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Surface Modification Protocols of Zirconia: A Literature Review

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Abstract

Achieving reliable bonding between resin cements and high-strength ceramics, such as zirconia, is challenging due to the material's chemical inertness and absence of silica, which prevents traditional etching. This lack of etchability and inability to undergo silanization has led to ongoing debates among clinicians and researchers. Since zirconia restorations may occasionally fail to withstand dislodging forces, in current literature various alternative protocols have been suggested to improve bond strength between resin cements, tooth structures, and zirconia surfaces.

For the long-term success and survival of of zirconia restorations, achieving sufficient bond strength is crucial to endure functional masticatory stresses. Consequently, the performance and bonding efficiency of these restorations are heavily dependent on the cementation procedure used. Despite extensive research, the literature on zirconia cementation presents conflicting results about the effectiveness of different luting agents, and no standardized protocol has been universally accepted.

This review aims to categorize and evaluate the existing techniques designed to enhance the adhesion of zirconia to dental substrates. It also explores current trends in surface conditioning methods, seeking to identify approaches that offer consistent and reliable bonding outcomes. By analyzing these methods, this review aims to provide a clearer understanding of effective bonding strategies for zirconia restorations.

Keywords: Bonding, Resin cement, Surface treatment, Tribochemical silica, Zirconia

Introduction

In recent years, the increasing demand for aesthetic solutions in dentistry has highlighted the growing significance of zirconia, valued for its excellent mechanical properties and biocompatibility.[1] The introduction of translucent zirconia with enhanced aesthetic qualities has further advanced its use, enabling the creation of monolithic prosthetic restorations.[2] These restorations offer several key advantages, such as improved resistance to chipping, greater mechanical strength compared to monolithic lithium disilicate, compatibility with CAD-CAM technology for standardized and cost-efficient production, reduced material thickness, and more conservative tooth preparation.[3]However, zirconia differs from glass ceramics in that it cannot be etched, which poses challenges for adhesive bonding.

Adhesive cementation plays a critical role in ensuring the durability and success of restorations, particularly in cases where tooth preparations lack retentive features or where enhanced mechanical integration between the restoration and tooth is required. The absence of a standardized adhesive protocol for zirconia has led to significant variability in clinical outcomes. Research has explored a wide range of approaches to improve zirconia adhesion, including various surface treatments, the application of primers and adhesives, and the use of resin cements. Despite these efforts, no universal protocol delivering consistent and reliable results has been established.[4-6] Thus the objective of this literature review is to examine the effectiveness of different zirconia surface treatments by synthesizing available evidence and contributing to improved clinical success.

Discussion

In the literature various surface treatments were evaluated to enhance micro-retention between monolithic zirconia and resin cement, addressing the challenge posed by the inability to perform acid etching. Zirconia surface treatments can be categorized into two main methods: mechanical or chemical treatments:

A. **Mechanical Treatment**

- Airborne-particle abrasion
- Tribochemical silica coating
- Diamond and disc grinding
- Electrical discharge machining
- Lasers

B. **Chemical Treatment**

- Using various acid solutions such as hydrofluoric acid (HF) and hydrochloric acid
- Silane coupling agent such as 10 MDP,Zirconate
- Plasma treament

Airborne particle abrasion

Airborne-particle abrasion, also known as sandblasting, plays a critical role in enhancing the mechanical interlocking of resin cement to dental materials, such as zirconia. This technique improves surface characteristics by cleaning the substrate, removing impurities, increasing roughness, and modifying surface energy and wettability. The mechanical impingement of abrasive particles creates micro-retentions on the surface, enabling resin cement to penetrate and establish a robust micromechanical interlock.[7,8]

Protocol for Airborne-Particle Abrasion

Ozcan (2013)[9] introduced a widely recognized protocol for preparing zirconia surfaces:

- **Abrasive particles:** Alumina with a diameter of 30–50 µm.
- **Pressure:** Between 0.5 and 2.5 bar.
- **Duration:** At least 20 seconds.
- **Distance:** The blast jet should be maintained 10 mm from the target surface.
- **Movement:** Continuous motion of the jet to avoid localized defects.

These parameters are designed to achieve optimal surface preparation while minimizing the risk of damage.

