INFLUENCE OF PHOSPHORIC ACID SURFACE TREATMENT ON SHEAR BOND STRENGTH DURABILITY OF RESIN CEMENT TO ZIRCONIA-BASED CERAMIC CONDITIONED WITH DIFFERENT PRIMERS

by

Eman Zuhair Alshehri

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Marco C. Bottino

Michael A. Cochran

Melvin R. Lund

Jeffrey A. Platt
Chair of the Research
Committee

Tien-Min Gabriel Chu
Program Director

Date____________________

DEDICATION

I dedicate this thesis to my loving Father and Mother; my Husband;
my sweet Daughters, Rital and Lana; my Sisters; my Brother, and my wonderful Friends.
Thank you for your encouragement, prayers, and
unconditional love.

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INTRODUCTION

After the discovery of various properties of zirconium oxide (zirconia) by Garvie et al. in 1975, there has been considerable focus on the use of zirconia in biomedical applications.[1] Zirconia (ZrO_2) is a silica-free, acid resistant, polycrystalline ceramic that possesses the ideal properties for dental use.[2] The yttrium oxide-stabilized tetragonal zirconia polycrystal (Y-TZP) is used in dentistry and it shows an outstanding mechanical, biocompatible, and aesthetic performance.[3, 4] Superior properties have made zirconium oxide ceramics a popular high strength ceramic with a large variety of clinical applications.[5, 6] However, its chemical inertness stood as an obstacle to establish a strong and a durable bond with other materials.[7, 8] The composition and physical properties of zirconia ceramics differ substantially from silica-based ceramics, and require alternative bonding techniques to achieve a strong and durable resin bond.[9]

The clinical success of resin bonding procedures for indirect ceramic restorations and ceramic repairs depends on the quality and durability of the bond between the ceramic and the resin cements. The quality of this bond depends on a variety of factors such as the bonding mechanisms that are controlled by the surface treatment, which promotes micromechanical and chemical bonding to ceramics.[10] Recent studies regarding bonding to zirconia ceramics have recommended different approaches of adhesion to improve this bond. Furthermore, contamination of bonded surfaces, and different cleaning methods can influence the long-term durability of resin cement to zirconia. [11]

Mechanical retention of adhesives to zirconia ceramics can be achieved by various methods such as sandblasting, tribochemical silica coating, laser or some other chemical approaches before using bonding agents. The chemical bonding agents were used in order to increase the bond strength between resin composite cement and zirconia by promoting a better interaction with the ceramic surface and improving the wettability.[12-15]

Several bonding agents and primers have previously been investigated and only those containing an organophosphate ester monomer have been proven to be effective in activation of zirconia surfaces. Acidic adhesive monomers, such as MDP, 6-MHPA, or MTU-6, have phosphate ester groups and show chemical bonding to zirconia-based ceramics. [16] The MDP monomer has a vinyl group which reacts with monomers in resin cements when the resin is polymerized, while the phosphate group of the MDP bonds strongly to zirconium oxide. [17]

Ceramic primers may be based on silane and/or an acidic adhesive monomer. Silane monomers alone do not promote chemical bonding to zirconia-based ceramics. These agents have been described in the literature as being able to increase the wettability of ceramic surfaces, thus improving the adhesion to luting resins, and to bond with hydroxyl groups of polar ceramic surfaces.[16-18] However, zirconia itself has an insufficient number of surface hydroxyl groups for chemical bonding.[8] As a consequence, a variety of surface activation procedures have been proposed in the literature to improve the wetting properties and adhesion of resin cement to zirconia.[19-22]

Various studies have shown that air abrasion, which is one of the most common methods of conditioning ceramics surface, and using the phosphate monomer (MDP)-containing luting agents, can help in the formation of high and durable bond strengths.[23-25] However, it is important to note that air abrasion might affect the ceramic surfaces through the creation of microcracks, which in turn reduce the fracture strength of the ceramic.[26] On the other hand, some authors argue that resin luting agents provide a strong and durable bond through repairing minor surface defects that are caused by air abrasion.[27,28]

Moreover, it is evident that the adhesive bonding to some extent depends on the surface energy as well as the wettability of the ceramics by the adhesive. The adhesion that occurs between the dental ceramics and resin-based cements is a result of the physicochemical interaction that happens at the interface between the adhesive and the substrate. In relation to this, the physical contribution of the adhesion process also depends on the surface topography of the substrate and can be characterized by its surface energy. Various changes in the surface topography in most cases result in changes in the surface area, wettability and the surface energy of the substrate. Therefore, the wetting behavior of resin cements on the treated ceramic substrate can be characterized using the contact angle data as well as the surface energy. This wetting is also known to favor the adhesion process and at the same time improve the chemical interaction between resin cement and the zirconia surface.[29,30]

A strong resin-ceramic bond might be compromised in the clinical situation due to contamination of restorative luting surfaces by saliva, blood or other contaminants. Using phosphoric acid as a chemical cleaning method seems to be effective to remove saliva and other organic contaminants.[31] However, phosphoric acid was not able to regain the bond strength of uncontaminated surfaces and the bond strength was significantly decreased after thermocycling.[32] Researchers assumed that results might be due to residual phosphate on the zirconia surface[31] and its effect on the surface free energy of the ceramic surface.[32] Phark et.al showed that the phosphoric acid might have changed the surface energy of the ceramic surface and therefore reduced the bonding strength although the organic contamination was removed.[11]

Recently, manufacturers have developed several surface primers to enhance bonding of zirconia to resin cement, and this makes it difficult for clinicians to choose the appropriate system after phosphoric acid treatment. There is no research has been published evaluating the interaction between phosphoric acid treatment and different primers. Therefore, the effect of phosphoric acid treatment on the conditioned zirconia ceramic surface and how it might affect the long-term durability of the resin cement bonding to pretreated zirconia with different primers has to be further investigated.

We have selected commercial resin-composite cement: Variolink II to use in this study. Variolink II is adhesive resin cement that does not contain the phosphate ester monomer. This will rule out its effect on the bond strength, and it is better to test the effect of different surface treatments and different primers without any additional effect from the cement.

We evaluated the effect of phosphoric acid on zirconia surface roughness and compared the effect of different interactions of different primers on shear bond strength of resin cement to zirconia. The shear bond strength values were compared to air-abraded and untreated zirconia surfaces. A failure mode analysis was also examined after the test.

The objectives of this study were: 1) To compare the shear bond strengths of resin cement to Y-TZP after phosphoric acid pretreatment and different chemical conditioning protocols; 2) To compare SBS between immediate and long-term storage and thermal cycling conditions; 3) To investigate the effect of phosphoric acid on the surface roughness of a yttrium-stabilized tetragonal zirconia polycrystal ceramic (Y-TZP).

Hypotheses

The null hypotheses of this study were: 1) Treating the zirconia surface with 35% H_3PO_4 does not affect the shear bond strength of resin cements to conditioned zirconia. 2) There are no differences between SBS after the application of different ceramic primers on pretreated zirconia surfaces. 3) Artificial aging does not affect resin bond strengths. 4) H_3PO_4 surface pretreatment does not affect the surface roughness of the zirconia.

The alternative hypotheses were: 1) Treating the zirconia surface with 35% H_3PO_4 decreases the shear bond strength of resin cements to conditioned zirconia. 2) The application of different ceramic primers on pretreated zirconia surfaces results in different shear bond strength of resin cements. 3) Artificial aging decreases resin bond strengths. 4) H_3PO_4 surface pretreatment increases the surface roughness of the zirconia.

REVIEW OF LITERATURE

BONDING TO Y-TZP CERAMICS

The frequent use of all-ceramic restorations is mainly a result of the high demand for metal-free, esthetic restorations and the emergence of high fracture resistance ceramics. Yttria partially stabilized tetragonal polycrystalline zirconia (Y-TZP) ceramics are commonly used in dentistry. One of the most important features of this material is the transformation toughening where the partially stabilized zirconium oxide can actively resist crack propagation through a transformation from a tetragonal to a monoclinic phase at the tip of a crack, which is in turn accompanied by a volume increase up to 5%.[9]

The conventional methods that are in most cases applied in the bonding to silica-based ceramics are not successful for bonding to zirconia ceramics. Therefore, various in vitro studies have tried to investigate the bonding ability of the adhesive systems to zirconia. Initial suggestions for achieving strong and durable bonding to zirconia would be a combination of the airborne particle abrasion and MDP-containing adhesive.[10] Currently, the combination of surface treatment with airborne particle abrasion and specific adhesive monomer containing a hydrophobic phosphate monomer has provided a reliable strategy for bonding zirconia ceramics.[33]

Moreover, the successful bond strength of ceramics is influenced by numerous factors during the bonding procedures, which include properties of the ceramic (wettability, surface roughness). Other properties that influence the strength of the bond are the adhesive and luting resin viscosity as well as its composition.[10] The durability of an indirect restoration is closely related to the integrity of the cement at the margin.

While the use of zirconia ceramics in dentistry is growing, the ideal approach to provide superior bond strengths is still unknown.[33] However, it is important to note that using hydrofluoric acid etching and the common silane agents is not effective for the zirconia ceramics. Therefore, zirconia ceramics require alternative techniques in order to achieve long-term durable resin bonding.

RESIN LUTING AGENTS AND PRIMERS

Various studies indicate that the full-coverage zirconia ceramic restorations and FPDs might not require adhesive cementation since they can be cemented by conventional cement including zinc phosphate or glass ionomer cements.[33] On the other hand, resin cements are known to have some advantages compared with other classes of cement materials since they have considerably lower solubility, as well as better esthetic characteristics.[34] In addition, the adhesive bond between the resin cement and ceramic can to some extent increase the restoration's resistance during occlusal loads, provide better marginal seal and good retention. This resin bond can, therefore, be adequate in some clinical situations such as for compromised retention and short abutment teeth.[34] Two common types of resin-based cements used for cementation to zirconia are phosphate monomer-based and traditional dimethacrylate-based resin cements.[34] It has been reported that phosphate ester monomers in phosphate monomer-based resin cements bond with metal oxides of the ceramic, theoretically improving the bond durability between the resin cement and ceramic.[19]

Another way to enhance the bonding of zirconia to resin cement is the use of a bifunctional surface primer. The primers play a critical role in adhesive procedures, especially in the zirconia-based ceramics since the untreated surface of the zirconia is not active to react with the resin cement. The role of a primer is to connect the ceramic or the metal surface to the resin cement. An important component that may be present in the primer is the 10-methacryloxydecyly dihydrogen phosphate monomer (MDP). Initially, this molecule was added to resin cement in order to bond to the crystalline ceramic, which has low glass content, thereby resulting in improved adhesion. Organo-phosphate monomers are known to have polymerizable functional groups (e.g. methacrylates), which are able to polymerize with the matrix of the methacrylate-based dental resin cements, composite and adhesive.[27] Recent research has confirmed that there exists a covalent bond between the oxygen, phosphorus and zirconia (P-O-Zr).[35] The silane-based primers have the ability to form bonds both to the organic and inorganic surfaces and their uses have been shown to increase the bond strength between resin cement and the zirconia ceramics after silica deposition surface treatment.[21]

