Thesis

Effects of surface treatment on bonding resin to polyetherketoneketone-based material

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1.1 Introduction

Polyetherketoneketone (PEKK) is a semicrystalline linear thermoplastic polymer, containing carbonyl and ether groups bridged by aromatic rings (Fig. 1). PEKK was first prepared by Bonner [1] in 1962, whereas polyetheretherketone (PEEK) was patented by Rose and Staniland [2] in 1982.

Both PEKK and PEEK belong to the family of polyaryletherketones (PAEKs); these compounds are characterized by high melting points (over 300˚C), excellent resistance against chemicals and abrasion, and mechanical properties suitable for prosthesis applications [3,4]. PAEKs have been used in dental implants [5-7], temporary abutments [8], crowns [9], fixed partial dentures [10,11], and removable dentures [12].

However, the natural color of tooth or gum cannot be fully reproduced using PAEKs alone, because these materials have a monochromatic opaque appearance. For this reason, machine-milled or heat-pressed PAEKs are usually veneered with light-curing resin composites to fulfill the esthetic demands of patients. Therefore, adhesive bonding between the PAEKs and the resin composite veneering materials is an
essential requirement for fabricating esthetic restorations.

Several studies have investigated the adhesive bonding of resin-based materials to PEEK. Silica coating, applied using the Rocatec system (3M ESPE, Seefeld, Germany), was shown to affect the bond strength [3,13,14]. The bond strength was also significantly influenced by plasma treatment [15,16]. Etching PEEK materials with sulfuric acid (SA) resulted in improved bond strengths, and this effect was dependent on the concentration [17,18]. A piranha solution, a mixture of SA and hydrogen peroxide, was also used for etching PEEK [19,20]. Whereas SA etching was found to produce higher bond strengths than hydrofluoric acid or piranha solution [15,21], it is unclear whether it also improves the adhesive bonding of a resin to PEKK.

In contrast to PEEK or other prosthetic materials, limited information is available on the surface treatments that may be effective for bonding to PEKK, with the exception of plasma treatment [22] and silica coating [3]. Although etching PEKK with 95% SA was compared to air-abrasion or silica coating [23], the optimum concentration of SA and etching duration have not been determined.

The hydrophilic vinylsulfonic acid (VSA, Fig. 1) is the smallest monomer
(molecular weight 108.12) made of a vinyl and a sulfonic acid group (-SO$_3$H), whose anions are highly soluble in water. It can be used to prepare pigment dispersants, dye stabilizers, thickeners, cosmetic ingredients, battery binders, high-molecular electrolytes, and adhesives in industrial products. However, no previous studies have investigated the use of VSA in dentistry, as a surface treatment agent for PEKK prior to bonding.

In this context, the present study aims to evaluate the effects of SA and VSA etching agents on the bond strength between an indirect resin composite and PEKK. The testable hypothesis was that neither SA nor VSA improves the bond strength.

![Chemical structures of PEKK and VSA](image)

**Fig. 1** Chemical structures of PEKK and VSA.
1.2 Materials and methods

1.2.1 Materials used

The substrate, veneering, and primer materials used in this work are listed in Table 1. A total of 200 disc specimens (11 mm diameter and 3 mm thickness) were cut from a PEKK block (Pekkton ivory press blanks, Cendres+Métaux SA, Biel/Bienne, Switzerland) and divided into 25 groups of 8 specimens. All specimens were ground with #400 and 600 silicon carbide papers (BuehlerMet2, Buehler, IL, USA), ultrasonically cleaned in sequence with distilled water and ethanol (Wako Pure Chemical Ind., Osaka, Japan) for 5 min each, and then air-dried.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Substrate material, resin composite, and primer used for shear bond strength tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Component</td>
</tr>
<tr>
<td>Substrate material</td>
<td>polyetherketoneketone (PEKK) 90%, TiO2 10%</td>
</tr>
<tr>
<td>Resin composite</td>
<td>urethane dimethacrylate, silica micro powder</td>
</tr>
<tr>
<td>Grada Opaque OA3</td>
<td>urethane dimethacrylate, silica micro powder, glass powder, organic composite filler</td>
</tr>
<tr>
<td>Etching agent</td>
<td>sulfuric acid (80, 90, or 95%), water</td>
</tr>
<tr>
<td>φSA</td>
<td>vinylsulfonic acid (90 or 95%), water</td>
</tr>
<tr>
<td>Primer</td>
<td>Metal Primer Z</td>
</tr>
</tbody>
</table>

