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Adhesion/cementation to zirconia and other non-silicate ceramics: Where are we now?

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Abstract

Non-silicate ceramics, especially zirconia, have become a topic of great interest in the field of prosthetic and implant dentistry. A clinical problem with use of zirconia-based components is the difficulty in achieving suitable adhesion with intended synthetic substrates or natural tissues. Traditional adhesive techniques used with silica-based ceramics do not work effectively with zirconia. Currently, several technologies are being utilized clinically to address this problem, and other approaches are under investigation. Most focus on surface modification of the inert surfaces of high strength ceramics. The ability to chemically functionalize the surface of zirconia appears to be critical in achieving adhesive bonding. This review will focus on currently available approaches as well as new advanced technologies to address this problem.

Keywords

Adhesion; Bonding; Surface Modification; Surface Functionalization; Zirconia

INTRODUCTION

Developments over the last 10–15 years in ceramic materials science for dental applications have led to a class of high strength materials (i.e. zirconia-based ceramics) which potentially provide better fracture resistance and long-term viability when compared to porcelain and other inorganic, non-metallic alternatives. There is a wealth of information in the scientific literature regarding the use of zirconia (ZrO₂) in dental applications [1–3]. Although superior in terms of mechanical performance (strength, toughness, fatigue resistance), there are some inherent problems associated with ZrO₂. One problem is with adhesion to the variety of substrates (synthetics or tissues) that that can be encountered in dental or other biomedical applications. Conventional cementation/attachment techniques used with ZrO₂ components do not provide sufficient bond strength for many of these applications [4–6]. It is important for high retention, prevention of microleakage, and increased fracture/fatigue resistance, that bonding techniques be optimized. Strong resin bonding relies on micromechanical interlocking and adhesive chemical bonding to the ceramic surface, which

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requires surface roughening for mechanical bonding and surface activation for chemical adhesion. In some instances, high strength ceramic restorations do not require adhesive bonding to tooth structure and can be placed using conventional cements which rely only on micromechanical retention. However, resin bonding is desirable in many clinical situations – e.g., when the prepared tooth structure is unusually short or tapered. In addition, it is likely that strong chemical adhesion would lead to enhanced long-term fracture and fatigue resistance in the oral environment. Non-destructive methods for treating inert ceramics to produce an activated/functionalized surface are desirable in such cases. These methods could also be used in endodontic and implant applications, where ZrO₂ has become a prominent material for fabricating posts and implant components [7–12], and where resin-based endodontic filling materials are often now employed, and adhesive bonding is desired.

Bonding to traditional silica-based ceramics, generally employing both mechanical and adhesive retention, has been well researched, and bond strengths are predictable. A strong resin bond relies on chemical adhesion between the cement and ceramic (by way of silane chemistry), and on micromechanical interlocking created by surface roughening. Current roughening techniques are: (1) grinding, (2) abrasion with diamond (or other) rotary instruments, (3) air abrasion with alumina (or other) particles, (4) acid etching (typically HF), and (5) a combination of any of these techniques. Unfortunately, the composition and physical properties of ZrO₂ differ from conventional silica-based materials like porcelain. Zirconia is not readily etched by HF, and requires very aggressive mechanical abrasion methods to be used to increase surface roughness, possibly creating strength reducing surface flaws [13–15]. Therefore, in order to achieve acceptable cementation in a wide range of clinical applications, alternate attachment methods, ideally utilizing chemical adhesion in addition to mechanical retention, are required for zirconia ceramics. Various approaches to this problem will be discussed in this review.

ZIRCONIA AS A BIOMATERIAL

Zirconium oxide (ZrO₂), or zirconia, is a metal oxide that was identified as a reaction product of heating the gem, zircon, by the German chemist Martin Heinrich Klaproth in 1789 [16]. Zirconia is polymorphic in nature, meaning that it displays a different equilibrium (stable) crystal structure at different temperatures with no change in chemistry. It exists in three crystalline forms: monoclinic at low temperatures, tetragonal above 1170°C and cubic above 2370°C [17,18]. A characteristic of this behavior is a change in crystal structure from tetragonal to monoclinic during cooling, which results in a volume increase (3–4 %) that can induce large stresses. These stresses can produce cracks that result in spallation, crumbling, and failure. Work by Ruff [19] showed that the cubic phase could be stabilized in ZrO₂ with the addition of small amount of calcia (CaO), making it possible to use ZrO₂ as an engineering material.

