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ORIGINAL ARTICLE

In vitro comparative bond strength of contemporary self-adhesive resin cements to zirconium oxide ceramic with and without air-particle abrasion

Markus B. Blatz · Jin-Ho Phark · Fusun Ozer · Francis K. Mante · Najeed Saleh · Michael Bergler · Avishai Sadan

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Abstract This study compared shear bond strengths of six self-adhesive resin cements to zirconium oxide ceramic with and without air-particle abrasion. One hundred twenty zirconia samples were air-abraded (group SB; $n=60$) or left untreated (group NO). Composite cylinders were bonded to the zirconia samples with either BisCem (BC), Maxcem (MC), G-Cem (GC), RelyX Unicem Clicker (RUC), RelyX Unicem Applicator (RUA), or Clearfil SA Cement (CSA). Shear bond strength was tested after thermocycling, and data were analyzed with analysis of variance and Holm–Sidak pairwise comparisons. Without abrasion, RUA (8.0 MPa), GC (7.9 MPa), and CSA (7.6 MPa) revealed significantly higher bond strengths than the other cements. Air-particle abrasion increased bond strengths for all test cements ($p<0.001$). GC (22.4 MPa) and CSA (18.4 MPa) revealed the highest bond strengths in group SB. Bond strengths of self-adhesive resin cements to zirconia were increased by air-particle abrasion. Cements containing adhesive monomers (MDP/4-META) were superior to other compositions.

Keywords Zirconia ceramic · Air abrasion · Self-adhesive cements · Bond strength

M. B. Blatz (✉) · F. Ozer · F. K. Mante · N. Saleh · M. Bergler
Department of Preventive and Restorative Sciences,
School of Dental Medicine, University of Pennsylvania,
240 S. 40th Street,
Philadelphia, PA 19104, USA
e-mail: mblatz@dental.upenn.edu

J.-H. Phark · A. Sadan
Department of Comprehensive Care, School of Dental Medicine,
Case Western Reserve University,
Cleveland, OH, USA

Introduction

Clinical success of all-ceramic restorations is influenced by the type of luting agent and technique for definitive cementation [4, 8]. The main influencing parameter seems to be adequate adhesion between ceramic restoration and the supporting tooth structures [8] to increase retention, marginal adaptation, and fracture resistance of the restored tooth and the restoration. Adequate adhesion is determined by luting agent type and its ability to successfully bond—with or without pretreatment steps—to the ceramic substrate as well as to enamel and dentin [21].

In recent years, the increasing demand for all-ceramic restorations led to development of ceramic materials with optimized mechanical properties such as densely sintered aluminum oxide and zirconium oxide ceramics [27]. The inherent esthetic and functional advantages of these materials have broadened the range of clinical indications [10]. CAD/CAM fabricated high-strength ceramic restorations are now even used for treatment options that require resin bonding for clinical success (e.g., laminate veneers, all-ceramic resin bonded fixed partial dentures) [1, 8], making the adequate selection and use of luting and bonding agents a necessity. Composite resin luting agents and bonding systems that provide strong and long-term durable adhesive bonds to high-strength ceramic materials not only increase retention, but also marginal seal and fracture strength [8]. Because of the diversity of products and their ingredients, physical properties of resin cements reveal great variations, but certain generalization can be made: compressive and tensile strength, toughness, and resilience of resin cement equal or exceed those of other luting agents; solubility is exceptionally low; and esthetic qualities are good, with color choices available [12].

