ACP AMERICAN COLLEGE OF PROSTHODONTISTS
Your smile. Our specialty.

Bond Strength of Resin Cements to Zirconia Ceramic Using Adhesive Primers

Ariovaldo Stefani, DDS, MSc,[1,2] Rui Barbosa Brito Jr, DDS, MSc, PhD,[1] Sidney Kina, DDS, MSc,[1] Oswaldo Scopin Andrade, DDS, MSc, PhD,[3] Gláucia Maria Bovi Ambrosano, MSc, PhD,[4] Andreia Assis Carvalho, DDS, MS,[5] & Marcelo Giannini, DDS, MS, PhD[6]

[1]Sao Leopoldo Mandic - School of Dentistry, Campinas, Brazil
[2]Private Practice, Sao Paolo, Brazil
[3]Graduation Center, National Service of Commercial Learning, Sao Paulo, Brazil
[4]Department of Social Dentistry/Statistics Piracicaba School of Dentistry, Campinas State University, Piracicaba, Brazil
[5]Department of Prevention and Oral Rehabilitation, Federal University of Goiás, Goiânia, Brazil
[6]Department of Restorative Dentistry, State University of Campinas, Piracicaba, Brazil

Keywords
Bond strength; resin cements; adhesive primers; zirconia ceramics.

Correspondence
Ariovaldo Stefani, Sao Leopoldo Mandic - School of Dentistry, Rua Dr. José Rocha Junqueira, 13 - Campinas - SP, Campinas, Sao Paulo 13045-755, Brazil.
E-mail: aristefani@uol.com.br

This study was performed in partial fulfillment of requirements for a master's degree.

Previously presented at the 90th IADR Annual Session - Iguaçu Falls - Brazil – 2012.

Funded by grants from CAPES *(No.* 3110/2010 and *No.* 840/2010*) and* CNPq *(No.* 305777/2010-6*), Brazil.*

The authors have no conflicts of interest to report.

Accepted February 2, 2015

doi: 10.1111/jopr.12334

Abstract

Purpose: To evaluate the influence of adhesive primers on the microshear bond strength of resin cements to zirconia ceramic.
Materials and Methods: Fifty zirconia plates (12 mm × 5 mm × 1.5 mm thick) of a commercially available zirconium oxide ceramic (ZirCad) were sintered, sandblasted with aluminum oxide particles, and cleaned ultrasonically before bonding. The plates were randomly divided into five groups of 10. Three resin cements were selected (RelyX ARC, Multilink Automix, Clearfil SA Cement self-adhesive resin cement), along with two primers (Metal-Zirconia Primer, Alloy Primer) and one control group. The primers and resin cements were used according to manufacturers' recommendations. The control group comprised the conventional resin cement (RelyX ARC) without adhesive primer. Test cylinders (0.75 mm diameter × 1 mm high) were formed on zirconia surfaces by filling cylindrical Tygon tube molds with resin cement. The specimens were stored in distilled water for 24 hours at 37°C, then tested for shear strength on a Shimadzu EZ Test testing machine at 0.5 mm/min. Bond strength data were analyzed statistically by two-way ANOVA and Dunnett's test (5%).
Results: The bond strength means in MPa (± s.d.) were: RelyX ARC: 28.1 (6.6); Multilink Automix: 37.6 (4.5); Multilink Automix + Metal-Zirconia Primer: 55.7 (4.0); Clearfil SA Cement: 46.2 (3.3); and Clearfil SA Cement + Alloy Primer: 47.0 (4.1).
Conclusion: Metal-Zirconia Primer increased the bond strength of Multilink Automix resin cement to zirconia, but no effect was observed for Alloy Primer using Clearfil SA Cement. RelyX ARC showed the lowest bond strength to zirconia.

