Zirconia-reinforced dental restorations

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CHAPTER 3

*Effect of an experimental zirconia-silica coating technique on micro tensile bond strength of zirconia in different priming conditions*
3.1 Abstract

Objectives: This study aimed to evaluate the adhesive properties of a MDP-containing resin cement to a colored zirconia ceramic, using an experimental zirconia-silica coating technique under different priming conditions.

Methods: 18 zirconia ceramic discs (Cercon base colored) were divided into two groups: the control group, and the experimental zirconia-silica coating group. Specimens in each group were further divided into 3 subgroups (n = 3) according to the priming conditions: no primer, a MDP-containing primer (ED Primer II) or a silane coupling primer (RelyX™ Ceramic Primer). Then resin-composite discs (Filtek™ Z250) were bonded to the treated surface using a MDP-containing resin cement (Panavia F 2.0). The bi-layered specimens were cut into microbars and 20 microbars were randomly selected from each specimen, half of which were stored in 37°C water bath for 24 hr, and the other half were stored for 30 days. After water storage, the samples were exposed to a Micro Tensile Bond Strength test (MTBS). The results were analyzed by ANOVA, while the fracture surfaces were examined by SEM.

Results: After 24 hr water storage, zirconia-silica coating followed by silanization showed a significantly (P < 0.001) higher MTBS value 45.0 (10.9) MPa. Water storage affected (P < 0.05) MTBS in the control group (24.1–30.3 MPa to 2.8–3.1 MPa), but only partially in the zirconia-silica coating group (20.0–45.1 MPa to 17.4–25.9 MPa). SEM analysis revealed a failure mode change after water storage.

Significance: The combination of zirconia-silica coating with silane coupling can improve the bonding of resin cement to this colored zirconia.
3.2 Introduction

The popularity of zirconia based core materials has increased in recent years because of its favourable biocompatibility, esthetic and mechanical properties. However, a long-term durable bonding to zirconia ceramics is reported to be difficult [1, 2], because of its surface stability. When zirconia is aimed to be used in adhesive dentistry applications this might be a determining factor in obtaining clinical success.

As zirconia is a monolithic ceramic not containing a glass phase, conventional hydrofluoric acid etching does not lead to changes of the surface roughness of zirconia, nor does it enhance the bond strength [3, 4]. Without surface pre-treatment, a single silane coupling agent may also not improve the bond strength to zirconia [1, 2, 5, 6], which lacks the required silica phase for the chemical reaction to form a siloxane network. Although the real function is still not clear, MDP (10-methacryloyloxydecyl dihydrogen phosphate) is assumed to have a chemical reaction to zirconia surface, and can improve the initial bond strength of resin cement to zirconia ceramics. However, this bond strength will always be compromised by artificial aging, indicating the high bond strength based on MDP is not stable in water [7-10].

The pre-treatment of airborne-particle abrasion is suggested to roughen the zirconia surface, since it could increase the micro mechanical interlocks and surface bonding area [2, 10-13]. However, it can also produce surface defects, which will result in a reduced strength of the zirconia restorations [14]. Moreover, it could also affect the long-term performance of zirconia ceramics [15], due to the surface flaws and the tetragonal to monoclinic phase transformation [14, 16]. Therefore, alternative surface modification methods are required for improving the resin bond strength to zirconia ceramics. Several alternatives to roughen zirconia surface are reported in literature, such as SIE (selective infiltration etching) technique [17], plasma spraying [6], coating with nano-structured alumina (Al₂O₃) [18], coating with zirconia ceramic powder and pore former [19, 20], different ways of coating with silica-based ceramic [2, 6, 12, 21], and coating with silica-like seed layers [22].

Among these techniques, coating with a silica-based layer seems to be easy and more reliable, since the bonding of resin cement to zirconia ceramics may be further improved via silane coupling agents [21, 23]. However, according to previous reports, there are still several weaknesses of the existing silica coating methods. For example, the coating layer could be too thick, hence influencing the clinical fitness [23]; the zirconia surface may not be fully covered by the coating layer [6] or the coating layer
may not firmly attached to the zirconia surface [2, 9]; most of them were still based on air-abrasion [2, 12, 21] which may cause micro defects due to a high blasting pressure.

The purpose of this study was to examine the effect of an experimental zirconia-silica coating technique on durability of the bond strength between resin cement and a colored zirconia ceramic, under different priming conditions. The micro tensile bond strength test (MTBS) and Scanning Electron Microscopy (SEM) were used as a method to evaluate the bond quality.

