth29.fr/adhesifs-52/clearfil-ceramic-primer--757.html

Monobond N is the universal primer for the conditioning of all types of restoration surfaces (glass and oxide ceramics, metal, composites, fiber-reinforced composite). The primer enables users to achieve a strong and durable bond to any dental restorative material because it combines three different functional methacrylates (silane methacrylate, phosphoric acid methacrylate and sulfide methacrylate) [71].

Figure 7 Monobond N and structural formula of Silane

Source: https://www.ivoclarvivadent.in/en-in/p/all/monobond-n

Table 1 Primer in this study

Product	Compositions	Manufacturer	Lot No.
V-Primer	VBATDT, Acetone	Sun Medical Co., Ltd., Moriyama, Shiga, Japan	SG1
Alloy Primer	VBATDT, MDP, Acetone	Kuraray Noritake Dental Inc., Kurashiki, Okayama, Japan	5E0101
Clearfil Ceramic Primer	MDP, Silane coupling agent, Ethanol	Kuraray Noritake Dental Inc., Kurashiki, Okayama, Japan	1G0041
Monobond N	Silane methacrylate, Phosphoric methacrylate, Sulfide methacrylate	Ivoclar Vivadent AG, Schaan, Liechtenstein	X41367

Cementation

Several methods of connecting a titanium base and zirconia coping have been reported. Maltzahn and colleagues found that the use of the resin-based luting cements Panavia F 2.0 or RelyX Unicem are appropriate for connecting titanium and zirconia components in two-piece zirconia abutments although the chemical composition of the resin cements are different [30]. Gehrke, et al. [10] found that using resin-based luting cements Panavia 21 provides the highest adhesion value when compared to Multilink Implant and SmartCem2. The luting cement that consists of phosphate monomer such as MDP can increase the bond strength between a titanium base abutment and zirconia coping [72]. The chemical bond between MDP and zirconia is received from the chemical interaction between the phosphate ester group of MDP and the hydroxyl group of the zirconia. The chemical bond between MDP and Bis-GMA (bisphenol-A-diglycidyl-methacrylate) composite resin is achieved through the chemical interaction between the methacrylate group of MDP and the composite resin matrix of the luting cement [69]. In vitro studies demonstrated that the application of resin-based cement, which contains an adhesive phosphate MDP monomer (Panavia resin group; Kuraray) in combination with air-abrasion of zirconia resulted in bond strengths higher than 50 MPa with no decline in bond strength after long term water storage and thermal cycling [73] and resulted also in high strength dependable bonding to titanium [74].

Figure 8 Adhesive resin cement: Panavia V5

Source: https://www.kuraraynoritake.com/world/product/cements/panavia_v5.html

Shear bond test

The masticatory force is shearing in nature. The adhesive strength at the inter surface of the materials is measured by the shear bond strength [75]. Shear bond strength was measured to define the strength of the bond between titanium and zirconia by universal test machine (8872, Instron, Norwood, Massachusetts, USA) which is load at a crosshead speed of 1 mm/min until failure of the titanium-zirconia bond. Maximum forces were recorded and the shear bond strength was calculated from the following formula: $Rt = F/S$, which Rt is the shear bond strength values [MPa], F is the force acting on the specimen [N] and S is the surface area of the specimen [mm^2].

Figure 9 Universal test machine

Atomic Force Microscope (AFM)

Atomic Force Microscope (AFM) is a type of scanning probe microscopes (SPMs), which a probe or tip is used to determine the characteristics and measure surface roughness of the sample. During operational mode, the tip connected to a cantilever is scanned over the surface of the sample, with a small repulsive force present between the sample and the tip. The cantilever may be deflected due to fluctuations in the surface topography. AFM can be used on a wide range of surfaces, including conductive surface, insulated surface, smooth solid surface, soft surface, polymer surface and other flat synthetic surfaces. A wide range of particle sizes can be characterized in the same scan from 1 nm to 8 µm. The sample should have a surface roughness less than 15 µm and maximum scan size less than 100x100 µm. AFM offers high resolution and visualization in 3D images from the tip movement with high resolution [76].

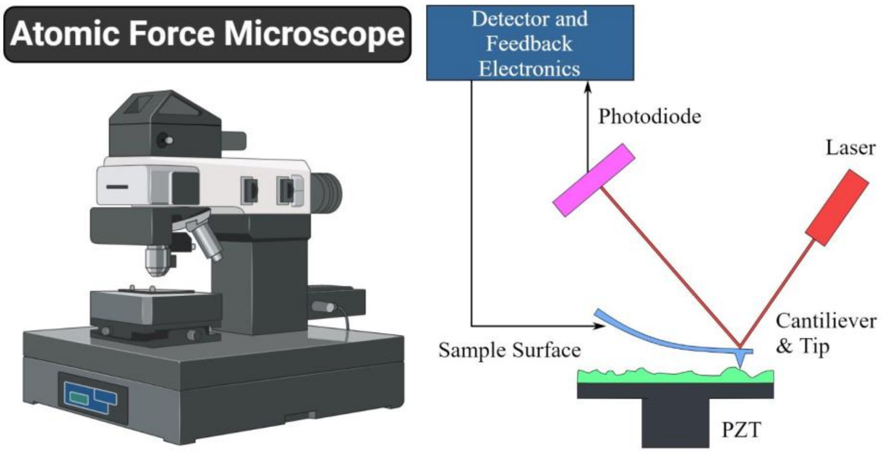

Figure 10 Atomic Force Microscope (AFM)

Source: https://microbenotes.com/atomic-force-microscope-afm/

Failure mode

Failure mode plays a significant part in determining the weak point of bond failure. The failure modes were classified to 3 categories [77].

1. Adhesive failure: the fracture is located at the resin cement-adherend interface, resulting in cement residues on only one of the adherend surfaces.

2. Cohesive failure: the fracture occurred within the resin cement layer, resulting in cement residues on both surfaces of the adherend and maybe the presence of voids and defects such as impurities and cracks in the resin cement layer.

3. Mixed failure: the fracture occurred both within the resin cement and at the resin cement-adherend interface.

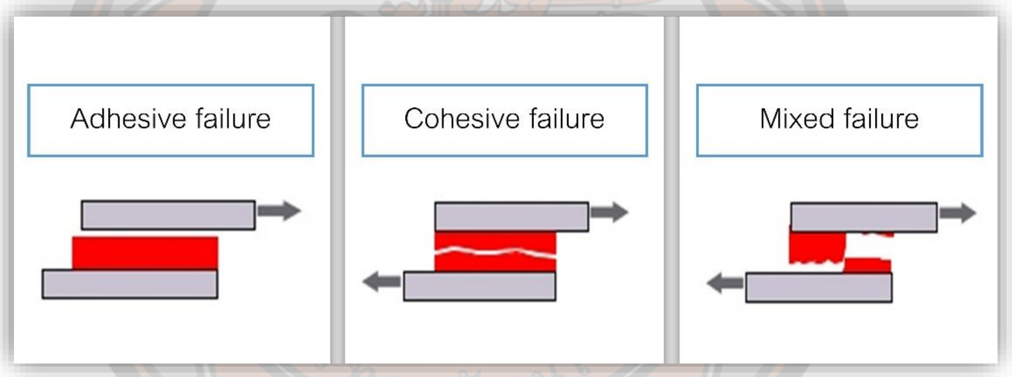

Figure 11 Failure mode

Source: https://tombrowninc.com/blog/understanding-adhesive-failures/

CHAPTER III

Research Methodology

Population and Sample

Calculation of sample size using a G * Power program based on results of the pilot study. The average shear bond strengths in each group were 7.92, 8.99, 12.72, 28.86, 25.20, 36.04 MPa and the average value of standard deviation was 1.91. Using a one-way ANOVA formula from the G * Power program at the 95% confidence of interval yields the sample size of 10 per group.

1. Preparation of specimens

1.1 Titanium

Titanium rods (CP Ti Grade IV) with 10 millimeter (mm) diameter were cut to 5 mm thickness by linear precision saw (Isomet 5000, Buehler, Lake Bluff, Illinois, USA). Titanium disks were embedded in a polyvinyl chloride (PVC) tube (20 mm in diameter and 13 mm high), using auto-polymerized acrylic resin (Fast Curing Custom Tray Acrylic Resin; Instant Tray Mix, Lang Dental Manufacturing Company, Wheeling, Illinois, USA). The bonding surfaces of titanium disks were smoothed with 240, 400, 800, 1000 and 1200-grit silicon carbide grinding papers (Buehler-MET II, Buehler, Lake Bluff, Illinois, USA) using a grinder-polisher (Phoenix Beta, Buehler, Lake Bluff, Illinois, USA) under water cooling, and cleaned in an ultrasonic bath (Sonorex Super 10 P, Bandelin, Berlin, Germany) containing deionized water for 8 minutes (min) [78].

Figure 12 Titanium disk: 10 mm in diameter and 5 mm in thickness

Figure 13 Titanium block: 20 mm in diameter and 13 mm in high

1.2 Zirconia

Zirconia blocks (Zirlux 16^+, Henry Schein Inc., Melville, New York, USA) were milled and sintered to 5 mm diameter and 5 mm thickness by the dental technician. The bonding surfaces of zirconia disks were smoothed with 240, 400, 800, 1000 and 1200-grit silicon carbide grinding papers using a grinder-polisher under water cooling, and cleaned in an ultrasonic bath containing deionized water for 8 min. After that, zirconia disks were surface treated by blasting with 50 Al_20_3 particle at 2.5 bar pressure for 20 seconds (sec) at a distance of 10 mm following Mehl's protocol [79], Then, the specimens were washed in deionized water in an ultrasonic cleaning bath for 8 min, dried with compressed air, applied with Clearfil Ceramic Primer (Kuraray Noritake Dental Inc., Kurashiki, Okayama, Japan) and blown dry [59].

Figure 14 Zirconia disk: 5 mm in diameter and 5 mm in thickness

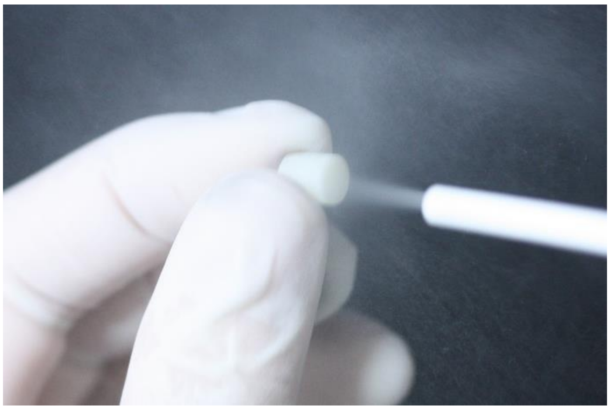

Figure 15 Sandblast of zirconia disk with 50 µm Al_20_3 for 20 sec at 2.5 bar

Figure 16 Application of Clearfil Ceramic Primer to zirconia disk

2. Testing of specimens

2.1 Part 1: To evaluate the effect of mechanical surface treatments

50 titanium disks were randomly divided into 5 groups according to the various surface treatments (n=10) as follows:

- Group 1: No surface treatment (Control)
- Group 2: Titanium disks were etched with 37% phosphoric acid (H_3PO_4) 15 min
- Group 3: Titanium disks were etched with 9% hydrofluoric acid (HF) 15 sec
- Group 4: Titanium disks were treated with 50% hydrogen peroxide (H_2O_2) 15 min
- Group 5: Titanium disks were blasted by 50 µm Al_20_3 particle at 2.5 bar for 20 sec at a distance of 10 mm