Until recently, resin cements were classified according to the adhesive system used to prepare the tooth structures prior to cementation. One group employs etch-and-rinse adhesive systems, while self-etching dentin- and enamel primers are used in the other group. Special ceramic priming agents have also shown to increase bond-strengths to high-strength ceramic materials [6–8]. The need for priming and bonding agents for both tooth and restoration bonding surfaces, however, makes the proper application of resin cements a time-consuming and technique sensitive, multiple-step undertaking. These significant shortcomings and respective demands from dental practitioners have led to the recent development of self-adhesive resin cements, which was based on the adaptation of the chemistry of resin cements and self-etching adhesives [26]. Self-adhesive resin cements are claimed to provide good bond strengths to tooth structures and restorative materials without any pretreatment or bonding agents. Therefore, their application is very simple and can be accomplished in a single clinical step, similar to the application procedures of conventional luting agents, such as zinc phosphate and glass ionomer cements. This most recent type of luting agents is indicated for adhesive cementation of all-ceramic, metal-alloy, or composite-resin indirect restorations and endodontic posts. The physical and functional advantages, the simplification of clinical steps, the low incidence of postoperative sensitivity, and the early clinical success has resulted in immediate market acceptance and achieved great popularity among dental clinicians in a very short time [19]. Various manufacturers have recently released a self-adhesive resin cement and claim similar properties.

For resin bonding of conventional silica-based ceramics, it is well established that treatment with hydrofluoric acid and silanization enhances the resin bond [5, 14, 18]. But as a completely bioinert material, zirconia provides unpolar surfaces with high corrosion resistance, thus lacking chemical adhesive potential or acid etch susceptibility [17]. In addition, aluminum trioxide and zirconium dioxide ceramics are not silica based, rendering the well-established micromechanical and chemical interlocking of silica-silane bonds useless. However, surface treatment via air-particle abrasion systems or abrasive particles has the ability to increase resin bonds to high-strength ceramic materials [4, 8, 11, 15, 22].

The scientific evidence on the composition and adhesive properties of many of the newly released self-adhesive resin cements to tooth and restorative materials is scarce. Their bond strength and the influence of air-particle abrasion to zirconia ceramics is still largely unknown.

This study evaluated and compared shear bond strengths of six self-adhesive resin cements to a zirconium-oxide ceramic substrate with or without air-particle abrasion. The null hypotheses tested were that different self-adhesive resin cements provide similar bond strengths to zirconium-oxide ceramic surfaces and that bonds are not influenced by air-particle abrasion of the bonding surfaces.

Materials and methods

One-hundred twenty square-shaped samples of densely sintered zirconium-oxide ceramic (Katana, Noritake, Nagoya, Japan) with the dimensions 10 mm×10 mm×1 mm were fabricated. All samples were cleaned in 98% isopropyl and an ultrasonic cleaning device for 3 min. Samples were randomly divided into two test groups (SB and NO). Bonding surfaces of specimens assigned to group SB were air-particle abraded with alumina oxide (50 µm particle size at a pressure of 2.8 bar for 12 s from a distance of 10 mm). The surfaces of samples in group NO were left untreated. An acrylic plastic tube with an inner diameter of 2.9 mm and a height of 3.0 mm was filled with composite resin (Z-250, Shade A2; 3M Espe, St. Paul, MN, USA) and light cured (Coltolux 4 Light-curing unit; Coltene Whaledent, Mahwah, NJ, USA) for 40 s from the top and two sides for a total of 120 s to fabricate cylindrical composite samples. The ceramic samples of two main test groups were randomly divided into six cement subgroups. Five minutes after light curing, the composite cylinders were bonded with one of the self-adhesive resin cements to the ceramic surfaces in a custom-made alignment apparatus with an added weight of 1,000 g for 10 min. The bonding method has been previously described in detail [6, 7]. The following self-adhesive luting cements for bonding zirconia were used in this study (Table 1): BisCem (BC), Maxcem (MC), G-Cem (GC), RelyX Unicem Clicker (RUC), RelyX Unicem Applicap (RUA), and Clearfil SA Cement (CSA).

