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Effects of sandblasting, H_2SO_4/HCl etching, and phosphate primer application on bond strength of veneering resin composite to commercially pure titanium grade 4

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This study investigated the effects of surface treatments on the bond strength of a resin composite to a commercially pure titanium. The bonding surfaces of all titanium specimens were ground with 1,000-grit silicon carbide paper and then subjected to one or more of these surface treatments: sandblasting with alumina (sand), etching with 45wt% H_2SO_4 and 15wt% HCl (SH-etchant) at 70°C for 10 min, and/or phosphate primer (MDP-primer) application. Specimens not subjected to any surface treatment were used as controls. After resin composite veneer placement and 24-h water immersion, the shear bond strengths of the specimens in descending order were: sand/SH-etchant/MDP-primer, sand/SH-etchant/no primer, no sand/SH-etchant/MDP-primer, sand/no etch/MDP-primer, no sand/SH-etchant/no primer, sand/no etch/no primer, no sand/no etch/MDP-primer, no sand/no etch/no primer. Scanning electron microscope observations revealed that sandblasting and SH-etchant created many micro- and nanoscale cavities on the titanium surface. Results showed that a combined use of sandblasting, SH-etchant, and MDP-primer application had a cooperative effect on titanium bonding.

Keywords: Titanium, Acid etching, Adhesive bonding

INTRODUCTION

Titanium is widely used for dental prostheses such as crowns, fixed partial dentures, removable dentures, and implant-supported superstructures because of its high corrosion resistance, light weight, excellent biocompatibility, and adequate mechanical properties[1-3]. However, the mechanical properties of titanium can be adversely affected by the chemical reaction between molten titanium and investment material or oxygen during casting[4]. This problem can be prevented by using computer-aided design/computer-assisted manufacturing (CAD/CAM) systems[5,6]. Then, there is another issue of inevitable distortions with cast frameworks. An additional advantage of using CAD/CAM systems is that they produce more accurate precision of fit than conventional casting techniques[7-9].

Resin composites are commonly used for veneering metal frameworks. However, complications such as fracture and detachment are occasionally observed for resin composite veneers. For cast restorations, retention beads are affixed to restoration surfaces to improve bonding with composite veneers. However, the milling drill of CAD/CAM systems cannot shape narrow undercuts such as those under retention beads. Therefore, there must be an alternative approach to achieve a strong and reliable adhesive bonding between resin composites and CAD/CAM titanium frameworks so that veneered prostheses could withstand the stresses of the oral environment.

To improve the adhesive bonding of resins to titanium, several physical and chemical surface modification techniques were investigated: sandblasting[10], silica coating[11-13], application of adhesive primers[14-21], plasma irradiation[22], alkaline treatment[23,24], and acid etching[25,26]. On the use of adhesive monomers in primers, the authors previously reported that a primer containing 10-methacryloyloxydecyl dihydrogen phosphate (MDP) monomer promoted resin bonding to titanium[14]. On the use of acids in acid etching, they are also used to modify titanium surfaces to promote biological interactions for osseointegration[27-29].

Various acids have been used to chemically etch titanium surfaces to improve resin bonding: HF, H_3PO_4, H_2SO_4, and HCl[25,26]. With commercially pure titanium (cpTi), etching with 48% H_2SO_4 at 60°C for 60 min reportedly resulted in high bond strength[25]. In previous studies[30,31], the authors reported that cpTi surfaces microscopically roughened by etching with ammonium hydrogen fluoride (NH_4FHF) or sodium hydrogen fluoride (NaFHF) also yielded markedly improved bond strengths. A combined treatment of sandblasting with 250–500 µm alumina and acid etching with a mixture of H_2SO_4 and HCl improved the bone response of a titanium implant (Straumann, Basel, Switzerland) [32,33]. However, it remained to be investigated if such a combined treatment would improve the adhesive bonding of resin composites to cpTi.