The esthetic and mechanical properties of all-ceramic, metal-free, indirect restorations have shown significant improvement. Ceramic systems available for clinicians include feldspathic, lithium disilicate, leucite-reinforced ceramics, alumina, and yttrium-stabilized tetragonal zirconia polycrystalline (Y-TZP) materials. The zirconia system used in dentistry is 90% zirconium dioxide and glass-infiltrated ceramics with 35% partially stabilized zirconia. Y-TZP has superior mechanical properties compared to other types of ceramics, leading to a wide range of clinical applications in dentistry.[1-7]

Disadvantages of Y-TZP ceramics are related to its hardness and poor adhesion of resin cement. Some techniques and materials have been suggested to overcome the poor adhesion of resin cement to its surface. These techniques include priming, sandblasting, laser application, and silicatization.[6,8-10] Of these techniques, priming is a good option because of its ease of use and low cost, and the clinician can apply it immediately before cementing. Primers contain adhesive monomers, which react chemically with zirconium dioxide, increasing the bond strength between resin cements and zirconia.[9,11]

Resin cement has different activation modes and bonding mechanisms to dentin and zirconia. The most common resin cements are dual-cure luting agents used in combination with a bonding agent. Self-adhesive resin cements were introduced

Table 1 Composition and lot number of the materials tested

Material (type)	Composition	Lot number
Multilink Automix (resin cement)	Base and catalyst: pastes of dimethacrylates, HEMA, inorganic fillers, ytterbiumtrifluoride, initiators, stabilizers, pigments	LM0577
Metal Zirconia Primer (primer)	Tert-butylalkohol, methylisobutylketon, phosphonic acid acrylate, dibenzoyl peroxide	L45953
Clearfil SA Cement (resin cement)	Bis-GMA, sodium fluoride, triethylene glycol dimethacrylate, 10- MDP, hydrophobic aromatic dimethacrylate, hydrophobic aliphatic dimethacrylate, silanated barium glass filler, silanated colloidal silica, dl-camphorquinone, initiators, accelerators, catalysts, pigments	5AA
Alloy Primer (primer)	6-(4-vinylbenzyl-n-propyl)amino-1,3,5-triazine-2,4-dithione, 10-MDP, acetone	330A
RelyX ARC (resin cement)	Silane-treated ceramic, TEGDMA, Bis-GMA, silane-treated silica, functionalized dimethacrylate polymer	GE9JG

some years ago and do not need a bonding agent, thus facilitating the cementation procedure.[11,12] Studies have shown similar performance between traditional and self-adhesive resin cements; however, adhesive monomers present in the composition of some resin cements have affinity and react with dental zirconia, improving the adhesion of resin cement to zirconia.[11,13,14]

The purpose of this study was to evaluate the bond strength between Y-TZP ceramic and three resin cements containing different monomeric composition, and to investigate the effect of adhesive primers on the bond strength between resin cements and Y-TZP ceramic. The null hypothesis to be tested was that monomeric composition and adhesive primer application do not influence the bond strengths between resin cements and Y-TZP ceramic.

Materials and methods

Fifty zirconia plates ($12 \times 5 \times 1.5$ mm^3) were obtained consisting of ceramic materials containing zirconia (IPS e.max Zir-CAD blocks; Ivoclar Vivadent AG, Schaan, Liechtenstein). The plates were air-abraded for 15 seconds with 50 μm aluminum oxide particles (Danville Engineering Inc., San Ramon, CA), then ultrasonically cleaned with water for 5 minutes (Ultrasonic Cleaning Unit; Cristófoli Biosafety Equipmentos Ltda., Campo Mourão, Brazil) and randomly divided into five experimental groups ($n = 10$) and allocated for testing the resin cements and the use of primers.

The materials used in this study are described in Table 1. Two conventional dual-cure resin cements (RelyX ARC [RX]; 3M ESPE, St. Paul, MN and Multilink Automix [MA]; Ivoclar Vivadent AG) and a self-adhesive resin cement: Clearfil SA Cement (CC) (Kuraray Noritake Dental Inc., Tokyo, Japan) were tested. MA and CC were tested with (MA/P and CC/P) and without (MA and CC) use of adhesive primers (Metal-Zirconia Primer; Ivoclar Vivadent AG and Alloy Primer; Kuraray Noritake Dental Inc.). The manufacturers' recommendations were followed when using the resin cements and primers. Alloy Primer was applied for 15 seconds to dry air-abraded zirconia plates with a sponge and left undisturbed for drying. Metal-Zirconia Primer was also applied to dry zirconia plates for the same time, but using a disposable brush and left undisturbed for 180 seconds. Afterward, this primer solution was dispersed by strong stream air.