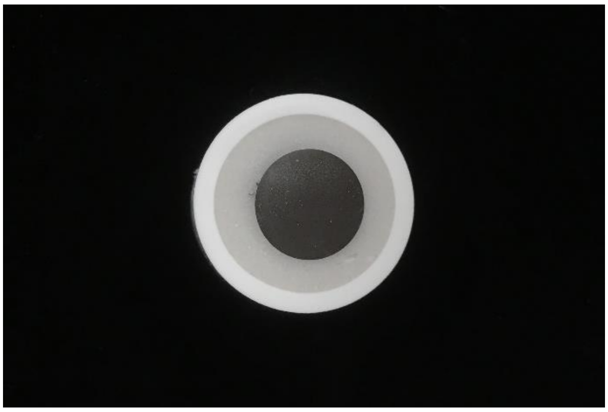

Figure 17 No surface treatment of titanium disk for Group 1

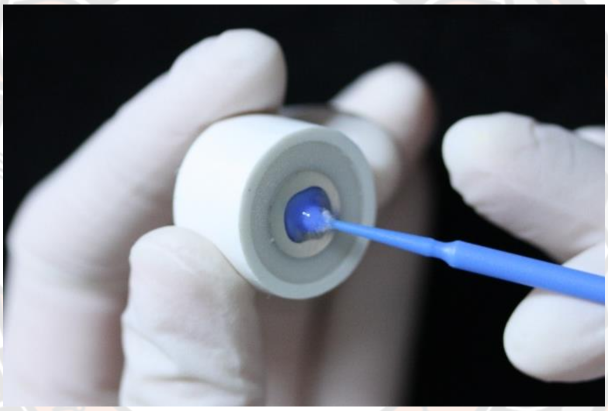

Figure 18 Etched of titanium disk with 37% H_3PO_4 15 min for Group 2

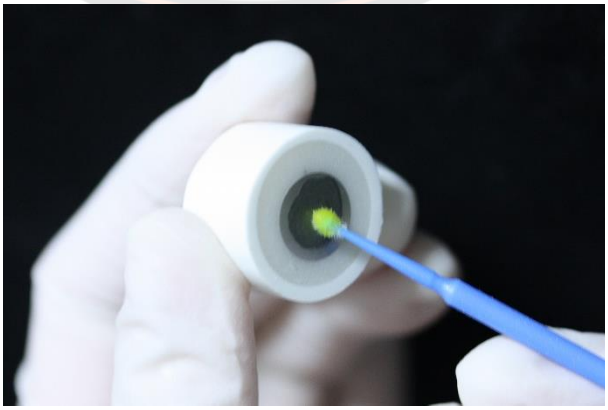

Figure 19 Etched of titanium disk with 9% HF 15 sec for Group 3

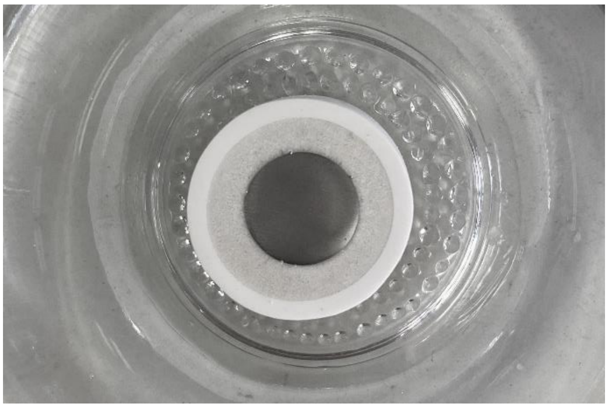

Figure 20 Treated of titanium disk with 50% H_2O_2 15 min for Group 4

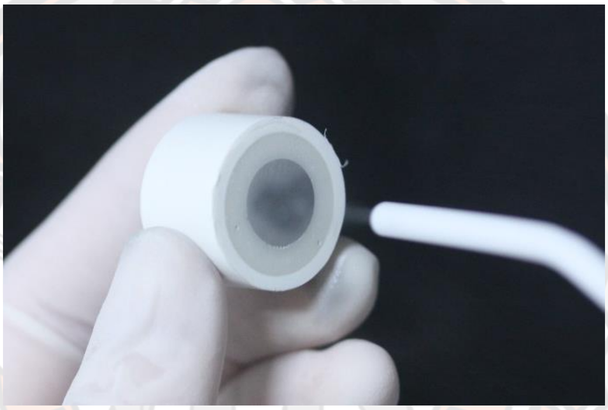

Figure 21 Sandblast of titanium disk with same pressure and time for Group 5

After the surface treatment, all specimens were washed in deionized water in an ultrasonic cleaning bath for 8 min and dried with compressed air [79]. All specimens were bonded to zirconia disks with dual-cures resin cement (Panavia V5) (Kuraray Noritake Dental Inc., Kurashiki, Okayama, Japan) [72] and seated with a constant 1 kg force applied by a specimen preparation jig (S4660A, Instron, Norwood, Massachusetts, USA). Excess resin cement was removed with a microbrush. Cement were light polymerized for 20 sec through each 4 sides of the specimen with an LED curing light at a distance of 10 mm to initiate polymerization (S.P.E.C. 3, Coltene Whaledent Inc., Cuyahoga Falls, Ohio, USA; 1600 mW/cm^2) and left final polymerization for 5 min. All specimens were stored in water for 24 hours at 37°C. After that, all specimens were aged by thermocycling for 5,000 cycles between 5°C and 55°C and a 15 sec dwell time.

Figure 22 Panavia V5 cement kit

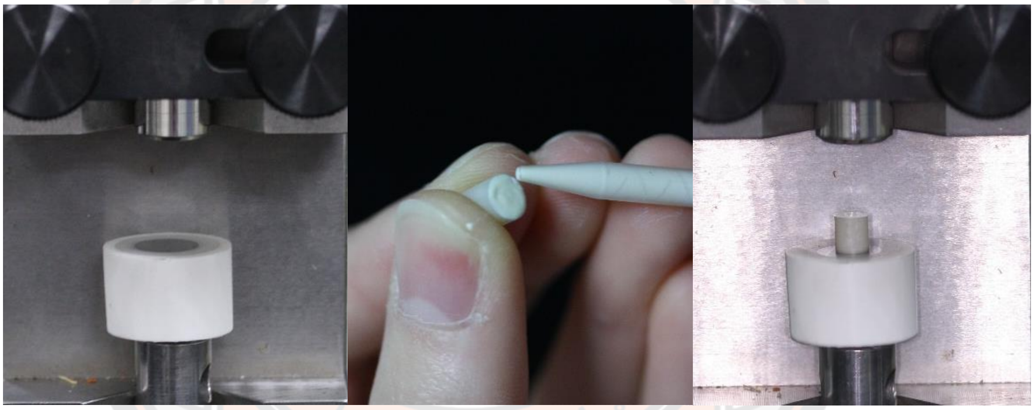

Figure 23 Cementation sequence of zirconia disk with titanium disk

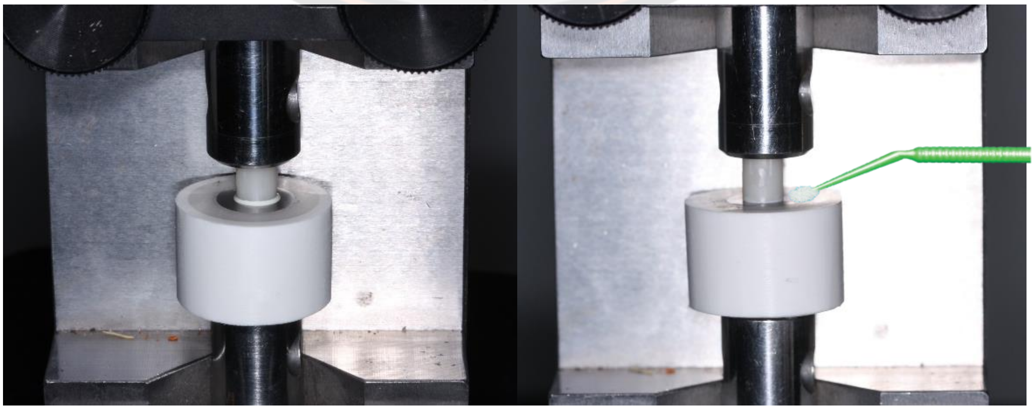

Figure 24 Fixation device and removal of excess cement

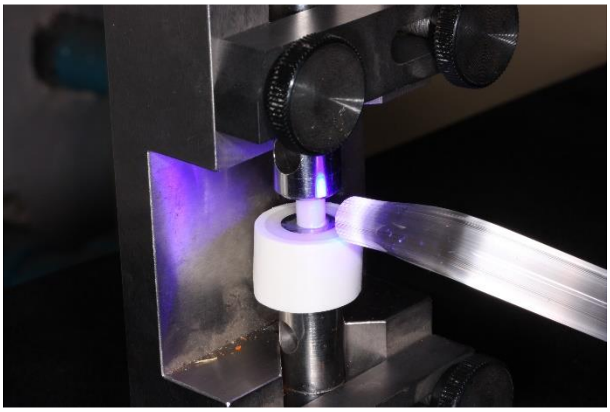

Figure 25 Polymerization for 20 sec through each 4 sides of the specimen

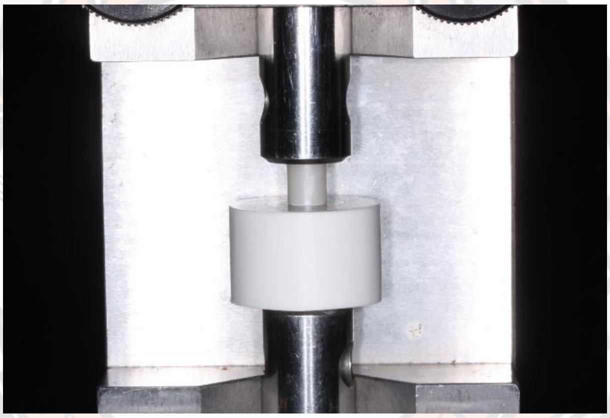

Figure 26 Final polymerization for 5 min

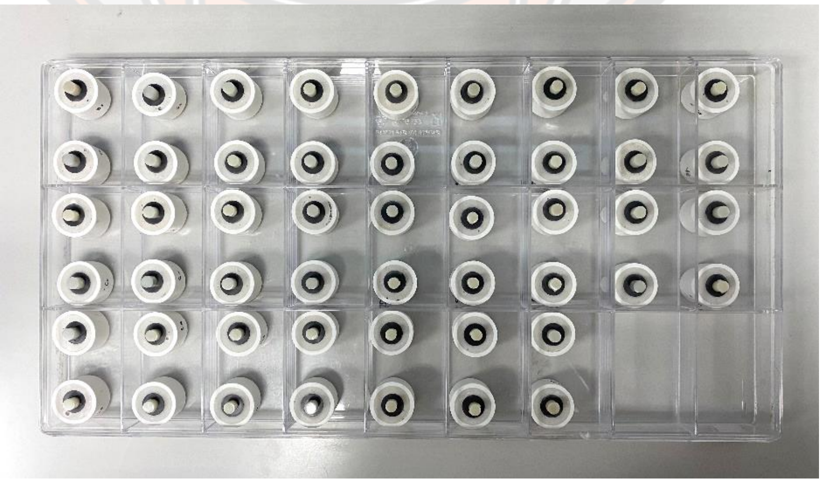

Figure 27 Stored all specimens in water for 24 hours at 37°C

2.2 Part 2: To evaluate the effect of mechanico-chemical surface treatments

50 titanium disks and 50 sintered zirconia disks were used in the experiment. Titanium disks were randomly divided into 5 groups depending on the various surface treatments (n=10). All experimental groups of titanium disks were sandblasted in the same procedure as part 1. Due to the result of part 1, the sandblast group provides the highest value of shear bond strength. After that, the specimens were washed in deionized water in an ultrasonic cleaning for 8 min and dried with compressed air. Then, the specimens will be chemically surface treated as follows:

- Group I: Titanium disks were sandblasted (Control)
- Group II: Titanium disks were sandblasted and applied with V-Primer
- Group II: Titanium disks were sandblasted and applied with Alloy Primer
- Group IV: Titanium disks were sandblasted and applied with Clearfil Ceramic Primer
- Group V: Titanium disks were sandblasted and applied with Monobond N

After the surface treatment, all specimens were bonded to zirconia disks using the same protocol in part I. After that, all specimens were aged by thermocycling for 5,000 cycles between 5°C and 55°C and a 15 sec dwell time.