It has been established that a better bond to Y-TZP ceramic is acquired using the resin cement with phosphate ester monomers, such as the MDP monomer. Furthermore, there is evidence demonstrating that the phosphate ester group might chemically bond to metal oxides such as zirconium oxide.[35] Wolfart and other researchers have tried to establish the strength and durability of the bond with two resins cements (MDP-based and Bis-GMA-based) to a zirconia ceramic. They found that the bond was able to survive over 150 days of water storage when using the MDP-based material and when the surface was air abraded with alumina particles.[20] Similarly, other studies have established that resin cements with phosphate ester groups can increase the bond strength of air-abraded and tribochemically-coated zirconia surfaces.[9,10,23,24,34,35]

Other monomers, such as the anhydride group that is present in the 4-META monomer and the phosphoric methacrylate ester, can also form a chemical bond to the zirconia ceramics.[34] Studies indicate that the bond strength of the polymethylmethacrylate (PMMA) resin cement containing 4-META was initially high, although this bond was not strong enough to resist thermal aging.[16] The weakening of this bond is because of water absorption during the thermal cycling. However, the application of the self-adhesive cement containing phosphoric methacrylate ester has resulted in the same bond strength of MDP-based resin cements after 14 days of thermal cycling and water storage.[16]

A previous study showed that the application of an MDP-containing bonding/ silane coupling agent is the main factor for a durable resin bond to Y-TZP ceramics and is not affected by the resin luting agent used.[13] Presently in the dental market, priming agents that contain special adhesive monomers are present to develop adhesive bonding to metal alloys. In addition to MDP, these substances have other monomers, such as VBATDT (6-(4-vinylbenzyl-n-propyl) amino 1,3,5-triazine-2,4-dithione), MEPS (thiophosphoric methacrylate) and MTU-6 (6-methacryloyloxyhexy1-2-thiouracil-5-carboxylate).[16] Yoshida and others confirmed that the bond strength of resin cement to zirconia increased significantly when surfaces were covered with an MDP-based metal primer.[18] However, this bond could not withstand thermal aging. This study also showed that a combination of MDP- based metal primer with a zirconate agent (2,2-di [allyloxymethy] butyltrimethacryloylzirconate) improved the bond between resin cement and zirconia ceramic.[18] This combination might be a clinically successful way to improve bonding to zirconia ceramics and should be further investigated.

EFFECTS OF SURFACE TREATMENT ON BONDING OF ZIRCONIA

Various surface pretreatments, including alumina sandblasting, tribochemical silica coating, chemical etching, ceramic coating, and laser irradiation, have been used to provide mechanical micro-interlocking retention to zirconia. In addition to surface pretreatment, chemical conditioning using primers containing MDP or other functional monomers has resulted in better bond strengths to zirconia.[13] In the literature, the highest decrease in bonding strength occurred in the aged samples when zirconia did not receive any mechanical pretreatment.[36] Moreover, mechanical pre-treatment appeared necessary to provide long-lasting bonding to zirconia ceramics. Even with the application of an MDP-containing primer or any other primer, the bond strength of the cement to zirconia after the aging process was lower than when zirconia was also mechanically pretreated.[33] When zirconia underwent abrasion with alumina particles, adding the MDP-containing primer led to higher aging resistance.[36] In general, combined techniques to improve mechanical microretention and chemical reactiveness appeared crucial to acquire durable bonding to zirconia ceramics.

Air abrasion with aluminum oxide particles is regularly performed to remove layers of contaminants, and increase micromechanical retention between the restoration and the resin cement.[28] In the literature, both positive and negative effects of air abrasion on the mechanical properties of zirconia have been reported.[36] Studies have verified that air abrasion improves the flexural resistance of zirconia ceramics as a result of tetragonal (T) to monoclinic (M) phase transformations, creating compressive layers on the surface.[36] It seems that the depth of the surface flaws resulting from the air abrasion does not go beyond the thickness of the compressive layers, clarifying the enhanced properties of air-abraded surfaces.[37] Furthermore, in a long-term clinical study with alumina and zirconia restorations, the authors noted that fractures occurred only at untreated sites, never at air-abraded surfaces.[21]

On the other hand, some other studies have reported that air abrasion surface treatment might increase ceramic degradation over time. It was verified that the strength of air abraded Y-TZP ceramic decreases considerably when specimens are submitted to fatigue. This might reflect the presence of surface flaws, which propagate with repeated cyclic loading, and they can negatively affect the material's properties. During the luting procedure, the superficial flaws resulting from air abrasion might grow if any additional grinding or abrasion is carried out, resulting in fracture propagation.[36]

Using air abrasion at lower pressure (1-2 bars) with particles up to 50 μm in size should be performed to keep away from the reported transformation and subsurface damage produced by big particle size and high pressure.[36] In the literature, the bond strength was considerably lower when zirconia was neither mechanically nor chemically pretreated. The use of an MPD-containing primer resulted in higher predicted bond strength than when zirconia was treated with another primer or received no pretreatment.[37]

CLEANING METHODS OF CONTAMINATED ZIRCONIA

During the laboratory manufacturing procedures and clinical try-in, contamination occurs and leaves a thin layer of contaminants on the luting ceramic surface. This contamination affects the formation of a stable bond by reducing the adaptation of the cement material to the bonded surface. It has been shown that cleaning the bonding substrates and the materials is required to gain a stable long-term bonding strength.

Cleaning procedures include firing, ultrasonic cleaning, airborne particle abrasion, applying alcohol or other organic solvents, and phosphoric acid etching.[11]

Nicholls et al. evaluated the effect of ceramic surface contamination with saliva and the subsequent cleaning with phosphoric acid and alcohol. They compared two different surface cleaning methods, cleaning with acetone and with phosphoric acid, and they showed higher bond strength values with phosphoric acid cleaning than acetone. But the effects of long-term water storage and long-term thermal cycling were not measured, so there is no indication of the bonding durability.[38]

Phosphoric acid treatment as a cleaning method successfully removes organic contaminants, but leaves some residues of phosphate, which lower the shear bond strength mostly after aging.[11] Other researchers reported the same results and assumed that phosphoric acid might change the surface energy of the ceramic surface and therefore reduce the bonding properties, but that organic contaminants, as measured by x-ray photoelectron spectroscopy (XPS), were removed.[38]

SHEAR BOND TEST VS MICROTENSILE BOND TEST

Different laboratory tests have been used to evaluate bonding effectiveness to zirconia ceramics. These methods include tensile, microtensile, shear bond strength and pull out tests. Shear bond strength testing was chosen for this study because it is a commonly used method and has proven to be reliable.[36]

Literature has shown that macro-shear testing was the most commonly used method of testing only because it does not need any further specimen processing of fully sintered zirconia when the bonding procedure is completed. But the mean predicted shear bond strength was lower than that of any of the three other tests. Shear bond strength testing has shown that non-uniform interfacial stresses might result in cohesive failures in the bonding substrate, causing misinterpretation of the resultant data. In addition, stress concentrations near the loading site lower the calculated shear bond strength below the true failure stress levels.[33] Valandro et al. found a higher percentage of adhesive failures when they compared shear to micro-tensile bond strength between the resin cement and high strength ceramics. However, the authors did not observe significant differences in the bond strength results from both tests.[39]

THERMOCYCLING AND STORAGE (AGING)

Before proceeding with long-term clinical trials, laboratory testing is usually used to evaluate the performance of the bonding systems. The thermocycling test is the in vitro process by which specimens are subjected to temperature extremes that simulate oral cavity conditions. Researchers do not agree on or provide a standard method in the different thermocycling studies in the literature.[36] When little or no thermocycling was done, high bond strength can be found but it will not represent in vivo experiences.[33, 36] In the present study, 5000 thermal cycles were chosen to evaluate the durability of the resin cement bond to zirconia ceramics.

To simulate aging, a combination of long-term water storage and thermal cycling is commonly employed. Thermocycling utilizes differences in the coefficients of thermal expansion between the ceramic and resin cement material to stress the adhesive bond, while water storage evaluates the resistance of the adhesive bond to hydrolytic degradation.[24]

In the aging procedure, both storage time in water and the number of thermocycles significantly affected the bond strength values and the bond resistance to the aging. It has been shown that long-term water storage might be needed to achieve full water saturation of the specimens and finally test the bond's ability to withstand long-term hydrolytic effects. In aging groups, the weak bonding to Y-TZP resulted from water infiltration, sorption, and degradation of the bonding interface.[24, 25]

Zirconium oxide surfaces show a strong affinity to the phosphate group of phosphoric acid. In various primers, with adhesive monomers this affinity is utilized in a targeted fashion. Consequently, the zirconia surface becomes inert after the formation of zirconium phosphate and resists the effect of primer. Recently, manufacturers have developed several primers with different organophosphate monomers to enhance bonding of zirconia, and this makes it difficult for clinician to choose the appropriate primer after phosphoric acid cleaning.

Therefore, the interaction between phosphoric acid treatment and different phosphate ester containing primers, and how it might affect the durability of the bonding of resin cement to pretreated zirconia has to be further investigated.

MATERIALS AND METHODS

In this study, shear bond strength (SBS) was tested for one resin cement material (Variolink II Table III) to zirconia ceramic.

PREPARATION OF ZIRCONIA SPECIMENS

Sixty rectangular bars of zirconia (30 × 5 × 2 mm) were supplied by Shofu. Plastic clear tubes with an inner diameter of 16 mm and a height of 26 mm were filled with acrylic resin (Bosworth Fastray) to support the specimens during testing by gluing each zirconia bar on the top of the plastic tube (Fig 1,2). Before gluing, the specimens were mounted over Struers mounting blocks and serially polished with water-cooled silicon carbide abrasive discs (500-, 1200-, 2400- and 4000-grit Al_2O_3 papers; (Struers RotoPol 31/RotoForce 6 polishing units, USA) under running water to make them uniform as our baseline (Fig 4). Ten mm of each bar was assigned to one of three groups according to different surface pretreatments: no treatment (negative control), pretreated with 35% H_3PO_4, pretreated with airborne-particle abrasion (positive control) (Fig 3). The control and phosphoric acid parts of each bar were covered before starting the abrasion by using a piece of double-coated tape, the same has been done during phosphoric acid treatment. The effect of adhesive tape and cleaning it with alcohol on bonding effectiveness has been studied, and no statistical significant difference was found between the group that used the tape and untaped group (P = 0.73).

The specimens were divided into five groups (n=12) to receive different primers: No primer (control), Clearfil ceramic primer (Kuraray), Z-prime plus (Bisco), Monobond plus (Ivoclar), and AZ primer (Shofu) (Fig 7).

SURFACE PRETREATMENT

Airborne-particle abrasion was applied to one part only of each bar using 50 µm aluminum oxide (Al_2O_3) particles at an air pressure of 2.8 bar for 15 sec at a distance of 10 mm (Fig 5). The literature review shows that abrasion of zirconia ceramics (our positive control) with 50µm alumina resulted in high and durable bond strengths.[40] After abrasion, the specimens were cleaned ultrasonically in DI water for 5 minutes and air-dried for 10 seconds. Phosphoric acid (35%) was applied on the middle third of each zirconia bar for 5 min then we rinsed it with distilled water for 20 s and dried with oil-free air spray for 10 s.

