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Adhesion to dental zirconia: A literature review

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Abstract
Introduction: Yttria-stabilized tetragonal zirconia polycrystals have become increasingly popular in dental restorations because of their aesthetic appeal, biocompatibility, and mechanical strength. However, currently there is no standardized treatment for zirconia.
Aims: Analyze the literature of adhesion to dental zirconia. Zirconia, decontaminating the internal surface of zirconia restorations, importance of 10-MDP in zirconia bonding and cementation protocol will be analyzed.
Methodology: A comprehensive literature review was conducted on the subject of Adhesion to Zirconia. The literature review consisted of 40 articles, which were obtained from different databases: PubMed, Springer Link, Wiley Online Library, Elsevier, using the terms "Zirconia", "Air-abrasion", "Adhesion", "MDP", "Dental Materials".
Results: When considering adhesion to zirconia the following factors should be taken into account: Zirconia, is a versatile ceramic with different crystalline phases, stabilized for dental use by doping with yttria. Decontaminating the internal surface of zirconia restorations, is crucial for strong bonding, with air abrasion being the most effective method. Importance of 10-MDP in zirconia bonding, improve zirconia's adhesion to composite resins by chemically bonding with zirconia and aiding polymerization. Cementation protocol, with adhesive cements offering better bond strength and aesthetics than traditional cements.
Conclusion: Bonding zirconia restorations requires effective surface preparation, contamination removal, and the use of specialized bonding agents. Air-particle abrasion and cleaning solutions like Ivoclean or ZirClean help remove contaminants, while primers with adhesive phosphate monomers like 10-MDP enhance bond strength. Dual-cure or self-cure composites ensure proper polymerization beneath the zirconia. The APC zirconia-bonding concept, which involves abrasion, primer application, and composite resin cement, provides a reliable method for strong, durable bonds, ensuring both mechanical stability and aesthetic quality in clinical use.

Keywords: Zirconia, adhesion, dental materials, air-abrasion, MDP

Introduction

Yttria-stabilized tetragonal zirconia polycrystals, commonly referred to as zirconia, have become increasingly popular in dental restorations due to their aesthetic qualities, particularly with the development of translucent and ultra-translucent versions [1]. Additionally, zirconia is valued for its biocompatibility and mechanical properties, including high flexural strength (> 900 MPa) [2].

This material provides long-term stability due to its high crystallinity and inertness [3]. However, this same property makes bonding difficult. In addition to enhancing the aesthetic qualities of zirconia, research has also focused on achieving reliable bonding between oxide ceramics and the tooth surface [4, 5].

There is no universal treatment for zirconia, but surface treatment is necessary to achieve durable bond strength [6]. The internal surface of zirconia cannot be etched with hydrofluoric acid because it lacks a glass ceramic phase [7, 8].

Contamination by saliva, blood, or silicone during the try-in or cementation process is a major cause of adhesive failure, as it can reduce the bond between the cement and zirconia, compromising adhesion [9, 10].

Many studies have focused on determining the most effective cleaning methods for decontaminating the restoration surface after try-in, using techniques such as water [11], alcohol [12], phosphoric acid [13], aluminum oxide (Al2O3) sandblasting [14], plasma [15], sodium hypochlorite [15], and commercial cleaning solutions like Ivoclean (Ivoclar Vivadent AG), ZirClean (Bisco Inc.), and Katana Cleaner (Kuraray Noritake Dental Inc.) [16].

A crucial element examined in the bonding of zirconia restorations is the application of adhesive composite resin luting agents containing particular adhesive phosphate monomers, notably 10- methacryloyloxydecyl-dihydrogen phosphate (MDP). This article examines the research regarding adhesion to dental zirconia, emphasizing the decontamination of the internal surface of zirconia restorations, the importance of 10-MDP in zirconia bonding, and the cementation technique.

Methodology

A comprehensive literature review was conducted about adhesion to zirconia. The literature review consisted of 43 articles, which were obtained from different databases: PubMed, Springer Link, Wiley Online Library, Elsevier; *In vitro* experimental studies were excluded, and articles from longitudinal studies, theoretical framework, control studies, observational studies, cohort study, systematic reviews, clinical trial type studies were included. We limited the search publication date from 2015 to 2024.

