The Effect Of Different Cleaning Agents On The Bond Strength Of Contaminated Zirconia

Thesis

Master of Science in Oral Biology (MSOB) degree program

By

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THESIS

Presented to the Faculty of Penn Dental Medicine in Fulfilment of the Requirements for the Degree of Master of Science in Oral Biology

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Dedication

I want to dedicate this manuscript to my father, Dr. Awni Musharbash, my mother Nidaa Naffa, and my siblings Rozan and Ziad Musharbash. My family is my source of support, strength and motivation and I would not be here without them.

Acknowledgement

I would like to acknowledge the Department of Preventive and Restorative Sciences at Penn Dental Medicine, Dental Materials Laboratory and Singh Center for Nanotechnology at University of Pennsylvania for providing the opportunity and facilities for this research. I want to express my sincere gratitude to Dr. Blatz for his vision and guidance throughout this project. I want to thank Dr. Conejo, Dr. Ozer and Dr. Mante for their support and guidance at each step. Special thanks to Dr. Anadioti, the founding director for the Advanced Education Program in Prosthodontics for being an inspiration and mentor.

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Abstract

Objectives: This study evaluated the influence of saliva contamination and the effect of several cleaning methods, on the resin bond durability to zirconia. Shear tests were performed to assess the shear bond strength of specimens after 24 h of storage or after thermocycling as an aging method.

Methods: One hundred KATANA Zirconia STML (n=20) specimens were sectioned and sintered in an induction furnace (CEREC SpeedFire, Dentsply Sirona, Germany). Specimen surfaces were ground finished with 800 grit silicon carbide abrasive with cooling water and cleaned with ultrasonication in alcohol. Specimens were air-particle abraded with 50 μm aluminum oxide at 2.8 bar pressure. All samples were equally divided into 5 groups (n = 20) according to the cleaning method. Groups were contaminated with saliva, and subjected to different cleaning protocols, namely: APC, Katana Cleaner (KC), Ivoclean(IC) and Zirclean(ZC). Cylindrical composite resin specimens (2.1 mm in diameter, 3 mm in height) were bonded to the zirconia samples with dual-cure multi-step composite resin cement Panavia V5 following manufacturers' instructions. A load of 1000 g was applied to the composite

cylinders during bonding in an alignment apparatus, then light cured for 80 s. Samples were stored in distilled water at 37° C for 48 h, then subjected to 10,000 thermal cycles. Shear bond strength was determined using a universal testing machine at a crosshead speed of 0.5 mm/min expressed in MPa. The fractured surfaces of specimens were inspected with a stereo microscope and classified as adhesive, cohesive, or mixed failures. Paired t-test and pairwise comparisons (Posthoc bonferroni test) with $\alpha=0.05$ were applied for statistical analysis.

Results: Shear bond strength values [MPa] under normal conditions (NC) were for Control 22.2 (10.26 SD), APC 52.78 (2.76 SD), KC 33.45 (13.59 SD), IC 34.66 (9.97 SD), and ZC 32.77 (14.53 SD). Shear bond strength values [MPa] under thermocycling (TC) conditions were for Control 6.51 (2.44 SD), APC 18.97 (8.67 SD), KC 17.11 (9.60 SD), IC 16.26 (3.62 SD), and ZC 15.13 (2.90 SD). Intragroup analysis using paired t-test revealed statistically significant differences in shear bond strength in every group between normal condition (NC) and thermocycling conditions (TC) ($p<0.05$). Intergroup analysis using Bonferroni Post-hoc test revealed statistically significant difference in shear bond strength among the tested groups ($p>0.5$) when compared to the control group with group 2-APC having significantly higher shear bond strength when compared to the other test groups ($p<0.05$).

Conclusions:

According to the results of this in vitro study, Zirconia ceramics' cleaning protocol must be considered after exposure to saliva during intraoral try-in procedures. Application of zirconia cleaning agents to the contaminated zirconia surfaces is as effective as mechanical surface abrasion and offers a simple step-by-step cleaning method for restoring zirconia surfaces after contamination.

Introduction

Ceramic materials are widely used in dentistry, because of their high esthetic potential, easily mimicking color, texture, and shape, while restoring function. [1]

The introduction of zirconia into modern dental practice has greatly advanced the development of metal-free dentistry. [2] Currently, various types of zirconia ceramics are being used extensively to fabricate dental restorations owing to their high fracture toughness and aesthetic properties. [3 4 5 6]

In terms of fracture resistance, zirconia -based fixed partial dentures (FDPs) have the potential to withstand physiologic forces of occlusion in the posterior region and therefore provide an interesting alternative to metal ceramic restorations. [7]

Moreover, because of its excellent biocompatibility and chemical stability, zirconia has been used in the fabrication of dental implants and abutments. It has now gained more attention from dentists and researchers. However, the application of zirconia-based restoration is constrained by its chemical inertness and the resultant relative weak bonding properties, including resin to zirconia, and porcelain to zirconia bonding. Therefore, many investigations were carried out to improve zirconia's bonding ability. Typically, resin cements are used for luting zirconia crowns or frameworks to the tooth abutments. [8 9 10 11 12]

However, a clinical problem with the use of zirconia restorations is the difficulty in achieving a reliable and durable bond between the resin luting agent and the ceramic. [4 8 9 12 13 14 15 16]

A strong resin bond relies on chemical adhesion and/or micromechanical interlocking created by surface conditioning methods such as roughening. Current roughening techniques consist of grinding, abrasion with diamond rotary instrument, airborne particle abrasion with alumina or silica-modified alumina particles, acid etching, or a combination of these techniques. [17 18 19 20]

The composition and physical properties of zirconia differ from those of conventional glass-based ceramics. Zirconia is densely sintered and does not contain a glassy phase; therefore, it cannot be etched with hydrofluoric (HF) acid to create a micro-retentive etching pattern. Thus, to achieve a reliable and durable bond in various clinical applications, alternative bonding strategies are required. [5]

Meanwhile, another major issue pertaining to bonding of ceramic restorations is related to its potential contamination before cementation. After sandblasting and clinical try-in procedures, zirconia can get contaminated with saliva and/or blood. As with many metals, zirconium shows a strong affinity toward the phosphate group found in saliva and other fluids, which reacts with the zirconia surface and makes bonding difficult. [21]

Many methods have been tested to clean the contaminated zirconia surface, such as sandblasting with aluminum oxide particles; silica coating; applying hydrofluoric acid, phosphoric acid, and sodium hypo- chlorite solutions; oil-free air streams; air–water spraying; ultrasonic cleaning; alcohol; plasma treatment (argon or air); laser treatment; selective infiltration etching; and enzymatic cleaning agents 25–30. However, mechanical cleaning methods such as sandblasting, can cause cracks and deformations on the material surface, and chemical agents can cause changes in the zirconia phase. [22] [23] Nonabrasive universal cleaning agents and pastes have increased in use. [24] [25] [26] [27]

A cleaning agent called Ivoclean® (Ivoclar-Vivadent, Schaan, Liechtenstein), which is an alkaline suspension of zirconium oxide particles, was developed to remove the contamination from zirconia in an effort to improve bonding to resin cements. Due to its size and the concentration of the particles in the medium, phosphate contaminants are much more likely to bond to them than to the surface of the ceramic restorations. Ivoclean adsorbs the phosphate contaminants preferentially, thus leaving behind a clean zirconium oxide surface. [28]

After the removal of the temporary crown before cementing a restoration, traditional cleaning methods of the abutment may not be sufficient for removing residual temporary cement, which will reduce the bond strength. KATANA Cleaner has a high cleaning effect due to the surface active characteristic of MDP Salt, which is formed from a phosphate monomer "MDP" and an alkaline compound. It is a simple way to optimize your cementation procedures and recover the bond strength. [29]

Additionally, ZirClean is a cleaning gel designed for the non-abrasive cleaning of the bonding surfaces of zirconia (and other prosthetic restorations) after intraoral try-in. ZirClean helps achieve reliable adhesive cementation results by removing the phosphate contamination of zirconia (as well as ceramic and metal restoration surfaces) that occurs during try-in. KOH works as an active ingredient to pull phosphate contaminates off zirconia surface, cleaning it and prepping it for bonding to primer.[30]

	KATANA CLEANER	IVOCLEAN	ZIRCLEAN
Intraoral Use on Tooth Structure	YES	NO	NO
Intraoral Use on Implant Abutments	YES	NO	NO
Extraoral Use	YES	YES	YES
Active Ingredient	MDP SALT	Sodium Hydroxide	Potassium Hydroxide
pH	4.5	13-13.5	13
Application Time	10 s	20 s	20 s
Handling	No Shaking	Shake Before Use	No Shaking

Table 1: Cleaners Comparison.

Statement of the problem

Ceramic indirect restorations are increasingly becoming the choice for crowns due to esthetic considerations and structural properties of the materials. However, regardless of the material used, the restoration must be cemented in place, and the bond strength of a permanent indirect restoration is critical to the success of the restoration. The bond of the cement to the ceramic crown imparts strength to the restoration by preventing microfractures from propagating from the intaglio surface. Bond strength only gains its maximum potential through a precise, controlled bonding technique. Imprecise technique or contamination can impede the bond, potentially decreasing the lifespan of a restoration. Cleaning methods have been proposed to remove contamination and restore bond strength. A clear understanding of the material to be bonded, the type of cement used, and the technique to bond the materials are paramount.

