Dilemmas in Zirconia Bonding: A Review

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SUMMARY
This article presents a literature review on the resin bond to zirconia ceramic. Modern esthetic dentistry has highly recognized zirconia, among other ceramic materials. Biocompatibility of zirconia, chemical and dimensional stability, excellent mechanical properties, all together could guarantee optimal therapeutical results in complex prosthodontic reconstruction. On the other hand, low thermal degradation, aging of zirconia as well as problematic bonding of zirconia framework to dental luting cements and tooth structures, opened the room for discussion concerning their clinical durability. The well known methods of mechanical and chemical bonding used on glass-ceramics are not applicable for use with zirconia. Therefore, under critical clinical situations, selection of the bonding mechanism should be focused on two important points: high initial bond strength value and long term bond strength between zirconia-resin interface. Also, this paper emphases the use of phosphate monomer luting cements on freshly air-abraded zirconia as the simplest and most effective way for zirconia cementation procedure today.

Keywords: ceramics; zirconia; resin cements

INTRODUCTION
Very good optical properties, wear resistance, strength and biocompatibility are the main positive characteristics which promote ceramic materials among the clinicians and patients. But, the shortcomings of these materials, such as brittleness, unpredictable crack propagation, low repair potential and marginal accuracy, could bring the limitations in their use. In addition, proper diagnosis in clinical practice and patient selection are factors critical for success and longevity of all ceramic restorations in oral conditions.

BACKGROUND CONCEPTS IN ZIRCONIA CERAMICS
Zirconia is a polycrystalline material, which can exhibit structural polymorphism (monoclinic, tetragonal and cubic form) depending on pressure and temperature conditions. Pure zirconia is monoclinic at room temperature and could be stable up to 1179°C. Above this temperature, it transforms into more dense, tetragonal phase, with volume decrease (5%) and initiation of cracks within its structure. The tetragonal form is stable between 1170 and 2370°C, while at higher temperatures ZrO₂ acquires a cubic structure. Reversely, during cooling, T-M transformation occurs, followed by volume expansion (3-4%).

The addition of stabilizing oxide to pure zirconia, enables inhibition of phase transformations and allows generation of a multiphase material at room temperature, termed stabilized zirconia. Fully stabilized zirconia (additives: CaO, MgO, Y₂O₃) has a cubic form and presents material of increased hardness and high thermal shock resistance, familiar in engineering ceramics [1]. The other type of multiphase zirconia with desirable mechanical properties is partially stabilized zirconia (PSZ). Its microstructure, at room temperature, consists generally of cubic zirconia as main phase, and monoclinic and tetragonal zirconia precipitates as minor phase. In a presence of small amount of stabilizing oxide, it is possible to produce PZS ceramic with a tetragonal phase only, material used in dentistry, called tetragonal zirconia polycrystals, TZP. Subsequently, the addition of approximately 2-3% mol yttria (Y₂O₃) in zirconia allows the sintering of tetragonal fine grained zirconia, made of 100% small metastable tetragonal grains, (0,8 µm), termed Y-TZP, yttrium-tetragonal zirconia polycrystals.

Zirconia materials differ from other high strength dental ceramics due to their stress-induced transformation toughening. This characteristic means that material undergoes microstructural changes when submitted to stress and can actively resist crack propagation through transformation from tetragonal to monoclinic phase at the tip of a crack. Described phenomenon is accompanied by a local expansion which favors crack closure. Such an increase in volume results in compressive stresses zone generated around and at the tip of crack, which then counteract the tensile stresses acting on the fracture tip. Subsequently,
Y-TZP exhibits high values of flexural strength (900–1200 MPa) and fracture toughness (K_{IC}) of 5–9 MPa-m^{1/2}, which are at least three times higher compared to alumina and lithium disilicate-based ceramics [2–7].