Seventy-two specimens (nine groups of eight specimens) were used to investigate the effects of three different concentrations (80, 90, and 98%) of SA and three etching durations (5, 30, and 60 s), in order to identify the optimum etching conditions. Forty-eight specimens (six groups of eight specimens) were used to investigate the effects of two concentrations (90 and 95%) of VSA and three etching durations (5, 30, and 60 s) and determine the optimum etching conditions corresponding to VSA. In addition, 80 specimens (10 groups of 8 specimens) were used to evaluate the effects of three etching conditions (SA etching, VSA etching, and no etching) and primer application on the bond strength of the sample before and after thermocycling.

1.2.2 Preparation of bonded specimens

The SA and VSA etching agents (100 µL) were applied to the PEKK surface with a micropipette (Eppendorf AG, Hamburg, Germany) for 5, 30, or 60 s, rinsed with water spray for 5 s, and then air-dried. A piece of masking tape with a circular hole of 5 mm diameter was attached to the surface of each specimen to delineate the bonding area (Fig. 2). A primer (1 µL, Metal Primer Z, GC Corp., Tokyo, Japan) was applied to the
specimens with a micropipette and gently air-blown. Gradia Opaque (GC Corp., Tokyo, Japan) was applied with a brush to each specimen and light-polymerized for 30 s in a laboratory light emitting diode (LED) unit (Labocure L, GC Corp., Tokyo, Japan). An acrylic ring (6 mm internal diameter, 2 mm height) was placed around the bonding area, filled with Gradia Body (GC Corp., Tokyo, Japan), and then light-cured for 120 s.

Fig. 2  Schematic illustration of the bonding procedure.

1.2.3  Shear bond strength tests

All bonded specimens were stored at room temperature for 30 min and then immersed in water at 37°C for 24 h. This state was denoted as thermocycle 0. The bonded specimens of four groups (a group comprising specimens etched under optimum etching conditions and three control groups without etching or primer application) were subjected to 20,000 thermocycles using a thermocycling machine (Higuchi Corp., Nagasaki, Japan), alternating between water baths held at 4 and 60°C, with a dwell time
of 1 min at each temperature. All specimens (with and without the thermocycling) were embedded in an acrylic resin mold and fitted to a shear-testing device (ISO/TR11405JIG, Wago Industrial, Nagasaki, Japan) (Fig. 3) in order to apply a shearing load parallel to the bonded interface. The shear bond strength, defined as the ratio between the force at failure and the bonded surface area (5 mm), was determined using a universal testing machine (AGS-10kNG, Shimadzu Corp., Kyoto, Japan) at a cross-head speed of 0.5 mm/min. Eight specimens were tested for each test group.

Fig. 3  Schematic illustration of the shear testing device.
1.2.4 Failure mode analysis

After the shear bond strength tests, the debonded surfaces of all specimens were observed through an optical microscope (SMZ-10, Nikon Corp., Tokyo, Japan) at 20× magnification. Failure modes were classified as adhesive failure at the interface between PEKK and veneered resin composite (Ad), cohesive failure within the resin composite (Co), partial fracture within the PEKK material (Fr), as well as three combinations of these failure modes (Ad/Co, Ad/Fr, and Ad/Co/Fr).