SURFACE CONDITIONING AND BONDING PROCEDURE

Before placing the specimen into a bonding jig (Ultradent, South Jordan, UT, USA), each primer was applied according to manufacturer’s instructions. Four surface primers were used: Clearfil ceramic primer, Monobond plus, Z-Prime plus and AZ Primer. One group did not receive a primer and was used as a control group. After that, the resin-luting agent was built as a cylinder (three per each bar) by positioning the specimen under a mold 2.38 mm in diameter and 3.5 mm in height (Fig 8). A small amount of cement was extruded onto a mixing pad prior to inserting the plastic dispensing tip directly into the mold. The plastic dispensing tip was positioned to ensure that adequate contact was made with the zirconia bar and that cement was extruded directly into the mold as the tip was retracted. After cement placement a disposable cotton tip was used to smooth the exposed surface and remove excess cement for easy removal of the resin cylinder.

The resin luting agent was light polymerized from the top as per manufacturer's instructions by placing the tip of the light cure unit directly on the insert of the mold and using LED light curing system (DEMI LED, Kerr, Orange, CA, USA). To remove the bonded specimen, the thumbnuts (or tension spring washers) were loosened and the resin cylinder was pressed down with an instrument while lifting the upper plate of the bonding clamp (Fig 8,9). Light irradiance was monitored using Managing Accurate Light Curing (MARC, BlueLight Analytical Inc., Hailfax, NS, Canada). Light irradiance=1024mW/cm^2.

Half of the specimens were rinsed and stored in distilled water for 24 h at 37˚C before testing. The remaining specimens were tested after storage for 90 days in distilled water and thermocycling at 5000 cycles (6˚C to 48˚C with a 30-second dwell time and transfer time of 10 seconds).

SHEAR BOND STRENGTH TEST

The Ultradent testing device (Ultradent Products Inc, South Jordan, Utah) was positioned to make contact with the bonded specimen at the cement and zirconia interface with a semicircular loading surface (2.4 mm in diameter, Fig. 10). Shear test to failure was performed using a screw-driven universal testing machine (Sintech ReNew 1123, MTS, Shakopee, MN) at a crosshead speed of 1 mm/min. Loads were converted to megapascals by dividing the failure load (N) by the bonding area (mm^2).

The control and phosphoric acid parts of each bar were covered before starting the abrasion by using a piece of double-coated tape; the same has been done during phosphoric acid treatment. The effect of adhesive tape and cleaning it with alcohol on bonding effectiveness has been studied. Twenty Y-TZP zirconia (Diazir®, Ivoclar-Vivadent) mounted specimens (10×10×2 mm) were polished with SiC papers and randomly assigned to two groups (n = 10). One group covered with double-coated tape for 10 min then the tape was removed, and the specimens were wiped with 70% isopropanol alcohol using cotton tip applicators. The other group did not receive anything after polishing procedure. After that, the specimens were cleaned ultrasonically in DI water for 5 minutes and air-dried for 10 seconds. Rely X Unicem resin cement (3M-ESPE) buttons were built (2.38 mm in diameter × 2 mm in thickness) over the specimens and polymerized according to the manufacturer's instructions. Samples were subjected to shear bond strength (SBS) testing after 24h of water storage at 37°C. No statistical significant difference was found between the group that used the tape and untaped group (p = 0.73).

The specimens were divided into five groups (n = 12) to receive different primers: No primer (control), Clearfil ceramic primer (Kuraray), Z-prime plus (Bisco), Monobond plus (Ivoclar), and AZ primer (Shofu) (Fig 7).

SURFACE ROUGHNESS MEASUREMENT

To assess the effect of treatment on surface roughness, three specimens from each pretreatment group (no treatment, phosphoric acid and abrasion groups) were scanned by a non-contact 3D optical profilometer (Proscan 2000, Scantron, Taunton England) using the S5/03 chromatic sensor (Fig.12). Three areas were scanned, each measuring 0.5 × 0.5

mm (step size of 0.1 × 0.1) on different places of each specimen to determine the surface roughness. The scans were done at 100 Hz frequency, with full sensor speed (100%).

FAILURE AND STEREOMICROSCOPIC ANALYSIS

To assess the mode of failure at the ceramic or the resin cement surface, the specimens' surfaces were examined with a light microscope (Nikon Measurescope UM-2, Tokyo, Japan) at original magnification X40 (Fig.13). The failure modes were classified as adhesive failure within the primer layer, cohesive failure in zirconia or cement, or mixed failure (adhesive and cohesive). Two specimens of each group were randomly selected for scanning electron microscopic analysis. Specimens were sputter coated with gold in a vacuum cold sputter (Desk II Cold Sputter, Denton Vacuum LLC, Moorestown, NJ, USA, Fig.14), and evaluated by scanning electronic microscopy under 35x, 2000x and 5000x magnification (SEM, Model 515, Philips Eindhoven, The Netherlands) to confirm the mode of failure that was seen under light microscopy (Fig.15).

STATISTICAL ANALYSIS

Shear bond strength results (mean, standard deviation, standard error, range) and failure mode (adhesive, mixed, cohesive percentages) were summarized for each pretreatment-primer-storage time combination. The effects of surface pretreatment, primer, and storage time on shear bond strength were evaluated using mixed-model ANOVA, which had included fixed effects for the three factors and all interactions and a random effect to allow correlations among the three surface pretreatments on each bar. Pair-wise comparisons between groups were made using Fisher's Protected Least

Significant Differences to control the overall significance level at 5%. Failure mode was compared among the groups using Mantel-Haenszel chi-square tests for ordered categorical responses.

ANOVA with a random effect was used to test the effect of pretreatment on surface roughness. The sample size calculations were based on a within-group standard deviation of 8.5 based on the pilot data. We conservatively assumed no correlation among the three surface pretreatments on each bar. With a sample size of 6 bars per primer for each storage time with all three surface pretreatments included on each bar (60 total zirconia bars), the study had 80% power to detect a shear bond strength difference of 10.2 MPa between any two surface pretreatment-primer combinations, assuming two-sided tests conducted at a 5% significance level and assuming the interaction with storage time was not significant.

RESULTS

SHEAR BOND STRENGTH (SBS)

Mean values of shear bond strength (SBS) and standard deviations in MPa are shown in Tables V and VI for the 24-hour and aged groups, respectively. Tables V and VI also show the number of specimens per group that debonded prior to testing.

Surface treatment (F = 62.67; $P < 0.0001$), Primer (F = 15.23; $P < 0.0001$) and time (F = 54.99; $P < 0.0001$) significantly affected the mean SBS values. Interactions between the factors were also significant except for treatment and time interaction.

THE EFFECT OF PHOSPHORIC ACID SURFACE TREATMENT ON SBS OF RESIN CEMENT TO CONDITIONED ZIRCONIA

After phosphoric acid treatment and 24 hours storage, shear bond strength of this group listed in decreasing order were: PMon > PClr > PZp > PAZp > P. There were no statistically significant differences among PZp, PAZp, and P, which had significantly lower shear bond strengths than PMon, PClr; PMon had significantly higher bond strength than PClr ($p = 0.0007$). PAZp and P groups showed no difference ($p = 0.7091$) in shear bond strength; PAZp also showed no difference to PZp ($p = 0.191$); PZp showed no difference to P group ($p = 0.094$).

After 90 days storage and thermocycling, the phosphoric acid groups listed in decreasing order of shear bond strength were: PMon > PZp > PClr > PAZp > P. All phosphoric acid treated groups after 90 days storage and thermocycling showed no statistically significant differences from each other. PMon showed no difference from PClr ($p = 0.8142$) or PAZp ($p = 0.5786$); and PZp showed no difference from PAZp (p =

0.5995).

For PMon and PClr primer groups, there were significant differences between the 24 hours and 90 days groups ($p < 0.05$), indicating that there was a statistically significant effect of water storage time and thermocycling on the shear bond strength of those materials. The SBS of PMon ($p < 0.0001$) and PClr ($p = 0.017$) groups decreased significantly after storage and thermocycling. The PAZp ($p = 0.478$), PZp ($p = 0.1363$), and P ($p = 0.736$) groups showed no statistically significant effect from the extended water storage time and thermocycling on shear bond strength.

COMPARISION OF SBS OF PHOSPHORIC ACID SURFACE TREATMENT GROUPS TO AIR-ABRASION TREATMENT GROUPS

SBS of all air-abrasion groups were higher than that of phosphoric acid groups after 24 hours. However, in groups using Monobond primer, there was no statistically significant difference in the mean SBS between abrasion and phosphoric acid after 24 hours storage in DI water ($p = 0.138$).

After 90 days storage and thermocycling, there was no statistically significant difference in SBS between abrasion and phosphoric acid in the no primer group only. However, there were statistically significant differences between abrasion and phosphoric acid treated groups in the following primer groups AZp ($p = 0.0014$), Clr ($p< 0.0191$), Zp ($p < 0.0001$) and Mon ($p = 0.0007$). In summary, the long-term storage in water with thermocycling led to a statistically significant decrease in shear bond strength for all test groups except SMon ($p = 0.4957$), SZp ($p = 0.7019$) and SAZp ($p = 0.3952$).

COMPARISION OF SBS OF PHOSPHORIC ACID SURFACE TREATMENT GROUPS TO CONTROL (NO SURFACE TREATMENT) GROUPS

There were no statistically significant differences between control and phosphoric acid treated groups with all primer groups in both 24-hour and aged conditions, except for Mon group at 24 hours storage ($p = 0.0016$) showed higher SBS when treated with phosphoric acid compared to control group.

The overall SBS in abrasion groups in all primers (Clearfil, Monobond, AZ or Z prime) was significantly higher than control groups in the same condition.

MODE OF FAILURE

The modes of failure as assigned using the light microscope at X40 magnification and calculated in percentages of the bonding areas for all groups, are presented in Table VII and VIII. Initially after 24 hours of water storage, the failure mode with phosphoric acid treatment was mostly mixed for all primer groups except with AZ prime where 33.3% of failures were adhesive. In abrasion 24 hours groups, the failure mode was mostly mixed, 16% of adhesive failure in Monobond and AZ prime groups, and 66.7% of cohesive failure in Zp group. In control groups, all primers groups showed mixed failure mode after 24 hours.

After 90 days storage in water and thermocycling, debonded specimens showed more adhesive failure patterns in all groups than after 24 hours storage. In phosphoric acid groups, the failure mode was mostly mixed, 83.33% of adhesive failure in No primer group (P) and 16.67% in PAZp, PZp and PMon primer groups. In abrasion-aged groups, the failure mode was mostly mixed, 16% of adhesive failure in SMon group and 33.33%

in no primer (S) group, and 33.33% of cohesive failure in SMon group. While in control-aged groups, all primer groups showed more adhesive failure than mixed failure mode.

SURFACE ROUGHNESS

The mean average surface roughness (Ra) values for the control, phosphoric acid and air-abrasion pretreatments were; 0.88, 0.96, 0.99 μm respectively and the (Rq) for the same groups were; 1.06, 1.16, 1.22 μm respectively (Table IX, Fig.16). No statistically significant differences were found ($p > 0.05$) among the groups. SEM images of different surface pretreatments are presented in Figures 20, 21, and 22. The images at X2000 showed a trend of increase of surface roughness with abrasion treatment and showed differences in surface topography comparable to the roughness values obtained from the Proscan measurements.