Although, the first recommended use of zirconium as biomaterial in the form of hip (knee) joint prosthesis has been well-known since the late 1960s [8, 9], its use in dentistry is relatively recent. The proofs of in vitro biocompatibility of ZrO₂ and advances in CAD/CAM technology were the essential facts that promoted this material in modern dentistry in a variety of clinical applications; root canal posts, orthodontic brackets, implants, implant abutments and frameworks for all-ceramic restorations.

**WHY IS BONDING OF ZIRCONIA THE SUBJECT OF CONCERN?**

The introduction of adhesive bonding systems and resin cements in dental practice, give the opportunity to practitioners to increase the retention of conventionally cemented crowns (in spite of critical values of taper, height and surface area of prepared teeth) and to achieve the optimal esthetic results in prosthetic reconstruction [10]. Those two goals: durability and pleasant esthetic appearance of all ceramic restorations are the guarantee for the longevity of these restorations in mouth conditions. Obviously, this “team work” could be obtained through the strong bond which must be established between three different structures: ceramic core surface, cement layer and dentin. The paramount aim in this direction, presents possible chemical, mechanical and chemical/biological bonding approaches [11].

Due to chemical inertness and resistance to aggressive chemical agents (strong acid, alkalis, organic and inorganic dissolving agents), bonding of zirconia to tooth tissues or other synthetic materials is difficult when compared to silica-based ceramic material [12].

The bonding of traditional glass-containing ceramics or silica based ceramics utilizes mechanical and adhesive way [13]. Mechanical bonding assumed micromechanical interlocking between the resin cement and roughen surface of silica-based ceramics. Phosphoric acid or hydrofluoric acid etching is the method commonly used for roughening the silica-based ceramics surfaces [13]. Chemical adhesion of glass ceramic and resin cements is achieved with use of bi-functional compounds, silanes that promote connection between dissimilar organic and inorganic counterparts. Also, silanes could influence increasing surface energy and wettability of ceramic surfaces, which enhances both mechanical and chemical bonding [14].

The well-known methods of mechanical and chemical bonding used on glass-ceramics are not applicable for use with zirconia. The most important reason for this is the absence of silica in the zirconia microstructure which ignores the viability of etching as a roughening method essential for mechanical bonding, as well as nullified the use of silanes, forming surfaces hydroxyls and developing the chemical bond [15].

**DIFFERENT APPROACHES IN ZIRCONIA/CEMENT BONDING**

In order to obtain the strong bond to zirconia ceramics in clinical conditions, it is important for the bonding surface to be roughened, activated for chemical bonding and free of any contaminants [16]. This objective premise offers different clinical and scientific answers which will be depicted through the following text.

**Surface abrasion or roughening**

Surface abrasion or roughening (grinding, airborne-particle abrasion, rotary abrasion using diamond burs) establishes adhesion only through micro-mechanical retention. There is a general consensus that airborne particle abrasion with 50–110 µm alumina particles at 0.25 MPa is effective in roughening and cleaning the bonding surface of zirconia [17]. However, the effect of those treatments on the mechanical properties of Y-TZP materials is controversial and both positive and negative results have been described in the literature [18, 19]. Also, it has been reported that particle abrasion creates sharp crack tips and structural defects, making zirconia more susceptible to radial cracking during function [20]. Therefore, the recommendation of reducing the pressure during air-abrasion and using particles up to 50 µm in size, could be beneficial [21].

Additionally, the particle air abrasion of zirconia, with alumina or other particles, produces lower bond strength compared to that of porcelain. The authors, who are standing behind those results, reinforced the opinion that mechanical adhesion alone is not suitable for providing the optimal resin bond strength. So, they promote the chemical adhesion in zirconia bonding [14, 22]. On the contrary, some others stated that elimination of particle abrasion as surface treatment would result in a dramatic reduction in bond strength. According to them, surface roughness is a key factor for adhesion to zirconia [23, 24].