1.2.5 Scanning electron microscopy observation

The PEKK specimens treated with nine representative etching conditions including a control (no etching, 80% SA for 5 s, 90% SA for 5 s, 90% SA for 60 s, 98% SA for 5 s, 90% VSA for 30 s, 95% VSA for 5 s, 95% VSA for 30 s, and 95% VSA for 60 s) were prepared for scanning electron microscopy (SEM) observation. The surface of the PEKK specimens was sputter-coated with gold using an ion coater (IB-3, Eiko Engineering Co. Ltd., Hitachinaka, Japan), and observed by SEM (JCM-6000Plus, JEOL Ltd., Tokyo, Japan) at 2000× and 5000× magnifications.
Two additional PEKK specimens were ground with #400 and #600 silicon carbide papers. One specimen was etched with 90% SA for 5 s, while the other specimen was etched with 90% VSA for 30 s. Each specimen was modified with Metal Primer Z, and then the light-curing resin composites were veneered as described above. Thirty minutes after bonding, both of the specimens were cut perpendicular to the bonded interface. Following sputter-coating with gold (Ion Coater IB-3; Eiko Engineering Co. Ltd., Mito, Japan), the cross-section was observed using a scanning electron microscope (JCM-6000Plus, JEOL Ltd., Tokyo, Japan) at 5000× magnification.

1.2.6 Statistical analysis

The mean bond strength and standard deviation (SD) of eight specimens were calculated for each test group. Normality and homoscedasticity were analyzed by Shapiro-Wilk and Levene tests, respectively. The bond strength values were examined using a nonparametric (Steel-Dwass) test with the statistical significance set at 0.05. The statistical analysis was carried out using the JMP Pro software system (Ver. 11, SAS Institute Japan Ltd., Tokyo, Japan).
1.3 Results

The mean bond strengths ranged from 9.6 to 26.2 MPa. The relation between concentration of SA and etching duration is illustrated in Fig. 4. When 80% SA was used, no significant difference was found among the bond strengths obtained with etching durations of 5, 30, and 60 s. The highest bond strength was achieved when the PEKK material was etched with 90% SA for 5 s (the corresponding group was labeled 90-5 SA). Longer etching times in 90% and 98% SA resulted in lower bond strengths.

![Fig. 4](image.png)

**Fig. 4** Effects of SA concentration and etching duration on the bond strength between a light-curing indirect resin composite and the PEKK material. Identical lowercase letters indicate values that are not statistically different ($P \geq 0.05$).
The influence of VSA concentration and etching duration on the bond strength is illustrated in Fig. 5. When 90% VSA was used, no significant difference was found among the bond strengths obtained with etching durations of 5, 30, and 60 s. A significantly higher bond strength was obtained with 95% than with 90% VSA. The group of specimens treated with 95% VSA for 30 s (labeled 95-30 VSA) exhibited the highest bond strength.

Fig. 5 Effects of VSA concentration and etching duration on the bond strength between a light-curing indirect resin composite and the PEKK material. Identical lowercase letters indicate values that are not statistically different ($P \geq 0.05$).
The bond strengths, before and after thermocycling, of the specimens treated with 90-5 SA or 95-30 VSA etching agents and the primer are listed in Table 2. Four groups (90-5 SA/unprimed, 90-5 SA/primed, 95-30 VSA/unprimed, and 95-30 VSA/primed) exhibited higher bond strength than the unetched controls (with and without primer) before and after thermocycling. No significant difference was found between the 90-5 SA and 95-30 VSA groups, irrespective of the application of the primer.

<table>
<thead>
<tr>
<th>Group</th>
<th>Mean (SD) (MPa) Therocycle 0</th>
<th>20,000 cycles</th>
<th>Failure modes (Number of specimens) Therocycle 0</th>
<th>20,000 cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>unetched/unprimed</td>
<td>9.6 (1.4)</td>
<td>12.2 (1.7)</td>
<td>Ad(8)</td>
<td>Ad(8)</td>
</tr>
<tr>
<td>unetched/primed</td>
<td>12.6 (2.9)</td>
<td>9.5 (2.7)</td>
<td>Ad(8)</td>
<td>Ad(8)</td>
</tr>
<tr>
<td>90-5 SA/unprimed</td>
<td>22.6 (1.0)</td>
<td>24.3 (4.3)</td>
<td>Ad(6), Ad/Co(2)</td>
<td>Ad(6), Ad/Co(1), Ad/Fr(1)</td>
</tr>
<tr>
<td>90-5 SA/primed</td>
<td>23.1 (2.7)</td>
<td>26.2 (3.2)</td>
<td>Ad(5), Ad/Co(3)</td>
<td>Ad(6), Ad/Co(2)</td>
</tr>
<tr>
<td>95-30 VSA/unprimed</td>
<td>25.1 (2.7)</td>
<td>23.7 (2.5)</td>
<td>Ad/Co/Fr(8)</td>
<td>Ad/Co/Fr(8)</td>
</tr>
<tr>
<td>95-30 VSA/primed</td>
<td>26.2 (3.0)</td>
<td>24.3 (4.1)</td>
<td>Ad/Co(1), Ad/Co/Fr(7)</td>
<td>Ad/Fr(2), Ad/Co/Fr(6)</td>
</tr>
</tbody>
</table>

