Resin Bonding to Zirconia

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The use of zirconia for dental applications has increased substantially over the past decade. This is evident from the wide variety of commercial products available on today's market and the wealth of information in the scientific literature. Its uses range from single-unit crowns and fixed-partial dentures to entire dental implant systems and nanoparticle fillers in composite resins. Zirconia, sometimes described as "ceramic steel," possesses the ideal properties for dental use: superior strength, toughness, and fatigue resistance, excellent wear properties, and biocompatibility. However, the nonreactive surface of zirconia presents a consistent issue of poor adhesion to other materials (synthetic or tissue). Here, we look at several research manuscripts that describe approaches and pretreatments to increase zirconia surface reactivity for enhanced adhesion with resin cements.

Effect of Surface Treatments on the Resin Bond to Zirconium-Based Ceramic

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International Journal of Prosthodontics 2005 (18:60–5)

ABSTRACT

Objective: This study tested the hypothesis that a tribochemical silica coating on ceramic surfaces increases the bond strength of resin cement to a glass-infiltrated zirconium-based ceramic.

Materials and Methods: Fifteen blocks of In-Ceram Zirconia (VITA Zahnfabrik, Bad Säckingen, Germany) from CEREC InLab (Sirona, Charlotte, NC, USA) (five per group) and 15 composite blocks (Filtek Z-250, 3M ESPE, St. Paul, MN, USA) 5 mm × 5 mm × 4 mm were made. The ceramic surfaces were polished, and the blocks were divided into three groups: (1) airborne abrasion with 110-μm aluminum oxide particles; (2) Rocatec (3M ESPE) tribochemical silica coating; and (3) CoJet (3M ESPE) tribochemical silica coating. The ceramic blocks were cemented to the composite blocks using Panavia F (Kuraray, Tokyo, Japan) according to the manufacturer's specifications. All samples were stored in 37°C distilled water for 7 days and later sectioned in two axes using a diamond disk to obtain specimens with a cross-sectional area of approximately 1 mm^2. Each specimen was then attached with cyanoacrylate glue to an adapted device for the microtensile test, which was carried out on a universal testing machine.

Results: Group 2 (23.0 MPa) and Group 3 (26.8 MPa) had higher mean bond strengths than Group 1 (15.1 MPa). The means of Groups 2 and 3 were not significantly different. All failures were adhesive in nature.

Conclusions: The hypothesis was confirmed—i.e., the tribochemical systems increased adhesion of a resin cement to a zirconia ceramic substrate.

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COMMENTARY

Earlier adhesion research focused on creating a surface for silanation and/or increasing the surface area for micro-mechanical attachment. Because conventional silanation techniques used for silica-containing materials such as porcelain do not apply for zirconia, solutions for adhesion range from physical to chemical alterations to the surface. One such technique, tribochemical abrasion, allows the clinician to physically impart a silica layer on the surface (as well as roughen), then use traditional silanation techniques for bonding.

The authors report a significant increase in adhesion with using products (Rocatec and CoJet) as compared with simple surface abrasion. However, later reports showed that long-term stability can be an issue.

This article highlights initial products that were developed at the early stages of zirconia use in dental applications. The use of zirconia has increased exponentially and so has the development of alternative solutions (e.g., silica coating using elaborate deposition techniques, highly specialized etchants, phosphate-containing primers, etc.).

Hydroxylation of Dental Zirconia Surfaces: Characterization and Bonding Potential

U. LOHBAUER, M. ZIPPERLE, K. RISCHKA, A. PETSCHELF, F.A. FULLER

Journal of Biomedical Materials Research Part B: Applied Biomaterials 2008 (87B:461–7)

ABSTRACT

Objective: Bioinert zirconia surfaces exhibit a low chemical bonding potential for resin-based luting agents. The aim was to hydroxylate dental zirconia surfaces and to examine tensile bond strengths using commercial luting agents.

Materials and Methods: The measured bond strength was compared with established mechanical conditioning techniques. Five acidic and one alkaline hydroxylation pretreatments were applied and compared with air abrasion and tribochemical silica coating. For the chemical characterization of hydroxyl groups and hydroxyl value, zirconia powders were used, chemically modified, and analyzed using Fourier-transformed infrared (FTIR) spectroscopy and a titrimetric method according to the International Organization for Standardization (ISO) 4629. All acidic pretreatment procedures exhibited increased hydroxyl values. The highest values were recorded after treatment with phosphoric acid or Piranha solution (mixture of sulfuric acid and hydrogen peroxide typically used in the microelectronic industry as an aggressive etchant). Tensile bond strengths were determined using a universal testing machine and the commercial dual-cure resin luting agents Multilink (Ivoclar Vivadent, Schaan, Principality of Liechtenstein) and Panavia F2.0 (Kuraray).

Results: Surface hydroxylation with Piranha solution in combination with the luting agent Multilink resulted in a mean bond strength of 12.5 MPa. Tribochemical silica-coated/silanized zirconia surfaces with Multilink produced the highest bond strength of 19.3 MPa. Using the luting agent Panavia F2.0, statistically homogenous values for the untreated (11.6 MPa) and for the hydroxylated surface (12.5 MPa) were measured.

