SUMMARY

**Purpose:** To evaluate the influence of different surface preparation methods on the bond strength of 2 composite resins to zirconium oxide ceramic restorations.

**Material and Methods:** 80 specimens 2 mm thickness of IPS e.max ZirCAD blocks were prepared and divided into 4 groups. The first group was left as a control (C). In the second group, specimens were treated with sand blasting (SB). In the third group, specimens were treated with roughening the surfaces with diamond burs (DB). Laser irradiation was applied for the last group (LI). Specimens were divided into 2 subgroups (n: 10) for each surface treatment protocol followed by the application of 2 resin cements: Multilink Automix (MA) and Multilink Sprint (MS). The shear bond strength was measured using the universal testing machine with a crosshead speed of 0.5 mm/min. The retentions force required to remove the specimens was recorded. After debonding of specimens, the fractured surfaces were evaluated with an optical microscope to classify the failure modes and selected specimens for each group were examined in a scanning electron microscope for determining interfacial morphologies of surface treatment. Data were submitted to 2-way ANOVA, Kruskal-Wallis and Mann-Whitney U tests (P<.05).

**Results:** The bond strengths were significantly influenced by the resin cement and surface treatment (P<.05). Both cements showed the highest bond strength values when specimens were treated with sandblasting. The bond strength of the MA adhesive cement to the sandblasted zirconia resulted in the highest bond strength values (5.42 ± 1.28 MPa).

**Conclusions:** Applying sandblasting surface treatment improves the bond strength of self-adhesive resin cement to zirconia.

**Keywords:** Zirconium Oxide; Resin Cements; Surface Treatment; Bond Strength
important for the long-term performance of a ceramic material, the clinical success of fixed ceramic prostheses seems to be strongly dependent on the cementation procedure. There is a common thought that conventional methods of adhesive cementation, which include prior acid etching of the ceramic surface with hydrofluoric acid and further silanation, are not efficient for Y-TZP ceramics, because of their lack of silica and glass phase\(^{10-12}\). Even though some Y-TZP manufacturers suggest the use of air abrasion or tribochemical coating prior to adhesive cementation, the effect of those surface treatments on the mechanical properties of Y-TZP materials is controversial, and both positive and negative results have been described in the literature\(^{10}\). Therefore, the most appropriate surface treatment for Y-TZP ceramics still has to be determined. Moreover, there are some possibilities for improving bonding to Y-TZP ceramics that need to be tested, including modern techniques for surface treatments and adhesive primer materials.

Therefore, the **aim** of this study was to compare the effect of various surface treatment methods on the zirconium oxide all ceramic restorations while using common alternative products for adhesive cementation of such restorations. The null hypothesis was that there is no difference in zirconia-composite cement bonding effectiveness among 4 different surface preparations.

### Material and Method

80 specimens 15x12x1.6 mm in diameter were obtained of \(\text{ZrO}_2\) (87-95%) stabilized by 5% \(\text{Y}_2\text{O}_3\) ceramic (IPS e.max ZirCAD, Ivoclar Vivadent AG, Schaan, Liechtenstein). They were ground with 600 grit silicon carbide polishing paper (DCCS, Sankyo Fuji star, Japan) under water cooling and ultrasonically cleaned in acetone and distilled water for 15 minutes.\(^2\) A total of 80 specimens were randomly divided into 4 groups (n: 20) according to the surface treatments. Group 1: No surface treatments (C); Group 2: Specimens were sandblasted (Easy Blast BEGO, Wilhelm-Herbest-Strabe, Bremen, Germany) for 60 seconds with 110 \(\mu\) particle size \(\text{Al}_2\text{O}_3\) sand (BEGO, Wilhelm-Herbest-Strabe, Bremen, Germany) from a distance of 1 cm under 2.8 atmospheres of air pressure (SB). Group 3: Specimens were roughened from various directions by the same investigator with a porcelain finishing diamond bur (Edenta AG, Dental Produkte St., St.Gallen, Switzerland), using a micro motor hand piece revolving at a speed of 15000 cycles (DB); Group 4: Er: YAG laser irradiation (LI). The specimens were roughened with a Fotona Fidelis Plus III Er: YAG laser device (Fotona Fidelis Plus 3 Lazer, Fotona dd, Ljubljana, Slovenia) The irradiation procedure was carried out using a pulsation frequency of 10 Hz and pulsation energy of 150 mJ at a 100 microseconds blasting time for a duration of 60 seconds. The wavelength of the device was 2940 nanometers and its focal spot size was 0.8 mm. During irradiation, the laser point was kept approximately 8 to 10 mm away from the surface and the whole surface was treated for 60 seconds.