Over the years, other metal oxides like cesium oxide (CeO₂), magnesia (MgO), and yttria (Y₂O₃) have been used to create a range of partially stabilized zirconia (PSZ) compositions, which are primarily cubic phase at room temperature, with monoclinic and tetragonal precipitates as a minor phase [17]. For example, the addition of 8 mol % MgO to ZrO₂ results in the creation of a stable matrix of cubic phase grains, with a metastable phase of tetragonal crystals that precipitate during cooling. In the Y₂O₃ - ZrO₂ system, the addition of 2–3 mol % Y₂O₃ to ZrO₂ produces a metastable matrix of tetragonal crystals referred to as tetragonal zirconia polycrystals (TZP) [20,21]. PSZ is of particular interest because of its transformation toughening properties [22]. As a crack initiates and propagates in PSZ during application of an external load, the tetragonal phase can transform to a monoclinic phase around and near the tip of the crack. The resulting volume expansion caused by the transformation creates compressive stresses at the crack tip. This actively hinders

propagation, because excess energy is now necessary for the crack to continue to propagate, thus increasing PSZ's resistance to fracture.

PSZs have gained popularity in many industries due to exceptional wear resistance, fracture toughness (7–8 MPa-m^{1/2}), and flexural strength (0.9–1.5 GPa) [23,24]. Because of this, PSZs have been used in blades to cut Kevlar, incorporated into magnetic tape, and as a structural component in a variety of filters [16]. PSZ's toughness, corrosion resistance, and thermal conductivity make it a good refractory material used in abrasives or as a thermal barrier coating on manufactured parts operating in aggressive environments, like extrusion dies, valves, and port liners for combustion engines [16,25]. PSZ is used as a refractory liner or valve part in foundries due to its thermal shock resistance [16]. Its high refractive index and transparency in the visible and near-infrared spectrum make it useful in optical filters, and laser mirrors [26]. It is used in high temperature oxygen separation, oxygen sensors, and fuel cell membranes due to its high ionic conductivity [27,28] and as an alternative gate dielectric in microelectronics because of its high dielectric constant [29,30].

In recent years, ZrO₂ has gained attention as a biomaterial due to superior mechanical properties, compared to alumina (Al₂O₃), and chemical and biological inertness that makes it very biocompatible [31]. Exploration into ZrO₂ as a biomaterial began in the 1960s [32], with most of the work over the years focused on the use of ZrO₂ in orthopedics, specifically in the area of femoral heads for total hip replacements [33,34]. Recently, ZrO₂ has been introduced in dentistry due to its superior esthetic potential when compared to metal-ceramic constructs. Zirconia has been explored as a dental material for a variety of clinical applications: orthodontic brackets [35], endodontic posts/dowels [36–38] and abutments [39,40], single crowns [41,42] and fixed partial dentures [43,44].

Bonding to ZrO₂ has become a topic of great interest in recent years [4,5,45–67]. As previously stated, traditional adhesive chemistry is ineffective on ZrO₂ surfaces, since they are essentially non-polar and inert. Additionally, acid etchants like HF do not sufficiently roughen the surface for simple micromechanical attachment. Surface abrasion with Al₂O₃ particles and application of a tribochemical silica coating allows for chemical bonds to a silane coupling agent and to resin cement. This is a somewhat complicated procedure that does not produce bond strengths as high as those reported for silane bonded porcelain [4,65,68]. In addition, there is some speculation that air particle abrasion should not be used, particularly with ZrO₂ ceramics, because it might cause microfractures that would reduce functional strength and lead to premature, catastrophic failure. *In vitro* analysis has shown that surface flaw generation can reduce the fracture strength of ZrO₂ significantly [13,15,69]. The use of phosphoric acid primers or phosphate-modified resin cements has been shown to produce silane-like adhesion, through a similar type of hydroxylation-driven chemistry. However, bond strength values reported in the literature through use of these agents are generally lower than the values reported for tribochemical silica coating, coupled with silane and resin cement. The currently available approaches for adhesive bonding of ZrO₂ bioceramics are not adequate for all clinical applications, and long-term durability is currently unknown [49]. Other hydroxylation approaches are also being developed, but they often utilize very powerful acidic or basic chemistries, and their utility, especially for biomedical application is not yet known [70–74].