*Superscripts indicate values that are not statistically different (P>0.05).

**Ad: adhesive failure at the interface between PEKK and veneered resin composite; Co: cohesive failure within the veneered resin composite; Fr: fracture within the PEKK material; Ad/Co, Ad/Fr, Ad/Co/Fr: combinations of Ad, Co, and Fr.
All unetched control specimens (with and without priming) showed complete adhesive failure. After etching with 90-5 SA (with and without priming), more than half of specimens showed complete adhesive failure, and the remaining specimens exhibited mixed failures (Ad/Co or Ad/Fr). On the other hand, most specimens etched with 95-30 VSA exhibited Ad/Co/Fr, and no complete adhesive failure was observed in this case.

The SEM images of representative PEKK surfaces are shown in Figs. 6 and 7. The unetched specimen (a) showed plain surfaces with slight flaws. The 80-5 SA specimen (b) displayed a complex fiber network. After etching with 90-5 SA (c), the specimens exhibited numerous round microcavities with sharp edges (honeycomb structure). In the specimen etched for longer time, 90-60 SA (d), the number and depth of the microcavities decreased. In the case of 98-5 SA (e), the microcavities appeared to disintegrate and lose their honeycomb structure.

The surface structures of the specimens etched with VSA (f–i) were clearly different from those etched with SA (b–e). The 90-30 VSA specimen (f) exhibited relatively plain surfaces, similar to the unetched specimen (a). The 95-5 VSA
specimen (g) displayed an irregularly structured surface with many rounded hollows, whereas etching with 95-30 VSA (h) led to a microporous (felt-like) surface. The surface of the 95-60 VSA specimen (i) was not considerably different from that of the 95-30 VSA specimen (h).

Secondary electron and backscattered images of the cross-section of the bonded specimens are shown in Figs. 8 and 9. When the PEKK surface was etched with SA, micro gap was observed at the interface between the PEKK specimens and the resin-based materials. On the other hand, the VSA etched specimen exhibited better continuity of the bonded interface, suggesting a resin-PEKK interdiffusion.
Fig. 6 SEM images of PEKK specimens at original magnification of 2000×: ground with #600 silicon carbide paper (a), and then etched with 80% SA for 5 s (b), 90% SA for 5 s (c), 90% SA for 60 s (d), 98% SA for 5 s (e), 90% VSA for 30 s (f), 95% VSA for 5 s (g), 95% VSA for 30 s (h), or 95% VSA for 60 s (i).
Fig. 7  SEM images of PEKK specimens at original magnification of 5000×:  ground with #600 silicon carbide paper (a), and then etched with 80% SA for 5 s (b), 90% SA for 5 s (c), 90% SA for 60 s (d), 98% SA for 5s (e), 90% VSA for 30 s (f), 95% VSA for 5 s (g), 95% VSA for 30 s (h), or 95% VSA for 60 s (i).
Fig. 8  Secondary electron (a) and backscattered (b) images of the veneered specimen cut in cross-section. The PEKK surface was etched with 90% SA for 5 s, primed Metal Primer Z, and then the light-curing resin composites were veneered. Arrows indicate the bonded interface. Original magnification was 5000×.

