Bonding of Resin Composite Luting Cements to Zirconium Oxide by Two Air-particle Abrasion Methods

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Clinical Relevance
The results of this in vitro study suggest that, in combination with air-particle abrasion methods, Panavia F and RelyX Unicem resin composite luting cements with phosphoric-acid methacrylate content provide a strong resin bond to zirconium oxide.

SUMMARY
Objective: This study evaluated the shear bond strength of two resin composite luting cements to zirconium oxide ceramic substrate using two air-particle abrasion methods. Methods: Two resin composite cements, RelyX Unicem (3M ESPE) and Panavia F (Kuraray), each with an acidic composition, were used in combination with a zirconium oxide (DCS Dental AG) substrate containing Al₂O₃ and SiO₂ (Rocatec system, 3M ESPE) and two air-particle abrasion methods. The shear bond strength of the resin composite cement to the substrate was tested after the samples were either water-stored for one week or thermocycled following 24 hours of water storage. Results: The RelyX Unicem resin composite cement specimens with the Rocatec treatment (20.9±4.6 Mpa and 20.1±4.2 MPa, respectively, n=12) demonstrated the highest shear bond strength. Alternatively, the lowest values were obtained for the Panavia F resin cement samples, with Al₂O₃ air-particle abrasion in both storage conditions, water storage for one week (17.7±8.9MPa) or thermocycling after 24 hours of water storage (16.3±4.9 MPa). Neither storage condition or particle abrasion system significantly affected shear bond strengths (ANOVA, p>0.05). Conclusion: It was concluded that two different surface conditioning methods and storage conditions did not significantly affect the bonding properties of Panavia F and RelyX Unicem resin composite luting cements to Zirconia.

INTRODUCTION
The use of all-ceramic restorations has increased in recent years. In load-bearing applications, aluminum trioxide and zirconium dioxide ceramics have made their breakthrough due to their improved mechanical
properties (Hahn & Lösth, 1992; Luthardt & others, 1998). These ceramics are used in posts, crowns, fixed partial dentures (FPD), implants and implant abutments (Blatz, 2002; Friederich & Kern, 2002; McLaren, 1998; Tinschert & others, 2001).

A successful bond between ceramic and a resin luting cement is achieved through the formation of chemical bonds and the micromechanical interlocking of resin to the ceramic surface (Blatz, Sadan & Kern, 2002). With conventional silica-based ceramics, acid etching and the application of a silane-coupling agent can create a moistened rough surface for successful ceramic-resin bonding (Blatz & others, 2002). Aluminum trioxide and zirconium dioxide ceramics are not silica-based; therefore, the well-established micromechanical interlocking of silica-silane bonds cannot be achieved (Awliya & others, 1998; Blatz, Sadan & Kern, 2003b). However, the use of air-particle abrasion systems utilizing Al₂O₃ or silica (SiO₂) abrasive particles can increase the surface area of the ceramic substrate and offer micrometer scale roughness for resin composite luting cements (Awliya & others, 1998; Blatz, Sadan & Blatz, 2003a; Blatz, Sadan & Kern, 2003b; Derand & Derand, 2000; Kern & Thompson, 1994; Kern & Thompson, 1995; Wegner & Kern, 2000; Wegner, Gerdes & Kern 2002).

Some studies (Kern & Wegner, 1998; Wegner & Kern, 2000; Wegner & others, 2002) evaluated different methods and materials for bonding resin composite luting cements to zirconium dioxide, while others tested the durability of bonding after long-term water storage (Berry, Barghi & Chung, 1999) and thermal cycling (Palmer, Barco & Billy, 1992). However, it still remains unclear as to which resin composite luting cement and which ceramic surface conditioning method produced the most durable bond strengths. This study evaluated the shear bond strength of two resin composite luting cements to zirconium dioxide ceramic substrate utilizing two air-particle abrasion methods.

### METHODS AND MATERIALS

The materials and test groups of this study are presented in Table 1. All materials were prepared and handled in accordance with the manufacturers’ instructions. Pieces of zirconium dioxide ceramic substrate (DCS Zirconia, Dental AG, Allschwil, Switzerland) (10 x 10 x 7 mm³) were used. The surface of the substrate was wet-ground with 500 and 1200 grit (FEPA) silicone carbide abrasive paper (Struers RotoPol 11, Struers A/S, Rodovre, Denmark), cleaned for 10 minutes in an ultrasonic water bath and air dried.