MECHANICAL BONDING

Bonding of ZrO₂ to tooth structure or other substrates requires a strong resin bond. The success of resin bonding relies on mechanical bonding through micromechanical interlocking from surface roughening, and if possible, chemical bonding between ceramic and cement. Phosphoric acid (H₃PO₄) or hydrofluoric acid (HF) etching are commonly

recommended methods used to surface roughen silica-based ceramics [75]. This creates a rough, clean surface, which improves wettability and increases surface area available for mechanical interlocking. Unfortunately, H_3PO_4 and HF cannot be used effectively on non silica-based ceramics, like ZrO_2 , making it difficult to roughen the surface for mechanical retention [4,54]. The lack of silica also removes the chemical bonding between silica-silane necessary for silanization.

Because of the difficulty in creating mechanical and chemical bonding in ZrO_2 , alternative methods have been explored to bond ZrO_2 using resins. Surface grinding is a commonly used alternative for roughening the surface of ZrO_2 to improve mechanical bonding. There are several methods used for surface grinding: grinding using abrasive paper or wheels (SiC or Al_2O_3), particle air-abrasion using Al_2O_3 or other abrasive particles ranging in size from 50 to 250 μm [76–78], and grinding using a diamond bur [78]. The advantage of these surface grinding methods is that they are generally easy to apply in a dental environment. However, research has shown that surface grinding techniques, using tradition resin cements, have no significant effect on increasing the bond strength of zirconia to resin cements [6,47,54,76,78,79].

Another problem with these techniques is that they can create surface microcracks [80,81]. These flaws act as crack initiation sites that can decrease strength and apparent fracture toughness. However, surface grinding also results in a tetragonal to monoclinic phase change on the surface of zirconia. This can theoretically produce a compressive stress layer that counteracts the flaw-induced reduction in strength [80,82]. Work by Guazzato *et al.* and Kosmač *et al.* showed that sandblasting produced the most effective tetragonal to monoclinic phase change when compared to fine polishing, grinding with an abrasive wheel, or grinding using a diamond bur [80,82]. It was determined that sandblasting was able to induce transformation at low temperature, with minimal surface damage. Care has to be taken with the amount of surface grinding, as an excess amount can diminish the strength enhancing effect.

Care also has to be taken when heat treating surface-ground ZrO_2 . It has been shown that heat treatment temperatures for bonding veneering porcelain to ZrO_2 substructures, around 900–930°C, can cause a decrease in flexure strength. The temperature applied during heat treatments, coupled with existing residual stresses, can sometimes be sufficient to cause a transformation of the monoclinic phase back to the tetragonal phase, which relieves the compressive stress in the surface layer and reduces the flexure strength of ZrO_2 .

The application of fused glass micro-pearls to the surface of ZrO_2 has been shown to increase the bond strength of resin cements to ZrO_2 [52,83]. In these studies, a slurry of micro-pearls was painted on a ZrO_2 surface and fired in a furnace. The fused glass film increased surface roughness of ZrO_2 , allowing increased micro-retention. The silica-rich film also allows for silanization of ZrO_2 before bonding, making it possible to form siloxane bonds to resin cement. Derand *et al.* showed that use of this fused micro-pearl film significantly increased the bond strength of ZrO_2 (11.3–18.4 MPa) compared to untreated or silanized ZrO_2 (0.5–1.5 MPa).

A novel surface roughening technique that has been explored for ZrO_2 is selective infiltration etching (SIE) [84]. SIE uses a heat-induced maturation process to pre-stress surface grain boundaries in ZrO_2 to allow infiltration of boundaries with molten glass. The glass is then etched out using HF, creating a 3D network of inter-granular porosity that allows nano-mechanical interlocking of resin cement. The advantage of SIE is that it only involves grains that are exposed to molten glass, allowing control of the area to be etched. Aboushelib *et al.* showed that using SIE on ZrO_2 resulted in increased microtensile bond

strength (49.8 ± 2.7 MPa) when compared to particle air-abraded ZrO_2 (33.4 ± 2.1 MPa). The use of SIE improved nano-mechanical retention of zirconia by increasing the surface area available for bonding. This was confirmed by AFM work done by Casucci *et al.* [85] showing that the surface roughness of ZrO_2 is significantly greater after SIE, when compared to particle air-abrasion or HF etching.

Recently, another experimental method has been examined for surface roughening of ZrO_2 . The use of a hot chemical etching solution has been proposed to etch the wings of Maryland bridges [86]. Although there has not been any reported research on the bond strength of ZrO_2 to resin cements using this treatment, AFM has shown that the application of hot chemical etching solution produces a surface roughness that is significantly greater than SIE [85]. It is possible that this technique could enhance the mechanical retention of ZrO_2 .