Fig. 9  Secondary electron (a) and backscattered (b) images of the veneered specimen cut in cross-section. The PEKK surface was etched with 90% VSA for 30 s, primed with Metal Primer Z, and then the light-curing resin composites were veneered. Original magnification was 5000×.
1.4 Discussion

The present study revealed that both SA and VSA etching agents are effective in improving the bond strength of a resin to PEKK, whereas the phosphate primer had no significant effects. Therefore, the testable hypothesis that neither SA nor VSA improves the bond strength was rejected.

Two sets of experiments, the results of which are shown in Figs. 4 and 5, were performed to select the most suitable SA and VSA concentrations and etching durations for bonding to PEKK. Based on the bond strength results, we selected two optimum etching conditions (90% SA for 5 s and 95% VSA for 30 s).

Preclinical in vitro tests of the bonding durability of adhesive systems are important for assessing the long-term stability of fabricated prostheses in the relatively harsh oral environment. Thermocycling represents a standard technique for evaluating the bonding durability against repeated thermal stress. The thermal stress induces expansion and contraction of the materials, accelerating the diffusion of water into the bonded interface. The bond strengths attained after 20,000 thermocycles at 50°C were comparable to those obtained at 60°C [24]. Many studies investigated the bond
strengths between resin and PEEK materials after 10,000-20,000 thermocycles [14,25-27]. Therefore, 20,000 thermocycles were employed in the present study.

Although 24-hour bond strength of resin composites to a PEKK material etched with 95% SA for 60 s was reported to be 14-18 MPa [23], the present findings suggest that this condition was not optimum. Specifically, the bond strengths of the specimens etched with 90–98% SA for 5 s were about two times higher than those etched with 90–98% SA for 60 s (Fig. 4).

SA not only attacks carbonyl and ether groups to break the chemical bonds of PEEK [19], but also sulfonates its surface [28-30], and the chemical structures of PEEK and PEKK are very similar. Therefore, we speculate that SA may attack the carbonyl groups or ether linkages of PEKK, and the detached PEKK molecular fragments could be washed away during the etching procedure.

The SEM observations indicate that SA etching increased the surface area and micromechanical retention, and more PEKK substrate was etched away as the concentration of SA increased from 80 to 98%. When using 98% SA, the optimal etching duration for bonding PEEK with resin cements was reported to be 60–90 s [16].
However, the results of the present tests carried out with 98% SA suggest that the optimal etching duration (5 s) for PEKK is shorter than that (60–90 s) reported for PEEK. Since the PEKK molecule has a larger number of carbonyl groups than PEEK, SA may break the carbonyl groups more than the ether linkages.

A wide range of duration times promoting high bond strength is advantageous for handling. When using 90 or 98% SA, the bond strengths were very sensitive to the duration time (Fig. 4). In contrast, the bond strength generated with 95% VSA was not significantly affected by duration times ranging from 5 to 60 s (Fig. 5).

To the best of our knowledge, this is the first study to compare the roles of chemical etching with organic and inorganic acid in the bonding behavior of PEKK. The surface structures of the etched specimens strongly suggest that the chemical reaction between VSA and PEKK is essentially different from that between SA and PEKK.

Most unetched PEKK specimens showed complete adhesive failure, and the failure mode was also affected by the type of etching agent employed. The failure modes tended to shift from adhesive failure to cohesive failure within the resin
composite as the bond strength increased. Fracture within the PEKK material suggests that cohesive strength of PEKK was locally weakened by the VSA etching. The occurrence of adhesive failure indicates that the adhesive force is lower than the cohesive strengths of the substrate materials. In contrast to the unetched or 90-5 SA group, none of the specimens etched with VSA exhibited complete adhesive failure, which suggests that a strong adhesive force was generated at the bonded interface.

We speculate that, in addition to the mechanical interlocking, a chemical reaction between VSA and PEKK surface may contribute to the increased bond strength. If grafted or residual VSA monomers exist on the PEKK surface after the etching procedure, their vinyl group could be copolymerized with the primer or opaque resin components. Therefore, analyzing whether VSA grafts PEKK surface is worth further study.

Although we had expected bonding between the functional monomers (10-methacryloyloxydecyl dihydrogen phosphate, MDP, and 10-methacryloyloxydecyl dihydrogen thiophosphate, MDTP) and the titanium TiO₂ pigments of the PEKK material [31], the phosphate primer did not significantly affect the bond strength, which
may be due to lack of bonding between the TiO$_2$ pigments and PEKK.