The American Society for Testing and Materials (ASTM) and Japan Industrial Standards (JIS) classify cpTi into four categories (grades 1–4) based on the amount of interstitial elements. Oxygen content increases with increasing titanium grade, and cpTi grade 4 has the highest oxygen content of about 0.40%. The increased oxygen content of cpTi grade 4 accounts for its higher tensile strength, higher proof stress, and lower elongation than cpTi grades 1–3[34]. However, little is known if cpTi grade 4 also produces higher bond strength to resin composites. In terms of commercial use, Procera® Implant Bridge (Nobel

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Biocare AB, Gothenburg, Sweden) and Compartis® ISUS (Dentsply Prosthetics, York, PA, USA) frameworks and restorations are milled from a solid block of cpTi grade 4 using computer numeric control milling machines.

The present study evaluated the bond strength of a resin composite to cpTi grade 4 subjected to a combination of these surface treatments: sandblasting with alumina, etching by H_2SO_4 and HCl, and/or application of a phosphate primer. We hypothesized that the combined use of sandblasting, etching, and primer application would produce a greater effect on titanium bonding than when used individually.

MATERIALS AND METHODS

Table 1 lists the details of the materials used in this study. For the acid etchant used in the present study, SH-etchant contained 45wt% H_2SO_4 and 15wt% HCl in water.

Specimen preparation

Sixty-four disk-shaped titanium specimens were machine-milled to a diameter of 10 mm and a thickness of 3 mm. All disk specimens were sequentially ground with 600- and 1,000-grit silicon carbide papers.

The surfaces of half of the specimens (*i.e.*, 32 specimens) were sandblasted (Pen-Blaster, Shofu Inc., Kyoto, Japan) with alumina (Hi-Aluminas, Shofu Inc., Kyoto, Japan; average grain size: 50 µm) for 15 s and then air-blown. Air pressure for sandblasting was 0.45 MPa, and the nozzle was located approximately 10 mm from the specimen surface.

The remaining 32 specimens were rinsed with tap water for 15 s, air-dried for 5 s, and then rinsed with acetone. They were divided into four subgroups of eight specimens: SH-etchant/MDP-primer, SH-etchant/no primer, no etch/MDP-primer, no etch/no primer. In SH-etchant/MDP-primer and SH-etchant/no primer subgroups, specimens were immersed in the SH-etchant at 70°C for 10 min, rinsed with tap water for 15 s, and then air-dried for 5 s. In SH-etchant/MDP-primer and no etch/MDP-primer subgroups, 1 µL of primer was applied to the titanium surface with a micropipette (Eppendorf AG, Hamburg, Germany) and then air-dried for 5 s.

After the surface treatments, a piece of 50-µm-thick masking tape with a 5-mm-diameter hole was placed on each specimen to define the bonding area. Estenia C&B Body Opaque paste (Kuraray Noritake Dental Inc., Tokyo, Japan) was applied to each specimen with a brush and light-cured for 90 s using a light curing apparatus (α-Light II, J. Morita Corp., Osaka, Japan). A round acrylic mold (inside diameter: 6 mm; height: 2 mm) was placed on top of the bonding area. The acrylic mold was filled with Estenia C&B Dentin paste (Kuraray

Table 1 Materials used in this study

Name (Abbreviation)	Composition	Manufacturer	Lot no.
Titanium			
Grade 4 of cpTi	Ti ≥ 99.4578%, O: 0.32–0.36%, Fe: 0.16–0.17%, H: 0.001–0.0012%, N: 0.005%, C: 0.006%	Kobe Steel Ltd., Kobe, Japan	1039C65001
Etching agent			
SH-etchant	45wt% H_2SO_4, distilled water 15wt% HCl, distilled water	Wako Pure Chemical Ind., Ltd., Osaka, Japan Wako Pure Chemical Ind., Ltd.	DCF1559 DCR1606
Primer			
Estenia C&B Opaque Primer (MDP-primer)	MDP, methacrylate monomer, solvent, others	Kuraray Noritake Dental Inc., Tokyo, Japan	0173BA
Resin composite			
Estenia C&B Body Opaque OA3	Bis-GMA, methacrylate monomer, photoinitiator, pigment, filler (quartz, composite), others	Kuraray Noritake Dental Inc.	0115AA
Estenia C&B Dentin DA3	UTMA, methacrylate monomer, photoinitiator, pigment, filler (surface-treated alumina microfiller, silanated glass ceramic filler), others	Kuraray Noritake Dental Inc.	0080BA

