Surface Treatments for Zirconia Bonding – "A Clinical Perspective"

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Abstract:

There is a monumental shift of the use of Zirconia in aesthetic/restorative dentistry. Zirconia-based restorative materials exhibit improved strength, versatility of clinical indications, ability to be CAD/CAM milled and an alternative to increasingly high costs of precious metals. The creation of surface adhesive primers that create covalent bonding to Zirconia will only help to propagate Zirconia's use in Clinical Dentistry.

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 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 significant affinity for non-silica based Oxides such as Zirconia. Research is showing the combination of light air-abrasion and MDP-based Zirconia primers are necessary to achieve long-term durable bonding to Zirconia (29). It is imperative for the Clinician to optimize adhesive performance in less-than-retentive preparation designs with the use of TE or SE Adhesives onto Dentin such as All Bond 3 or All Bond SE (Bisco); MDP containing Primers onto the Zirconia indirect substrate such as ZPRIME 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) or RelyX Unicem (3M ESPE) 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 aesthetic restorative dentistry.

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

The goal of replicating the cohesive hydrophobic interface (DEJ) with the use of resin luting cements is first dependent upon the clinician addressing the individual needs of the tooth substrate (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 has been the challenge that has limited the use of Zirconia and Alumina[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*) [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***, *3M ESPE*) showed that it did not offer improved bonding and could be prone to degradation. Other research showed that tribo-chemical bonding improved bonding with the use of primers [19]. Internal studies at Bisco have shown ZPRIME PLUS adhesion not to 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*), ***Clearfil Ceramic Primer*** (*Kuraray America*), ***Metal/Zirconia Primer*** (*Ivoclar Vivadent*), ***Monobond Plus*** (*Ivoclar Vivadent*), and ***Z-PRIME PLUS*** (*Bisco Dental Products*). 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 covalent bonds with the Zirconia surface and have resin terminal ends that bond to the resin cements. 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. Monobond Plus and Clearfil Ceramic Primers incorporate Silane with the intended additional use on Silica-based surfaces.

Silane is known to be unstable in acidic environments (Figure 2). 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*** (*Bisco Dental Products*) does not contain Silane.

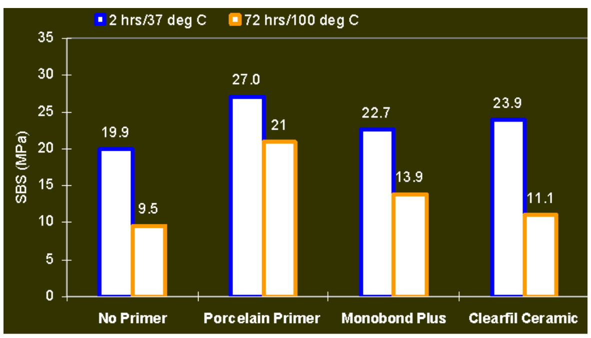
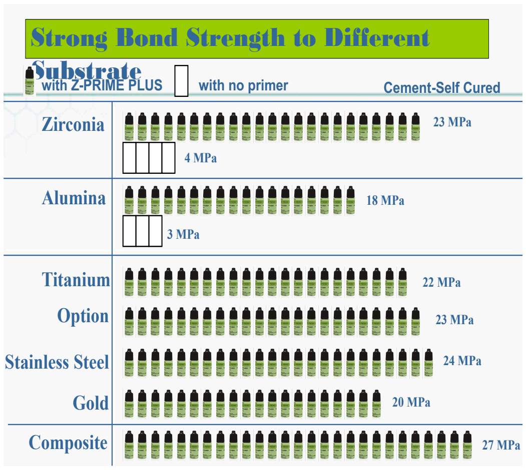


Figure 2. Shear bond strengths of different primers on etched lithium disilicates before and after accelerated aging.(Internal Bisco Data)

Z-PRIME PLUS (*Bisco Dental Products*) 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.



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 show 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 (Fig. 1) [22-23]

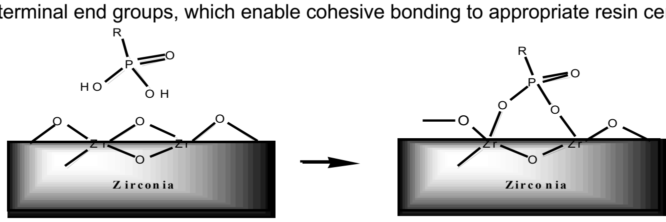


Figure 1. Demonstration of how the hydrogen (-H) group of phosphate-monomer interacts with the Zr-O group of zirconia and forms the phosphate monolayer on the zirconia surface.