Potential Risks and Concerns

Despite its benefits, airborne-particle abrasion poses some risks to zirconia:

1. **Microcrack Formation:** The high stresses from particle impingement can lead to microcrack formation, which may reduce the material's flexural strength.[10]
2. **Phase Transformation:** In Y-TZP zirconia, the tetragonal-to-monoclinic phase transformation occurs under stress, leading to a volume expansion of 4–5%. This transformation can introduce structural instability and impact material reliability.[11]

Benefits

While airborne-particle abrasion is effective for creating micro-retentions and improving bonding, care must be taken to select appropriate parameters and techniques to minimize damage to zirconia.[12,13]

Further research is needed to refine the method and assess the long-term implications of surface treatment on structural integrity.

Tribochemical Silica Coating

The tribochemical silica coating method is indeed a sophisticated approach designed to overcome the challenges of bonding resin cement to zirconia. Here's a structured overview of the key points you provided:

Tribochemical Silica Coating Mechanism

1. **Silica Deposition:** Enhances the silica content on the ceramic surface, essential for chemical bonding.
2. **Surface Roughening:** Improves mechanical interlocking and promotes bonding durability.

Benefits

- **Silica Deposition & Silanization:**
    - Facilitates chemical bonding via silane coupling agents and hydroxyl groups in resin cement.Application of silane enables chemical bonding through the formation of siloxane (Si–O–Si) bonds.Silanol groups (Si–OH) on silica-coated zirconia interact with hydroxyl groups in resin cements.
    - Improved Durability: When properly executed, provides a reliable bond for zirconia-based restorations.Demonstrates higher bond strength compared to untreated zirconia surfaces.[14]

Challenges and Observations

Bond Degradation Over Time:

- Studies have observed that while tribochemical silica-coating initially results in high bond strength between resin cement and zirconia, values decrease after long-term storage or thermocycling.[15,16]
- The weakening of bond strength has been suggested to be linked to the presence of a thin layer of silica deposited on the zirconia surface. This silica layer may have facilitated the penetration of water, thereby contributing to a more pronounced degradation of the zirconia bonding. Unfortunately, there are no clinical trials available to confirm the long-term bonding efficacy to silica-coated zirconia . Overall, the difference in bond strength

values and stability between zirconia abraded with alumina particles or with silica-embedded alumina particles is unclear.

Laser

The use of lasers as a surface treatment method for zirconia ceramics in dentistry has been extensively studied, with mixed outcomes depending on the type of laser and specific application:

Er:YAG Laser: Some studies suggest that Er:YAG lasers can enhance the surface roughness of zirconia ceramics, potentially improving the bond strength to resin cement. However, its effectiveness appears to be less consistent compared to sandblasting techniques.[17]

CO_2 Laser: Research indicates that CO_2 lasers can significantly increase the bond strength between resin cement and zirconia ceramics. This is attributed to zirconia's high absorption of CO_2 laser wavelengths, leading to localized heating, surface destruction, and the creation of porosity. These changes enhance micromechanical retention. CO_2 lasers are often reported to outperform other laser types, including Er:YAG and diode lasers, in this regard.[18]

Nd:YAG Laser: The application of Nd:YAG lasers for zirconia surface treatment has yielded less promising results. Some studies report that Nd:YAG laser treatment may be ineffective or even detrimental, reducing bond strength compared to methods like sandblasting or Er:YAG lasers. This could be due to insufficient surface modification or undesirable thermal effects on the zirconia.[18,19]

Mechanisms of Bond Improvement

The effectiveness of laser treatments depends on their ability to:

- **Create Porosity**: Laser interaction with zirconia can generate micro-scale porosities, enhancing micromechanical retention.
- **Increase Surface Roughness**: This provides a larger surface area for bonding with resin cement.
- **Thermal Effects**: Controlled heating can modify the surface properties, but excessive heat might lead to undesirable effects like cracking or reduced structural integrity.

The selection of a laser type should consider the clinical situation, desired bonding outcomes, and the potential side effects on the zirconia's mechanical properties. While CO_2 lasers show promise, further research is needed to optimize parameters and compare their efficacy with conventional methods like sandblasting.