Contamination during the bonding process can degrade the final bond strength. A common source of contamination is with saliva during try-in, which can affect the final bond adversely due to salivary proteins on the intaglio surface of the crown that inhibit cement binding sites. Therefore, the restorations must be cleaned appropriately before cementing in place, but in a manner that itself does not reduce bond strength by chemical modification of the surface. Thus, the cleaning technique must be related to the chemistry of the crown material and the bonding agent.

There is also a need to simplify the cementation/bonding process. This standardization becomes important for dentists due to the economics of materials, patient treatment time, and the technique sensitivity of the cementation/bonding process. One area of the bonding protocol that can be simplified is the cleaning of the prosthesis after try-in.

Ceramic cleaning methods after try-in procedures have a significant influence on the resin-ceramic bond strength.

With the introduction of a new cleaning mechanism, the bond strength must be examined to ensure the successful cleaning of the intaglio surface and maintenance of overall bond strength.

Research objective

Purpose

This study evaluated the influence of saliva contamination and the effect of several cleaning methods, on the resin bond durability to zirconia. Shear tests will be performed to assess the shear bond strength of specimens after 24 h of storage or after thermocycling as an aging method.

Null Hypothesis

The null hypothesis to be tested is that cleaning methods or storage conditions will not influence bonding to zirconia.

Alternative Hypothesis

The cleaning methods employed after saliva contamination positively influence bonding to zirconia. More specifically, the shear bond strength of resin cement to zirconia was improved after cleaning with one or more cleaning agents both immediately and after thermal aging (thermocycling).

Review of Literature

Dental ceramics

Dental ceramics have increasingly become the choice for indirect restorations because of their esthetic and structural properties. Ceramic restoration materials can be divided into two different subgroups: silica-based glass and nonsilica–based ceramics [31]. Kelly [32] described dental ceramics in three different categories based on their composition; predominantly glass, particle-filled glass, and polycrystalline. Predominantly, glass and particle-filled glass ceramics can generally be classified under silica-based ceramics, while polycrystalline ceramics describe the non-silica-based ceramics. Each group has different attributes and properties that lend themselves to different clinical situations that will be further discussed. Kelly [32] also finds it important to understand that any dental ceramic within these categories is also considered a composite, meaning a composition of two or more entities. The addition of materials into the glass matrix or the crystalline structure will impart different properties to ceramics.

Zirconium-Oxide Ceramics

Recently, zirconia has become very popular due to its favorable esthetic properties, mechanical properties, and biocompatibility. [3] The fracture toughness of densely sintered zirconia ceramics is more than 1000MPa. The first biomedical application of zirconia occurred in 1969, but its use in dentistry started in the early 1990s. Zirconia ceramics are currently used for fixed restorations as a framework material because of their mechanical and optical properties. In terms of fracture resistance, zirconia-based fixed partial dentures have the potential to withstand physiological occlusal forces applied on the teeth and therefore provide an interesting alternative to metal-ceramic restorations. Zirconia ceramics have been used in the fabrication of ceramic veneers, single crowns, inlays and onlays, fixed partial denture prosthesis frameworks, dental implants, implant abutments, orthodontics brackets, endodontic posts, and surgical instruments. [33]

Zirconium oxide, also known as zirconia, is a white crystalline oxide of the metal element zirconium. It is processed and purified to produce porous bodies, which can be milled through CAD/CAM with great precision. Zirconia blocks can be milled at three different stages: green, pre-sintered, and fully sintered.[34] The original zirconia frameworks are milled from the green stage and pre-sintered zirconia blocks are enlarged to compensate for prospective material shrinkage (20 percent to 25 percent) that occurs during the final sintering stage.[35] The milling of green stage and pre-sintered zirconia blocks is faster and less wear-and-tear producing on hardware than the milling of fully sintered blocks. Due to the increased hardness of the fully sintered zirconia material, they are not subject to dimensional changes such as shrinkage after milling. Once densely sintered, a polycrystalline ceramic is produced that does not contain a glass phase like other dental ceramics.

Transformation Toughening

Depending on the temperature, zirconia crystals can have a monoclinic (M), tetragonal (T), or cubic structure. At high temperature, zirconia has a cubic structure. As temperature is lowered to 2370 C, the atoms rearrange themselves and the structure becomes tetragonal. Then, the tetragonal structure transforms to a monoclinic structure below 1170 C. The transformation from tetragonal to monoclinic results in a volume change (4 percent to 5 percent), which makes zirconia stronger and tougher than aluminum oxide. Some oxides such as yttrium oxide (Y2O3), magnesium oxide (MgO), calcium oxide (CaO), and others are added to zirconia to stabilize tetragonal crystal structure at room temperature. This partially stabilized zirconia has high flexural strength and fracture toughness.[4] A phenomenon of transformation toughening occurs when an increase in the tensile stresses at a crack tip causes the transformation form tetragonal to monoclinic phase, resulting in a localized expansion of 4 percent to 5 percent. Localized expansion triggers compressive stresses at the crack tip, which counteract the external tensile stresses, resulting in retarding crack propagation. Thus, the crack is closed until a much higher stress is applied. Yttrium-oxide stabilized tetragonal zirconia polycrystal (Y-TZP) has desirable mechanical properties for restorative dentistry.

Adhesion In Dentistry/Resin To Zirconia Bonding

Despite the good mechanical properties of zirconia, another major issue arises pertaining to the bonding of ceramic restoration to resin cements. [3] When bonding ceramic to tooth structure, two interfaces determine the final bond strength of the restoration: dentin- resin cement and ceramic-resin interfaces. Therefore, it is important to ensure optimal bond strength at these interfaces. The wettability of the conditioned adherent surface with resin cement is important for the bonding of ceramics regardless of the mechanism of bonding, for example, chemical micromechanical interlocking, or combination.[36] Zirconia is densely sintered and does not contain a glass phase; therefore, it cannot be etched with hydrofluoric acid to create micro retentive etching patterns. It does not contain any silica, so silanes cannot be used to promote bonding.

Composite Cements

Resin-based composite cements are currently the recommended material for adhesive luting of ceramic restorations.[37] Resin cements contain inorganic fillers and resin monomers, such as bisphenol A glycidyl methacrylate (BisGMA)/triethylene glycol dimethacrylate (TEGDMA), and urethane dimethyl acrylate(UDMA).[38] The amount of filler determines the viscosity and flow of the material. Filler-containing composite cements revealed higher bond strengths than resins without fillers, and hybrid composites showed better results than micro-filled resin composites. [37] Highly filled cements may improve abrasion resistance at the marginal area, reduce polymerization shrinkage, and facilitate removal of excess cement. Traditional resin cements do not contain an adhesive functional monomer such as methacryloxydecyl dihydrogen phosphate (MDP). Cement film thickness has been shown to have an effect on short and long term bond strengths. [38]

Resin composite cements can be classified into 3 different groups according to their initiation mode: auto polymerizing, photo activated, or dual-activated3. Each type of composite cement has its advantages and disadvantages. Photo activated cements have long handling times and rapid hardening when exposed to light. However, they can only be photo-initiated if light can pass through the ceramic material to an effective depth of cure. Auto polymerizing cements have fixed setting times, and are indicated for opaque materials and high-strength ceramics. Dual-activated cements have extended working times and controlled polymerization. Most dual-activated cements still need to be light cured for final polymerization and hardness.

Contamination

A good resin-ceramic bond obtained in a strictly controlled clean situation in-vitro might be compromised in clinical situations, leading to a significantly reduced bond. During the try-in procedure of the restoration, contamination of the intaglio surface by saliva, blood, or silicone is difficult to avoid. Saliva contamination is frequently one of the main reasons for decreased resin bond strength. [39]

Surface Treatments Of Zirconia

The composition and mechanical properties of zirconia crystalline ceramics differ from those of classic ceramics. Thus, bonding to zirconia has become a topic of interest. A strong resin bond relies on micromechanical interlocking and chemical bonding to the ceramic surface. To obtain durable retention of zirconia restoration, various surface treatments should be carried out before cementation to improve the bond strength of the resin cement to zirconia. Several treatments like sandblasting, acid etching, selective infiltration etching, surface coating, and laser irradiation have been studied in the recent years for adequate surface activation. [82640]

It was claimed that the sandblasted (with 50-um alumina particles) zirconia samples produce higher shear bond strength than others. The treatment of sandblasting was found to result in the loss of surface materials and to increase the surface roughness. However, this technique creates surface micro cracks resulting in apparent decrease in the strength, and fracture toughness of the zirconia.37 In 1998, Kern et al. achieved durable bond to airborne particle abraded (110 Al2O3 at 0.25 MPa) zirconia ceramic after 150 days of water storage with thermocycling using resin composite with a special adhesive monomer. In this study, airborne particle abrasion, silane application and use of Bis- GMA resin cement resulted in an initial bond that failed spontaneously after simulated aging. These findings were verified by a long-term study conducted by Wegner, in which specimens were subjected to two years of water storage and repeated thermocycling. [41]

As a different surface preparation method for bonding, tribochemical silica coating (Rocatec System) of zirconia ceramics air abraded with Al2O3 particles modified with silica has been introduced. [89424344] The authors indicated that the use of MDP- containing resin cements in conjunction with alumina particles air-abrasion is required to achieve a durable bond. The functional phosphate group of MDP (10- Methycryloxydecyl dihydrogen phosphate) forms a water-resistant chemical bond with zirconia. The MDP resin cements are hydrolytically stable and therefore tend not to decrease in bond strength overtime.[45]

It is somewhat debatable whether ultrasonic cleaning should be carried out after tribochemical silica coating treatment. Ultrasonic cleaning was suggested for enhancing the strength and durable bond between resin cement and titanium [46] but no significant influence was detected when testing the tensile bond strength between resin and zirconia after 30 days of water storage combined with 150 days of thermocycles.[47] Nishigawa et al. reported a negative effect of ultrasonic cleaning in distilled water in bonding to silica-coated zirconia ceramic compared to groups that were bonded without ultrasonic cleaning. [48] The study demonstrated that the ultrasonic bath in distilled water for 1 min reduced mean shear bond strength. Extending the ultrasonic bath time to 5 min even further reduced the shear bond strength. Thus, it was declared that ultrasonic cleaning of tribochemically silanized zirconia should be avoided. The decrease in bond strength was attributed to the fact that ultrasonic cleaning removed loose silica particles, and a significant amount of silica coating layer from the ceramic surface. However, a negative effect of ultrasonic cleaning in alcohol was not found. Thus, one may speculate that the negative effect on bonding might be related to the effect of water on the highly reactive silica-coated surface rather than to the ultrasonic cleaning itself.

