Adhesion of Resin Cement to Zirconia Using Argon Plasma and Primer

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Abstract

Purpose: To evaluate the effectiveness of nonthermal atmospheric plasma (NTAP) and priming on the shear bond strength (SBS) of a resin cement to two zirconia ceramics after 24
hours and 1 year of water storage. **Materials and Methods:** A total of 120 plates (9 x 7 x 2 mm) were obtained from two types of zirconia (Katana, Kuraray Noritake; and ZirCAD, Ivoclar Vivadent) plates randomly divided into 12 groups (n = 10 each). Zirconia ceramic plates were submitted to the following treatments: (1) untreated (control); (2) treated with Z-Prime Plus (Bisco Dental) primer; (3) NTAP (Surface Plasma Tool Model SAP, Surface Engineering and Plasma Solution) application for 10 seconds; (4) NTAP for 30 seconds; (5) NTAP for 10 seconds followed by priming; and (6) NTAP for 30 seconds followed by priming.

Two silicone molds (2.37-mm diameter x 2-mm height) were positioned on the treated surface of each zirconia plate, and the resin cement (Panavia F 2.0, Kuraray Noritake) was manipulated and inserted into the molds. After light activation, two resin cement cylinders (specimens) were obtained from each plate. One specimen was tested after 24 hours, and the other after 1 year. The shear load was applied to the base of the resin cement cylinders until failure. Data were analyzed using three-way ANOVA and post hoc Tukey test (α = .05). **Results:** NTAP application alone (groups 3 and 4) increased SBS compared to the control group only at 24 hours. After 1 year, the NTAP/primer combination showed higher SBS than the other groups. Water storage for 1 year reduced the bond strength for all groups. **Conclusion:** NTAP, combined or not combined with primer, had a beneficial effect on adhesion after 24 hours and after 1 year. Water storage negatively influenced the adhesion in all groups. *Int J Prosthodont* 2021. doi: 10.11607/ijp.7118

**Introduction**

Zirconium dioxide or zirconia is a polycrystalline ceramic composed by metastable tetragonal phase that presents high fracture toughness and strength. The esthetic property of the first generation of zirconia ceramics was not considered adequate as glass ceramic and new ones are being developed to increase its translucent characteristics and their esthetic features.
The manufacture of indirect glass-ceramic and resin-based restorations by CAD/CAM technology is considered faster and simpler than traditional methods. Specifically for zirconia ceramics, the manufacture is based only on CAD / CAM technology (1), (2), (3).

Regarding to luting properties, some protocols for cementing an indirect restoration of zirconia have been recommended and they can be achieved micro-mechanically and chemically (4). Zirconia ceramics present low surface energy, low hydrophilicity and are chemically unreactive (5), (6), (7), (8). Therefore, differently from glass ceramics, zirconia is not etchable with 5 to 10% hydrofluoric acid due to its crystalline phase, without silica phase (5), (7), (9), (10), (11). Regarding the method to create micro-porosities, sandblasting with or not silica-coated particles has evidence in the literature as methods to improve the adhesion of resin cements to zirconia (12), (13). On the other hand, chemical adhesion can be obtained with surface treatments, such as primer applications (14).

Thus, to improve the adhesion to Zirconia some surface treatments have been suggested (15), (16), (17) and although comparing these studies is a difficult task due to the different methods used (12), (18), (19), (20), many authors have suggested the use of sandblasting, primers and specific resin cements (4), (12), (13), (14), (15), (16), (17). Regarding primers, studies have indicated that the acidic monomers such as 10-metacryloxydecyl dihydrogen phosphate (10-MDP) can chemically react with metal oxides, such as zirconia and alumina (4), (13), (21). Commercially, 10-MDP is contained in the primer solutions and resin cements, which are specific to be used in zirconia ceramic cementation (22).

An alternative zirconia surface treatment that has been suggested is the non-thermal atmospheric plasma (NTAP) application, which can improve surface hydrophilicity and wettability, reduce contact angle (5), (6), (8) and also used as decontamination method (23), (24). NTAP produces reactive species that are created by the interaction of ions and electrons.
of argon gas with the oxygen from atmosphere. Reactive species are able to break chemical stabilized bonds, forming polar groups and chemical sites on the surface to provide adhesion of other materials (25), (26), (27).

Studies have shown positive effects of primers and NTAP application in short-term analysis, however evaluations after long storage times are necessary to determine the importance of primer and NTAP applications for zirconia cementation (6), (7), (8), (28). Thus, this study aimed to evaluate the effectiveness of NTAP and priming on the shear bond strength of a resin cement to two zirconia ceramics, after 24-hours and one-year of water-storage. The null hypotheses tested were: 1- the use of NTAP and/or primer would not improve the bond strength of resin cement to zirconia compared to control and 2- the water-storage for one year would not reduce the bond strength promoted by the use of NTAP and/or primer.