Conclusions: Bioinert zirconia surfaces were successfully hydroxylated in terms of tensile bond strength. Resin bonding with Multilink can be strongly increased by acidic treatment with Piranha solution. Bonding with Panavia F2.0 is not affected by hydroxylation, which is likely due to the incorporation of specific functional monomers in the material.

COMMENTARY

A well-accepted concept for increased adhesion is to increase the chemical bonding and micro-mechanical attachment. The chemical bond between zirconia surfaces and phosphate monomers is often reported as a reaction with surface –OH groups. However, zirconia

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itself is described as hydrophobic and having very low surface concentrations of –OH groups. The authors here report that native surfaces had approximately 5.4% –OH coverage, suggesting only limited chemical binding between zirconia and adhesive monomer. They did improve the hydroxylation and bond strength by using an aggressive Piranha solution (mixture of sulfuric acid and hydrogen peroxide), but unfortunately this procedure would be not suitable for clinical settings. This research article is an excellent study on zirconia surfaces and reports exactly how difficult it is to chemically functionalize with the use of monomers.

Bonding of Primed Zirconia Ceramics: Evidence of Chemical Bonding and Improved Bond Strengths

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American Journal of Dentistry 2012 (25:103–8)

ABSTRACT

Objective: This study investigated changes of zirconia surface hydrophobicity (contact angle) following the application of a zirconia primer as a function of post-priming storage period and after exposure to harsh conditions and analyzed whether a chemical bond forms between a zirconia primer and zirconia ceramics.

Materials and Methods: Zirconia ceramics were treated with a zirconia primer (Z-Prime Plus, BISCO, Inc., Schaumburg, IL, USA) and were left undisturbed for specific times (reaction time). Storage was followed by ultrasonic cleansing in ethanol or acetone bath, and then contact angles were measured ($n = 10$). The primed zirconia ceramics also were subjected to harsh conditions (strong acid or boiling water) prior to contact angle testing. The chemical change of zirconia surface with and without being primed was analyzed by time-of-flight secondary ion mass spectroscopy (TOF-SIMS). Shear bond strengths of resin to zirconia were tested using different zirconia primers.

Results: Contact angles on primed zirconia surface (56–72° for different primers) were significantly higher than on unprimed zirconia (15°). Contact angles were maximized as the reaction time increased within 5 minutes (from 58° at 10 seconds to 72° at 5 minutes). Exposure to harsh conditions caused no significant change in contact angle values. The time-of-flight secondary ion mass spectrometry (TOF-SIMS) detected fragmentations with mass of 549 and 411, indicating that a chemical group of phosphate monomer(P)-O-Zr existed. This indicates that a chemical bond was formed between zirconia and Z-Prime Plus. All of the zirconia primers tested in the study significantly improved resin-zirconia bond strengths (4 MPa for unprimed zirconia and 17–23 MPa for primed zirconia).

Conclusions: Current zirconia primers significantly improved the hydrophobic nature of the zirconia surface and improved resin bond strengths. Zirconia primer was able to create a chemical (covalent) bond between resin and zirconia. The zirconia priming process reached its optimal effect within 5 minutes. The contact angle studies indicated that the primed zirconia could survive harsh conditions such as boiling water and strong acids, and could be stored up to 6 months before cementation with no adverse effects.

COMMENTARY

This article provides an excellent analysis of chemical bonding at the zirconia surface using specialized priming agents. As noted by the authors, the most successful surface treatment in terms of increased adhesion of resin to zirconia has been the use of an organo-phosphate monomer (10-methacryloxydecyl dihydrogen phosphate [MDP]). Enhanced adhesion between the primers and zirconia surfaces using MDP-based primers are predicated on chemical bonding either through covalent (P-O-Zr bond formation) bonds, hydrogen bonds, and weaker surface interactions such as Van Der Waals forces. This

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study included other similar commercial primers that do not contain a carboxylate monomer as Z-Prime Plus does. Results and discussion provided a conclusive analysis of P-O-Zr bonding using Z-Prime Plus by using time-of-flight secondary ion mass spectrometry (TOF-SIMS), which is a sensitive technique that provides elemental composition of a sample or molecule. Additionally, aggressive cleaning and time-based contact angle measurements confirmed that Z-Prime Plus was more stable than the other primers studied.

Manufacturers of the various primers still suggest the using of roughening the surface (particle air-abrasion), which some argue could be detrimental to the lifetime of the restoration due to the potential for induced surface flaws; however, clinical data to date have yet to confirm this as a failure issue.

SUGGESTED READING

Review Papers

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THE BOTTOM LINE

- Research has focused on adhesion and bond strengths to zirconia, but the question is "what is the gold standard—what is the bond strength we are trying to achieve?"
- Clinical data are needed to further understand adhesion issues—and studies are just now being published. Preliminary clinical research indicates that some failures are due to loss of adhesion but more are due to chipping of veneer porcelain.
- Commercial adhesion products are continuously being developed and optimized for clinical use.
- It is anticipated that the use of zirconia in dentistry will increase in the future, so reliable clinical adhesion solutions are needed.
- Based on the literature and the commercial products available to clinicians today, using novel primers (e.g., Z-Prime Plus) coupled with low pressure air-abrasion would be more than sufficient for adequate bonding of resin cement.

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