MDP: 10-methacryloyloxydecyl dihydrogen phosphate; Bis-GMA: bisphenol-A-glycidyl methacrylate; UTMA: urethane tetramethacrylate

Noritake Dental Inc., Tokyo, Japan), light-cured for 180 s, and heated at 110°C for 15 min in an oven (KL100, J. Morita Corp., Osaka, Japan). Eight test groups of bonded specimens (no sand/no etch/no primer, no sand/no etch/MDP-primer, no sand/SH-etchant/no primer, no sand/SH-etchant/MDP-primer, sand/no etch/no primer, sand/no etch/MDP-primer, sand/SH-etchant/no primer, and sand/SH-etchant/MDP-primer) were thus prepared as described above.

Shear bond strength test

After leaving the bonded specimens at room temperature for 30 min, they were immersed in distilled water at 37°C for 24 h. After water storage, the specimens were embedded in an acrylic resin mold and fitted to a shear testing jig (Wago Industrial Ltd., Nagasaki, Japan) which was used to apply a shearing load parallel to the bonded interface. Shear bond strengths were determined using a universal testing machine (AGS-10kNG, Shimadzu Corp., Kyoto, Japan) at a crosshead speed of 0.5 mm/min.

Mean bond strength and standard deviation of eight specimens were calculated for each test group. All data were analyzed by analysis of variance (ANOVA), and the mean values were compared by a *post-hoc* Tukey compromise test at a statistical significance of 0.05.

After shear testing, the titanium surfaces of the debonded specimens were observed with an optical microscope (SMZ-10, Nikon Corp., Tokyo, Japan) at a magnification of ×20 to determine the failure mode. Failure modes were categorized as: adhesive failure at resin composite-titanium interface (Ad), cohesive failure in resin composite (Co), and mixed adhesive-cohesive failure (Ad/Co).

Scanning electron microscope observation

One titanium specimen from each of these four test groups was selected for microscopic observation: sand/no etch, no sand/no etch, sand/SH-etchant, and no sand/SH-etchant. Their surface characteristics were observed using a scanning electron microscope (SEM; S-3500N, Hitachi Corp., Tokyo, Japan) at ×1,000 and ×8,000 magnifications.

Surface roughness measurement

Four test groups were selected for surface roughness measurement: sand/no etch, no sand/no etch, sand/SH-etchant, and no sand/SH-etchant. The surfaces of all titanium specimens from these four test groups were analyzed using a color laser 3D profile microscope (VK-8500, Keyence Corp., Osaka, Japan) at ×2,000 magnification.

Arithmetic mean roughness (Ra), maximum height (Ry), and 10-point mean roughness (Rz) within a 50 µm×50 µm area were determined using an analysis software (VK shape analysis application VK-H1W, Keyence Corp., Osaka, Japan). For each test group, the mean and standard deviation of eight measurements were calculated. All data were analyzed by ANOVA, and the mean values were compared by a *post-hoc* Tukey compromise test at a statistical significance of 0.05.

RESULTS

Shear bond strength

Table 2 shows the ANOVA results for shear bond strength data shown in Table 3. Bond strength was influenced by sandblasting, SH-etchant, and MDP-primer when used individually. The combined treatments of sandblasting/SH-etchant, sandblasting/MDP-primer, SH-etchant/MDP-primer, and sandblasting/SH-etchant/MDP-primer did not significantly affect bond strength.

