Cleaning and Surface Treatment Protocols for Repair of Aged Y-TZP with Composite Resin

The purpose of this study was to evaluate the cleaning and surface treatment techniques in the repair of aged and contaminated yttrium oxide-stabilized tetragonal polycrystalline zirconia (Y-TZP). From a total of 80 specimens of Y-TZP, 60 were subjected to aging simulation in a buccal environment with degradation in an autoclave for 24 hours (127°C/1.5 bar) and contaminated with Streptococcus mutans. The surfaces were cleaned with a triple syringe (air/water jet; n = 20) or isopropyl alcohol (n = 20), or by prophylaxis (n = 20) with pumice and water. The remaining 20 specimens comprised the control group. All specimens were then treated with silicatization (n = 10 per group) or adhesive (n = 10 per group) and repaired with composite resin. Analyses of shear strength, failure mode, and roughness were performed by electron microscopy. Data were analyzed by two-way analysis of variance (ANOVA) and t test (α = .05). Statistical significance was set at P < .05. Two-way ANOVA was significant for aging and surface treatments (P = .049), but was not significant for surface cleaning (P = .05). ANOVA results were statistically significant for surface treatments (P < .0001), with higher resistance for the silicatization groups. The failure mode was mostly adhesive for all specimens. The roughness was not significant for aging and control groups (P > .05). Triple-syringe and prophylaxis cleansing followed by silicatization was the most efficient treatment for the repair of aged and contaminated Y-TZP. There is reduced repair efficiency with the aging of Y-TZP.

The use of yttrium oxide-stabilized tetragonal polycrystalline zirconia (Y-TZP) is well accepted in the dental community for the production of fixed prostheses as an infrastructure material for the replacement of lost or fractured dental elements. However, the greatest concern with this type of restoration is related to ceramic veneer chipping and, consequently, the loss of the prosthetic restoration.1–15 The chipping of the veneering porcelain (Fig 1) can be the result of several factors, including the thermal expansion coefficient difference between ceramics,10,16,17 defects due to the processing technique, thick porcelain layers, low thermal conductivity, infrastructure anatomy,5,18 or even parafunctional habits.8 However, chipping can sometimes be repaired or polished without removal of the restoration, avoiding further trauma to the remaining tooth and at lower cost to the patient.3,5,6,8,9,11,13–15 In these cases, the dentist may opt for the indirect technique, in which another porcelain coating is made and cemented into the delaminated region,18 or the direct technique, in which the chipped area is repaired directly in the mouth with resin.5,14,15 In both cases, it is important to create a suitable (clean) surface for adhesion.

In addition, surface treatments are important for successful resis-
tance at the repair site. While several methods for bonding Y-TZP and resin can be found in the literature, the best results have been seen with silicatization and silane application\(^3,6,9,14,18,19\) or conditioning with primer/silane containing 10-MDP (10-methacryloyloxydecyl dihydrogen phosphate)\(^3,6,9,18,19\)

Once chipped, the zirconia infrastructure is exposed to humidity and temperature variations in the buccal environment. Studies have shown that the presence of water at low temperatures in contact with zirconia can induce transformation from the tetragonal to the monoclinic phase, with concomitant changes in properties.\(^14,20–22\)

However, there is no evidence that contamination in degraded zirconia can affect the shear strength of repaired resin. Thus, this in vitro study aimed to evaluate the cleaning methods and surface treatments used to repair the zirconia structure with composite resin after the structure was shattered, exposed in the buccal environment, and undergoing degradation and contamination.

The following null hypotheses were tested: (1) The cleaning methods will not be statistically significantly different with respect to shear strength after biofilm removal; (2) surface treatment techniques will not influence the shear strength; and (3) the shear resistance of aged zirconia will not differ from that of unaged zirconia.