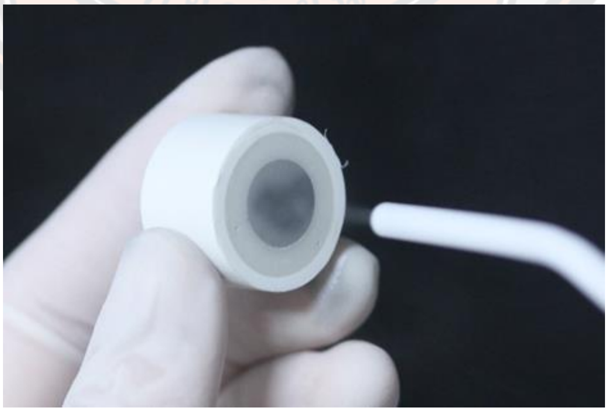

Figure 28 Sandblast of titanium disk with same pressure and time for Group I

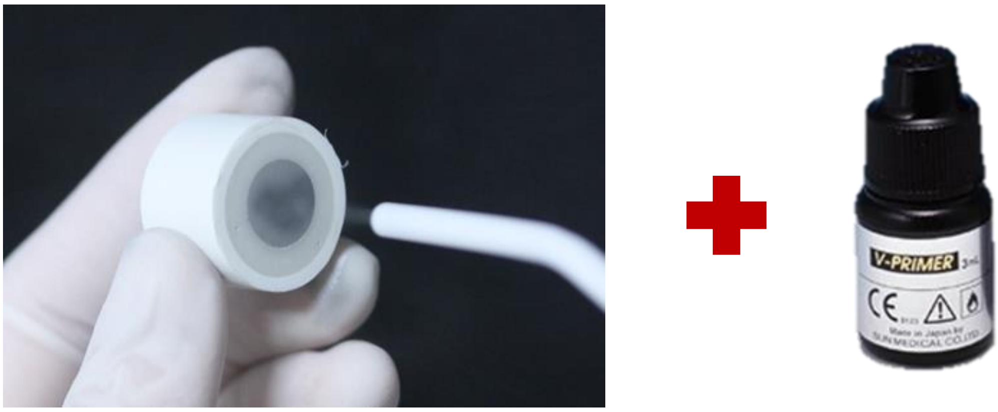

Figure 29 Sandblast of titanium disk and applied with V-Primer for Group II

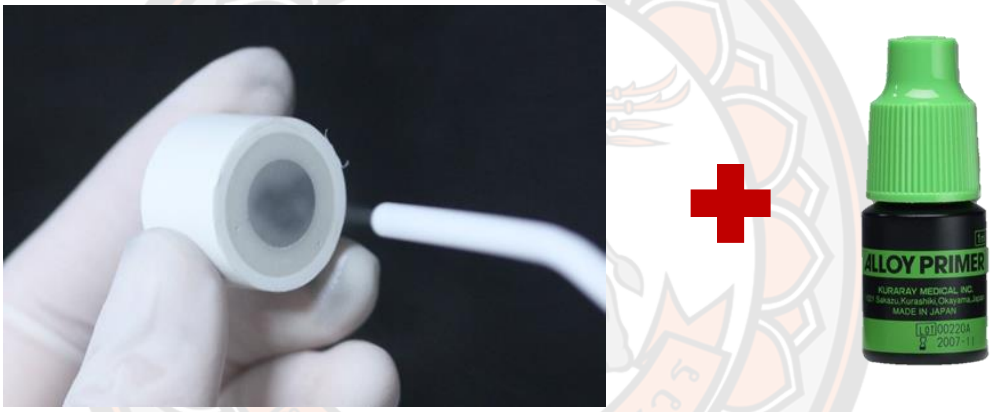

Figure 30 Sandblast of titanium disk and applied with Alloy Primer for Group III

Figure 31 Sandblast of titanium disk and applied with Clearfil Ceramic Primer for Group IV

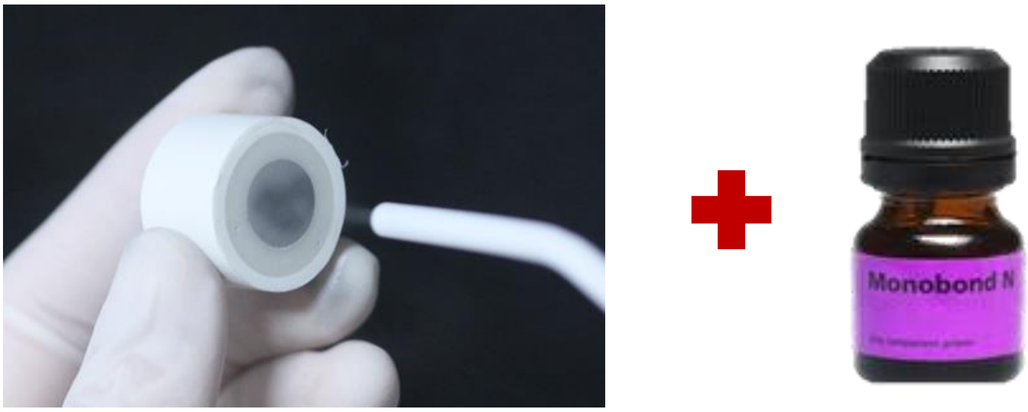

Figure 32 Sandblast of titanium disk and applied with Monobond N for Group V

3. Stimulated aging

All specimens were exposed to alternating thermal loads in moist air to stimulate the humid atmosphere and variations in temperature in the oral cavity. Following water storage, the specimens were thermocycled for 5,000 cycles between 5°C and 55°C and a 15 sec dwell time [80] by thermocycling machine (THE 1100/1200, SD Mechatronik Dental research equipment, Feldkirchen-Westerham, Germany) correspond to six months of clinical service [81].

Figure 33 Thermocycling machine

4. Shear bond test

Specimens were tested for the shear bond strength using a universal test machine with a 10 kN load cell. A knife-edge-shearing rod running at a crosshead speed of 1 mm/min were used to load the specimens until fracture.

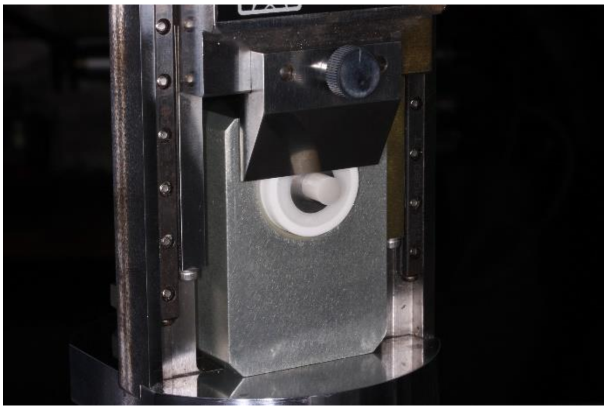

Figure 34 Tested specimens with a universal test machine

5. Microsurface characterization

Each untreated and treated specimen were examined under an atomic force microscope (AFM) (Flex-axiom, Nano-surf, Liestal, Switzerland) and a scanning electron microscope (SEM) (SEM Zeiss (Leo) 1455VP, Jena, Germany) to examine the surface roughness and surface topography of specimens. The roughness of specimens was analyzed at three different areas in the critical zone using an AFM that represent morphological nanoscale features. The resolution of images at lateral size scanning for 50×50 μm^2. The roughness was calculated by using the Nanosurf analysis tool (C3000 control software version 3.10.0, Nano-surf, Liestal, Switzerland). One parameter will be considered: Sa corresponding to the arithmetic average of the absolute values of the roughness profile. In part 1, the control group that untreated surface was selected with a surface roughness value in the range of 165-175 nm. In part 2, the control group that sandblasted surface was selected with a surface roughness value in the range of 600-615 nm. After the shear bond strength testing, the fractured surfaces were examined with a stereomicroscope (Olympus SZX16, Spacemed, Tokyo, Japan) at 20x and determined the mode of failure. Failure modes were recorded by a single calibrated observer as either adhesive (fracture between titanium/zirconia and resin cement), cohesive (fracture within the resin cement) or mixed (fracture areas of adhesive and cohesive failure). Representative specimens were analyzed by SEM with an acceleration voltage of 10 kV after sputtering using a gold alloy conductive layer of approximately 30 nm to define the nature of the fractures formed in the shearing procedure.

Research Instrument

- Liner precision saw (Isomet 5000, Buehler, Lake Bluff, Illinois, USA)
- Grinder-polisher (Phoenix Beta, Buehler, Lake Bluff, Illinois, USA)
- Ultrasonic cleaning bath (Sonorex Super 10 P, Bandelin, Berlin, Germany)
- Specimen preparation jig (S4660A, Instron, Norwood, Massachusetts, USA)
- LED curing light (S.P.E.C. 3, Coltene Whaledent Inc., Cuyahoga Falls, Ohio, USA)
- Universal test machine (8872, Instron, Norwood, Massachusetts, USA)
- Thermocycling machine (THE 1100/1200, SD Mechatronik Dental research equipment, Feldkirchen-Westerham, Germany)
- Atomic Force Microscope (Flex-axiom, Nano-surf, Liestal, Switzerland)
- Scanning Electron Microscope (SEM Zeiss (Leo) 1455VP, Jena, Germany)
- Stereomicroscope (Olympus SZX16, Spacemed, Tokyo, Japan)

Data Collection

Shear bond strength was measured in a universal testing machine with 1 mm/min crosshead speed. Maximum forces were recorded and the shear bond strength was calculated from the following formula: $Rt = F/S$, which Rt is the shear bond strength values [MPa], F is the force acting on the specimen [N] and S is the surface area of the specimen [mm^2].

Mode of failure and surface characteristics were examined. A fractographic analysis was performed with stereomicroscope and SEM.

Analysis of Data

The mean values and standard deviations of all specimens were calculated for each group. Data was analyzed and evaluated with SPSS programs (SPSS version.22, IBM, Armonk, NY, USA) by comparison between independent samples at the level of confidence of 95%. If the data had a normal distribution, they were analyzed using a one-way analysis of variance (ANOVA) and Tukey HSD (Honestly Significant Difference) post-hoc test for all pairwise comparisons. However, the Kruskal-Wallis was used if the data are not normally distribution.

CHAPTER IV

Results

Part 1

The shear bond strength, reported in Megapascal Pressure Unit (MPa). The mean ± standard deviation (SD) bond strength values range from 3.64 ± 2.11 MPa (control group) to 36.01 ± 2.80 MPa (sandblast group), as shown in Table 2 and Figure 35. The data were analyzed for significant differences using a one-way analysis of variance (ANOVA) with $P<.05$. Differences between groups were determined by Tukey HSD (Honestly Significant Difference) post-hoc test.

Statistical analysis revealed a significant influence of titanium surface treatment on the shear bond strength ($P<.05$). The Tukey HSD test revealed that the titanium surface treated with sandblasting (36.01 ± 2.80 MPa) and with H_2O_2 (33.57 ± 2.74 MPa) exhibited significantly higher shear bond strengths compared to the other groups ($P<.05$), while the group that underwent surface treatment with HF (21.27 ± 2.76 MPa) exhibited a significantly higher shear bond strength than the control group (3.64 ± 2.11 MPa) ($P<.05$). In contrast, the group surface treated with H_3PO_4 (5.29 ± 2.50 MPa) showed no significant differences compared to the control group (3.64 ± 2.11 MPa) ($P>.05$).

Table 2 Means and standard deviations of shear bond strength of part 1

Group	N	Mean	Std Dev	Std Error	Lower 95%	Upper 95%
Control	10	3.64	2.11	.67	2.13	5.15
H_3PO_4	10	5.29	2.50	.79	3.50	7.08
HF	10	21.27	2.76	.87	19.29	23.24
H_2O_2	10	33.57	2.74	.87	31.61	35.53
Sandblast	10	36.01	2.80	.88	34.01	38.01

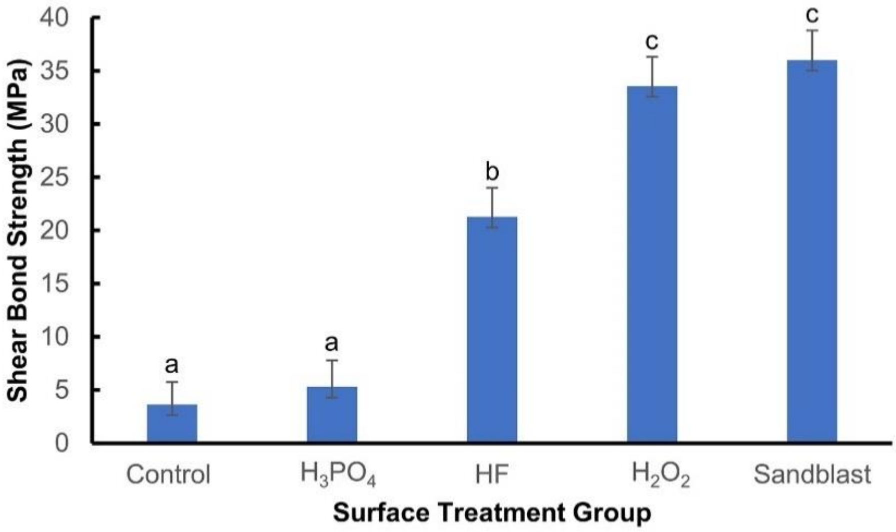

Figure 35 Means and standard deviations of shear bond strength of part 1

Note: The different superscripts indicate significant difference among groups (*P*<.05)

The mean and SD values of the titanium surface roughness before and after surface treatment were shown in Figure 36. The titanium surface roughness values of the control, H_3PO_4 treated and H_2O_2 treated groups were significantly lower than those of the HF and sandblast groups (*P*<.05). The group that was surface treated through sandblasting showed the highest surface roughness value among all groups (*P*<.05).