Combined surface treatment with airborne particle abrasion and a specific adhesive monomer with a hydrolytic phosphate monomer has been proven for bonding to zirconia ceramics. Thus, several published research articles [78411594043474950] have demonstrated that the combination of surface grinding techniques and traditional resin cementation significantly increases the bond strength of zirconia to resin cement.

Cleaning Contaminated Zirconia

Saliva contamination is frequently one of the main reasons for reducing resin bond strength. [13 51 47 48 21 52 39 12 53 54 21] Yang et al. found a strong influence of saliva contamination and cleaning methods on resin bonding to zirconia and its durability. In his study, he found that non-covalent adsorption of salivary proteins on roughened “activated” air- borne particle abraded surface occurred during saliva immersion, which could not be removed by water rinsing as shown by XPS. Zirconia has a strong affinity for the phosphate group, which is found in saliva and other fluids. After saliva contamination, XPS (X-ray photoelectron spectroscopy) analysis revealed an organic coating that resisted complete removal with water rinsing, isopropanol, or phosphoric acid.[39]

According to Phark and colleagues, conventional contaminants like saliva, blood and die stone plays a significant role in bonding to modified zirconia surfaces.[16] They concluded that procedures such as clinical try-ins and laboratory-manufacturing procedures impart a thin layer of contaminants on the surface of the modified ceramic surface detrimental to bonding. The mechanism behind the contamination of zirconium oxide surfaces is well explained by Kweon et al. [17] Zirconium shows a strong affinity to the phosphate group in that the zirconium surfaces react with phosphoric acid in an acid-base reaction. Consequently, saliva and other body fluids that contain various phosphate groups, such as phospholipids, can react irreversibly with zirconium surface and thus make cleaning a very difficult task.

Zhang found that saliva contamination adversely affects resin bonding to zirconia because it deposits an organic adhesive coating on the restorative materials in the first few seconds of the exposure, which is washing-resistant. [51] The finding by Aboush study suggested that ceramic surfaces should be treated with silane before try-in procedures. After intraoral try-in, it is recommended to treat ceramic surfaces with phosphoric acid before applying fresh layers of silane to ensure proper bonding.[52] But according to Zhang et al., phosphoric acid cleaning effectively removed saliva contamination from coated bonding surfaces, but was not so effective in the removal of the silicone disclosing agent.[51] Cleaning with acetone was only effective in the elimination of silicone contaminants, but not for removing salivary residues. Therefore, phosphoric acid or acetone might not serve as an effective cleaning agent. Kern observed a significant decrease in the bond strength of the resin to zirconia after cleaning with phosphoric acid.[40]

Therefore, factors influencing resin bonding to zirconia ceramic include the wettability of ceramic by adhesive resin, the roughness of ceramic surface, the composition of adhesive resin, the handling performance of adhesive resin, and possible contamination during bonding procedures. Several studies have shown different methods to remove contamination, but none of the methods has been proven to be the best. So, this study investigated the effect of saliva contamination and subsequent cleansing methods on zirconia shear bond strength durability with resin cement. Nonabrasive universal cleaning agents were used to clean saliva contamination, and shear bond strength was determined by a universal testing machine. The failure mode was checked under a light microscope.

Testing Conditions and Methods

Intraoral conditions produce chemical, thermal, and mechanical influences on the ceramic-resin bond.[31] It is necessary to try and replicate these in the laboratory to draw conclusions on the bonds durability. Wegner et al.[9] showed that different storage conditions can affect the tested bonding systems differently regarding the durability of the bond. Long-term water storage and thermocycling of bonded specimens are accepted as ways to simulate aging and to stress the bond interface. Water storage and thermocycling affect the resin itself due to the different coefficient of thermal expansions of the filler particles and surrounding matrix.[9] Significant reduction in bond strength occurs after mechanical cyclic loading.

Preferred bond strength tests are the 3-point bending test, the tensile and micro- tensile test, and the shear and micro-shear test. The most common testing method is the shear bond test. The modified tensile tests may be preferred to eliminate the occurrence of non-uniform interfacial stresses typical to conventional tensile and shear bond tests.[31] The Ultradent shear bond strength testing apparatus is an available system to prepare and test samples for shear bond strength. The Ultradent system provides a standard way to prepare samples by providing a known area for bonding and uniform resin cement addition. The resin piece fits precisely into the crosshead assembly to ensure the force is placed directly on the bonded area and perpendicular to the resin piece.

Materials and methods

Specimen Fabrication

Square-shaped samples of unprocessed zirconium-oxide ceramic (KATANA Zirconia STML, Kuraray Noritake, Japan) with the dimensions 9 mm × 8 mm × 3 mm were fabricated and then sintered in an induction furnace (CEREC SpeedFire, Dentsply Sirona, Germany) N=20, total N=100. **(Fig 1)** Specimens were embedded in copper molds using PMMA (Polymethyl methacrylate) with one surface exposed for bonding. **(Fig 2)** Specimens were ground finished with up to 800-grit silicon carbide abrasive under cooling water. Cylindrical composite resin specimens (2.1 mm diameter, 3 mm height) were fabricated using a standardized mold and packable composite resin material. **(Fig 3)** Composite resin specimen surfaces were standardized using 800-grit silicon carbide abrasive. The zirconia specimens were cleaned with ultrasonication in alcohol for 3 min and air-particle abraded with 50 um aluminum oxide particles, 2.8 Bar pressure from a distance of 1 cm at a 90-degree angle for 15 seconds.

Contamination Protocol and Experimental Design

Following air-abrasion treatment, the zirconia specimens were divided into five groups according to the experimental design.

Specimens were immersed in 2 mL-stimulated saliva (from saliva bank under IRB approval #1303010880) for 1 min and divided into four experimental groups according to the cleaning methods, as follows:

Group 1: Control

Zirconia samples were air-particle abraded with 50 um aluminum oxide particles, 2.8 Bar pressure from a distance of 1 cm at a 90-degree angle for 15 seconds, contaminated with saliva and cleaned in an ultrasonic cleaning bath in alcohol for 5 min. **(Fig 4)**

Group 2: APC

After the saliva contamination, samples were cleaned in an ultrasonic cleaning bath in alcohol for 5 min and air-particle abraded with 50 um aluminum oxide particles, 2.8 Bar pressure from a distance of 1 cm at a 90-degree angle for 15 seconds. **(Fig 5)**

Group 3: Katana (KC)

After the saliva contamination, samples were rinsed with water spray and dried with oil-free air. The bonded surface of the restoration was covered with a layer of Katana cleaner. After 10 seconds, the samples were rinsed with water spray and dried with oil free air. **(Fig 6)**

Group 4: Ivoclean (IC)

After the saliva contamination, samples were rinsed with water spray and dried with oil-free air. The bonded surface of the restoration was covered with a layer of Ivoclean. After 20 seconds, the samples were rinsed with water spray and dried with oil free air. **(Fig 7)**

Group 5: ZirClean (ZC)

After the saliva contamination, samples were rinsed with water spray and dried with oil-free air. The bonded surface of the restoration was covered with a layer of ZirClean. After 20 seconds, the samples were rinsed with water spray and dried with oil free air. **(Fig 8)**

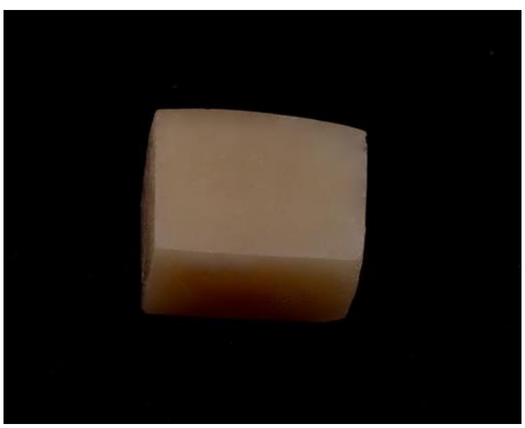

Fig 1: Sintered samples of zirconium-oxide ceramic.

