Surface Treatments for Zirconia Bonding: A Clinical Perspective

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ABSTRACT

There has been a monumental shift in the use of zirconia in esthetic/restorative dentistry. Zirconia-based restorative materials exhibit improved strength, versatility of clinical indications, and the ability to be CAD/CAM milled. They are also an alternative to the increasingly higher cost of precious metals. As well, the creation of surface adhesive primers that create covalent bonding to zirconia will only help to propagate zirconia's use in clinical dentistry.

RÉSUMÉ

Il y a eu un changement monumental dans l'utilisation de la zircone (oxyde de zirconium) en dentisterie esthétique ou de restauration. Les matériaux de restauration à base de zircone possèdent une résistance améliorée et une versatilité des indications cliniques et peuvent être utilisés avec la technologie CAO/FAO. Ce sont également une solution de rechange aux métaux précieux dont le prix ne cesse d'augmenter. De plus, la création de couches adhésives superficielles favorisant une fixation par liaison covalente à la zircone permettra de propager l'utilisation de la zircone en dentisterie clinique.

Zirconia (ZrO_2) is a silica-free, acid-resistant, polycrystalline ceramic that does not contain amorphous silica (SiO_2) glass. Traditional ceramic surface treatments (such as hydrofluoric acid [HF] etching and/or silane primer application) are ineffective on the silica-free surfaces of zirconia, alumina, and metal. New research has shown phosphate monomers to have a significant affinity for non-silica-based oxides such as zirconia. Research has shown that the combination of light air abrasion and methacryloyloxydecyl dihydrogen phosphate (MDP)-based zirconia primers is necessary to achieve long-term durable bonding to zirconia. It is imperative for the clinician to optimize adhesive performance in less-than-retentive preparation designs with the use of etch-and-rinse (total etch) or etch-and-dry (self-etch) adhesives onto dentin, such as All Bond 3 or All Bond SE (Bisco, Schaumburg, IL); MDP-containing primers onto the zirconia indirect substrate, such as Z-PRIME PLUS (Bisco); and dual-cure resin cements such as DuoLink or DuoLink SE (Bisco). When preparation designs are fully retentive (and strong adhesion is not critical), organophosphate-containing, self-adhesive, dual-cured resin cements, such as BisCem (Bisco), Maxcem Elite (Kerr, Orange, CA), and RelyX Unicem (3M ESPE, St. Paul, MN), can be used.

The incorporation of proven monomers into new product innovation aimed at addressing clinical challenges is exciting. The use of primers to enhance bonding to zirconia has led to the development of improved material alternatives in metal-free esthetic restorative dentistry.

Treating the Zirconia Surface: Low-Pressure Al_2O_3 and Zirconia Primers

The goal of replicating the cohesive hydrophobic interface (dentin-enamel junction, or DEJ) with the use of resin luting cements is first dependent upon the clinician addressing the individual needs of the tooth substrates (dentin, enamel) and the indirect substrates (zirconia, alumina, ceramic, metal). Adhesive bonding agents onto the tooth substrate and primers onto the indirect substrate are critical in optimizing this cohesion.

Zirconia has been used in clinical dentistry for several years with much success.[1–8] Creating adhesion to non-silica-based oxide ceramics such as zirconia, alumina, and metal was the challenge that limited their use.[9–14] This is changing with our current understanding of zirconia. Zirconia is a silica-free, acid-resistant, polycrystalline ceramic. It does not contain amorphous silica glass (like feldspathic porcelain, leucite-reinforced ceramics, and lithium disilicate ceramics); thus, traditional ceramic surface treatments such as HF etching followed by silane application are ineffective.[9–14]

It is now understood that the combination of low-pressure Al_2O_3 with primers specific to zirconia may contribute to long-term stability of its bonding. The use of pyro-chemical (Pyrosil, Sura Instruments, Jena, Germany)[15,16] or tribo-chemical treatments (Cojet/Rocatec, 3M ESPE)[12,14,17–22] to create a pseudo-silane attached surface is an alternative method. Internal research at Bisco Dental Products with tribo-chemical bonding (Cojet/Rocatec) showed that it did not offer improved bonding and could be prone to degradation. Other research has shown that tribo-chemical bonding improved bonding

