The Influence of Surface Treatments on the Shear Bond Strength of Resin Cements to Zirconia

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“In the name of Allah, the Entirely Merciful, the Especially Merciful”

“Praise is to Allah, Lord of the worlds”

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Abstract

Purpose: The aim of this *in vitro* study was to evaluate the effect of a hot chemical etching solution (HES) as new surface treatment on the shear bond strength (SBS) of zirconium-oxide ceramic to resin cements and the influence of different resin cements and their primers on the retention of zirconia.

Materials and Methods: 120 Zirconia specimens 6 x 6 x 4mm were fabricated from zirconia blocks, sintered, and divided into three groups according to their surface treatment: control group (no treatment), airborne-particle abrasion (APA), and (HES) group. Each group was randomly divided into five subgroups according to the resin cement technique used: subgroup A cemented by RelyX™ Unicem, subgroups B cemented by Panavia F2.0, subgroup C cemented by Panavia F2.0 plus its ceramic primer, subgroup D cemented by Multilink Automix, and subgroup E cemented by Multilink Automix plus its ceramic primer. The zirconia blocks were bonded to composite cylinders. SBS was tested in a universal testing machine (Instron) after 30 days of water storage and 5000 thermal cycles. Statistical analysis was performed using 2-way ANOVA (α =0.05) and multiple comparisons were performed by Tukey's HSD.

Results: APA resulted in significantly higher SBS (*P* <0.001) than the two other surface conditioning methods. Bond strength of Panavia F2.0 (11.9 MPa) and RelyX™ Unicem (9.7 MPa) cements to zirconia was significantly higher than that of Multilink Automix regardless of the surface treatment (*P* <0.001). Using zirconia primer with Multilink Auomix resin cement showed significant improvement in the shear bond strengths (*P* <0.001). Zirconia primer with Panavia F2.0 did not show any statistically significant in the bond strengths (*P* =0.885).

Conclusion: The use of the phosphate monomer-containing luting system (Panavia F2.0 and RelyX™ Unicem) with APA can be recommended as promising bonding method. Using zirconia primer with non MDP- containing resin cement is necessary to achieve durable bond to densely sintered zirconia ceramics.

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Introduction

Interest for using high-strength zirconium oxide ceramics for the fabrication of computer-manufactured full coverage crowns and bridge frameworks is growing in recent years. This is due to Zirconia's improved mechanical properties in comparison to more conventional alumina or lithium disilicate-based ceramics.[1,2,3]

In contrast to conventional feldspathic ceramic, the matrix pressure on the tetragonal particles of zirconium oxide is reduced by tensile stresses that induce a transformation of the tetragonal to a monoclinic phase. This is associated with a localized volumetric increase of 3% to 5%, resulting in compressive stresses that counteract the external tensile stresses and, in this way, may prevent cracks from propagating.[4,5]

Although conventional cementation of zirconium oxide restorations with traditional luting agents (such as zincphosphate or resin-modified glass ionomer cements) may provide adequate clinical fixation, adhesive cementation is preferable for ensuring better retention and marginal adaptation.[3,6,7]

Multiple clinical studies document excellent long-term success of resin-bonded restorations, such as porcelain laminate veneers, ceramic inlays and onlays, resin-bonded fixed partial dentures, and all-ceramic crowns.[1]

A strong, durable resin bond provides high retention, improves marginal adaptation, prevents microleakage, and increases fracture resistance of the restored tooth and the restoration.[3]

Bonding to traditional silica-based ceramics is a predictable procedure yielding durable results when certain guidelines are followed. However, the composition and physical properties of high-strength ceramic materials, such as aluminum oxide-based (Al_2O_3) and zirconium oxide-based (ZrO_2) ceramics, differ substantially from silica-based ceramics and require alternative bonding techniques to achieve a strong, long-term, durable resin bond.[1]

The achievement of reliable adhesion to ceramics conventionally requires surface pre-treatments. However, neither hydrofluoric acid etching nor silanization result in a satisfactory resin bond to zirconia because of the high crystalline content and the limited vitreous phase (below1%) of this high strength core ceramic.[7,8,9]

Airborne particle abrasion has been employed in the attempt to enhance the surface area available for bonding.[10-12] Although an improvement in the average surface roughness has been recorded on a micrometer scale; the treatment appeared inadequate to establish reliable ceramic/cement bonds.[1]

A hot chemical solution has been proposed to etch the wings of Maryland bridges. It has the effect of roughening the surface and promoting retention.[14] This solution now represents an effective method for conditioning zirconia surfaces, and enhancing micromechanical retention.[15]

Aims of Study:

- The purpose of this *in vitro* study is to evaluate the effect of the hot chemical etching solution as new surface treatment on the shear bond strength of zirconium-oxide ceramic to dual-cured resin cements.
- The influence of different resin cements and their primers on the retention of zirconia.

The Hypotheses:

- Using a hot etching chemical solution as surface treatment will increase the mean shear bond strength between zirconia and adhesive cements, compared to sandblasting and control.
- Using the self adhesive resin cement will result in higher mean shear bond strength than multi-step system adhesive cements.
- Among the Panavia F2.0 and Multilink Automix cements, using a zirconia primer will increase the mean shear bond strength.

Clinical Significant of the Study:

The results of this study could affect the decision of the clinician on:

- Selecting the type of surface treatment that provides more durable bonds of zirconia ceramics to adhesive cements.
- Selecting the type of cementing medium for cementation of the zirconium oxide ceramics.

Historical Background

Zircon has been known as a gem from ancient times. The name of the metal, zirconium comes from the Arabic *Zargon* (golden in color) which in turn comes from the two Persian words *Zar* (Gold) and *Gun* (Color). Zirconia, the metal dioxide (ZrO_2), was identified as such in1789 by the German chemist Martin Heinrich Klaproth as the reaction product obtained after heating some gems, and was used for a long time blended with rare earth oxides as pigment for ceramics.[16]

The first paper concerning biomedical application of zirconia was published in 1969 by Helmer and Driskell.[17] While the first paper concerning the use of zirconia to manufacture ball heads for Total Hip Replacements (THR), which is the current main application of this ceramic biomaterial, was introduced by Christel *et al.*, in 1988.[18]

In the early stages of the development, several solid solutions (ZrO_2-MgO, ZrO_2-CaO, and ZrO_2-Y2O_3) were tested for biomedical applications. But in the following years the research efforts appeared to be more focused on zirconia-yttria ceramics, characterized by fine grained microstructures known as Tetragonal Zirconia Polycrystals (TZP).[16]

The recent introduction of zirconia-based ceramics as restorative dental materials has generated considerable interest in the dental community. The mechanical properties of zirconia are the highest ever reported for any dental ceramic. This may allow the realization of posterior fixed partial dentures and permit a substantial reduction in core thickness. These capabilities are highly attractive in prosthetic dentistry, where strength and esthetics are paramount.

Review of literature

Properties of Zirconia

The attractive properties of zirconium oxide such as high strength, excellent mechanical properties,[4,13] and biocompatibility[16] allow several applications in restorative dentistry. One of which is as a core material for all ceramic crowns and fixed partial dentures (FPDs).

Unalloyed zirconia is a well-known polymorph that occurs in three forms: Monoclinic (M), Tetragonal (T), and Cubic (C). Pure zirconia is monoclinic at room temperature. This phase is stable up to 1170^0C, above this temperature it transforms into tetragonal and then into cubic phase at 2370^0C. During cooling, a T→M transformation takes place in a temperature range of about 100^0C below 1070^0C.[19,20] The phase transformation taking place while cooling is associated with a volume expansion of approximately 3 to 5%. Stresses generated by the expansion originate cracks in pure zirconia ceramics that, after sintering in the range 1500 to 1700^0C, break into pieces at room temperature. This vast volumetric expansion precludes the use of pure zirconia in ceramic systems.[21,22]

Alloying pure zirconia with stabilizing oxides such as CaO, MgO, Y_2O_3 or CeO_2 allows the retention of the tetragonal structure at room temperature and therefore the control of the stress-induced T→M transformation, efficiently arresting crack propagation and leading to high toughness.[21,22]

Three classes of zirconia materials can be obtained: Cubic stabilized zirconia (CSZ), partially stabilized zirconia (PSZ), which is a mixture of cubic and tetragonal/monoclinic phases, and

Tetragonal zirconia polycrystals (TZP).[21,22] Among these three classes, the (TZP) materials have the best fracture toughness and mechanical strength, especially when 3 mol % yttria is used as stabilizer. Such results are related to the greater extent of yttria solubility in tetragonal zirconia solid solution when compared to others oxides,[23] and this is the most commonly used type of zirconia in dentistry.

Zirconium dioxide content in yttrium-stabilized tetragonal zirconia is higher than 90% (Y-TZP), while glass-infiltrated ceramics have only 35% of partially-stabilized zirconia.[5,6]

I. Transformation Toughening

The 3 mol% yttria-stabilized zirconia (3Y-TZP) exhibits a very important feature, related to the polymorphic transformation for monoclinic phase when a mechanical stress is applied. This phenomenon, known as transformation toughening, it gives (3Y-TZP) superior mechanical properties compared with other ceramics,[10,16] and can explain why this material is referred to as a “ceramic steel” by some authors. This phenomenon can prevent crack growth resulting in a material with high toughness and mechanical strength.[16] At a crack tip, the matrix constraint on the tetragonal particles of 3Y-TZP is reduced by tensile stresses so that a transformation to the monoclinic structure takes place. This transformation produces a local 4% increase in volume, which results in compressive stresses within the matrix, thereby increasing the energy necessary for further crack growth.[13,24] On the other hand, this transformation also altering the phase integrity of the material and increasing the susceptibility to aging.

II. Aging or the Low Temperature Degradation (LTD) of Ziconia

Aging is a well-documented phenomenon exacerbated notably by the presence of water.[25-27] The consequences of aging are many and include surface degradation with grain pullout and micro cracking as well as strength degradation.

The LTD, as well as the ‘‘transformation toughening’’ phenomenon mentioned previously, results in reverse transformation of the material from the tetragonal to the monoclinic phase with simultaneous volumetric expansion. Transformation toughening that is initiated by a crack is desirable because the excess volume ‘‘seals’’ the crack. However, LTD is, in general, considered unfavorable because the excess volume causes micro-and macro cracking at the surface that proceeds to the interior, reducing the material’s mechanical properties.

