©Operative Dentistry, 2013, **38-2**, 168-176

Effect of Artificial Aging and Surface Treatment on Bond Strengths to Dental Zirconia

J Perdigão • SD Fernandes • AM Pinto
FA Oliveira

Clinical Relevance

In case the veneering ceramic of a zirconia-based restoration fractures in the mouth to expose the zirconia coping, a phosphate/carboxylate monomer–based primer may be a good adhesion enhancer to repair the fracture.

SUMMARY

The objective of this project was to study the influence of artificial aging and surface treatment on the microtensile bond strengths (µTBS) between zirconia and a phosphate monomer–based self-adhesive cement. Thirty zirconia disks (IPS e.max ZirCAD, Ivoclar Vivadent) were randomly assigned to two aging regimens: AR, used as received, which served as a control, and AG, artificial aging to simulate low-temperature degradation. Subsequently, the disks of each aging regimen were assigned to three surface treatments: NT, no surface treatment; CO, surface silicatization with CoJet sand (3M ESPE); and ZP, zirconia surface treated with Z-Prime Plus (Bisco Inc). Thirty discs were made of Filtek Z250 (3M ESPE) composite resin and luted to the zirconia discs using RelyX Unicem (3M ESPE). The specimens were sectioned with a diamond blade in X and Y directions to obtain bonded beams with a cross-section of 1.0 ± 0.2 mm. The beams were tested in tensile mode in a universal testing machine at a speed of 0.5 mm/min to measure µTBS. Selected beams were selected for fractographic analysis under the SEM. Statistical analysis was carried out with two-way analysis of variance and Dunnett T3 post hoc test at a significance level of 95%. The mean µTBS for the three AR subgroups (AR-NT, AR-CO, and AR-ZP) were significantly higher than those of the corresponding AG groups ($p<0.0001$). Both AR-CO and AR-ZP

---

*Jorge Perdigão, DMD, MS, PhD, University of Minnesota, Department of Restorative Sciences, Minneapolis, MN, USA

Sara D. Fernandes, DMD, Center for Interdisciplinary Research (CiiEM), Egas Moniz Institute for Health Sciences, Monte da Caparica, Portugal

Ana M. Pinto, DMD, MS, Center for Interdisciplinary Research (CiiEM), Egas Moniz Institute for Health Sciences, Monte da Caparica, Portugal

Filipe A. Oliveira, PhD, University of Aveiro, Department of Ceramic and Glass Engineering, Campus Universitário de Santiago, Aveiro, Portugal

*Correspondence: 515 SE Delaware St, 8-450 Moos Tower, Minneapolis, MN 55455, USA; e-mail: perdi001@umn.edu

DOI: 10.2341/11-489-L

resulted in statistically significant higher mean bond strengths than the group AR-NT ($p<0.006$ and $p<0.0001$, respectively). Both AG-CO and AG-ZP resulted in statistically significant higher mean bond strengths than the group AG-NT (both at $p<0.0001$). Overall, AG decreased mean μTBS. Under the SEM, mixed failures showed residual cement attached to the zirconia side of the beams. CO resulted in a characteristic roughness of the zirconia surface. AR-ZP was the only group for which the amount of residual cement occupied at least 50% of the interface in mixed failures.

INTRODUCTION

Zirconia is a high-strength and flaw-tolerant material[1,2] that has shown potential as a biomaterial in orthopedics and dentistry.[3] The high strength of zirconia is derived from a stress-induced transformation from the metastable tetragonal form to the stable monoclinic form ($t \rightarrow m$).[2,4] This transformation enhances the mechanical properties of zirconia through an increase in crack resistance during the course of crack propagation, as a result of compressive stresses that form in the vicinity of the crack.[4,5]

Tetragonal zirconia stabilized with 3mol% yttria (or 3Y-TZP) is the material currently used in dentistry. Several commercial 3Y-TZP dental materials are available, including Cercon (Dentsply Prosthetics, York, PA, USA), IPS e.max ZirCAD (Ivoclar Vivadent, Principality of Liechtenstein), and Lava (3M ESPE, St Paul, MN, USA). The advent of CAD/CAM technology has given clinicians the opportunity to prescribe complex but precise 3Y-TZP–based restorations.[6,7]

Acid-resistant ceramics (such as alumina- and zirconia-based) are not etchable with hydrofluoric acid because they lack a vitreous phase. In lieu of etching, clinicians have used airborne particle abrasion to create micro-retentive features for the luting agent.[8,9] Chairside air abrasion with 30-μm silica-coated aluminum particles (tribochemical silica coating, also known as *silicatization*) has been recommended to create surface irregularities on acid-resistant ceramics.[9–11] The rationale behind silica coating is to embed the ceramic surface with silica particles,[12] which are chemically more reactive to the resin via priming agents.[13]