3.3 Materials and methods

Zirconia specimens: Eighteen zirconia ceramic discs were cut from Cercon base colored blanks (Cercon base 38 colored, Shade: ivory; Degudent, Germany), with a diamond-coated cutting disc (Diamond Wafering Blade, No 11-4254; Buehler, USA) applied in a sawing machine (Isomet 1000; Buehler, USA). The blank zirconia discs were then placed in a sintering oven (Cercon Heat, Degudent, Germany) and sintered for 6:40 hr at the maximum temperature of 1350ºC, according to manufacturer’s instructions. The fully sintered zirconia discs (3.0 mm in thickness and 19.5 mm in diameter) were cleaned in an ethanol ultrasonic bath (Branson 3510; Branson Ultrasonics Corp, USA) for 10 min. The 18 discs were divided into two groups (i) the control group with no pre-treatment and (ii) the zirconia-silica coating group.

The experimental coating technique: The experimental zirconia-silica coating technique applied in this study was based on sintering the filler particles (at 1200°C for 10 min) of a flowable resin composite which was coated on the zirconia surfaces. A thin layer of Filtek supreme XT Flowable Restorative (A3 Shade; 3M ESPE, USA) was spread on one surface of the zirconia disc by a micro brush and remained uncured. Filtek supreme XT Flowable is a bis-GMA based resin composite containing silica and zirconia nanofillers and nanoclusters (65% by weight, 55% by volume). During firing of the nine discs, the resin matrix will burn, leaving the filler particles on the zirconia surface to be sintered. For the sintering procedure, a computer programmed dental porcelain furnace (STRATOS; Elephant Dental BV, The Netherlands) was used, at a heating rate of 15°C/min and holding on for 10 min at the highest temperature of 1200°C. After that the specimens were cooled down to room temperature in 100 min. All the coated specimens were ultrasonically cleaned in ethanol for 10 min.
Table 3.1  Materials used in this study

<table>
<thead>
<tr>
<th>Material</th>
<th>Basic Composition</th>
<th>LOT</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cercon base colored</td>
<td>Zirconia 93 wt %, Yttrium oxide 5 wt%, Hafnium oxide &lt; 2 wt%, Aluminium oxide and silicon oxide &lt; 1 wt%</td>
<td>2002369</td>
<td>DeguDent GmbH Germany</td>
</tr>
<tr>
<td>Filtek Supreme XT</td>
<td>Bis-GMA*, TEGDM**, Bis-EMA#, 75 nm silica nanofiller, 5-10 nm zirconia nanofiller, 0.6 - 1.4 μm zirconia/silica nanoclusters</td>
<td>6CB</td>
<td>3M ESPE USA</td>
</tr>
<tr>
<td>Filtek Z250 Universal</td>
<td>Bis-GMA, UDMA**, Bis-EMA, 0.01–3.5μm silica/zirconia particles, 82% by weight (60% by volume)</td>
<td>N193019</td>
<td>3M ESPE USA</td>
</tr>
<tr>
<td>ED Primer II Liquid A</td>
<td>2-hydroxyethyl methacrylate, 10-Methacryloyloxydecyl dihydrogen phosphate, N-Methacryloyl-5-aminosalicylic acid, Water, Accelerators</td>
<td>00283B</td>
<td>Kuraray Medical Inc. Japan</td>
</tr>
<tr>
<td>ED Primer II Liquid B</td>
<td>N-Methacryloyl-5-aminosalicylic acid, Water, Catalysts, Accelerators</td>
<td>00158A</td>
<td>Kuraray Medical Inc. Japan</td>
</tr>
<tr>
<td>Panavia F 2.0 Paste A</td>
<td>10-Methacryloyloxydecyl dihydrogen phosphate, Hydrophobic aromatic dimethacrylate, Hydrophobic aliphatic dimethacrylate, Hydrophilic aliphatic dimethacrylate, Silanated silica filler, Silanated colloidal silica, dl-Camphorquione, Catalysts, Initiators, Others</td>
<td>00437A</td>
<td>Kuraray Medical Inc. Japan</td>
</tr>
<tr>
<td>Panavia F 2.0 Paste B</td>
<td>Sodium fluoride, Hydrophobic aromatic dimethacrylate, Hydrophobic aliphatic dimethacrylate, Hydrophilic aliphatic dimethacrylate, Silanated barium glass filler, Catalysts, Accelerators, Pigments, Others</td>
<td>00223B</td>
<td>Kuraray Medical Inc. Japan</td>
</tr>
<tr>
<td>RelyX Ceramic primer</td>
<td>Ethyl Alcohol 70 - 80 wt%, Water 20 - 30 wt%, Methacryloxypropyltrimethoxysilane &lt; 2 wt%</td>
<td>N198785</td>
<td>3M ESPE USA</td>
</tr>
</tbody>
</table>