Table 3 lists the mean shear bond strengths, standard deviations, and failure modes of all the eight test groups in this study. Mean bond strength ranged from 7.4 to 29.9 MPa, and data were obtained in this descending order: sand/SH-etchant/MDP-primer, sand/SH-etchant/no primer, no sand/SH-etchant/MDP-primer, sand/no etch/MDP-primer, no sand/SH-etchant/no primer, sand/no etch/no primer, no sand/no etch/MDP-primer,

Table 2 Analysis of variance results for shear bond strength

Source of variation	d.f.	Sum of squares	Mean square	*F*-value	*p*-value
Sandblasting	1	594.3	594.3	84.3	≤0.0001
SH-etchant	1	1628.0	1628.0	230.8	≤0.0001
MDP-primer	1	466.4	466.4	66.1	≤0.0001
Sandblasting/SH-etchant	1	9.5	9.5	1.3	0.3
Sandblasting/MDP-primer	1	2.6	2.6	0.4	0.5
SH-etchant/MDP-primer	1	6.2	6.2	0.9	0.4
Sandblasting/SH-etchant/MDP-primer	1	13.4	13.4	1.9	0.2
Residual	56	394.9	7.1	—	—

no sand/no etch/no primer. There were no statistical differences between sand/SH-etchant/no primer and no sand/SH-etchant/MDP-primer, between sand/no etch/MDP-primer and no sand/SH-etchant/no primer, and between sand/no etch/no primer and no sand/no etch/MDP-primer.

Failure mode

In Table 3, five specimens of no sand/no etch/no primer group exhibited adhesive failure at the resin composite-titanium interface (Ad) and three specimens exhibited mixed adhesive-cohesive failure (Ad/Co). For the remaining seven test groups, all specimens exhibited mixed failure with opaque resin fragments remaining on the titanium surface.

Surface characteristics

Figures 1–4 show the SEM images of cpTi grade 4 surfaces with and without surface treatments. At ×1,000 magnification, the surface texture of the specimen treated with sandblasting and SH-etchant (Fig. 4a) was different from the other specimens (Figs. 1a, 2a, and 3a). At higher ×8,000 magnification, their differences became sharper (Figs. 1b, 2b, 3b, and 4b). The surfaces of specimens treated with SH-etchant (Figs. 2b and 4b) were clearly rougher and had more cavities than the specimens not treated with SH-etchant (Figs. 1b and 3b). The cavities in Fig. 4b were smaller and deeper than those in Figs. 2b and 3b. Many microcavities, and even more nanoscale cavities, were observed in Fig. 4b. The nanoscale cavities had sharp edges with a honeycomb structure (Fig. 4b). In contrast, no such nanoscale cavities were observed when treated with SH-etchant (Fig. 2b) or sandblasting (Fig. 3b) only.

Surface roughness

Table 4 shows the ANOVA results for Ra data shown in Table 5. Ra values were significantly influenced by

Table 3 Shear bond strengths and failure modes

Test group	Mean (SD)* (MPa)	Failure mode** (Number of specimens)
No sand/no etch/no primer	7.4 (3.6)[a]	Ad(5), Ad/Co(3)
No sand/no etch/MDP-primer	14.7 (1.9)[b]	Ad/Co(8)
No sand/SH-etchant/no primer	19.8 (1.5)[c]	Ad/Co(8)
No sand/SH-etchant/MDP-primer	24.1 (3.1)[d]	Ad/Co(8)
Sand/no etch/no primer	15.6 (1.9)[b]	Ad/Co(8)
Sand/no etch/MDP-primer	20.3 (1.3)[c]	Ad/Co(8)
Sand/SH-etchant/no primer	24.6 (2.4)[d]	Ad/Co(8)
Sand/SH-etchant/MDP-primer	29.9 (4.1)[e]	Ad/Co(8)

*Identical small letters indicate that values are not statistically different (p>0.05).
**Ad: Adhesive failure at resin composite-titanium interface; Co: cohesive failure in resin composite;
Ad/Co: Mixed adhesive-cohesive failure