Several recent resin cements, known as self-adhesive cements, contain phosphorylated methacrylate monomers. These materials may interact chemically with the zirconia surface. With two phosphate groups and at least two double-bonded carbon atoms, self-adhesive cements are expected to bond to zirconia similarly to other phosphate-based adhesive materials.[14] In addition, new phosphate monomer–based primers are now available to promote chemical adhesion between resin materials and hydroxyl groups present on the zirconia surface.[15–17] One of these phosphate-based materials, Z-Prime Plus (Bisco Inc, Schaumburg, IL, USA), is a primer that includes a mixture of phosphate and carboxylate monomers to enhance the bonding to zirconia and metals, according to the respective manufacturer. This primer has been shown to enhance the adhesion of conventional and self-adhesive resin cements to air-abraded zirconia.[18]

Aging occurs experimentally in zirconia, mostly in humid atmosphere or in water.[19,20] The lack of long-term stability has been a major issue for medical use and has led to the replacement of several zirconia femoral heads in orthopedic patients.[21] Low-temperature degradation (LTD) has been associated with several 3Y-TZP–based biomaterials[22] but is difficult to simulate in the laboratory. Consequently, a standard *in vitro* hydrothermal accelerated aging test using steam and pressure has been developed.[23] The ISO Standard 13356 recommends that "the Y-TZP specimens are placed in a suitable autoclave and exposed to steam at (134 ± 2)°C under a pressure of 0.2 MPa for a period of 5 h."[23]

In addition to studying adhesion to zirconia as received from the dental laboratory, it is therefore clinically relevant to study adhesion to aged zirconia, in case there is a need to repair the fractured restoration when the zirconia coping becomes exposed to the oral environment. In fact, clinical studies have reported an incidence of chipping of the zirconia veneering porcelain as high as 10%-15% at 3 years.[24,25] Veneering zirconia with glass-based ceramic reduces the fracture resistance of zirconia copings compared with those copings that are subjected only to cyclic loading.[26] The reduction in fracture resistance associated with the hydrothermal degradation of 3Y-TZP[22] may be responsible, at least partially, for the clinical failures associated with chipping of the veneering ceramic.

The null hypotheses to test in this study were 1) artificial aging of zirconia does not result in a reduction of microtensile bond strengths (μTBS) of a phosphate-based self-adhesive resin cement, and 2) zirconia surface treatment with silicatization or with a specific primer does not increase μTBS of a phosphate-based self-adhesive resin cement.

METHODS AND MATERIALS

Thirty IPS e.max ZirCAD (IPS, Ivoclar Vivadent) discs (d=13.0 mm; h=3.0) were prepared from CAD-CAM blocks and sintered following the manufacturer's instructions (Table 1). All disks were cleaned ultrasonically in distilled water for five minutes prior to use in this project.[14] The disks were randomly and equally assigned to two aging regimens: 1) AR, as received (control), and 2) AG, artificial aging to simulate LTD: disks were immersed in distilled water in an autoclave (SANOclav Las-3-13-MCS-J, Adolf Wolf SANOclav, Hausen, Germany) for five hours at a temperature of 134°C under a pressure of 0.2 bar, following ISO recommendations.[23]

Disks were further randomly assigned to one of three surface treatments: 1) NT, no treatment; 2) CO, silicatization with CoJet sand (3M ESPE) for 20 seconds, under a pressure of 2.5 bar, from a distance of 7 mm,[27] with a tip inclination of 45°; and 3) ZP, two coats of Z-Prime Plus (Bisco Inc) were applied with a microbrush (Microbrush International, Grafton, WI, USA) to uniformly wet the zirconia surface, followed by drying with air for three to five seconds.[28]

Thirty composite resin disks (d=13.0 mm; h=3.0) were made of Filtek Z250 shade A2 (3M ESPE) in a silicone mold. The composite was polymerized with an Elipar S10 curing light (3M ESPE) in four areas for 60 seconds each to include the entire disk surface. RelyX Unicem Aplicaps (3M ESPE) shade A2 was activated, mixed for 15 seconds, and applied on the irradiated surface of the composite disc, which was seated on top of the zirconia disc. This bonded setup was loaded with 50N for 60 seconds,[14] excess cement was wiped off, and the specimen was light polymerized from the composite side with the same curing unit at four different locations for 60 seconds each.

Bonded specimens were sectioned in X and Y directions with a 0.5-mm-thick diamond disk (Cafro SRL, Fino Mornasco, Como, Italy) in a Secotom-10 apparatus (Struers A/S, Ballerup, Denmark) to obtain approximately 20 beams per bonded disk, with a cross section of 1.0 ± 0.2 mm^2.

After 24 hours in distilled water at 37°C,[14] each beam was individually attached to a stainless-steel jig using cyanoacrylate glue (Zapit, Dental Ventures of America, Corona, CA, USA). The zirconia-resin μTBS were measured in MPa by applying a tensile load to the bonded interface using a universal testing machine (Shimadzu Autograph AG-IS, Tokyo, Japan) at a crosshead speed of 0.5 mm/min. A digital caliper (Mitutoyo Corp, Kanagawa, Japan) with an accuracy of 0.001 mm was used to measure the sides of the bonding interface and calculate the bonding area in millimeters squared. The load at fracture and the bonding surface area of the specimen were registered and μTBS calculated in MPa. Pretesting failures (PTFs), which corresponded to spontaneous debonding that occurred prior to testing, were computed as zero MPa.[29–31] The fractures were analyzed under a stereo microscope (Leica MZ6,