*Bis-GMA, bisphenol glycidylmethacrylate; **TEGDMA, triethylene glycol dimethacrylate; #Bis-EMA, ethoxylated bisphenol A dimethacrylate; ##UDMA, urethane dimethacrylate.
**Resin composite discs:** Eighteen resin composite discs (3.0 mm in thickness and 19.5 mm in diameter) were made of Filtek Z250 Universal Restorative (A3 Shade, 3M ESPE, USA) with a plastic mold. The composite discs were cured using Elipar FreeLight 2 (3M-ESPE, St Paul, MN, USA), according to the manufacturer’s instructions. The discs were stored in water at 37°C for at least 24 hr before bonding.

**Priming and luting:** The specimens in each group were further divided into three subgroups (n = 3), according to the priming conditions: (A) no primer, (B) a MDP-containing primer (ED primer II; Kuraray Medical Inc, Japan) and (C) a silane coupling agent containing primer (RelyX ceramic primer; 3M-ESPE, USA). A MDP-containing resin cement (Panavia F2.0; Kuraray Medical Inc, Japan) was mixed and applied on the surface of the resin composite disc, which was then seated on top of the zirconia disc at a constant load of 50 N for 60 s. Excess cement was wiped off and the specimen was light cured at four different locations for 60 s each.

**Micro Tensile Bonding Strength (MTBS) test:** All the cemented bi-layered specimens were stored in water at 37°C for 24 hr and sectioned into microbars of 1.0 × 1.0 mm [17] by using the sawing machine and a 0.3 mm thick diamond-coated cutting disc. The microbars were examined under a stereomicroscope (SZ; Olympus, Tokyo, Japan) and only intact microbars were selected. 20 microbars from each specimen were selected for the micro tensile bonding strength (MTBS) test, ten of them were tested after 24 hr in 37°C water, and the other ten microbars were tested after 30 days storage in 37°C water. Each microbar was bonded to a stainless steel attachment unit [17, 24] using a light-polymerized adhesive resin (Clearfil SE bond; Kuraray Medical Inc, Japan). The zirconia–resin MTBS was measured by applying tensile load to the bonded interface using a universal testing machine (Instron 6022; Instron Corp, High Wycombe, England) at a crosshead speed of 0.5 mm/min. Microbars which debonded spontaneously before test were included as 0 MPa in the statistical analysis.

**Analysis of failure mode:** The fractured zirconia surfaces after MTBS test were examined under a Scanning Electron Microscopy (SEM) (XL 20; Philips, The Netherlands), after gold coating. Failure mode was classified either as the four types below:

- **Type 1** adhesive mode, complete zirconia surface was visible;
- **Type 2** a mixed mode in zirconia surface and cement, both (partial) zirconia surface and a (partial) cement cover were visible;
Type 3  a cohesive fracture within the cement layer, almost all of the fracture surface was covered with cement;

Type 4  a mixed mode in zirconia surface, cement and resin composite, both cement and resin composite were detected on the zirconia surface.

Statistics: MTBS values were analyzed by three-way analysis of variance (ANOVA) to examine the effects of zirconia-silica coating pre-treatment, priming conditions and water storage periods. Post hoc multiple comparisons were conducted using Dunnett T3 tests at $\alpha = 0.05$ level, for the variances were not equal from the homogeneity test.