### Bonding Procedure

After appropriate surface treatment, each adhesive resin cement was applied according to the manufacturers’ instructions at room temperature (23.0 ± 1.0\(^\circ\)C) and relative humidity (50% ± 5%)\(^{10}\). Application mode and chemical composition of the investigated materials are reported in table 1. To standardize the cementing of resin cements on zirconium specimens, specially prepared ring-shaped plastic moulds with 5 mm inner diameter and 2 mm height were used. Resin cements were applied into the plastic ring from a syringe using an automatic mixing tip, which allows a homogeneous mixture. The ring was covered with a cellulose tape and a standard weight of 400 gm was applied on the specimen. Excess cement was removed with a dental explorer. It was left to rest for 10 minutes in the room temperature for the cement to cure by itself. Specimens were stored in distilled water at 37\(^\circ\)C for 24 hours before testing shear bond strength.

### Shear Bond Strength Test

Shear bond strength was determined according to ISO/TS 11 405:2 003 using a Universal Testing Machine (TSTM 02500, Elista Ltd Şti, Istanbul, Türkiye) at a crosshead speed of 0.5 mm/min\(^2\). The force at separation (N) was divided by the cross-section area (100 mm\(^2\)) to provide results in units of stress (MPa). After debonding, the fractured surfaces were evaluated with an optical microscope (100x magnification) to classify the failure modes into 1 of the following categories (A) adhesive failure at the interface between the ceramics and resin-luting agent (C) cohesive failure within the ceramics, within the resin-luting agent only and (M) adhesive and cohesive failure at the same site or a mixed failure\(^2\).

Representative interfacial morphologies of surface treatment and debonded specimens were examined in a Scanning electron microscopy (SEM) (JEOL JSM-6060LV Scanning Electron Microscope, Tokyo, Japan). Prior to analysis, specimens were dried and gold coating was applied with a sputter coater (Polaron SC 502 Sputter Coater, SPI supplies/ Structure Probe, Inc. West Chester, USA)\(^10\).

### Statistical Analysis

The values obtained as a result of the shear test were assessed using 2-way ANOVA, Kruskal-Wallis test, which is a non-parametric statistical analysis, and Mann-Whitney U statistical tests with Bonferroni correction. The statistical analyses were carried out in Windows XP environment using SPSS 13.0 package programme.
In all groups, the MA cement had higher bond strength than MS cement \((P<.05)\). With the groups cemented with MA, SB and DB resulted in significantly higher bond strengths, while LI and C presented similar results. The same order was seen for the groups luted with the MS (Tab. 2). There were statistically significant differences between all groups for both cements except C and LI.

Table 3 describes the distribution of failure modes in the groups. Adhesive failures were most prevalent in all the experimental groups, with an average of 77\% adhesive failure between the ceramics and resin luting agent. No cohesive failure was observed. SEM images showed morphologic differences among the groups after surface treatments (Fig. 1). SA (Fig. 1b) created rougher surface compared to DB, LI and C (Figs. 1a and 1c). Er: YAG laser irradiation originated a smooth surface (Fig. 1d).