Table 1: *Composition of Materials Used in This Study (Batch Numbers in Parentheses)*

Material	Manufacturer	Batch Number	Composition
IPS e.max ZirCAD[a]	Ivoclar Vivadent	(M40290)	ZrO_2 (87.0–95.0wt%), Y_2O_3 (4.0–6.0wt%), HfO_2 (1.0–5.0wt%), Al_2O_3 (0.1-1.0wt%), Other oxides (<0.2wt%)
CoJet Sand	3M ESPE	(433711)	Aluminum oxide, amorphous silica
Z-Prime Plus	Bisco Inc	(1000003112)	Organophosphate monomer (MDP), carboxylic acid monomer (BPDM); HEMA, ethanol
RelyX Unicem Aplicap	3M ESPE	(435042), (431825)	Powder: glass powder, silica, calcium hydroxide, pigment, substituted pyrimidine, peroxy compound, initiator; liquid: methacrylated phosphoric ester, dimethacrylate, acetate, stabilizer, initiator
Filtek Z250	3M ESPE	(N234284)	BisEMA, BisGMA, TEGDMA, UDMA, zirconium, silica, pigments, camphorquinone

Abbreviations: bis-GMA, bisphenol A diglycidyl methacrylate; BisEMA-(6), bisphenol A polyetheylene glycol diether dimethacrylate; BPDM, biphenyl dimethacrylate; HEMA, 2-hydroxyethyl methacrylate; TEGDMA, triethyleneglycol-dimethacrylate; UDMA, urethane dimethacrylate.
[a] *Sintering temperature is 1500°C in a program of eight hours divided in three cycles: (1) 90 minutes, (2) two hours 45 minutes, (3) three hours 30 min.*

Leica Microsystems AG, Heerbrugg, Switzerland) at 20×. The mode of failure was classified as adhesive, mixed, and cohesive. Failures were considered adhesive if they occurred at the zirconia-cement interface, which included PTFs; of mixed nature if there was residual cement at the zirconia side of the interface; and of cohesive nature if the fracture occurred solely in composite resin.

Data were submitted to two-way analysis of variance (ANOVA). As Levene's statistics showed that there was an inhomogeneity of variances ($p>0.05$), the Dunnett T3 pairwise comparison test was used for the μTBS data ($p<0.05$). Failure modes were analyzed with chi-square followed by Cramer's V. The software PASW Statistics 18.0 (SPSS Inc, Chicago, IL, USA) was used for the analyses.

SEM Analysis

Randomly selected fractured beams (six for each experimental condition) were mounted on Al stubs (Ted Pella Inc, Redding, CA, USA) with carbon adhesive tape and colloidal silver paint (Ted Pella Inc). Then, specimens were sputter coated with gold-palladium by means of an E-5100 sputter coater (Polaron Ltd, Watford, UK) at 20 mA for 45 seconds and observed under an S-4700 FESEM (Hitachi High Technologies America Inc, Pleasanton, CA, USA) at an accelerating voltage of 5.0 kV and working distance of 11.8-12.2 mm.

RESULTS

Means, standard deviations, number of beams per group, and number of PTFs are displayed in Table 2. Two-way ANOVA found significant differences for both factors "aging" and "surface treatment" (both at $p<0.0001$). There were no significant interactions between these variables ($p>0.097$).

The highest mean μTBS was obtained with group AR-ZP (17.4 MPa), which was statistically higher than any other mean μTBS. The lowest mean μTBS was obtained with group AG-NT (0.7 MPa), which also resulted in the highest number of PTFs (91.9% of the beams). AG-CO was the only other group that had PTFs (36.8% of the beams).

The three groups for which zirconia was used as received (AR) resulted in statistically higher mean μTBS than the corresponding AG groups (AR-NT > AG-NT; AR-CO > AG-CO; AR-ZP > AG-ZP).

Table 3 displays the statistical significance for each pair of means. For the AR groups, AR-NT resulted in statistically lower mean μTBS than either AR-CO or AR-ZP ($p<0.006$ and $p<0.0001$, respectively). The means for AR-CO were statistically lower than those of AR-ZP at $p<0.022$. For the AG groups, mean μTBS for AG-NT were statistically lower than those of either AG-CO or AG-ZP ($p<0.0001$). The mean μTBS for AG-CO were statistically lower than those for AG-ZP at $p<0.009$.

Most failures were of adhesive nature (Table 4). There was a statistical difference for failure modes among groups ($p<0.0001$, Cramer's V). Overall, AR specimens had a statistically lower number of adhesive failures (and greater number of mixed failures) than AG specimens.

SEM Analysis

Adhesive failures displayed residual scratches from the zirconia manufacturing finishing procedures

Table 2: *Means ± SD, Number of Bonded Beams, and PTFs*

	Surface Treatment	**Mean ± SD** (MPa)	**Number of Beams**	**PTFs (%)**
As received (AR), n=15	No treatment	9.2 ± 4.7	99	0
	CoJet	13.1 ± 7.2	96	0
	Z-Prime Plus	17.4 ± 8.8	112	0
Aged (AG), n=15	No treatment	0.7 ± 2.7	99	91.9
	CoJet	7.7 ± 7.8	114	36.8
	Z-Prime Plus	11.0 ± 5.8	101	0

Abbreviation: PTFs, pretesting failures.

