A focus on zirconia: an in-vitro lifetime prediction of zirconia dental restorations

Rosentritt, M.

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CHAPTER 8

Shear bond strength between cement and zirconia.

Keywords: zirconia, bonding, self-adhesive, resin, cement
8.1 Abstract

Objective. This study investigated the shear bond strength of various cements to zirconia ceramic.

Materials and Methods. Eighty coplanar zirconia disks (20 mm x 10 mm x 2 mm; n = 8 per group) were bonded to CoCr-cylinders. All bonding areas were sandblasted using 110 μm Al₂O₃. Four self-adhesive resin cements and four resin cements were investigated, partly in combination with a tribochemical/silane treatment. All cements were auto-polymerizing. The shear bond strength (SBS) was determined after 24 h, 30 and 90 days of water storage, and after 12 000 thermal cycles. Statistics: Mann Whitney U test; α=0.05.

Results. SBS after 24 hours varied between 9.5 MPa for the control and 37.3 MPa for Multilink. After thermal cycling, the values for Maxcem, Variolink with Rocatec and RelyX increased between 0.9 (Variolink with Rocatec) and 6.3 MPa (Maxcem). SBS for all other bonding systems decreased between 1.0 (RelyX HM) and 16.8 MPa (Multilink). Thirty days of storage in water reduced the SBS in comparison to the results after 24 h for all materials. Only RelyX and Variolink with Rocatec showed an increase between 3.4 and 11.6 MPa. After 90 days of storage, the different systems provided a SBS above 9.1 MPa. All samples of Maxcem failed after 90 days of storage. The failure mode in most cases was adhesive.

Conclusions. The systems with additional procedure steps are not superior to the simple self-adhesive methods. Some self-adhesive bonding concepts can successfully bond to the zirconia. The durability of the bonding between resin and zirconia can only be judged after long-term water storage.
8.2 Introduction

During the 1950s, standards for crown retention were described on the basis of taper, height, and surface area [1]. Decreasing taper and increasing both the preparation height and surface area increased the retention of the conventionally cemented crowns. Investigations by Palacios [2] and Ernst [3] evaluated the axial retention stress of low tapered (10° Palacios, 5° Ernst) abutments. They found that resin-modified glass ionomers retained experimental crowns as well as adhesive resin cements. It has been reported that the retentive values of adhesive resins at 24° taper were 20% higher than the retention values of conventional cements at 6° taper [4]. The retention standards of tapers less than 10 degrees cannot be fulfilled in all clinical cases and, therefore, adhesive bonding is promoted to safely lute a restoration if the mechanical retention is insufficient. In contrast to cast dentures, CAD/CAM restorations have a rough surface, due to the manufacturing process [5] that promotes an additional micromechanical interlocking of the luting agent. Nevertheless, for the restoration of ceramic implant abutments, the standards of crown retention are often not ensured: the height of an abutment is often low, the surface area is small due to screw channels or small diameters and depending on the implant insertion path the taper-degrees are high. Additionally a contamination during try-in may reduce bond strength [6]. Therefore, the cementation of the zirconia restorations on teeth, but especially on zirconia abutments/implants may require special bonding technologies. In these cases, the chair-side treatment is improved if the dentist may resign to expensive ceramic pre-treatments. Hydrofluoric acid etching does not work with zirconia surfaces because of a lacking glass phase. Some investigations describe roughening with sandblasting to achieve a resin-to-zirconia bond [5]. Good bonding qualities are described with these treatments [7, 8], but their application may also change the state and phase of the zirconia surface and damage the ceramic in the long-term [9, 10]. Sandblasting may damage thinly designed crown margins, and if it is applied in-vivo, it may harm the gingival tissue or implant body.