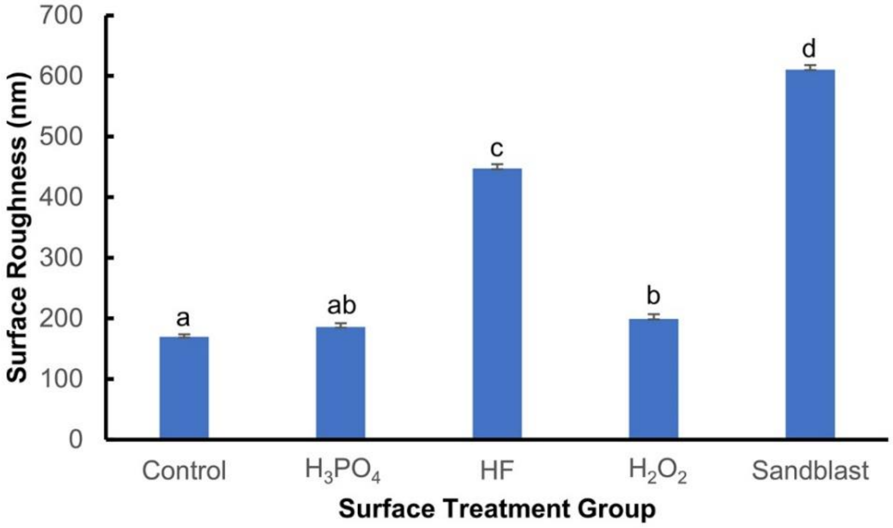

Figure 36 Means and standard deviations of surface roughness of part 1

Note: The different superscripts indicate significant difference among groups (*P*<.05)

Figure 37 shows selected AFM and SEM images of titanium disks surface before and after surface treatment. In the control group, AFM and SEM images exhibited a macroscopically and microscopically smooth surface, with evident minor parallel grooves, owing to polishing process (Figures 37A and 37B). The H_3PO_4 and H_2O_2 treated groups showed mean values of roughness similar to those of the control group. The H_3PO_4 and H_2O_2 treated disks exhibited slight alterations in the surface topography. As a result, the parallel groove on the titanium surface became less obvious (Figures 37C, 37D, 37G, and 37H). In the groups that underwent surface treatment through sandblasting and with HF, the mean roughness values were significantly higher than those of the other groups, and a significant difference between the above two groups was observed ($P<.05$). The HF treated disks showed several peaks on a flat surface and protruded particles, which appeared as small and large irregular shapes with round edges (Figures 37E and 37F). The sandblast treated disks revealed numerous irregular cavities, cracks, and sharp edges, which differed from the other groups (Figures 37I and 37J)

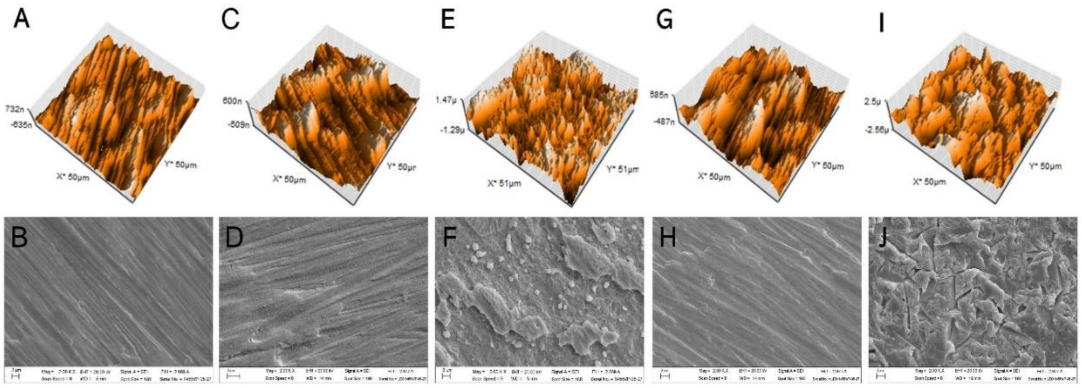

Figure 37 AFM (Upper row) and SEM (Lower row) images for the control group (A and B), H_3PO_4 group (C and D), HF group (E and F), H_2O_2 group (G and H) and sandblast group (I and J)

After the shear bond strength testing, the specimens were examine using a stereomicroscope (20x) to record the failure mode, and the distribution of fracture patterns is summarized in Table 3. The analysis of fracture patterns showed that the control and H_3PO_4 treated groups demonstrated only the adhesive fracture pattern between the titanium disks and resin cement. In these two groups, no resin cement remnants were found on the titanium surfaces; however, all the resin cement layers were found on the zirconia surface (Figures 38 and 39). The groups surface treated with HF, H_2O_2, and sandblasting have mixed fracture patterns, and more residual cement tended to remain on the zirconia surfaces than on the titanium surfaces (Figures 40-42).

Table 3 Fracture pattern distribution of part 1

Group	Adhesive fracture between titanium surface and resin cement	Mixed fracture pattern
1	10	-
2	10	-
3	6	4
4	3	7
5	3	7

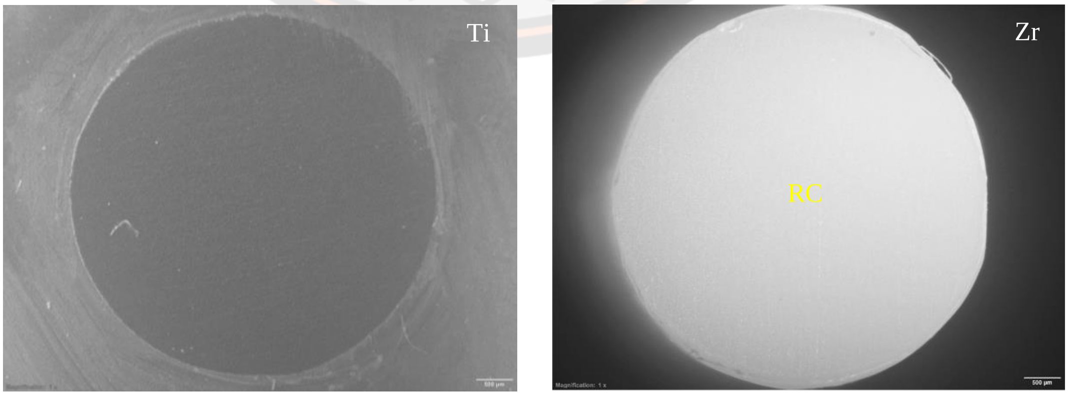

Figure 38 Adhesive fracture pattern between titanium surface (Ti) (left) and resin cement (RC) on zirconia surface (Zr) (right) of group 1

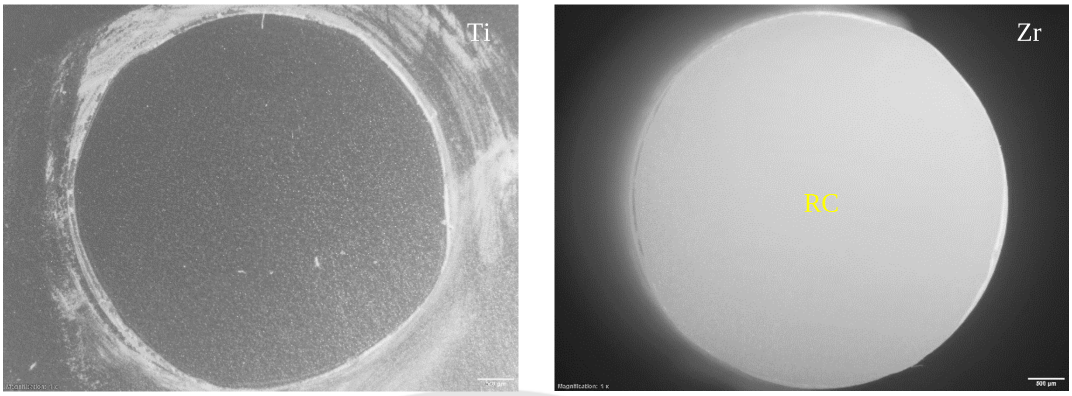

Figure 39 Adhesive fracture pattern between titanium surface (Ti) (left) and resin cement (RC) on zirconia surface (Zr) (right) of group 2

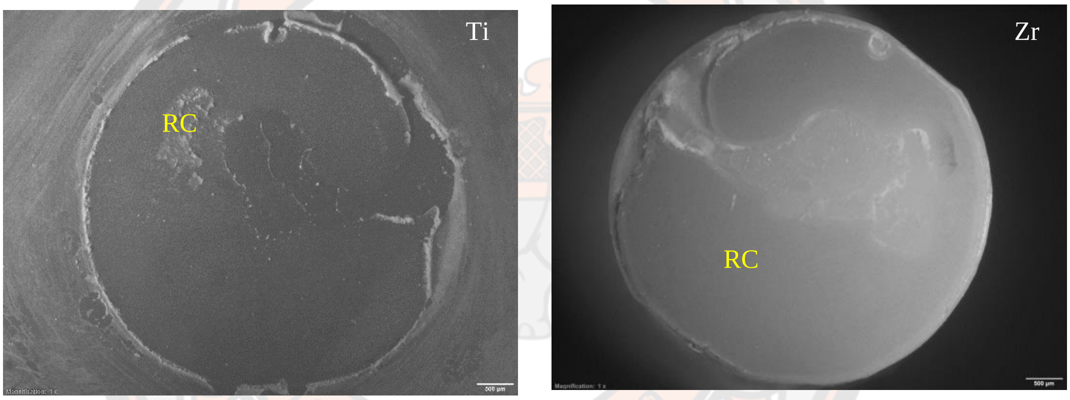

Figure 40 Mixed fracture pattern between titanium (Ti)-resin cement (RC) (left) and zirconia (Zr)-resin cement (right) interfaces of group 3

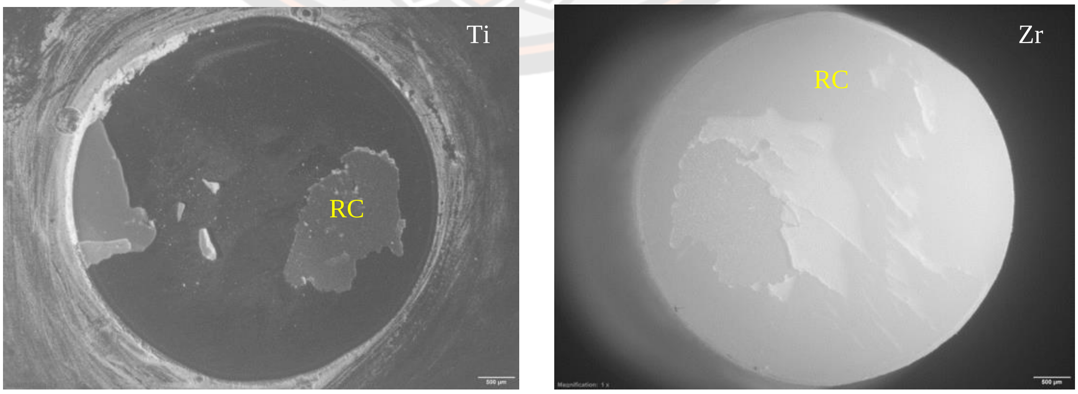

Figure 41 Mixed fracture pattern between titanium (Ti)-resin cement (RC) (left) and zirconia (Zr)-resin cement (right) interfaces of group 4

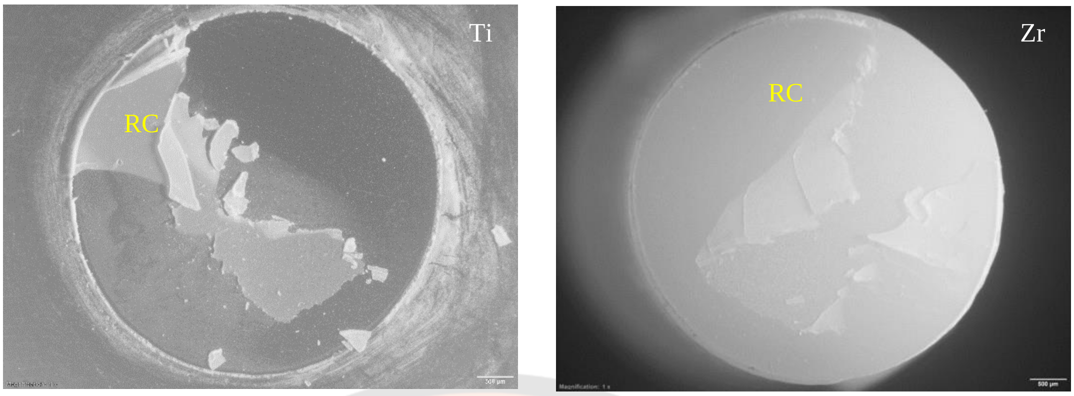

Figure 42 Mixed fracture pattern between titanium (Ti)-resin cement (RC) (left) and zirconia (Zr)-resin cement (right) interfaces of group 5

The representative SEM images of the surface morphology of specimens after the shear bond strength testing are shown in Figures 43-47. High-magnification (×1,000) SEM images revealed all resin cement residues on the zirconia surface in group 1 and group 2 for the adhesive fracture pattern (Figures 43 and 44). Other groups demonstrated resin cement residues on both the titanium and zirconia surfaces in a mixed fracture pattern (Figures 45-47).