Results

Zirconia

Zirconia (ZrO2) is a metastable ceramic material characterized by three distinct crystalline phases: monoclinic, tetragonal, and cubic. At room temperature, pure zirconia maintains stability in its monoclinic phase. In dental applications, zirconia is commonly doped with 3 mol% yttria to maintain the stabilization of the tetragonal phase at room temperature. The first version of 3Y- TZP dental zirconia encountered limitations because of its opacity, which can be somewhat attributed to the inclusion of alumina. Alumina acts as a sintering aid, helping to minimize pore formation during the firing process of green-state zirconia in the furnace. The accumulation at the grain boundaries contributes to the stabilization of the tetragonal zirconia phase [17].

Dental zirconia has been formulated with an increased yttria content of 5 mol% to enhance translucency. This modification results in the formation of partially stabilized zirconia, which consists of approximately 50% cubic phase zirconia. The cubic phase demonstrates isotropy in various crystallographic directions, thereby reducing light scattering at the grain boundaries [17, 18].

Although 5Y-ZP is well-suited for anterior restorations due to its enhanced translucency, its inferior mechanical properties may limit its application in posterior fixed partial dentures. Nevertheless, 5Y-ZP continues to be simple to work with and wear-resistant [17, 19]. Zirconia is a highly versatile ceramic material with different crystalline phases, stabilized for dental use by doping with yttria. The development of 5Y-ZP zirconia improves translucency, making it ideal for anterior restorations. 5Y-ZP remains wear-resistant and user-friendly, offering a promising material for dental prosthetics.

Decontaminating the internal surface of zirconia restorations

Nearly all ceramic restorations intended for cementation are generally subjected to abrasion with airborne particles in a dental laboratory to ensure both micromechanical and chemical adhesion with the luting agent. The try-in technique for zirconia restorations has the potential to introduce contaminants to the intaglio surface, including fluids like blood, saliva, or fitting indicators such as try-in pastes or silicone. The presence of this contamination significantly contributes to the reduction in binding strength, given that zirconia exhibits a strong affinity for the phosphate groups present in saliva and fluids [20].

Multiple cleaning techniques have been evaluated to eradicate these pollutants and guarantee a robust resin adhesion. For instance, cleansing contaminated surfaces with water or employing ultrasonic cleaning in isopropanol demonstrated negligible or no efficacy, rendering these procedures inappropriate. An imperceptible organic coating from saliva establishes ionic connections on the zirconia surface, rendering water ineffective in dissolving salivary proteins or decontaminating the surface [22].

In a comparable investigation conducted by Klosa *et al*., a protective lacquer (1% ethyl cellulose in ethanol) was administered to the bonding surface before exposure to saliva or silicone, followed by cleaning in an ultrasonic bath utilizing 99% ethanol. The bond strength attained was markedly inferior to that of uncontaminated zirconia, suggesting that lacquer and contaminant residues remained post-cleaning, underscoring the necessity for enhanced cleaning techniques [40].

Acidic cleaning is an alternative technique employed to eliminate organic pollutants. Cleaning with phosphoric acid gel was successful in eliminating saliva but ineffective against silicone residues. The presence of these inorganic silicone residues obstructs the cement's adhesion to the zirconia surface, yielding the lowest bond strength compared to all cleaning techniques [23, 22].

The application of hydrofluoric acid (HF) produced favorable outcomes following water rinsing, as HF engages with organic impurities and removes them from the zirconia surface. Research repeatedly indicates that airborne particle abrasion is the most efficacious technique for eliminating impurities from saliva-contaminated zirconia ceramics and reinstating a robust connection between resin cement and zirconia. Air particle abrasion with alumina particles between 50 and 110 μm at 0.25 PSI shown efficacy in cleansing and reinstating bond strength to values akin to uncontaminated zirconia [24].

Nonetheless, owing to the expense associated with acquiring an air abrasion device, along with the supplementary time and effort required, dentists may opt to assign this treatment to dental technicians. An alternative may involve the utilization of gas plasma. Plasma, one of the four fundamental states of matter, is a gas that is either partially or completely ionized. Its interaction with materials can alter their surfaces, removing organic substances, inducing chemical restructuring, or activating gaseous species. These alterations, referred to as plasma surface modification (PSM), are extensively utilized in industrial operations owing to their efficacy and cost-effectiveness. In the biomedical sector, PSM has been employed for sterilizing and disinfection purposes. Plasma can decompose big molecules without compromising stable materials like ceramics [15].