The materials were used under temperature and relative humidity control. The methodology developed by Shimada et al[15] was used to prepare specimens for the microshear test. Three cylindrical translucent molds (Tygon tubing, TYG-030; Saint-Gobain Performance Plastic, Clearwater, FL) were positioned over the zirconia plate surface, and freshly mixed dual-cure resin cements were placed in the molds to fill their internal volume, using a modified composite spatula (Duflex No. 3; SS White, Juiz de Fora, Brazil). Plates were stored in distilled water at 37°C for 24 hours. The tube molds were then removed with a surgical scalpel blade (No. 15; Swann-Morton, Sheffield, UK) to expose resin cement cylinders measuring 0.75 mm diameter $\times$ 1.0 mm high bonded to the zirconia surface. Thus, three cylindrical resin cement specimens were obtained for bonding to each zirconia plate. Before testing, all resin cylinders were checked under an optical microscope (30$\times$) for defects at the bonding interface (Fig 1).

Each zirconia plate was attached to the testing device with cyanoacrylate adhesive (Super Bonder; Loctite, Itapevi, Brazil), and the shear bond strength was measured (72% relative humidity at 25°C) in a universal testing machine (EZ Test; Shimadzu Corp., Tokyo, Japan). A shear load was applied at the base of the resin cement cylinder by a thin wire (0.20 mm diameter) at a 0.5 mm/min crosshead speed until failure (Fig 1). The shear bond strengths were calculated and expressed in MPa (N/m^2). The failure load was obtained in Kgf and converted to Newtons. The bonded area presented a diameter of 0.7 mm, and its radius was used to calculate the circular area bonded with resin cement.

The bond strength value for each plate was represented by the mean of the three resin cement cylinders of each plate. The results were analyzed by two-way ANOVA (resin cement + use of primer) and Dunnett's test (5% level of significance).

After testing, the debonded zirconia plates were mounted on aluminum stubs, gold/palladium sputter-coated (SCD 050; Baltec, Vaduz, Liechtenstein) and examined under high vacuum by a scanning electron microscope (SEM; VP-435; Leo, Cambridge, UK). Photomicrographs of representative areas of the fractured surfaces were taken at 100$\times$ and 120$\times$