III. Zirconia's Fracture Toughness

It is between 8 and 10MPa which is almost twice as high as that of aluminum oxide ceramics. This is due to transformational toughening, which gives zirconia its unique mechanical properties.[28]

IV. The Flexural Strength of Zirconia Oxide

It has been reported that the flexural strength of ZrO_2 is in the range of 900 to 1,100MPa. This is approximately twice as strong as alumina oxide ceramics currently on the market and 5 times greater than standard glass ceramics. These values exceed the maximal occlusal loads during normal chewing.[29]

In addition, without any glass matrix, zirconia oxide materials are generally stronger and offer more resistance to cracking than other ceramics. Further, chemical corrosion occurs on glass substrates, which can lead to clinical failure. The aqueous component in saliva can react with glass in ceramic material, causing corrosion. This can increase the rate of crack propagation and lead to failure of the material.[30]

Type of Zirconia Blanks

Three types of zirconia blanks are available for the CAD/CAM milling systems. One is the completely sintered dense blanks for direct machining by CAD/CAM (hard machining). The other two types of blanks for CAD/CAM fabrication require post machining sintering to obtain final products with sufficient strength (soft machining). They are namely blanks at the green stage or pre-sintered blocks, while another type are blanks at the raw stage in the form of partially stabilized zirconia powder mixed with binder.[31]

Fabrication of Zirconia Substructure

The most common method to fabricate a zirconia substructure is by CAD/CAM milling from a solid block. The partially sintered zirconia is milled 20% to 25% larger than the desired final size due to shrinkage caused by the post machining sintering process (soft machining), while the fully sintered zirconia is milled at a 1:1 ratio (hard machining). For both the partially sintered and the fully sintered techniques, the die is scanned, and then the computer program designs the framework or the coping.[31]

I. Soft Machining of Pre-Sintered Blanks

Since its development in 2001,[32] direct ceramic machining of pre sintered 3Y-TZP has become increasingly popular in dentistry and is now offered by a growing number of manufacturers. Briefly, the die or a wax pattern is scanned, an enlarged restoration is designed by computer software (CAD) and a pre-sintered ceramic blank is milled by computer aided machining (CAM). The restoration is then sintered at high temperature. Several variations of this process exist depending on how the scanning is performed and how the large sintering shrinkage of 3Y-TZP (~25%) is compensated for. For example, both contact scanners and non-contact scanners are available. Overall, non-contact scanners are characterized by a higher density of data points and a greater digitizing speed compared to contact scanners.[31]

Typically the 3Y-TZP powder used in the fabrication of the blanks contains a binder that makes it suitable for pressing. The binder is later eliminated during the pre-sintering step. It also contains about 2wt% HfO_2, classically difficult to separate from ZrO_2. These powders have only minor variations in chemical composition. The blanks are manufactured by cold isostatic pressing.[31]

The binder is eliminated during a pre-sintering heat treatment. This step has to be controlled carefully by manufacturers, particularly the heating rate and the pre-sintering temperature. If the heating rate is too fast, the elimination of the binder and associated burn out products can lead to cracking of the blanks. Slow heating rates are therefore preferred. The pre-sintering temperature of the blanks affects the hardness and machinability. These two characteristics act in opposite directions: an adequate hardness is needed for the handling of the blanks but if the hardness is too high, it might be detrimental to the machinability of the blank. The temperature of the pre-sintering heat treatment also affects the roughness of the machined blank. Overall higher pre-sintering temperatures lead to rougher surfaces. The choice of a proper pre-sintering temperature is thus critical. The density of each blank is carefully measured so that the appropriate compensating shrinkage is applied during final sintering. The final density of the pre-sintered blanks is about 40% of the theoretical density.[31]

Machining is better accomplished in two steps. A first rough machining is done at a low feed rate while the final fine machining is performed at a higher feed rate.[32] The soft machining technique prevents the stress-induced transformation from tetragonal to monoclinic and leads to a final surface virtually free of monoclinic phase unless grinding adjustments are needed or sandblasting is performed. Most manufacturers of 3Y-TZP blanks for dental applications do not recommend grinding or sandblasting to avoid both the t → m transformation and the formation of surface flaws that could be detrimental to the long-term performance despite the apparent increase in strength due to the transformation-induced compressive stresses.[31]

Restorations can be colored after machining by immersion in solutions of various metal salts such as cerium, bismuth, iron or a combination thereof.[33] The color develops during the final sintering stage. Alternatively, colored zirconia can be obtained by small additions of various metal oxides to the starting powder.[33]

Sintering of the machined restorations has to be carefully controlled, typically by using specifically programmed furnaces. Shrinkage starts at 1000^0C and reaches ~25% at final temperature. Sintering conditions are product-specific. Final sintering temperatures between 1350 and 1550^{0}C with dwell times between 2 and 5 hours lead to densities greater than 99% of the theoretical Density. The restorations are furnace-cooled to a temperature below 200^{0}C to minimize residual stresses.[31]

On average, manufacturers recommend that the minimal thickness for a zirconia coping should be 0.3mm for anterior teeth and 0.5mm for posterior teeth. For a fixed prosthesis fabricated with zirconia, the cross –sectional dimension for a connector should be $9mm^2$. This is much smaller than the $16mm^2$ connector recommended for conventional glass ceramics. This decrease in connector dimension is due to zirconium’s greater strength, allowing for a smaller connector and thus resulting in a more aesthetic appearance.[30]

Representative systems utilizing soft machining of 3Y-TZP for dental restoration are Cercon® (Dentsply International), Lava™ (3M™ ESPE™), Procera® zirconia(Nobel Biocare™), YZ cubes for Cerec InLab® (Vident™)and IPS e.max® ZirCAD (Ivoclar Vivadent).[31]

II. Hard Machining of 3Y-TZP

At least two systems, Denzir® (Cadesthetics AB) and DCZirkon® (DCS Dental AG) are available for hard machining of zirconia dental restorations. Y-TZP blocks are prepared by presintering at temperatures below 1500^{0}C to reach a density of at least 95% of the theoretical density. The blocks are then processed by hot isostatic pressing at temperatures between 1400 and 1500^{0}C under high pressure in an inert gas atmosphere.[34,35] This latter treatment leads to a very high density in excess of 99% of the theoretical density.

Processing of zirconia in its densely sintered stage has the advantage of avoiding undesirable dimensional changes as the result of the sintering shrinkage that occurs during machining heat treatment. However, it makes the milling procedures difficult, time consuming and leads to high wear of milling instruments. The restorations produced by hard machining of fully sintered 3Y-TZP blocks have been shown to contain a significant amount of monoclinic zirconia.[23] This is usually associated with surface microcracking, higher susceptibility to low temperature degradation and lower reliability.[37]

Veneering of Zirconia

Current processing technologies unfortunately cannot make zirconia frameworks as translucent as natural teeth, so they have to be veneered with weaker porcelain to achieve acceptable esthetics.

The coefficient of thermal expansion of substructure and porcelain should be matched. Porcelain that is used in porcelain-fused-to metal restorations cannot be used with a zirconia substructure, since delamination will occur. Further, proper firing of a bonding layer of porcelain to the zirconia core is essential to create a stable interface between the two materialas.[38] The nature of the interface between 3Y-TZP and the veneering porcelain has not been thoroughly studied.

The typical failure pattern of a veneering material in the daily clinical practice is known as ceramic chipping.[27,39] This fracture pattern is associated with a thin layer of glass-ceramic that remains on the zirconia framework.[39-40] This indicates a reliable bond of veneering ceramics to the framework, but also reveals a weakness of the veneering porcelain. A possible reason for the incidence of ceramic chippings may be found in the former limited CAD- software options by which crown and fixed dental prosthesis (FDP) frameworks could not be machined to an anatomically reduced form which can offer an adequate support to the veneering material. Modern CAD/CAM systems are able to provide a considerably better anatomically cut back framework design. Future clinical long-term results may be more favorable.[41,42] Another potential reason may be that the powder buildup technique frequently results in the incorporation of voids and flaws.[43] Use of more stable veneering materials might reduce the chipping rate compared to traditional veneering porcelains. The porcelains used in the powder technique have a flexural strength in the range of 80MPa,[44] while the ceramics used for the over-pressing technique to veneer zirconia show a flexural strength of 120MPa. However, several in vitro studies reported no difference in load-bearing capacity of crown systems with over-pressed veneering ceramics and powder buildup veneering porcelain.[43]

All manufacturers of porcelains for dental Y-TZP ceramics now provide “liner” materials, presumably to increase porcelain bonding as well as to provide some chroma and fluorescence. Although “bonding” does not appear to be at issue, perhaps these liners help assure wetting or have chemistries adjusted to reduce possible interactions with the Y-TZP. It does not appear that prostheses have needed to be replaced in any studies due to porcelain crazing or minor chipping.[31]

Adaptation of Zirconia

CAD/CAM techniques involve scanning, software and machining procedures, each single step could contribute to the overall fit of the crown. Systems dependent upon an optical impression experience problems with rounded edges due to the scanning resolution and positive error, which simulates peaks at the edges.[45] Other systems that use a surface contacting probe cannot accurately reproduce proximal retentive features less than 2.5mm wide and more than 0.5mm deep. Feather-edge finish lines, deep retentive grooves, and complex occlusal morphology are not recommended, not only for scanning and milling prerequisites, but also to decrease stress that would develop in a restoration with inadequate preparation and margin geometry.[46] An additional problem with computer-milled ceramic restorations is that the internal cutting bur may be larger in diameter than some parts of the tooth preparation, such as the incisal edge. This would result in a larger internal gap than with other fabrication techniques.[45] Research has shown that the internal gaps and marginal adaptations of zirconia frameworks were significantly larger than that of metal frame works.[37,40]

Marginal Adaptation of Zirconia

When evaluating the clinical success and quality of a restoration marginal discrepancy is an essential criterion.[47] Absolute marginal discrepancy was defined as an angular combination of the horizontal and vertical error and would reflect the total misfit.[48] McLean suggested that 120µm should be the limit for clinically acceptable marginal discrepancies.[49]

The long-term clinical success of all-ceramic prosthodontics can be influenced by marginal discrepancies.[50] Poor marginal adaptation of fixed prostheses increases plaque retention and changes the distribution of the micro flora, which can induce the onset of periodontal disease.[2] Also, poor marginal fit can cause secondary caries and lead to clinical failure of fixed prosthodontics.[51] Micro leakage from the oral cavity may cause endodontic inflammation.[52]

Internal Gaps of Zirconia

An internal gap is the perpendicular measurement from the axial wall to the internal casting surface. Compared with the traditional casting of metal, the computer-aided fabrication of ceramic frameworks may lead to critically large internal gaps between them and their underlying abutments, depending on the system used.[37,40]

The internal adaptation plays an important role for the long-term stability of all-ceramic reconstructions. The important factors to be considered are the thickness of the cement layer, an increase in cement thickness caused by a larger internal gap can have a significant impact on the long-term stability of a ceramic reconstruction. Because increase in thickness of the cement layer, resulting from a larger internal gap, leads to a significant decrease of the flexural failure load of ceramics, as *in vitro* studies have shown.[53]

There are two main factors which have influences on the marginal adaptation and the internal fit of zirconia, computer fixed cement space, and convergence angle of the abutment tooth.

I. Computer Fixed Cement Space

The cement spaces set by the CAD/CAM system for all ceramic restorations need to be taken into consideration because they have influence on improving their marginal adaptation. 60μm cement space fixed by the CAD/CAM system might be favorable from the aspect of marginal adaptation of zirconia ceramic copings.[54,55] These findings probably related to the disappearance of the premature contacts between the abutments and coping internal surfaces in the increased computer-fixed cement spaces.