**Materials and Methods**

**Sample Processing**

Presintered blocks of Y-TZP ceramic (In-Ceram 2000 YZ cubes, VITA Zahnfabrik) were sectioned \((n = 80)\) using a saw under water cooling (IsoMet 1000 Precision Sectioning Saw, Buehler). The blocks were polished with silicon-carbide paper of decreasing grit size (from 1,200 to 400) under water irrigation, then cleaned in an ultrasonic isopropyl alcohol bath. Sintering of specimens was performed in a furnace (Zyrcomat T, VITA Zahnfabrik). In sequence, the blocks were divided into the aged \((n = 60)\) or control groups \((n = 20)\). Specimens belonging to the aged group were subjected to aging in an autoclave \((127^\circ C/1.5\) bar) for 24 hours as well as contamination, whereas the control groups were not subjected to any type of degradation + contamination. All specimens of aged groups were further sterilized for 15 minutes in an autoclave for standardization and then contaminated with *Streptococcus mutans* for 48 hours.

**Biofilm Adhesion**

Biofilm adhesion was achieved by a modified version of the technique proposed by Anami et al.\(^23\) and a standard suspension of *S. mutans* (ATCC 35688) was then prepared. The bacteria were plated in brain-heart infusion agar (Difco) and incubated in CO\(_2\) for 24 hours at 37°C. After incubation, the growth was suspended in a sterile physiologic solution (0.9% sodium chloride), where the number of suspended cells was 106 cells/mL, counted by spectrophotometry (Micronal B582 Deuterium Lamp). The optical density and wavelength parameters were 0.620 and 398 nm, respectively. These parameters were previously established by means of a standard curve of CFU/mL vs absorbance. Adherence of the biofilm was then checked in an aseptic environment.
in a laminar air-flow chamber. Each specimen was positioned in a single well of sterile 24-well polystyrene tissue-culture plates, with 2.0 mL of broth and 0.1 mL of standardized S. mutans suspension. The plates were then sealed and incubated in CO$_2$ for 48 hours at 37°C.

### Cleaning and Repairing Contaminated Y-TZP Blocks

After degradation and contamination with S. mutans, the specimens were subjected to one of the cleaning methods described in Table 1 (n = 20 per cleaning method). In sequence, the aged specimens and the control group were subjected to silicatization or adhesive surface treatments (n = 10 per surface treatment per group), detailed in Table 2. Figure 2 shows a schematic of the study design. After surface treatment, the composite resin (Opallis shade A2E, FGM) was applied with increments of approximately 2 mm to a transparent polyethylene mold (3.5-mm diameter, 4-mm height) on the surfaces of the Y-TZP specimens, and photopolymerization (Radii-cal, SDI) was performed for 20 seconds. The specimens were then stored in water for 24 hours.

### Shear Bond Strength

The shear strength test was performed on all specimens in a universal testing machine (EMIC DL-1000, Instron). A metal device was used to position the specimen on the test machine so that the ceramic/resin interface was perpendicular to the horizontal plane. A metal wire was attached to the load cell (50 kgf) and around the resin, and then pulled at the ceramic/resin interface with a constant velocity of 0.5 mm/minute until fracture. The load to failure (N) was recorded, and the mean shear bond strengths (MPa) were calculated ($\sigma = F/A$).

### Failure Mode Analysis

After debonding, the specimens’ surfaces were analyzed qualitatively by stereomicroscopy, and the failure modes were classified as: (1) adhesive failure between zirconia and resin; (2) predominantly adhesive failure between zirconia and resin; (3) cohesive resin failure; or (4) mixed failure.

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**Table 1 Methods of Cleaning Specimens Contaminated by S. mutans**

<table>
<thead>
<tr>
<th>Cleaning methods</th>
<th>Application procedures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triple syringe</td>
<td>Water/air jet was applied for 20 s, and the sample was dried with an air jet for 10 s.</td>
</tr>
<tr>
<td>Alcohol</td>
<td>Isopropyl alcohol was applied for 20 s using a sterile cotton ball, and an air jet was applied for 10 s.</td>
</tr>
<tr>
<td>Prophylaxis</td>
<td>Prophylaxis with pumice and water was performed for 20 s using a contra-angle and brush. A water/air jet was applied for 10 s, and the sample was dried with an air jet for 10 s.</td>
</tr>
</tbody>
</table>