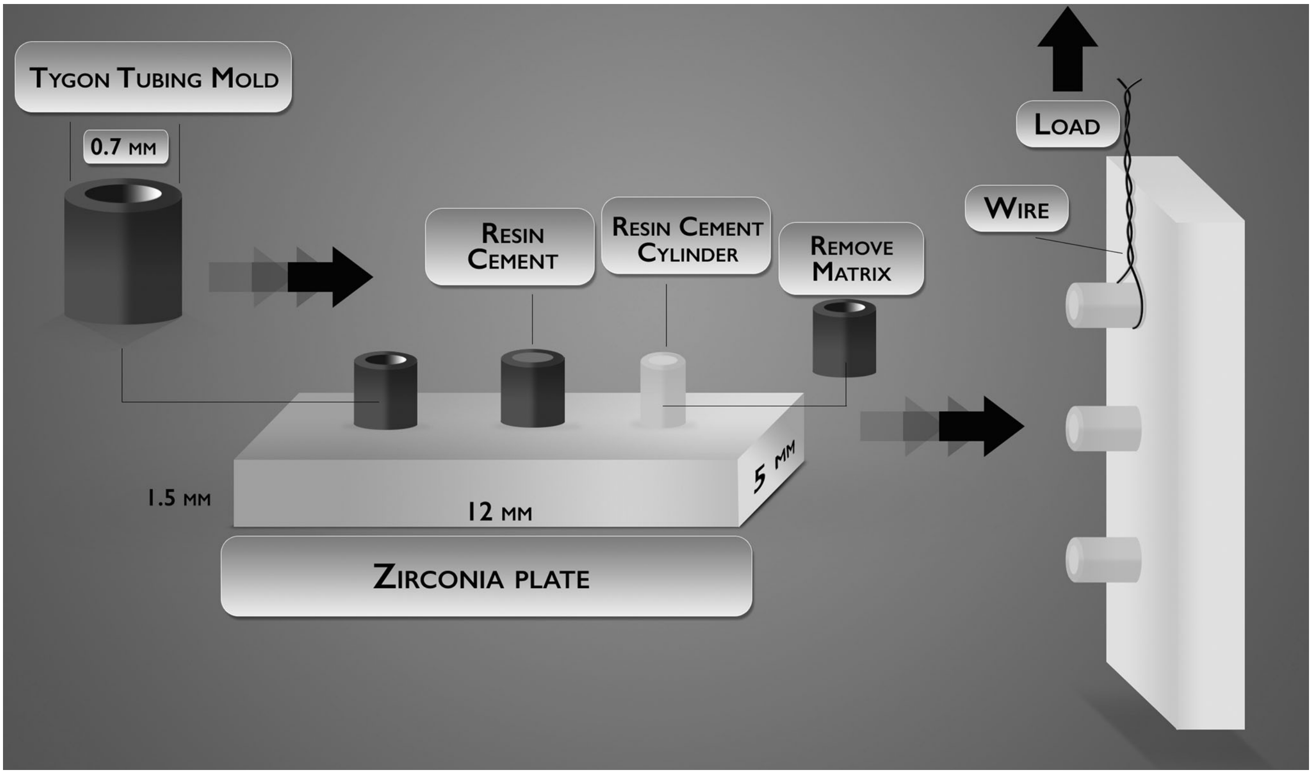

Figure 1 Schematic representation of specimen preparation.

Table 2 Means (standard deviation) of shear bond strength of resin cements to zirconia ceramic using adhesive primers (in MPa)

	Primer	
Resin cement	Without	With
Multilink Automix	[a]37.6 (4.5) B a	[a]55.7 (4.0) A a
Clearfil SA Cement	[a]46.2 (3.3) A a	[a]47.0 (4.1) A a
RelyX ARC (Control Group)	28.1 (6.6)	----------

Values of groups having similar letters were not significantly different ($p = 0.05$) (uppercase letters = rows; compared the use of primer or not and lower case letters = column, compared Multilink Automix and Clearfil SA Cement resin cements).

[a]Significant differences from the control group by Dunnett´s test ($p < 0.05$).

Table 3 Distribution of failure modes among experimental groups (%)

Group	Adhesive failure	Mixed failure
RelyX ARC	100	–
Multilink Automix	100	–
Multilink Automix + Metal Zirconia Primer	100	–
Clearfil SA Cement	70	30
Clearfil SA Cement + Alloy Primer	30	70

magnifications for fracture pattern evaluation. These were classified as: (1) adhesive along the zirconia surface or (2) mixed, when simultaneously exhibiting the zirconia surface and remnants of resin cement.

Results

Two-way ANOVA indicated that the factors “primer” ($p < 0.0001$) and “interaction” (primer + resin cement, $p < 0.0001$) significantly influenced the bond strength results, whereas the factor “resin cement” was not significant ($p = 0.9556$). Table 2 summarizes the statistics for the different experimental groups. Regarding the differences in the “primer” factor, the bond strength to zirconia for MA resin cement was significantly increased by the prior application of Metal-Zirconia Primer ($p < 0.05$); however, the use of Alloy Primer did not improve the bond strength of CC to zirconia ($p > 0.05$). MA and CC resin cements showed no difference whether or not primer was used ($p > 0.05$). Both of these produced higher bond strengths than RX ($p < 0.05$).

The distribution of failure modes among treatments is depicted in Table 3. Figures 2 to 5 are representative images of the failure modes. Adhesive failures along the zirconia surface were the predominant failure pattern observed for all resin cements, with and without adhesive primer (Figs 2 and 4). Primer application tended to change the failure pattern to mixed failure only for CC. Figures 3 and 5 show a mixed failure mode, with remnants of resin cement over the zirconia surface.

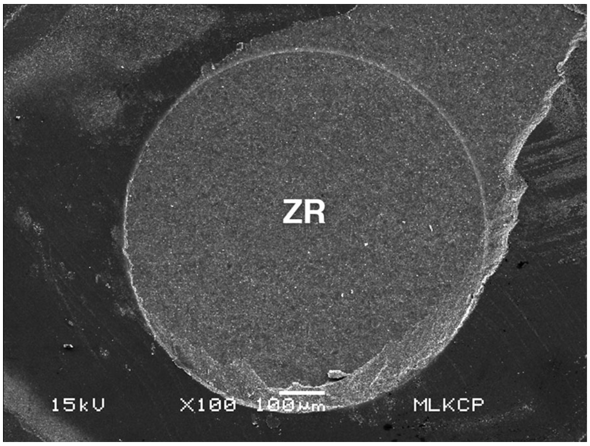

Figure 2 SEM photomicrograph illustrating an adhesive failure along the zirconia surface for the Multilink Automix resin cement tested with Metal Zirconia Primer (ZR: zirconia surface, original magnification 100×).