CHEMICAL BONDING - SILANE COUPLING AGENTS

Organo-silanes, generally referred to simply as “silanes” in dentistry, are compounds that contain a silicon (Si) atom or atoms, are similar to orthoesters in structure, and display dual reactivity. Their use in clinical dentistry and affect on adhesive bonding has been described in detail in the scientific literature [4,48,58,59,87–94]. One end of a silane molecule is organically functional (e.g., vinyl $-CH=CH_2$, amino $-NH_2$), and can polymerize with an organic matrix (e.g., a methacrylate). The other end is generally comprised of alkoxy groups (e.g., methoxy $-OCH_3$, ethoxy $-OCH_2CH_3$), which can react with a hydroxylated, silica containing surface, like porcelain. Silanes are commonly used in dentistry to coat glass filler particles in polymer matrix composites, to achieve adhesive bonding of porcelain (or other silica-containing ceramics) to resin luting cements for restorative applications, and with certain ceramic or ceramic-containing composite posts for endodontic applications employing resin-based filling materials. Silanes are also believed to promote surface wetting, which enhances potential micromechanical retention with low viscosity resin cements [58,67]. Traditional silane chemistry is not truly effective with ZrO_2 , as it possesses a relatively non-polar surface, is more chemically stable than silicacontaining ceramics, and not easily hydrolyzed.

Experimentation with different silane coupling agents has resulted in enhancement of luting of ZrO_2 . Matinlinna *et al.* [58] researched use of three trialkoxysilanes, 3-methacryloyloxypropyl-trimethoxysilane (MPS), 3-acryloyloxypropyl-trimethoxysilane (ACPS), and 3-isocyanatopropyl-triethoxysilane (ICS), in enhancing the bonding of two resin cements, an experimental Bis-GMA and commercial Bis-GMA (RelyX ARC, 3M-ESPE, Seefeld, Germany), to ZrO_2 . They determined that application of a tribochemical coating, followed by silanization with MPS and ACPS, were successful in bonding the two cements to ZrO_2 . It is thought that the RelyX ARC has a coefficient of thermal expansion that matches more closely with ZrO_2 , which results in enhanced bonding. Artificial aging using thermocycling showed that only RelyX ARC was able to maintain its shear bond strength after using MPS and ACPS. The decrease in bonding using ICS is due to the absence of acrylate and methacrylate groups in ICS that could polymerize and bond with the dimethacrylate groups in RelyX ARC. Matinlinna *et al.* [59] has also worked on a novel silane system, 3-mercaptopropyltrimethoxysilane (MEPS) blended with 1,2-bis-(triethoxysilyl)ethane (BTSE), that has shown promising results. This novel silane system demonstrated similar shear bond strength to MPS under dry conditions on particle air-abraded and silica-coated ZrO_2 . However, after thermocycling, bond strength obtained with the novel silane system decreased significantly and was significantly less than MPS. Further work in optimizing this novel silane system may provide stronger bonding after thermocycling.

Aboushelib *et al.* [95] showed that application of silane alone resulted in low bond strength. The use of five silanes (MPS, ACPS, and ICS along with styrylethyltrimethoxysilane and 3-(*N*-Allylamino)propyltrimethoxysilane) to aid in luting of as-received ZrO₂ resulted in bond strengths that were significantly less than when using the silanes on SIE ZrO₂. It was shown that MPS produced greater bond strength when used on SIE ZrO₂ compared to the other silanes. However, bond strength of SIE ZrO₂ using the silanes decreased significantly after long-term storage [96]. This decrease in bond strength demonstrates that use of silanes does not aid in producing a hydrolytically stable bond with ZrO₂. Although bond strength decreased after time, SIE does create a retentive surface for mechanical bonding. It is also possible that SIE could chemically modify the surface to improve bonding between the silane and ZrO₂.

Alternatively, the use of a zirconate coupling agent has been explored for pure zirconium and ZrO₂ [67,97]. The ZrO₂ coupling agent acts like a silane coupling agent by bonding ZrO₂ with hydroxyl groups. This coupling agent enhanced bonding to resin cements but exhibited a significant decrease in bond strength after thermocycling.