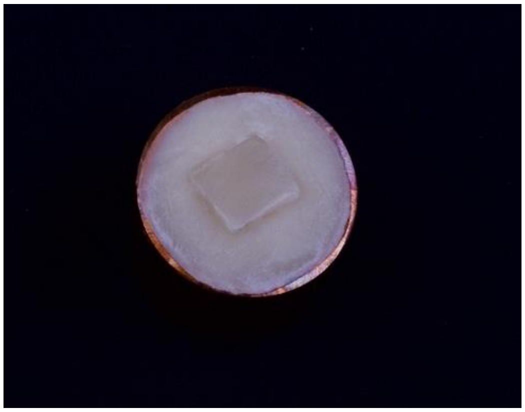

Fig 2: Specimens embedded in copper molds with one surface exposed for bonding.

Fig 3: Cylindrical composite resin specimens.

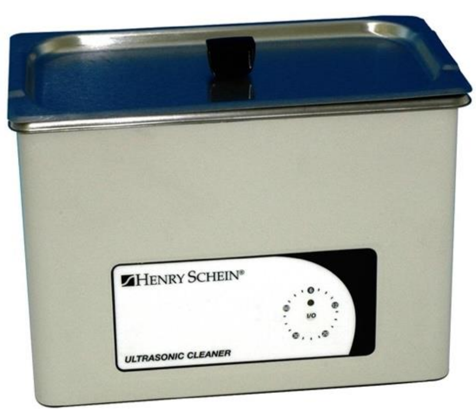

Fig 4: Ultrasonic cleaner.

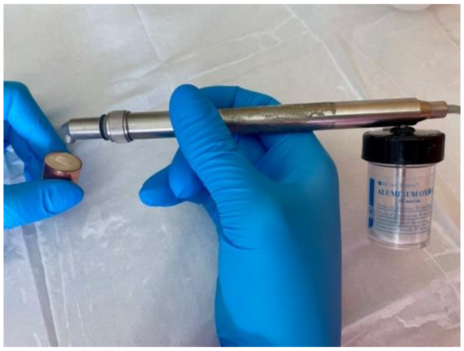

Fig 5: Chair-side Air Abrasion.

Fig 6: Katana Cleaner.

Fig 7: Ivoclean Cleaner.

Fig 8: ZirClean Cleaner.

Bonding Procedure

After the samples received the assigned cleaning regimen a single-component adhesive primer (Clearfil ceramic primer plus, Kuraray Noritake) was applied with a brush on the samples and then dried with using mild, oil-free air flow.

Cylindrical composite resin specimens (2.1 mm diameter, 3 mm height) were bonded to the zirconia surfaces with dual cure resin cement (Panavia V5; Kuraray Noritake) according to manufacturer's instructions. **(Fig 9,10) (Table2)**

A load of 1000 g was applied for 10 min during the cementation process and light irradiated for 20 s from the buccal, lingual, mesial and distal sides for 80 seconds with a hand- held light curing device. Excess cement was removed.

Aging method

Specimens were stored in distilled water at 37° C for 24 h. Short-term thermocycling of 10,000 cycles was applied over 9 days 30 s dwell time and 5 seconds between baths. **(Fig 11)**

Shear bond strength

Specimens were placed in a fixture on a universal testing machine (Instron), aligned with the shearing blade just touching the bonding interface. A shear load was applied until failure at a crosshead speed of 0.5 mm/min. Loads were converted to MPa by dividing the failure load by the bonding surface area. **(Fig 12)**

Failure analysis

The fractured surfaces were inspected using a stereo microscope to evaluate the failure mode and were classified as adhesive, cohesive, or mixed failures approximated by the amount of remaining resin cement on the ceramic surface with respect to the bonding surface area. **(Fig 13)**

Statistical analysis

The data were analyzed by one-way ANOVA and pairwise comparisons (Posthoc bonferroni test) with α=0.05.

Fig 9: Cylindrical composite resin specimens bonded to the zirconia surfaces with dual cure resin cement.

Fig 10: Dual cure resin cement (Panavia V5; Kuraray Noritake).

Properties:

- Filler loading: 61 gew% (38 vol%)
- Flexural strength[1,2]: 127 MPa
- Flexural modulus[1,2]: 6,3 GPa
- Compressive strength[1]: 310 MPa
- Water sorption[1,2]: 21 µg/mm³
- Film thickness[1,2]: 12 µm

- Radiopacity[2]: 180% Al
- Fluoride releasing (28 days)[1]: 58 µg/g
- Working time: (23˚C) 2 min.
- Curing time: (light) 10 sec.

[1]Dual curing of the paste (combination of self- and light-curing)
[2]According to ISO 4049:2009. Source: Kuraray Noritake Dental Inc.

Paste A/Paste B
• Bisphenol A diglycidylmethacrylate (Bis-GMA)
• Triethyleneglycol dimethacrylate (TEGDMA)
• Hydrophobic aromatic dimethacrylate
• Hydrophilic aliphatic dimethacrylate
• Initiators
• Accelerators
• Silanated barium glass filler
• Silanated fluoroalminosilicate glass filler
• Colloidal silica Bisphenol A
• diglycidylmethacrylate (Bis-GMA)
• Hydrophobic aromatic dimethacrylate
• Hydrophilic aliphatic dimethacrylate

• Silanated barium glass filler
• Silanated alminium oxide filler
• Accelerators
• dl-Camphorquinone
• Pigments
CLEARFIL™ Ceramic Primer Plus
• 3-Methacryloxypropyl trimethoxysilane
• 10-Methacryloxypropyl dihydrogen phosphate (MDP)
• Ethanol
PANAVIA™ V5 Tooth Primer
• 10-Methacryloyloxydecyl dihydrogen phosphate (MDP)
• 2-Hydroxyethyl methacrylate (HEMA)
• Hydrophilic aliphatic dimethacrylate
• Accelerators
• Water

Table 2: Dual cure resin cement (Panavia V5; Kuraray Noritake) Contents.

Fig 11: Huber SD Mechatronik Thermocycler.

Fig 12: Universal testing machine Instron.

Fig 13: Scanning electron microscope (FEI Quanta 600 ESEM; FEI Co)

Results

Shear Bond Strength

The mean, standard deviation, and standard error values of shear bond strength (SBS) are summarized in Tables 3-7 and Figures 14-18 for five different cleaning groups and the two different storage conditions. The cleaning method, storage condition, and their interaction had significant impacts on shear bond strength.

The intergroup comparisons of mean shear bond strength under normal conditions and under thermocycling are summarized in Tables 8-11 and in Figures 19-20.

<u>The intra-group comparisons: Group 1-Control</u>

A two-tailed t-test for independent samples showed that the difference between Group 1 - Control (NC) and Group 1 - Control (TC) with respect to the dependent variable was **statistically significant**, $t(10.02) = 4.71$, $p = .001$, 95% confidence interval [8.28, 23.14]. Thus, the null hypothesis is rejected.

Group 1 Control	Descriptive statistics			Paired *t*-test	*P*-value (2-tailed)
	Mean	Std. Deviation	Std. Error Mean		
NC	52.78	2.76	0.87	11.75	<0.001*
TC	18.97	8.67	2.74		

*Unequal variances

Table 3: Paired t-test statistical analysis for Group 1-Control

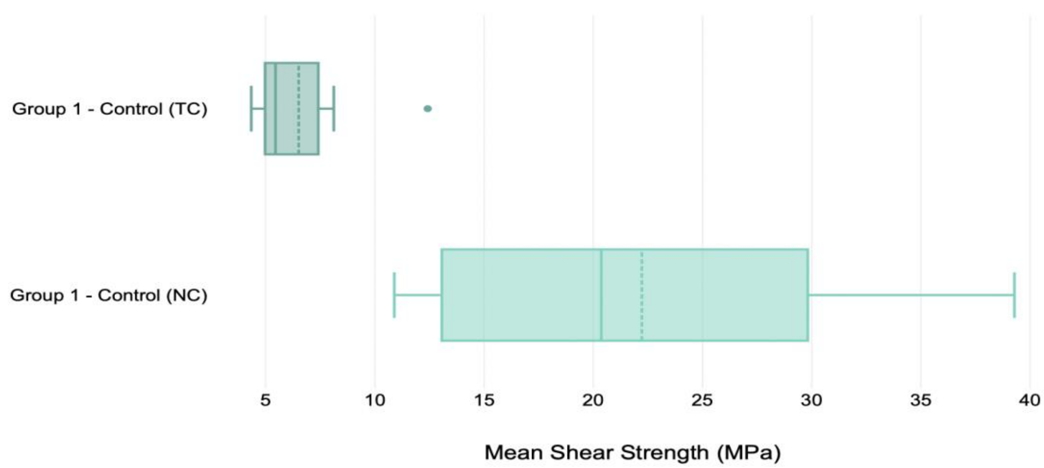

Fig 14: Box Plot showing mean and standard deviation values for Group 1-Control

The intra-group comparisons: Group 2-APC

A two-tailed t-test for independent samples showed that the difference between Group 2 - APC (NC) and Group 2 - APC (TC) with respect to the dependent variable was **statistically significant**, $t(10.8) = 11.75$, $p = <.001$, 95% confidence interval [27.46, 40.16]. Thus, the null hypothesis is rejected.