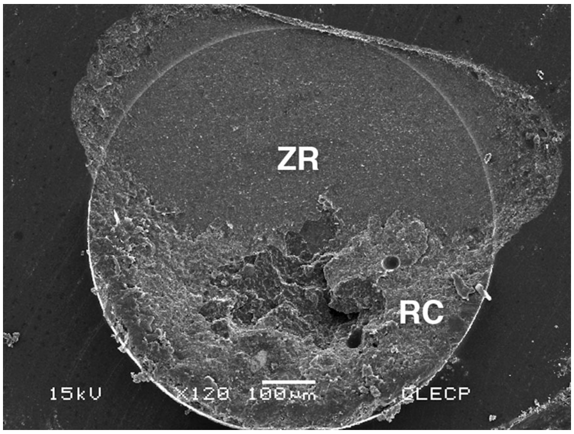

Figure 3 SEM photomicrograph illustrating a mixed failure for the Clearfil SA Cement resin cement tested with Alloy Primer (ZR: zirconia surface, RC: resin cement, original magnification 120×).

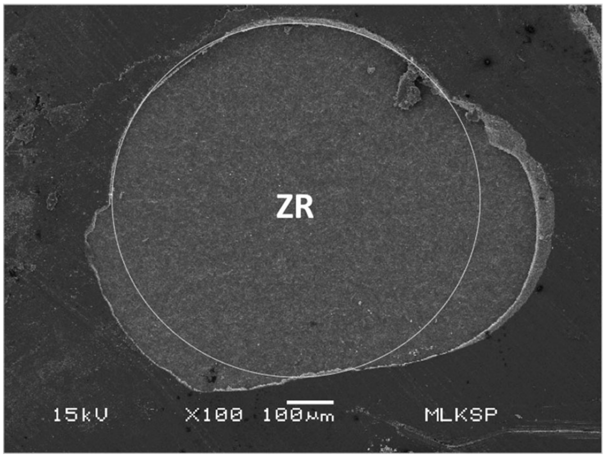

Figure 4 SEM photomicrograph illustrating an adhesive failure along the zirconia surface for the Multilink Automix resin cement tested with no primer (ZR: zirconia surface, original magnification 100×).

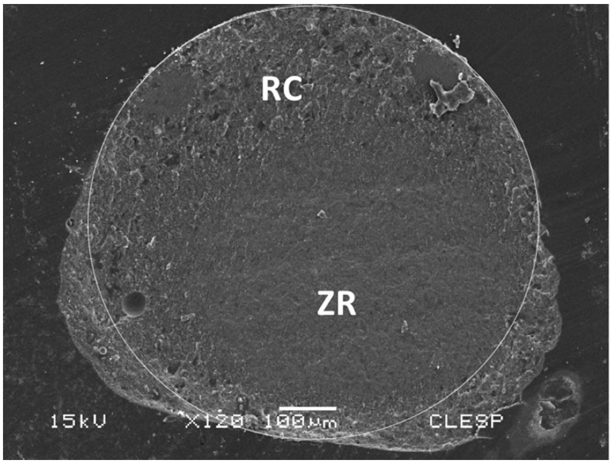

Figure 5 SEM photomicrograph illustrating a mixed failure for the Clearfil SA Cement resin cement tested with no primer (ZR: zirconia surface, RC: resin cement, original magnification 120×).

Discussion

The null hypotheses tested that monomeric composition and adhesive primer application do not influence bond strengths of resin cement to Y-TZP ceramic was accepted. The results indicated no significant difference between MA and CC resin cements, and the Alloy Primer did not increase the bond strength for CC resin cement. There was little variation in the failure pattern for all resin cements; failure of the adhesive was the most predominant outcome.