Bonding Zirconia to Preparations with Retention/Resistance Form

Self-adhesive resin cements, such as ***BisCem*** (*Bisco Dental Products*), ***Maxcem Elite*** (*Kerr Corporation*), ***RelyX Unicem*** (*3M ESPE*), 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(efficiency of mix) and self cure chemistry (polymerization conversion, setting times). These properties are significantly affected with ageing dependent upon the brand. Bond strengths of Self-adhesive cements are lower than bonded resin cements to both Dentin and Zirconia, but in retentive preparations, the ease of placement is a compelling benefit (Table 1).

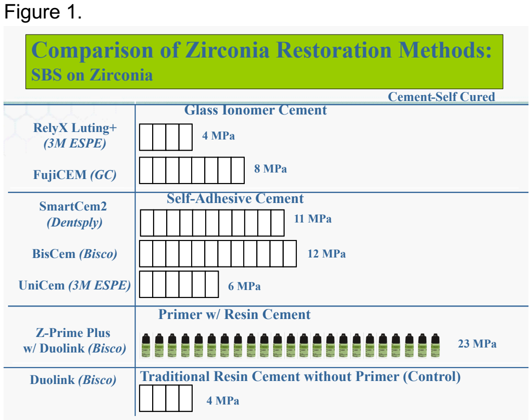
Table 1. Shear Bond Strength (MPa) of Self-Adhesive Resin Cements to Zirconia

	Light-Cured Cement		Self-Cured Cement	
	Initial*	Aging*	Initial*	Aging*
Zirconia Bonding Systems	37°C/2 hours	100°C/3 days	37°C/2 hours	100°C/3 days
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+/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 strength (MPa) tested on sandblasted zirconia using 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 ($p>0.05$).(Intenal Bisco Data)

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 Clinicians 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 [24-28] (Figure 1)

Figure 1.



(Internal Bisco Data)

Creating Adhesion between Direct and Indirect Substrate 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, Bisco), primers specific to Zirconia/Metal (Z-PRIME PLUS, Bisco), and the use of dual-cure hydrophobic resin cements (DuoLink, Bisco).

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 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 defines cements chemistry and has been shown to significantly affect bond strengths. (Table 2).

Table 2, Shear Bond Strength (MPa) of Resin Cements to Zirconia (Internal Bisco Data)

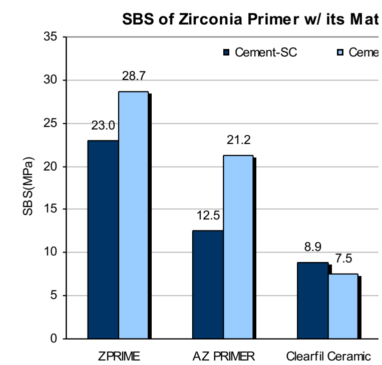
Zirconia Bonding Systems	Light-Cured Cement		Self-Cured Cement	
	Initial* 37°C/2 hours	Aging* 100°C/3 days	Initial* 37°C/2 hours	Aging* 100°C/3 days
AZ Primer/ResiCem	21.2 (8.3) [1, a]	17.7 (5.5) [1, b]	12.5 (5.9) [1, b]	5.8 (1.9) [2, b]
Clearfil Ceramic Primer/ Panavia F2.0	7.5 (4.5) [1, b]	3.2 (2.2) [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]

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 six minutes allows for interproximal flossing, whereas one that 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 3)

Figure 3. Comparison of shear bond strength using corresponding brands (Z-Prime+/DuoLink, AZ Primer/ResiCem, Clearfil Ceramic Primer/Panavia F2.0, Monobond Plus/Multilink Automix, Metal Zr Primer/Multilink Automix).(Internal Bisco Data)

Internal testing at Bisco has shown ***Z-PRIME PLUS*** (*Bisco Dental Products*) to significantly improve the Self-Cure efficiencies of competitive brands of resin cements. It is theorized the Proprietary combination of Monomers addresses acidity issues inherent within many formulas.