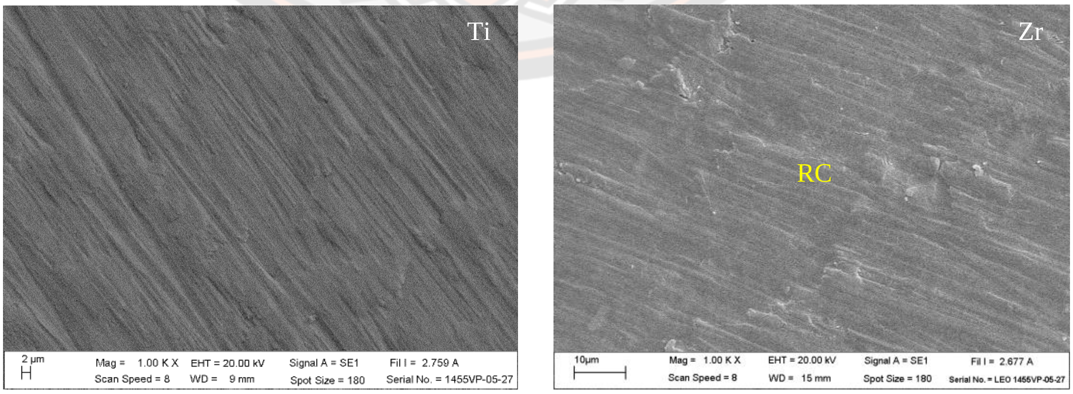

Figure 43 SEM images of the titanium and zirconia surface after the shear bond strength testing of group 1 (Magnification x1000)

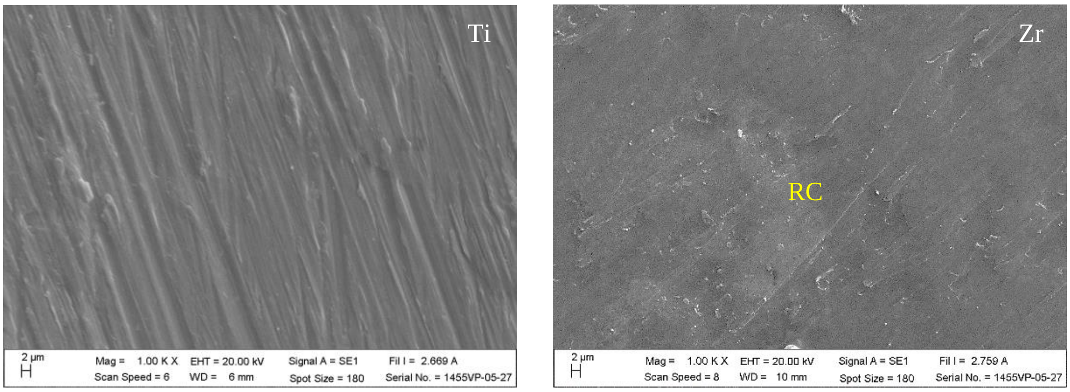

Figure 44 SEM images of the titanium and zirconia surface after the shear bond strength testing of group 2 (Magnification x1000)

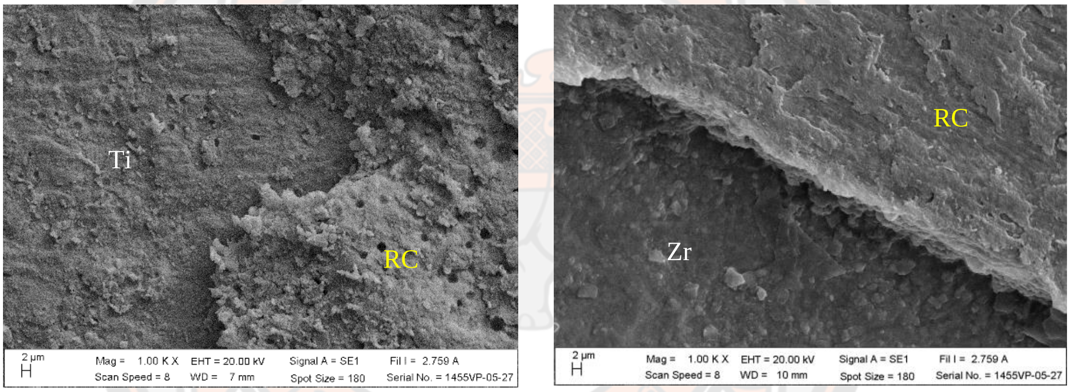

Figure 45 SEM images of the titanium and zirconia surface after the shear bond strength testing of group 3 (Magnification x1000)

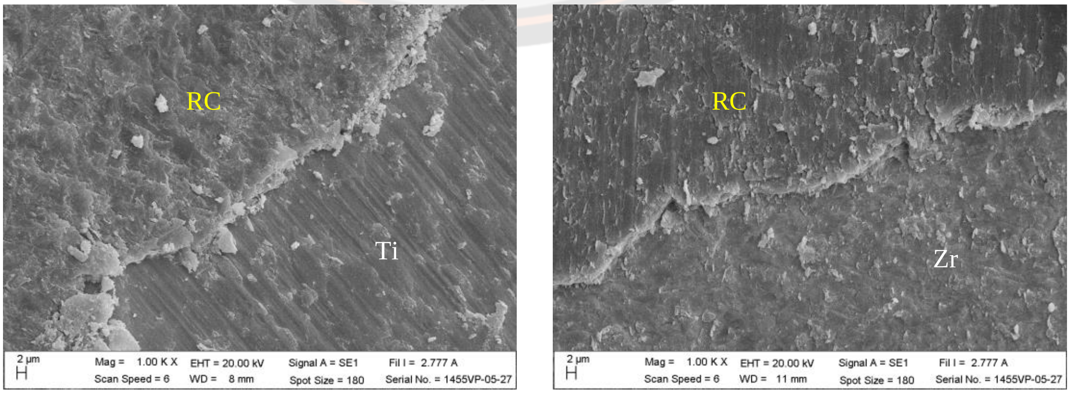

Figure 46 SEM images of the titanium and zirconia surface after the shear bond strength testing of group 4 (Magnification x1000)

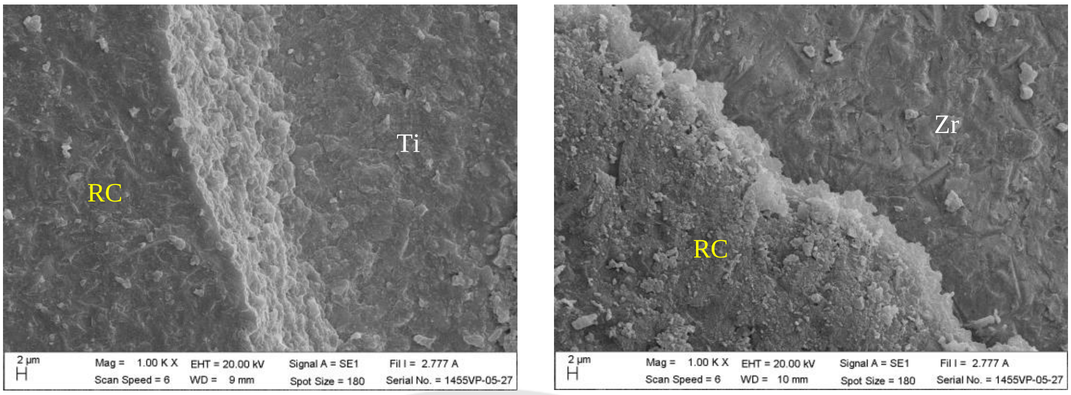

Figure 47 SEM images of the titanium and zirconia surface after the shear bond strength testing of group 5 (Magnification x1000)

Part 2

The mean ± SD bond strength values range from 32.28 ± 5.90 MPa (V-Primer group) to 51.99 ± 2.98 MPa (Monobond N group), as shown in Table 4 and Figure 48. The data were analyzed for significant differences using a one-way analysis of variance (ANOVA) with *P*<.05. Differences between groups were determined by Tukey HSD (Honestly Significant Difference) post-hoc test.

Statistical analysis revealed that the surface treatment of titanium disks with chemical treatments had a significant increase in the shear bond strength when compared to the control group (*P*<.05) except the V-Primer group. The Tukey HSD test revealed that the surface treatment with Monobond N group (51.99 ± 2.98 MPa) and Clearfil Ceramic Primer group (51.05 ± 4.43 MPa) had a statistically significant highest of the shear bond strength compared to the other group (*P*<.05). While the surface treatment with Alloy Primer group (43.89 ± 4.59 MPa) had a statistically significant higher shear bond strength than the control group (35.88 ± 2.51 MPa) (*P*<.05). On the other hand, the surface treatment with V-Primer group (32.28 ± 5.90 MPa) had the lowest shear bond strength and no significant differences compared to the control group (35.88 ± 2.51 MPa) (*P*>.05)

Table 4 Means and standard deviations of shear bond strength of part 2

Group	N	Mean	Std Dev	Std Error	Lower 95%	Upper 95%
Sandblast (S)	10	35.88	2.51	.79	34.09	37.68
S+V-Primer	10	32.28	5.90	1.86	28.07	36.50
S+Alloy Primer	10	43.89	4.59	1.45	40.60	47.17
S+Clearfil	10	51.05	4.43	1.40	47.88	54.22
S+Monobond N	10	51.99	2.98	.94	49.86	54.12

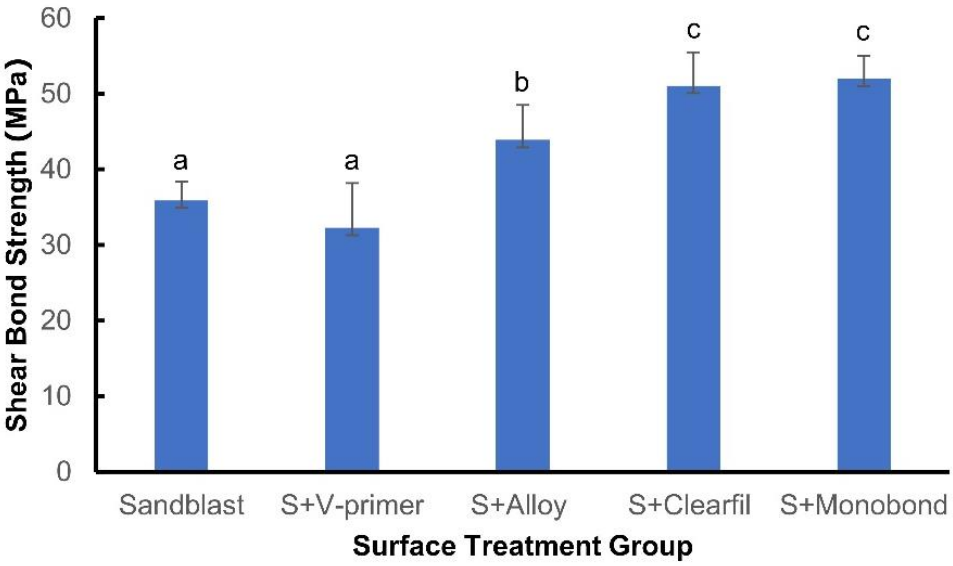

Figure 48 Means and standard deviations of shear bond strength of part 2

Note: The different superscripts indicate significant difference among groups (*P*<.05)

After the shear bond strength testing, the specimens were examine using a stereo microscope (20x) to record the failure mode, and the distribution of fracture patterns is summarized in Table 5. The analysis of fracture patterns showed that the control and the surface treatment with V-Primer groups demonstrated the adhesive fractures pattern between the titanium disks and the resin cement which no resin cement remnants were found on the titanium surfaces. However, all the resin cement layers were found on the zirconia surface (Figures 49 and 50). While the surface treatment with Alloy Primer, Clearfil Ceramic Primer, and Monobond N groups were found only the mixed fracture patterns with residual cement observed on each surface. (Figures 51-53).