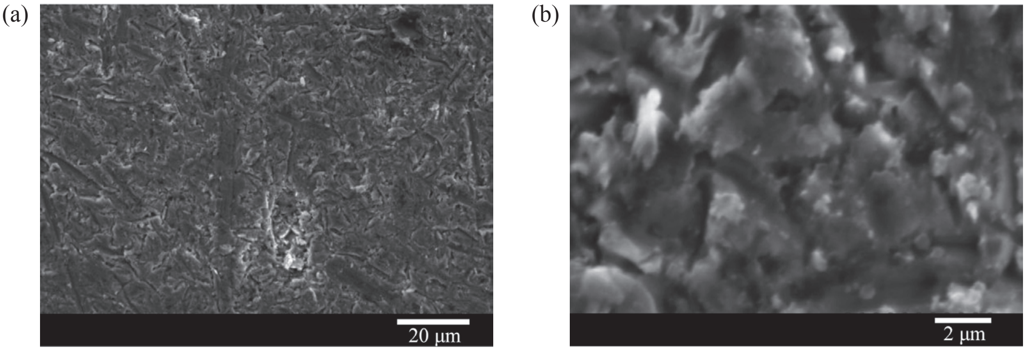

Fig. 1 SEM micrographs of cpTi grade 4 surface ground with 1,000-grit silicon carbide paper only: (a) ×1,000 magnification; (b) ×8,000 magnification.

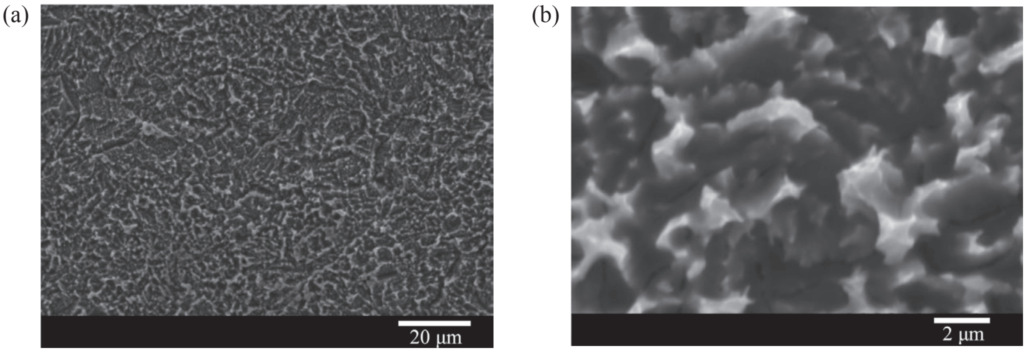

Fig. 2 SEM micrographs of cpTi grade 4 surface etched with SH-etchant only: (a) ×1,000 magnification; (b) ×8,000 magnification.

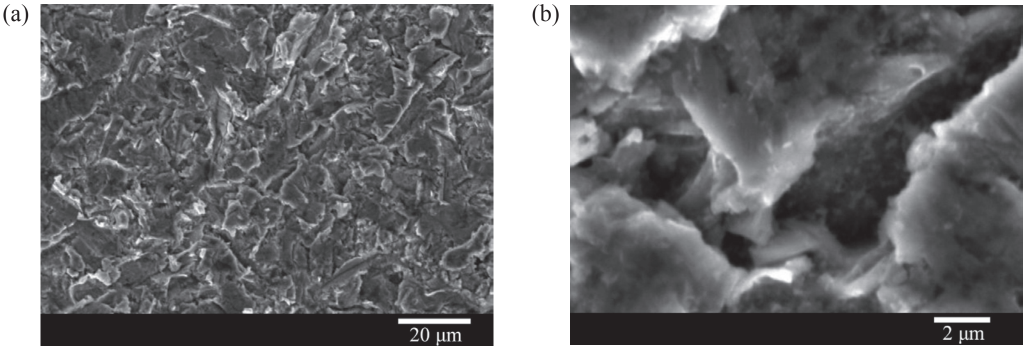

Fig. 3 SEM micrographs of cpTi grade 4 surface sandblasted with alumina only: (a) ×1,000 magnification; (b) ×8,000 magnification.