II. Convergence Angle of the Prepared Tooth

To improve marginal and internal adaptation of zirconia restorations, manufacturers need preparing the abutment with wider convergence angle to improve the scanning power.[55] In one study, preparing the tooth with a 20° convergence angle produced statistically significantly smaller internal spaces and Marginal discrepancies as compared with teeth prepared with 6° and 12° convergence angles. The scanning accuracy of abutments could have been enhanced with a larger convergence angle of abutment, since the increase in convergence angles makes the scanning more precise.[55] These findings would indicate that the internal spaces reduce as the convergence angles of abutments increase. On the other hand, retention of the restoration is in inverse proportion to the convergence angle of the abutment tooth, as the convergence angle of the abutment tooth increases the retention of the restoration decreases.[56] However, some researchers have shown a positive relationship between convergence angles of the abutments and internal spaces of all-ceramic restorations fabricated by using the CAD/CAM system.[54,57]

In general, studies have demonstrated that internal gap widths are higher than marginal gaps.[47,58-60] This finding has implications for glass-ceramic restorations which may be dependent upon the mechanical properties of the luting cement to resist functional forces.[61] Most of the literature reports marginal discrepancies in the range of clinical acceptability recommended by McLean and Christensen.[49,62]

Clinical Implication

Considering zirconia's high strength, this material enables the clinician to place the ceramic restoration almost anywhere in the mouth. Single crowns, implant abutments, and bridges can be fabricated from zirconia.[63,64] Although some manufacturers indicate that zirconia ceramics allow for the fabrication of a prosthesis involving the full arch, FPDs with a maximum of five units seem to be more reliable.[65] This material can also be used for posts and cores or implant abutments in prosthetic dentistry.[65]

Y-TZP ceramics can be colored to simulate tooth structure; however, they are highly opaque. This radiopacity can be very useful for monitoring their marginal adaptation through radiographic analysis, especially when intrasulcular and proximal preparations are performed.[65] On the other hand, opacity might limit the esthetic outcome of zirconia restorations compared with those made of conventional dental ceramics. Additionally, it has been shown to be biocompatible, without any reported cases of toxicity, patient allergy, or sensitivity.[66]

Tooth Preparation of Zirconia

The tooth preparation needed to accommodate a zirconia restoration is essentially that of a porcelain-fused-to-metal crown with a few modifications. Preparations must follow the free gingival margin, incisal/occlusal reduction should be at least 1.5mm and axial reduction should be a maximum of 1.5mm. The range of reduction is related to the aesthetic needs. The more tooth reduction, the more available space for the lab technician to appropriately layer various porcelains to achieve better aesthetics. Some clinicians and technicians advocate 2.0 to 2.5mm of incisal/occlusal reduction for optimal appearance and anatomical form.[3] Excessively tapered preparations should be avoided.[65,67] Chamfer or rounded-shoulder preparations are recommended, because they increase material thickness at the restoration margins.[65] Knife-edge preparations might also be appropriate, since the fracture load required for Y-TZP copings with this type of preparation was greater than that required for chamfer preparations, regardless of coping thickness.[68] Due to the limitations of the die-scanning process and the subsequent machine milling, sharp angles in the preparation must be avoided. Ninety-degree shoulders, undercuts, or sharp line angles are not acceptable.[65]

Cementation of Zirconia

The cementation process is vital for the clinical success of all-ceramic restorations. Although superior in terms of mechanical performance (strength, toughness, and fatigue resistance) there is an inherent limitation associated with high strength ceramic materials. Bonding of resins to these materials is more difficult than it is for silica-based ceramics. Fortunately, it is possible to conventionally lute zirconia crowns that rely only on micromechanical retention, due to their high flexural strength.[69,70] With traditional preparations, which provide mechanical retention and resistance form.[71] in addition to classical composite luting systems, conventional zinc-phosphate and glass- ionomer cements are used, as are resin-modified glass-ionomer and compomer cements. The more recent generation of self-adhesive luting cements are also indicated. These conventional cements are less technique-sensitive. However, conventional cementation techniques do not provide sufficient bond strength for some clinical applications. These include compromised retention and short abutment teeth.[72] Good adhesion is important for high retention, prevention of microleakage, and increased fracture and fatigue resistance, these are maximized by the use of resin-based cements.[1]

Investigations have been conducted to determine the ability of commonly used luting agents to retain high noble metal-ceramic crowns.[73-77] For better simulation of clinical conditions, investigation of the retentive strength of luting agents should be studied using axial dislodgment forces with crowns cemented on extracted human teeth.[75,76] Currently, only a recent publication by Ernst *et al*., evaluated the retentive strength of zirconium oxide–based crowns with several luting agents and different ceramic pretreatments, using a new in vitro model for connection to a crown during retention testing.[67] However, the results may have been affected by the low 5 degrees of taper used. On the other hand, some investigators have examined and measured the shear bond strength of different cements on zirconium oxide ceramic surfaces after different pretreatments; these studies provided varying and controversial results.[78,79]

Luting agents of interest are those in common use with the potential of creating a strong interface between dentin and the internal surface of the zirconium oxide–based restoration. In the Ernst *et al*., study, several types of cements demonstrated relative high zirconium oxide coping retention.[67] Studies of shear bond strength to zirconia ceramic have shown that a composite resin cement containing an adhesive phosphate monomer (MDP) provided significant bond strength values.[78,79] The self-adhesive modified composite resin cement represents a new type of cement and was developed with the goal of combining the ease of handling and absence of required pretreatment steps, along with favorable esthetics and higher adhesion to tooth structure.[80] This cement has also demonstrated high shear bond strength to zirconia ceramics under specific conditions.[81]

The success of the cementation process is dependent on the composition of the ceramic material. The bond of the resin luting cement to the tooth structure is enhanced by acid etching of enamel or dentin and by the use of a dentin adhesive. The penetration of monomers into the demineralized dentinal matrix, followed by polymerization, promotes the micromechanical bond via hybrid layer formation.[82-84] In a similar way, the internal surface of the ceramic restoration must be prepared to optimize the micromechanical bond between the ceramic and the resin.

Surface Treatments and Resin-Ceramic Bonding

Ceramic/resin cement bonds may be more effective and durable if associated with micromechanical retentions: the achievement of roughened ceramic surfaces may allow the resin cement to penetrate and flow into these microretentions, thus creating a stronger micromechanical interlock.[15,85–87] The common treatment options available for surface treatment are (1) grinding,[88] (2) abrasion with diamond rotary instruments,[89,90] (3) airborne particle abrasion with aluminum oxide,[91,92] (4)acid etching,[93] and (5) combinations of any of these methods.

- **Acid Etching**

Acid etching with solutions of hydrofluoric acid (HF) or ammonium bifluoride can achieve proper surface texture and roughness to silica-based ceramics.[93-97] The glassy matrix is selectively removed, and crystalline structures are exposed. Hydrofluoric acid solutions between 2.5% and 10% applied for 2 to 3 minutes seem to be most successful.[95-97] The number, size, and distribution of leucite crystals influence the formation of microporosities that acid etching creates.[98] For the leucite-reinforced feldspathic porcelain IPS Empress, solutions of 9% HF applied for 60 seconds were most successful.[99] The lithium-disilicate glass-ceramic IPS Empress 2 has a high crystalline content and exhibits significantly higher bond strengths than IPS Empress independent from surface conditioning. It seems that the ceramic microstructure has a significant influence on the fracture resistance of the composite-ceramic adhesion zone.[100] Application of a silane coupling agent to the pretreated ceramic surface provides a chemical covalent and hydrogen bond,[101,102] and is a major factor for a sufficient resin bond to silica-based ceramics.[96-100,101,104] Silanes are bifunctional molecules that bond silicone dioxide with the OH groups on the ceramic surface. They also have a degradable functional group that copolymerizes with the organic matrix of the resin.[98,105] Silane coupling agents usually contain a silane coupler and a weak acid, which enhances the formation of siloxane bonds.[98] Silanization, also increases wettability of the ceramic surface. Sorensen *et al*., showed that ceramic etching and silanization significantly decreased microleakage, which was not achieved by exclusive silane treatment.[106]

Unfortunately, because of the chemistry and the high crystalline content of zirconia that differ from those of conventional silica-based materials, neither hydrofluoric acid etching nor silanization result in a satisfactory resin bond to zirconia.[8,107-110]

- **Air-Abrasion**

Air-abrasion with aluminum oxide particles is routinely performed to remove layers of contaminants, thus increasing micromechanical retention between the resin cement and the restoration.[111,112] Usually, air abrasion units use aluminum oxide particles with sizes ranging from 25μm to 250μm. The application of a tribochemical silica coat that allows for chemical bonds to a silane coupling agent and to composite has been recommended.[113-115]

The effect of air abrasion on the mechanical properties of zirconia has been repeatedly discussed in the literature, and both positive and negative results have been described.[10,116,117] Some authors have stated that air abrasion increases the flexural resistance of zirconia ceramics, because it induces T→M phase transformations, creating compressive layers on the surface.[10,116] Apparently, the depth of the surface flaws induced by air abrasion do not exceed the thickness of the compressive layers, justifying the improved properties of air-abraded surfaces.[116] When the effects of air abrasion and milling with fine-grained diamond instruments (20µm-40µm) were compared with the use of coarse diamond burs (125µm-150µm), it was observed that less severe protocols reduced surface roughness and provided the formation of compressive layers on the surface. Conversely, coarse diamond burs reduced the flexural strength and reliability of Y-TZP ceramics.[117] In a different study, air abrasion and coarse diamond burs also presented opposite effects on the flexural resistance of a zirconia ceramic. The authors of that study added that, during milling with the diamond bur, a vast amount of material was removed and sparks were commonly observed despite the use of constant water spray, indicating that both stress and temperature were high during the operation.[10]

- **Tribochemical Coating**

Tribochemical coating is an effective method to roughen glass-infiltrated-based ceramic. In this technique, air pressure impregnates the ceramic with silica particles, and further silane application renders the impregnated surface chemically reactive to the resin cement.[112] Rocatec (3M ESPE) system is an example of this method, This system involves cleaning the surface to be coated with 110µm of high-purity aluminum oxide (Rocatec Pre; 3M ESPE) at 250KPa for 14 seconds, creating a uniform pattern of roughness. This is followed by a tribochemical coating with 110µm (Rocatec Plus; 3M ESPE) or a less abrasive 30µm (Rocatec Soft; 3M ESPE) of silica modified high purity aluminum oxide. The aluminum oxide leaves the surface partially coated with SiO_2, which is then conditioned with silane (3M ESPE Sil; 3M ESPE) to create a bond to the silicate surface of the metal or oxide ceramic and with the composite resin.[113] The volume loss through this tribochemical process was found to be 36 times less for a glass-infiltrated alumina (In-Ceram Alumina; VITA Zahnfabrik) than for a feldspathic glass ceramic (IPS Empress; Ivoclar Vivadent) and did not change its surface composition.[113] Pretreatment of a glass-infiltrated alumina (In-Ceram Alumina; VITA Zahnfabrik) with the tribochemical process (Rocatec; 3M ESPE) resulted in a durable resin bond over5 years.[118]

Tribochemical seems to be less effective for zirconia ceramics than for glass-infiltrated ceramics.[67,79] Siloxane bonds (including silica, silane and resin cement) are formed only if the surface presents oxygen and silica, because both molecules present linking sites between silane and the ceramic. Y-TZP ceramics present greater hardness compared with systems with a glassy structure, which prevents the impregnation of silica onto the surface.[119] For this reason, silane agents do not bond adequately to zirconia ceramics.[79] Although some studies have demonstrated good results with tribochemical treatment,[7,120] the question might be posed whether the improved bonding was caused by the siloxane bond or micromechanical retention, and this fact should be investigated in further studies.

According to some other studies, surface treatments, such as air abrasion, might increase ceramic degradation over time. It was demonstrated that the strength of air abraded Y-TZP ceramic decreases significantly when specimens are submitted to fatigue. This might be indicative of the presence of surface flaws, which increase with cyclic loading, and they can negatively affect the material's properties. Any further grinding or abrasion performed during the luting procedure might exacerbate superficial flaws created by air abrasion, resulting in fracture propagation.[121] In such cases a non-destructive, simple method for treating the ceramic surfaces would be very useful.