Materials and Methods

Two commercial zirconia ceramics were tested: Katana (Kuraray Noritake Dental, Tokyo, Japan – lot # BNAHZ,) and ZirCAD (Ivoclar Vivadent AG, Schaan, Liechtenstein – lot # M60517). CAD/CAM blocks were sectioned to obtain one hundred and twenty zirconia plates, which were sintered according to their manufacturers’ instructions. The final dimension of each plate was 9 mm length x 7 mm wide x 2 mm thick. Afterwards, zirconia plates were embedded in an acrylic resin and the samples divided in six groups that represented the surface treatments:

1- control (untreated – resin cement applied to zirconia without primer or NTAP applications)
2- primer application for 10 seconds and dried for 5 seconds (Z-Prime Plus, Bisco Dental Products, Schaumburg, IL, USA)
3- NTAP application for 10 seconds
4- NTAP application for 30 seconds
5- NTAP application for 10 seconds + Z-Prime Plus for 10 seconds and dried for 5 seconds

6- NTAP application for 30 seconds + Z-Prime Plus or 10 seconds and dried for 5 seconds

Plasma tool model SAP - Lab applications (Surface – Engineering and Plasma Solution LTDA, Campinas, SP, Brazil) was the equipment used to treat the zirconia samples. Argon was used as the working gas (Praxair 4.8, White Martins Gases Ind. S.A., Rio de Janeiro, RJ, Brazil), with an output of 1.0 liter per minute. The application was performed in a dried surface for either 10 or 30 seconds, with nozzle at 10 mm distance from the zirconia surface. The zirconia surface activation was tested using contact angle evaluation (5) before performing this study.

Two silicon molds (Virtual, Ivoclar Vivadent) with central hole (2.37 mm diameter X 2 mm height) were positioned over each treated zirconia surface and filled with uncured resin cement (Panavia F 2.0, Kuraray Noritake). After light activation (Valo, Ultradent Products Inc., South Jordan, UT, USA), molds were removed, and two resin cement cylinders bonded to each zirconia plate were obtained. Plates were stored in distilled water for 24 hours at 37°C and for each plate, one of resin cylinder was tested in a shear device, while the other one kept stored for one year before testing (n = 10).

The shear bond strength test of samples was performed in a universal testing machine (Ez-Test, Shimadzu Corp., Kyoto, Japan) with the shear load applied to the base of the resin cement cylinder with a loop orthodontic wire (0.20 mm diameter) at speed of 0.5 mm/min until failure. Bond strength values were obtained by dividing the maximum load by bonding area (MPa). Data attended all assumptions related to normal distribution and homoscedasticity. Three-way ANOVA analyzed the bond strength data (SAS V9 software, SAS Institute, Cary, NC, USA) that was conducted in a factorial mode (2x2x2 / factors: type of zirconia, surface treatment and evaluation time) (α = 0.05). The post hoc Tukey Test identified differences among groups.
Results

Bond strength means are presented in Table 1. Three-way ANOVA demonstrated that the type of zirconia, the surface treatment and the evaluation time factors significantly influenced the bond strength results, with significant interaction between the factors ($p < 0.01$). NTAP combined with primer or not increased the bond strength compared with control and priming only at 24 hours ($p < 0.05$), except for NTAP applied to Katana for 10 seconds ($p > 0.05$).

The water-storage for one year decreased significantly the bond strength of resin cement to both zirconia ceramics and bond strength obtained for NTAP combined with priming was higher than other groups such as control, priming and NTAP only, after one year storage ($p < 0.05$). The bond strength of the resin cement was higher to the ZirCAD group than Katana, for the control and in the NTAP application only, all at 24 hours ($p < 0.05$). The failure mode of tested samples was 100% adhesive, i.e., the fracture occurred at the zirconia-resin cement interface, with no remnant of resin cement over zirconia surface.