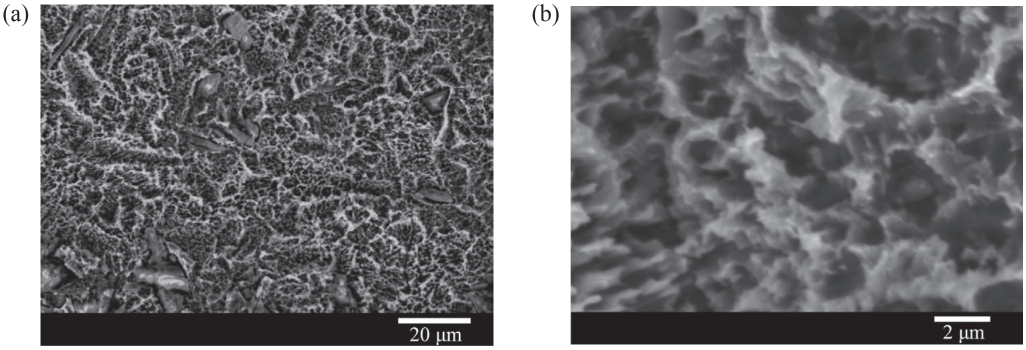

Fig. 4 SEM micrographs of cpTi grade 4 surface sandblasted with alumina and etched with SH-etchant: (a) ×1,000 magnification; (b) ×8,000 magnification.

both sandblasting and SH-etchant, and their interaction was also significant. Table 5 shows the mean Ra values obtained, which were found in this descending order: sand/SH-etchant (1.29 µm), sand/no etch (1.13 µm), no sand/SH-etchant (0.83 µm), no sand/no etch (0.25 µm). There were significant differences in Ra value among the four groups of surface treatments.

Table 6 shows the ANOVA results for Ry data shown in Table 7. Ry values were significantly influenced by both sandblasting and SH-etchant, and their interaction was also significant. Table 7 shows the Ry values obtained, which were found in this descending order:

Table 4 Analysis of variance results for arithmetic mean roughness (Ra)

Source of variation	d.f.	Sum of squares	Mean square	*F*-value	*p*-value
Sandblasting	1	3.60	3.60	511.11	≤0.0001
SH-etchant	1	1.08	1.08	152.74	≤0.0001
Sandblasting/SH-etchant	1	0.34	0.34	48.45	≤0.0001
Residual	28	0.20	0.01	—	—

Table 5 Arithmetic mean roughness (Ra) of specimens modified by four surface treatment combinations

Test group	Mean (SD)* (µm)
No sand/no etch	0.25 (0.02)^a
No sand/SH-etchant	0.83 (0.08)^b
Sand/no etch	1.13 (0.10)^c
Sand/SH-etchant	1.29 (0.11)^d

*Identical small letters indicate that values are not statistically different (p>0.05).

Table 6 Analysis of variance results for maximum height (Ry)

Source of variation	d.f.	Sum of squares	Mean square	*F*-value	*p*-value
Sandblasting	1	343.42	343.42	419.54	≤0.0001
SH-etchant	1	26.45	26.45	32.31	≤0.0001
Sandblasting/SH-etchant	1	417.39	417.39	509.91	≤0.0001
Residual	28	22.92	0.82	—	—

Table 7 Maximum height (Ry) of specimens modified by four surface treatment combinations

Test group	Mean (SD)* (µm)
No sand/no etch	10.58 (1.09)^a
No sand/SH-etchant	19.62 (1.32)^b
Sand/no etch	24.36 (0.52)^c
Sand/SH-etchant	18.95 (0.30)^b

*Identical small letters indicate that values are not statistically different (p>0.05).

sand/no etch (24.36 µm), no sand/SH-etchant (19.62 µm), sand/SH-etchant (18.95 µm), no sand/no etch (10.58 µm). There was no statistical difference between no sand/SH-etchant and sand/SH-etchant.