Both SA and VSA etching could reduce fracture or debonding of veneered resin composites from PEKK-based frameworks. However, care should be taken to protect skin and eyes when using the etching agents. In addition, buffering of the waste liquid in the laboratory is essential for safety.
1.5 Conclusions

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

1. The concentration of SA and VSA, along with the etching duration, significantly affected the bond strength between the indirect resin composite and the PEKK material.

2. Etching with 90% SA for 5 s or 95% VSA for 30 s provided the highest bond strength, irrespective of the application of a phosphate primer.

3. SEM observations revealed that numerous microcavities were generated on the PEKK surface etched with 90% SA for 5 s. On the other hand, the PEKK surface etched with 95% VSA for 30 s exhibited a microporous, felt-like appearance.
1.6 References


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Effect of different surface pre-treatments and luting materials on shear bond

B. Effect of sulfuric acid etching of polyetheretherketone on the shear bond

19. Hallmann L, Mehl A, Sereno N, Hämmerle CHF. The improvement of
adhesive properties of PEEK through different pre-treatments. Appl Surf Sci.
2012; 258:7213-8.

Influence of PEEK surface modification on surface properties and bond

Keul C. PEEK surface treatment effects on tensile bond strength to veneering


27. Stawarczyk B, Keul C, Beuer F, Roos M, Schmidlin PR. Tensile bond


1.7 List of journal publications

1.7.1 Main research article

1. Sakihara M, Taira Y, Sawase T.

Effects of sulfuric and vinyl sulfonic acid etchants on bond strength of resin composite to polyetherketoneketone.

Odontology. doi: 10.1007/s10266-018-0375-0.

Summary

This study aims to evaluate the effects of etching with sulfuric acid (SA) and vinyl sulfonic acid (VSA) on the bond strength between a light-curing indirect resin composite and polyetherketoneketones (PEKK). PEKK specimens were ground with 600 silicon carbide papers, etched with 90% SA for 5 s (90-5 SA) or 95% VSA for 30 s (95-30 VSA), and then modified with a phosphate primer; afterward, a light-curing resin composite was veneered on the specimens. Two control groups were also prepared without etching (unetched/unprimed and unetched/primed). After 20,000 thermocycles in water at 4 and 60°C, the shear bond strengths of the specimens were determined and subjected to a
nonparametric (Steel-Dwass) test ($\alpha=0.05$, $n=8$). The etched surfaces were observed by scanning electron microscopy (SEM) at 2000× magnification. Higher bond strengths were obtained when the PEKK surface was etched with 90-5 SA or 95-30 VSA (90-5 SA/unprimed 24.3±4.3 MPa, 90-5 SA/primed 26.2±3.2 MPa, 95-30 VSA/unprimed 23.7±2.5 MPa, 95-30 VSA/primed 24.3±4.1 MPa), and these values were not statistically different, whereas the two control groups exhibited significantly lower bond strengths (unetched/unprimed 12.2±1.7 MPa, unetched/primed 9.5±2.7 MPa). SEM observations revealed that 95-30 VSA led to a microporous (felt-like) surface, which was different from the surface structure etched with 90-5 SA. Etching the PEKK surface with SA or VSA significantly improved the bond strength between resin composite and PEKK in contrast with the application of the phosphate primer. Appropriate chemical etching could be a useful option when fabricating prostheses using PEKK-based materials and indirect resin composites.
1.7.2 Other research contributions

2. Egoshi T, Taira Y, Sakihara M, Kamada K, Sawase T, Murata H.

Effects of air abrasion and glow-discharge plasma treatment on bonding resin cement to ceria-stabilized zirconia/alumina nanocomposite.