**Table 2 Surface Treatments After Cleaning Specimens Contaminated by S. mutans**

<table>
<thead>
<tr>
<th>Surface treatments</th>
<th>Application procedures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicatization</td>
<td>Airborne-particle abrasion was performed with 30-μm silica-modified Al$_2$O$_3$ particles (Rocatec Soft, 3M ESPE) with an abrasion unit (2.5 bar/4 seconds; DENTO-PREP, Rønvig Dental). An air jet was then applied for 20 s, and then a microbrush was used to apply silane (Monobond N, Ivoclar Vivadent) for 60 s.</td>
</tr>
<tr>
<td>Adhesive</td>
<td>Application of one layer of 10-MDP-containing adhesive (Scotchbond Universal Adhesive, 3M ESPE) using a microbrush, then photopolymerized (Radii-cal, SDI) for 20 s at an intensity of 1,200 mW/cm$^2$.</td>
</tr>
</tbody>
</table>
**Scanning Electron Microscope**

The qualitative analysis of bacterial colonization on the Y-TZP surfaces was performed by scanning electron microscopy (SEM). Five specimens (one from each of the following groups: control, autoclaved, triple syringe, alcohol, and prophylaxis) that had not been treated with adhesive or silicatization were fixed for 1 hour in a 2.5% glutaraldehyde solution and dehydrated in sequential ethanol baths (10%, 25%, 50%, 75%, and 90% for 20 minutes, and 100% for 1 hour), as suggested by Pereira et al.24 The plates were then incubated at 37°C for 24 hours to dry the discs. Specimens were then fixed in a metallic base with carbon adhesive tape (SPI Supplies), sputter-coated with a gold-palladium alloy (SC7620, Quorum Technologies; 130 seconds, 10 to 15 mA, 130 mTorr vacuum, 3.5 nm/minute metallization rate, 80Å Pd-Au layer [approximate]), and observed by SEM (20 kV; Inspect S50, FEI).

**Roughness**

For roughness analysis, a rugosimeter (SJ-400, Mitutoyo) was used with an analyzing tip. The parameters used were: Ra (mean roughness), corresponding to the arithmetic mean of the absolute values of the spacing ordinates (peaks and valleys) in relation to the midline within the measurement path; and Rz (mean depth roughness), corresponding to the arithmetic mean of the absolute values of the greatest distance point of ordinates above and below the midline. A different selection of 20 aged and control specimens that had not been surface-treated with adhesive or silicatization (4 from each of the following groups: control, autoclaved, triple syringe, alcohol, and prophylaxis) were used to evaluate the effectiveness of the cleaning methods. For each specimen, three parallel measurements were made in one direction and three parallel measurements in another direction, for a total of six measurements. The analyzer tip ran a total of 3 mm, at

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**Fig 2** Schematic of the study design. First part of the study: Test specimens were aged (autoclaving) and contaminated before cleaning and surface treatment. Second part of the study: Application of adhesive or silicatization was performed on the test and control specimens.
a speed of 0.5 mm/second for each measurement. After these six measurements, the average values were obtained for Ra and Rz.

**Statistical Analysis**

A power analysis was performed for bond strength testing. Thus, for a sample size of 10 and an SD of ±3 MPa, the means comparison with the Tukey test \((P < .05)\) showed a difference of 5.5 MPa and power above 80%. Two-way analysis of variance (ANOVA) and Tukey test were then used for bond strength comparisons between the control and aged/contaminated groups (experimental groups) after surface treatments, and also for comparison between the aged/contaminated groups after cleaning methods and surface treatments. For statistical analysis of roughness \((n = 20\) specimens), \(t\) test was used. Differences were considered statistically significant at \(P < .05\).

**Results**

Two-way ANOVA \((P < .05)\) and the bond-strength Tukey tests (control vs experimental groups) showed a clear drop in bonding in experimental groups (Table 3), and silicatization as a superior surface treatment compared to adhesive, for which an interaction effect was found \((F_{\text{df}}[2;48] = 3.568; \; P = .036)\) and far superior bond strength for silicatization, whereas the cleaning method was not statistically significant \((P = .050)\). However, the decrease in shear bond strength values observed after cleaning with alcohol is worth mentioning, mainly in the alcohol+adhesive group, which presented five specimens with pretest failure (not included in the statistical analysis; Table 4). No cohesive or mixed failures were observed (Table 5).