**Application of a tribochemical silica coating**

This is a technique which uses alumina particles modified with silica for air abrasion at 0.28 MPa and embedding silica particles in the ceramic surface. Silica particles create a base for micromechanical bonding and interlocking in ceramic. The next step is application of a silane which enables chemical adhesion between ceramic and resin cement. Silane coupling agents act on various manners;
lower the surface tension of a substrate, wet it and increase surface energy, improving effectiveness of bonding. Thus, hydrophobic luting resin could adhere to hydrophilic surfaces of silica (glass, glass-ceramic). Additionally, due to inorganic-organic silanes nature, this hybrid agent is capable of forming strong covalent bonds to the silica coated zirconia through formation of silanol groups [22, 25, 26].

Interesting question concerning the mechanism of this bonding covers the dilemmas whether transfer of silica is caused by particles embedded in target surface, mechanical/chemical transference (tribochemistry) or both. It is supposed that in case of very hard zirconia cores, (target material) embedding of silica coated particles is difficult. Therefore, it is possible that silica-coated particles „bounce off” ceramics, but after actual transference of silica from particles to ceramic substrate [8, 27].

The results regarding the efficiency and long-term bond durability obtained by this relatively simple technique (silica-coated 30 μm aluminum oxide particles, commercial product: Cojet, Rocatec 3M ESPE, followed by application of silane) are conflicting. There are data in the literature showing increasing bond strength of zirconia and different resin cements after Cojet device application in pretreatment activity [25, 28, 29, 30].

Some shortcuts have to be made to this technique. It is possible that TBC (tribochemical coating) could produce a non-uniform silica layer (user variability) on the bonding surface which in opposite results in variation in bond strength. Another weak point of this method is hardness of zirconia, which contributes to the low concentration of silica on the bonding surface. This problem may be addressed by increasing operating pressure, which could increase resin bonding [31]. Also, there is still the issue of creating surface micro-flaws with possible fracture from particle abrasion [14]. However, this is not of essential importance, as it has been shown that the application of resin luting agents can „heal” surface flaws [32].

On the other hand, there are articles with the data which confirmed that tribocohemical treatment provided no advantages in combination with the self-adhesive cements; such situation is explained by the inert zirconia surface [10, 21]. These authors emphasized that all procedures and results could be judged only by following prolonged water storage in excess of 30 days, monitoring the impact of hydrolysis on the zirconia-resin bond [10]. The majority of contemporary articles use long term water storage (till 6 months) and thermal cycling in order to determine the artificial aging of zirconia [14, 33, 34].

Silica coating techniques

These techniques are used to facilitate a siloxan bond between a zirconia surface and resin cement. Fusion of glass beads and plasma spray seem to be complicated technique to achieve sufficient coverage [21]. Information about quality of bonding of different zirconia ceramics through the literature is confusing. Some articles have confirmed that silica coating produced significant resin bonding for zirconia ceramics [22], while others certified reduced bond strength after artificial aging, with explanation that silica coverage was not firmly attached to zirconia. The usage of vapor-phase deposition technique, where silicon tetrachloride is combined with water vapor, is worth mentioning. This modification with silanization and bonding technique, improved adhesion of zirconia ceramic framework to resin cement [25]. The next study, which compared long-term microtensile bond strength of different thickness of silica seed layers (3.2 nm, 5.8 nm, 30.4 nm) deposited on the zirconia substrate, showed similar or superior bond strength to resin cement, when compared to traditional silanization, but lower than that for silane–treated dental porcelain [14]. Also, the authors discussed the importance of the layer thickness to bond strength in a function of time (up to six months). They concluded that silica layer may be only bonded to zirconia through mechanical and/or secondary chemical bonding (van der Waals bonds), which is not strong as covalent bonding formed between silane and resin cement. At the time, water absorption at the interface (between the layers) could decrease the bond strength of the silica coating. It is desirable to get homogeneous structure of deposited films to improve their resistance to degradation. Additionally, there is a report about negative effect of ultrasonic cleaning in distilled water on bonding to silica coated zirconia. This fact was addressed to possibility of ultrasonic cleaning to remove significant amount of silica-coating layer from the ceramic substrate. On the contrary, ultrasonic cleaning in alcohol did not show negative effect on bond strength. Therefore, it was speculated that the effect of water on reactive silica coated surface was of the greater importance than ultrasonic cleaning itself [35].