TABLES AND FIGURES

TABLE I

Description of the materials

Materials	Description	Manufacturer	Batch no.
Zirconia	YTZP	Shofu Dental	Experimental block supplied by Shofu
Variolink II	Adhesive resin cement	Ivoclar	R42504, R69476 R60512
Clearfil ceramic primer	Silane coupling agent	Kuraray Dental	0022DA
Z-prime plus	Priming agent	Bisco	1300001898
Monobond plus primer	Universal primer	Ivoclar Vivadent	R85610
AZ primer	Zirconia Primer	Shofu Dental	011314
35% H_3PO_4 (Ultra-Etch)	Etchant	Ultradent	B7WPQ
Isopropyl Alcohol 70%	Solvent	VWR	070213B

TABLE II

Composition of primers

Primer	**Composition**
Clearfil Ceramic Primer (Kuraray America,Inc.)	Ethanol>80% 3-trimethoxysilylpropyl methacrylate<5% (silane) 10-methacryloxydecyl dihydrogen phosphate (MDP)
Monobond Plus Primer (Ivoclar Vivadent,Inc.)	Ethanol 50-80% 3-trimethoxysilylpropyl methacrylate< 2.5% (silane) Methacrylated phosphoric acid ester < 2.5%
Z-prime Plus (Bisco,Inc.)	Ethanol 10-methacryloxydecyl dihydrogen phosphate (MDP) Hydroxyethyl methacrylate < 20% Biphenyl dimethacrylate < 10%
AZ primer (Shofu Dental Corporation)	Acetone > 99% Phosphonate monomer/thioctic monomer, silane

TABLE III

Description of the resin cement

Material	**Composition**	
Variolink II (Ivoclar Vivadent)	**-Monomer matrix:** Bis-GMA*, UDMA[#], TEGDMA[@] **-Inorganic fillers:** Barium glass Ytterbium trifluoride, Barium-Aluminum-fluorosilicate glass, spheroid mixed oxide **-Additional contents:** catalysts, stabilizers, and pigments.	Dual curing resin cement

*Bis-GMA = Bisphenol A glycidyl methacrylate,[#]UDMA = Urethane dimethacrylate,
[@]TEGDMA = Triethylene glycol dimethacrylate.

TABLE IV

Tested groups and respective codes

Surface treatment	Primer	Label
Control (as sintered)	No primer	C
	Clearfil Primer	CClr
	Monobond primer	CMon
	Z Prime Plus	CZp
	AZ primer	CAZp
Phosphoric acid	No primer	P
	Clearfil Primer	PClr
	Monobond primer	PMon
	Z Prime Plus	PZp
	AZ primer	PAZp
Air abrasion	No primer	S
	Clearfil Primer	SClr
	Monobond primer	SMon
	Z Prime Plus	SZp
	AZ primer	SAZp

TABLE V

Mean shear bond stress (SBS), standard deviation (SD), and statistical significance level (*) between primers within each surface pretreatment group and statistical significance level (*') between surface treatment groups within each primer group ($p < 0.05$) after 24h water storage

Group	N	Pre-test failures	Mean SBS (MPa)	SD	*	*'
C	6	0	0.12	0.09	b	B
CClr	6	0	3.27	2.09	a	B
CMon	6	0	4.58	2.92	a	A/B
CZp	6	0	3.72	1.82	a	B
CAZp	6	0	0.63	0.52	a/b	B
P	6	0	0.52	0.80	c	B
PClr	6	0	4.2	1.13	b/c	B
PMon	6	0	9.54	8.04	a	A
PZp	6	0	3.1	1.62	c	B
PAZp	6	0	1.09	1.08	c	B
S	6	0	4.93	1.85	b	A
SClr	6	0	15.77	2.58	a	A
SMon	6	0	7.25	4.36	b	A
SZp	6	0	7.06	3.05	b	A
SAZp	6	0	6.31	3.95	b	A

TABLE VI

Mean shear bond stress (SBS), standard deviation (SD) and statistical significance level (*) between primers within each surface pretreatment group and statistical significance level (*') between surface treatment groups within each primer group ($p < 0.05$) after aging

Group	N	Pre-test failures	Mean SBS (Mpa)	SD		*
C	6	6	0	0	a	A
CClr	6	4	0.695	1.1	a	B
CMon	6	1	1.11	1.3	a	B
CZp	6	1	1.03	1.5	a	B
CAZp	6	4	0.04	0.05	a	B
P	6	6	0	0	a	A
PClr	6	4	0.49	0.66	a	B
PMon	6	1	0.85	.068	a	B
PZp	6	3	0.81	1.1	a	B
PAZp	6	6	0	0	a	B
S	6	4	0.18	0.29	c	A
SClr	6	2	4.13	2.64	b	A
SMon	6	1	6.21	5.08	a/b	A
SZp	6	1	7.65	4.97	a	A
SAZp	6	2	5.01	2.09	a/b	A

TABLE VII

Failure mode of specimens (%) after 24 hours

Time	Surface Treatment	Primer	Mixed (%)	Adhesive (%)	Cohesive (%)
24h	Control	Control	6(100%)	0 (0%)	0 (0%)
		Clearfil	6(100%)	0 (0%)	0 (0%)
		Monobond	6(100%)	0 (0%)	0 (0%)
		Z Prime	6(100%)	0 (0%)	0 (0%)
		AZprime	6(100%)	0 (0%)	0 (0%)
	Abrasion	Control	4 (66.67%)	2 (33.33%)	0 (0%)
		Clearfil	6(100%)	0 (0%)	0 (0%)
		Monobond	5(83.33%)	1(16.67)	0 (0%)
		Z Prime	2(33.33%)	0 (0%)	4 (66.67%)
		AZprime	5(83.33%)	1(16.67)	0 (0%)
	Phosphoric	Control	6(100%)	0 (0%)	0 (0%)
		Clearfil	6(100%)	0 (0%)	0 (0%)
		Monobond	6(100%)	0 (0%)	0 (0%)
		Z Prime	6(100%)	0 (0%)	0 (0%)
		AZprime	4 (66.67%)	2 (33.33%)	0 (0%)

TABLE VIII

Failure mode of specimens (%) after aging

Time	Surface Treatment	Primer	Mixed (%)	Adhesive (%)	Cohesive (%)
Aged	Control	Control	2 (33.33%)	4 (66.67%)	0 (0%)
		Clearfil	2 (33.33%)	4 (66.67%)	0 (0%)
		Monobond	5(83.33%)	1(16.67)	0 (0%)
		Z Prime	3(50 %)	3(50 %)	0 (0%)
		AZprime	2 (33.33%)	4 (66.67%)	0 (0%)
	Abrasion	Control	4 (66.67%)	2 (33.33%)	0 (0%)
		Clearfil	6(100%)	0 (0%)	0 (0%)
		Monobond	3(50 %)	1(16.67)	2
		Z Prime	6(100%)	0 (0%)	(33.33%)
		AZprime	6(100%)	0 (0%)	(0%)
					0 (0%)
	Phosphoric	Control	1(16.67)	5(83.33%)	0 (0%)
		Clearfil	6(100%)	0 (0%)	0 (0%)
		Monobond	5(83.33%)	1(16.67)	0 (0%)
		Z Prime	5(83.33%)	1(16.67)	0 (0%)
		AZprime	5(83.33%)	1(16.67)	0 (0%)

TABLE IX

Zirconia mean surface roughness values (Ra and Rq in µm) for the different groups along with standard deviation (SD), standard error (SE), minimum values (Min), Maximum values (Max) and Statistical significance level between groups (*)

Outcome	**Group**	**Mean (SD)**	**SE**	**Min**	Max	*
Ra	Control	0.88 (0.04)	0.02	0.85	0.93	a
	Phosphoric acid	0.96 (0.04)	0.02	0.93	1.00	a
	Abrasion	0.99 (0.09)	0.05	0.93	1.10	a
Rq	Control	1.06 (0.06)	0.04	1.02	1.13	a
	Phosphoric acid	1.16 (0.04)	0.03	1.13	1.21	a
	Abrasion	1.22 (0.10)	0.06	1.15	1.33	a

TABLE X

ANOVA table for shear bond strength (SBS)

Effect	**Num DF**	**Den DF**	**F Value**	**P Value**
Pretreatment	2	100	62.67	<.0001
Primer	4	100	15.23	<.0001
Pretreatment*primer	8	100	3.23	0.0026
Time	1	100	54.99	<.0001
Pretreatment*time	2	100	1.80	0.1703
Primer*time	4	100	5.96	0.0002
Pretreat*primer*time	8	100	4.86	<.0001

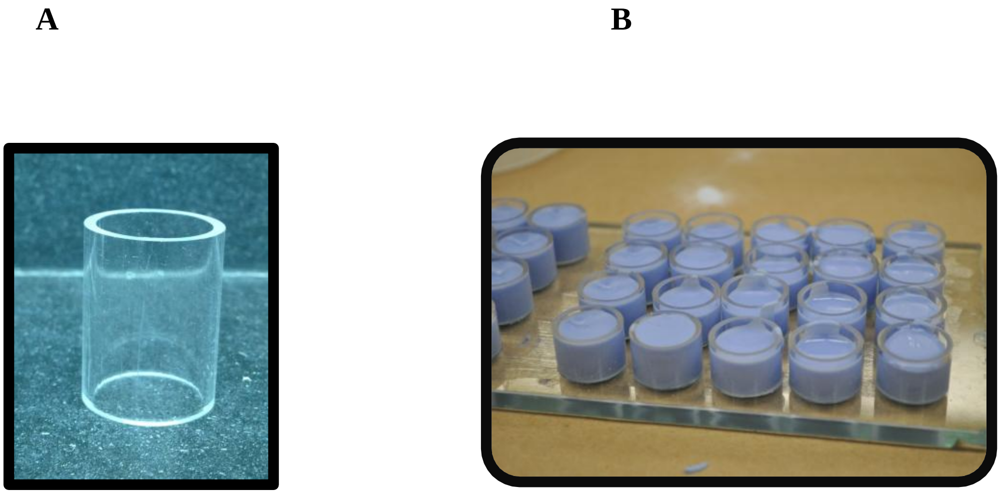


FIGURE 1. Illustrations of mounting the tubes using the acrylic resin to support the samples during testing. (A) The plastic tube. (B) Mounting of the tubes.

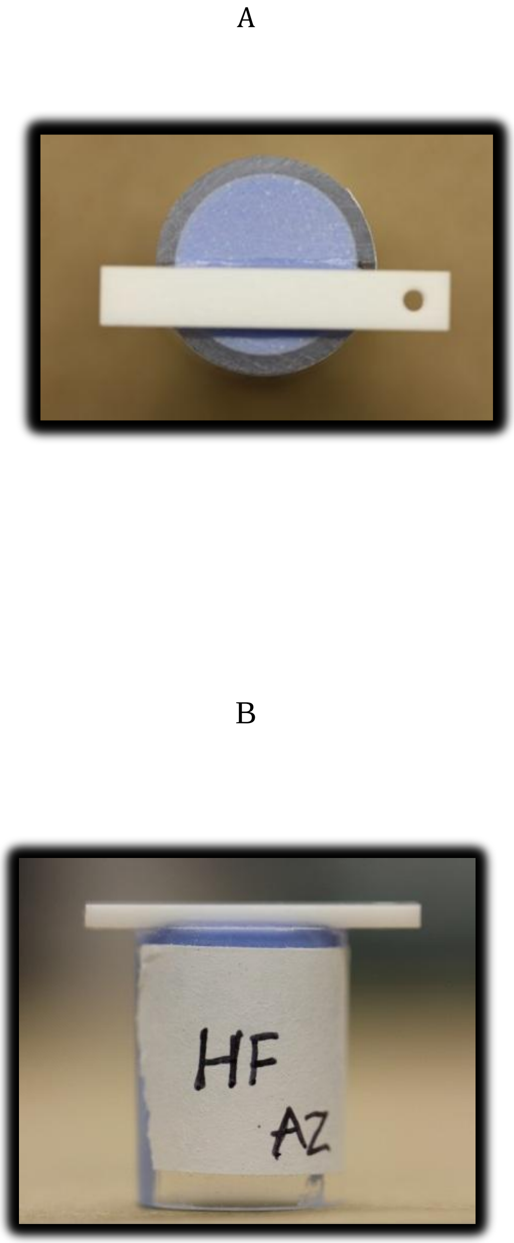


FIGURE 2. A, B. Y-TZP zirconia bar after being mounted on the acylic resin tube.