Discussion

The first null hypothesis stating that the use of NTAP and/or primer would not improve the bond strength of resin cement to zirconia was rejected, because NTAP and/or primer increased the bond strength after water storage for 24 hours and one year. The second hypothesis was also rejected because the bond strength values promoted by NTAP and/or primer at one year were lower than those obtained at 24 hours. Thus, this study showed that NTAP and/or primer improved the bond strength compared to the control (untreated) at 24 hours, but this bond strength was not stable, reducing significantly after one year, regardless the type of zirconia ceramics. This reduction seemed to be more significant when the primer and NTAP were applied alone. On the other hand, their combination showed less reduction in the bond strength and had the highest values at one year.
Two generations of zirconia ceramics were tested, and few differences were found between them. These differences were found only at 24 hours and the bond strength was always lower for the Katana zirconia. ZirCAD belongs to a third generation of zirconia ceramics (4Y-PSZ), while Katana to the second one (3Y-PSZ). Thus, ZirCAD has more cubic phase (> 25%) being more translucent, while Katana has less cubic phase (< 15%C), which provides more resistant to fracture and opacity (1). In addition, ZirCAD is a pre-sintered yttria-stabilized zirconium dioxide, while Katana is non-pre-sintered one. This might influence on zirconia wettability, contact angle and porosity (5), (7). Also, polar fraction of both zirconia ceramics is different and according to a theoretical simulation, the presence of a majority of non-polar groups in the zirconia surface explains the low hydrophilic properties and the low surface energy of zirconia ceramics (29).

In order to change zirconia surface hydrophilic properties, NTAP was applied and the results of this study at 24 hours showed that NTAP application significantly increased the bond strength of resin cement compared with control, except for Katana treated with NTAP for 10 seconds. A study (29) reported higher surface energy levels resulted from the polar components after treatment with NTAP. In that study, the contact angle decreased approximately 50% when compared to untreated surfaces, because new polar groups were formed on the zirconia surface following the exposure to NTAP. Besides new polar groups, the interaction of ions and electron from argon plasma with zirconia also opens chemical sites to further bonding (30), (31), (32). Additionally, studies have showed that the application of NTAP on the zirconia surface seems to remove organic residues, promotes a surface restructure (30), decreases carbon amount, and enhances oxygen ones (23), (29). As consequence, the zirconia surface becomes more hydrophilic, which improves its wettability, reduces surface contact angle (24) and promotes a better resin bonding (7), (8) without changing the surface morphology.
Traditional methods to create micromechanical retentions are commonly recommended to silica- and zirconia-based ceramics, which increases the microporosities, clean surfaces and improves wettability due to the surface area available for mechanical interlocking of resin cement (36). Sandblasting with aluminum oxide (Al₂O₃ / 25-50 µm) and the use of 10-MDP containing primers are widely used and has already been shown to be effective in clinical and in vitro studies (4), (12), (35), (36), (37). Therefore, to evaluate the chemical interactions only of primer and NTAP with zirconia, in this study zirconia ceramics were not sandblast with Al₂O₃, in order to have a more smooth surface without microporosities that could interfere on results by increasing the bond strength, which would impaired the evaluation of the adhesion promoted by primer e NTAP. Thus, all failures observed in the tested samples were adhesive, i.e. there was no remnant of the resin cement on the zirconia surface, due to absence of sandblasting of the zirconia that would produced more surface roughness and then, more retention of resin cement on its surface.

Regarding to chemical adhesion to zirconia, it was used a primer and a resin cement containing 10-MDP acidic monomer (21), (38). Z-Primer Plus can be used with various resin cements and is a single-bottle priming agent indicated to treat zirconia and alumina oxide-based ceramics, as well as other types of metals/alloys, composites and endodontic posts. The use of Z-Primer Plus alone did not differ from control at 24 hours and one year, showing that 10-MDP based-resin cement presented the same outcome when using in combination with this primer. Perhaps, another type of resin cement without 10-MDP could be benefited with the use of this primer based on 10-MDP (13), (14). Panavia F 2.0 is a dual-cured resin-based cement commonly used in prosthetic dentistry, and consists of two pastes that which contains 10-MDP, other dimethacrylates, silanated fillers, initiators, catalysts, reaction accelerators and a previous priming step corresponding a 10-MDP-based bonding agent. It combines auto- and light-curing polymerization reactions for several clinical conditions, in either the presence or
absence of the light (39), but the light-activation still important to achieve better mechanical properties for this resin cement (40).

Previous studies already reported the bond strength reduction of resin cement to zirconia over the years, even using primers and resin cements containing functional monomers in order to improve the adhesion (7), (21), (41), (42), (43). The aging method used in this study was the water-storage for one-year. The aging results also showed significant zirconia bond strength reduction of resin cement, even when zirconia was treated with NTAP and/or primer. Hydrolytic degradation may explain in parts the loss of adhesive effectiveness of primers and resin cements (7), (21), (40), (41). The first step of hydrolytic degradation is the uptake of water into the polymer and the second one is the chemical bond breaks, and diffusion of low molecular weight products out of the polymer (44). The bonding loss between the zirconium dioxide and functional monomers also occurs under influence of water (21,45). Besides, even though NTAP promotes a contact angle reduction and bonding improvement, the adverse effect of increased wettability is the attraction of water, which can accelerate hydrolytic degradation (28), explaining the decrease in bond strength using NTAP and/or primer.