Chloro-silane treatment

Chloro-silane treatment is introduced earlier as a pretreatment of zirconia surfaces by a group of authors [14, 25]. Actually, chloro-silane combined with vapor phase technique allowed pretreatment that deposits a silica-like layer on the zirconia substrate. The result is very thin coating (till 2.6 nm) which increased the number of chemical binding sites (Si\textsubscript{4}O\textsubscript{4}) for the subsequent organ-saline primer, used in conventional adhesive technique. Application of the chloro-silane film increases the bond strength to resin cements enabling the values of microtensile bond strength similar to clinically common bonding technique. Further, the obtained effects are strongly influenced by layer thickness and surface topography. Also, deposition of a thin Si\textsubscript{3}O\textsubscript{4} layer demonstrated a 60% mixed (adhesive/cohesive) failure mode for roughened surface [21].

Selective infiltration etching (SIE)

SIE is based on inter-grain metastable tetragonal grains, created during thermal pre-stressing of the surface grains using a specific thermal regime. Due to this procedure, the
bonding zirconia surface is ready to accept the adhesive resin which infiltrates and „interlocks” the bond [36]. SIE transforms dense, nono-retentive, relatively smooth and low energy surface of zirconia to highly active and well bonding surface [12, 37]. The proposed technique utilized the characteristics of zirconia on an ultrastructural level [38]. Despite the facts which describe zirconia as steel ceramic material, it is less known that zirconia possesses dynamic nature. On a nano-scale, crystal level, zirconia has the ability to transform from tetragonal to slightly larger monoclinic phase in response to mechanical and thermal stresses, demonstrating high fracture toughness. On a grain, micro-level, the surface and bulk grains can grow in size when given sufficient stimuli (temperature, time). Additionally, grain boundary parts allow diffusion of various elements, such as silica, calcium, sodium, potassium and titanium. This phenomenon changes the surface features of zirconia, exerts high capillary and tension forces, consequently enhancing nano-rearrangement movements of grains, their splitting and sliding [39].

In SIE method the surface of zirconia is coated with a glass-containing conditioning agent silica (65% wt), alumina (15% wt), sodium oxide (10% wt), potassium oxide (5% wt) and titanium oxide (5% wt) with closely-matched thermal expansion coefficient to zirconia. Later on, the material is heated above glass transition temperature, until the optimal grain boundary diffusion is achieved. After cooling to room temperature, the glass is dissolved in an acidic bath to eliminate all traces of conditioning agent. The cooling and heating rates are controlled by a computer-calibrated induction furnace [12].

The promising results with infiltration etching emphasize the effect of a sealed interface of modified zirconia surface, which is capable to resist the nano-leakage during artificial aging. Beside the affirmative results, still there is point of concern related to the effect of intergran porosities on the mechanical properties of SIE zirconia. Some additional studies suggest that proposed treatment creates porosities approximately of 1.5 µm which are not critical [12].

**Nanostructured alumina coating**

Nanostructured alumina coating is presented as a new approach which is able to provide a strong and durable resin bond to Y-TZP [36, 40]. It is based on the idea of a rapid precipitation of aluminium hydroxides that originate from the hydrolysis of AlN powder in a diluted aqueous suspension. The result is heterogeneous nucleation of lamellar boehmite (γAlOOH) onto the surface of the immersed Y-TZP substrate. The nanostructured coatings consist of 6 nm thick and 240 nm long interconnected polycrystalline γAlOOH lamellas that grow perpendicular to the zirconia surface. During a heat treatment up to 900°C, these coatings are transformed into transient alumina, but without any change in the morphology [41]. This non-invasive process can be classified as chemical pretreatment method that increases the surface area and penetrates the lamellar network, implying good wetting. The proposed technique offers some advantages over conventional surface treatment. Firstly, it does not create any flaws that can decrease the strength of zirconia ceramics. Secondly, functionalization of zirconia surface is more effective compared to air abraded and polished surface, even after thermo cycling procedures. Thirdly, technique is simple and can be easily transferred to dental laboratories [36].