Table 3: *Statistical Significance Between Pairs of Microtensile Bond Strengths Means*

	AR-NT	AR-CO	AR-ZP	AG-NT	AG-CO	AG-ZP
AR-NT		0.006	**0.0001**	**0.001**	0.836	0.325
AR-CO	**0.006**		**0.022**	**0.0001**	**0.0001**	0.601
AR-ZP	**0.0001**	**0.022**		**0.0001**	**0.0001**	**0.0001**
AG-NT	**0.0001**	**0.0001**	**0.0001**		**0.0001**	**0.0001**
AG-CO	0.836	**0.0001**	**0.0001**	**0.0001**		**0.009**
AG-ZP	0.325	0.601	**0.0001**	**0.0001**	**0.009**	

The p-values in bold denote a statistical significant difference between the respective pair of means.

(Figure 1). Mixed failures showed residual cement attached to the zirconia side of the beams (Figure 2a). CO resulted in a characteristic roughness of the zirconia surface (Figure 2b). AR-ZP was the only group for which the amount of residual cement occupied at least 50% of the interface in mixed failures (Figure 3a). For the same group AR-ZP, areas of the zirconia side of the interface displayed 3- to 5-μm-long neddle-like crystals (Figure 3b). For AG-NT specimens, there were no specific morphologic features. AG-CO specimens displayed a similar surface roughness compared with their AR counterparts with areas showing the zirconia crystals intermingled with others without signs of surface abrasion (Figure 4). Mixed failures in the AG-ZP group displayed a minimal amount of residual cement at the interface compared with AR-ZP (Figure 5).

DISCUSSION

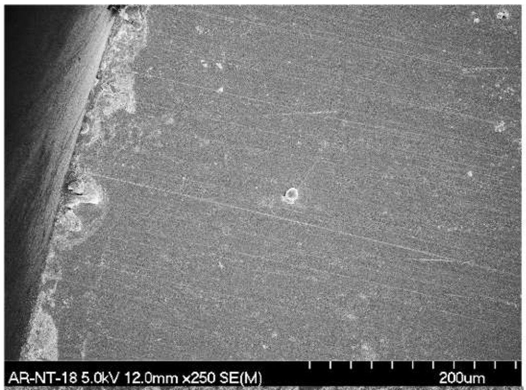
The use of toughened ceramics such as 3Y-TZP has enabled the use of all-ceramic restorations in posterior regions where high-strength structures are required. Ceramic materials applied in dentistry may exhibit significant subcritical crack growth due to thermal fatigue and the aqueous environment during mastication.[32]

Veneering of the zirconia coping is usually carried out at a relatively high temperature (750–900°C). During this process, the zirconia frameworks are exposed to moisture from the veneering porcelain. The firing process is repeated two to five times.[3] Residual stresses accumulate each time the zirconia is fired at high temperatures followed by cooling to ambient temperature during the laboratory process of making crowns and bridges.[33] A study evaluated the fracture resistance of 3Y-TZP bridge frameworks after mechanical fatigue, heat treatment similar to that used during veneering of the zirconia or after veneering.[26] Multiple firings may affect the resistance of the framework to fracture and the adhesion of the veneering porcelain to the zirconia coping.[26]

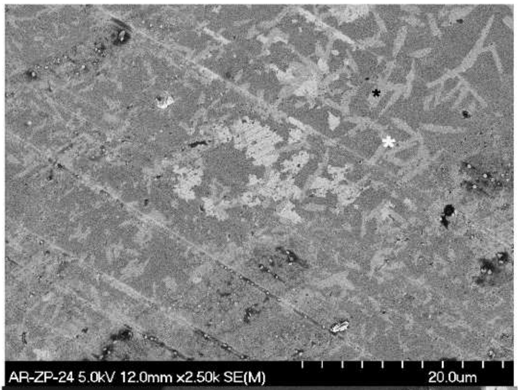
In addition to this reduction in physical properties from firing, zirconia undergoes a slow transformation process under a humid environment (known as LTD) from the tetragonal phase to the monoclinic phase.[34,35] The fracture of the veneering ceramic

Table 4: *Type of Fractures per Group (%)*

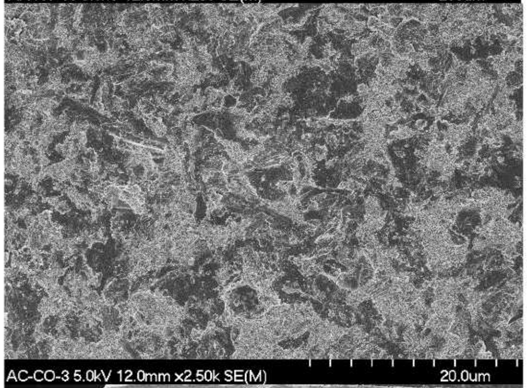
	AR-NT	AR-CO	AR-ZP	AG-NT	AG-CO	AG-ZP
Adhesive	69.7	68.8	70.4	99.0	80.7	89.1
Cohesive	0	0	0	0	0	0
Mixed	30.3	31.2	29.6	1.0	19.3	10.9