Group 2 APC	Descriptive statistics			Paired *t*-test	*P*-value (2-tailed)
	Mean	Std. Deviation	Std. Error Mean		
NC	52.78	2.76	0.87	11.75	<0.001*
TC	18.97	8.67	2.74		

*Unequal variances

Table 4: Paired t-test statistical analysis for Group 2-APC

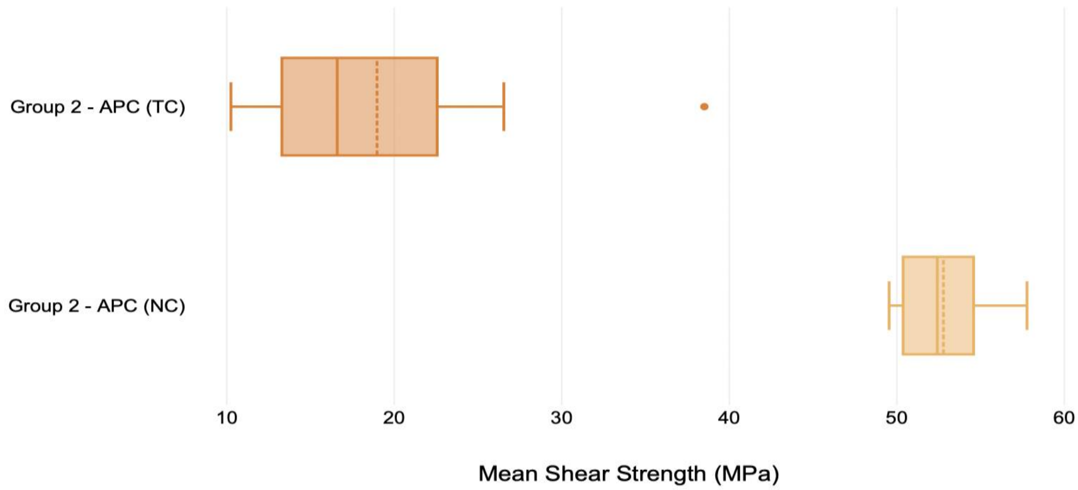

Fig 15: Box Plot showing mean and standard deviation values for Group 2-APC

<u>The intra-group comparisons: Group 3-Katana Cleaner (KC)</u>

A two-tailed t-test for independent samples showed that the difference between Group 3 - Katana Cleaner (KC) (NC) and Group 3 - Katana Cleaner (KC) (TC) with respect to the dependent variable was **statistically significant**, $t(16.19) = 3.1$, $p = .007$, 95% confidence interval [5.19, 27.49]. Thus, the null hypothesis is rejected.

Group 3 Katana Cleaner (KC)	Descriptive statistics			Paired *t*-test	*P*-value (2-tailed)
	Mean	Std. Deviation	Std. Error Mean		
NC	33.45	13.59	4.3	3.1	0.007*
TC	17.11	9.6	3.04		

*Unequal variances

Table 5: Paired t-test statistical analysis for Group 3-Katana Cleaner (KC)

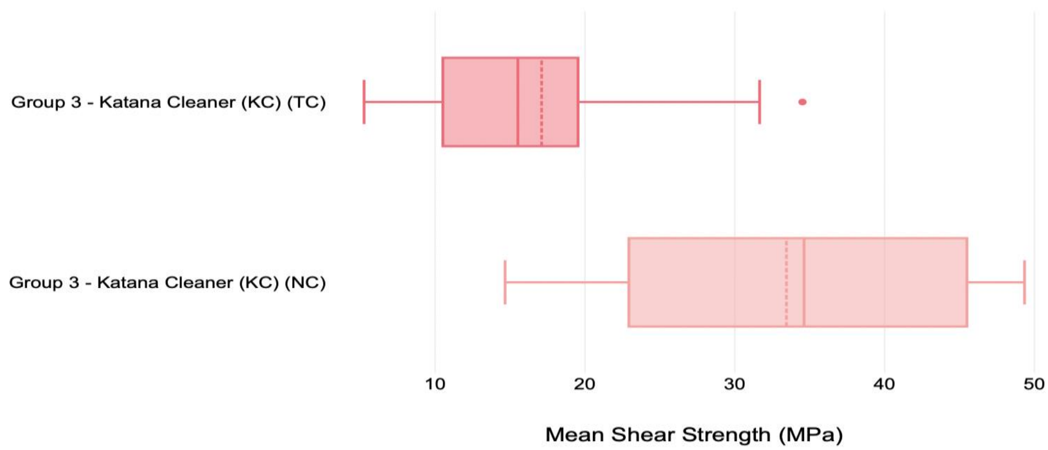

Fig 16: Box Plot showing mean and standard deviation values for Group 3-Katana Cleaner (KC)

The intra-group comparisons: Group 4-Ivoclean (IC)

A two-tailed t-test for independent samples showed that the difference between Group 4 - Ivoclean (IC) (NC) and Group 4 - Ivoclean (IC) (TC) with respect to the dependent variable was statistically significant, $t(11.34) = 5.49$, $p = <.001$, 95% confidence interval [11.05, 25.76]. Thus, the null hypothesis is rejected.

Group 4 Ivoclean (IC)	Descriptive statistics			Paired *t*-test	*P*-value (2-tailed)
	Mean	Std. Deviation	Std. Error Mean		
NC	34.66	9.97	3.15	5.49	<0.001*
TC	16.26	3.62	1.15		

*Unequal variances

Table 6: Paired t-test statistical analysis for Group 4-Ivoclean (IC)

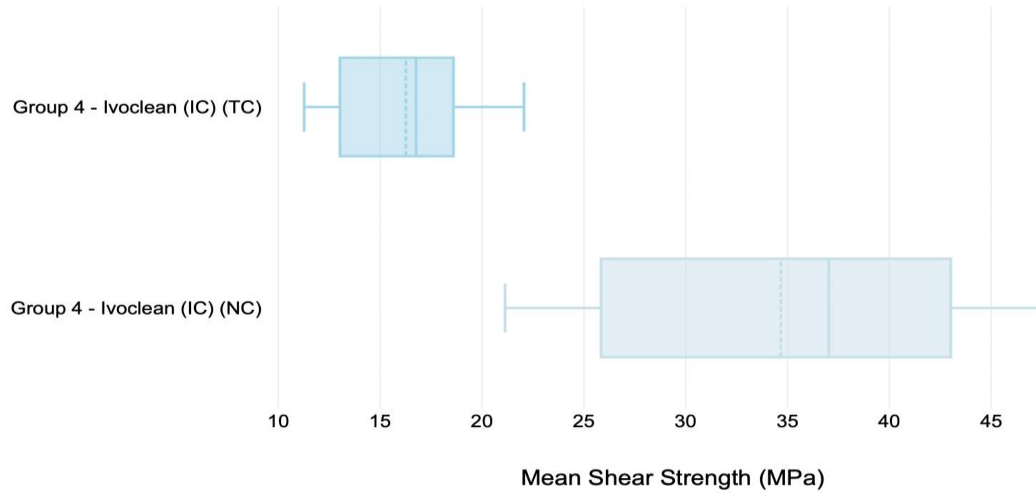

Fig 17: Box Plot showing mean and standard deviation values for Group 4-Ivoclean (IC)

<u>The intra-group comparisons: Group 5-Zirclean (ZC)</u>

A two-tailed t-test for independent samples showed that the difference between Group 5 - ZirClean (ZC) (NC) and Group 5 - ZirClean (ZC) (TC) with respect to the dependent variable was **statistically significant**, $t(9.72) = 3.76$, $p = .004$, 95% confidence interval [7.15, 28.12]. Thus, the null hypothesis is rejected.

Group 5 ZirClean (ZC)	Descriptive statistics			Paired *t*-test	*P*-value (2-tailed)
	Mean	Std. Deviation	Std. Error Mean		
NC	32.77	14.53	4.6	3.76	0.004*
TC	15.13	2.9	0.92		

*Unequal variances

Table 7: Paired t-test statistical analysis for Group 5-ZirClean (ZC)

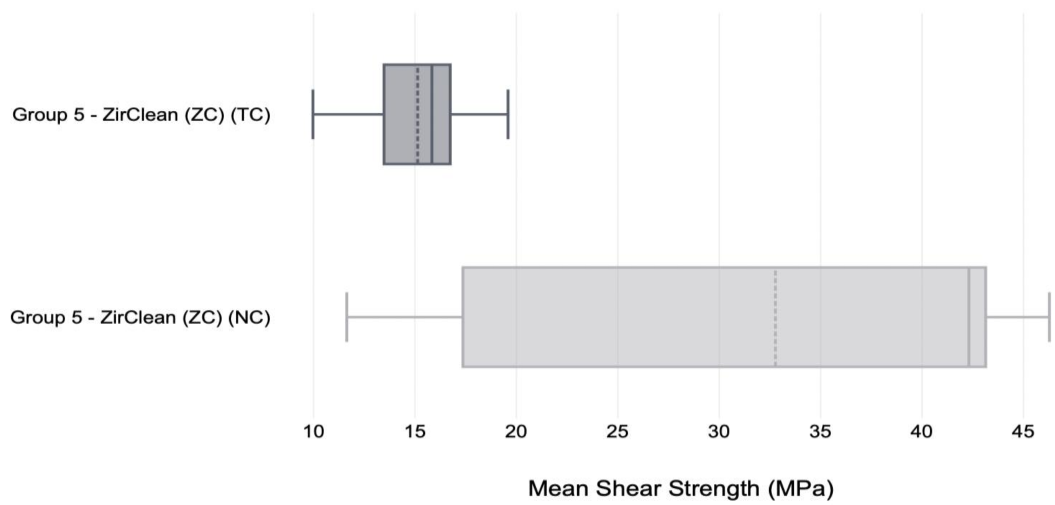

Fig 18: Box Plot showing mean and standard deviation values for Group 5-ZirClean (ZC)

Inter-group comparison (NC)