Dent Mater J (In press)

Summary

The aim of this study was to evaluate the effects of air abrasion and plasma treatment on the bond strength between resin and ceria-stabilized tetragonal zirconia polycrystals/alumina (Ce-TZP/Al₂O₃). Ce-TZP/Al₂O₃ specimens were ground with #1000 silicon-carbide paper, air abraded with alumina, and then exposed to glow-discharge plasma (Abrasion/Plasma). Specimens without air abrasion and/or plasma exposure were also prepared as controls (Abrasion/No plasma, No abrasion/Plasma, and No abrasion/No plasma). The specimens were bonded to resin composite disks with a self-adhesive resin cement (SA) or a luting composite containing no functional monomer (LC). Shear bond strengths were determined after 10,000 thermocycles at 4 and 60°C, and the data were analyzed by
non-parametric tests ($\alpha=0.05$, n=8/group). When using SA, the Abrasion/Plasma specimens exhibited the highest bond strength, followed by the Abrasion/No plasma, No abrasion/Plasma, and No abrasion/No plasma specimens. For LC, neither air abrasion nor plasma treatment exhibited any significant effect on bond strength.

Effect of tetrabutylammonium dihydrogen trifluoride treatment on durability of resin–titanium bond strengths.

J Dent Sci (In press)

Summary

This study investigated the effect of titanium surface treatment with tetrabutylammonium dihydrogen trifluoride (TDTF) on the bond between the titanium and resins for dental applications. Commercially pure titanium (cpTi) specimens were air-abraded with alumina particles, surface-treated with an etchant containing TDTF (Monobond Etch & Prime; ETCH) for 10 s (ETCH10) or 30 s (ETCH30), rinsed with water, treated with a phosphoric monomer-based primer, and bonded to an indirect resin composite. Non-ETCH-treated specimens (no-ETCH) were prepared as a control. The shear bond strengths were determined before and after 100,000 thermocycles, and the means and standard deviations for eight specimens were calculated and statistically analyzed using a non-parametric Steel-Dwass test ($\alpha = 0.05$). The ETCH10 and ETCH30 specimens exhibited the
highest bond strengths, which were maintained for 100,000 thermocycles, while significantly lower values were obtained for no-ETCH specimens. In conclusion, the surface treatment with a TDTF-containing etchant considerably improved the durability of the resin–cpTi bond strength. Appropriate surface treatment of cpTi should be selected for achieving longer-lasting treatments and better clinical solutions for patients.
4. Shinohara A, Taira Y, Sakhara M, Sawase T.

Effects of three silane primers and five adhesive agents on the bond strength of composite material for a computer-aided design and manufacturing system.


Summary

The objective of this study was to evaluate the effects of combinations of silane primers and adhesive agents on the bond strength of a composite block for a computer-aided design and manufacturing system. Three silane primers [Clearfil Ceramic Primer (CP), Super-Bond PZ Primer (PZ), and GC Ceramic Primer II (GP)] were used in conjunction with five adhesive agents [G-Premio Bond (P-Bond), Repair Adhe Adhesive (R-Adhesive), Super-Bond D-Liner Dual (SB-Dual), Super-Bond C&B (SB-Self), and SB-Dual without tributylborane derivative (SB-Light)]. The surface of a composite block (Gradia Block) was ground with silicon carbide paper. After treatment with a silane primer, an adhesive agent was applied to each testing specimen. The specimens were then bonded with a light-curing resin composite. After 24 h, the shear bond strength values were
determined and compared using a post hoc test ($\alpha = 0.05$, $n = 8$/group). We also prepared control specimens without primer (No primer) and/or without adhesive agent (No adhesive). PZ/SB-Dual and GP/SB-Dual presented the highest bond strength, followed by GP/P-Bond, CP/SB-Dual, CP/R-Adhesive, No primer/SB-Dual, GP/R-Adhesive, CP/P-Bond, No primer/R-Adhesive, PZ/R-Adhesive, CP/SB-Self, PZ/P-Bond, PZ/SB-Self, and GP/SB-Self in descending order of bond strength. No primer/P-Bond, No primer/SB-Self, and all specimens in the SB-Light and No adhesive groups presented the lowest bond strengths. A dual-curing adhesive agent (SB-Dual) containing a tributylborane derivative in combination with a silane primer (GP or PZ) presents a greater bond strength between the composite block and the repairing resin composite than the comparators used in the study.