Table 3 Shear Bond Strength (MPa) in the Comparison Between Control and Aged Groups

<table>
<thead>
<tr>
<th>Groups</th>
<th>Shear bond strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control group</td>
<td></td>
</tr>
<tr>
<td>Adhesive</td>
<td>11.83 ± 3.21\textsuperscript{B}</td>
</tr>
<tr>
<td>Silicatization</td>
<td>17.39 ± 4.15\textsuperscript{A}</td>
</tr>
<tr>
<td>Aged group</td>
<td></td>
</tr>
<tr>
<td>Adhesive</td>
<td>2.71 ± 0.89\textsuperscript{C}</td>
</tr>
<tr>
<td>Silicatization</td>
<td>12.87 ± 4.43\textsuperscript{B}</td>
</tr>
</tbody>
</table>

Values are shown as mean ± SD. The same superscript letter indicates no statistically significant difference.

For the aged group. Student \(t\) test showed no statistically significant differences in Ra \((P = .541)\) and Rz \((P = .059)\) between the aged and control groups.

**Discussion**

Metal-free ceramic systems with a zirconia and veneering porcelain have thermal residual stresses\(^{10,16,17}\) and may experience chipping\(^{1–15}\). The possibility of chipping being repaired with composite resin, without total loss of the indirect restoration, must be considered\(^{3,5,6,8,9,11,13–15}\). The first null hypothesis was accepted in the present study because the bond strengths did not differ significantly depending on the cleaning methods for biofilm removal. The second and third null hypotheses were rejected, since the surface treatment techniques influenced shear bond strength values, and the control zirconia behaved differently from aged zirconia in terms of bonding.

In this study, zirconia aging was simulated prior to cleaning and repair to provide an analogy to the
Table 4 Shear Bond Strength (MPa) by Cleaning Method with Comparison Analysis (Tukey Test)

<table>
<thead>
<tr>
<th>Surface treatment</th>
<th>Cleaning method</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Triple syringe</td>
<td>Alcohol</td>
<td>Prophylaxis</td>
</tr>
<tr>
<td>Adhesive</td>
<td>2.71 ± 0.89&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.91 ± 0.46&lt;sup&gt;c,*&lt;/sup&gt;</td>
<td>3.17 ± 1.09&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Silicatization</td>
<td>12.86 ± 4.43&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7.98 ± 2.66&lt;sup&gt;a&lt;/sup&gt;</td>
<td>11.36 ± 3.03&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Values are shown as mean ± SD. This group presented five specimens with pretest failure, which were not included in the statistical analysis. Uppercase letters indicate statistically significant differences within rows.

Table 5 Failure Percentages

<table>
<thead>
<tr>
<th>Group</th>
<th>Failure mode</th>
<th>Adhesive</th>
<th>Predominantly adhesive*</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS-S</td>
<td>80%</td>
<td>20%</td>
<td></td>
</tr>
<tr>
<td>TS-A</td>
<td>100%</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>AL-S</td>
<td>100%</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>AL-A</td>
<td>100%</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>PX-S</td>
<td>50%</td>
<td>50%</td>
<td></td>
</tr>
<tr>
<td>PX-A</td>
<td>80%</td>
<td>20%</td>
<td></td>
</tr>
</tbody>
</table>

TS = triple syringe; AL = alcohol; PX = prophylaxis; A = adhesive; S = silicatization.

*Sixty percent or higher of the substrate (zirconia) is exposed after debonding.

Fig 3  SEM of the Y-TZP specimens: (a) Control, (b) autoclaved zirconia, (c) aged (autoclaved and contaminated), (d) aged and cleaned with a triple syringe, (e) aged and cleaned with prophylaxis (arrow indicates remnants of stone pumice), and (f) aged and cleaned with alcohol.
clinical situation, as zirconia will probably suffer low-temperature degradation after delamination. None of the surface treatments in the aged ceramic group were able to present shear strength compatible with that of the control group, demonstrating the importance of aging before simulation of a repair protocol, as it may contribute to decreased adhesion values.