PRIMERS - SILICA COATING

Due to the lack of silica in ZrO₂, silica-coating techniques have been explored to utilize the chemical bonding provided by silanization. The use of a tribochemical silica coating is a common practice for coating metal alloys and alumina- and zirconia-based dental ceramics with silica [12,47,51,54,79,98–104] with the CoJet and Rocatec systems (3M ESPE, Seefeld, Germany) being the most heavily favored commercial products utilized for applying the coating. The tribochemical technique air-abrades the ceramic surface with alumina particles that have been coated with silica, embedding/coating the surface with silica [105,106]. This results in not only preparing a surface for silanization, but also creates micromechanical retention. Research has shown that the application of a tribochemical coating, before silanization, significantly enhances bond strength between a treated substrate and resin cement. However, there can be significant loss in bond strength over the long-term when using traditional resin cements used for silica-based ceramics. This might be a result of a low concentration of silica on the surface due to difficulty in particle abrasion caused by the high hardness of ZrO₂.

Cleaning of a tribochemical coated ZrO₂ before resin bonding can be deleterious to bond strength. Nishigawa *et al.*, [107] determined that ultrasonic cleaning of tribochemical coated ZrO₂ before silanization and resin bonding significantly decreases bond strength. Cleaning for 2 or 5 minutes resulted in bond strength statistically similar to air-abrading alone before bonding. It was shown that ultrasonic cleaning results in decreased silica content on the surface. This decrease, along with surface morphology changes, is thought to cause the loss of bond strength. Air pressure has also been shown to affect bond strength when applying a tribochemical coating. Heikkinen *et al.* [108] determined that increasing the air pressure at which tribochemical coating is applied significantly increases the bond strength of ZrO₂ to resin cement. It was also determined that increasing pressure increased the amount of silica on the ZrO₂ surface. It is thought that increasing air pressure, which increases kinetic energy of particles, causes an increase in surface roughness and the number of particles that contact the surface. This increases mechanical retention and the amount of silica available for chemical bonding.

Another method that had been used to apply a silica layer to ZrO₂-based ceramics is silicoating [109]. Silicoating involves pyrolytically applying a silica coating on a substrate surface, followed by application of silane, before bonding using a resin cement [110]. Using a lab device, butane gas is burned with atmospheric oxygen and guided over a container

filled with tetraethoxy silane. The gas is lit and the silane decomposes in the flame, coating the material with a layer of $\text{SiO}_x\text{-C}$ fragments that bond adhesively to the surface of the material [111]. Silicoating, marketed under the Silicoater-Technology (Silicoater, Kulzer Co., Friedrichshof, Germany), has been successful in improving the bond strength of resin cements to metals and decreasing the degradation of bond strength after thermocycling [105,106,112–114]. However, it was expensive and too complex to be commercially viable for standard dental applications.

Recent innovations in silicoating, *i.e.*, the PyrosilPen-Technology (PyrosilPen, SurA Instruments, Jena, Germany), have made it easier to use for chair-side applications. Application of the PyrosilPen-Technology had been researched on ZrO_2 -based ceramics [111]. Although there was no significant difference in bond strength, the ZrO_2 -based ceramics had lower bond strength than that of silicoated silica- and alumina-based ceramics. This could be due to a lack of micromechanical bonding since the surface of the ceramic was only abrasively ground using 800 grit grinding paper [111]. It is possible that bond strength could be improved if the surface was particle air-abraded before silicoating. Further research is required before the PyrosilPen-Technology can be used as an acceptable method to enhance bonding of ZrO_2 to resin cements.

Another form of silicoating uses a plasma spray technique to deposit a siloxane coating on ZrO_2 [52]. Derand *et al.* used a high-frequency generator to deposit hexamethyldisiloxane (HMDS) on the surface of ZrO_2 . When polymerized, HMDS acts like a silane, resulting in a siloxane bond between ZrO_2 and resin cement. The application of the plasma produced a bond strength that was significantly greater than untreated or silanized ZrO_2 but was significantly less than ZrO_2 coated with a film of porcelain micropearls. Using air-abrasion or surface grinding to increase mechanical retention could increase bond strength of plasma coated ZrO_2 .