Diamond and disc grinding

Numerous studies[20,21] have concluded that the mechanical behaviours of Y-TZP are affected by thermal ageing and surface treatments such as grinding because the transformation from the tetragonal phase to the monoclinic phase can be induced by water or stress under certain conditions. The water species penetrated the zirconia lattice and disturbed the charge conservation, as well as the stability of the tetragonal phase, compared to thermal ageing or low-temperature degradation (LTD). According to some results, grinding with dental diamond burs reduced the LTD susceptibility of zirconia materials in spite of the increased surface roughness and the generated monoclinic zirconia. The surface roughened by grinding did not accelerate the LTD of zirconia; however, at the zone near the ground surface, a compressive stress layer was created along the grain boundary as the grains moderately expanded as a result of phase transformation. This compressive stress layer delayed the penetration of water and the subsequent propagation of microcracks.[20,21]

Electrical Discharge Machine

Electrical discharge machining (EDM) is a nonconventional process, that creates a desired shape by eroding material with electrical sparks in a dielectric medium. The process was introduced into dentistry by Rubeling in 1982 to produce precision attachments. Any electrically conductive material can be machined via this method, regardless of its hardness, shape or strength. However, it was reported that a resistivity lower than 100 V cm is necessary for any material to be machined with EDM. If that is the case, zirconia would be categorized as a nonconductive material for EDM purposes as its resistivity is nearly 109 –1010 V cm. Subsequently, Kucukturk and Cogun developed a method in 2010 to machine of electrically nonconductive workpieces with EDM. In this method graphite powder is mixed with the dielectric liquid and the maching is achieved via a conductive coating layer (CL) on the workpiece surface. Kucukturk and Cogun further reported the highest material removal rate of material and the most stable machining regime for ZrO2 (via addition of Y2O3) ceramic workpieces.[22,23] Rona *et al*[24] found that electric discharge machining (EDM) may be an alternative surface treatment method for increasing zirconia-resin bonding strength considering its higher shear-bond strength than specimens surface treated with sandblasting, tribochemical silica coating and laser. The flexural strength tests performed in this study revealed that EDM surface treatment does not significantly affect strength properties of zirconia

Drawbacks

EDM displays unsatisfying rates of material removal and poor surface finish

Chemical treatment

The chemical etching methods have the advantage that it can produce surface roughness without significantly affecting the properties of the zirconia

Hydrofluoric Acid

It has been established that a mixture of high-concentration HF and various strong acids increases the surface roughness of zirconia.[25] Zirconia, being a non-silica-based ceramic, is resistant to HF etching at room temperature. However, prolonged immersion in high-concentration HF at elevated temperatures can successfully etch the zirconia surface.[26] Casucci *et al.*[27] reported that hot-etching zirconia with a low concentration of HF produced a surface roughness comparable to that achieved using high-concentration HF at room temperature.

Despite its effectiveness, the dangers associated with HF are well known. HF is not a particularly strong acid, but it penetrates cells and disrupts their metabolism, leading to cell death. Contact with HF on the skin may not result in an immediate burn; symptoms often appear 24–48 hours later and can include severe tissue necrosis. Even low concentrations, such as a 2% aqueous HF solution, can cause significant harm, including corneal erosion.[28]

Silane coupling agents

Zirconia presents unique challenges for adhesive bonding due to its dense polycrystalline structure. Traditional adhesive chemistries and acid etchants like HF, which work effectively on silica-based ceramics, are ineffective for zirconia. The lack of selective etching prevents simple micromechanical attachment, and the use of silane coupling agents alone results in insufficient adhesion.[29]

To address these challenges, a tribochemical silica-coating method has been proposed as a surface preparation technique. This method creates a hydrolysable and hydrophilic silica layer on the zirconia surface, enabling the application of silane coupling agents for bonding mediation. However, concerns about hydrolytic stability persist. In humid oral environments, the siloxane bonds formed between zirconia and resin composites are susceptible to degradation by water molecules, potentially reducing clinical longevity.[29] Laboratory studies have demonstrated significant reductions in shear bond strength following 8000 thermo-cycles or four years of water storage when using commercial silanes .[30] Nonetheless, novel silane systems blending different silanes have shown promise in enhancing hydrolytic stability and improving zirconia–resin bonding performance .[31]

Alternative adhesion methods, including the use of phosphoric acid primers or phosphate-modified resin cements, mimic silane-like adhesion via hydrolyzation-driven chemistry. Despite this, reported bond strengths are generally lower than those achieved with tribochemical silica coating combined with silane and resin cement.[32] Selective infiltration etching and advanced silane-based zirconia primers have also demonstrated increased bond strength.[33] Yet, the current methods for bonding zirconia ceramics remain inadequate for all clinical applications, and their long-term reliability is uncertain. Optimizing the coupling agent appears critical for improving adhesion performance.