3.4 Results

Mean MTBS values and their standard deviations observed in the tested groups are summarized in Table 3.2. Three-way ANOVA showed that the zirconia-silica coating pre-treatment ($F = 366.0; P < 0.001$), the priming conditions ($F = 81.0; P < 0.001$), and the storage period ($F = 845.1; P < 0.001$) significantly affected the MTBS to zirconia. The interactions of zirconia-silica coating/priming conditions ($F = 92.7; P < 0.001$), zirconia-silica coating/storage period ($F = 231.4; P < 0.001$), priming conditions/storage period ($F = 32.7; P < 0.001$), and zirconia-silica coating/priming conditions/storage period ($F = 27.2; P < 0.001$) were also significant. After 24 hr water storage, zirconia-silica coating without primer did not significantly affect the MTBS ($P > 0.05$) compared to the control. Zirconia-silica coating followed by silanization (RelyX
Ceramic primer) showed a significantly (P < 0.001) higher MTBS value of 45.0 (10.9) MPa, while a significantly lower value of 20.0 (2.9) MPa with MDP-primer (ED primer II) was observed, compared to specimens in the control group with the same primer. However, after 30 days of water storage, all the subgroups pre-treated with zirconia-silica coating showed a higher MTBS value compared to the control group at the same priming condition (P < 0.001). Specimens primed with ED primer II showed a higher MTBS in the control group, but no statistical difference was detected among

**Figure 3.1** Percentage of different failure modes in each group at different storage periods after MTBS test, (top) failure modes after 24 hr in water (bottom) failure modes after 30 days in water.
Figure 3.2  SEM images (100x magnification) of different failure type. (A) Type 1, adhesive mode, complete zirconia surface was visible. (B) Type 2, a mixed mode in zirconia surface and cement, both (partial) zirconia surface and a (partial) cement cover were visible. (C) Type 3, a cohesive fracture within the cement layer, almost all of the fracture surface was covered with cement. (D) Type 4, a mixed mode in zirconia surface, cement and resin composite, both cement and resin composite were detected on the zirconia surface.

the subgroups at the same storage period (P > 0.05). Water storage could significantly (P < 0.001) decrease MTBS in the control group, from 24.1 – 30.3 to 2.8 – 3.1 MPa. The trend of decrease in the zirconia-silica coating group was only significant (P < 0.001) in silane priming subgroup (RelyX Ceramic primer), from 45.1 (10.9) to 25.9 (7.9) MPa.
Figure 3.3  SEM images of zirconia-silica coating surface. (A) (200x magnification) Zirconia surface coated with a zirconia-silica layer, showing small cracks in the coating layer. (B) (5,000x magnification) Zirconia-silica coating layer, priming with RelyX Ceramic primer. (C) (100x magnification) Fracture surface after MTBS test, zirconia-silica coating/ no primer/ 24 hr, showing cement merged into the cracks. (D) (1,000x magnification) Larger magnification of fracture surface after MTBS test, zirconia-silica coating/ no primer/ 24 hr.

SEM analysis revealed a failure mode change in the control group after 30 days of water storage, from mainly cohesive or mixed fracture into adhesive type in the control group, but in the coating group, the fracture mode was always mixed or cohesive. The percentages of different failure types in each test group are shown in
3.5 Discussion

Zirconia restorations can be bonded to teeth structures by various cements, such as zinc phosphate cement, glass ionomer cements, resin-modified glass ionomer cements, and resin cements. Although resin cements performs better than other conventional cements [25, 26], bonding to zirconia ceramics, especially for adhesive dentistry, still remains a challenge [1, 2]. Our results showed that applying zirconia-silica coating layer based on nanoparticles on the zirconia surface can improve the bond strength and maintain it for at least 30 days in water at 37°C. In contrast, the untreated specimens showed hardly any bonding after 30 days. The bonding to zirconia differed from silica-based glass ceramics. Etching the zirconia surface with for example HF, did not improve the bond strength because the ceramic structure of zirconia was resistant to acid etching [4, 27]. Furthermore, chemical bond by silane coupling agents did not provide sufficient bond strength to zirconia ceramics [6, 28]. Airborne-particle abrasion, tribochemical silica coatings, selective infiltration, plasma spraying with hexamethyldisiloxane, and chemical bonding with cements with adhesive phosphate monomers, like 10-methacryloyloxydecyl dihydrogen phosphate, can improve the bond strength to the zirconia surface [2, 6, 10-13, 17, 21]. In the present study the nano roughness and the chemical properties zirconia-silica nanoparticles were used to provide a micro retention and chemical bonding to this intermediate layer. Similar technology is used in solar cell devices, where a nanoparticle slurry with wax is fired on an electro conductive layer [29]. During the firing process the wax is burned and the nanoparticles are partially sintered resulting in nano porous network. In our study a layer of zirconia-silica embedded in an uncured resin was applied on the zirconia surface. During the firing the resin was burned and a surface as in Figure 3.3 was created. Since this surface contains silica, chemical bonding through the silica molecules is in principle possible.