Cements were mixed, applied to the zirconia surfaces, and cured according to manufacturers' recommendations without any primer or adhesive. After fabrication, the specimens were removed from the alignment device and stored in deionized water and thermocycled for 20.000 cycles between 5°C and 60°C with a dwell time of 15 s. Finally, the bonded specimens were placed in a jig for shear bond strength testing described in ISO/TR 11405 and loaded to failure with a crosshead speed of 1 mm/min by using Universal Testing Machine (Model 4411; Instron, Canton, MA, USA). The loads were converted to MPa by dividing the failure load (N) by the bonding area (mm^2).

The data were analyzed by two-way analysis of variance (ANOVA) models and pairwise multiple comparison procedures (Holm-Sidak method) with α=0.05. Specimen surfaces were examined with a light microscope (SM LUX; Ernst Leitz GmbH, Wetzlar, Germany) at original magnification ×25 to assess the mode of failure

Table 1 List of self-adhesive resin cements

Cement	Components	Main composition	Manufacturer	Lot #
BisCem (BC)	Two pastes	Bis(Hydroxyethyl methacrylate) phosphate, Tetra ethylene glycol dimethacrylate, Dental Glass	Bisco Inc, USA	0700012333
RelyX Unicem Clicker (RUC)	Two pastes	Methacrylate monomers containing phosphoric acid groups, Methacrylate monomers, Silanated fillers, Alkaline fillers	3M Espe, USA	311818
RelyX Unicem Applicap (RUA)	Powder and liquid	Methacrylate monomers containing phosphoric acid groups, Methacrylate monomers, Silanated fillers, Alkaline fillers	3M Espe, USA	310241
Maxcem (MC)	Two pastes	Methacrylate ester monomers, Inert mineral fillers, Ytterbium fluoride, Activators, Stabilizers	Kerr Corp,USA	2882112
G-Cem (GC)	Powder and liquid	4-META, UDMA, Alumina-silicate glass, Phosphoric ester monomer, camphorquinone, Pigments	GC Corp. Japan	0704231
Clearfil SA Cement (CSA)	Two pastes	MDP, Hydrophobic aromatic dimethacrylate, Hydrophobic aliphatic dimethacrylate, Colloidal silica, Barium glass fillers	Kuraray, Japan	SA CA-A-061211, SACA-U-070329H

(cohesive, adhesive, or mixed failure at the ceramic or the composite surface).

Results

The results of the shear bond strength test for the study test groups are presented in Table 2 and Fig 1. Statistically significant differences between the test groups and between the surface treatments are indicated in the table. ANOVA analyses showed statistically significant interaction between cements and surface conditions (ρ<0.001). All test cements revealed higher bond strengths to air-particle abraded zirconia surfaces than to the untreated surfaces (ρ<0.001). However, these differences were not statistically significant for groups BC (ρ=0.167) and MC (ρ=0.373). Mean bond strength values of test cements were 4.3 MPa in group NO and 11.6 MPa in group SB. Without pretreatment (group NO), RUA, GC, and CSA revealed higher bond strengths than the other test cements. The highest mean bond strength values to air-particle abraded zirconia (Group SB) were found with GC (22.4 MPa) and CSA (18.4 MPa), which were not significantly different (ρ=0.027) from each other. RUA, in return, provided bond strengths that were in the same statistical grouping as CSA (ρ=0.031), but significantly lower than GC (ρ=0.000). In this group, BC (2.8 MPa) and MC (3.0 MPa) revealed the lowest values.

Failure modes were 100% adhesive at the ceramic bonding interface for all test cements and with both surface conditions.

Discussion

The results of this study disapproved our null hypotheses that different self-adhesive resin cements provide similar bond strengths to zirconium oxide ceramic surfaces and that air-particle abrasion of the zirconia bonding surfaces does not influence bond strength values.

The newest type of luting cement is the self-adhesive resin cement. The benefits of conventional and adhesive luting techniques have been combined in these materials by incorporating the advantages and different components from many of the earlier generations of cement material classes. The first self-adhesive resin cement introduced to the market is RelyX Unicem (3M Espe), a dual-cure powder and liquid material. More recently, newer paste and paste versions have been commercialized [19]. It should be noted that, in the meantime, some of the materials tested in this study were updated or even replaced. For example, Maxcem (Kerr) was replaced by Maxcem Elite. G-Cem is also available as G-Cem Automix.