Recent research has explored other silane and phosphate-based coupling agents to enhance zirconia adhesion. These agents utilize mechanisms such as improved surface wettability, restrained layer theory, and chemical binding. For instance, 10-methacryloyloxydecyl dihydrogen phosphate (MDP) has gained attention as a potential alternative to silane due to its enhanced bonding and hydrolytic stability. [34] However, findings regarding MDP's stability after artificial aging have been inconsistent. Its phosphate ester group exhibits strong chemical affinity for zirconia surfaces, with additional surface treatments improving bond durability.[35]

Zirconate coupling agents have also been proposed as a promising alternative, though limited research exists on their effects.[36] Tribochemical treatments combined with zirconate agents, such as zirconium(IV)-2,2(bis-2-propenolatomethyl), show potential for achieving stronger and more durable bonds between resin composites and yttria-stabilized tetragonal zirconia polycrystals (Y-TZP). Zirconate compounds, commonly used to enhance adhesion between inorganic fillers and organic matrices, may be incorporated into resin composites at concentrations of 0.1–1 wt% to improve bonding performance.[36]

Plasma Surface treatment

Plasma is the most prevalent state of matter in the universe and is characterized as a fully or partially ionized neutral gas containing electrons, ions, and neutral particles. Often referred to as the fourth state of matter, it complements the traditional states of solids, liquids, and gases.[37] Plasma-based methods for zirconia surface treatment offer several unique advantages over conventional approaches. Specifically, plasma treatments modify only the surface of materials—typically within a range of a few to a dozen nanometers—while preserving the intrinsic properties of the underlying substrate.

Valverde et al.[38] demonstrated that non-thermal atmospheric pressure plasma (NTP) chemically modifies zirconia surfaces, increasing surface energy and improving the shear bond strength (SBS) between yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) and resin cement. NTP contains numerous reactive species that give it distinctive properties, setting it apart from conventional gases. Studies have shown that NTP facilitates the formation of reactive groups on Y-TZP surfaces through mild etching and chemical functionalization. This process reduces carbon contamination, enhances surface wettability, and significantly improves SBS without causing substantial changes to the surface morphology or mechanical properties of Y-TZP.[39,40]

Additionally, NTP is a simple and environmentally friendly surface treatment technique. It effectively cleans surfaces without generating harmful pollutants, making it well-suited for future clinical applications. However, the effectiveness of plasma treatment depends on the type of gas used, with different gases yielding varying outcomes. As such, determining the optimal plasma gas composition remains a critical area of ongoing research to maximize treatment efficacy.

Conclusion

The literature presents a range of surface treatment methods for zirconia in dentistry, emphasizing both its effectiveness and limitations:

Tribochemical Silica Coating: This is regarded as the best surface treatment method for zirconia. It enhances bonding by increasing surface roughness and promoting chemical adhesion between resin cement and zirconia ceramics.

Airborne-Particle Abrasion with Alumina: This method significantly increases the zirconia surface area, facilitating better interaction with resin cement. It effectively enhances the mechanical interlocking between zirconia and resin cement.

Laser Surface Treatment: Lasers are gaining interest as an alternative due to their ability to avoid the potential damage caused by grit-blasting. They may offer a less invasive way to prepare the zirconia surface.

Chemical Treatment: These methods, commonly used for other ceramics, are not effective for zirconia. This is because zirconia's chemical structure does not allow effective interaction with hydrofluoric acid or silane.

Advancements in product chemistry, development and a deeper understanding of zirconia are making zirconia bonding more reliable and effective than ever before. By gaining insight into the fundamental properties of zirconia, clinicians can select the most suitable products and follow optimal protocols to achieve strong, lasting bonds. This ensures they can deliver durable and esthetically pleasing restorations that meet their patients' needs.

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