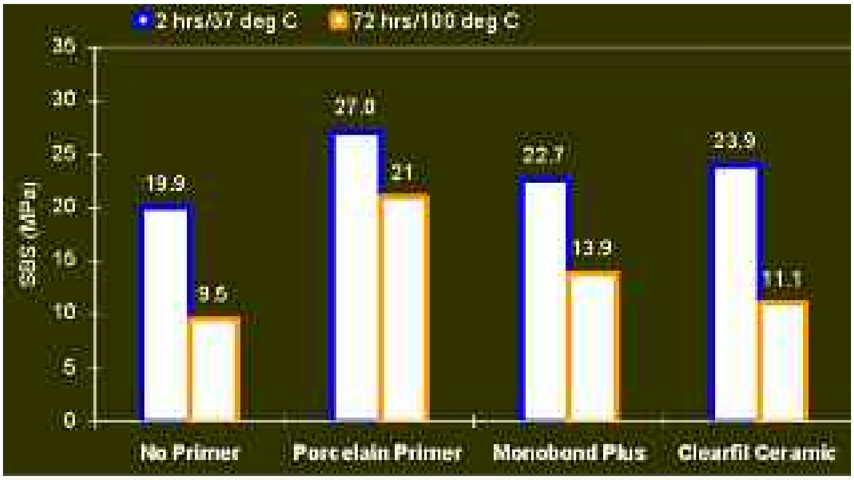

Figure 1. Shear bond strengths (SBSs) of different primers on etched lithium disilicates before and after accelerated aging (internal Bisco data).

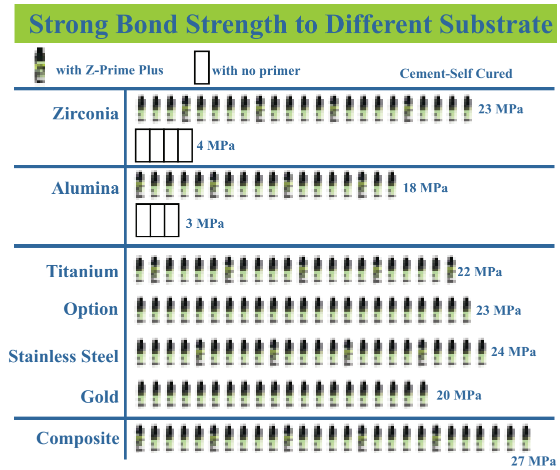

Figure 2. Bond strengths of Z-PRIME PLUS to various substrates.

with the use of primers.[19] Internal studies at Bisco have shown Z-PRIME PLUS adhesion does not require mechanical altering of the zirconia surface.

Phosphate Monomers Specific to Zirconia

There are five commercial ceramic primer systems intended for use with zirconia: AZ Primer (Shofu Dental Corporation, San Marcos, CA), Clearfil Ceramic Primer (Kuraray America, Houston, TX), Metal/Zirconia Primer (Ivoclar Vivadent, Amherst, NY), Monobond Plus (Ivoclar Vivadent), and Z-PRIME PLUS. These products differ in the type and concentration of phosphate monomers used, clinical technique for use, time of application, and proprietary formulas. Phosphate monomers form chemical bonds with the zirconia surface and have resin terminal ends that bond to the resin cements. MDP is the most time-tested of the commonly used phosphate monomers and has been shown to have a special affinity for non-glass-based substrates of zirconia, alumina, and metal. MDP is a relatively hydrophobic monomer due to its 10-carbon chain and contains both a hydrophilic phosphate terminal end that chemically adheres to zirconia and a polymerizable methacrylate terminal end that adheres to resin.

Bond strengths are a function of the mode of curing, stability of the resin chemistry, compatibility of primer to cement, and contamination potential dependent upon clinical application times. The acidic nature of phosphate monomers does pose a chemical challenge with creating formulas that are both durable and stable. Monobond Plus and Clearfil Ceramic Primer incorporate silane with the intended additional use on silica-based surfaces. Silane is known to be unstable in acidic environments (Figure 1). The acidic nature of organophosphates (phosphate/phosphonate monomers) placed in products such as Monobond Plus and Clearfil Ceramic Primer may lead to instability of the silane component of these individual formulas. Z-PRIME PLUS does not contain silane.