#### Surface Treatment of the Substrate

To increase the surface area for bonding and to decrease surface tension, the surfaces of the substrates were air abraded with either 50 µm grain-sized aluminum trioxide particles at a pressure of 200 kPa from a distance of approximately 10 mm for 14 seconds, or they were abraded with tribochemical silica coated with Rocatec Plus abrasive, which is 110 µm grain-sized aluminum trioxide modified with silisic acid (referred as as silica, SiO₂) at a pressure of 280 kPa from a distance of 10 mm for 13 seconds. After air abrasion, the ceramic substrates were cleaned for 10 minutes in an ultrasonic water bath and air dried.

#### Cementing

The Panavia F (Kuraray, Osaka, Japan) resin composite luting cement system was used, and K-Etchant gel was applied on the substrate surface for five seconds. After water rinsing and air drying, a mixture of Clearfil Porcelain Bond Activator and Clearfil SE Bond primer was applied for 10 minutes in an ultrasonic water bath and air dried.
composite cement was light cured (Optilux 501, Kerr, Orange, CA, USA; light intensity 800 mW/cm²) for 20 seconds for each increment. Before light curing, Oxyguard 2 was applied to all margins and rinsed off after 3 minutes.

RelyX Unicem Aplicap (3M ESPE) self-adhesive universal resin composite luting cement was used in all test groups. The luting cement capsules were inserted into the activator and activated by pressing down and holding the handle for four seconds. The capsules were then inserted into the mixing device (Silamat Plus, Ivoclar-Vivadent, Schaan, Liechtenstein) and mixed for 15 seconds. The resin composite luting cement from the capsules was applied incrementally into translucent polyethylene molds. The samples were light cured (Optilux 501, Kerr; light intensity 800 mW/cm²) for 20 seconds for each increment.

**Storage Conditions**

The test specimens in each group were divided into two subgroups. Forty-eight specimens from each group were stored in distilled water at (37±1)°C for one week before evaluating the shear bond strength of the resin composite luting cement to the substrate. An additional 48 specimens of each group were stored in distilled water at (37±1)°C for 24 hours and thermocycled for 2000 cycles in water baths of 5°C and 55°C (dwelling time 30 seconds).

**Shear Bond Test**

The specimens were mounted in the shear bond jig (Bencor Multi-T shear assembly, Danville Engineering Inc, San Ramon CA, USA) of a universal testing machine (Lloyd LRX, Lloyd Instruments Ltd, Fareham, UK). The crosshead speed of continuous loading was 1.0 mm/minutes until fracture or debonding occurred, and the load deflection curve was recorded with Nexygen 4.0 software (Lloyd LRX, Lloyd Instruments Ltd).

**SEM/EDS Analysis**

Scanning electron microscopy (SEM) (Model JSM 5500, JEOL Ltd, Tokyo, Japan) and energy dispersive x-ray spectroscopy (EDS) (Spirit, Princeton Gamma-Tech Inc, Princeton, NJ, USA) were carried out for the substrate surfaces after each air-particle abrasion treatment (n=5/surface treatment). For analysis, the substrate surfaces were coated with a layer of carbon 10–15 nm-thick using a sputter coater (Model BAL-TEC SCD 050 Sputter Coater, Liechtenstein). SEM micrographs and EDS analysis were carried out using a standardized method, with an accelerating voltage of 20 kV in a vacuum using a working distance of 20 mm. A liquid-nitrogen-cooled Lithium-drifted Silicon (Si(Li)) x-ray detector with a 30 mm² active area (PRISM 2000, Princeton Gamma-Tech Inc) was used to collect x-ray spectra. Carbon was deconvoluted away from the spectra. The analysis was done using 400x magnification with an area of 294 x 220 μm. The elements, in the form of oxides found on the substrate surfaces and their amounts in weight%, are listed in Table 2. The topographical changes on the substrate surfaces followed by the air-particle abrasion methods were examined with SEM. Furthermore, the position-tagged spectrometry of the element map was applied to illustrate the morphology and location of oxides on the substrate surface. The failure modes on the substrate surfaces following the shear bond test were also examined with SEM analysis.