In the CC/P group, some mixed failures were observed (approximately 30%), which revealed cohesive fracture of the resin cement and also adhesive failure that exposed the zirconia surface. Some parts of resin cement were retained on the zirconia surface after testing because of the interaction of 10-methacryloyloxydecyl dihydrogen phosphate (MDP) from resin cement and primers. Both Alloy Primer and CC resin cement contain an efficient adhesive monomer 10-MDP responsible for the high bond strength to zirconia.[13,14] The resin cement remnants on the zirconia may have resulted from the interaction between 10-MDP and zirconia (Fig 3).

Alloy Primer contains the phosphoric acid group 10-MDP that bonds chemically to nonprecious metal atoms and oxide groups, such as zirconium dioxide and aluminum oxide, while the double bonds at the other end of the molecule react with the resin cement. For precious metals, the sulfur atom of the VBATOT molecule bonds chemically to precious metal atoms, and the double bonds have the same function of interacting with the resin cement.

The CC is a self-adhesive resin cement and also contains 10-MDP. This is one reason why Alloy Primer did not influence the results for CC. Perhaps, for resin cements that do not contain 10-MDP, primer application would be important for increasing the bond strength of resin cement to Y-TZP ceramic. Studies have demonstrated that the use of resin-based luting and priming agents containing the adhesive monomer MDP provide a higher bond strength to zirconia than do other systems, such as Monobond Plus.[16,17] Some primers are not effective for bonding of resin cements to Y-TZP ceramics. In this case, the combination with sandblasting seems to improve the bond strength of resin cement to Y-TZP ceramics.[18]

The lowest bond strength was obtained for RX resin cement (28.1 ± 6.6 MPa). In this study, this product was used as a control group because it possesses the basic constituents of dual-cured resin cements: TEGDMA, Bis-GMA, and dimethacrylate polymer. It does not contain a functional monomer to bond with zirconium dioxide, which explains why it had the lowest shear strength of all the resin cements tested. The application of an adhesive primer may be indicated for RX; however, the interaction between 10-MDP-based primers and conventional resin cements is little known.

MA resin cement contains the resin monomers dimethacrylates and 2-hydroxyethyl methacrylate (HEMA), but does not contain functional monomers or an adhesion-promoter component. In this case, Metal-Zirconia Primer increased the bond strength to Y-TZP ceramic. Metal-Zirconia Primer is also a single-component primer that promotes an adhesive bond between resin cements and indirect restorations made of zirconium oxide and aluminum oxide ceramic, or metal and metal–ceramic. The functional monomer is the phosphonic acid methacrylate;[19] the methacrylate cross-linking agent reacts with resin monomers of the composite luting agent.

Attia et al[20] found that the tensile bond strength of MA to ZirCad zirconia ranged from 31.5 to 45.2 MPa after 3 days storage in water with thermocycling, and from 10.6 to 38.8 MPa after 30 days. The artificial aging decreased the bond strength significantly for the groups that used conventional silane after silica coating. Silva et al[21] and Smith et al[22] also demonstrated that a primer/resin cement combination provides early adequate bond strength to zirconia; however, the adhesion of resin cements to Y-TZP ceramics was unstable when the specimens were submitted to artificial aging. Cura et al[23] studied the adhesion of two resin cements to zirconia ceramics, both glazed and unglazed. The resin cements tested, including MA, were used in combination with Metal/Zirconia Primer (MA/P group). This combination provided early adequate bond strength to zirconia, and the thermocycling method did not decrease the results significantly.

This study was performed in in vitro conditions, which did not consider the oral moisture affects; however, this fact can affect the clinical application or interpretation of the test results. Also, this study obtained only immediate bond strength values (24 hours). The in vitro conditions and short-term bond strength results are considered the limitations of this study. Clinically, the reduction of chair-time, such as by simplifying cementing procedures, is always important during the appointment. To obtain higher bond strength, application of an adhesive primer is indicated for some resin cements, while self-adhesive resin cements containing functional monomers can be used without a coupling agent. The decision to use the primer or not is related to the composition of each cementing system.

Conclusion

Application of an adhesive primer can increase the bond strength of resin cement to Y-TZP ceramic; however, results are product-dependent. Metal-Zirconia Primer increased the bond strength of MA resin cement to zirconia, but no effect was observed for CC/P. Resin cement containing 10-MDP functional monomer does not need the primer, and the RX showed the lowest bond strength to zirconia.