Despite the possible negative outcomes of surface treatments on the mechanical properties of Y-TZP materials, the application of resin cements to untreated surfaces apparently result in low bond strength, which is unable to resist water storage. This fact might indicate that some surface alteration is fundamental in order to obtain a durable bond to zirconia.[111] Additionally, in a long-term clinical study with alumina and zirconia FPDs, the authors noted that fractures only occurred at untreated sites, never at air abraded surfaces.[122]

Although an improvement in the average surface roughness by airborne particle abrasion has been recorded on a micrometer scale, the treatment appeared inadequate to establish reliable ceramic/cement bonds.[13]

- **Selective Infiltration Etching**

Alternative technologies are advocated in the attempt to change these high-strength ceramic cores into more retentive substrates. Selective infiltration etching (SIE) has been recently proposed achieving promising results in terms of bond strengths values at the zirconia–resin cement interfaces.[123] This treatment, that is based on the principle of the heat-induced infiltration process, may determine zirconia crystal rearrangements as well as intergrain nano-porosities formation where low-viscosity resinous materials may flow and interlock after polymerization.[107,12]

- **Hot Chemical Etching Solution**

Considering the metallic nature of pure zirconium, it can be assumed that treatments originally performed for conditioning metals or alloys may be somewhat beneficial for etching zirconium dioxide crowns or bridge frameworks. The application of the hot etching solution resulted in modifications to the zirconia surface, and significant increase in surface roughness. These results are similar of those previously achieved by Ferrari when etching high strength Ni–Co alloys for enhancing the retentive potential of Maryland bridges wings.[14] The action of this hot acid solution is basically a corrosion-controlled process. It can be speculated that the hot chemical etching solution may determine a chemical dissolution of the grain structure on the zirconia surface,[125] enlarging the grain boundaries throughout the preferential removal of the less-arranged, high-energy peripheral atoms.[126] Etching rate depends on solution movement over the ceramic surface and on temperature. The temperature tested 100^0C was suitable for conditioning the substrate in a reasonable application time 10 min. Improvement in HCL concentration would also increase the etching rate, although this approach may not be recommendable for dental purposes. Once resin cement systems penetrate the intergrain spaces forming micromechanical interlocks with the substrate, a superior strength would be necessary to debond it.[15]

Materials and Methods

Experimental Design

This study measures the shear bonding strength between different resin adhesive cements and zirconium-oxide ceramic specimens treated with various surface conditioning methods.

One hundred twenty 9 x 9 x 7mm (±0.3, ±0.3, and ±0.4mm, respectively) blocks were milled from partially sintered 3% Y-TZP (IPS e.max ZirCAD C15L Blocks; Ivoclar Vivadent AG, Schaan, Liechtenstein) using an electrical high precision saw (IsoMet 1000 Precision Saw; Buehler Ltd, Lake Bluff, IL) under water irrigation with a diamond wafering blade (4-inch wafering blade, High Concentration, M412H; MetLab Corp, Niagara Falls, NY). The blocks were sintered at 1500°C for 2 hours in a high temperature sintering furnace for zirconia (Programat S1; Ivoclar Vivadent AG). The dimensions of the blocks following 25% volumetric shrinkage associated with the sintering were 6 x 6 x 4mm (±0.2, ±0.2, and ±0.3mm, respectively). Ceramic blocks were randomly divided into three major groups (40 samples per group) according to the different mechanical and/or chemical treatment performed:

1) Group I (C): No surface treatment (control group).

2) Group II (APA): Airborne particle abrasion using 50µm aluminum oxide powder (Al_2O_3).

3) Group III (HES): Experimental hot etching solution.

Each group was randomly divided into five subgroups A, B, C, D, and E (8 samples per group) according to the resin cement technique used: subgroup IA, IIA, and IIIA were cemented by RelyX™ Unicem (3M ESPE, St. Paul, MN), subgroups IB, IIB and IIIB were cemented by

Panavia F2.0 (Kuraray America CO, NY), subgroups IC, IIC, AND IIIC were cemented by Panavia F2.0 plus its ceramic primer (Clearfil ceramic primer), subgroups ID, IID, and IIID were cemented by Multilink Automix (Ivoclar Vivadent AG), and subgroups IE, IIE, and IIIE were cemented by Multilink Automix plus its ceramic primer (Monobound Plus). (Fig1)

The test specimens in each bonding group, after they have been bonded to composite cylinders by using different resin cement techniques, were stored in distilled water at room temperature for 30 days, during which they underwent 5000 cycles in thermocycling machine. After thermocycling all specimens were stored in distilled water at room temperature before starting of shear strength test.

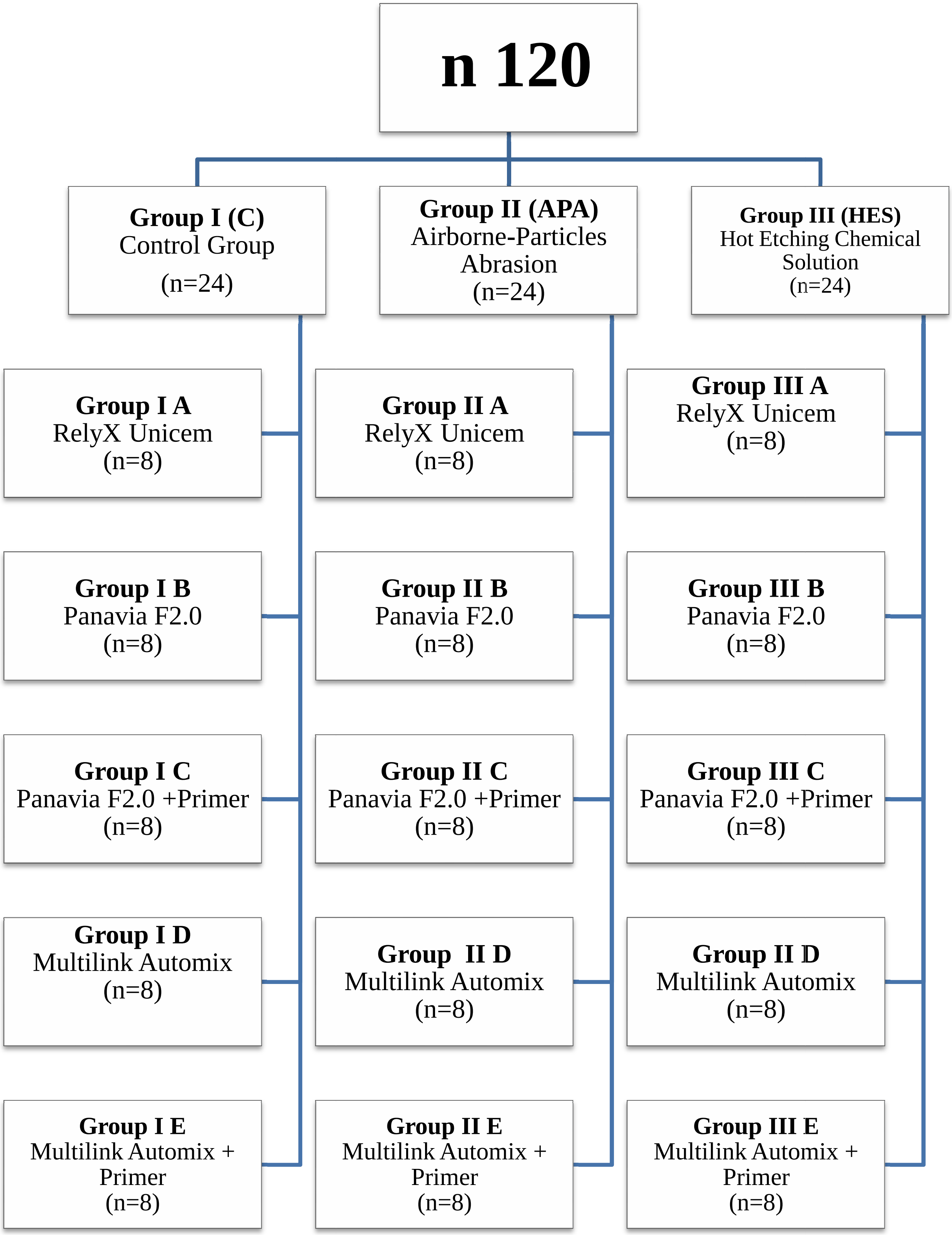

Fig 1: Flow chart of the groups and subgroups

Surface Treatment of the Substrate

To increase the surface area for bonding and to decrease surface tension, the surfaces of the substrates were treated by one of the following methods.

1) Group I (C): Underwent no mechanical or chemical surface treatment following sintering

2) Group II (APA): Airborne particle abrasion performed perpendicularly to the ceramic surface by means of a 50µm Al_2O_3 Particles (Aluminum Oxide Blasting Compound, 50µm/240 grit fine grain size; Ivoclar Vivadent, Inc, Amherst, NY) applied for 10s at a working distance of 10mm and a pressure of 3 bars (KaVo EWL Type 5423; KaVo Dental GmbH, Biberach, Germany).

3) Group III (HES): Experimental hot etching solution (a solution with 800ml of methanol, 200ml of 37% HCI, and 2gr of ferric chloride) that was heated up to 100^{0}C in water path and applied for 30 minutes according to a protocol previously proposed by Ferrari when he etched high strength Ni–Co alloys for enhancing the retentive potential of Maryland bridges wings.[14]

After being treated, specimens were ultrasonically cleaned in distilled water for 10min and gently air-dried prior to bonding.

One hundred twenty composite cylinders (Filtek™ Supreme Ultra Universal Restorative, capsules and gun dispenser shade A1B, 3M ESPE, St. Paul, MN) were prepared by filling a plastic mold with an inner diameter of 4.7mm and a height of 3mm. The top and 2 sides were each light-polymerized (Elipar®2500, Halogen Curing Light, 3M ESPE, St. Paul, MN) for

40 seconds for a total of 120 seconds and at equal light source-composite cylinder distance for each cylinder. The output was measured for each group of specimens to ensure adequate output.

Luting procedure

Five minutes after light curing, the composite resin cylinders were bonded to the treated ceramic surfaces using five different bonding techniques with dual-cured resin cements which resulted in five subgroups for each surface treatment:

(A) RelyX™ Unicem (3M ESPE, St. Paul, MN). (RXU)

(B) Panavia F2.0 (Kuraray America CO, NY). (Pan)

(C) Panavia F2.0 with Clearfil ceramic primer (Kuraray America CO, NY). (Pan+)

(D) Multilink Automix (Ivoclar Vivadent AG). (Multi Auto)

(E) Multilink Automix with Monobond® Plus (Ivoclar Vivadent AG). (Multi Auto+)

All the materials were handled following manufacturer's recommendations at room temperature. The chemical compositions of the investigated materials are reported in Table 1.

Product	Composition	Manufacturer
Panavia F 2.0 Cement	**Paste A** BPEDMA/MDP/DMA/silica/ barium sulfate/dibenzoylperoxide **Paste B** N,N-diethanol-*p*-toluidine/silica sodiumfluoride	Kuraray America CO, NY
RelyX™ Unicem	Methacrylated phosphoric ester, dimethacrylate, inorganic fillers, fumed silica, chemical and photoinitiators	3M ESPE, St. Paul, Minn, USA
Multilink Atuomix	**Base and Catalyst** Hydroxyethyl methacrylate (HEMA), Dimethacrylates, Inorganic fillers, Ytterbiumtrifluoride, Initiators, Stabilizers and Pigments	Ivoclar Vivadent AG
Monobond®Plus	Alcohol solution of silane methacrylate, phosphoric acid methacrylate and sulphide methacrylate.	Ivoclar Vivadent AG
Clearfil™ceramic	MDP,Trimethoxysilylpropyl methacrylate, Ethanol	Kuraray America CO, NY

Table 1: materials that were used in the study

The Ceramic-cement-composite resin set were placed in a bonding clamp (Ultradent Products, Inc) with the interface perpendicular to a vertical load 300g (Fig 2) at room temperature, in order to standardize the applied pressure.