Studies indicate that reactive gas-based plasma treatments, such as oxygen, oxygen-argon, and air plasma, efficiently eliminate saliva impurities from zirconia restorations. A decrease in binding strength was noted following age [15, 25].

While low-pressure non-thermal plasma can moderately cleanse saliva and silicone, it is inferior to alumina abrasion in efficacy. Recent investigations indicate that the combination of ultrasonic cleaning with isopropanol and plasma treatment constitutes an efficient approach for cleansing saliva-contaminated zirconia specimens [15, 25]. Furthermore, certain studies indicate that sodium hypochlorite (NaOCl) can efficiently eliminate saliva from zirconia, presenting a more economical option compared to specialized zirconia cleaning agents. The efficacy of NaOCl as a disinfectant is contingent upon its concentration (7.5% NaOCl was utilized) and the length of application. The findings indicated that extending the scrub duration enhanced the bond strength, elevating it from 14.7 MPa to 16 MPa [22].

Residual NaOCl may interfer resin polymerization by producing oxygen; therefore, a comprehensive rinse with water is essential post-application. The AD Gel cleaning agent, comprising NaOCl and alumina, effectively eliminates saliva impurities and reinstates bond strength to values comparable to uncontaminated zirconia [23].

The introduction of ceramic cleansers has provided professionals with a structured and effective method for decontaminating ceramic surfaces. Every solution function through a distinct mechanism. Ivoclean is an alkaline cleanser that features hyper-saturated zirconia particles, which effectively attract pollutants via a chemical gradient, enabling their removal with water before the cementation process. Zirclean is a non-abrasive gel with an alkaline composition of potassium hydroxide, which effectively disrupts the ionic interaction between contaminants and the restorative surface. Katana Cleaner is an acidic cleaning agent with a pH of 4.5, featuring a 10-methacryloyloxydecyl dihydrogen phosphate (MDP) salt. It is designed to effectively remove pollutants both intraorally and extraorally [28]. The shear bond strength remains consistent across these cleansers, as each one effectively eliminates organic contaminants and rejuvenates the bonding surface [22]. Some studies suggest that air abrasion outperforms cleaning paste in removing spit contamination from zirconia surfaces [23].

Regardless of the decontaminant used, MDP has been suggested as a preventive approach to early contamination, as its phosphate group binds to the zirconia surface, exposing the hydrophobic termini of the methacrylate monomer [29]. This creates a barrier that prevents saliva from hydrating the surface. Angkasith *et al*. found that using an MDP primer before testing facilitates effective surface cleaning with a 20-second water rinse [30].

Cleaning zirconia restorations is crucial for strong bonding, with air abrasion being the most effective method. While plasma treatment and ceramic cleaners like Ivoclean and Zirclean also

help, their effectiveness varies. Combining these cleaning methods with MDP primers can improve bond strength and reduce contamination during dental procedures.

Importance of 10- MDP in zirconia bonding

Primers containing 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP) have demonstrated promising results in improving the adhesion strength between zirconia and composite resins, particularly after alumina sandblasting. The chemical connection between 10- MDP and Y-TZP provides a direct, non-invasive method for ceramic substrates, resulting in enhanced bonding effectiveness [30, 31].

The 10-MDP molecule has a phosphoric acid group at one terminus, a vinyl group at the opposing terminus, and a ten-carbon ester spacer chain that interposes these two functional groups. The vinyl group promotes polymerization and improves chemical interaction with unsaturated carbon bonds in the resin matrix of the substrate. The phosphate group is essential for enhancing adhesion to hydroxyapatite or metal oxides, like alumina and zirconia. The phosphate group is essential for the chemical attachment of 10-MDP to the non-polar and chemically inert zirconia surfaces [8, 32].

10-MDP is commonly employed in primers or universal adhesives for the preparation of zirconia restorations before bonding. Universal adhesives containing 10-MDP are especially preferred for zirconia due to their ease of use and effectiveness. The functional monomer 10-MDP is thought to chemically engage with zirconia via its phosphate group, while its unsaturated bonds connect with residual, non-polymerized monomers of bisphenol A-glycidyl dimethacrylate (Bis- GMA) [32, 33].

In clinical practice, Y-TZP crowns are often attached to the tooth structure, predominantly dentin, or to a base material, with composite resin being the most commonly utilized substance. Furthermore, utilizing particular primers can reduce the contact angle between zirconia and resin, thereby improving bond strength [34].