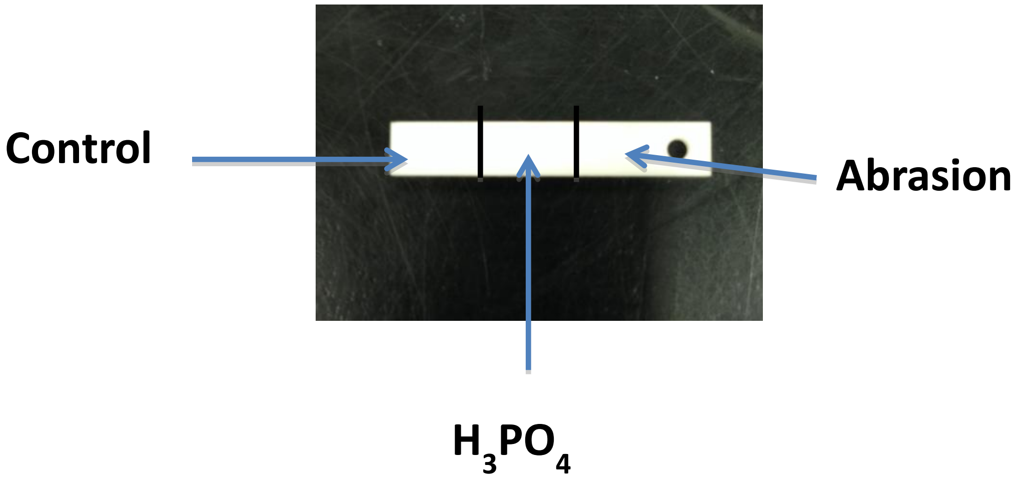


FIGURE 1. Zirconia bar: showing the shape and each part to be treated.

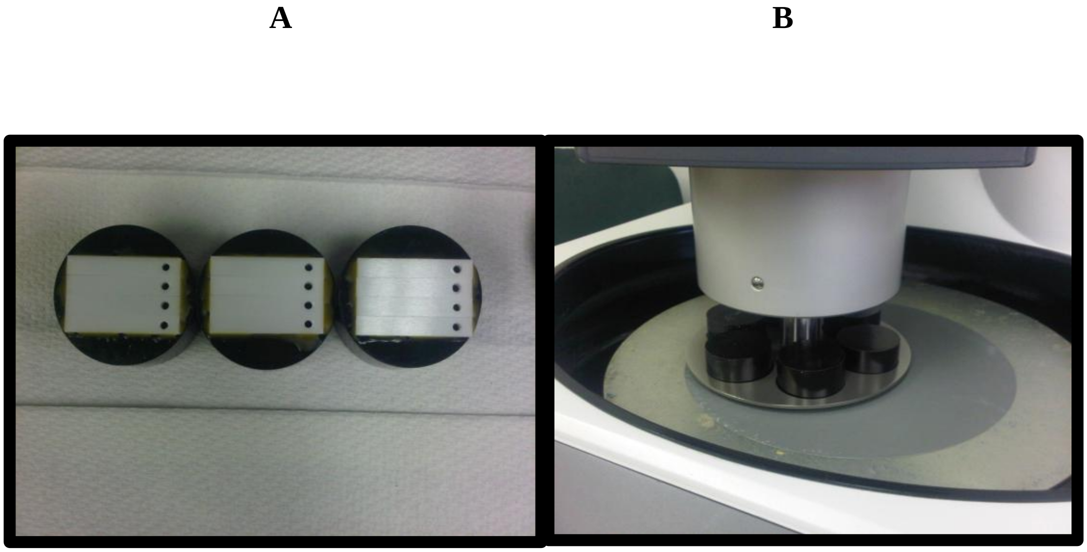


FIGURE 4. Polishing Zirconia bars. A) Zirconia bars mounted on Struers blocks using sticky wax before polishing procedure. B) The Struers polishing machine used for polishing the zirconia bars sequentially using silicon carbide grinding papers (Struers RotoPol 31/RotoForce 6 polishing units, USA).

FIGURE 5. Illustration of airborne-particle abrasion of Y-TZP.
A) Airborne-particle abrasion machine.
B) Abrasion the zirconia bar with the customized distance wire.

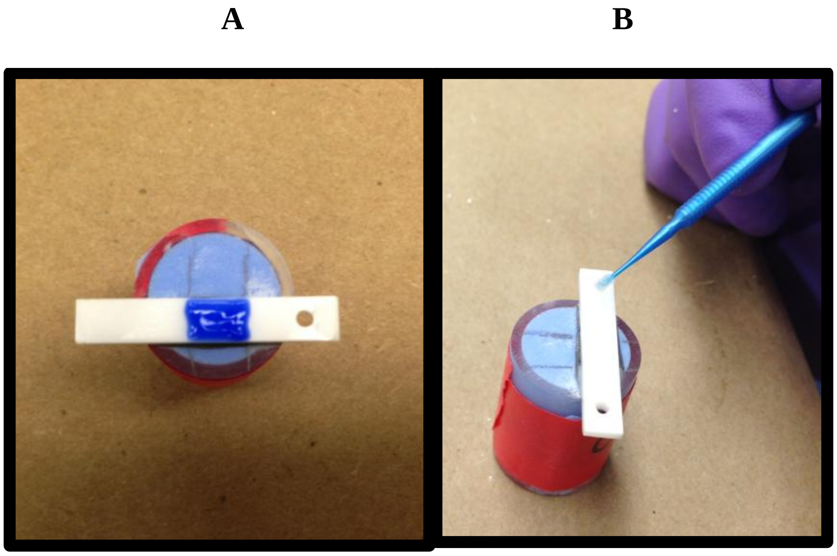


FIGURE 6. A) Illustration of 37% phosphoric acid application on Y-TZP bar. B) Application of primer on Zirconia bar using microbrush applicator.

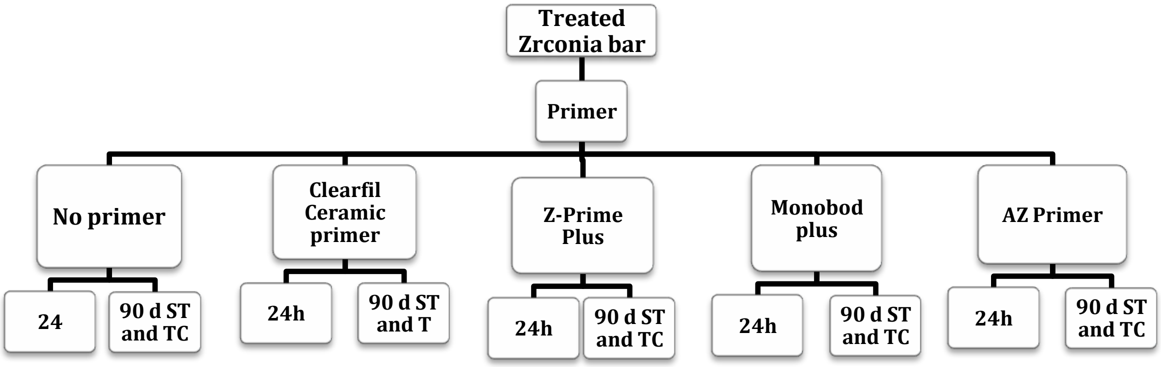


FIGURE 7. Flowchart describing the experimental study design. Surface-treated specimens were conditioned with five different primers. Each group was either tested for shear bond strength after 24 hours or after 90 days water storage and thermocycling (ST and TC). Abbreviations: 24h (24 hours), 90 d (90 days), ST (water storage) and TC (thermocycling).

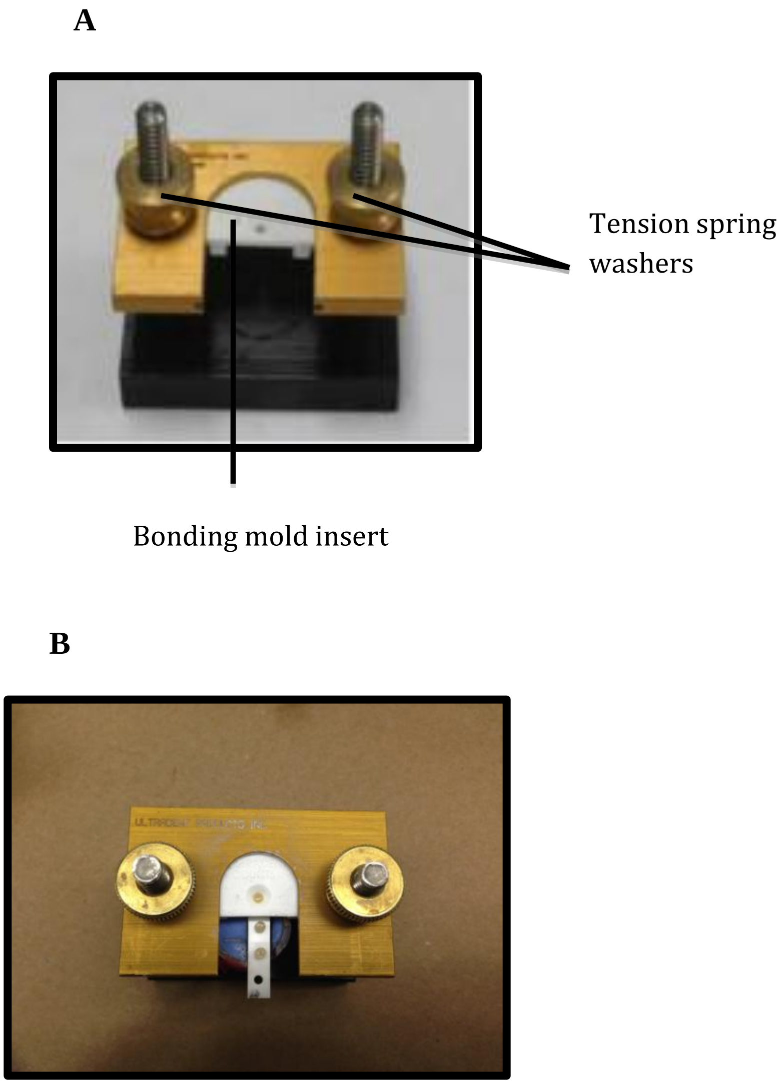


FIGURE 8. A) Illustration of a bonding jig parts. B) Ultradent jig with button preparation on zirconia bar.