Studies in which x-ray diffraction was used to evaluate zirconia degradation in a hydrothermal medium for 8 and 12 hours reported monoclinic phase formation; those results can be compared with the results of the present study, in which aging occurred for 24 hours with a probable shift from a tetragonal to a monoclinic phase, which may have favored the microstructural changes, resulting in low shear bonding at the interface. On the other hand, the present study and a study by Galvão Ribeiro et al did not find a reduction in bond strength after aging.

Although ceramic materials exhibit low bacterial adhesion, biofilm formation begins a few hours after first material exposure in the oral cavity. Surface irregularities can favor the accumulation of biofilm, but in the present study, there were no statistically significant differences between the surface roughness of the aged and control groups.

The different cleaning methods did not influence bond strength values, which is in agreement with the results reported by Phark et al, who also evaluated shear strength after contamination and cleaning. The cleaning protocols used in the present study (triple syringe, isopropyl alcohol, and prophylaxis) are the most common methods. Feitosa et al demonstrated that, among all methods, a relatively new material containing zirconia beads (Ivoclean) was the only one to provide a fresh zirconia surface for bonding after saliva contamination. In this regard, one critical point of the present study is that one bacteria strain may be removed more easily, whereas saliva and/or a more complex biofilm (of several species) may be more difficult to remove with the cleaning methods used herein. This needs further investigation.

It could be seen by SEM that (1) bacteria still remained on the surface after being cleaned with a triple syringe; (2) with the prophylaxis method, fragments of pumice could be observed; and (3) the surface seemed cleaner with the alcohol cleaning method. The cleaning method with alcohol presented the lowest bond strength, and five samples were lost before testing. Previous studies showed the same trend but did not perform additional surface treatments afterwards. The presence, even trace amounts, of organic elements (such as carbon, oxygen, and nitrogen) probably impaired adhesion to the composite.

It was observed that silicatization followed by the application of silane, regardless of the cleaning method, presented significantly higher shear strength values for all groups compared with the groups treated with 10-MDP–containing adhesive, probably due to chemical bonding as well as micromechanical retention caused by air-abrasion. Silicatization allows for the generation of a silica-rich surface, facilitating stronger adhesion between the resins and the silanated surface. In a recent study about methods for repairing zirconia that was aged for 8 hours in an autoclave, it was observed that silicatization followed by silanation was the best method for bonding; this was also observed in the present study with no change in bond strengths, even for contaminated and aged zirconia.

In the failure mode analysis, it was observed that there was total adhesive failure in most specimens, as was found in other studies. This was due to the weak bonding of the resin to the zirconia. However, clinically, the veneering porcelain may also be involved in the area of fracture, in which case the dentist should evaluate the fracture and select the best method of repair, taking both ceramics into consideration. Studies reporting repairs on feldspar porcelain, as well as repairs on both zirconia and feldspar porcelain, found better results after hydrofluoric acid conditioning was used followed by silane and adhesive, whereas zirconia was treated with airborne-particle abrasion (silicatization) and silane.

If it is clinically considered that delaminated ceramic will be susceptible to aging due to oral fluids and contamination, it should be repaired as soon as possible. The surface treatment, preferably silicatization, of aged zirconia prior to resin repair should also be performed in order to obtain the highest bonding quality.
Conclusions

Among the evaluated methods for the repair of chipped and degraded zirconia, cleaning contaminated zirconia with prophylaxis (pumice stone and water) or a triple syringe (water and air jet), followed by silicatization and slame treatment, was most effective for bonding. This treatment should occur as soon as possible, as this would reduce the aging of zirconia resulting from exposure in the buccal environment, which was also a determinant for decreased bonding.

Acknowledgments

The authors would like to thank Dr Ivan Balducci (Institute of Science and Technology, Universidade Estadual Paulista) for providing helpful research statistics. The authors declare no conflicts of interest.

References