Z-PRIME PLUS contains a propriety formula of concentrated MDP and carboxylic monomers formulated specific to zirconia, alumina, and metal. The versatility of these primers is a compelling feature for use on many different indirect substrates (Figure 2).

Adherence of Resin Cements to Zirconia: The Science

Phosphate monomers in self-adhesive cements are proven to be effective in adhering to non-silica-based polycrystalline materials of zirconia, alumina, and metal.[17–20] It is with this information that primers specific to zirconia, alumina, and metal were created. Numerous research studies have shown that phosphate /phosphonate monomers are very effective in improving zirconia bonding. In theory, phosphate monomers form chemical bonds with the zirconia, alumina, and metal oxide surfaces and have resin terminal end groups, which enable cohesive bonding to appropriate resin cements (Figure 3).[22,23]

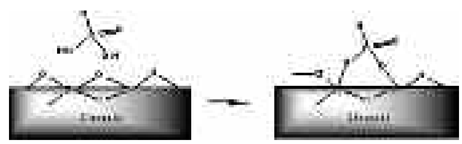

Figure 3. Demonstration of how the hydrogen (-H) group of a phosphate monomer interacts with the Zr-O group of zirconia to form a phosphate monolayer on the zirconia surface.

Bonding Zirconia to Preparations with Retention/Resistance Form

Self-adhesive resin cements, such as BisCem, Maxcem Elite, and RelyX Unicem, are dual-cured, contain organophosphate monomers, and can be used when preparation designs are fully retentive; however, these cements are hydrophilic due to the acidic resin components and have lower physical and mechanical properties than resin cements. Self-adhesive resin cements differ in viscosity

Table 1. Shear bond strengths (MPa) of self-adhesive resin cements to zirconia

	Light-Cured Cement		Self-Cured Cement	
Zirconia Bonding Systems	Initial*: 37°C/2 h	Aging*: 100°C/3 d	Initial*: 37°C/2 h	Aging*: 100°C/3 d
BisCem	20.0 (3.6) 1, bc	12.1 (2.8) 2, b	12.4 (2.6) 1, b	9.6 (2.4)2, b
RelyX Unicem	11.6 (6.2) 1, d	4.2 (2.9) 2, c	6.2 (2.6) 1, c	2.7 (2.0) 2, c
SmartCem2	16.2 (3.7) 1, cd	5.5 (1.9) 2, c	10.8 (3.0) 1, b	3.8 (1.8)2, c
Z-PRIME PLUS/DuoLink	28.7 (5.7) 1, a	28.3 (4.4) 1, a	23.0 (5.3) 1, a	15.8 (2.7) 2, a

*Means and standard deviations (n = 8) of shear bond strengths (MPa) tested on sandblasted zirconia using the Ultradent jig method. Results with the same numerical superscripts in the same row and same curing mode or same letter superscripts in the same column are statistically the same ($p > .05$) (internal Bisco data).

Table 2. Shear bond strength (MPa) of resin cements to zirconia

	Light-Cured Cement		Self-Cured Cement	
Zirconia Bonding Systems	Initial* 37°C/2 h	Aging* 100°C/3 d	Initial* 37°C/2 h	Aging* 100°C/3 d
AZ Primer/ResiCem	21.2 (8.3) 1, a	17.7 (5.5) 1, b	12.5 (5.9) 1, b	5.8 (1.9) 2, b
Clearfil Ceramic Primer/Panavia F2.0	7.5 (4.5) 1, b	3.2 (2.2) 2, c	8.9 (4.0) 1, b	1.7 (2.1) 2, c
Monobond Plus/Multilink Automix	26.4 (8.8) 1, a	15.5 (5.4) 2, b	10.8 (3.3)1, b	6.7 (1.8) 2, b
Z-PRIME PLUS/DuoLink	28.7 (5.7) 1, a	28.3 (4.4) 1, a	23.0 (5.3) 1, a	15.8 (2.7) 2, a

*Means and standard deviations (n = 8) of shear bond strengths (MPa) tested on sandblasted zirconia using the Ultradent jig method. Results with the same numerical superscripts in the same row and same curing mode or same letter superscripts in the same column are statistically the same ($p > .05$) (internal Bisco data).