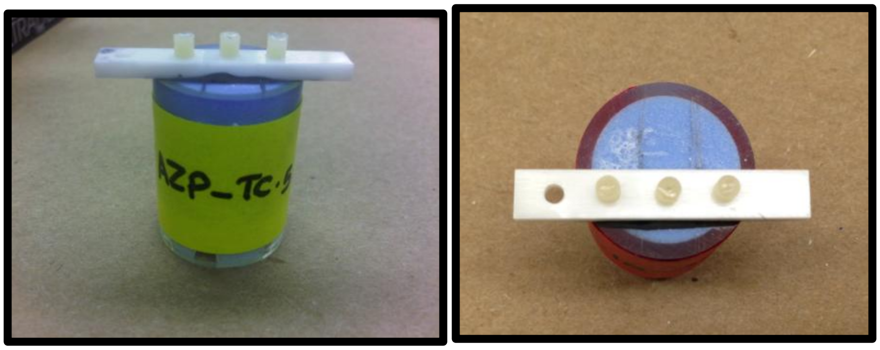


FIGURE 9. A) Side view of the prepared buttons on the zirconia bar B) Top view of the buttons prepared on zirconia bar.

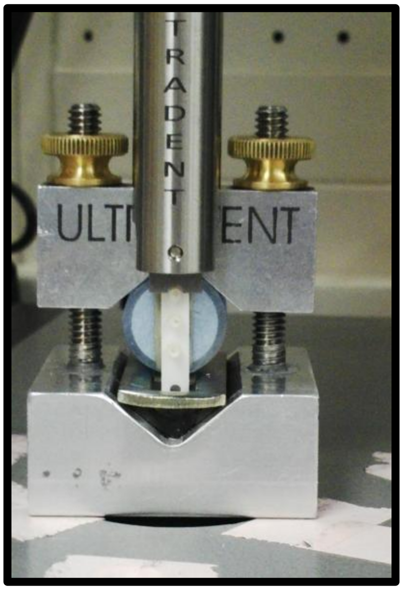


FIGURE 10. A) Illustration of specimen placed in a universal testing machine
B) (Sintech ReNew 1123, MTS) with a semicylindrical loading surface.

FIGURE 11. Illustration of thermocycling machine.

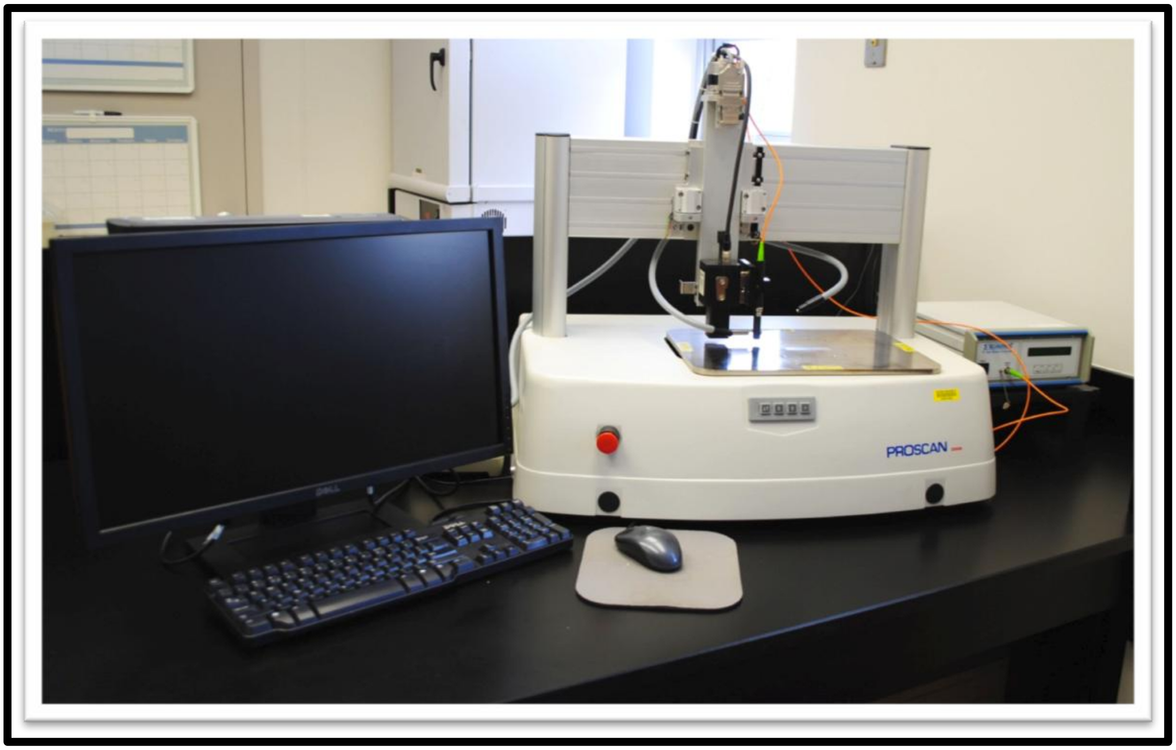


FIGURE 12. Non-contact optical profilometer (Proscan 2000, Scantron, Taunton, England).

FIGURE 13. Light microscope (Nikon Measurescope UM-2, Tokyo, Japan).

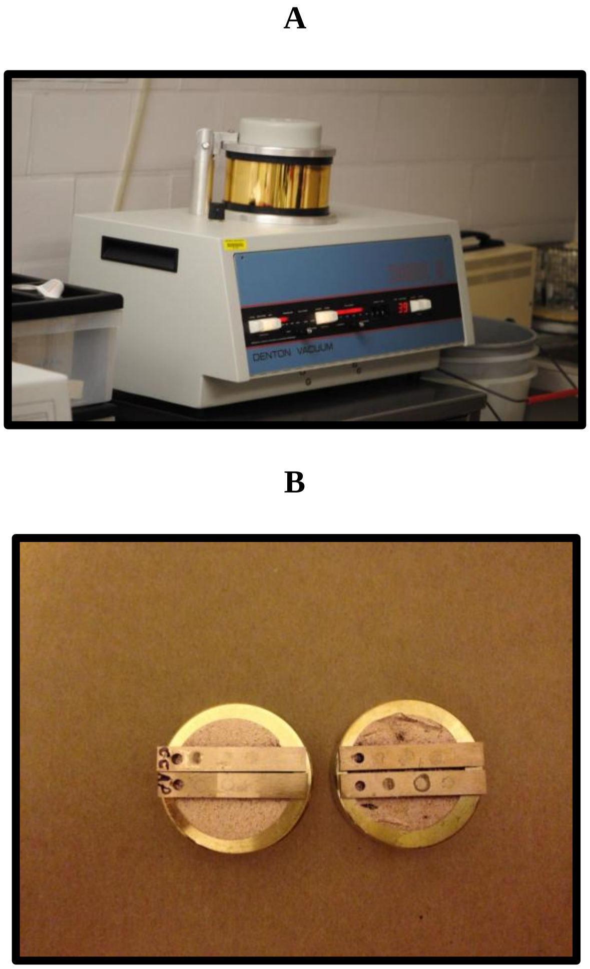


FIGURE 14. A) Sputter-coater (Denton Vacuum Desk II) and B) Zirconia bars sputter-coated with gold prior to SEM imaging.

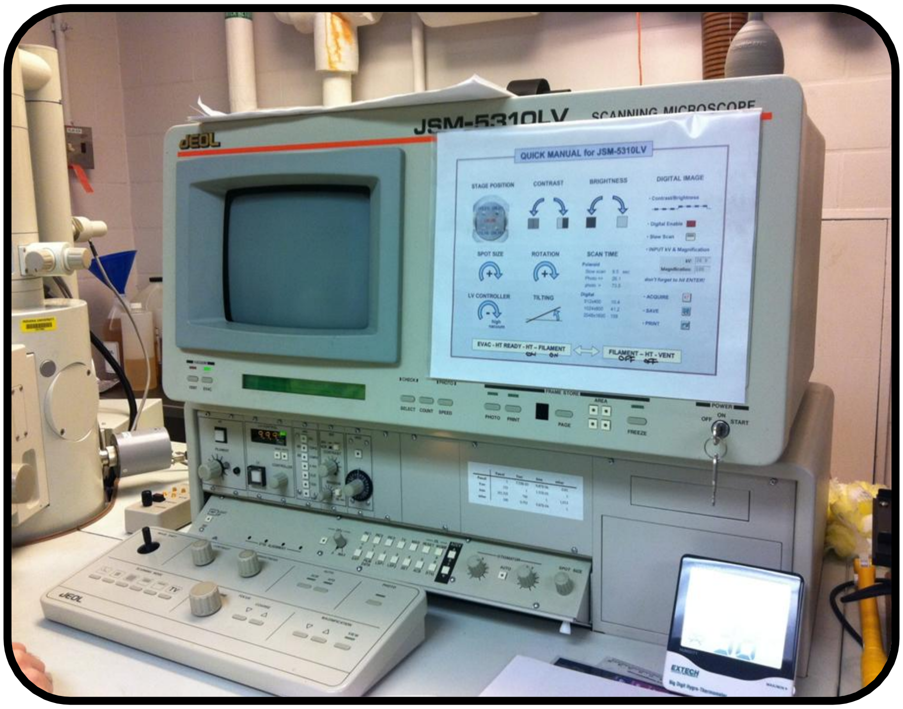


FIGURE 15. Scanning electron microscope (SEM, Model 515, Philips Eindhoven, The Netherlands).