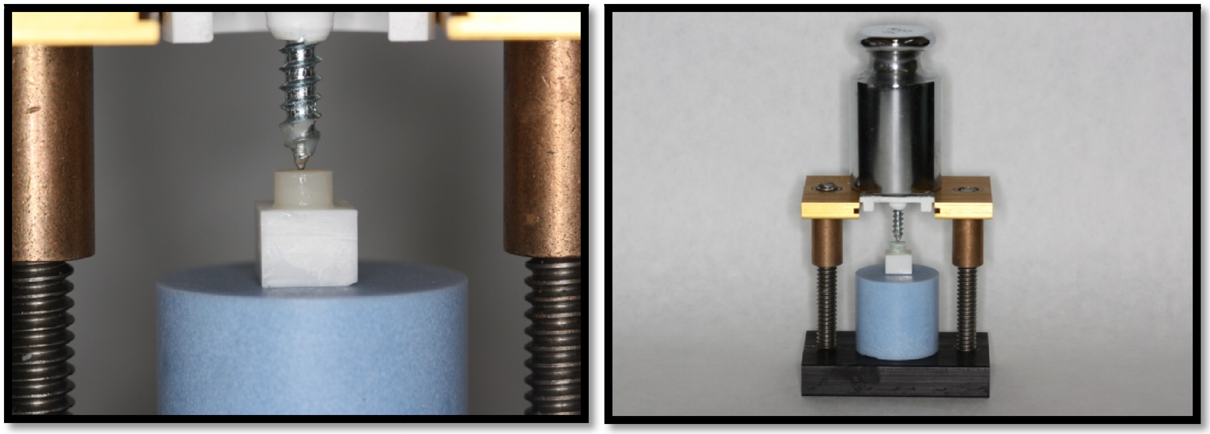

Fig 2: The Ceramic-cement-composite resin set in a bonding clamp

The excess resin luting agent was removed with Foam pellets (Disposable mini-sponge applicators; 3M ESPE St. Paul, MN) and microbrushes (Microbrush Disposable Micro-Applicator; Grafton, WI). (Fig 3) The specimens were light polymerized from 4 sides for 20 seconds for each side. (Fig 4) The specimens were then removed from the alignment device after 10 minutes, and stored in distilled water.

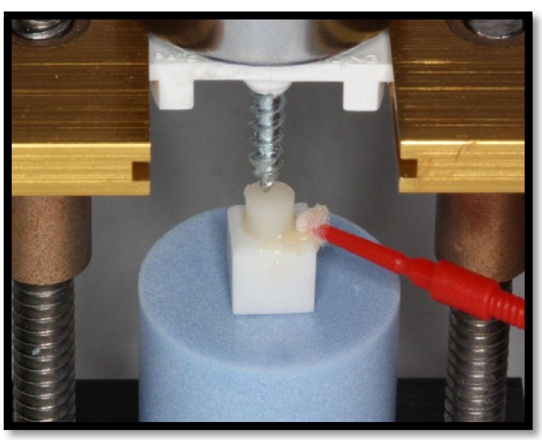

Fig 3: removing cement excess

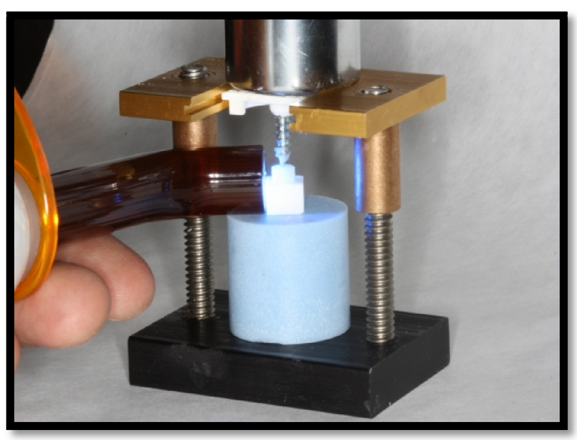

Fig 4: Light curing

The cementation procedure was conducted immediately after the required surface preparation for every test group to prevent possible contamination of the specimens.

Aging Methods

The test specimens in each bonding group were stored in distilled water at room temperature for 30 days, during which they underwent 5000 cycles in water baths of 5°C and 55°C (dwelling time 15 seconds). After thermocycling all specimens were stored in distilled water at room temperature before starting of shear strength test.

Shear Bond Test (SBS)

The bonded specimens, after water storage and thermocycling were placed in a jig for shear bond strength testing and loaded to failure with a crosshead speed of 1mm/min by using Universal Testing Machine (Model 5566; Instron, Canton, MA, USA) (Fig 5). The universal testing machine were controlled via a computer software system (Bluehill®2 Software, MAUSA), which also will complete the stress-strain diagram and records the breaking load. The bond strength (α) values (expressed in MPa) were calculated using the formula:

$\alpha = L/A$

(L) is the load at failure (in Newton) and (A) is the adhesive area (in mm^2).

Fig 5: Universal Testing Machine (model 5566, Instron Corp. Canton, Mass)

Statistical Analysis

1. The statistical analysis was processed using the PASW 18.0 version statistical software.

2. Data was analyzed with a two-way ANOVA with surface treatments, and cement types as variables. Multiple comparisons were performed by Tukey's HSD. The critical level of alpha was set at 0.05.

3. Means and standard deviations were calculated for each group and presented as tables. Box plot graphs were also used to illustrate the results.

Debonded specimen surfaces were examined by the same observer with an optical microscope (Busch & Lomb, Rochester, New York) to assess the mode of failure. Adhesive and/or cohesive failure of bonding could occur in 3 locations:

(1) Adhesive failure at the interface between the ceramic and resin luting agent or between the resin luting agent and the composite resin interface.

(2) Cohesive failure within the ceramic, within the resin luting agent, or within the composite resin only.

(3) Adhesive and cohesive failure at the same site or a mixed failure.

Results

The shear bond strength (SBS) values, for the fifteen bonding groups, are summarized in Table 2. The shear bond strengths between zirconia and adhesive cements were significantly influenced by the surface treatment (*P* <0.001), and the cementing medium (*P* <0.001). ANOVA analyses showed no statistically significant interaction between cements and surface treatment (*P* =0.240).

Luting Cement	Control	Air Particle Abrasion	Hot Etching Solution
RelyX^{TM} Unicem	8.3 (2.4)	13.8 (3.2)	7.1 (1.8)
Panavia F2.0	8.1 (2.8)	16.5 (7.5)	11.2 (6.1)
Panavia F2.0 + primer	8.6 (1.9)	14.3 (2.3)	10.02 (6.4)
Multilink Automix	0 (0)	2.7 (3.01)	1.5 (2.1)
Multilink Automix + primer	6.2 (0.9)	10.3 (2.1)	4.6 (0.8)

Table 2 Mean shear bond strength values [MPa] and Standard Deviation (SD) to zirconia ceramic with different treatment methods

The Tukey honestly significant difference (HSD) post-hoc pair-wise comparison test indicated that all test cements revealed higher bond strengths to air-particle abraded zirconia surfaces than to the untreated or the chemical etched surfaces (*P* <0.001). Mean bond strength values of test cements were 6.2, 11.5 and 6.9MPa for the control, APA, and the HES, respectively. The hot etching chemical solution show better results than the control group but was not statistically significant (*P* =0.726).

Specimens bonded with Panavia bn F2.0 (MDP-containing resin cement) showed higher bond strengths than specimens bonded with the RelyX™ Unicem resin in the airborne- particle abrasion and the hot etching solution groups, and it showed lower bond strengths than the RelyX™ Unicem in the control group. However, all these differences were not statistically significant (*P* =0.244). Multilink Automix showed very low bond strengths, and these results were statistically significant from Panavia F2.0 and RelyX™ Unicem (*P* <0.001). Table 3

	Sample size	Mean	SD
RelyX Unicem	24	9.7 [a,c]	3.8
Panavia F2.0	24	11.9 [a]	6.6
Panavia F2.0 + primer	24	10.9 [a]	4.6
Multilink Automix	24	1.4 [b]	2.3
Multilink Automix + primer	24	7.05 [c]	2.8

Table 3 Mean shear bond strength values [MPa] and standard deviation (SD) of different adhesive cement techniques. Same lower case subscript letters indicate no statistical difference

Using zirconia primer (Monobond®Plus) with Multilink Auomix resin cement showed significant improvement in the shear bond strengths (*P* <0.001). Zirconia primer (Clearfil™ ceramic primer) with Panavia F2.0 did not show any statistically significant in the bond strengths (*P* =0.885). Table 3

When Multilink Automix was used without the Monobond®Plus primer (Subgroups D) all of the specimens debonded spontaneously in group ID (untreated zirconia). In group IID (sandblasted zirconia) four of the eight specimens did not debond. These four specimens showed low bond strengths of 4.8, 6.6, 6.2 and 4.2MPa, respectively. Additionally, in group IIID (chemical etched zirconia) four of the eight specimens did not debond, low bond strengths of 0.02, 5.3, 2.9 and 3.4 MPa, respectively where demonstrated in these four specimens.

Failure modes were 100% adhesive at the ceramic bonding interface for all test cements and with all surface conditions.

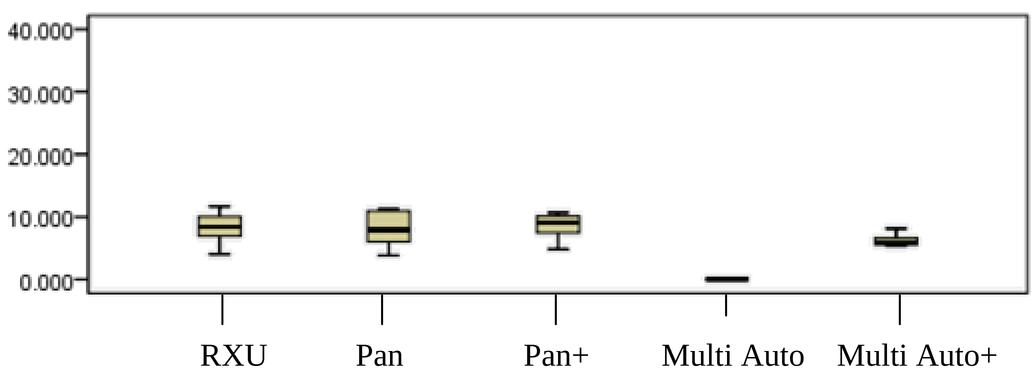

Fig 5: Box plot of SBS of all used adhesive cement with untreated surfaces.

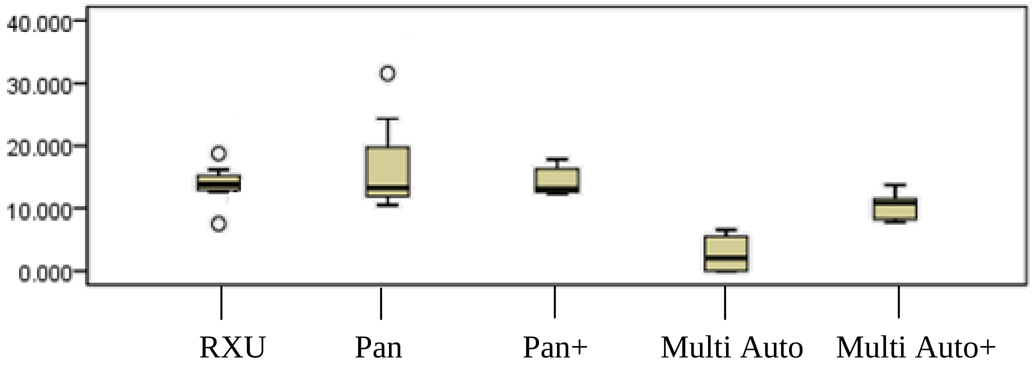

Fig 6: Box plot of SBS of all used adhesive cement with APA.

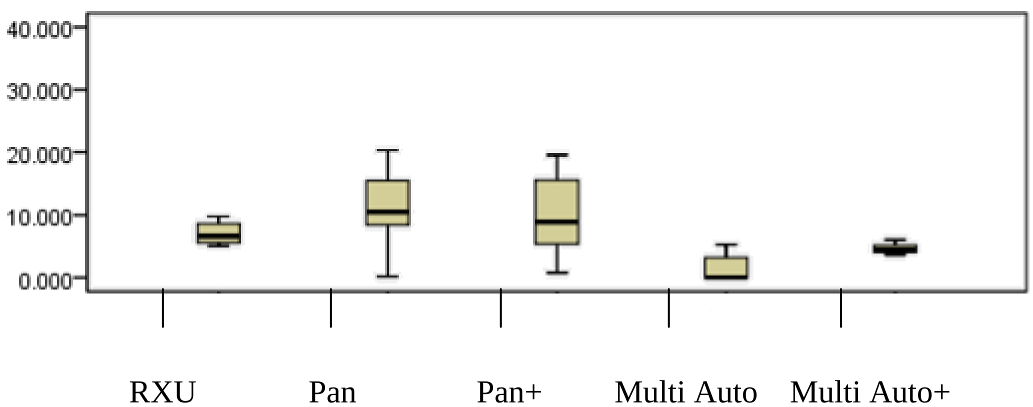

Fig 7: Box plot of SBS of all used adhesive cement with HES.