The MDP patent was held by Kuraray for ten years, until 2011, after which several companies started integrating it into their products. MDP is utilized in a range of bonding and luting products, including primers, adhesives, and resins [34].

Primers with 10-MDP improve zirconia's adhesion to composite resins by chemically bonding with zirconia and aiding polymerization. Universal adhesives containing 10-MDP offer a simple and effective solution for bonding zirconia restorations. These primers also enhance bond strength by reducing the contact angle between zirconia and resin.

Cementation Protocol

Full-ceramic restorations, unlike metal-ceramic restorations, should not have any primary friction, as this can create tensile stresses that may cause cracks inside the restoration. This also applies to zirconia. One key role of the cementation material is to make up for the lack of primary friction to prevent retention losses. Generally, there are two types of cementation materials: traditional cements and composite resin cements. For cementation with conventional acid-based cements (e.g., zinc phosphate or glass-ionomer cement), an extremely close fit between the prepared tooth and the restoration is required. This ensures that, due to the hydrophilic properties of conventional cements, the restoration fits precisely. No pretreatment of the dental hard tissue is needed with traditional cements. Traditional cements should only be used for crown preparations with a stump height of 4 mm or more and a relatively steep preparation angle (6 to 15 degrees) [35].

In contrast, adhesive cementation using composite cements creates a force-fit bond due to the “sticking together” effect, which makes it somewhat more forgiving regarding fit. While adhesive cementation materials may be less user-friendly and more sensitive to moisture compared to traditional cements, they offer notable improvements in both mechanical and aesthetic properties. Additionally, adhesive cements exhibit high abrasion resistance and are nearly insoluble due to their hydrophobic characteristics [35, 36].

Studies demonstrate that although various bonding protocols for high-strength ceramics yield satisfactory results in the short term, the formation of resilient and enduring resin bonds requires meticulous surface preparation via air-particle abrasion and the application of an adhesive composite resin luting agent that incorporates specific adhesive phosphate monomers, such as 10-methacryloyloxydecyl-dihydrogen phosphate (MDP) [37, 19].

This simplified method consists of three steps: APC-Step A, which involves abrading the bonding surface with aluminum oxide particles; APC-Step P, where a specialized zirconia primer is applied; and APC-Step C, which includes the use of dual-cure or self-cure composite resin cement [37].

The restoration of zirconia involves a multi-step process to ensure optimal bonding and durability. First, after cleaning the restoration, zirconia should undergo air-particle abrasion with alumina or silica-coated alumina particles (50 µm to 60 µm) at low pressure (below 2 bar), commonly referred to as sandblasting or microetching. This step primarily serves to decontaminate the bonding surfaces rather than just enhancing surface roughness. Next, a specialized ceramic primer containing adhesive phosphate monomers, like MDP, is applied to the zirconia bonding surfaces. This primer improves the bonding strength of various cements, including resin-modified glass ionomers. Finally, dual-cure or self-cure composites are recommended for adequate polymerization beneath the zirconia, as the material limits light transmission. However, high-translucent zirconia allows sufficient light to pass through, meaning the shade of the cement or resin luting agent can affect the final appearance of the restoration [37].

The APC zirconia bonding concept is not confined to dental use; it is also for instance, in implant reconstructions that feature cemented zirconia components [37].

The utilization of airborne particle abrasion alongside primers or composite resin cements containing particular phosphate monomers results in strong resin bonds. Robust bonds can be formed between high-translucent zirconia and resin cements, and the materials and methods employed do not negatively impact the physical characteristics of the zirconia [38, 39].

Zirconia restorations require precise cementation, with adhesive cements offering better bond strength and aesthetics than traditional cements. Long-lasting bonds are formed by air-particle abrasion, applying a primer containing phosphate monomers such as MDP, and using dual-cure or self-cure composite resins.

Conclusion

According to the literature review carried out, it can be concluded that, bonding zirconia restorations requires effective surface preparation, contamination removal, and the use of specialized bonding agents. Air-particle abrasion and cleaning solutions like Ivoclean or ZirClean help remove contaminants, while primers with adhesive phosphate monomers like 10- MDP enhance bond strength. Dual-cure or self-cure composites ensure proper polymerization beneath the zirconia. The APC zirconia-bonding concept, which involves abrasion, primer application, and composite resin cement, provides a reliable method for strong, durable bonds, ensuring both mechanical stability and aesthetic quality in clinical use.

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