Table 5 Fracture pattern distribution of part 2

Group	Adhesive fracture between titanium surface and resin cement	Mixed fracture pattern
I	3	7
II	4	6
III	-	10
IV	-	10
V	-	10

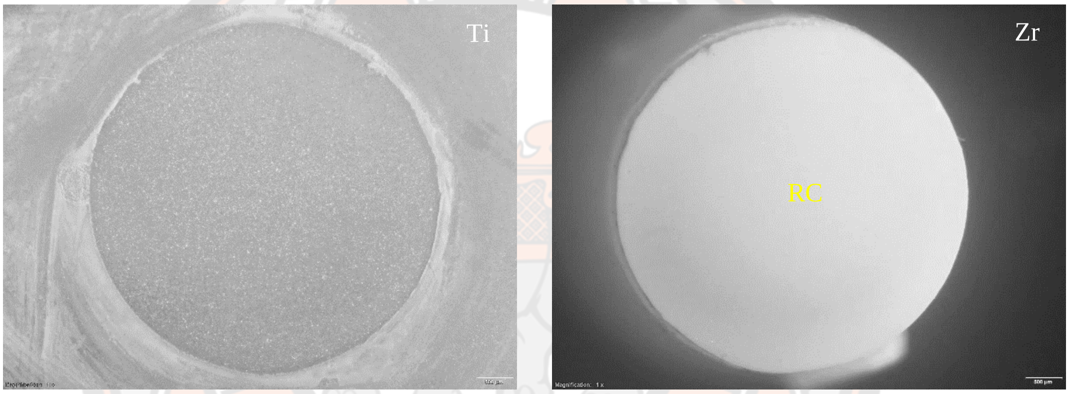

Figure 49 Adhesive fracture pattern between titanium surface (Ti) (left) and resin cement (RC) on zirconia surface (Zr) (right) of group I

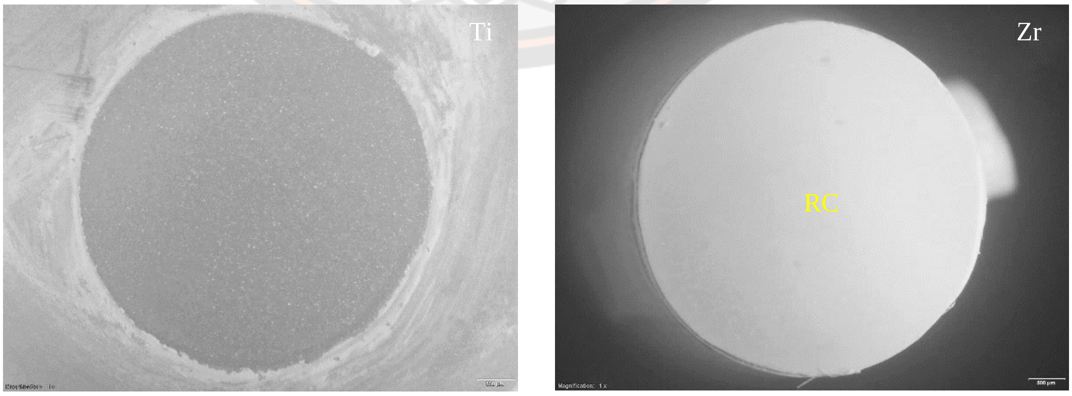

Figure 50 Adhesive fracture pattern between titanium surface (Ti) (left) and resin cement (RC) on zirconia surface (Zr) (right) of group II

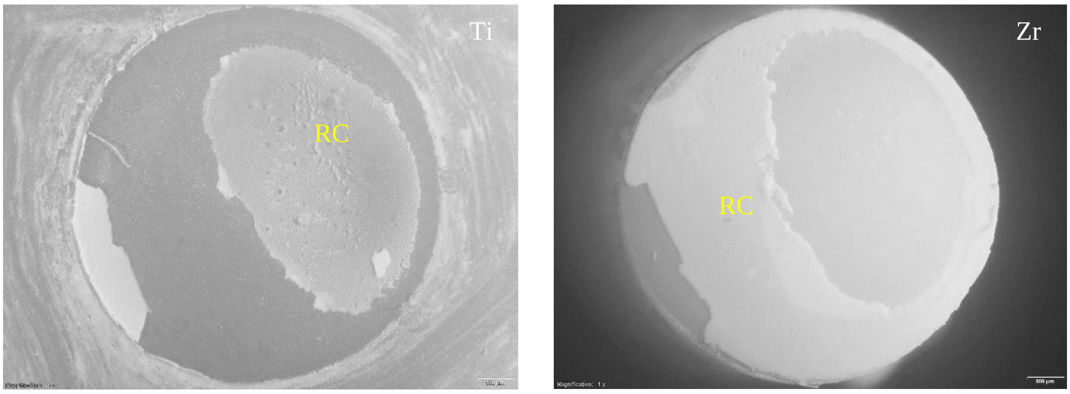

Figure 51 Mixed fracture pattern between titanium (Ti)-resin cement (RC) (left) and zirconia (Zr)-resin cement (right) interfaces of group III

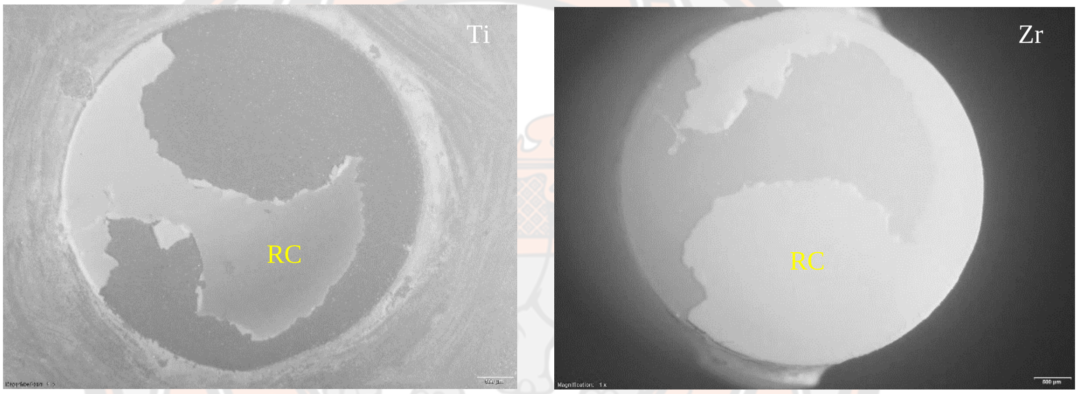

Figure 52 Mixed fracture pattern between titanium (Ti)-resin cement (RC) (left) and zirconia (Zr)-resin cement (right) interfaces of group IV

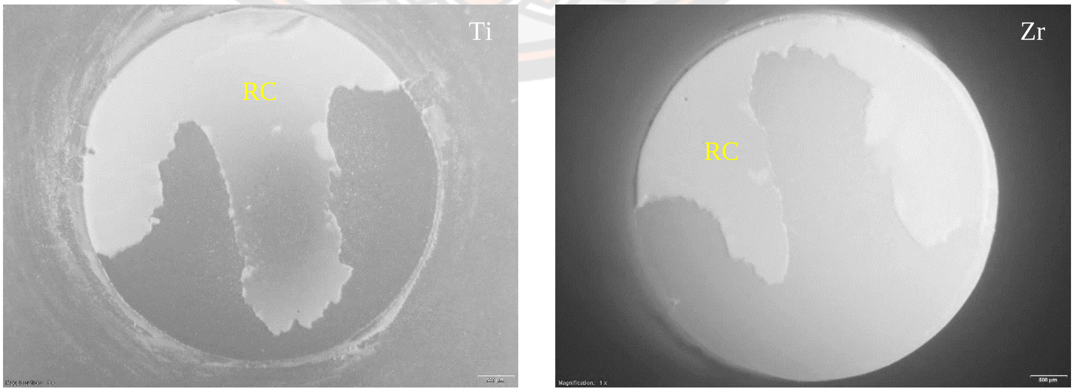

Figure 53 Mixed fracture pattern between titanium (Ti)-resin cement (RC) (left) and zirconia (Zr)-resin cement (right) interfaces of group V

The representative SEM images of the surface morphology of specimens after the shear bond strength testing are shown in Figures 54-58. High-magnification (×1,000) SEM images revealed all resin cement residues on the zirconia surface in group I and group II for the adhesive fracture pattern (Figures 54 and 55). Other groups demonstrated resin cement residues on both the titanium and zirconia surfaces in a mixed fracture pattern (Figures 56-58).

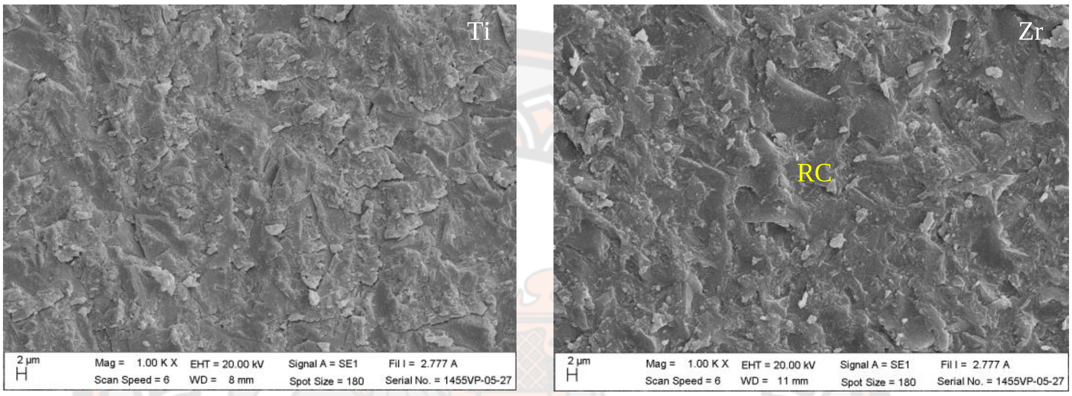

Figure 54 SEM images of the titanium and zirconia surface after the shear bond strength testing of group I (Magnification x1000)

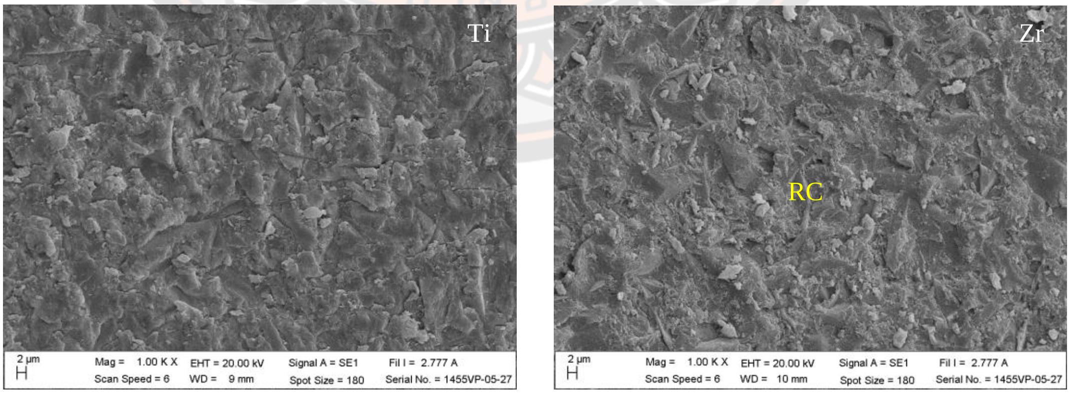

Figure 55 SEM images of the titanium and zirconia surface after the shear bond strength testing of group II (Magnification x1000)