Recently, another method has been proposed to apply a silica layer to the surface of ZrO_2 ceramics. Piascik *et al.* [68] have researched application of a unique vapor-phase deposition technique, in which a chloro-silane gas (SiCl_4) is combined with water vapor to form a Si_xO_y -functionalized surface on a ZrO_2 substrate. The process uses molecular vapor deposition (MVD), an enhancement on conventional vapor deposition, to deposit ultra-thin, uniform, organic molecular coatings on substrates using an in-situ surface plasma treatment [115]. MVD can produce hydrophobic, hydrophilic, biocompatible, protective, ordering, or otherwise reactive coatings on a variety of materials. The study conducted by Piascik *et al.* showed that ZrO_2 coated with a Si_xO_y film, followed by silanization and resin cement bonding, enhanced bond strength. Zirconia with a film thickness of 2.6 nm had significantly greater bond strength than tribochemical-coated ZrO_2 and was comparable to porcelain. The ZrO_2 that was bonded using a 23 nm Si_xO_y film had a significantly lower bond strength than the 2.6 nm film coated ZrO_2 but greater than untreated ZrO_2 . Based on these results, Piascik *et al.* stated that it is possible that bond strength of the Si_xO_y film is dependent on film thickness. The decrease in bond strength could be caused by a lack of chemisorption in the additional layers deposited on the ZrO_2 surface after the initial deposited layer. This would result in reducing the chemical adhesion between the layers, thus lowering the bond strength of the resin cement to the film. This would explain the increase in adhesive failure observed for the 23 nm film specimens compared the 2.6 nm film specimens. Further investigation into the optimal film thickness could result in expanding the use of ZrO_2 to more dental applications.

LUTING OF ZIRCONIA

Resin-based composite cements are the standard material used in luting a ceramic prosthetic to tooth structures [116]. Resin-based composite cements have compositions and characteristics similar to conventional restorative composites and consist of inorganic fillers embedded in an organic matrix (e.g., Bis-GMA, TEGDMA, UDMA). Retention of a dental restoration to tooth structure and sealing of the marginal gap between the restoration and tooth are dependent on the luting agent's ability to bond to the surface of the ceramic [117].

As previously mentioned, the non-silica composition of ZrO_2 makes it difficult to bond ZrO_2 to tooth structures using traditional resin composite cements. Previous research by Kern and Thompson [118] showed that use of Bis-GMA was unsuccessful in bonding to particle air-abraded alumina, but use of phosphate monomer-containing resin-based composite cement was able to form a durable bond to alumina. Kern and Wegner [54] were the first to report the long-term bond strength of phosphate monomer-containing resin-based composite cements to ZrO_2 . They compared the tensile bond strength of particle air-abraded ZrO_2 to several bonding systems: two chemical-cured phosphate monomer-containing resin-based cements, Panavia Ex (Kuraray Medical Inc., Kurashiki, Japan [10-methacryloyloxydecyl-dihydrogen-phosphate or MDP]) and Panavia 21 Ex (Kuraray Medical Inc., Kurashiki, Japan), BisGMA alone, BisGMA after silanization, BisGMA after tribochemical silica coating and silanization, BisGMA after acrylization, and chemical-cured polyacid-modified resin composite cement. After 150 days, it was determined that only the two phosphate containing cements exhibited high bond strength (Panavia: 49.7 ± 8.1 MPa; Panavia 21: 46.0 ± 7.4 MPa) and showed no significant difference in bond strength after artificial aging. Further work conducted by Wegner and Kern [76] on the 2-year tensile bond strength of resin cements to ZrO_2 confirmed the functional phosphate ester group of MDP forms a water-resistant chemical bond with zirconia. Based on their results, MDP-containing resin cements are recommended for luting bonding of ZrO_2 for clinical use.

Contrary to the research conducted by Wegner and Kern, Derand and Derand [78] found that Panavia Ex did not form a strong bond to ZrO_2 . Instead, they discovered that Superbond C & B (Sun Medical, Moriyama City, Japan), an autopolymerizing resin cement containing 4-META/TBB/PMMA, had significantly greater bond strength. Work by Ernst *et al.* [101] and Lee *et al.* [119] confirmed that Superbond C & B does produce greater bond strength than a MDP-containing resin cement (Panavia F [Kuraray Medical Inc., Kurashiki, Japan]). It is thought that the anhydride group in 4-META bonds with ZrO_2 and the tribochemical coating. However, there has not been any evidence to show that this chemical bond is significantly stronger than the bond of MDP to ZrO_2 . This was further confirmed by data in both studies showing that the bond strength of Superbond C & B was not significantly different than Panavia F. The low bond strength for Panavia Ex could be due to a difference in testing methods, shear vs. tensile. Tensile tests usually apply a standardized press for bonding while shear tests use a manual pressure, by hand, that clinically simulates pressure used to cement prosthetics to tooth structure during the cementation process [101,119]. Other factors that could affect bond strength are thickness of the cement film, the composition of the ZrO_2 ceramic used, the composite used for bonding, and the manner in which the ZrO_2 is resin-bonded to composite or tooth structure.