(efficiency of mix) and self-cure chemistry (polymerization conversion, setting times). These properties are significantly affected with aging, depending upon the brand. Bond strengths of self-adhesive cements are lower than those of bonded resin cements to both dentin and zirconia; but in retentive preparations, the ease of placement is a compelling benefit (Table 1).

Self-adhesive resin cements may not be strong enough to be used alone on both surfaces (tooth and zirconia) when cementing a non-retentive zirconia restoration. Primers should be part of the clinician's protocol to play a beneficial role for improved adhesion of self-adhesive cements to zirconia. Glass ionomer cements have minimal bond strengths to zirconia (4 MPa) and are susceptible to water degradation due to their chemistry[24–27] (Figure 4).

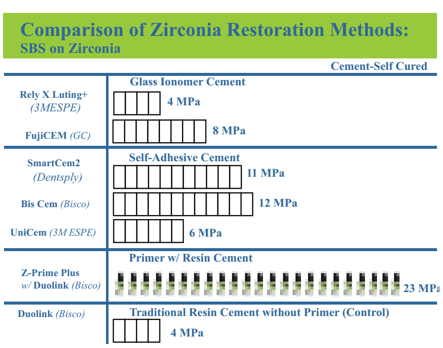

Figure 4. Comparison of shear bond strengths (SBSs) with various zirconia restoration methods.

Creating Adhesion between Direct and Indirect Substrates When Retention Is a Challenge

For slightly retentive or non-retentive designs, traditional adhesive protocols are time tested and required. Optimizing adhesive performance is the goal in less-than-retentive preparation designs and demands the use of dentin adhesives including self-etch (ACE/All Bond SE, Bisco) or total etch (All Bond 3) primers specific to zirconia/metal (Z-PRIME PLUS) and the use of dual-cure hydrophobic resin cements (DuoLink).

Primers that address the specific needs of non-silica oxides (zirconia, alumina, and metal) are highly beneficial and warranted for the restorations when retention/resistance form is compromised. Ceramic and metal primers have been shown to be important to the success of bonding to these indirect materials in laboratory testing. Clinical experience with primers has indicated improved bonding to both direct and indirect substrates. The self-cure mode has been shown to significantly affect bond strengths (Table 2).

The Final Link: All Resin Cements Are Not Created Equal

Arguably, the most important factor in bonding to zirconia is the polymerization (setting) properties of resin cements. The self-cure modes of dual-cure cements are the link to optimizing adhesion between the tooth substrate and indirect restoration. To this date, most zirconia, alumina, and metal indirect restorations lack the ability to transmit the light required for proper polymerization of resin cements. The dual-cured mode is preferred over light-cured-only esthetic resin cements, removing the potential for limited light transmission through opaque copings.

It is important to note that all dual-cured cements are not created equal. Choose a dual-cured cement that performs equally well in both light-cured and self-cured modes, is not affected by aging (ask the manufacturer when the catalyst and base were made, not when they expire), and has an appropriate setting time. Resin cement that fully polymerizes in the self-cured mode within 6 minutes allows for interproximal flossing, whereas one that