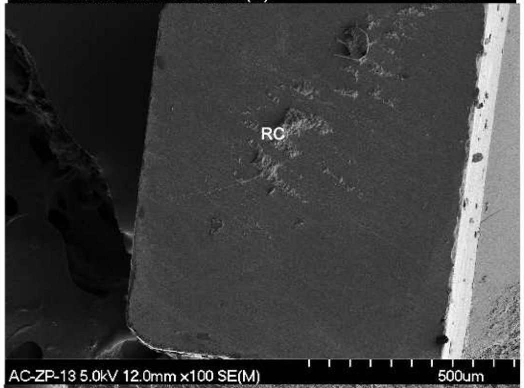
1



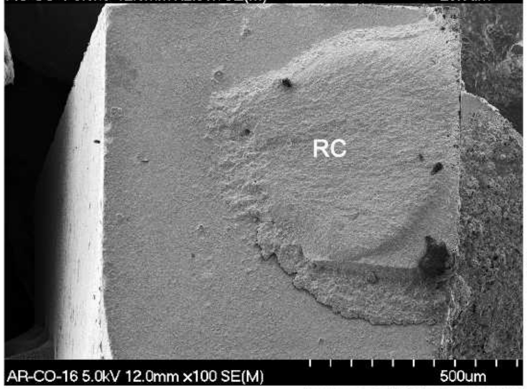
2 a



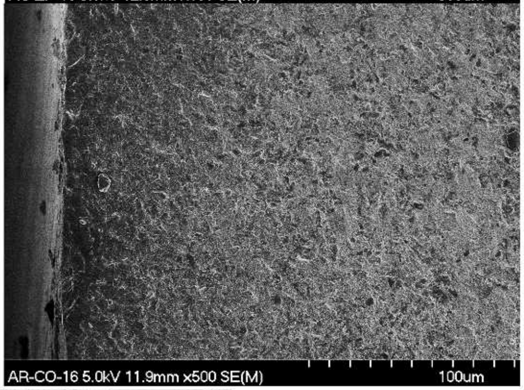
2 b



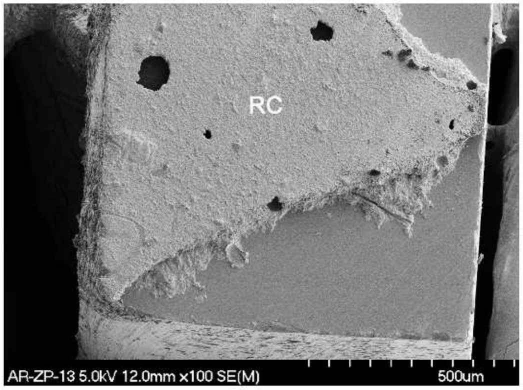
3 a



3 b



4



5

Figure 1. *Adhesive failure (zirconia side) of AR-NT specimen. Original magnification = 250×.* Figure 2. *(a): Mixed failure (zirconia side) of AR-CO specimen. RC, resin cement. Original magnification = 100×. (b): Higher magnification of the same specimen showing the zirconia surface roughness as a result of CO abrasion. Original magnification = 500×.* Figure 3. *(a): Mixed failure (zirconia side) of AR-ZP specimen. RC, resin cement. Original magnification = 100×. (b): Higher magnification of the same specimen showing needle-like deposits (asterisks) on the zirconia surface. Original magnification = 2500×.* Figure 4. *Morphological characteristics of the effect of CO on AG zirconia. Original magnification = 2500×.* Figure 5. *Mixed failure (zirconia side) of AG-ZP specimen showing small islands of resin cement (RC). Original magnification = 100×.*

may expose the core framework to the aqueous environment of the mouth. The long-term lifetime of zirconia-based bridges is then governed by the water-assisted subcritical crack growth behavior of the framework material.[31]