Discussion

The achievement of reliable bonds between zirconium oxide ceramics and resin-based luting agents is a prerequisite for ensuring clinical success and longevity.[3,107–110] Several studies have been concerned with choosing the best luting cement in order to gain optimal retention of bonded zirconia crowns and bridges.[13] However, concerns still remain regarding the identification of the best luting methodology. The purpose of this study was to evaluate the influence of surface treatments and cement type on bonding to zirconia.

The results of this study disapproved our first hypothesis which is using a hot etching chemical solution as surface treatment will increase the mean shear bond strength between Zirconia and adhesive cements, compared to airborne-particle abrasion and control. A hot chemical etching solution has been proposed by Ferrari *et al*., to etch the wings of Maryland bridges in 1989,[14] and recently he proved that the application of same solution resulted in modifications to the zirconia surface and significant increase in surface roughness comparing to airborne-particle abrasion.[15] These results have been shown by using the atomic force microscope (AFM) and scanning electron microscope (SEM). In this study, the hot chemical etching solution has been tested with different adhesive luting cements and showed higher bond strengths than the control group, but these results were not statistically significant. However, the bond strengths were significantly lower than they were for airborne-particle abrasion group. The possible explanation to this is that the hot chemical etching solution might increase the surface area of zirconia by widening the grain boundaries without creating undercuts which is important in forming the micromechanical interlocking with the cement.

Airborne-particle abrasion with Al_2O_3 is the preferred treatment method for high strength ceramic materials.[78,110,114] Surface roughening methods increase energy and wettability and may decontaminate bonding surfaces.[110,127] Della Bona *et al.*, showed that treatment of In-Ceram Zirconia with airborne particle abrasion systems (sandblasting and silica coating) produced significantly greater Ra values, which should benefit the mechanical bond mechanisms to resin-based materials.[124] In a recent study, Quaas *et al.*, found that air-abrading contaminated zirconia surfaces led to significantly higher resin-ceramic bond strength values than cleaning the contaminated ceramic surfaces with phosphoric acid or alcohol.[127]

The results of the current study also confirm that air particle abrasion of zirconia surfaces with Al_2O_3 increases bond strength values of adhesive luting cements to ceramic surfaces. Qeblawi *et al.*, study was the only investigation identified in the literature on the resin bond strength to the same zirconia system (IPS e.max ZirCAD; Ivoclar Vivadent AG). They evaluated the bond strength of adhesive luting cement to a zirconia ceramic after performing four different surface treatments. They found that airborne-particle abrasion resulted in significantly higher initial bond strengths.[128]

In contrast to the majority of studies, which support the positive effect of air-particle abrasion on the bond strength of luting cements to zirconia surface. Derand *et al.*, evaluated the effect of different pretreatment of zirconia ceramics (Procera), and he found that sandblasting negatively affect the retention of ceramics with zinc phosphate cement.[129] Phark and Blatz have shown the same result after testing the shear bond strength of different adhesive cements to zirconia ceramics (Procera) with and without airborne-particle abrasion and concluded that an airborne-particle abrasion of the modified zirconia surface is not recommended. Apparently the production process of such ziconia ceramic (Procera) gives rougher surfaces than the sandblasting process that possibly polishs the surface.[130]

Although there are studies indicating that air abrasion affects the surface of zirconia ceramic which leads to a reduction of the flexural strength of these ceramics,[121] there are other authors who showed that air abrasion might even strengthen zirconia ceramics.[10] Furthermore, a negative effect of the microcracks on the ceramic surface caused by air abrasion on the clinical performance of resin-bonded all ceramic restorations is questionable. In a long-term clinical study with two- and single-retainer all-ceramic (In-Ceram alumina and In-Ceram zirconia) resin-bonded fixed partial dentures fractures occurred at the connector sites which were not air abraded, but never at the retainer wings which were air abraded prior to bonding.[122]

In this study three different types of resin cement, RelyX™ Unicem Clicker a self adhesive resin cement containing methacrylate monomers, Panavia F2.0 an adhesive resin cement containing MDP group and dentin bonding system, and Multilink Automix resin cement with dentin bonding system , were compared. The results reject the hypothesis, which states that using the self adhesive resin cement (RelyX™ Unicem) will result in the highest mean shear bond strength among the other adhesive cements, and showed that Panavia F2.0 exhibited the best performance in shear bond strength to the modified surface after artificial aging. But the difference in shear bond strength values was not significantly different compared to RelyX™ Unicem. However, both were significantly different from Multilink Automix. In agreement with these findings, study by Kumbuloglu *et al.*, has shown that in combination with air-particle abrasion methods, Panavia F 2.0 and RelyX^{TM} Unicem resin luting cements with phosphoric-acid methacrylate content provide a strong resin bond to zirconium oxide.[120]

The shear bond strength to zirconia ceramics study by Kern and Wegner has shown that only the phosphate modified composite resin cement with MDP (Panavia and Panavia 21) provided a long-term durable bond, and resulted in the highest bond strength values after airborne particle abrasion.[79] Aslo, Blatz *et al*., study of shear bond strength to zirconia ceramics has shown that composite resin cement containing an adhesive phosphate monomer MDP provided significant bond strength values.[78] Results of the two previous studies are in partial agreement with the results of this study; in group II (APA) and III (HES) the SBS values of Panvia F2.0 cement were the highest, while in group I (Control) RelyX^{TM} Unicem resin cement was the highest. However, the differences in the SBS values of these two cements in all groups were not statistically significant.

RelyX^{TM} Unicem showed the capability of bonding the substrate, regardless of the ceramic surface treatment and without additional coupling agent application. Bonding mechanism of RelyX^{TM} Unicem is similar to the self-adhesiveness of glass ionomer cements and a possible improvement in bond strength may occur after cement maturation overtime.[131] Higher shear bond strengths of the cement to sandblasted ceramics have been recently reported after 14 days of water storage and thermocycling.[81]

The last hypothesis, which states that among the Panavia F 2.0 and Multilink Automix cements, using a zirconia primer will increase the mean shear bond strength is rejected as well, because the zirconia primer did not show any improvement in the mean shear bond strength when it is used with Panavia F2.0. However, it provided significant bond strength values with Multilink Automix. The possible explanation for this observable fact is that Panavia F2.0 already has the MDP phosphate monomer in its composition, but Multilink Automix does not. Therefore, zirconia primer which contains MDP would be more beneficial when it used with Multilink Automix. In accordance to this study, Qeblawi *et al.*, evaluated the bond strength of Multilink Automix resin cement after different mechanical and chemical treatment of zirconia (IPS e.maxZirCAD, Ivoclar Vivadent AG) and found that air-particle abrasion followed by the application of a zirconia primer has resulted in improved resin bond strength.[128] Also, Atsu *et al.*, evaluated the SBS of Panavia F2.0 to zirconia ceramic (Cercon) after using different surface treatments and primer/bonding agents and showed no significant difference of using the MDP-containing bonding agent after the airborne-particle abrasion.[7]

Long-term water storage and thermal cycling are commonly used to simulate aging of resin bond interfaces. Because these 2 parameters coexist clinically, this study used the 2 techniques combined. In the literature, there is no consensus on a relevant regimen for artificial aging.[132] Gale and Darvel reviewed 130 thermal cycling studies and reported median temperatures of 5 and 55°C for the low and high temperature tanks, respectively. Harper *et al.*, noted that a patient would not tolerate direct contact of a vital tooth with extremely hot or cold substances for longer than 15 seconds.[133] Cycling numbers in the literature range from 100-50,000 cycles.[134,135] The number of cycles is usually arbitrarily set, which makes it difficult to compare results. The ISO

TR 11450 standard indicates that 500 cycles in water at 5-55°C is an appropriate aging regimen.[136] However, Gale and Darvell concluded that 10,000 cycles corresponds to approximately 1 year of *in vivo* function.[132] The number of cycles in this study was arbitrarily set at 5000 over 30 days.

In this study the ceramic were cemented to composite resin blocks, rather than to natural tooth structures, because of the uniform structure of the composite resin cylinders and the microstructural variations in tooth structure (enamel or dentin) that could result in incorrect interpretation of the results. Furthermore, the purpose of the present study is to evaluate only the bond strength of resin luting agent to ceramic, while varying the treatment applied to the ceramic surface.

In vitro studies such as this shear bond strength study do not replace clinical studies, and their outcomes should be interpreted with caution.[79] For this study, the shear bond strength test was used because it is a commonly used method and its reliability has been demonstrated in previous studies.[7,78,81] The limitation of the shear bond test is that it may fail to eliminate nonuniform interfacial stresses causing cohesive failures in the bonding substrate, which may result in misinterpretation of the data. However, the present study found primarily adhesive failures, which may indicate the validity of the applied testing method. The ceramic composition and intaglio surface are specific for each commercial system; thus, conclusions drawn for one zirconia ceramic system may not be applicable to others.

All *in vitro* studies have limitations and randomized clinical trials are the ultimate tools to evaluate the benefits of a certain clinical procedure. Numerous factors such as preparation design and 3-dimensional geometry of the restoration may influence the long-term clinical outcome of resin-bonded all-ceramic restorations and cannot be included in an in vitro study. Two of the primary objectives of *in vitro* studies are the elimination of influential parameters and limitation of the variables. Hypothesis-driven focus on narrowly defined parameters may not sufficiently simulate intraoral conditions, but allows for preliminary testing and identification of superior materials and methods that may later be tested in a more relevant setting.

Conclusion

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

1. Airborne-particle abrasion with Al_2O_3 is the preferred treatment method for zirconia.

2. The use of composite resin cement with a dentin bonding system did not yield greater retention.

3. Using zirconia primer with non MDP-containing resin cement is necessary to achieve durable bond to densely sintered zirconia ceramics.

References

1. Blatz MB, Sadan A, Kern M. Resin–ceramic bonding: a review of the literature: J Proshtet Dent 2003;89:268–74.

2. Raigrodski AJ, Chiche GJ, Potiket N, Hochstedtler JL, Mohamed SE, Billiot S, et al. The efficacy of posterior three unit zirconium-oxide-based ceramic fixed partial denture prostheses: a prospective clinical pilot study. J Proshtet Dent 2006; 96:237–44.

3. Burke FJ, Fleming GJ, Nathanson D, Marquis PM. Are adhesive technologies needed to support ceramics? An assessment of the current evidence. Journal of Adhesive Dentistry 2002;4:7–22.

4. Christel P, Meunier A, Heller M, Torre JP, Peille CN. Mechanical properties and short-term in-vivo evaluation of yttrium-oxide-partially-stabilized zirconia. J Biomed Mater Res 1989;23:45-61.

5. Luthardt RG, Holzhuter M, Sankuhl O, Herold V, Schnapp JD, Kuhlisch E, *et al*. Reliability and properties of ground Y-TZP-zirconia ceramics. J Dent Res 2002; 81:487-91.

6. Derand T, Molin M, Kvam K. Bond strength of composite luting cement to zirconia ceramic surfaces. Dent Mater 2005; 21:1158–62.

7. Atsu SS, Kilicarslan MA, Kucukesmen HC, Aka PS. Effect of zirconium-oxide ceramic surface treatments on the bond strength to adhesive resin. J Proshtet Dent 2006; 95:430–6.