	Group 1 - Control	Group 2 - APC	Group 3 - Katana Cleaner (KC)	Group 4 - Ivoclean (IC)	Group 5 - ZirClean (ZC)
Mean	22.22	52.78	33.45	34.66	32.77
Median	20.37	52.42	34.63	37.03	42.31
Modal	10.89	49.54	14.67	21.13	11.64
Std. Deviation	10.26	2.76	13.59	9.97	14.53
Minimum	10.89	49.54	14.67	21.13	11.64
Maximum	39.28	57.77	49.34	47.47	46.28
Range	28.39	8.23	34.67	26.34	34.64
95% Confidence interval	2.11; 42.34	47.37; 58.19	6.81; 60.09	15.13; 54.2	4.29; 61.25
Mean ± Std.	22.22 ± 10.26	52.78 ± 2.76	33.45 ± 13.59	34.66 ± 9.97	32.77 ± 14.53

Table 8: Descriptive Statistical Analysis for all groups (NC)

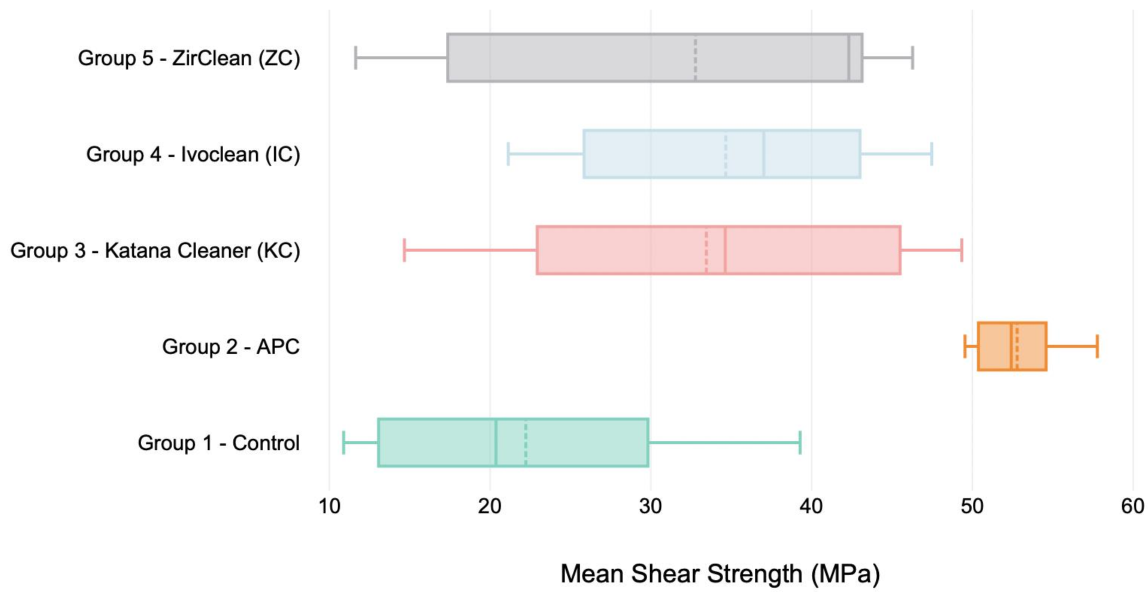

Fig 19: Box Plot showing mean and standard deviation values for all groups (NC)

Bonferroni Post-hoc-Test

A one factor analysis of variance has shown that there is a significant difference between the categorical variable and the dependent variable p=<.001 with group 2-APC having the highest mean shear bond strength in comparison to all other groups.

Variables	Average difference	t	p
Group 1 - Control - Group 2 - APC	-30.56	-6.2	<.001
Group 1 - Control - Group 3 - Katana Cleaner (KC)	-11.23	-2.28	0.028
Group 1 - Control - Group 4 - Ivoclean (IC)	-12.44	-2.52	0.015
Group 1 - Control - Group 5 - ZirClean (ZC)	-10.55	-2.14	0.038
Group 2 - APC - Group 3 - Katana Cleaner (KC)	19.33	3.92	<.001
Group 2 - APC - Group 4 - Ivoclean (IC)	18.12	3.67	0.001
Group 2 - APC - Group 5 - ZirClean (ZC)	20.01	4.06	<.001
Group 3 - Katana Cleaner (KC) - Group 4 - Ivoclean (IC)	-1.21	-0.25	0.807
Group 3 - Katana Cleaner (KC) - Group 5 - ZirClean (ZC)	0.68	0.14	0.891
Group 4 - Ivoclean (IC) - Group 5 - ZirClean (ZC)	1.89	0.38	0.703

Table 9: One factor analysis of variance for all groups (NC)

Inter-group comparison (TC)

	Group 1 - Control	**Group 2 - APC**	**Group 3 - Katana Cleaner (KC)**	**Group 4 - Ivoclean (IC)**	**Group 5 - ZirClean (ZC)**
Mean	6.51	18.97	17.11	16.26	15.13
Median	5.45	16.6	15.53	16.76	15.83
Modal	4.34	10.25	5.26	11.27	9.97
Sum	65.12	189.69	171.09	162.59	151.34
Std. Deviation	2.44	8.67	9.6	3.62	2.9
Variance	5.96	75.22	92.24	13.14	8.43
Minimum	4.34	10.25	5.26	11.27	9.97
Maximum	12.42	38.51	34.52	22.06	19.59
Range	8.08	28.26	29.26	10.79	9.62
Quartile 1	4.97	13.29	10.52	13.03	13.48

Quartile 2	5.45	16.6	15.53	16.76	15.83
Quartile 3	7.41	22.56	19.54	18.6	16.74
Skew	1.77	1.37	0.85	-0.06	-0.45
95% Confidence interval	1.73; 11.3	1.97; 35.97	-1.72; 35.93	9.15; 23.36	9.44; 20.83
Mean ± Std.	6.51 ± 2.44	18.97 ± 8.67	17.11 ± 9.6	16.26 ± 3.62	15.13 ± 2.9

Table 10: Descriptive Statistical Analysis for all groups (TC)

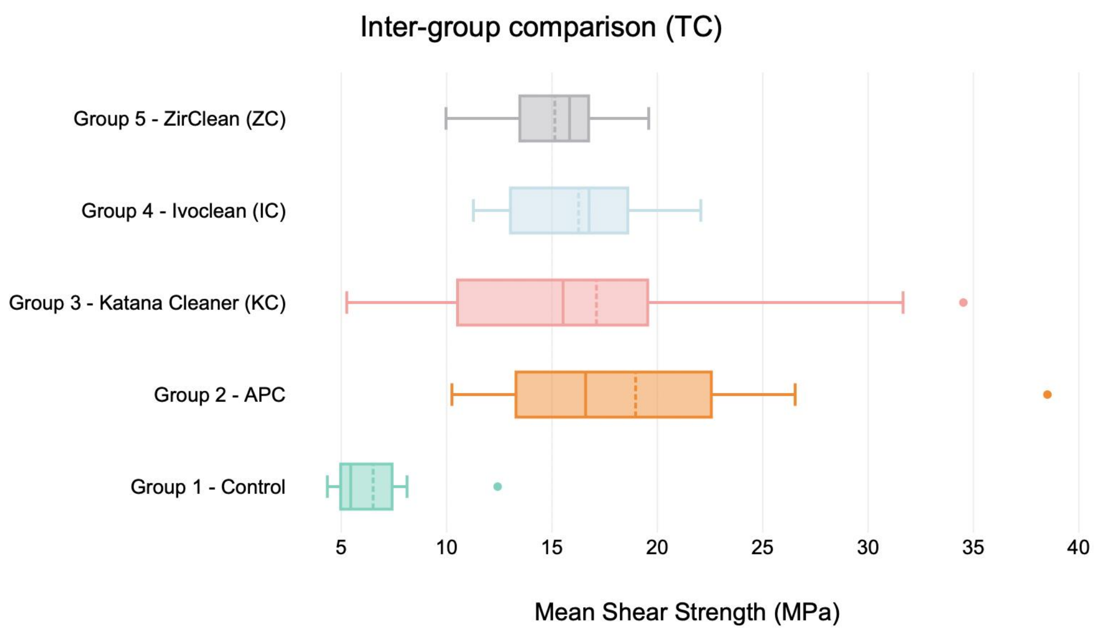

Fig 20: Box Plot showing mean and standard deviation values for all groups (TC)

Bonferroni Post-hoc-Test

A one factor analysis of variance has shown that there is a significant difference between the categorical variable and the dependent variable p=<.001 with groups 2-APC having the highest mean shear bond strength in comparison to all other groups.

Variables	Average difference	t	p
Group 1 - Control - Group 2 - APC	-12.46	-4.46	<.001
Group 1 - Control - Group 3 - Katana Cleaner (KC)	-10.6	-3.79	0.001
Group 1 - Control - Group 4 - Ivoclean (IC)	-9.75	-3.49	0.001
Group 1 - Control - Group 5 - ZirClean (ZC)	-8.62	-3.09	0.001
Group 2 - APC - Group 3 - Katana Cleaner (KC)	1.86	0.67	0.509
Group 2 - APC - Group 4 - Ivoclean (IC)	2.71	0.97	0.337
Group 2 - APC - Group 5 - ZirClean (ZC)	3.84	1.37	0.177
Group 3 - Katana Cleaner (KC) - Group 4 - Ivoclean (IC)	0.85	0.3	0.762
Group 3 - Katana Cleaner (KC) - Group 5 - ZirClean (ZC)	1.98	0.71	0.483
Group 4 - Ivoclean (IC) - Group 5 - ZirClean (ZC)	1.13	0.4	0.689

Table 11: One factor analysis of variance for all groups (TC)

SEM Analysis

The fractured surfaces were inspected with a stereo microscope to evaluate the failure mode and were classified as adhesive, cohesive or mixed failures approximated by the amount of remaining resin cement on the ceramic surface in respect to the bonding surface area.