**Different surface treatments**

**Hot chemical etching solution**

It is recommended for conditioning the zirconia substrate. This procedure based on corrosion-controlled process and metallic nature of pure zirconium. It selectively etches the zirconia and creates micro-retentions on the surface by modifying the grain boundaries through removal of the less arranged atoms. The authors state that hot etching solution increases the zirconia surface roughness enabling the optimal bonding to resin cements. According to the literature data, this novel method must be checked through further studies which would confirm its effects on bond strength of complex zirconia/cement combination [8, 42].

**Laser application**

Laser application and its capacity to increase the zirconia roughness for adhesive luting procedures have been discussed in details in other articles [9, 18, 43]. Er:YAG (erbium-doped yttrium aluminum garnet) laser has the ability to remove particles through ablation process by micro-explosions and vaporization. Laser effects obtained due to temperature changes (heating and cooling), induce phase transformation in the material leading to its damage. It has been suggested to lower the laser power and to enable surface irradiation with constant water cooling. But, the results are still questionable regarding the fact that laser irradiation is not as effective in increasing bond strength as air-particle abrasion under an in vitro experiment [18, 43].

**Zirconia ceramic powder coating**

It is presented as nondestructive approach to create unique surface characteristic of zirconia. It is produced by coating zirconia framework (presintered or fully sintered) with slurry containing zirconia powder and a pore former. During the sintering process pore former burns off leaving a porous modified surface. The advantage of this procedure is the possibility to change the pore size by using different sizes of pore former or repeating the coating process. Also, the modified surface is already present, applied by manufacturer of the framework. The restoration could be provided ready to bond without sintering process pore former burns off. There are a few clinical and in vitro data about the performance of this novel surface and its effects on...
shear bond strength. Additionally, current studies emphasize that bonding to the modified zirconia surface requires no airborne-particle abrasion or special cement. Although, this method could promote the wider application of zirconia, especially for the frameworks relying heavily on bonding (veneers and resin-bonded fixed partial dentures), it is too early for making any clinical recommendations before further evaluations [44].

**Gas-phase fluorination process**

This process presents a method to chemically modify zirconia by creating thin oxyfluoride conversion layer on its surface that is receptive to organosilane attachment. The recommended procedure is complex and involves fluorination of zirconia in a planar, inductively coupled plasma reactor, vacuum (≈35 mT), and handling of a fluorine concentration of zirconia in a planar, inductively coupled plasma reactor, vacuum (=35 mT), and handling of a fluorine containing precursor gas. Essentially, the goal of the process is to apply the fluorinated plasma to the zirconia surface, to convert the top 1-3 nm into a ZrO<sub>3</sub>F<sub>4</sub>, which would further react with organo-silanes, enabling silicon bonding to the surface. The recent studies show that the fluorination treatment on roughened or polished zirconia displayed higher shear bond strength as compared to commercially available treatments [21]. Therefore, this method could be useful on as-received substrates, where roughening or other modification techniques are not possible. Till now, the exact mechanism by which the fluorination improves bonding is unclear. It is hypothesized that oxyfluoride phase facilitates Zr-hydroxylation via H-F extraction in the presence of water, increasing the reactivity of zirconia surface with silane. But, ongoing experiments would bring more evidence on oxyfluoride stoichiometry and reaction pathways. Although, the creators of this procedure underlined some difficulties (research tool used in study does not exist), they offer, if this bonding protocol would be clinically adopted, to implement a small counter-top device as a clinical or dental lab setting [21].