Even though Superbond C & B has demonstrated a greater retentive strength during shear testing compare to MDP-containing resin cements, research over the years has focused on studying and improving the bond strength of MDP resin cements to ZrO_2 [6,7,49,57,⁶⁶,79,103,120,121]. This is because MDP resin cements are hydrolytically stable, and therefore, do not decrease in bond strength over time. The addition of a MDP-containing bonding/silane coupling agent to enhance bonding of MDP resin cements has produced

positive results. It was shown that particle air-abrasion or tribochemical coating, followed by the application of MDP-containing bonding/silane coupling agent, resulted in increased bond strength compared to MDP-containing cements only [6,47,49,104,122]. It is known that acidic monomers rapidly hydrolyze silane coupling agents, producing the siloxane bonds necessary for chemical bonding [123]. It is thought that the acidic nature of MDP enhances the polysiloxane bonding produced by silane coupling agents and results in improved retention of resin cements to ZrO₂ [122].

Other phosphate monomer-containing cements like RelyX Unicem (3M ESPE, Seefeld, Germany), a universal self-adhesive resin cement, and non-phosphate monomer-containing cements like RelyX ARC and Bifix QM (VOCO GmbH, Cuxhaven, Germany), Bis-GMA resin cements, and Multilink Automix (Ivoclar Vivadent, Amherst, NY, USA), a phosphonic acid-based cement, have exhibited statistically comparable bond strength to MDP-containing resin cements in laboratory studies [6,49,57,79,103,120,121,124]. Although these resin cements have shown good mechanical retention, MDP-containing resin cement continues to be the popular choice for luting ZrO₂ prosthetics in clinical applications due to their low incident of failure and loss of retention [125–129].

BONDING OF VENEERING MATERIAL TO ZIRCONIA

The ability to accurately fabricate ZrO₂ sub-structures (copings) has improved dramatically in recent years. However, ZrO₂ copings for crowns or multi-unit frameworks still require application of veneering ceramic, usually specialized porcelain, to achieve suitable esthetics. A high percentage of clinical failures of ZrO₂-based dental prosthetics reported in the literature are attributed to debonding and/or fracture of veneering ceramic. Failure rates due to veneer debonding and/or fracture as high as 15% for ZrO₂ restorations 2–5 years old have been reported [1,42,128–130]. Besides framework design, the durability of the interface between the ZrO₂ framework and veneer depends on many factors related to the two different material phases, including chemical bonding, mechanical interlocking, and extent of interfacial stress generated via thermal expansion mismatch and glass transition temperature differences [131]. Since ceramics are extremely susceptible to tensile stresses, achieving a slight compressive stress in the veneering ceramic is preferred, as in metal-ceramic (PFM) restorations. For this to occur, the veneering material must have a thermal expansion coefficient lower than the core material [132]. Zirconia ceramics have coefficients of thermal expansion (CTE) ranging from approximately 9–11 $\mu\text{m}/\text{m}^\circ\text{K}$, depending on stabilizing oxide and other variables, while specialty porcelains can have CTE values ranging from 7–13 $\mu\text{m}/\text{m}^\circ\text{K}$, depending on compositional variations. Achieving an appropriate CTE match/mismatch is possible, but other factors related to intimate and uniform contact, and adhesion between the two ceramic phases is also important for success. There is evidence that chemical bonding between ZrO₂ substructures and porcelain veneering materials is important in achieving a durable interface, even to the extent that surface roughening of the ZrO₂ prior to veneer application might not be necessary [133]. The use of ZrO₂ surface modifiers to achieve strong primary bonding between coping and veneering ceramic could improve the clinical failure rates observed to date. Application of a silicate intermediate layer, applied on the ZrO₂ surface via a tribochemical approach has been studied [133]. A vapor deposition approach could also enable conformal silicate surface modification without use of an aggressive physical process, which might result in damage to the coping surface.