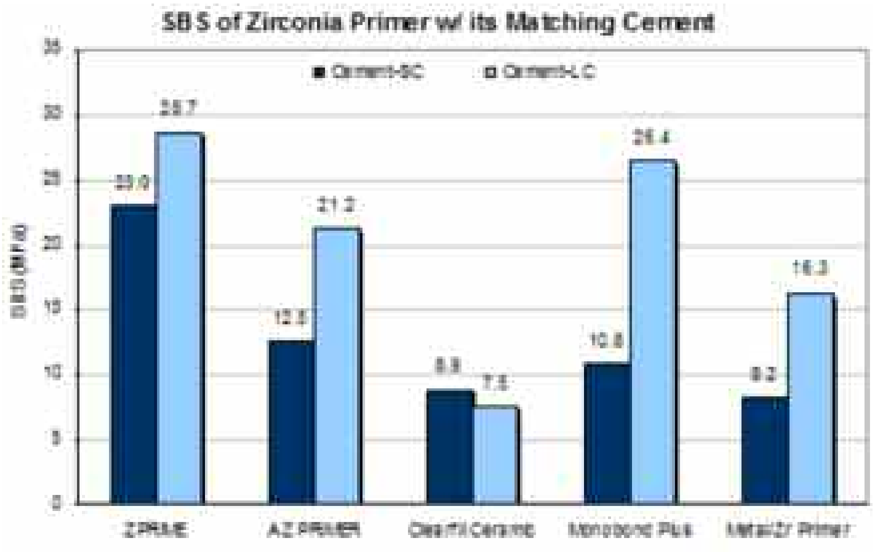

Figure 5. Comparison of shear bond strengths (SBSs) using corresponding brands (Z-PRIME PLUS/DuoLink, AZ Primer/ResiCem, Clearfil Ceramic Primer/Panavia F2.0, Monobond Plus/Multilink Automix, Metal Zr Primer/Multilink Automix) (internal Bisco data).

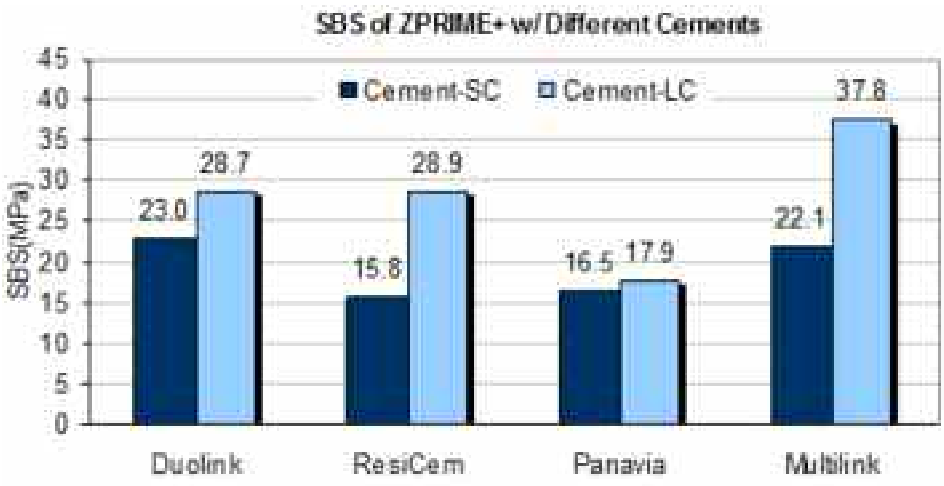

Figure 6. Shear bond strengths (SBSs) of Z-PRIME PLUS with various cements (internal Bisco data).

sets in 10 to 12 minutes requires appropriate measures not to interfere with the development of the bond. Internal testing at Bisco Dental Products supports previous data showing that self-cured modes of some resin cements significantly differ and many are further affected by aging of the chemistry (Figure 5).

Internal testing at Bisco has shown Z-PRIME PLUS to significantly improve the self-cure efficiencies of competitive brands of resin cements. It is theorized that the proprietary combination of monomers addresses acidity issues inherent within many formulas (Figure 6).

Case Report

Presentation

A 58-year-old female (a breast cancer survivor of 5+ years) presented to our practice. She had a retained deciduous tooth "h" with a mesio-angular impacted tooth #23 extending under teeth #21 through #24 (Figure 7) and was concerned about the darkening of this cuspid in addition to conservative enhancement of her smile (Figure 8). A comprehensive list of treatment options was discussed, including orthodontic repositioning. The accepted plan was for the extraction of tooth h, a zirconia framework/porcelain bridge to replace #23, a composite to correct the facial incisal of #21, and a composite on #13 to restore the cusp tip and to provide cuspid disclusion in excursive movements.

Preparation and Design

The laboratory prescription was for a zirconia framework bridge with add-on porcelain over an ovate pontic design (Figures 9 to 12). Zirconia has been widely used the past few years as a bridge framework because of its non-metalic colour, fracture resistance with flexural tests over 1,000 MPa, and excellent long-term clinical success. A major disadvantage of its use was the inability to

Figure 7. Lateral view of greying deciduous cuspid.

Figure 8. Maxillary anterior pre-treatment display.