In this study, RUA and GC were the only powder-and-liquid-type cements, while all others were two-paste materials. Those two cements as well as CSA revealed better bond strength values to the untreated zirconia surfaces than the other materials. GC, RUA, and CSA showed almost the same bond strength to intact zirconium-oxide surfaces even though they have different components to promote adhesive bonding mechanisms. RUA is a dual-cure liquid-and-powder resin material and contains methacrylate monomers with phosphoric acid groups. These phosphoric acid groups promote surface adhesion by hydrogen bonding with ceramic surfaces. In addition, its setting reaction resembles powder–liquid glass ionomers or hybrid ionomers by interacting with surface minerals.

It was also confirmed that 4-META (4-methacryloxyethyl trimellitate anhydride) products show chemical reactivity with tooth and metal-oxide layers [16, 19]. Its incorporation in resin luting agents facilitates adhesive bonds to metal oxides. GC contains 4-META as well as a UDMA methacrylate structure, which has a low molecular weight and less viscosity compared to BisGMA. These chemical properties may attribute to the excellent bonding ability

Table 2 Mean shear bond strength values [MPa] and standard error of means (SEM) of self-adhesive resin cements to untreated (NO) and air-particle abraded (SB) zirconia surfaces

Luting Cements	Surface treatment	Mean Bond strength [MPa]	SEM [MPa]
BC	NO	0.3[a]	0.3
	SB	2.8[a]	1.0
MC	NO	1.4[a]	0.9
	SB	3.0[a]	0.9
GC	NO	7.9[b]	1.6
	SB	22.4[c]	1.1
RUC	NO	0.6[a]	0.6
	SB	8.2[b]	2.0
RUA	NO	8.0[b]	1.5
	SB	14.6[d]	1.0
CSA	NO	7.6[b]	1.1
	SB	18.4[cd]	2.4

Same superscript letters indicate no statistical difference

Same superscript letters indicate no significant difference

of GC, which was, together with CSA, the highest in the air-particle abraded group (SB), followed by RUA.

10-Methacryloyloxydecyl dihydrogen phosphate (MDP) is an important component in CSA. The current evidence supports the use of modified priming and/ or resin composite luting agents containing special adhesive monomers (e.g., MDP) that provide chemical bonds to metal oxides and, therefore, long-term durable resin bonds to high-strength ceramic materials [3, 4, 6, 7]. Blatz et al. [7] indicated that airborne particle abrasion and an MDP-containing priming agent followed by application of MDP-containing resin composite luting agent provided superior bond strengths to zirconia. Ozcan and Vallittu [21] as well as Wolfart et al. [27] also concluded that a strong and long-term reliable resin bond to alumina and zirconia ceramics is achieved by air-particle abrasion and MDP-containing resin luting cements. The outcomes of the current study support these findings and the excellent bonding properties of MDP to high-strength ceramic materials.

A number of surface treatment methods and techniques have been reported to enhance the bond strength of luting cements to ceramic surfaces. Etching the intaglio surface of a

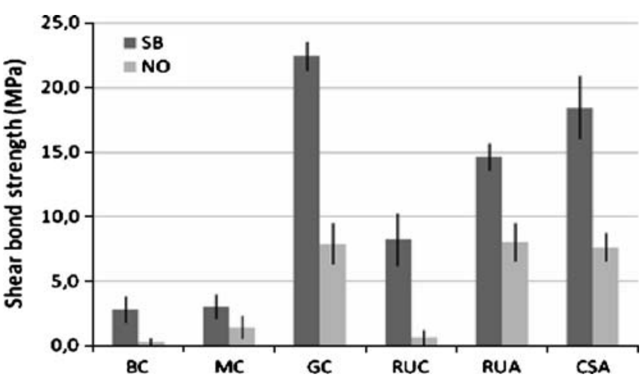

Fig. 1 Mean shear bond strength [MPa] and standard error of means (SEM) of self-adhesive resin cements to untreated (NO) and air-particle abraded (SB) zirconia surfaces