8. Amaral R, Ozcan M, Bottino MA, Valandro LF. Microtensile bond strength of a resin cement to glass infiltrated zirconia-reinforced ceramic: the effect of surface conditioning. Dent Mater 2006; 22:283–90.

9. Bottino MA, Valandro LF, Scotti R, Buso L. Effect of surface treatments on the resin bond to zirconium-based ceramic. Int J Prosthod 2005; 18:60–5.

10. Kosmac T, Oblak C, Jevnikar P, Funduk N, Marion L. The effect of surface grinding and sandblasting on flexural strength and reliability of Y-TZP zirconia ceramic. Dent Mater 1999; 15:426–33.

11. Guazzato M, Quach L, Albakry M, Swain MV. Influence of surface and heat treatments on the flexural strength of YTZ dental ceramic. J Dent 2005; 33:9–18.

12. Sato H, Yamada K, Pezzotti G, Nawa M, Ban S. Mechanical properties of dental zirconia ceramics changed with sandblasting and heat treatment. Dent Mater 2008; 27:408–14.

13. Luthardt RG, Sandkuhl O, Reitz B. Zirconia-TZP and alumina-advanced technologies for the manufacturing of single crowns. European Journal of Prosthodontics and Restorative Dentistry 1999; 7:113–19.

14. Ferrari M, Cagidiaco MC, Borracchini A, Bertelli E. Evaluation of a chemical etching solution for nickel–chromium– beryllium and chromium–cobalt alloys. J Proshtet Dent 1989;62:516–21

15. Casucci A, Osorio E, Osorio R, Monticelli F, Toledano M, Mazzitelli C , Ferrari M. Influence of different surface treatments on surface zirconia Frameworks. j.jdent.2009.06.013

16. Piconi C, Maccauro G. Zirconia as a ceramic biomaterial (Review). Biomaterials 1999; 20:1-25.

17. Helmer JD, Driskell TD. Research on bioceramics. Symp. On Use of Ceramics as Surgical Implants. South Carolina (USA): Clemson University, 1969.

18. Christel P, Meunier A, Dorlot J-M et al. Biomechanical compatibility and design of ceramic implants for orthopaedic surgery. Bioceramics: material charateristics versus in vivo behavior. Ann NY Acad Sci 1988;523:234-56.

19. Subbarao EC. Zirconia-an overview. In: Heuer AH, Hobbs LW, editors. Science and technology of zirconia. Columbus, OH: The American Ceramic Society; 1981. p. 1–24.

20. Kisi E, Howard C. Crystal structures of zirconia phases and their interrelation. Key Eng Mater 1998;153/154.

21. Garvie R, Nicholson P. Phase analysis in zirconia systems, J Am Ceram Soc 1972; 55: 303 –05.

22. Heuer A, Lange F, Swain M, Evans G, Transformation toughening: an overview, J Am Ceram Soc 1986; 69: i–iv.

23. Guazzato M, Albakry M, Ringer S, Swain M, Strength, fracture toughness and microstructure of a selection of all-ceramic materials. Part II. Zirconia-based dental ceramics, Dent Mater 2004; 20: 449–56.

24. Hannink RHJ, Kelly PM, Muddle BC. Transformation toughening in zirconia-containing ceramics. J Am Ceram Soc 2000; 83: 461–87.

25. Sato T, Ohtaki S, Shimada M. Transformation of yttria partially stabilized zirconia by low-temperature annealing in air, J Mater Sci 1985; 20: 1466-70.

26. Sato T, Shimada M. Crystalline phase-change in yttria-partially-stabilized zirconia by low-temperature annealing, J Am Ceram Soc 1984; 67: 212–13.

27. Sato T, Shimada M. Transformation of yttria-doped tetragonal ZrO2 polycrystals by annealing in water, J Am Ceram Soc 1985; 68: 356–59.

28. Evans AG. Perspective on the development of high toughness –ceramics J Am Gerem Soc. 1990;73:187-06.

29. White SN, Miklus VG, Mclarin EA. Flexural strength of layered zirconia and porcelain dental all -ceramic system. J Prosthet Dent 2005:94:125-31.

30. Parker R. Use of Zirconia in Restorative Dentistry. Denistry Today. March 2007:114-19.

31. Denry I, Kelly J. State of the art of zirconia for dental applications, Dent Mater 2008; 24: 299-07.

32. Filser F, Kocher P, Gauckler LJ. Net-shaping of ceramic components by direct ceramic machining. Assembly Autom 2003;23:382–90.

33. Suttor D, Hauptmann H, Schnagl R, Frank S, inventors; 3M Espe AG, assignee. Coloring ceramics by way of ionic or complex-containing solutions. US Patent 6,709,694; March 23, 2004.

34. Cales B. Colored zirconia ceramics for dental applications. In: LeGeros RZ, Legeros JP, editors. Bioceramics. New York: World Scientific Publishing Co. Pte. Ltd.; 1998.

35. Sundh A, Molin M, Sj ¨ ogren G. Fracture resistance of yttrium oxide partially-stabilized zirconia all-ceramic bridges after veneering and mechanical fatigue testing. Dent Mater 2005; 21:476–82.

36. Piconi C, Maccauro G, Pilloni L, Burger W, Muratori F, Richter HG. On the fracture of a zirconia ball head. J Mater Sci Mater Med 2006; 17:289–300.

37. Huang H. Machining characteristics and surface integrity of yttria stabilized tetragonal zirconia in high speed deep grinding, Mater Sci Eng A: Struct 2003; 345: 155–63.

38. Mclarin EA, Hyo L, CAD/CAM update technologies and materials and clinical perspective Inside Denistry. 2006; Nov/Dec:l02.

39. Larsson C, Vult von Steyern P, Sunzel B, Nilner K. All-ceramic 2–5-unit implant-supported reconstructions. A randomized, prospective clinical trial, Swed Dent J 2006; 30:45–53.

40. Tinschert J, Natt G, Mautsch W, Augthun M , Spiekermann H. Fracture resistance of lithium-disilicate-, alumina-, and zirconia-based three-unit fixed partial dentures: a laboratory study, Int J Prosthodont 2001;14: 231–38.

.

41. Tinschert J, Natt G, Hassenpflug S, Spiekermann H. Status of current CAD/CAM technology in dental medicine, Int J Comput Dent 2004;7:25–45.

42. Vult von Steyern P, Carlson, Nilner K. All-ceramic fixed partial dentures designed according to the DC-Zirkon technique. A 2-year clinical study, J Oral Rehabil 2005; 32:180–87.

43. Tsalouchou E, Cattell MJ, Knowles JC, Pittayachawan P, McDonald A. Fatigue and fracture properties of yttria partially stabilized zirconia crown systems. Dent Mater 2008; 24:308– 318.

44. Herrero AA, Sierraalta M, Razzoog ME. Flexural strength of several porcelain systems for zirconium ceramics. J Dent Res 2006;85:abstract 1355.

45. Reich S, Wichmann M, Nkenke E, Proeschel P. Clinical fit of all-ceramic three unit fixed partial dentures, generated with three different CAD/CAM systems. Eur J Oral Sci 2005; 113:174-9.

46. Lin MT, Sy-Munoz J, Munoz CA, Goodacre CJ, Naylor WP. The effect of tooth preparation form on the fit of Procera copings. Int J Prosthodont 1998; 11:580-90.

47. Bindl A, Mormann WH. Marginal and internal fit of all-ceramic CAD/CAM crown copings on chamfer preparations. J Oral Rehabil 2005; 32:441-7.

48. Holmes JR, Bayne SC, Holland GA, Sulik WD. Considerations in measurement of marginal fit. J Prosthet Dent 1989; 62:405-8.

49. McLean JW, von Fraunhofer JA. The estimation of cement film thickness by an in vivo technique. Br Dent J 1971; 131:107-11.

50. Mehl A, Hickel R: Current state of development and perspectives of machine-based production methods for dental restorations. Int J Comput Dent 1999;2:9-35.

51. Suttor D, Bunke K, Hoescheler S, et al: Lava—the system for all-ceramic ZrO2 crown and bridge frameworks. Int J Comput Dent 2001; 3:195-06.

52. Denry IL, Holloway JA, Rosenstiel SF. Effect of ion exchange on the microstructure, strength, and thermal expansion behavior of a leucite reinforced porcelain. J Dent Res 1998; 77:583-88.

53. Thompson P, Rekeow D. Dental ceramics and the molar crown testing ground. J Appl Oral Sci 2004; 12(Spec. Iss.): 26–36.

54. Nakamura T, Dei N, Kojima T, Wakabayashi K. Marginal and internal fit of Cerec 3 CAD/CAM all-ceramic crowns. Int J Prosthodont 2003; 16: 244-48.

55. Iwai T, Komine F, Kobayashi K, Saito A, Matsumura H. Influence of convergence angle and cement space on adaptation of zirconium dioxide ceramic copings. Acta Odontologica Scandinavic , 2008; 66: 214 –18.

56. Jorgensen KD. The relationship between retention and convergence angle in cemented veneer crowns. Acta Odontol Scand 1955; 13:35-40.

57. Luthardt RG, Bornemann G, Lemelson S, Walter MH, Huls A. An innovative method for evaluation of the 3-D internal fit of CAD/CAM crowns fabricated after direct optical versus indirect laser scan digitizing. Int J Prosthodont 2004; 17: 680-85.

58. Denissen H, Dozic A, van der Zel J, van Waas M. Marginal fit and short-term clinical performance of porcelain-veneered CICERO, CEREC, and Procera onlays. J Prosthet Dent 2000; 84:506-13.

59. Addi S, Hedayati-Khams A, Poya A, Sjogren. CAM-manufactured ceramic inlays/onlays in vitro. J Dent 2002; 30:53-8.

60. Coli P, Karlsson S. Fit of a new pressuresintered zirconium dioxide coping. Int J Prosthodont 2004;17:59-64.

61. Scherrer SS, de Rijk WG. The fracture resistance of all-ceramic crowns on supporting structures with different elastic moduli. Int J Prosthodont 1993; 6:462-7.

62. Christensen GJ. Marginal fit of gold inlay castings. J Prosthet Dent 1966; 16:297-305.

63. Sadan A, Blatz M, Lang B. Clinical considerations for densely sintered alumina and zirconia restorations:Part 1. Int J Periodontics Restorative Den t. 2005; 25:213-219.

64. Sorensen JA. The Lava system for CAD/CAM production of high strength precision fixed prosthodontics. Quintessence Dental Technol. 2003; 26:57-67.

65. Manicone PF, Rossi Iommetti P & Raffaelli L. An overview of zirconia ceramics: Basic properties and clinical applications Journal of Dentistry. 2007; 35:819-26.

66. Zirconia Supported ceramic dental prosthesis, CRA Newsletter. Nov2004:28:2-4.

67. Ernst CP, Cohnen U, Stender E & Willershausen B. In vitro retentive strength of zirconium oxide ceramic crowns using different luting agents The Journal of Prosthetic Dentistry. 2005; 93:551-58.

68. Reich S, Petschelt A & Lohbauer U. The effect of finish line preparation and layer thickness on the failure load and fractography of ZrO(2) copings The Journal of Prosthetic Dentistry.2008; 99:369-76.

69. Ardlin B. Transformation-toughened zirconia for dental inlays, crowns and bridges: Chemical stability and effect of temperature aging on flexural strength and surface structure. Dent Mater 2002; 82:238-42.

70. Chong K, Chai J, Takahashi Y, Wozniak W. flexural strength of in-ceram alumina and in-ceram zirconia core materials. Int J prosthodont 2002; 15:183-88.

71. Mou SH, Chai T, Wang JS, Shiau YY. Influence of different convergence angles and tooth preparation heights on the internal adaptation of Cerec crowns. J Prosthet Den 2002; 87: 248-55.