Table 8 shows the ANOVA results for Rz data shown in Table 9. Rz values were significantly influenced by both sandblasting and SH-etchant, and their interaction was also significant. Table 9 shows the Rz values obtained, which were found in this descending order: sand/no etch (22.75 µm), sand/SH-etchant (18.15 µm), no sand/SH-etchant (17.34 µm), no sand/no etch (5.82 µm). There was no statistical difference between sand/SH-etchant and no sand/SH-etchant.

Table 8 Analysis of variance results for 10-point mean roughness (Rz)

Source of variation	d.f.	Sum of squares	Mean square	*F*-value	*p*-value
Sandblasting	1	629.56	629.56	747.17	≤0.0001
SH-etchant	1	95.69	95.69	113.57	≤0.0001
Sandblasting/SH-etchant	1	519.35	519.35	616.38	≤0.0001
Residual	28	23.59	0.84	—	—

Table 9 Ten-point mean roughness (Rz) of specimens modified by four surface treatment combinations

Test group	Mean (SD)* (μm)
No sand/no etch	5.82 (0.56)[a]
No sand/SH-etchant	17.34 (1.06)[b]
Sand/no etch	22.75 (1.38)[c]
Sand/SH-etchant	18.15 (0.21)[b]

*Identical small letters indicate that values are not statistically different (p>0.05).

DISCUSSION

Results of the present study revealed that the shear bond strength of resin composite to cpTi grade 4 was significantly improved with a combined use of sandblasting, SH-etchant, and MDP-primer application. Therefore, the hypothesis of this study was accepted.

It was reported that sandblasting with 250–500 μm alumina particles prior to etching with a mixture of H_2SO_4 and HCl, sand-blasted large grit acid-etched (SLA) surface, improved osseointegration[32,33]. In the present study, however, smaller alumina particles (average grain size: 50 μm)[19,30,31,35] were used for sandblasting. The objective was to create nanoscale retention associated with nanoscale cavities for adhesive bonding.

On the efficacy of etchant formulations on titanium bonding, it was reported that the bond strength of cpTi modified with 48% H_2SO_4 was higher than that modified with 4.8% H_2SO_4 or 18% HCl alone[25]. Based on our preliminary experiments and findings of other studies[25-29,32,33], it was determined that the optimal formulation of SH-etchant would contain 45wt% H_2SO_4 and 15wt% HCl. In addition, several temperatures and etching times were tested in our preliminary experiments. The etchant temperature of 70°C and etching time of 10 min were found to be optimal and were thus employed in the present study.

The sand/SH-etchant specimen exhibited the highest Ra value and had many micro- and nanoscale cavities (Fig. 4b). However, the Ry and Rz values of sand/SH-etchant were lower than those of sand/no etch, which suggested that SH-etchant reduced the peak of surface irregularities on the alumina-blasted surface. Instead, the SEM images revealed that sand/SH-etchant (Fig. 4b) produced more undercuts than no sand/SH-etchant (Fig. 2b) and sand/no etch (Fig. 3b). Surface characteristics, especially undercuts and cavities, affect micro- and nano-mechanical retention, which in turn contributed to high bond strength in this study.

When comparing the effects of sandblasting and SH-etchant, no sand/SH-etchant/no primer (19.8 MPa) and no sand/SH-etchant/MDP-primer (24.1 MPa) exhibited significantly higher bond strengths than sand/no etch/no primer (15.6 MPa) and sand/no etch/MDP-primer (20.3 MPa). Interestingly, comparison with surface roughness results revealed that no sand/SH-etchant specimen had lower values of Ra (0.83 μm), Ry (19.62 μm), and Rz (17.34 μm) than sand/no etch specimen (Ra: 1.13 μm, Ry: 24.36 μm, and Rz: 22.75 μm). However, the SEM images (Figs. 2a, 2b, 3a, and 3b) indicated that the no sand/SH-etchant surface had more undercuts than the sand/no etch surface, which most probably contributed to mechanical interlocking and thus higher bond strength.