This study tested two different application times to two different generations of zirconia ceramics and when NTAP was applied alone no significant difference was found between times (10 and 30 seconds). When ZirCAD was treated with NTAP only, ten seconds was enough to produce higher bond strength than those obtained for control or primer application with outcomes comparable with the combination of primer and NTAP for 30 seconds at 24 hours. For Katana also at 24 hours, NTAP for 30 seconds and primer combination yielded higher bond strength than those obtained with control, primer and NTAP application alone, regardless the application time. However, the best bond strength results of
resin cement to zirconia ceramics at one year were obtained when the combination between NTAP and primer was used, regardless the NTAP application time.

Therefore, the suggestion for a technique to bond a resin cement to zirconia must consider the time-consuming, the need for equipment, the types of materials used and the complexity of the techniques (37). This study showed bond strength results after 24 hours and one year of water-storage, which were important to estimate the zirconia bonding durability formed with a resin cement, a primer, the NTAP and NTAP and primer combination. The comparison of the results of this study with previous ones should be done with caution, as the studies used different sources and type of plasma.

Finally, it is not known whether increasing the NTAP application time, beyond 30 seconds used in this study, could significantly improve the bond strength of resin cement to zirconia and produce an adhesion more stable over time. A study monitored the contact angle of water droplets for 70 hours in order to evaluate the longevity of the effect of NTAP on two zirconia ceramic surfaces. After NTAP application for one minute, the contact angle decreased approximately 50%. Regarding the recovery of hydrophobicity, the duration of the effect of plasma on zirconia surfaces was at least five hours (5). In addition to increasing the NTAP application time to improve the adhesion of resin cement, the duration of the NTAP effects can also vary depending on the type of zirconia.

Conclusion

The NTAP combined or not with primer can be beneficial to improve the bond strength of resin cement to zirconia ceramics, after 24 hours and one year. Results suggested that the bond strength of resin cement to zirconia ceramics decreased following the water-storage for one year, regardless the treatment used.
Disclosure statement

The authors of this article certify they have no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company in this article.

References


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Table

Table 1. Shear bond strength of resin cement to ZirCAD and Katana zirconia ceramics.

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>Surface Treatment</th>
<th>Control (Untreated)</th>
<th>Primer</th>
<th>NTAP 10s</th>
<th>NTAP 30s</th>
<th>NTAP 10s + Primer</th>
<th>NTAP 30s + Primer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>24 hours</td>
<td>1 year</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Katana</td>
<td>Control (Untreated)</td>
<td>4.5 (1.1) c B *</td>
<td>1.9 (0.5) b A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Primer</td>
<td>5.1 (1.0) c A *</td>
<td>2.8 (0.7) b A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NTAP 10s</td>
<td>6.9 (2.0) bc B *</td>
<td>2.9 (0.8) b A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NTAP 30s</td>
<td>7.7 (1.3) b B *</td>
<td>2.9 (0.4) b A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NTAP 10s + Primer</td>
<td>9.7 (1.9) ab A *</td>
<td>4.9 (0.9) a A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NTAP 30s + Primer</td>
<td>11.9 (2.1) a A *</td>
<td>4.6 (0.4) a A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZirCAD</td>
<td>Control (Untreated)</td>
<td>6.9 (1.2) b A *</td>
<td>2.2 (0.2) b A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Primer</td>
<td>7.6 (1.5) b A *</td>
<td>2.0 (0.6) b A</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>NTAP 10s</td>
<td>11.4 (2.2) a A *</td>
<td>3.0 (0.6) b A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NTAP 30s</td>
<td>10.7 (1.1) a A *</td>
<td>2.8 (0.4) b A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NTAP 10s + Primer</td>
<td>11.9 (2.3) a A *</td>
<td>5.2 (0.8) a A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NTAP 30s + Primer</td>
<td>9.6 (1.6) ab A *</td>
<td>5.5 (1.0) a A</td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

Means followed by different letters (lower-case letters compare treatments for the same zirconia and evaluation time; and capital letters compare zirconia ceramics within the same treatment and evaluation time) differ among them (p < 0.05). Mean followed by asterisks differ from the same treatment and zirconia after one year of water-storage (p < 0.05).