A scanning electron microscope (FEI Quanta 600 ESEM; FEI Co) in the Singh Center for Nanotechnology at University of Pennsylvania was used to image and evaluate the failure modes.
Images of the specimens were captured at 75x, and 500x magnification for detailed evaluation.

Majority of the specimens had a mixed failure mode and photos from SEM evaluation can be noted here.

<u>Failure Analysis: Group 1-Control</u>

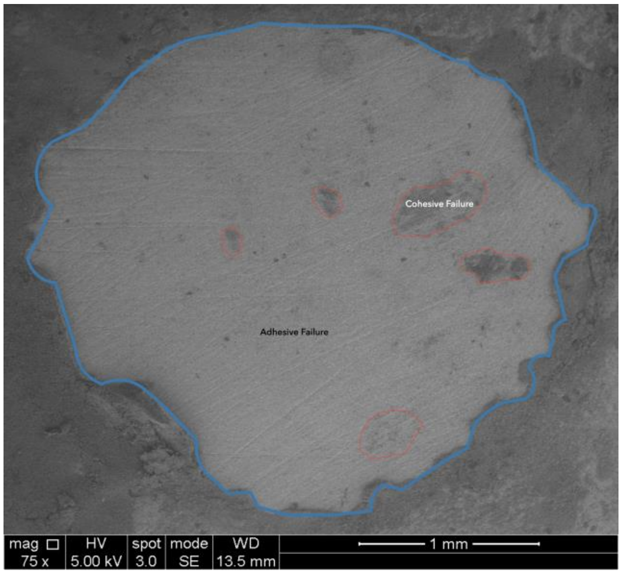

Fig 21: Sample with thermocycling (TC) has mixed failure with 17% of the specimen showing cohesive failure and 83% showing adhesive failure exposing the zirconia surface.

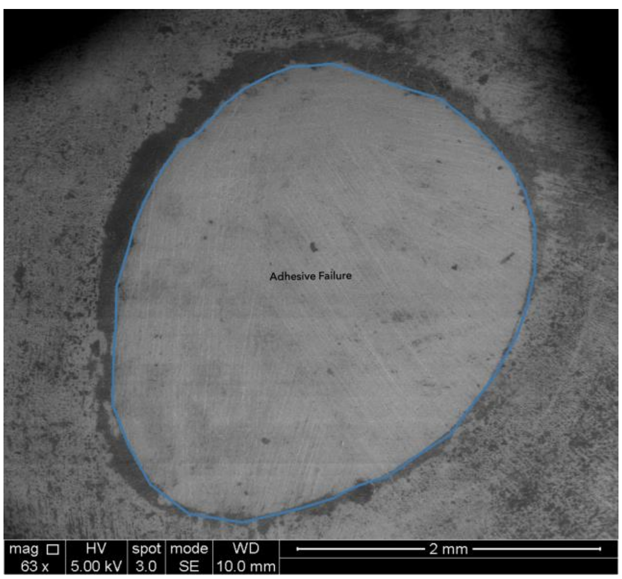

Fig 22: Sample without thermocycling (NC) has 100% showing adhesive failure exposing the zirconia surface.

Failure Analysis: Group 2-APC

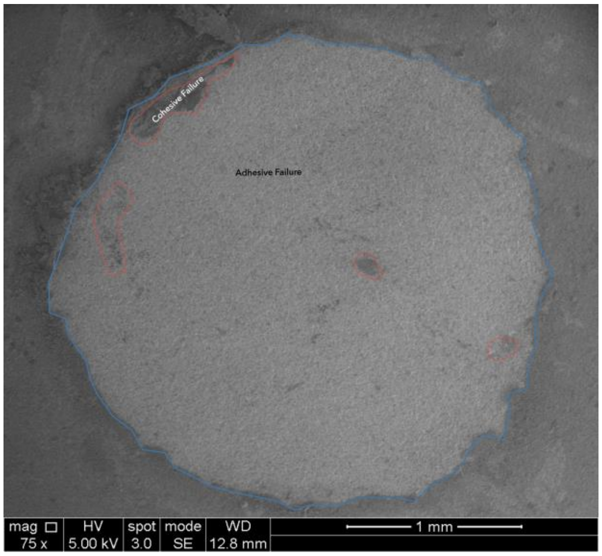

Fig 23: Sample with thermocycling (TC) has mixed failure with 15% of the specimen showing cohesive failure and 85% showing adhesive failure exposing the zirconia surface.

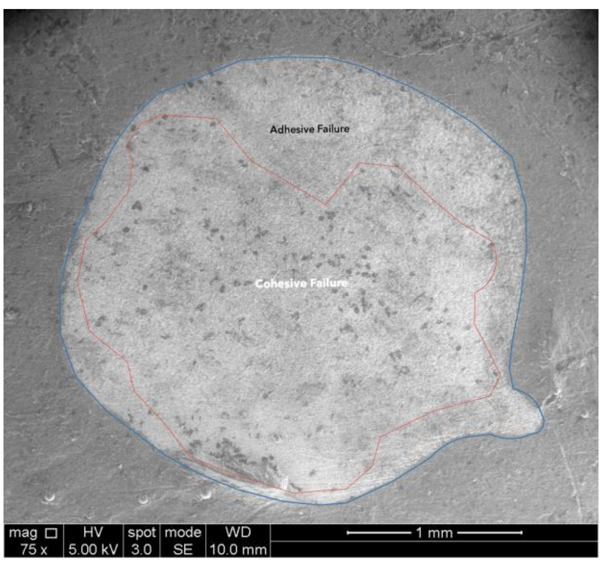

Fig 24: Sample without thermocycling (NC) has mixed failure with 70% of the specimen showing cohesive failure and 30% showing adhesive failure exposing the zirconia surface.

Failure Analysis: Group 3-Katana Cleaner (KC)

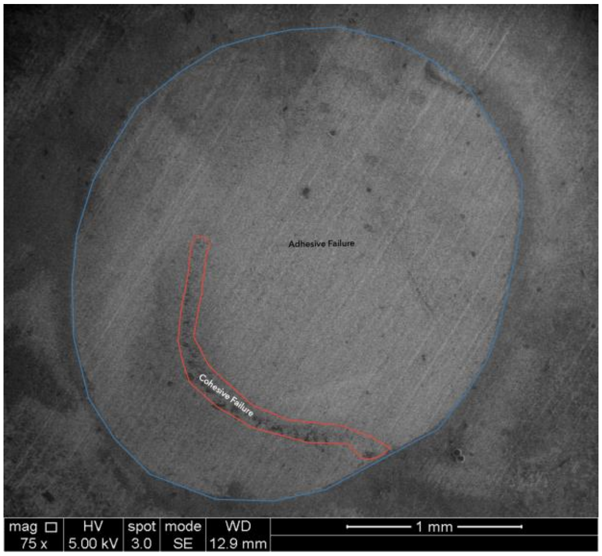

Fig 25: Sample with thermocycling (TC) has mixed failure with 17% of the specimen showing cohesive failure and 83% showing adhesive failure exposing the zirconia surface.

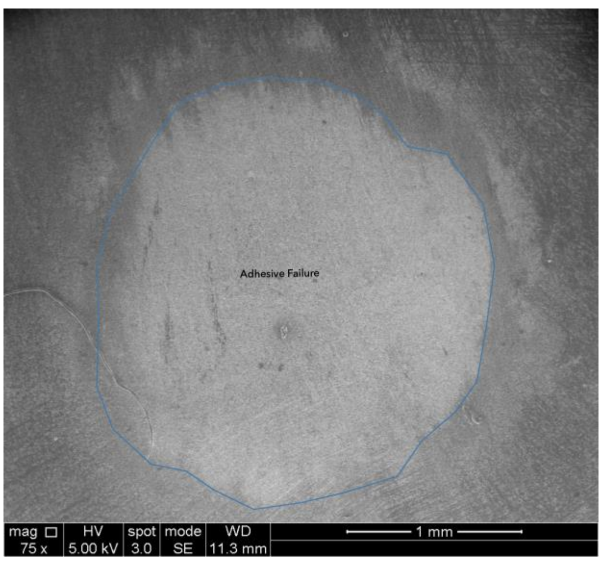

Fig 26: Sample without thermocycling (NC) has 100% showing adhesive failure exposing the zirconia surface.

<u>Failure Analysis: Group 4-IvoClean (IC)</u>

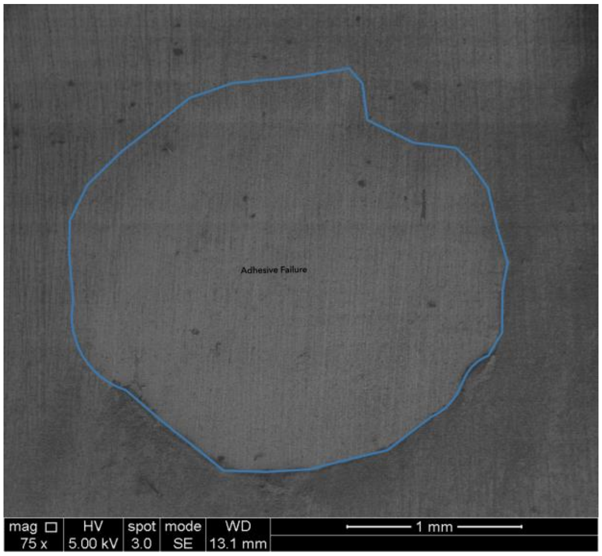

Fig 27: Sample with thermocycling (TC) has 100% of the specimen exposing the zirconia surface.