In the absence of MDP-primer, sand/SH-etchant/no primer specimen had a significantly higher bond strength (24.6 MPa) than no sand/SH-etchant/no primer (19.8 MPa) and sand/no etch/no primer (15.6 MPa). In the presence of MDP-primer, sand/SH-etchant/MDP-primer still had a significantly higher bond strength (29.9 MPa) than no sand/SH-etchant/MDP-primer (24.1 MPa) and sand/no etch/MDP-primer (20.3 MPa). These findings suggested a cooperative effect between sandblasting and SH-etchant treatments, irrespective of whether MDP-primer was used.

TiH_2 reportedly formed on cpTi when etched with H_2SO_4 and HCl[36], H_2SO_4[29], or HCl[37]. The average thickness was approximately 150 nm when etched with H_2SO_4 and HCl[36]. Upon exposure to moisture in the air, the TiH_2 layer was immediately covered by an oxide layer (TiO_2)[29,37]. In the present study, therefore, the bonding surfaces of titanium specimens were mainly constituted of TiO_2 rather than pure titanium.

After sandblasting with alumina, some alumina particles probably remained on the surface[17,38]. Through X-ray photoelectron spectroscopy (XPS), it was revealed that when titanium surface was pretreated with 1 N HCl, it became effectively decontaminated[26]. In the present study, it was speculated that acid etching with SH-etchant brought about several benefits to the titanium surface: increased micro- and nanoscale mechanical interlocking, increased effective bonding area, and decreased contaminants from the surface. In terms of commercial applicability, the SH-etchant seemed to augur well for reducing clinical complications such as fracture or debonding of resin composite veneers from titanium frameworks. However, utmost care and caution must be exercised when handling H_2SO_4 and HCl. The skin and eyes must always be protected, and fume chamber is necessary to prevent inhaling the vapors of evaporated acids.

Comparisons between no sand/no etch/no primer and no sand/no etch/MDP-primer, between no sand/SH-etchant/no primer and no sand/SH-etchant/MDP-primer, between sand/no etch/no primer and sand/no etch/MDP-primer, and between sand/SH-etchant/no primer and sand/SH-etchant/MDP-primer indicated that the MDP monomer improved titanium bonding irrespective of prior treatments to the titanium surface before MDP-primer application. These findings agreed with previous studies which reported that an MDP-containing primer improved the adhesive bonding between titanium and resins[15,16]. It was suggested that the phosphoric acid group of MDP monomer was effective in improving the adhesion of resins to titanium[20]. In the present study, it was speculated that the MDP monomer generated chemical bonding to the titanium surface and promoted the diffusion of other monomers into the micro- and nanoscale cavities created by sandblasting and acid etching. Strong mechanical interlocking was then achieved when diffused monomers were polymerized *in situ*.

In the present study, bond strength was evaluated at 24 h after the bonding procedure. In clinical situations, high bonding durability is a mandatory requisite for dental prostheses to function over a long time in the oral environment. Therefore, the next research target is to investigate the bonding durability produced by these surface treatments as well as to extend this investigation to other metal alloys.

CONCLUSIONS

Within the limitations of the present study, the following conclusions were drawn:

1. Different surface treatment combinations of sandblasting, acid etching, and primer application significantly improved the 24-h shear bond strength between cpTi grade 4 and a veneering resin composite.
2. Maximum bond strength was obtained when cpTi grade 4 was sandblasted with 50-µm alumina, etched with an aqueous solution containing 45 wt% H_2SO_4 and 15 wt% HCl, and treated with an MDP-containing primer.
3. Combined use of sandblasting and acid etching significantly increased arithmetic mean roughness (Ra) and created many micro- and nanoscale cavities on the titanium surface, thus enhancing mechanical interlocking at the bonded interface.

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