Figure 9. Pep Gen granular and flow graft materials were placed and a collagen membrane sutured in place for stabilization.

Figure 10. Conservative preparation designs with minimal reduction, rounded shoulders, and seating grooves parallel in nature.

Figure 11. Zirconia framework overlayed with Ceram porcelain.

Figure 12. Our reputation is built on adhesion.

Figure 13. Ten-second application of Z-PRIME PLUS, which would be followed by air-drying.

Figure 14. Maxillary anterior view of restoration.

bond zirconia to the tooth substrate. Our improved knowledge of non-glass-based oxides such as zirconia has resulted in the subsequent innovation of adhesives with special qualities. Z-PRIME PLUS is one of those special primers that have been shown to significantly increase bond strengths to zirconia allowing for more conservative removal of tooth tissue.

Treatment Completion

Following verification of the fit, the bridge was cleaned in an ethyl alcohol ultrasonic bath for 10 minutes. Two drops of zirconia primer (Z-PRIME) were placed on the internal surface of the porcelain abutments and dried after 10 seconds (Figure 13). It was my decision to optimize adhesion with the use of total etch on dentin/enamel, coupled with the use of a hydrophobic dual-cure resin cement.

The abutments were cleaned with slurry of pumice/water. The etch-and-rinse technique was accomplished using phosphoric acid (UNI-ETCH BAC, Bisco) followed by disinfecting/rewetting with a cavity cleanser CHX and an application of All Bond 3 primer/resin. DuoLink dual-cure resin cement was placed directly on the teeth, and the bridge was positioned with moderate digital pressure. Clean-up was initially accomplished using a microbrush and 2 × 2 cotton gauze. Margins were initially light-cured; then the dual cure was allowed to cement to complete polymerization in self-cure mode. Final clean-up was accomplished using 204S scaler and explorer. Occlusion was checked, cuspid disclusion verified, and anterior guidance was checked.

Teeth #13 and #21 were prepared lightly using a finishing diamond to remove old filling material, to make an irregular finish line, and to remove staining. The teeth were isolated with retractors (SeeMore, Discus Dental, Culver City, CA) and etched for 20 seconds with 37% phosphoric acid (UNI-ETCH BAC); subsequently, they were rinsed, and several coats of bonding agent (All Bond 3) were applied. Various layers of dentin, enamel, and incisal opacities of composite (Renamel, Cosmedent, Chicago, IL) were applied with Creative Color (Cosmedent) stain.

The lingual and bulk of the tip on #13 were completed using Renamel Universal

Figure 15. A smile to be proud of.

Microhybrid for strength, tinted with grey and honey yellow Creative Color and covered facially with Renamel Microfil Incisal Medium for polishability. Occlusion was checked and cuspid disclusion on #6 was confirmed. Polishing was completed with FlexiDisk rubber polishers (Cosmedent). Tooth #21 was restored using Renamel Microfil Incisal Medium, coupled with matching tints. Shaping was completed with SofLex disks (3M) and polishing with FlexiDisk (Cosmedent) rubber polishers.

A clear, vacuum-formed, 2 mm hard/soft nocturnal bruxism splint was made (Erkodent, Glidewell Labs, Newport Beach, CA), and the patient was encouraged to wear

it nightly to prevent parafunctional forces particularly under times of stress.
The final result was pleasing (Figures 14 and 15).

Conclusion

Patients demand esthetics. The incorporation of zirconia in clinical dentistry offers a new alternative to metal-free esthetic dentistry. New esthetic restorative materials demand adhesion. Recreating the DEJ is a function of addressing the needs of the individual substrates involved (enamel, dentin, and indirect materials such as zirconia). The use of adhesives on the tooth substrate and the use of primers on the indirect substrate in conjunction with quality resin-based cements are crucial in optimizing clinical outcomes to these new restorative materials.

Disclosure

Dr. Byoung Suh is the founder of Bisco Dental. Dr. Liang Chen is a senior researcher at Bisco Dental. Dr. Douglas Brown is senior manager of clinical affairs at Bisco Dental. Dr. Jack Griffin Jr. declares he has no financial interest in the materials mentioned in this article and is not receiving an honorarium for his contribution to this article. The content provided is based solely on his belief in translating science to the application of clinical dentistry.

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