The phosphate groups make self-adhesive cements acidic immediately upon mixing. RelyX Unicem (3M ESPE) reaches a pH close to neutrality after mixing.[36] Some authors have reported that RelyX Unicem has the ability to bond to zirconia, regardless of the zirconia surface treatment (no treatment, sandblasting with Al_2O_3 particles, or silicatization).[37] Other studies have shown that phosphate monomer–based resins bond better to zirconia than resins without these monomers.[38] We used only one resin cement in our study; therefore, it is not possible to generalize to other materials. In agreement with previous studies,[14,37] the resin cement used in our study has the ability to interact with zirconia without the need for additional surface treatment, as observed in the AR-NT subgroup (9.2 ± 4.7 MPa). However, this likely chemical interaction was lost when RelyX Unicem was applied on aged (AG) zirconia, for which the majority of the bonds failed spontaneously (0.7 ± 2.7 MPa, 91.9% PTFs). The use of CO improved the bonding ability of RelyX Unicem to AG zirconia (7.7 ± 7.8 MPa), but the number of spontaneous PTFs was still relatively high (36.8%). Although ZP was able to restore the bonding ability to the AG zirconia substrate, the bond strengths obtained for AG-ZP (11.0 ± 5.8 MPa) were only 62.5% of those measured when ZP was applied to AR zirconia (17.4 ± 8.8 MPa). In addition, mixed failures for AR-ZP specimens under the SEM displayed wider areas of residual fractured cement compared to AG-ZP specimens. This decrease in bond strengths and the different fracture pattern highlight the negative effects of artificial aging (LTD) on the bond strength of the self-adhesive cement to zirconia. The lower bond strengths to AG zirconia may have been a result of the structural changes induced by artificial aging or simulated LTD on the zirconia surface. When 3Y-TZP disks were implanted in a denture and worn for 24 hours/day for one year, the material underwent a degradation process in which the increase in the percentage of monoclinic phase was similar to that of zirconia aged in an autoclave at 134°C for six hours.[39] Aging through LTD has been reported to activate the transformation from the tetragonal to the monoclinic phase ($t \rightarrow m$), which is always accompanied by a slight volume change inducing stresses leading to microfissures on the zirconia surface.[35] This phenomenon may have clinical relevancy in case a zirconia-based restoration fractures in the mouth and needs to be repaired.

Other studies have investigated the influence of hydrothermal aging, thermocycling, and mechanical fatigue on bond strengths to zirconia.[40,41] In general, thermal and mechanical fatigue result in a reduction in bond strengths, which is in agreement with our study. Chevalier and others[35] observed nucleation sites in zirconia crystals with formation of nanofissures after the material had been submitted to an aging regimen similar to that used in our study.

Surface abrasion with a tribochemical silica-coated alumina (silicatization) has been shown to be an effective treatment method for zirconia by physically roughening the surface while also leaving behind physically bound silica. Silica coating, therefore, combines micromechanical retention, produced by airborne-particle abrasion, with chemical bonding, and the process is well documented.[40,42,43] However, the silica content on the Y-TZP surface after silica coating is too low for effective silanization.[17] In addition, one of the problems associated with the use of an air brasion method on zirconia has to do with the possibility of air brasion inducing the $t \rightarrow m$ transformation.[44] The presence of the monoclinic phase on the zirconia surface may result in surface alterations that compromise the establishment and durability of reliable micromechanical adhesion.

Piascik and others[45] obtained a mean μTBS of 18.6 MPa to silica-coated zirconia. In our study, the corresponding condition would be the subgoup AR-CO, for which we obtained a mean of 13.1 MPa. The difference may reside in the size of the microtensile specimens. While the cross section of our specimens was approximately 1.0 mm^2, those of Piascik and others were 1.5 mm × 1.5 mm.Z-Prime Plus includes both phosphate monomers and carboxylate monomers. Organophosphate monomers resemble silanes because their methacrylate groups can copolymerize with monomers in the resin cement.[17] Phosphate radicals may bond to metal oxides such as zirconia.[18] In the case of ZP, the carboxylate groups may also enhance the bonding ability of this primer to zirconia.[18] In our study, ZP improved mean μTBS significantly compared with those to NT and CO zirconia surfaces for each of the two aging regimens. Although studies have reported that primers containing phosphorylated monomers improve bonding to zirconia,[15–17] ZP, in the present study, may have also acted as a wetting agent for the resin cement, which would have promoted adhesion as reported for other phosphate monomers applied to alumina.[46] The resistance of this possible chemical bonding to hydrolysis and thermal fatigue in the mouth has not been established.[47]

The present study has several limitations, including the absence of mechanical fatigue to simulate clinically relevant loads. Furthermore, we used only one resin cement for two reasons. First, this specific self-adhesive resin cement has been shown to bond better to zirconia than a conventional dual-cured resin cement.[48,49] Second, our experimental hypotheses were not related to the type of resin cement used but to the effect of artificial aging and surface treatment of zirconia.

The results of the present study suggest that new developments in bonding to zirconia may depend on research on new surface treatments that establish chemical interaction with both luting cements and zirconia surfaces. Further studies must test luting agents and primers that include phosphate monomers and silanes in the same solution.

CONCLUSION

Within the limitations of this study, in which zirconia was not veneered with glass-based ceramic as in clinical situations, we have to reject both null hypotheses, as 1) artificial aging of zirconia resulted in a reduction of microtensile bond strengths and 2) zirconia surface treatment with silicatization and with Z-Prime Plus increased μTBS of a phosphate-based self-adhesive resin cement to zirconia.

Conflict of Interest

The authors of this article certify that they have no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company that is presented in this article.

Acknowledgements

Special thanks to 3M ESPE, Bisco Inc, and Ivoclar Vivadent for providing the materials used in this project.