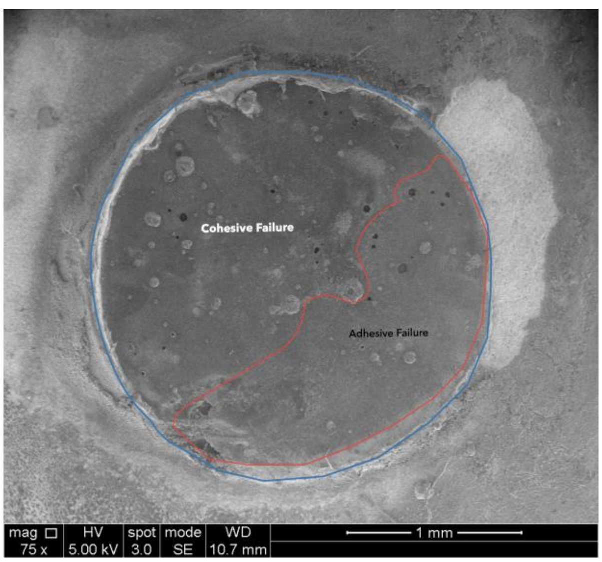

Fig 28: Sample without thermocycling (NC) has mixed failure with 40% of the specimen showing cohesive failure and 60% showing adhesive failure exposing the zirconia surface.

Failure Analysis: Group 5-ZirClean (ZC)

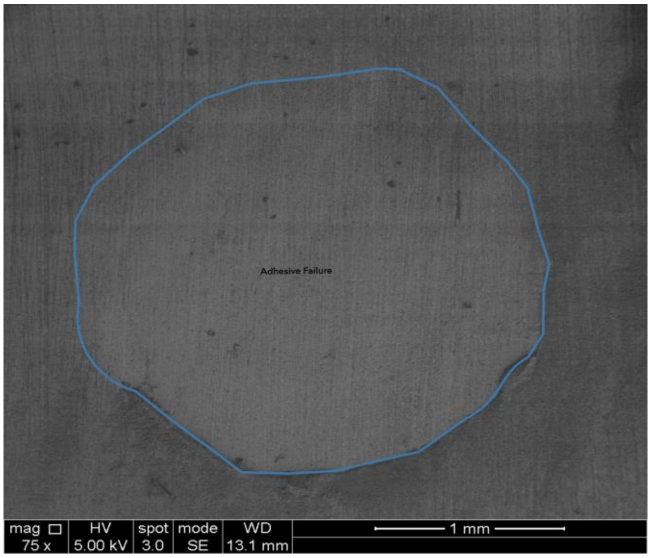

Fig 29: Sample with thermocycling (TC) has 100% of the specimen exposing the zirconia surface.

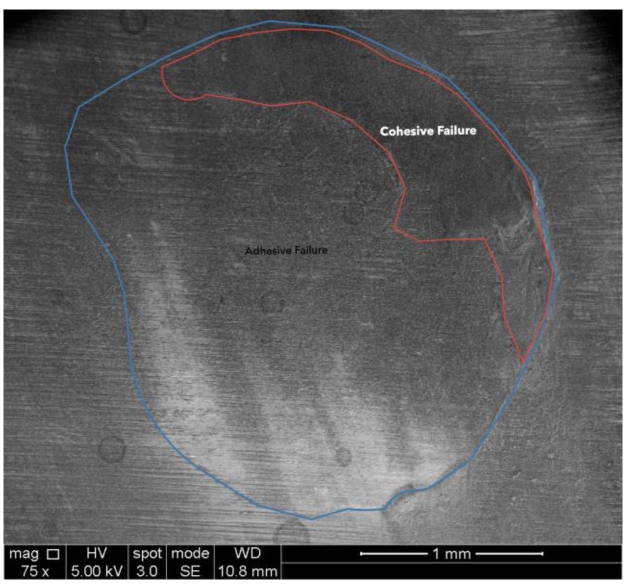

Fig 30: Sample without thermocycling (NC) has mixed failure with 25% of the specimen showing cohesive failure and 75% showing adhesive failure exposing the zirconia surface.

Discussion

The results of this study reject the null hypothesis that cleaning methods or storage conditions do not influence bonding to zirconia.

All tested groups had significantly higher bond strength compared to the control group and showed a significant effect of the aging protocol.

Air-borne particle abrasion produced the highest shear bond strength (36 MPa) of all tested cleaning methods, suggesting the complete surface restoral. Although mechanical surface abrasion has been reported to be the most effective way to decontaminate a ceramic surface, it remains a controversial method, nonetheless. [5326] Particle abrasion roughens the surface, which increases the wettability and surface energy in zirconia, allowing for improved retention.[39] However, particle abrasion may induce deleterious effects on the mechanical properties of zirconia. Phark et al., examined the effects of particle abrasion on the shear bond strength of zirconia.[26] They concluded that regardless of the particle size tested (50 and 110 μm), abrasion increased the shear bond strength. A similar study by Özcan et al. examined the effects of particle abrasion on the biaxial flexural strength of the zirconia using the same abrasion parameters.[55] Conversely, they concluded that an increase in the biaxial flexural strength after abrasion due to an increase in the monoclinic phase. Although the effect of abrasion on the mechanical properties of zirconia remains controversial, it is an effective method for mechanically detaching the contaminants from the surface.

The introduction of ceramic cleaners has provided clinicians with a simple step-by-step cleaning method for restoring ceramic surfaces after contamination. The manufacturer advertises Ivoclean as an alkaline extraoral universal ceramic cleaner. Ivoclean has been reported as an effective way of restoring ceramic surfaces. [218] Ivoclean is a solution composed of highly concentrated zirconia oxide particles that form a concentration gradient, creating an increased affinity for phosphate compared to the ceramic surface. Increased affinity in the solution removes organic contaminants from the zirconia surface, which can then be rinsed away with water. ZirClean is also an alkaline cleaner for use on zirconia and other ceramic restorations after try-in. Its alkalinity is due to potassium hydroxide, which interrupts the ionic bond formed between the contaminant and the zirconia surface. [19] Unlike Ivoclean and ZirClean, Katana Cleaner is acidic (pH 4.5) which allows either extraoral or intraoral application. The manufacturer advertises the product as a universal cleaner capable of removing contamination from a wide variety of dental materials and tooth structure. An MDP salt acts as the active ingredient, in which the hydrophobic methacrylate ends of the MDP molecule attach to the organic contaminants that weaken the bond to the restorative surface.[20] The hydrophilic phosphate heads surround the contaminants, which allow them to be washed away with water. Limited information regarding the cleaning effectiveness of Ivoclean, ZirClean and Katana Cleaner is available from previous in vitro studies. Based on the results of this study, there was no significant difference in shear bond strength between the ceramic cleaners, each effectively removing organic contamination and restoring the bonding surface.

Group comparison showed that all groups presented lower results after Thermocycling. The predominant failure mode in the tested group was adhesive which shows that the surface contamination of the zirconia ceramic with saliva is related to the decreased bond strength. This result is in the agreement with the study conducted by Quaas et al. The study was designed to test the resin-ceramic bond strength and its durability related to the cleaning methods of contaminated ceramic bonding surface. They found that no cleaning after the contamination group led to the lowest bond strength values.[12 53]

Saliva contamination adversely affects resin bonding because organic deposits remain on the restorative material after a few seconds of exposure in saliva.[56] Prior studies [48 39] reported that water rinsing may not be effective in removing some saliva contaminants from the zirconia surface. Saliva contains 99 percent water combined with some proteins, glycoprotein, sugar, amylase and inorganic particles. Noncovalent adsorption of salivary proteins occurs on the restorative surface after saliva contamination, creating a thin residual film of organic protein that cannot be removed with water. This results in decreased bond strength and the inability to establish the bond strength of uncontaminated zirconia. It prevents chemical bonding to zirconia ceramics, while thermocycling then further interferes with the formation of a durable bond. Lower bond strength values and a high percentage of adhesive failure modes can be explained by the fracture phenomenon at the surface area of zirconia ceramics.

Limitations of this study include the in vitro set up, short term thermocycling application as well as being single-operator study. The SBS test method was used in this study, but this does not provide a homogeneous stress distribution on the test surfaces [56 57 58]. Since the microtensile test method allows obtaining more precise and controlled data, it may provide more reliable results [59 60]. For this reason, the use of alternative methods should be considered in determining bond strength values in future studies.

Additionally, clinical studies with multiple operators and long-term performance in the oral environment can provide more clinically relevant data.

Conclusions

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

1. Zirconia ceramics' cleaning protocol must be considered after exposure to saliva during intraoral try-in procedures.
2. Mechanical surface abrasion is the most effective way to decontaminate the zirconia surface.
3. Application of zirconia cleaning agents to the contaminated zirconia surfaces is as effective as mechanical surface abrasion and offers a simple step-by-step cleaning method for restoring zirconia surfaces after contamination.

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