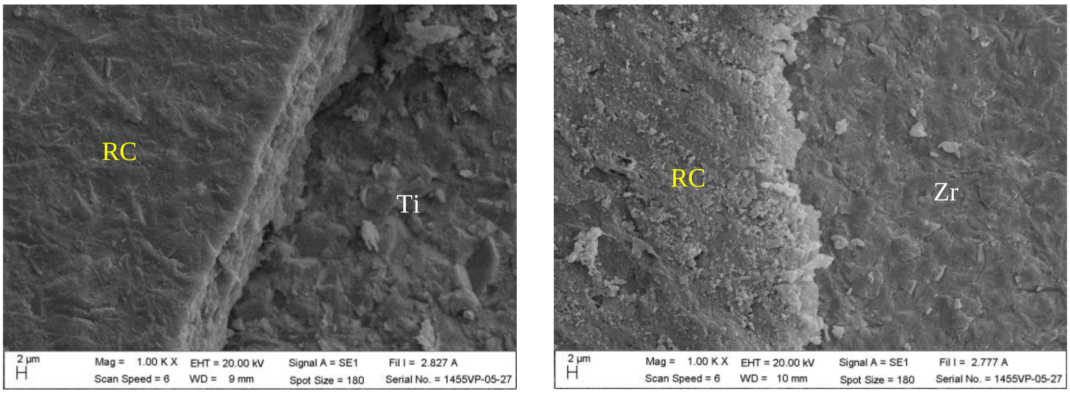

Figure 56 SEM images of the titanium and zirconia surface after the shear bond strength testing of group III (Magnification x1000)

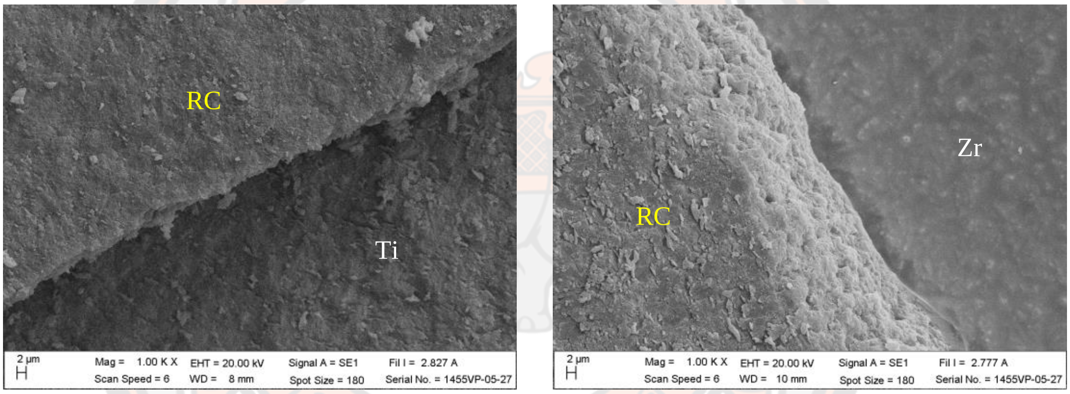

Figure 57 SEM images of the titanium and zirconia surface after the shear bond strength testing of group IV (Magnification x1000)

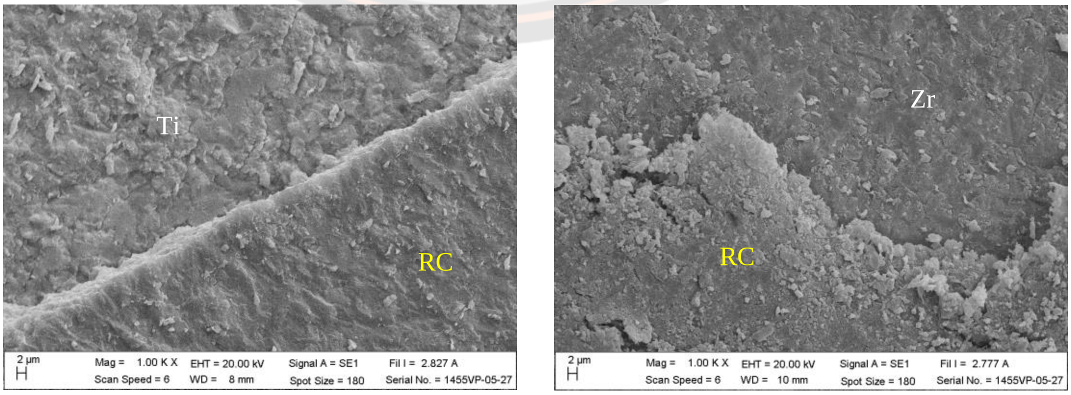

Figure 58 SEM images of the titanium and zirconia surface after the shear bond strength testing of group V (Magnification x1000)

CHAPTER V

Discussion

The use of a two-piece zirconia abutment as a prosthetic superstructure for dental implants requires an effective bond between the zirconia coping and titanium base abutment. The connection between these two materials is a key factor for long-term success of the abutment. The results of the present study reject the null hypothesis, which considers that different surface treatments of titanium surfaces do not influence the shear bond strength between the titanium and zirconia surfaces. The surface treatment methods significantly affected the shear bond strength between the titanium and zirconia surfaces ($P<.05$).

Although zirconia is an inert material that is difficult to treat the surface and no generally accepted protocol exists for zirconia to adhesion with other materials. Several methods have been proposed to enhance adhesion to zirconia. Air-abrasion with Al_20_3 particle has been suggested for roughening the adhesive surface of zirconia to improve retention of resin cement [62]. Previous studies have found that pretreatment zirconia surface by air-abrasion with Al_20_3 particle combined with the use of cement and primer containing MPD can achieve superior long-term tensile and shear bond strength between zirconia and resin cement [62, 66]. From the study of Valente et al.[82] reported that MDP-based primer has a more significant influence on improving bond strength of zirconia than resin cement with MDP components. Therefore, in the present study, sandblasting with 50 µm Al_20_3 particle at a pressure of 2.5 bar and applying Clearfil Ceramic Primer, which contains MDP components were selected for zirconia surface treatment. The resin cement is Panavia V5, even without MDP components, since it is manufactured by the same company as MDP primer and is a dual-cured resin cement that polymerizes without the light curing procedure. While the studies of surface modification on titanium for increasing the bond strength with zirconia surface was little research. Smielak et al.[78] reported that titanium without surface treatment resulting in low shear bond strength between titanium and zirconia. That result is consistent with the present study that the control group (no surface treatment on titanium) was the lowest value of the bond strengths and tended to result in all specimens were adhesive failure pattern between the titanium disks and the resin cement. The analysis of fracture pattern showed that the titanium surface seemed to be the weakest point of bonding construction. From this point, the authors focused on the method of modification of titanium surfaces to improve the bond strength.

Surface treatment of the material before adhesive bonding plays an important factor in the improvement of durability and strength of bonded joints. Previous studies have demonstrated that the shear bond strength was increased when increasing surface roughness of the adherend material because of the increase in the bonding surface area [19]. Treatment of titanium surface is considered an influential factor for increasing the bond strength at the titanium-resin cement interface [10, 22, 25]. Sandblasting is an favorable method of titanium surface modification for improving the potential of bonding to other materials [27]. Previous study reported etching titanium abutment with 9% HF for 15 sec can enhance retention of restorative materials [23]. From pilot study demonstrated surface treatment of titanium with 37% H_3PO_4 and 50% H_2O_2 for 15 min have higher bond strength values to zirconia when compared to 5 and 10 min which treatment time used in previous studies [24, 27]. Therefore, in part 1 of this study, titanium surface treatment was performed with sandblasting, etched with 9% HF 15 sec, etched with 37% H_3PO_4 15 min and treated with 50% H_2O_2 15 min to evaluate the effect of micromechanical surface treatments.

As the results of this study showed that the shear bond strength of titanium surface increased by using sandblasting, H_2O_2 and HF methods. The increasing shear bond strength of sandblasting and HF groups correlated with the increase of surface roughness, while the increasing shear bond strength of the H_2O_2 group was not related to surface roughness. The group treated with sandblasting method produced the highest roughest surface and the highest shear bond strength (36.01 ± 2.80 MPa) caused by increasing surface roughness result to enhance the bonding surface area. The cement can penetrate and occurred micromechanical interlock to the titanium surface. This is consistent with the findings of Gehrke et al.[10] that sandblasting which is a method to increase the surface roughness, improves the retention between the components of two-part abutments due to micromechanical interlock with resin cement, resulting in improved adhesion between titanium and zirconia. However, excessive pressure or prolong time of sandblasting resulted in the drastic change of the titanium surface [20].

Followed by a group that modification the titanium surface with HF, which has the second highest surface roughness and is associated with the third high of shear bond strength (21.27 ± 2.76 MPa), which is significantly different from the control group that does not treat the titanium surface. During the HF etching process, the etchant was agitated to improve the contact area of the chemical reaction and gas bubbles were formed [22]. The original brightness of the polished titanium disks changed into an opaque grey color could be related to micro level changes of the surface topography. Indeed, the topographical parameters showed a significant enhancement of the surface roughness. This finding was in accordance with a previous study, which reported that the HF etching effect will have micromechanical retention on the titanium surface, which improve the bond strength between titanium and restorative materials [23]. However, Smielak et al. [83] concluded that should not combination of airborne particle abrasion and HF etching titanium surface because it may cause over-etching or partial removal of the surface roughness. This results in the weakening of the surface structure bond.

In the group that modified the titanium surface with H_3PO_4 has low surface roughness and low shear bond strength (5.29 ± 2.50 MPa), which is not significantly different from the control group (3.64 ± 2.11 MPa). Similar to study of Tsuchimoto et al. [24] reported that when pretreating titanium with H_3PO_4, phosphoric acid was also strongly adsorbed on the titanium surface. As a result, phosphoric acid potentially inhibits the subsequent adsorption of the phosphoric groups of 10-MDP onto titanium. Therefore, the results in this study indicate that titanium surface should better not be pretreated with phosphoric acid, which would else significantly decrease the bond strength of the resin cement to titanium restoration.

On the other hand, the titanium surface was modified by immersion in H_2O_2 (33.57 ± 2.74 MPa) had a high shear bond strength and not significantly different from the sandblasting group**,** but the H_2O_2 group has a lower surface roughness compared with the sandblast and the HF groups. The results of this study showed that the improvement of shear bond strength for titanium treated with H_2O_2 not related to surface roughness value and micromechanical bonding. This might be due to H_2O_2 treatments resulted in increased oxide layer thickening, owing to increased titanium oxidation, and additionally supported by the coloration changes in H_2O_2 treated discs. The titanium surface leaned to be browner yellowish, implying that the surface oxide film was thickened. In agreement with the previous report that when titanium was immersed in H_2O_2, the titanium surface was oxidized to improved resin bond strengths [25]. The oxidation mechanism was supposed to be due to the Fenton reaction, by which the hydroxyl radicals were formed [26, 57]. It may be assumed that surface treatment by H_2O_2 solution altered the natural composition of the titanium surfaces, resulting in improve the bond strength of resin cement to titanium through a chemical adhesion mechanism. However, Yoshida et al. [25] reported that prolonged time of H_2O_2 treatment of titanium results in decreased bond strength due to the excessive thickness of the surface oxide film. Therefore, immersion titanium in H_2O_2 solution is an interesting method, but more studies still need to explain the mechanism of H_2O_2 improving the bond strength.

The analysis of fracture patterns and identifying the failure mode plays a significant part in determining the weak point of bond failure [84]. This study showed that the mode of failure in HF, H_2O_2, and sandblast groups were mainly mixed fracture with residual cement observed on both the titanium and zirconia surfaces, indicating adequate bonding on each surface. Similar to the study of Maltzahn et al. [21], who found mixed fracture between titanium and zirconia which surface treatment by sandblasting method. However, the control group (without treatment) and H_3PO_4 group showed the lowest shear bond strength values with adhesive fractures, demonstrating the presence of cement remnants at the zirconia surface. The fracture patterns analysis indicated that the bond strength between the titanium surface and the resin cement seems to be the weaker point. This is likely due to the titanium surface has not been modified or phosphoric acid is not suitable for titanium surface treatment. Additionally, the MDP primer was used only on the zirconia surface. This makes resin cement better adhere to zirconia than titanium. Previous study reported more cement remnants were found on the zirconia abutment when the MDP primer was applied to the zirconia [21].

From the result of this study, the use of 50% H_2O_2 for 15 min yielded high shear bond strength nearby to sandblasting method. The clinical implications are that using 50% H_2O_2 for 15 min is less required special equipment, more controllable, and easier method than sandblasting. If the results are not significantly different in clinical situations, this technique may be a useful alternative method for the clinician.