(Accepted 27 April 2012)

REFERENCES

1. Garvie RC, Hannink RH, & Pascoe RT (1975) Ceramic steel? *Nature* **258(25)** 703-704.
2. Heuer AH (1987) Transformation toughening in ZrO_2-containing ceramics *Journal of the American Ceramic Society* **70(10)** 689-698.
3. Chevalier J, & Gremillard L (2009) Ceramics for medical applications: a picture for the next 20 years *Journal of the European Ceramic Society* **29(7)** 1245-1255.
4. Hannink RHJ, Kelly PM, & Muddle BC (2000) Transformation toughening in zirconia-containing ceramics *Journal of the American Ceramic Society* **83(3)** 461-487.
5. Piconi C, Maccauro G, Muratori E, & Brach del Prever E (2003) Alumina and zirconia ceramics in joint replacements *Journal of Applied Biomaterials and Biomechanics* **1(1)** 19-32.
6. Rekow ED (2006) Dental CAD/CAM systems: a 20-year success story *Journal of the American Dental Association* **137(Supplement)** 5S-6S.
7. Aboushelib MN, de Jager N, Kleverlaan CJ, & Feilzer AJ (2005) Microtensile bond strength of different components of core veneered all-ceramic restorations *Dental Materials,* **21(10)** 984-991.
8. Awliya W, Odén A, Yaman P, Dennison JB, & Razzoog ME (1998) Shear bond strength of resin cement to densely sintered high-purity alumina with various surface conditions *Acta Odontologica Scandinavica* **56(1)** 9-13.
9. Dérand P, & Dérand T (2000) Bond strength of luting cements to zirconium oxide ceramics *International Journal of Prosthodontics* **13(2)** 131-135.
10. Özcan M, Alkumru H, & Gemalmaz D (2001) The effect of surface treatment on the shear bond strength of luting cement to a glass-infiltrated alumina ceramic *International Journal of Prosthodontics* **14(4)** 335-339.
11. Bottino MA, Valandro LF, Scotti R, & Buso L (2005) Effect of surface treatments on the resin bond to zirconium-based ceramic *International Journal of Prosthodontics* **18(1)** 60-65.
12. Sun R, Suansuwan N, Kilpaltrick N, & Swain M (2000) Characterisation of tribochemical assisted bonding of composite resin to porcelain and metal *Journal of Dentistry* **28(6)** 441-445.
13. Özcan M, & Vallittu PK (2003) Effect of surface conditioning methods on the bond strength of luting cement to ceramics *Dental Materials* **19(8)** 725-731.
14. Mirmohammadi H, Aboushelib MNM, Salameh Z, Feilzer AJ, & Kleverlaan CJ (2010) Innovations in bonding to zirconia based ceramics: part III. Phosphate monomer resin cements *Dental Materials* **26(8)** 786-792.
15. Yoshida K, Tsuo Y, & Atsuta M (2006) Bonding of dual-cured resin cement to zirconia ceramic using phosphate acid ester monomer and zirconate coupler *Journal of Biomedical Materials Research Part B: Applied Biomaterials* **77(1)** 28-33.
16. Yang B, Barloi A, & Kern M (2010) Influence of air-abrasion on zirconia ceramic bonding using an adhesive composite resin *Dental Materials* **26(1)** 44-50.
17. Matinlinna JP, Heikkinen T, Özcan M, Lassila LV, & Vallittu P (2006) Evaluation of resin adhesion to zirconia ceramic using some organosilanes *Dental Materials* **22(9)** 824-831.
18. Magne P, Paranhos MPG, & Burnett LH Jr (2010) New zirconia primer improves bond strength of resin-based cements *Dental Materials* **26(4)** 345-352.
19. Yoshimura M, Noma T, Kawabata K, & Sōmiya S (1987) Role of H_2O on the degradation process of Y-TZP *Journal of Materials Science Letters* **6(4)** 465-467.
20. Chevalier J, Gremillard L, & Deville S (2007) Low-temperature degradation of zirconia and implications for

biomedical implants *Annual Review of Materials Research* **37(1)** 1-32.