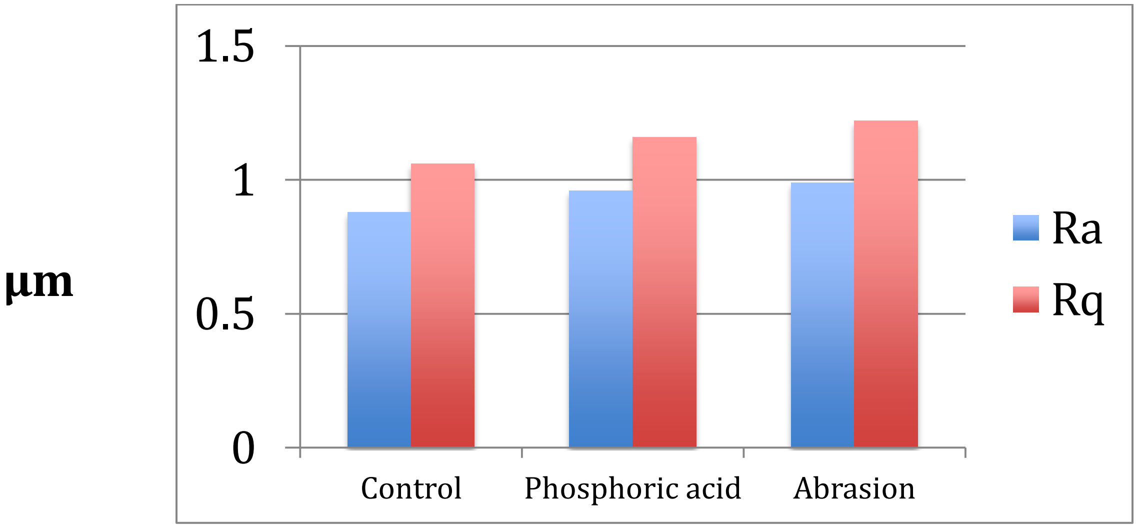
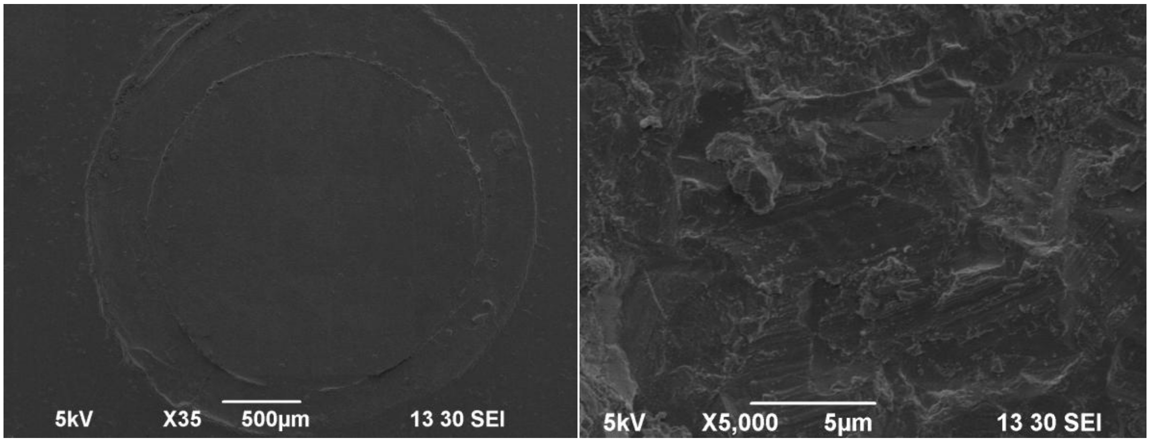
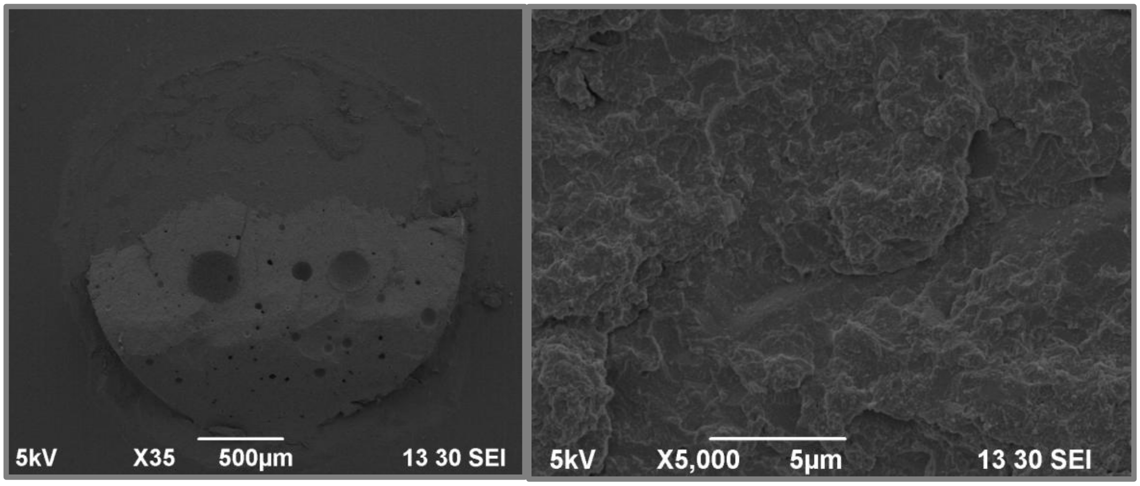


FIGURE 16. Summary of surface roughness measurements (Ra,Rq in µm) among the different surface treatments groups.



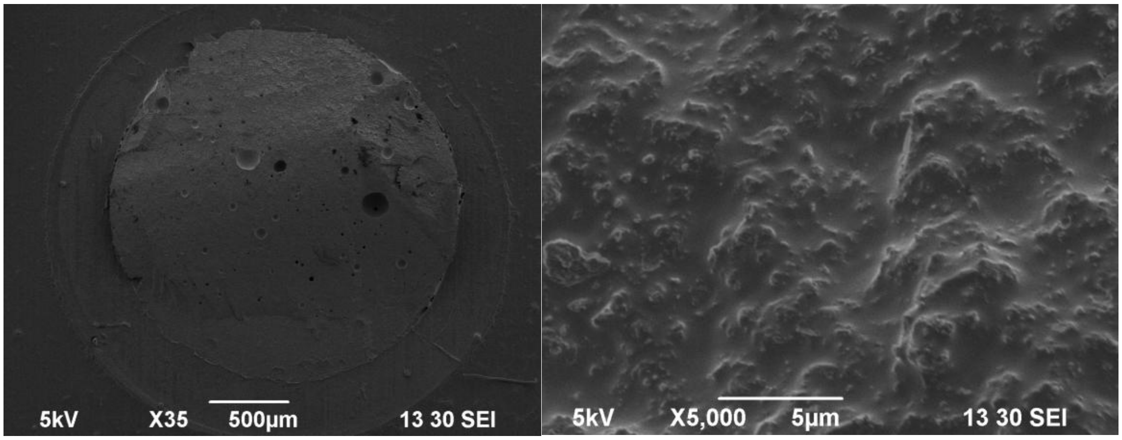
A) B)

FIGURE 17. SEM images of zirconia surface representing adhesive mode of failure after debonding at magnification A (X35) and B (X5000).



A) B)

FIGURE 18. SEM images of zirconia surface representing mixed mode of failure after debonding at magnification A (X35) and B (X5000).



A) B)

FIGURE 19. SEM images of zirconia surface representing cohesive mode of failure after debonding at magnification A (X35) and B (X5000).

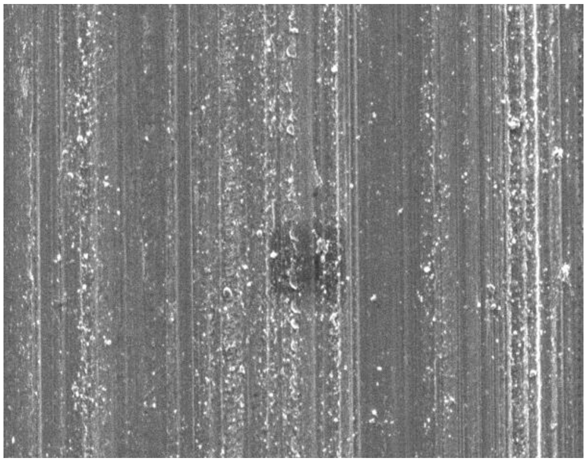


FIGURE 20. SEM images of Control surface treatment (zirconia bar after polishing with no surface treatment) at X2000.

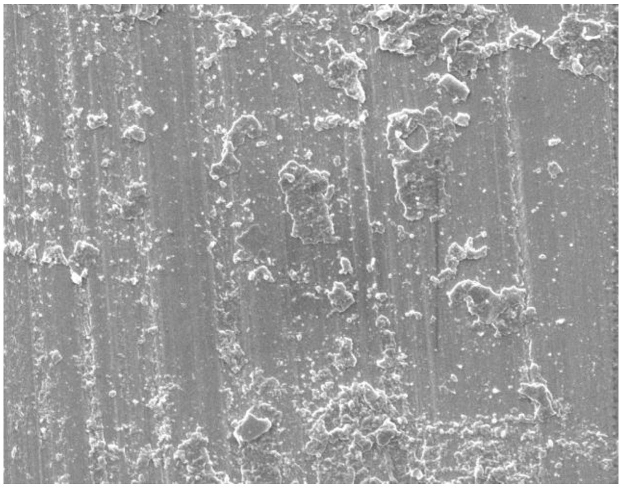


FIGURE 21. SEM image of Phosphoric acid treatment at X2000.

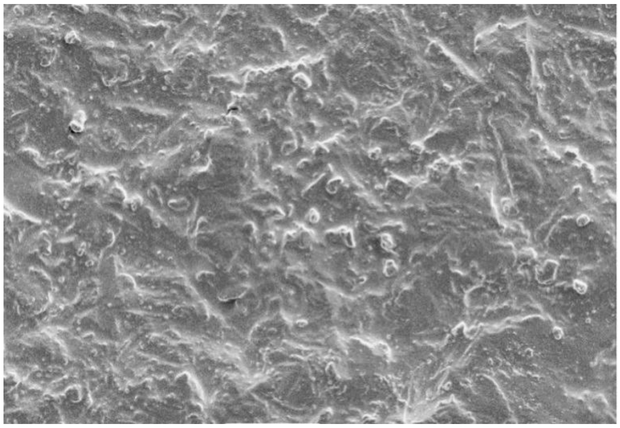


FIGURE 22. SEM image of Air-abrasion treatment at X2000.

DISCUSSION

Numerous factors affect the bond durability of resin cement to zirconia ceramics. These include roughness of the ceramic surface, the ability of resin cements to wet the ceramic surface, handling technique of the materials, composition of the resin cements, compatibility of the primer and cement, possible contamination during bonding procedures and cleaning methods of the restoration luting surface.[36] This present study evaluated the effect of using phosphoric acid as a chemical cleaning treatment on the bonding effectiveness of conditioned zirconia by different primers. A significant decrease in shear bond strength (SBS) was found by which the first null hypothesis was rejected. With phosphoric acid surface pretreatment, the initial bonding effectiveness of the primers was affected negatively after 24 hours except for Monobond Plus primer that was somewhat unexpected. The Monobond Plus primer (Ivoclar Vivadent) revealed significantly higher initial bonding effectiveness to zirconia after 24 hours but the bond strength dropped upon ageing (Table V, VI).

As outlined in the literature, zirconium oxide surfaces have strong affinity towards the phosphate group, as many metals do, and they react with phosphoric acid in an acid-base reaction.[11] Different primers contain phosphoric acid-containing reagents that utilize this affinity in the same way.[34] When restorations are cleaned with phosphoric acid gel, a stable phosphate layer forms on the restoration surface and provides a surface resistant to the effect of the primer.[11] Furthermore, the surface energy of the ceramic surface might be decreased due to the use of phosphoric acid, leading to reduced SBS values. Therefore, lower bond strength values are achieved after the restoration surface has been cleaned with phosphoric acid gel.[32] Consequently, contaminated zirconia restorations must never be cleaned with phosphoric acid gel.

For Monobond Plus primer, methacrylate monomers with a functional phosphoric acid group are used to establish a bond to zirconia, which has high affinity to phosphoric acid.[41] High initial SBS of the PMon group was recorded even after phosphoric acid treatment. This might be due to various parameters of the chemical reaction between zirconia and phosphate. These may include the size and concentration of the reactant. For example, if methacrylate monomers with a functional phosphoric acid group in Monobond Plus primer are more concentrated, the bond between this reactant and the zirconia is much more probable to form than to the phosphate of phosphoric acid gel or any other lower concentration reactant.[41] In addition, the range of the recorded bond strengths of PMon group was broadened after phosphoric acid treatment and 24 hours storage. Monobond Plus primer also contains silane methacrylate, 3-trimethoxysilylpropyl methacrylate (3-MPS), that can wet the zirconia surface by reducing the surface tension and increasing the surface energy of zirconia.[34]

The second null hypothesis was also rejected, as chemical conditioning of the zirconia surface using four different primers did not equally influence the bonding effectiveness of zirconia. All the primers tested do contain phosphate-based functional monomers to form chemical bonds with the zirconia surface, but appeared not equally effective (Table II).