### Results

The results showed that bond strengths were significantly influenced by the resin cement and surface treatment \((P<.05)\). The shear bond strength values and the results of multiple comparisons are summarized in Table 2 for all 2 resin cements and 4 surface treatments. The mean values were 1.84±0.27 to 2.47±0.31; Mean: 2.15±0.42 MPa for C, 4.35±0.72 to 5.42±1.28; Mean: 4.88±1.15 MPa for SB, 3.28±0.90 to 3.72±0.89; Mean: 3.50±0.90 MPa for DB and 1.74±0.30 to 2.37±0.39; Mean: 2.05±0.46 MPa for C. The bond strength of the MA adhesive cement to sandblasted zirconia resulted in the highest bond strength values (5.42±1.28 MPa). Both cements showed the highest bond strength values when specimens were treated with sandblasting (SB).
in zirconia-composite cement bonding effectiveness among 4 different surface preparations. Moreover, SEM images demonstrated considerable qualitative differences in the surface topography of Y-TZP specimens after the surface treatments. Sandblasting appeared to be a more efficient method to modify zirconia surfaces compared to diamond burr and laser irradiation. This finding could be directly related to bond strength results, which showed that both resin cements yielded higher bond strengths after sandblasting\textsuperscript{10,17-22}.

Untreated zirconium oxide ceramic is a relatively inert substrate, with low surface energy and wettability\textsuperscript{17}. De Oyague et al\textsuperscript{18} reported that atomic force microscopy analysis reveals a significant increase in surface roughness after sandblasting with 125 μm aluminum-oxide particles. Sand blasted surfaces might present an increased surface area, which favours wettability\textsuperscript{19-21}. However, some authors have stated that the micro porosities created by surface treatments may act as crack initiators, weakening ceramic materials\textsuperscript{22,23}. Thus, the effect of those alterations on the durability of Y-TZP restorations should be investigated in long-term clinical trials to determine whether the higher retention of sandblasted surfaces compensate for the changes in mechanical properties.

Some studies have suggested the use of Er:YAG (erbium-doped yttrium aluminum garnet) laser to enhance the bond strength of adhesive materials to resin composites used for indirect restorations and lithium based ceramics\textsuperscript{24,25}. However, the capacity of the Er:YAG laser to increase the roughness of Y-TZP ceramics for adhesive luting procedures has not been investigated. In this study, irradiation of Y-TZP surfaces with Er: YAG laser was proposed as a surface treatment method. Our results indicated that laser irradiation was not as effective in improving bond strength as treatment with sandblasting and diamond bur for both resin cements. Laser treated and untreated surfaces presented similar results\textsuperscript{10,24}. The Er: YAG laser has the ability to remove particles by micro explosions and by vaporization, a process called ablation. During laser treatment, local temperature changes due to heating and cooling phases create internal tensions that can damage the material\textsuperscript{10,24}. The mechanical properties of Y-TZP ceramics can be negatively affected by changes in temperature, which can induce phase transformation\textsuperscript{10}.

### Table 3. Percentage of the failure modes in each experimental group

<table>
<thead>
<tr>
<th>Resin cement</th>
<th>Surface Treatment</th>
<th>Adhesive</th>
<th>Mixed</th>
<th>Adhesive</th>
<th>Mixed</th>
<th>Adhesive</th>
<th>Mixed</th>
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<td>70</td>
<td>66</td>
<td>34</td>
<td>75</td>
<td>25</td>
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### Discussion

Previous studies investigated the bond strength of adhesive restorative materials to Y-TZP ceramics\textsuperscript{13-16}. Adhesion tests were applied in laboratory conditions in order to assess the effectiveness of the restoration systems being used, or to make a prior estimation of the status of a newly marketed adhesive system in the mouth. Clinical recommendations and selection of material related to resin adhesion to ceramics are based on mechanical laboratory tests which demonstrate significant differences in the choice of material and method. The widely preferred bond strength tests are 3-point bending test, tensile and micro-tensile tests, and shear and micro-shear tests. Shear bond test was used for measuring bond strength in a large number of studies in the literature to investigate adhesion of resin cements to porcelain surface\textsuperscript{13-16}. In this study shear bond test was used to measure the bond strength of 2 different resins cements on the zirconium surfaces that were roughened in a number of ways.