**Application of phosphate ester primers and phosphate modified resin cements**

This is promising and chair-side method to create a relatively stable bond zirconia/tooth structure, but alone insufficient to stand long-term intraoral conditions [8, 11, 21]. The literature data emphasize the beneficial effects of phosphate esters on bond strength zirconia/luting cements, only with the mechanical pretreatments (airborne particle abrasion, SI etching) in order to achieve durable bond values [37, 45] and omit the premature failure as well as gap formation [12]. The adhesive functional monomers are believed to have the ability to form chemical hydrogen bonds with metal oxides at the resin/zirconia interface, improving the wettability. On the other hand, the composition of resin cement, for example, large filler size and high viscosity could affect the wettability significantly. The most frequent phosphate monomer groups used in resin cement or metal primers are the following: 10-methacryloyl oxydecyl dihydrogen phosphate, MDP (the adhesive monomer in Panavia F 2.0, Alloy Primer, Clearfil SE Bond/Porcelain Bond activator, Clearfil Ceramic primer), methacrylated phosphoric ester (adhesive monomer in RelyX Unicem), and phosphoric acid acrylate (the adhesive monomer of multilink automix) [45]. The VBATDT (6-(N-(4-vinylbenzyl) propylamino)-1,3,5-triazine-2,4-dithione) monomer (Alloy Primer, Totalbond) [46] and a new generation of engineered zirconia primers are recommended to optimize the wetting and chemistry of non-primed zirconia or SIE treated zirconia substrate [37, 46, 47]. Recently, a new formula of universal primer which contains a silane and a phosphate monomer has been promoted (3-alcohol solution of methacryloxypropyl-trimethoxysilane, phosphoric acid methacrylate and sulphide methacrylate-Monobond Plus) [34]. It creates promising bond strength to zirconia after artificial aging when used after air-borne particle abrasion with ultrasonic cleaning or after silica coating [34]. In addition, there are studies which confirmed that different primers could react differently with etched zirconia surfaces due to chemical variations and bonding ability between the active agents. Further research is needed to develop more hydrophobic compounds that would resist hydrolytic effect of water under clinical conditions [47]. Also, addition of cross-linking monomers to primers would be helpful to enhance their bonding to the resin matrix not only to zirconia.

**CONCLUSION**

It is obvious that there are different options how to create durable bond zirconia/resin cements. But, it should be mentioned that under oral environment conditions, (masticatory forces, saliva influence, thermal factors, fatigue) bond reduction with various consequence, is often expected. Therefore, under critical clinical situations, selection of the bonding mechanism should be focused onto two important points: high initial bond strength value and long-term bond strength between zirconia-resin interface.

Very often, mechanical tests, like microtensile bond strength and shear bond strength are used to evaluate the bond quality between resin luting agent and zirconia substrate. But, it seems that these are not sufficient to show the behavior of the material under function, limiting the treatment effects. For the credibility of study results, it is proposed to combine mechanical tests with chemical analysis of bonding materials prior to clinical recommendation of technique or a new material [46].

Nevertheless, the problem of zirconia bonding to resin cement is still questionable. It is important to remember that zirconia crowns can also be luted with conventional cements if adequate crown preparation design provides sufficient retention without bonding. In closing this review, it is beneficial to focus on the experts’ opinion which emphasizes that the use of phosphate monomer luting cements on freshly air-abraded zirconia present the simplest and most effective way for zirconia cementation procedure today [48].
REFERENCES


КРАТАК САДРЖАЈ

Рад даје осврт на проблем везивања надокнада од цирконијума диоксида за зубна ткива. Цирконијум-диоксид (цирконија) је оксидни керамички материјал који у стоматологији – посебно у савременој естетској пракси – налази важно место. Добрих механичких карактеристика, високе биокомпатибилности и задовољавајућих оптичких особина, он представља материјал избора у великому броју протетичких индикација. Оно што може угрозити крајње терапијске резултате када је у питању клиничка експлоатација надокнада од цирконијум-диоксида јесте немогућност једнообразне припреме њене површине за везивање с различитим цементима и зубним структурама. У раду се описују и дискутују различити начина припреме површине цирконије. Наглашава се да у одабиру оптималне методе предност треба дати једноставнијим клиничким опцијама, пут пескирања површине цирконије и употребе композитног цемента са специјалним фосфатним мономерима.

Кључне речи: керамика; цирконија; композитни цементи

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