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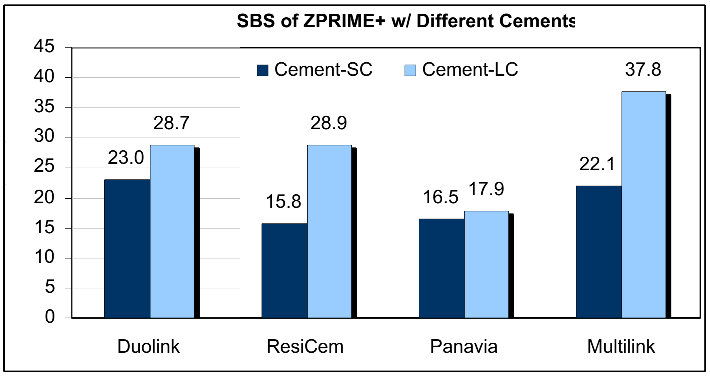

Figure 4, Shear bond strength of ZPRIME+ (Bisco) with Different. (Internal Bisco Data)

Case Presentation

Introduction

The patient, a 58 year old woman breast cancer survivor of 5+ years, is a long time patient in this practice and now healthy. She had a retained deciduous tooth “h” with a mesio-angular impacted #11 extending under teeth #9 through #12.(Fig 1) and was concerned about the darkening of this Cuspid in addition to conservative enhancement of her smile (Fig 2). A comprehensive list of treatment options were discussed including orthodontic repositioning. The accepted plan was for extraction of “h”, a zirconia framework/porcelain bridge replacing #11, composite to correct the facial incisal of #9, and composite on #6 to restore the cusp tip and to provide cuspid disclusion in excursive movements.

Figure 1. Lateral view of graying deciduous cuspid

Figure 2. Maxillary Anterior pre-treatment display

Figure 6, Pep Gen granular and Flow graft materials were placed and a collagen membrane sutured in place for stabilization.

Preparation and Design

The lab prescription was for a zirconia framework bridge with add-on porcelain over an ovate pontic design. Zirconia has been widely used the last few years as a bridge framework because of its non-metalic color, fracture resistance with flexural tests over 1000MPa, and excellent long term clinical success. A major disadvantage of its use was the inability to 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. ZPRIME PLUS is one of those special primers that has been shown to significantly increase bond strengths to Zirconia allowing for more conservative removal of tooth tissue.

Figure 7. Conservative preparation designs with minimal reduction, rounded shoulders and seating grooves parallel in nature.

Figure 10. Zirconia Framework overlayed with Ceram Porcelain

Figure 11. Our Reputation is built on Adhesion

Figure 12. 10 second application of ZPRIME PLUS followed by air drying.

Treatment Completion

Following verification of fit, the bridge was cleaned in an ethyl alcohol ultrasonic bath for 10 minutes. 2 drops of zirconia primer (Z-Prime, Bisco) was placed on the internal surface of the porcelain abutments and dried after 10 seconds.

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) followed by disinfecting/rewetting with Cavity Cleanser CHX and application of All Bond 3 primer/resin (Bisco). Duo-Link dual-cure resin cement (Bisco) was placed directly on the teeth and the bridge was positioned with moderate digital pressure. Clean up was initially accomplished using a microbrush and 2X2 cotton gauze. Margins were initially light cured followed by allowing the dual cure 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 #6 and #9 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), etched 20 seconds with 37% phosphoric acid (UNI-ETCH BAC, Bisco), rinsed, and several coats of bonding agent (All Bond 3, Bisco) were applied. Various layers of dentin, enamel, and incisal opacities of composite (Renamel, Cosmedent) were applied with Creative Color (Cosmedent) stain.

The lingual and bulk of the tip on #6 was completed using Renamel Universal Microhybrid for strength, tinted with gray and honey yellow Creative Color, and covered facially with Incisal Medium Microfill for polishability. Occlusion was checked and cuspid disclusion on #6 was confirmed. Polishing was completed with FlexiDisk rubber polishers (Cosmedent). #9 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 2mm hard/soft nocturnal bruxism splint was made (Erkodent, Glidewell labs) and the patient encouraged to wear it nightly to prevent parafunctional forces particularly under times of stress.

Figure 14. Renamel Microfill/ Flexi-Disk polishing system (Cosmedent)

Figure 18. A smile to be proud of

Conclusion

Patients demand esthetics. The incorporation of Zirconia in clinical dentistry offers a new alternative to metal-free Aesthetic Dentistry New aesthetic restorative materials demand adhesion. Re-creating 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, the use of Primers on the Indirect Substrate in conjunction with quality resin-based cements is crucial in optimizing clinical outcomes to these new Restorative Materials.

Disclosure:

Dr. Byoung Suh founder of Bisco Dental
Dr. Liang Chen, Senior Researcher Bisco Dental
Dr. Douglas Brown, Senior Manager Clinical Affairs Bisco Dental

Dr. Jack Griffin Jr., Private Practice Eureka, MO. Dr. Griffin 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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