restoration with hydrofluoric acid followed by the application of a silane coupling agent is well-documented method to increase resin bond strengths to silica-based ceramics [4, 5]. However, high-alumina and zirconia ceramics do not contain a silicon dioxide (silica) phase and, therefore, require alternative conditioning systems [1, 2, 6–8, 13, 14, 20, 21].

Airborne-particle abrasion with Al_2O_3 is the preferred treatment method for high strength ceramic materials [5–8, 13]. Surface roughening methods increase energy and wettability [5, 6,] and may decontaminate bonding surfaces. Della Bona et al. [9] showed that treatment of In-Ceram Zirconia with airborne particle abrasion systems (sandblasting and silica coating) produced significantly greater Ra values, which should benefit the mechanical bond mechanisms to resin-based materials. In a recent study, Quaas et al. [25] found that air-abrading contaminated zirconia surfaces led to significantly higher resin-ceramic bond strength values than cleaning the contaminated ceramic surfaces with phosphoric acid or alcohol. The results of the current study also confirm that air-particle abrasion of zirconia surfaces with Al_2O_3 increases bond strength values of self-adhesive luting cements to ceramic surfaces, especially in test groups GC, RUC, RUA, and CSA. Similarly, Piwowarczyk et al. [24] concluded that cements containing phosphoric-acid methacrylates (in their study RelyX Unicem and Panavia F) provide a strong physical interaction, such as hydrogen bonding, with the air-borne particle-abraded ceramic surface and bond strengths that were higher than other cementing agents. Another study by the same author [23] evaluated shear bond strengths of several luting cements and revealed that, after air-borne particle abrasion, the highest bond strength values were obtained with RelyX Unicem.

In contrast to the majority of studies, which support the positive effect of air-particle abrasion on the bond strength of luting cements to zirconia surfaces, Derand and Derand [11] tested different surface treatment and composite resin cements and found that acid-etching and airborne-particle abrasion had only minor influence on bond strengths. Kumbuloglu et al. [15] demonstrated that Al_2O_3 and SiO_2 air abrasion and two different storage conditions did not significantly affect the bonding properties of both Panavia F and RelyX Unicem resin cement to zirconia. While surface treatment was significantly influencing long-term bond strengths of resin cements to zirconia, it had no effect on the bond strength of a resin-modified glass-ionomer cement [7]. Heat-induced maturation and selective infiltration etching provided superior zirconia-resin bond strength compared to airborne-particle abrasion in a study by Aboushelib et al [1]. Their study follows a recent trend to identify alternative methods as the damage created by blunt surface treatment methods like air-particle abrasion may have detrimental effects on the overall clinical performance of bilayer all-ceramic restorations [8]. The focus on the sole effect of air-particle abrasion on the bond strength may, therefore, be one of the major limitations of the present study. Other limitations include the overall methodology and testing set-up, especially the frequently discussed validity of the shear test. This, however, is still the most commonly used bond strength test.

This is one of the first studies to test bond strengths of different recently released self-adhesive luting cements to zirconia. Due to the great popularity of self-adhesive resin cements and increasing use of zirconia restorations, the results may have important clinical implications. The present study confirms that the compositions of self-adhesive cements and the characteristics of the components play a fundamental role in bonding mechanisms of luting cements to zirconia surfaces.

Conclusion

Bond strengths of self-adhesive resin cements to zirconium-oxide ceramics were highly variable and increased by air-particle abrasion. Cements containing adhesive monomers such as MDP or 4-META provided better bonds than other compositions.

Conflict of Interest The authors declare that they have no conflict of interest.

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