**Statistical Analysis**

Statistical analysis was performed using SPSS System for Windows, Release 10.0.5/1999 (SPSS Inc, Chicago, IL, USA). The means of shear bond strengths of each group were analyzed by multivariate analysis of variance (ANOVA), with shear bond strength as the dependent variable and brand of resin luting cement and storage condition as independent variables. In all tests, p values less than 0.05 were considered to be statistically significant. Multiple comparisons were conducted using the Tukey Post-Hoc test.

The basic form of the Weibull distribution is shown below:

$$ P_f = 1 - \exp \left( - \frac{V \left[ \frac{\sigma - \sigma_u}{\sigma_o} \right]^m}{m} \right) $$

where the constant m is the Weibull modulus, which determines the slope of the distribution function, while σ characterizes the spread of the failure data with respect to stress. And σₚ is the stress level at which 63% of the specimens have failed, while σₚ is the theoretical failure stress at which the failure probability approaches zero, also known as the threshold stress. Weibull statistics were calculated with Weibull++ software (Reliasoft Corporation, Tucson, AZ, USA).

**RESULTS**

The results of the shear bond strength test are presented in Figure 1, while Figure 2 shows the results of the

<table>
<thead>
<tr>
<th>Element (wt%)</th>
<th>Al₂O₃ Abrasion</th>
<th>SD</th>
<th>SiO₂ Abrasion</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>6.22</td>
<td>0.31</td>
<td>85.28</td>
<td>0.72</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.81</td>
<td>0.14</td>
<td>8.50</td>
<td>0.53</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>95.19</td>
<td>0.09</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Weibull analysis. Table 2 shows the results of the EDS element analysis, where the oxide content (wt%) on the ZrO₂ substrate surface after air-particle abrasion (Al₂O₃ abrasion, SiO₂ abrasion) is displayed. The highest shear bond strengths in the water stored and thermocycled groups were obtained with RelyX Unicem resin composite cement and SiO₂ air-particle abrasion treatment (20.9±4.6 Mpa and 20.1±4.2 MPa, respectively). The lowest values in both the water stored (17.7±8.9MPa) and thermocycled (16.3±4.9 MPa) groups were observed with Panavia F adhesive resin cement with Al₂O₃ air-particle abrasion. ANOVA revealed that the shear bond strengths values were not significantly affected by thermocycling in all subgroups (p<0.05).

SEM/EDS micrographs of the zirconium dioxide substrate surface after Al₂O₃ and SiO₂ (Rocatec silica coating) air-particle abrasion are presented in Figures 3 and 4. Analysis revealed SiO₂ and Al₂O₃ particles on the sample surface corresponding to the air-particle abrasion systems.

**DISCUSSION**

Over the last decade, major improvements relating to the mechanical properties of dental ceramics have been made (Tinschert & others, 1999). Nevertheless, certain applications, especially those for minimal invasive treatments, require adhesive cementation (Kern, Knodle & Strubb, 1991; Wegner & others, 2002). Water absorption (Özcan, Alkumru & Gemalmaz, 2001), hydrolysis (Berry & others, 1999) and thermal changes (Palmer & others, 1992) are intra-oral conditions that influence the long-term stability of silane promoted adhesion to resins. Long-term water storage (Berry & others, 1999) and thermocycling (Palmer & others, 1992) are commonly used artificial-aging methods that significantly influence the resin bond to ceramics, especially “non-etchable” high-strength ceramics (Kern & Thompson, 1995; Kern & Wegner, 1998; Wegner & Kern, 2000; Wegner & others, 2002). Several laboratory studies have revealed that, while degeneration of the bonding interface of resin composite that is susceptible to hydrolytic degeneration is accelerated by thermocycling, hydrolytically stable resin composites show no or only a limited effect by thermocycling (Kern & Thompson, 1995; Pfeiffer & Schwickerath, 1985; Wegner & others, 2002). Similarly, the bond strengths of thermocycled samples were found to be lower than that of water-stored samples in this study.