The surface treatments investigated in the current study resulted in significantly different bond-strengths. So null hypothesis was rejected as there were differences in zirconia-composite cement bonding effectiveness among 4 different surface preparations. Moreover, SEM images demonstrated considerable qualitative differences in the surface topography of Y-TZP specimens after the surface treatments. Sandblasting appeared to be a more efficient method to modify zirconia surfaces compared to diamond burr and laser irradiation. This finding could be directly related to bond strength results, which showed that both resin cements yielded higher bond strengths after sandblasting\textsuperscript{10,17-22}.

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![Figure 1. SEM images (original magnifications 500X) of specimens’ surfaces: (a) Control (C); (b) Sandblasted (SB); (c) Diamond burr (DB); (d) Er: YAG laser irradiated (LI)](image-url)
Therefore, in this study, a lower power setting for the Er:YAG laser was selected (150mJ) and the surfaces were irradiated with constant water cooling. However, more studies need to be carried out in this area using different power and pulsation settings before and after the sintering process.

In this study of measuring bond strengths, the results of the shear test showed that the bond strength of MA (3.49±1.47) on zirconium surfaces was statistically significantly higher than that of MS (2.80±1.23). Multilink sprint (MS) is self etch, self adhesive resin based adhesive cement and designed for ease of use with no bonding application. Multilink Automix (MA), on the other hand, is a resin cement used with bonding applications on the teeth and metal/zirconia primer on the restoration in the aim of having higher bond strength. Metal/Zirconia Primer is only used with Multilink Automix. Metal/Zirconia Primer was used on the surfaces before applying MA as recommended by the manufacturer, but no zirconium primer was used before applying the new generation MS, which contains the etch and adhesive systems in its own composition. It was reported in previous studies that the use of resin cements containing phosphate-based monomer increased adhesion to zirconium surface. The phosphate-containing methacrylate in MA’s zirconium primer, which was used in this study, increased bond strength on zirconium surfaces in a similar way. Therefore, higher bonding values achieved by Multilink Automix may well be due to the application of Metal/zirconia primer. The reason for such increase was because phosphate-containing methacrylate in the primer formed a salt-like bond with zirconium. Due to low bond strength of Multilink Sprint, it is not on the market anymore. However, the purpose of this in vitro study was to evaluate the influence of different surface treatment methods on the bond strength of 2 composite resins to yttrium stabilized zirconium oxide ceramics.

It is not the bonding strength of Multilink Sprint that is important, but the effect of surface treatment methods on the shear bond strength of resin cements authors have focused on. The principal aim of this study was to compare the effect of various surface treatment methods on the zirconium oxide all ceramic restorations while using common alternative products for adhesive cementation of such restorations.

It was interesting that the bond strength values of this study were quite lower than previous stated. If the bond strength values were achieved in the region of 20-30 MPa (average bonding values of adhesive cements on tooth substances), there would be no problems as to adhesive bonding of resin cements on zirconium oxide restorations. Therefore, authors should question such high bonding values rather than suspect more realistic numbers found in this study.

In this study, failure mode results indicated that, regardless of the experimental group, most failures of the resin cement-Y-TZP ceramic were adhesive, which left the zirconia specimens free of remnants of adhesive materials. Fractures being caused mostly by adhesive failure indicated that no real chemical bond could be established between the resin cement and the yttrium stabilized zirconium oxide specimens.

Conclusions

Within the limitations of the present in vitro study, the following conclusions can be drawn:

1. Applying sandblasting surface treatment improves the bond strength of self-adhesive resin cement to zirconia;
2. In the surface treatment of sand blasted and diamond bur roughness, self-adhesive resin cement Multilink Automix shows the highest bond strengths to zirconia. The using of zirconium primer may have an effect on the mechanical strength of the cement;
3. Fractures were mostly adhesive failure, indicating that no real chemical bond could be established between the resin cement and the zirconium oxide specimens.

References


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