21. Fernandez-Fairen M, Blanco A, Murcia A, Sevilla P, & and Gil FJ (2007) Aging of retrieved zirconia femoral heads *Clinical Orthopaedics and Related Research* **462(1)** 122-129.
22. Guo X (2004) Property degradation of tetragonal zirconia induced by low-temperature defect reaction with water molecules *Chemistry of Materials* **16(21)** 3988-3994.
23. ISO-Standards (2008) ISO 13356 Implants for Surgery: Ceramic Materials Based on Yttria-Stabilized Tetragonal Zirconia (Y-TZP) Geneva: *International Organization for Standardization*
24. Vult Von Steyern P, Carlson P, & Nilner K (2005) All-ceramic fixed partial dentures designed according to the DC-Zirkon technique: a 2-year clinical study *Journal of Oral Rehabilitation* **32(3)** 180-187.
25. Sailer I, Fehér A, Filser F, Lüthy H, Gauckler LJ, Schärer P, & Hämmerle CHF (2006) Prospective clinical study of zirconia posterior fixed partial dentures: 3-year follow-up *Quintessence International* **37(9)** 685-693.
26. Sundh A, Molin M, & Sjögren G (2005) Fracture resistance of yttrium oxide partially-stabilized zirconia all-ceramic bridges after veneering and mechanical fatigue testing *Dental Materials* **21(5)** 476-482.
27. Scherrer SS, Cattani-Lorente M, Vittecoq E, Mestral F, Griggs JA, & Wiskott HWA (2011) Fatigue behavior in water of Y-TZP zirconia ceramics after abrasion with 30 μm silica-coated alumina particles *Dental Materials* **27(2)** e28-e42.
28. Z-Prime Plus Retrieved September 22, 2011 from: http://www.bisco.com/instructions/Z-PRIME%20Plus%20Technique.pdf
29. Pashley EL, Agee KA, Pashley DH, & Tay FR (2002) Effects of one versus two applications of an unfilled, all-in-one adhesive on dentine bonding *Journal of Dentistry* **30(2–3)** 83-90.
30. Ito S, Tay FR, Hashimoto M, Yoshiyama M, Saito T, Brackett WW, Waller JL, & Pashley DH (2005) Effects of multiple coatings of two all-in-one adhesives on dentin bonding *Journal of Adhesive Dentistry* **7(2)** 133-141.
31. Shiraia K, De Munck J, Yoshida Y, Inoue S, Lambrechts P, Suzuki K, Shintani H, & Van Meerbeek B (2005) Effect of cavity configuration and aging on the bonding effectiveness of six adhesives to dentin *Dental Materials* **21(2)** 110-124.
32. Studart AR, Filser F, Kocher P, Lüthy H, & Gauckler LJ (2007) Cyclic fatigue in water of veneer–framework composites for all-ceramic dental bridges *Dental Materials* **23(2)** 177-185.
33. Basu B (2005) Toughening of yttria-stabilised tetragonal zirconia ceramics *International Materials Reviews* **50(4)** 239-256.
34. Cales B, Stefani Y, & Lilley E (1994) Long term *in vivo* and *in vitro* aging of a zirconia ceramic used in orthopaedy *Journal of Biomedical Materials Research* **28(5)** 619-624.
35. Chevalier J, Cales B, & Drouin JM (1999) Low-temperature aging of Y-TZP ceramics *Journal of the American Ceramic Society* **82(8)** 2150-2154.
36. Saskalauskaite E, Tam LE, & McComb D (2008) Flexural strength, elastic modulus, and pH profile of self-etch resin luting cements *Journal of Prosthodontics* **17(4)** 262-268.
37. De Oyagüe RC, Monticelli F, Toledano M, Osorio E, Ferrari M, & Osorio R (2009) Influence of surface treatments and resin cement selection on bonding to densely-sintered zirconium-oxide ceramic *Dental Materials* **25(2)** 172-179.
38. Blatz MB, Sadan A, Martin J, & Lang B (2004) *In vitro* evaluation of shear bond strengths of resin to densely-sintered high-purity zirconium-oxide ceramic after long-term storage and thermal cycling *Journal of Prosthetic Dentistry* **91(4)** 356-362.
39. Kosmac T (2010) *In-vivo* ageing of zirconia ceramics: results after 12 months *Journal of Dental Research* **89(Special Issue B)** Abstract #3671 (www.dentalresearch.org).
40. Wegner SM, & Kern M (2000) Long-term bond strength to zirconia ceramic *Journal of Adhesive Dentistry* **2(2)** 139-147.
41. Aboushelib MN, Mirmohamadi H, Matinlinna JP, Kukk E, Ounsi H, & Salameh Z (2009) Innovations in bonding to zirconia-based materials. Part II: focusing on chemical interactions *Dental Materials* **25(8)** 989-993.
42. Wolfart M, Lehman F, Wolfart S, & Kern M (2007) Durability of the resin bond strength to zirconia ceramic after using different surface conditioning methods *Dental Materials* **23(1)** 45-50.
43. Valandro LF, Özcan M, Bottino MC, Bottino MA, Scotti R, & Bona AD (2006) Bond strength of a resin cement to high-alumina and zirconia-reinforced ceramics: the effect of surface conditioning *Journal of Adhesive Dentistry* **8(3)** 175-181.
44. Guazzato M, Quach L, Albakry M, & Swain MV (2005) Influence of surface and heat treatments on the flexural strength of Y-TZP dental ceramic *Journal of Dentistry* **33(1)** 9-18.
45. Piascik JR, Swift EJ, Thompson JY, Grego S, & Stoner BR (2009) Surface modification for enhanced silanation of zirconia ceramics *Dental Materials* **25(9)** 1116-1121.
46. Kern M, & Thompson VP (1995) Bonding to glass infiltrated alumina ceramic: adhesive methods and their durability *Journal of Prosthetic Dentistry* **73(3)** 240-249.
47. Aboushelib MN, Matinlinna JP, Salameh Z, & Ounsi H (2008) Innovations in bonding to zirconia-based materials: part I *Dental Materials* **24(9)** 1268-1272.
48. Nothdurft FP, Motter PJ, & Pospiech PR (2009) Effect of surface treatment on the initial bond strength of different luting cements to zirconium oxide ceramic *Clinical Oral Investigations* **13(2)** 229-235.
49. Miragaya L, Maia LC, Sabrosa CE, de Goes MF, & da Silva EM (2011) Evaluation of self-adhesive resin cement bond strength to yttria-stabilized zirconia ceramic (Y-TZP) using four surface treatments *Journal of Adhesive Dentistry* **13(5)** 473-480.