However, the highest shear bond strength value of part 1 was received from sandblasting method on titanium surface. The mechanical surface treatment with sandblasting is a popular method for titanium surface modification to increases the surface roughness and improves the retention between the components of two-part abutments [30]. Apart from mechanical surface treatments, chemical surface treatments also contain modifying titanium. According to the manufacturer, there are many types of activating primers for increasing the bond strength to the metal such as V-Primer [28], Alloy Primer [29], Clearfil Ceramic Primer [30], and Monobond N [31]. But it is still unclear which activating primers would be suitable for titanium surface treating.

From the present study, sandblasting combined with chemical surface treatments had a significant influence on shear bond strength between titanium and zirconia surfaces compared to only mechanical method with sandblasting. The highest values of shear bond strengths were found in the surface treatment with Monobond N group (51.99 ± 2.98 MPa) and Clearfil Ceramic Primer group (51.05 ± 4.43 MPa).

Monobond N is a universal primer for the pretreatment of all types of restoration surfaces such as fiber-reinforced composite, oxide ceramics and metal. The primer achieves a strong and long-lived bond to any dental restorative material because it consists of a combination of the three different functional methacrylates including silane methacrylate, phosphoric acid methacrylate and sulfide methacrylate [71]. Clearfil Ceramic Primer is a single-component adhesive primer used to enhance the bond strength between resin-based materials and ceramic materials. This primer contains the 3-methacryloxypropyl trimethoxy silane, 10-MDP and ethanol. It is indicated for the surface treatments of lithium disilicate ceramics, zirconia ceramics, hybrid ceramics, composite resins and metal surfaces [31]. According to the manufacturer, Monobond N and Clearfil Ceramic Primer improve the bond strength of metal surfaces. Both of these primers have a silane composition. Silane is probably the one that makes titanium adhesion well to resin cement. Previous studies showed that silane establishes a chemical bond between the resin cement and the metal surface due to their bifunctional characteristics [85]. The non-hydrolyzable organic group contains carbon-carbon double bond which can polymerize with monomers of resin cement. The hydrolyzable groups react with an inorganic hydroxyl-rich (-OH) surface such as oxide layer of titanium surface. Silane promotes hydrogen and covalent bonds on titanium surfaces and increases the wettability of resin cement, which infiltrates more easily in the rough surface of titanium produced by sandblasting. Moreover, the bifunctional monomers chemically bond to the alumina layer remaining on the titanium surface after sandblasting, it provides hydrolytically =Al-O-Si≡ bonds [70]. Therefore, the application of silane after sandblasting maybe improve the bond strength between titanium and resin cement. However, more studies on chemical bonds by Fourier-transform infrared spectroscopy (FTIR) may be needed to confirm that silane is a component that makes titanium adhere to resin cement well.

The Alloy Primer group (43.89 ± 4.59 MPa) had higher shear bond strength than the sandblast group (35.88 ± 2.51 MPa) and the V-Primer group (32.28 ± 5.90 MPa). Alloy Primer is a metal primer used to increase the bond strength between dental metal and resin base materials. It consists of acetone, 10-MDP and VBATDT. Alloy Primer is a pretreatment agent for conditioning metal and is used to secure the adhesive capability of resins and acrylic ester to gold, titanium and other dental alloys [30]. V-Primer is an acetone solution with adhesive monomer VBATDT that contains thiol group. Thiol group of VBATDT has sulfur to react chemically with the oxides on the metal surface. It used to enhance the bond durability to noble metals [70]. The Alloy Primer and V-Primer containing VBATDT composition, which is the mercapto group chemically bonds to noble metal [86]. Titanium is considered a base metal, and the surface is covered with a passive layer of metallic oxides with the hydrophilic group in the atmospheric environment [87]. Several studies have shown that functional monomer VBATDT have affinity to noble metals but not base metal [87, 88]. In the present study, the V-Primer group containing only VBATDT exhibited the lowest shear bond strength value. However, the Alloy Primer group containing not only VBATDT but also MDP exhibited higher shear bond strength. These results agree with Kunt et al. [29] indicated that sandblasting plus Alloy Primer increased bond strength between the titanium abutment and crown. This is most likely due to the content of MDP in Alloy Primer, which provides an effective bond between resin cement and titanium. This bond occurs through a chemical reaction between the phosphate ester group of MDP and the hydroxyl group in the metal oxide layer of the titanium surface.

The analysis of fracture patterns showed that the failure modes in the groups which surface treatment with Alloy Primer, Clearfil Ceramic Primer and Monobond N were only mixed fractures with residual cement on both the titanium and zirconia surfaces. The cement remnants tended to attach to the titanium surface more than the zirconia surface, indicating that good effective titanium surface treatment occurred due to resin cement could more adhesion to the titanium surface. However, the sandblast group and the V-Primer group showed the lowest shear bond strength values with still have adhesive fractures, which demonstrate the presence of cement remnants at the zirconia surface. The analysis of fracture patterns indicated that the bond strength between the titanium surface and the resin cement seems to be the weaker point.

The results of the present study showed that shear bond strength between titanium and zirconia surfaces could be significantly improved by the combination of mechanical and chemical surface treatment. Monobond N and Clearfil Ceramic Primer have been suggested for bonding to titanium.

However, this study still has some limitations include the geometry of the tested specimen used to measure shear bond strength was different from the clinical used abutment. Due to the specimen geometry was selected to be appropriate to the study methodology, which allowed the specimens to be mounted in the universal test machine. Further study should be tested in the clinical abutment to represent realistic geometry of dental abutment and clinical application protocol should be confirmed in clinical study.

CHAPTER VI

Conclusions

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

1. The procedure of surface treatment both mechanical and chemical on the titanium surfaces before bonding had a significant influence on the shear bond strength between the titanium and zirconia surfaces.

2. For the mechanical surface treatment, the group of titanium surface treatment with sandblasting and the group of treated with H_2O_2 had a statistically significant higher of the shear bond strength than the other groups.

3. When combined surface treatment by both of mechanical and chemical methods, the shear bond strength between the titanium and zirconia surfaces were significantly increased when compared with treated surface only mechanical method.

4. From the result of this study, the combination of mechanical surface treated by sandblasting and chemical surface treated by applying Monobond N or Clearfil Ceramic Primer were the most effective titanium surface treatment method to improved bonding between titanium and zirconia, that may be recommended for clinical guideline of bonding between the zirconia coping and titanium base abutment.

5. Although sandblasting was widely accepted as the most effective method for titanium surface treatment, but from the result of this study, titanium surface treatment with H_2O_2 might be the promising alternative technique as more simple method with a high shear bond strength value.

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Appendix

Table 6 Shear bond strength values of Group 1

Test specimen	**Shear bond strength (MPa)**
1	4.01
2	0.93
3	5.40
4	6.83
5	4.47
6	6.19
7	3.49
8	1.13
9	1.62
10	2.32
Mean	3.64 MPa

Table 7 Shear bond strength values of Group 2

Test specimen	**Shear bond strength (MPa)**
1	2.00
2	3.70
3	8.10
4	8.69
5	8.30
6	6.11
7	1.81
8	5.06
9	4.04
10	5.08
Mean	5.29 MPa

Table 8 Shear bond strength values of Group 3

Test specimen	**Shear bond strength (MPa)**
1	17.96
2	20.50
3	20.47
4	20.45
5	21.73
6	21.70
7	24.27
8	27.12
9	20.57
10	17.90
Mean	21.27 MPa

Table 9 Shear bond strength values of Group 4

Test specimen	**Shear bond strength (MPa)**
1	31.73
2	30.68
3	36.95
4	37.00
5	30.72
6	33.52
7	32.42
8	34.70
9	37.27
10	30.69
Mean	33.57 MPa

Table 10 Shear bond strength values of Group 5

Test specimen	Shear bond strength (MPa)
1	33.44
2	38.19
3	32.69
4	31.94
5	35.75
6	37.11
7	34.49
8	37.21
9	39.66
10	39.62
Mean	36.01 MPa

Table 11 ANOVA Sum of Squares of part 1

Source	Sum of Squares	DF	Mean Square	F Ratio	Sig.
Between Groups	9260.81	4	2315.20	343.94	.000*
Within Groups	302.91	45	6.73		
Total	9563.73	49			

Table 12 Tukey’s Post Hoc Test of part 1

Level - Level	Mean Dif	Std Err	Low CL	Up CL	Sig.
Control - H_3PO_4	1.64	1.16	4.94	1.65	.618
Control - HF	17.63	1.16	20.92	14.33	.000*
Control - H_2O_2	29.93	1.16	33.22	26.63	.000*
Control - Sandblast	32.37	1.16	35.67	29.07	.000*
H_3PO_4 - HF	15.98	1.16	19.27	12.68	.000*
H_3PO_4 - H_2O_2	28.28	1.16	31.58	24.98	.000*
H_3PO_4 - Sandblast	30.72	1.16	34.02	27.42	.000*
HF - H_2O_2	12.30	1.16	15.60	9.00	.000*
HF - Sandblast	14.74	1.16	18.04	11.45	.000*
H_2O_2 - Sandblast	2.44	1.16	5.74	.85	.236

Note: *The mean difference is significant at the 0.05 level.

Table 13 Means for groups in homogeneous subsets of part 1

Method	**N**	**1**	**2**	**3**
Control	10	3.64		
H_3PO_4	10	5.29		
HF	10		21.27	
H_2O_2	10			33.57
Sandblast	10			36.01
Sig.		.618	1.000	.236

Note: Subset for alpha = 0.05

Table 14 Shear bond strength values of Group I

Test specimen	**Shear bond strength (MPa)**
1	32.44
2	32.69
3	33.44
4	34.49
5	35.75
6	37.11
7	37.21
8	37.91
9	38.19
10	39.62
Mean	35.88 MPa

Table 15 Shear bond strength values of Group II

Test specimen	**Shear bond strength (MPa)**
1	24.12
2	25.18
3	25.81
4	27.90
5	33.75
6	34.95
7	36.91
8	37.25
9	37.42
10	39.55
Mean	32.28 MPa

Table 16 Shear bond strength values of Group III

Test specimen	**Shear bond strength (MPa)**
1	37.45
2	38.98
3	39.01
4	42.30
5	43.60
6	43.83
7	45.91
8	47.15
9	49.88
10	50.77
Mean	43.89 MPa

Table 17 Shear bond strength values of Group IV

Test specimen	**Shear bond strength (MPa)**
1	45.48
2	47.27
3	48.30
4	48.31
5	49.64
6	51.06
7	51.14
8	52.34
9	57.57
10	59.42
Mean	51.05 MPa

Table 18 Shear bond strength values of Group V

Test specimen	**Shear bond strength (MPa)**
1	48.49
2	48.50
3	48.64
4	50.16
5	51.52
6	53.05
7	53.54
8	53.87
9	55.94
10	56.22
Mean	51.99 MPa

Table 19 ANOVA Sum of Squares of part 2

Source	Sum of Squares	DF	Mean Square	F Ratio	Sig.
Between Groups	3119.67	4	779.92	43.03	.000*
Within Groups	815.70	45	18.13		
Total	3935.37	49			

Table 20 Tukey’s Post Hoc Test of part 2

Level - Level	Mean Dif	Std Err	Lo CL	Up CL	Sig.
S – S+V Primer	3.60	1.90	1.81	9.01	.337
S - S+Alloy Primer	8.00	1.90	13.41	2.59	.001*
S - S+Clearfil	15.17	1.90	20.58	9.76	.000*
S - S+Monobond N	16.11	1.90	21.52	10.70	.000*
S+V Primer - S+Alloy Primer	11.60	1.90	17.01	6.19	.000*
S+V Primer - S+Clearfil	18.77	1.90	24.18	13.36	.000*
S+V Primer - S+Monobond N	19.71	1.90	25.12	14.30	.000*
S+Alloy Primer - S+Clearfil	7.17	1.90	12.58	1.75	.004*
S+Alloy Primer - S+Monobond N	8.11	1.90	13.52	2.69	.001*
S+Clearfil - S+Monobond N	0.94	1.90	6.35	4.47	.988

Note: *The mean difference is significant at the 0.05 level.

Table 21 Means for groups in homogeneous subsets of part 2

Method	N	1	2	3
S+V-Primer	10	32.28		
Sandblast (S)	10	35.88		
S+Alloy Primer	10		43.89	
S+Clearfil Ceramic Primer	10			51.05
S+Monobond N	10			51.99
Sig.		.337	1.000	.988

Note: Subset for alpha = 0.05