Core-veneer all-ceramic restorations have gained popularity as a substitute to metal-veneer restorations over the years. Although the mechanical properties of all-ceramic restorations are not superior to those of metal-veneer restorations, their esthetic appearance and biocompatibility make all-ceramic restorations more appealing for dentistry. The use of

ZrO₂, as a core material, has increased the mechanical strength and fracture toughness of all-ceramic restorations, allowing them to withstand occasional forces that occur during mastication. The strength of an all-ceramic restoration is determined by the core-veneer interface or the veneer material. A weak bond between the core and veneer can result in delamination or fracture of the veneer itself. There are several factors that play a role in determining the strength of any all-ceramic restoration: thickness of ceramic layers, elastic modulus of the core material, size and location of occlusal contact areas, coefficient of thermal expansion (α) of the core and veneer, residual stresses induced by processing, interfacial bond strength, environmental effects, and the direction, magnitude, and frequency of occlusal loads [134].

The bond strength of porcelain veneers to ZrO₂ has been examined using shear and microtensile bond strength test [135–141]. It was determined that bond strength of veneer to ZrO₂ is comparable to that of veneer to metal [138]. Differences in materials and testing condition could lead to differences in veneer bond strengths when comparing metal to ZrO₂[139], however bond strength of veneers to ZrO₂ is thought to be sufficient for dental applications.

As mentioned, differences in CTE between veneer and core is one of the possible reasons for chipping and delamination of veneers. Differences in α can cause tensile stress or compressive stress in the veneer or at the interface of the core and veneer. Residual compressive stresses are favorable because they have to be overcome first before failure occurs, thereby requiring a greater applied stress necessary for failure. On the other hand, residual tensile stresses lower failure strength of the veneer since less stress has to be applied to cause failure. Because of this, the optimal veneer used should have α equal to or slightly less than that of the core to minimize tensile stresses in the veneer. Clinically, failure of veneers (chipping and/or delamination) to ZrO₂ prosthetics is an issue. Failure rates of veneers as great as 15 % have been reported in two year [42] and five year studies [128], which is greater than the failure rates reports for porcelain fused to metal prosthetics [142]. Over the years, a decrease in failure rates as low as 2 % have been reported for veneers bond to ZrO₂. However, failure is still a concern and thermal mismatch is thought to be a leading cause of clinical failures.

The effect of thermal mismatch on bond strength has been studied for veneer- ZrO₂ core bonding. Aboushelib *et al.* [135] determined that use of an experimental veneer ($\alpha = 12.5$ ppm/°C) on ZrO₂ (Cercon Base, Hanau, Germany, [$\alpha = 10.5$ ppm/°C]) resulted in delamination and a weaker bond than when veneering with a commercial veneer (Cercon Ceram S, Hanau, Germany, [$\alpha = 9.5$ ppm/°C]). Fischer *et al.* also measured bond strength of different veneers, with varying α , to ZrO₂ [143,144]. It was determined that there was no correlation between fracture load/strength and α for veneers in which α is equal to or lower than the ZrO₂ core. However, it was shown that glass transition temperature (T_g), coupled with α , has an effect on bonding of veneers to ZrO₂ cores since stresses only develop below T_g [143]. Above T_g , effect of thermal mismatch between veneer and core is compensated by plastic flow, which allows for relaxation of stresses in materials through deformation in the presence of applied stress. Fischer *et al.* showed that there was a positive linear correlation between fracture load and the difference in the coefficient of thermal expansion between the veneer and core ($\Delta\alpha$) and the difference between T_g of the veneer and room temperature (ΔT) for the range of 185 ppm to 1120 ppm.

The application of a liner, used to modify the color of white ZrO₂ for esthetics, has shown mixed results in bond strength when used on veneers. Aboushelib *et al.* showed that addition of a liner increased bond strength in Cercon Base/Ceram S core-veneer system [135,136] but decreased bond strength when used in the Cercon Express core-veneer system [136,137].

The bond strength of colored ZrO₂ frameworks, which require thinner veneers, and eliminate the need for liners to veneers, increased when a liner were applied before veneering [137]. Aboushelib *et al.* determined that use of liner with layered veneers resulted in increased bond strength, except for Nobel Rondo (Nobel Biocare, Sweden) and a decrease in bond strength for pressable veneers [136,137]. It was also observed that application of a liner increased incidence of adhesive failure for pressable veneers but decreased it for layered ceramics. It is thought that application of a liner for pressable veneers inhibits surface contact between veneer and ZrO₂ that would normally result in improving bond strength. The decrease in surface contact could increase the size and amount of gaps at the interface that would serve as sites for failure.

SUMMARY

Although the science and technology applied to adhesion/bonding issues with ZrO₂ have improved, there is still much to be learned to make this a predictable behavior for clinical use.

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