Silane coupling agents are wetting the bonding surface and lower the surface tension. It was demonstrated that silane can strengthen the bond between silica-based ceramic and resin cement [11, 12]. However, silanes in general fail to link between the resin and zirconia oxide-ceramic [13]. A sufficient bond between these components was demonstrated only for special silane coupling agents and after short term water storage [12], but this bond fails with increasing storage time due to hydrolysis [8, 13, 14]. Other pre-treatment methods are plasma spray treatment, addition of low-fusing porcelain layers [15], tribochemical silica coating (Rocatec, 3M Espe) [5, 13], or phosphate acid ester monomers [8, 16]. The latter was described to successfully bond resin to zirconia [13, 16]. However, Kern and co-workers emphasized that all these procedures can only be judged if a water storage time was prolonged...
over a period of 30 days [13]. Unfortunately, many investigations only take thermal cycling and storage less than one week into consideration. Therefore, they were not able to show the impact of hydrolysis on the zirconia-to-resin bond. This study investigated different zirconia-to-resin bonding concepts after different storage conditions. The aim was to favour methods which are easy to use. Self-adhesive composite cements were compared with silicoating and phosphate-ester monomer systems. The hypothesis was stated that after thermal cycling or long-term water storage of 90 days, the shear bond strength of easily applied self-adhesives could not maintain the level of sophisticated multi-step systems.

8.3 Materials and Methods

Specimen preparation
Eighty coplanar specimens of a zirconia ceramic (Cercon base, colour white; 93 wt % zirconium oxide, 5 wt % yttrium oxide, > 2 wt% hafnium oxide, > 1 wt % aluminium oxide and silicon oxide, DeguDent, G) were cut. The specimens were ground flat using a trimming device (Reco GMT 5330, Ritter, G) and sintered for six hours (1350°C) to their final dimensions (thickness 2 mm, length 20 mm, width 10 mm). The resulting surface was comparable to the surface after milling. The surface roughness was 0.9 μm.

A total of eighty cobalt-chromium (CoCr; Dentitan; 69.5 wt % Co, 24 wt % Cr, 4.5 wt % Mo and 2 wt % Ti; Krupp, G) cylindrical specimens were cast (Globocast HF3, Krupp, G). The specimens had a diameter of 5 mm and a height of 3 mm. The front sides of the cylinders were ground flat using a Motopol grinding machine (Al₂O₃, grain 800). The surface roughness after treatment was 1.2 μm.

The zirconia specimens and the front sides of the CoCr cylinders were all airborne particle abraded with 110 μm Al₂O₃ for 10 seconds at 2.8 HPa. A punched tape coated the zirconia specimens in order to restrict the working area to a diameter of 5 mm (bonding area: 19.625 mm²). The CoCr surface was treated with Metal Primer (GC, Tokyo, J).

Application of the luting agents
All resin cements (Table 8.1) were mixed and applied at room temperature under orange room light to hinder light-triggered polymerisation and to guarantee auto-polymerization. A thin cement layer was placed onto the front side of the CoCr cylinder and then pressed onto the bonding area of the zirconia specimens. The cement was allowed to set under a constant weight of one kilogram for five minutes. Surplus cement was removed. The specimens were randomly assigned into four subgroups with eight specimens per group. Group 1 was stored for 24 hours in distilled water at 37°C. The second group underwent 12,000 thermal-cycles in
distilled water with an alternating temperature of 5°C/55°C changing every 2 minutes. The entire thermal cycling process lasted 17 days. The third group was stored for 30 days and the fourth group for 90 days in distilled water at 37°C.