References

1. Trinschert J, Natt G, Mautsch W: Fracture resistance of lithium disilicate-, alumina-, and zirconia-based three-unit fixed partial dentures: a laboratory study. Int J Prosthodont 2001;14:231-238
2. Manicone PF, Rossi Iommetti P, Raffaelli L: An overview of zirconia ceramics: basic properties and clinical applications. J Dent 2007;35:819-826
3. Yilmaz H, Aydin C, Gul BE: Flexural strength and fracture toughness of dental core ceramics. J Prosthet Dent 2007;98:120-128
4. Cavalcanti AN, Foxton RM, Watson TF, et al: Y-TZP ceramics: key concepts for clinical application. Oper Dent 2009;34:344-351
5. Cavalcanti AN, Foxton RM, Watson TF, et al: Bond strength of resin cements to a zirconia ceramic with different surface treatments. Oper Dent 2009;34:280-287
6. Miyazaki T, Nakamura T, Matsumura H, et al: Current status of zirconia restoration. J Prosthodont Res 2013;57:236-261
7. Ritter RG: Use of high translucency zirconia in the aesthetic zone. Dent Today 2013;32:116,118-119
8. Behr M, Proff P, Kolbeck C, et al: The bond strength of the resin-to-zirconia interface using different bonding concepts. J Mech Behav Biomed Mater 2011;4:2-8
9. Amaral M, Belli R, Cesar PF, et al: The potential of novel primers and universal adhesives to bond to zirconia. J Dent 2014;42:90-98
10. Miragaya L, Maia LC, Sabrosa CE, et al: Evaluation of self-adhesive resin cement bond strength to yttria-stabilized zirconia ceramic (Y-TZP) using four surface treatments. J Adhes Dent 2011;13:473-480
11. Sá Barbosa WF, Aguiar TR, Francescantonio MD, et al: Effect of water storage on bond strength of self-adhesive resin cements to zirconium oxide ceramic. J Adhes Dent 2013;15:145-150
12. Aguiar TR, André CB, Correr-Sobrinho L, et al: Effect of storage times and mechanical load cycling on dentin bond strength of conventional and self-adhesive resin luting cements. J Prosthet Dent 2014;111:404-410
13. Yoshida K, Tsuo Y, Atsuta M: Bonding of dual-cured resin cement to zirconia ceramic using phosphate acid ester monomer and zirconate coupler. J Biomed Mater Res B Appl Biomater 2006;77:28-33
14. Souza GM, Silva NR, Paulillo LA, et al: Bond strength to high-crystalline content zirconia after different surface treatments. J Biomed Mater Res B Appl Biomater 2010;93:318-323
15. Shimada Y, Yamaguchi S, Tagami J: Micro-shear bond strength of dual-cured resin cement to glass ceramics. Dent Mater 2002;18:380-388
16. Koizumi H, Nakayama D, Komine F, et al: Bonding of resin-based luting cements to zirconia with and without the use of ceramic priming agents. J Adhes Dent 2012;14:385-392.
17. Kitayama S, Nikaido T, Takahashi R, et al: Effect of primer treatment on bonding of resin cements to zirconia ceramic. Dent Mater 2010;26:426-432

18. Yun J, Ha S, Lee J, et al: Effect of sandblasting and various metal primers on the shear bond strength of resin cement to Y-TZP ceramic. Dent Mater 2010;26:650-658
19. Van Landuyt KL, Snauwaert J, De Munck J, et al: Systematic review of the chemical composition of contemporary dental adhesives. Biomaterials 2007;28:3757-3785
20. Attia A, Lehmann F, Kern M: Influence of surface conditioning and cleaning methods on resin bonding to zirconia ceramic. Dent Mater 2011;27:207-213
21. Silva LH, Costa AKF, Queiroz JRC, et al: Ceramic primer heat-treatment effect on resin cement/Y-TZP bond strength. Oper Dent 2012;37:634-640
22. Smith RL, Villaneuva C, Rothrock JK, et al: Long-term microtensile bond strength of surface modified zirconia. Dent Mater 2011;27:779-785
23. Cura C, Ozcan M, Isik G, et al: Comparison of alternative adhesive cementation concepts for zirconia ceramic: glaze layer vs zirconia primer. J Adhes Dent 2012;14:75-82