72. Burke FJ. Fracture resistance of teeth restored with dentin-bonded crowns: the effect of increased tooth preparation. Quintessence Int. 1996; 27:115-21.

73. Kaufman EG, Coelho DH, Colin L. Factors influencing the retention of cemented gold castings. J Prosthet Dent 1961; 11:487-02.

74. Eames WB, O'Neal SJ, Monteiro J, Miller C, Roan JD Jr, Cohen KS. Techniques to improve the seating of castings. J AmDent Assoc 1978; 96:432-7.

75. Johnson GH, Hazelton LR, Bales DJ, Lepe X. The effect of a resin-based sealer on crown retention for three types of cement. J Prosthet Dent 2004; 91:428-35.

76. Johnson GH, Lepe X, Bales DJ. Crown retention with use of a 5% glutaraldehyde sealer on prepared dentin. J Prosthet Dent 1998; 79:671-6.

77. Gorodovsky S, Zidan O. Retentive strength, disintegration, and marginal quality of luting cements. J Prosthet Dent 1992; 68:269-74.

78. Blatz MB, Sadan A, Martin J, Lang B. In vitro evaluation of shear bond strengths of resin to densely-sintered high-purity zirconium oxide after long-term storage and thermal cycling. J Prosthet Dent 2004; 91:356-62.

79. Kern M,Wegner SM. Bonding to zirconia ceramic: adhesion methods and their durability. Dent Mater 1998; 14:64-71.

80. Piwowarczyk A, Lauer HC. Mechanical properties of luting cements after water storage. Oper Dent 2003; 28:535-42.

81. Piwowarczyk A, Lauer HC, Sorensen JA. The shear bond strength between luting cements and zirconia ceramics after two pre-treatments. Oper Dent 2005; 30:382-8.

82. Gwinnett AJ, Matsui A. A study of enamel adhesives. The physical relationship between enamel and adhesive. Arch Oral Biol 1967; 12:15-20.

83. Fusayama T, Nakamura M, Kurosaki N, Iwaku M. Non-pressure adhesion of a new adhesive restorative resin. J Dent Res 1979; 58:1364-70.

84. Nakabayashi N, Kojima K, Masuhara E. The promotion of adhesion by the infiltration of monomers into tooth substrates. J Biomed Mater Res 1982; 16:265-73.

85. Spohr AM, Sobrinho LC, Consani S, Sinhoreti MA, Knowles JC. Influence of surface conditions and silane agent on the bond of resin to IPS Empress 2 ceramic. Int J Prosths 2003; 16:277–82.

86. Kamada K, Yoshida M, Atsuta M. Effect of ceramic treatments on the bond of four resin luting agents to a ceramic material. J Prosthet Dent1998; 79:508–13.

87. Ozcan M, Alkumru HN, Gemalmaz D. The effect of surface treatment on the shear bond strength of luting cement to a glass-infiltrated alumina ceramic. Int J Prosthodont 2001; 14:335–9.

88. Semmelmann JO, Kulp PR. Silane bonding porcelain teeth to acrylic. J Am Dent Assoc 1968; 76:69-73.

89. Jochen DG, Caputo AA. Composite resin repair of porcelain denture teeth. J Prosthet Dent 1977; 38:673-9.

90. Ferrando JM, Graser GN, Tallents RH, Jarvis RH. Tensile strength and microleakage of porcelain repair materials. J Prosthet Dent 1983; 50:44-50.

91. Lacy AM, LaLuz J, Watanabe LG, Dellinges M. Effect of porcelain surface treatment on the bond to composite. J Prosthet Dent 1988; 60:288-91.

92. Calamia JR. Etched porcelain veneers: the current state of the art. Quintessence Int 1985; 16:5-12.

93. Bailey LF, Bennet RJ. DICOR surface treatments for enhanced bonding. J Dent Res 1988; 67:925-31.

94. Wolf DM, Powers JM, O'Keefe KL. Bond strength of composite to porcelaintreated with new porcelain repair agents. Dent Mater 1992; 8:158-61.

95. Sorensen JA, Engelman MJ, Torres TJ, Avera SP. Shear bond strength of composite resin to porcelain. Int J Prosthodont 1991; 4:17-23.

96. Chen JH, Matsumura H, Atsuta M. Effect of different etching periods on the bond strength of a composite resin to a machinable porcelain. J Dent 1998; 26:53-8.

97. Chen JH, Matsumura H, Atsuta M. Effect of etchant, etching period, andsilane priming on bond strength to porcelain of composite resin. Oper Dent 1998; 23:250-7.

98. Barghi N. To silanate or not to silanate: making a clinical decision. Compend Contin Educ Dent 2000; 21:659-62, 664.

99. Estafan D, Dussetschleger F, Estafan A, Jia W. Effect of prebonding procedures on shear bond strength of resin composite to pressable ceramic. Gen Dent 2000; 48:412-6.

100. Della Bona A, Anusavice KJ, Shen C. Microtensile strength of composite bonded to hot-pressed ceramics. J Adhes Dent 2000; 2:305-13.

101. Horn HR. Porcelain laminate veneers bonded to etched enamel. Dent Clin North Am 1983; 27:671-84.

102. Bailey JH. Porcelain-to-composite bond strengths using four organosilane materials. J Prosthet Dent 1989; 61:174-7.

103. Kato H, Matsumura H, Atsuta M. Effect of etching and sandblasting on bond strength to sintered porcelain of unfilled resin. J Oral Rehabil 2000; 27:103-10.

104. Frankenberger R, Kramer N, Sindel J. Repair strength of etched vs silicacoatedmetal-ceramic and all-ceramic restorations. Oper Dent 2000; 25: 209-15.

105. Soderholm KJ, Shang SW. Molecular orientation of silane at the surface of colloidal silica. J Dent Res 1993; 72:1050-4.

106. Sorensen JA, Kang SK, Avera SP. Porcelain-composite interface microleakage with various porcelain surface treatments. Dent Mat 1991; 7:118-23.

107. Oyagu e RC, Monticelli F, Toledano M, Osorio E, Ferrari M, Osorio R. Effect of water aging on microtensile bond strength of dual-cured resin cements to pre-treated sintered zirconium-oxide ceramics. Dent Materl 2009; 25:392–9.

108. Senyilmaz DP, Palin WM, Shortall AC, Burke FJ. The effect of surface preparation and luting agent on bond strength to a zirconium-based ceramic. Operative Dentistry 2007; 32:623– 30.

109. Derand P, Derand T. Bond strength of luting cements tozirconium oxide ceramics. Int J Prosthodont 2000; 13:131–5.

110. Blatz MB, Chiche G, Holst S, Sadan A. Influence of surface treatment and simulated aging on bond strengths of luting agents to zirconia. Quintessence Int 2007; 38:745–53.

111. Wolfart M, Lehmann F, Wolfart S & Kern M. Durability of the resin bond strength to zirconia ceramic after using different surface conditioning methods. Dent Mater 2007; 23:45-50.

112. Valandro LF, Ozcan M, Bottino MC, Bottino MA, Scotti R & Bona AD Bond strength of a resin cement to high-alumina and zirconia-reinforced ceramics: The effect of surface conditioning J Adhes Dent. 2006; 8:175-81.

113. Kern M, Thompson VP. Sandblasting and silica coating of a glass infiltrated alumina ceramic: volume loss, morphology, and changes in the surface composition. J Prosthet Dent 1994; 71:453-61.

114. Kern M, Thompson VP. Bonding to glass infiltrated alumina ceramic:adhesive methods and their durability. J Prosthet Dent 1995; 73:240-9.

115. Sadoun M, Asmussen E. Bonding of resin cements to an aluminous ceramic: a new surface treatment. Dent Mater 1994; 10:185-9.

116. Papanagiotou HP, Morgano SM, Giordano RA & Pober R. In vitro evaluation of low-temperature aging effects and finishing procedures on the flexural strength and structural stability of Y-TZP dental ceramics. J Prosthet Dent 2006; 96:154-164.

117. Curtis AR, Wright AJ & Fleming GJ. The influence of surface modification techniques on the performance of a YTZP dental ceramic. J Dent 2006; 34:195-06.

118. Kern M, Strub JR. Bonding to alumina ceramic in restorative dentistry: clinical results over up to 5 years. J Dent 1998; 26:245-9.

119. Matinlinna JP, Heikkinen T, Ozcan M, Lassila LV & Vallittu PK Evaluation of resin adhesion to zirconia ceramic using some organosilanes. Dent Mate 2006; 22:824-31.

120. Kumbuloglu O, Lassila LV, User A & Vallittu PK. Bonding of resin composite luting cements to zirconium oxide by two air-particle abrasion methods. Oper Dent 2006; 31:248-55.

121. Zhang Y, Lawn BR, Rekow ED & Thompson VP. Effect of sandblasting on the long-term performance of dental ceramics Journal of Biomedical Materials Research Part B Applied Biomaterials 200; 71:381-86.

122. Kern M. Clinical long-term survival of two-retainer and single-retainer all-ceramic resin-bonded fixed partial dentures Quintessence International. 2005; 36(2) 141-147.

123. Aboushelib MN, Kleverlaan CJ, Feilzer AJ. Selective infiltration-etching technique for a strong and durable bond of resin cements to zirconia-based cements. J Prosthet Dent 2007; 98:379–88.

124. Della Bona A, Donassollo TA, Demarco FF, Barrett AA, Mecholsky Jr JJ. Characterization and surface treatment effects on topography of a glass-infiltrated alumina/ zirconia-reinforced ceramic. Dent Mater 2007; 23:769–75.

125. Javid AH, Hassani AH, Golshan G. Selective removal of heavy metals from ferric chloride caused by etching processes by using sulfide precipitation. Journal of Environmental Science and Technology 2004; 20.

126. Anusavice KJ. Mechanical properties of materials. In: Saunders WB, editor. Phillips' science of dental materials. 11^{th} ed. 2003. pp. 115–18.

127. Quaas AC, Yang B, Kern M Panavia F 2.0 bonding to contaminated zirconia ceramic after different cleaning procedures. Dent Mater 2007; 23:506–512.

128. Qeblawi D, Muñoz C, Brewer J, Monaco E. The effect of zirconia surface treatment on flexural strength and shear bond strength to resin cement. J Prosthet Dent 2010; 103:210-20.

129. Derand T, Molin M, Kleven E, Hagg P, Karlsson S. Bond strength of luting materials to ceramic crowns after different surface treatments. Eur.J. Prosthodont. Rest, Vol.16, No. 1, pp 35-38.

130. Phark J, Blatz MB, Sadan A. An in vitro evaluation of the long-term resin bond to a new densely sintered high-purity zirconium-oxide ceramic surface. J Prosthet Dent 2009; 101:29-38.

131. Yap AU, Tan AC, Goh AT, Goh DC, Chin KC. Effect of surface treatment and cement maturation on the bond strength of resin modified glass ionomers to dentin. Oper Dent 2003; 28:728–33.

132.Gale MS, Darvell BW. Thermal cycling proceduresfor laboratory testing of dental restorations. J Dent 1999; 27:89-99.

133. Harper RH, Schnell RJ, Swartz ML, Phillips RW. In vivo measurements of thermal diffusion through restorations of various materials. J Prosthet Dent 1980; 43:180-5.

134. Crim GA, Garcia-Godoy F. Microle akage: the effect of storage and cycling duration. J Prosthet Dent 1987; 57:574-6.

135. Inoue S, Koshiro K, Yoshida Y, De Munck J, Nagakane K, Suzuki K, *et al*. Hydrolytic stability of self-etch adhesives bonded to dentin. J Dent Res 2005; 84:1160-4.

136. International Standards Organization. ISO TR 11405:1994. Dental materials- guidance on testing of adhesion to tooth structure. Geneva: ISO; 1994. Available at: http://www.iso.ch/iso/en/ prods-services/ISOstore/store.html.