The SEM images of the zirconia-silica coating showed that the zirconia surface was completely covered by the coating layer, and even after MTBS test, no chipping between the coating layer and zirconia surface was found, indicating that the coating layer was firmly attached on the zirconia surface. This maybe because the higher coating temperature was used in this technique, and also the coating agent contains both zirconia and silica nanoparticles. It is known that zirconia will transform from a
monoclinic phase into a tetragonal phase between 1170 and 2370ºC. In this study, the coating temperature was as high as 1200ºC, which may induce a phase change in zirconia fillers. So that the zirconia component in the coating layer may be sintered as a whole together with the zirconia base surface, which may generate a tight junction between the zirconia-silica coating layer and the zirconia base, through the agglomerated zirconia/silica nanocluster fillers in the coating flowable resin. However, the hypotheses of phase change and tight junctions need to be confirmed in further studies. From the SEM images, micro cracks could be found on the surface of coated zirconia surface, which is assumed to increase the surface roughness and micro interlocks. Nonetheless, the results of this study also showed that the experimental zirconia-silica coating technique could not improve the initial MTBS at the absence of silane primer. Similar phenomena were reported previously [1, 21, 30], where a weak correlation between surface roughness and the MTBS was found. As a result, it is assumed that the surface roughness of the zirconia specimen has only little influence on tensile bond strength results [1, 31], and the higher surface roughness will not guarantee a higher bond strength [16]. These studies indicated the concept that mechanical adhesion alone is not enough for providing the maximum resin bond strength to zirconia, and that chemical adhesion is also necessary for achieving optimal bond strength [32].

It is reported that some reactions may occur between the zirconium oxide and the phosphate ester monomer [13], so that MDP-containing primers or MDP-containing resin cements [33] could improve the bond strength to zirconia ceramics. The adhesive monomer is believed to have the ability to form chemical bonds with metal oxides, through van der Waals forces or hydrogen bonds at the resin–zirconia interface. These interfacial forces can improve the surface wettability of zirconia ceramic surface and then enhance the resin bond strength with low percentage of adhesive failure from ceramic surface [9]. However, in this study, the MDP-containing primer could not significantly improve the MTBS to zirconia compared with no primer subgroups. The explanation may be that the chemical reactions between MDP component and zirconia surface have certain reaction sites, and the amount of these sites is limited, which means the chemical effect has an upper limit that cannot be surpassed. Meanwhile, the resin cement Panavia F2.0 is also containing MDP monomer, which can also react with zirconia, so that the additional priming with MDP is not necessary. Silane coupling agents can also reduce surface tension and improve the wettability of a bonding agent [1]. In addition, a chemical bond can be formed between the silane coupling agent and silica layer on the ceramic surface or the resin
Experimental zirconia-silica coating

cement [13], through the formation of siloxane (–Si–O–Si–O–) network. This may explain the result that the zirconia-silica coating combined with silane primer got a significantly higher initial MTBS value in this study. Similarly, bond strength of zirconia could be increased by silanization after tribochemical silica coating [1], or an internal coating technique [21].

Even though 30 days of water storage seems a quite short time, there was already a significantly sharp decrease of MTBS after 30 days storage at 37ºC water in the control group. Meanwhile in the zirconia-silica coating group, the decrease was only significant in the silane priming condition. These results showed that although there may be some chemical reaction between MDP and zirconia surface, it’s still not stable in the water without surface pre-treatment [7-10]. Additionally, the chemical reaction between silica and silane may also not be stable in water. Similar results were also reported in previous studies, that both water storage and thermo cycling can reduce the bond strength when silane was used [34-36]. However, in this study, the MTBS of zirconia-silica coating with no primer or with ED primer II did not change significantly after 30 days of water storage.

Behr et al. (2011) [1] assumed bond strength higher than 10 MPa was considered clinically sufficient [1]. Given this estimation, after 30 days of water storage, none of the investigated bond strengths reached this level in the control group, while all the mean MTBS values in zirconia-silica coating group surpassed 10 MPa. This may suggest that even if there was a strong tendency for a reduced bond strength during a long term water storage, the bond strength of zirconia might still be clinically sufficient when zirconia-silica coating is applied. In order to get more solid proof of the effectiveness of this coating method, a longer time of water storage or a thermo-cyclical aging would be done in the future study.

3.6 Conclusion

Durable bonding to zirconia cannot be established without surface pre-treatment. The combination of zirconia-silica coating with silane coupling can improve the bonding of resin cement to zirconia.
3.7 Reference


Experimental zirconia-silica coating