The highest mean value of SBS (15.77 MPa) was observed when zirconia was air abraded and chemically conditioned using the 10- MDP/silane-based ceramic primer, Clearfil Ceramic Primer (Kuraray Noritake) after 24 hours of water storage. However, the other ceramic primers, Z-Prime Plus (Bisco,Inc.), AZ Primer (shofu) and Monobond Plus (Ivoclar Vivadent), showed equal values of bonding effectiveness to zirconia after abrasion and 24 hours storage but less than the mean SBS of Clearfil primer. As outlined above, application of the Monobond Plus primer after phosphoric acid treatment revealed significantly higher initial SBS to zirconia after 24 hours compared to the other three primers that showed low values.

Therefore, the differences in the **S**BS measured might be influenced by different factors related to the functional monomers. These include actual concentration of the functional monomer, the purity of the primer and the presence of silane methacrylate monomer (3-MPS) that has efficient wetting capabilities. In addition, having many ingredients mixed into one primer may mutually compete to contact the zirconia surface. Consequently, there may be interferance with the effective interaction of the actual functional monomers with the zirconia surface.[34]

In the air abrasion group, the shear bond strength increased statistically significantly, but it did not remain stable over storage time and thermal cycling in the SClr group and no primer S group. On the other hand, the shear bond strength of SMon, SZp and SAZp groups were stable and did not decrease significantly after 90 days storage in water with thermal cycling. A possible explanation might be that the phosphate monomer in these three ceramic primers might have bonded to the zirconia ceramic, and form chemical bonds at the resin zirconia interface through covalent bonds, hydrogen bonds or van der Waals forces as previously stated.[35] They also have resin terminal ends that bond to the resin cements. For instance, the universal primer (Monobond Plus) contains an alcohol solution of silane methacrylate, phosphoric acid methacrylate, and sulfide methacrylate.[34] The phosphate monomer was able to promote durable resin bonding to zirconia ceramic in the SMon group that is in agreement with results of Kern et al. [42]and with Attia et al.[38] Z-prime plus primer composed of 10-methacryloyloxydecyl dihydrogen phosphate (MDP) and the carboxylic monomer biphenyl dimethacrylate (BPDM). The MDP monomer helps the reaction between BPDM and metal oxide of the zirconia, resulting in increased bond strength.[34] In addition, both monomers in Z-prime plus primer have chemical binding affinity to the zirconia surface. The acidic monomer MDP has two active points and at least two points in BPDM that are able to bond with ZrO_2. Moreover, the phosphoric acid monomer in AZ primer is the main ingredient that has two active sites capable of reacting with the Zr atom, and it also contains thioctic-acid monomer.[43] In agreement with other studies, this study showed that phosphate monomers are chemical agents that provide durable bond strength to zirconia.[10,20,23,33,36]

Several studies have reported that application of MDP/silane-containing bonding improves bond strength between sandblasted zirconia and resin cement.[10,16,21,24,34,35] Clearfil primer contains both an MDP monomer and a silane monomer 3-MPS, which is commonly used in dentistry. In this current study, SClr group had high initial SBS but it decreased statistically significantly after aging.

The Monobond and Clearfil Primers contain silane monomers. As reported in the literature, the silane increases the bond strength by performing two functions. Firstly, it provides a chemical bond between silica-based surfaces and resin composite; unfortunately, this does not apply to the zirconia ceramics used in this study. Secondly, the wettability of the ceramic surface increases by the organic portion of the silane molecule.[33, 36] This increase in wettability enhances the flow of resin cement into the ceramic surface, resulting in a stronger micromechanical bond. It is also known that silane is unstable in acidic environments.[34, 35] The acidic composition of phosphate monomers in the primers such as Monobond Plus and Clearfil Ceramic Primer may result in instability of the silane component of these primers. On the other hand, Z-Prime plus primer does not contain silane monomer to allow for greater concentrations of the phosphate monomer and to minimize the potential hydrolysis of the silane if it is applied as recommended by Bisco, Inc.[34]

To test durability of resin bonding, water storage and thermal cycling are two significant factors that decrease bond strength as reported in several studies.[10,20,23,33,36] Therefore three months storage in water and thermocycling for 5000 cycles were used as the aging regime in this study. After 90 days storage in water and thermocycling, SBS was significantly decreased for groups using Clearfil primer with all the three surface-pretreatment groups and Monobond primer with the control and phosphoric acid surface-pretreatment groups. As reported in several previous studies, this decrease might be due to the hydrolytic effect of water at the resin cement/ceramic interface.[10,20,23,28,33,36] Furthermore, stresses at the bonded interfaces resulted from the difference between coefficients of thermal expansion of (zirconia ceramic, monomers, and luting resin) during thermal cycling.[20] Therefore, the combined effect of water storage and thermal cycling might be responsible for the negative effects on bond strength of all tested groups although the decrease was significant only for Clearfil and Monobond groups. According to these results, the third hypothesis was partially rejected.

After 90 days storage in water and thermocycling (Table VI), there were statistically significant differences in SBS between abrasion and phosphoric acid treated groups in all primers groups; AZp ($p = 0.0014$), Clr ($p = 0.0191$), Mon ($p = 0.0007$), and Zp ($p < 0.0001$). However there were no statistically significant differences between abrasion and phosphoric acid groups in the No primer group ($p = 0.9082$). Compared to the controls, phosphoric acid treatment groups had no statistically significant difference between all the primers after aging. For PAZp, the aging even resulted in premature failures after phosphoric acid treatment, while other primers groups revealed low bond strengths similar to the control value.

Fractographic analysis revealed that most of the experimental groups exhibited more **‘**mixed**’** failures after 24 hours, except for S, SMon, SAZp and PAZp groups where 33.33%, 16.67%, 16.67%, and 33.33% of specimens showed an adhesive failure pattern, respectively (Table VII, VIII). Mixed mode of failure would indicate more effective bonding between the cement and parts of zirconia surface in which stresses were experienced in the cement bulk and resulted in some areas of cohesive failure. Only 66.67% of specimens in SZP group showed cohesive failure within the resin cement after 24 hours. Also noteworthy is that all aged groups exhibited relatively low bond strengths, in particular the control and phosphoric acid treated groups, and typically failed adhesively, entirely at the cement-zirconia interface. SEM failure analysis revealed minimal adhesive remnants on the fractured surfaces, indicating a weak interaction with zirconia.

After aging, 33.33% of specimens that were air-abraded and chemically pre-treated using Monobond failed cohesively**.** This agrees well with SBS results that show significantly higher bond strength values in this group. In addition, specimens subjected to phosphoric acid pretreatment using Monobond Plus primer seldom failed entirely 'adhesively' at the interface (Table VIII). At a microscopic level, many composite remnants were still found attached to the surface (Fig.17).

Airborne particle abrasion promotes the formation of resin-ceramic micromechanical interlocking by increasing the bonding area, inducing an activated micro-roughened zirconia surface, and modifying wettability and surface energy of the ceramic surface.[2,6,9,10,19,20,22, 23, 37] In our study, air abrasion surface treatment increased the average surface roughness Ra and Rq values, but with no statistically significant differences among the three surface treatment groups. Air-abraded groups presented more specimens that were fractured cohesively, as shown in the SZP 24h group and SMon in aged group, and less adhesive fracture compared to other surface pretreatment groups. SEM images (Figs. 20 to 22) illustrate the surface of zirconia after no treatment, phosphoric acid, and air abrasion treatment. Surface roughness of Proscan (quantitative) and SEM images (qualitative) confirm an increase in surface roughness and irregularities with phosphoric acid and air-abrasion treatment, although it was not statistically significant.

SUMMARY AND CONCLUSIONS

From these results, it can be concluded that:

- Monobond Plus primer provided the highest SBS to zirconia after phosphoric acid treatment.
- The chemical conditioning of zirconia ceramics with dedicated ceramic primers (Z-prime Plus (Bisco,Inc.); Monobond Plus, Ivoclar Vivadent; and AZ primer (Shofu Dental Corporation)) resulted in the most favorable bond durability of resin cement to air-abraded zirconia.
- Air abrasion is the best surface treatment after contamination of zirconia surface.

Manufacturers' attempts to improve zirconia bonding will likely continue with further development of surface primer technology to provide high and durable bonds in all clinical situations.

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ABSTRACT

INFLUENCE OF PHOSPHORIC ACID SURFACE TREATMENT ON SHEAR BOND STRENGTH DURABILITY OF RESIN CEMENT TO ZIRCONIA-BASED CERAMIC CONDITIONED WITH DIFFERENT PRIMERS

by

Eman Zuhair Alshehri

Indiana University School of Dentistry
Indianapolis, Indiana

BACKGROUND: Phosphoric acid treatment has been reported to be relevant for zirconia cleaning after contamination. However, its interaction with different primers is not well known and needs to be investigated. OBJECTIVES: To compare the shear bond strengths (SBS) of resin cement to Y-TZP after phosphoric acid pretreatment and different chemical conditioning protocols, and to test the durability of SBSs after long-term storage and thermal cycling conditions. To investigate the effect of phosphoric acid on the surface roughness of a yttrium-stabilized tetragonal zirconia polycrystal ceramic (Y-TZP). METHODS: Sixty bars of zirconia (30 X 5 X 2 mm) were polished and glued to acrylic tubes. Each bar received 3 different surface treatments (control, phosphoric acid and air-abrasion). The bars were randomly assigned into five groups according to different primers applied (No primer, Clearfil ceramic primer, Monobond Plus, Z-prime plus and AZ primer). After that, resin cement was mixed, injected into a mold, and light cured. The specimens were tested in shear on a universal testing machine. Half of the specimens were tested after 24 h water storage and the other half were tested after 90 days of water storage and thermocycling. Non-contact profilometer was used to assess the effect of the three surface pretreatments on surface roughness of zirconia. Mode of failure and surface roughness were evaluated with SEM. Statistical analyses were conducted with mixed-model ANOVA and chi-square tests. RESULTS: The results indicated that Monobond Plus primer showed higher SBS after phosphoric acid treatment compared to other primers used. SBS of all air abrasion groups were higher than phosphoric acid groups. Long term water storage and thermocycling led to a statistically significant decrease in SBS for all groups except Monobond Plus, Z-prime plus and AZ primer after air abrasion treatment. Surface roughness measurements showed no significant differences among the surface treatments. CONCLUSION: Monobond Plus provided the highest SBS to zirconia after phosphoric acid treatment. The findings suggest that the air abrasion is the best surface treatment after contamination of zirconia surface. Monobond Plus, Z-prime plus and AZ primer showed durable SBS after air abrasion treatment and aging process.

CURRICULUM VITAE

Eman Zuhair A. Alshehri

May 1983	Born in Jeddah, Saudi Arabia
June 2000	High School Diploma 1st High School. Jeddah, KSA
July 2000 to July 2006	Bachelor of Dental Medicine & Surgery (BDS) Faculty of Dentistry, King Abdul Aziz University (KAU) Jeddah, KSA
July 2007 to present	Demonstrator (Teaching Assistant) Dental Materials Division, Department of Restorative Dentistry, College of Dentistry, King Saud University, Riyadh, Saudi Arabia.
June 2011	Dental Materials Graduate Program, Indiana University School of Dentistry, Indianapolis, Indiana.

Professional Organizations

The Academy of Operative Dentistry
Saudi Dental Society
American Dental Education Association (ADEA)