**Table 8.1:** Resin cements and their application procedure on zirconia.

<table>
<thead>
<tr>
<th>Resin cements</th>
<th>Manufacturer</th>
<th>Primer on zirconia</th>
<th>Mixing procedure</th>
<th>Linking agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxcem</td>
<td>Kerr, Orange, CA, USA</td>
<td>No primer</td>
<td>Self-mixing</td>
<td>Phosphate-groups</td>
</tr>
<tr>
<td>Multilink</td>
<td>Ivoclar-Vivadent, Schaan, FL</td>
<td>SR Link allow to dry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Multilink Sprint</td>
<td></td>
<td>No primer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rely X Unicem</td>
<td>3M Espe, Seefeld, G</td>
<td>No primer</td>
<td>automatic mixing 15s (Aplicap)</td>
<td></td>
</tr>
<tr>
<td>Rely X Unicem</td>
<td></td>
<td>Rocatec Plus 13s Silane: Espe Sil</td>
<td></td>
<td>Silicoating</td>
</tr>
<tr>
<td>Rely X Unicem hand-mixing</td>
<td></td>
<td>No primer</td>
<td>hand-mixing 15s</td>
<td>Phosphate-groups</td>
</tr>
<tr>
<td>Variolink II low viscosity</td>
<td>Ivoclar-Vivadent, Schaan, FL</td>
<td>Rocatec Plus 13s Silane: Espe Sil</td>
<td>hand-mixing 20s</td>
<td>Silicoating</td>
</tr>
<tr>
<td>Variolink II low viscosity</td>
<td></td>
<td>No primer CONTROL</td>
<td></td>
<td>---</td>
</tr>
<tr>
<td>Calibra</td>
<td>Dentsply, Konstanz, G</td>
<td>Two times silane, 40s allow to dry mixture of Prime&amp;Bond XP and SCA (self-cure Activator)</td>
<td></td>
<td>Silane coupling agent</td>
</tr>
<tr>
<td>Panavia F</td>
<td>Kuraray, Osaka, J</td>
<td>No primer</td>
<td></td>
<td>Di-phosphate</td>
</tr>
</tbody>
</table>

Shear bond strength test
Shear bond strength (SBS) was determined following ISO TR 11405. The specimens were fixed in a shear bond device that allowed the shear chisel to strike the CoCr cylinder. The
distance between chisel and alloy panel was 0.1 mm to avoid a cantilever effect on the adhesive surface. The universal testing machine Zwick 1446 (Zwick, G) pushed the chisel down at a cross-head speed of 1 mm/min. SBS was calculated using the formula:

Shear strength [MPa] = maximum force [N] / bonding area [mm²].

The fracture type was analysed using a Stereoscan reflected-light microscope (Zeiss, Jena, G). A fracture was defined “adhesive” if more than 75% of the alloy surface (of the restricted area) was visible. A “cohesive” fracture showed more than 75% of the surface covered with resin. All other cases were classified as “mixed fractures”. Means and standard errors of means were calculated. Statistical differences were determined using one-way ANOVA. The level of significance was set at \( \alpha = 0.05 \).

### 8.4 Results

Detailed information about the SBS results is provided in **Fig. 8.1**.

**Fig. 8.1:** Shear bond strength (means, standard error of means, *: total failure; Roc= Rocatec; cont=control; TC = thermal cycling).

The shear bond strength after 24 hours varied between 9.5 MPa for the control and 37.3 MPa for Calibra. The lowest values were found for the control Variolink without bonding (9.5 MPa) and Variolink with Rocatec treatment (13.2 MPa). Significantly highest results could be determined for Calibra with bonding pre-treatment (37.3 MPa). After thermal cycling (TC), the values for Maxcem, Variolink with Rocatec and RelyX increased by between 0.9 (Variolink with Rocatec) and 6.3 MPa (Maxcem). The shear bond
strength for all other bonding systems decreased by between 1.0 (RelyX HM) and 16.8 MPa (Multilink).

30 days of storage in water reduced SBS in comparison to the results after 24 h for all materials except Variolink with Rocatec and RelyX, where an increase of between 8.5 and 11.6 MPa was found.

After 90 days of storage, the different systems provided a SBS above 9.1 MPa. The systems RelyX and RelyX with Rocatec showed the highest values between 24.3 and 28.6 MPa. All samples of Maxcem failed after 90 days of storage.