Air abrasion with Al₂O₃ is the preferred surface treatment method for high-strength ceramic materials (Awliya & others, 1998; Blatz & others, 2003b; Kern & Thompson, 1994, 1995; Wegner & Kern, 2000; Wegner & others, 2002). Micromechanical bonding systems utilize air-particle abrasion, which improves micromechanical bond and increases the bonding surface area (Özcan, Pfeiffer & Nergiz, 1998). Also, surface roughening methods increase surface energy and, therefore, wettability (Blatz & others, 2003b). Although satisfactory bonding between ceramic and resin is achieved in current dental practice, many attempts have been made to develop better bonding techniques. One such technique is silica coating, in which the tribochemical effect of air abrasion results in the deposition of a molecular coating of SiO₂ on the surface. The surface is then coated with silane to render it more chemically reactive to the resin (Hansson & Moberg, 1993; Özcan, 2003). In this study, air-particle abrasion with SiO₂...
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The use of (Rocatec) yielded slightly higher bond strengths for both groups than was obtained with Al₂O₃ particles. However, it should be noted that, due to high deviation, statistics did not reveal significant differences between the two different air abrasion systems.

A regression line, including a coefficient, has been included in the graph (Figure 2), as the coefficient was ≥0.95. The data was considered to exhibit a good fit to the Weibull model (McCabe & Carrick, 1986; Robin & others, 2002). From the Weibull graphs, it can be concluded that Rocatec revealed better values in all groups if lower values are examined. These results are in accordance with previous studies (Blatz, Sadan & Blatz, 2003; Blixt & others, 2000; Hansson & Moberg, 1993; Kern & Wegner, 1998; Özcan & Vallittu, 2003; Özcan, 2002, 2003). The SEM/EDS analysis revealed SiO₂ content on the Rocatec-treated ZrO₂ substrate surface. The existence of silica likely increased the affinity of silane to the ZrO₂ surface, which improved the adhesion of resin composite cements.

Failure modes were observed to be completely adhesive at the ceramic surface after water storage and thermal cycling in this study. This general finding is similar to the results of a study by Blatz and others (2004). Short-term water storage and thermocycling were used in the Blatz and others study, which partly explains why no statistically significant differences between storage conditions were found.

Air abrasion procedures supposedly produce surface micro-irregularities that may function as crack initiators and therefore weaken ceramic materials. However, it has been shown that resin luting agents, which have been proven to provide durable resin bonds, have the ability to “heal” minor surface flaws.
created by acid etching or air abrasion and, therefore, significantly strengthen ceramic materials (Blatz & others, 2003b; Burke & others, 2002). Air abrasion causes a transformation of the monoclinic phase of Zirconia, creating a layer of compressive stresses on the surface that counteracts flaws induced by air abrasion (Guazzato & others, 2005).

Current bonding systems require multiple adhesive steps and may be technique sensitive, unpredictable and time-consuming. A self-adhesive, dual-polymerizing universal resin composite luting cement has been recently introduced. According to the manufacturer, bonding to the tooth structure can be achieved without any pretreatment steps, such as etching, priming or bonding (Piwowarczyk, Lauer & Sorensen, 2004). RelyX Unicem, a self-adhesive resin composite luting cement, has revealed higher bond strengths than the highly reputed Panavia F in both water-stored and thermocycled groups in accordance with the results of a study by Bulot and others (2003). Panavia F and RelyX Unicem contain phosphoric-acid methacrylates that provide a strong physical interaction, such as hydrogen bonding, with the air abraded ceramic surface (Piwowarczyk & others, 2004). In addition, the compressive strength and microhardness of RelyX Unicem were found to be higher than with Panavia F in the literature (Kumbuloglu & others, 2004).

**CONCLUSIONS**

Within the limitations of this study, it was concluded that two different surface conditioning methods, using Al₂O₃ and SiO₂ air abrasion and two different storage conditions, water storage for one week or thermocycling after water storage for 24 hours, did not significantly affect the bonding properties of both Pavina F and RelyX Unicem resin composite cements to Zirconia.
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References