With the exception of encapsulated Rely X, all samples failed at the ceramic, but not on the alloy side. Cohesive fractures were observed only for Rely X. All other systems showed adhesive or mixed failure modes.

8.5 Discussion

The results of the shear bond test cannot be transferred directly to the clinical situation, but this investigation allows for ranking and comparing different bonding concepts. The shear bond test may be limited when the bending influence of the components increases with increasing inner stress of all components (cylinder, coplanar plates, resin) under high shear forces [17]. The measured SBS then represents the resistance of the single components against bending and not the adhesive properties of the bonding itself. Therefore, cobalt-chromium (E~ 200GPa) was used instead of composite cylinders as described elsewhere [15, 18] in order to try to concentrate the stress at the bonding area. The loading on the bonding between the zirconia and adhesive was verified by the failure mode, which showed that the interface alloy-resin was stronger than the interface ceramic-resin. The influence of the surface roughness on the bond strength, which is a limiting factor of the quality of the testing procedure, was reduced by guaranteeing surface roughness values of about 1 μm. These values were achieved on zirconia by a sandblasting treatment with 100-150 μm grit Al₂O₃ [8]. Self-adhesive composite cements promise a simple luting procedure, because they allow a bond between the resin and zirconia without additional primer application. Both types of Rely X Unicem, Multilink Sprint and Panavia F seemed to fulfil this promise and they simplified the luting procedure on the zirconia surface. These systems showed stable SBS values under different conditions or at least sufficient values after 90 days of storage in water. The results may presumable be an effect of phosphate groups in the cement that have been described earlier [7, 13, 16, 19]. Indeed, the low results for Maxcem may allow the suggestion that phosphate components alone may not produce a sufficient long-term bond to the zirconia.

This study indicated that the different bonding systems have different sensitivity to hydrolysis. Some systems showed a strong (Panavia, RelyX handmixing or Multilink) or even
drastic (Calibra) reduction of SBS compared to the results after 24 hours but remained on a
good or at least sufficient bonding level. This is in agreement with other studies [13, 19].
Astonishingly, one self-adhesive system totally failed after 90 days of water storage.
Sandblasting of zirconia results in a remarkable initial SBS to a dual-curing composite like
Variolink. Sandblasting may activate and modify the zirconia surface, but beyond this,
sandblasting effects may not be stable and the SBS may be reduced after long-term storage [9,
10]. The addition of a silane coupling agent does not enhance the bond strength in the long-
term. The initially high SBS of Calibra with Silane was not durable. This indicates that the
silane coupling agent used did not bond to zirconia in contrast to silica-based ceramics. These
results are in agreement with other investigations [20] and studies where sufficient bond
values were reported only with special silane agents [12].
The tribochemical treatment provided no advantages for the combination with the self-
adhesive cement RelyX and only some minor advantages when it was combined with the
resin cement Variolink. These results may be explained by the hard/inert zirconia surface and
support earlier investigations where tribochemical treatment did not enhance bond strength [3]
or even did not result in durable bonding [13]. A similar result is reported on alloys where
tribochemical silica coatings work more successfully with softer alloys than with harder ones
[21]. In contrast to these results, Atsu and co-workers [18] recommended these treatments to
increase the adhesive resin bond strength to zirconium-oxide ceramic. These investigations
were performed only after 24 hours storage in water, leaving unconsidered the long-term
hydrolysis. Some authors even reported that an auto-polymerizing resin cement exhibited high
bond strength regardless of the surface treatment such as silica coating, airborne particle
abrasion, HF etching or grinding with a diamond bur [20].
Overall, the systems with additional procedure steps are not superior to the simple self-
adhesive methods, and, therefore, the hypothesis stated in the introduction had to be rejected.
Some self-adhesive bonding concepts can successfully bond to zirconia. The durability of the
bonding between the resin and zirconia can only be judged after long-term water storage.
8.6 References