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Short Communication

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

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Abstract: 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.

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Introduction

Titanium is widely used in fixed partial dentures, removable dentures, and implant-supported superstructures, which are commonly fabricated using casting techniques or computer-aided design/computer-assisted manufacturing systems. Although titanium has excellent biocompatibility, high corrosion resistance, and adequate mechanical properties,[1] strong bonding between the metal framework and resin composites is required for titanium prostheses to withstand the severe conditions in the oral cavity.

A number of titanium surface modification techniques have been investigated to improve the strength and durability of resin—titanium adhesive bonds, e.g., air abrasion,[2] silica coating,[3] primer application,[4] alkaline treatment,[5] acid etching,[6] and plasma treatment.[7] Previously, we reported that chemical etching with ammonium hydrogen fluoride or sodium hydrogen fluoride significantly improves the strength of commercially pure titanium (cpTi)—resin bonds.[8]

Chemical etching is characterized by ease of operation, low running costs, and short treatment times, and does not require the use of special equipment; however, the toxicity of some fluorides (e.g., hydrogen fluoride) is a matter of great concern. Recently, an etching agent (Monobond Etch & Prime (ETCH); Ivoclar Vivadent AG, Schaan, Liechtenstein) containing tetrabutylammonium dihydrogen trifluoride (TDTF) has been introduced onto the market as a clinically acceptable product for bonding glass ceramics. Since the chemical structure of TDTF is close to that of ammonium hydrogen fluoride, we hypothesized that the former may facilitate resin—cpTi bonding.

Currently, increasingly strict requirements are being placed on the durability of esthetic prostheses and the use of potentially allergenic metal alloys, which necessitates the development of methods for improving resin—titanium bonding. To address this challenge, we herein evaluated the effects of the surface treatment of titanium with ETCH on the durability of the bond strength between an indirect resin composite and cpTi, where the null hypothesis is that this treatment has no effect on bond strength.

Materials and methods

Preparation of bonded specimens

The characteristics of cpTi, etching agent, primer, and resin composite used are summarized in Table 1. A total of 72 cpTi disks (diameter: 10 mm; thickness: 3 mm) were ground with #600 and #1200 silicon carbide papers and air-abraded (Jet Blast III, J. Morita Corp., Kyoto, Japan) with alumina (Hi-Alumina, Shofu Inc., Kyoto, Japan; average grain size 50—70 μm) for 10 s using an air pressure of 0.40 MPa and a metal surface-to-nozzle distance of 10 mm. The abraded disks were ultrasonically cleaned in distilled water for 5 min (SUC-110, Shofu Inc., Kyoto, Japan).

The specimens were divided into three groups of eight specimens each, depending on the ETCH treatment time: ETCH10 (ETCH-treated for 10 s), ETCH30 (ETCH-treated for 30 s), and no-ETCH (untreated control samples). ETCH was applied to the cpTi surface using disposable brush applicators (Shofu Inc., Kyoto, Japan). Then the etched samples were rinsed with a water spray for 30 s, ultrasonically cleaned in distilled water for 5 min, and air-dried.

A piece of 50-μm-thick masking tape with a 4-mm-diameter circular hole was attached to each cpTi specimen to define the bonding area and Metal Link Primer (Shofu Inc., Kyoto, Japan) was applied to the specimens with a brush. Ceramage Duo Pre-Opaque and Opaque (Shofu Inc., Kyoto, Japan) were applied to the specimens with a brush

Table 1 Titanium metal, etching agent, primer, and resin composite used in this study.

Name (Abbreviation)	Manufacturer	Composition	Batch No.
<Titanium metal>			
Commercially pure titanium grade 4 (cpTi)	Kobe Steel Ltd., Kobe, Japan	Ti, ≥99.4578%; O, 0.32—0.36%; Fe, 016—0.17%; H, 0.001—0.0012%; N, 0.005%; C, 0.0006%	
<Etching agent>			
Monobond Etch & Prime (ETCH)	Ivoclar Vivadent AG, Schaan, Liechtenstein	Tetrabutylammonium dihydrogen trifluoride, methacrylated phosphoric acid ester, bis-(triethoxysilyl)ethane, butanol	V09353
<Primer>			
Metal Link Primer	Shofu Inc., Kyoto, Japan	10-MDDT, 6-MHPA, acetone	111591
<Resin composite>			
Ceramage Duo	Shofu Inc., Kyoto, Japan	Pre-Opaque: UDMA, silica powder, pigment, photoinitiator	111601
		Opaque A3O: UDMA, silica powder, pigment, photoinitiator	111601
		Body resin A3B: UDMA, urethane diacrylate, zirconium silicate, pigment	121602

10-MDDT: 10-methacryloyloxydecyl-6,8-dithiooctanate, 6-MHPA: 6-methacryloyloxyhexyl phosphonoacetate, UDMA: urethane-dimethacrylate.

and light-cured for 30 and 90 s, respectively, using a laboratory light-emitting-diode (LED) unit (Labocure L, GC Corp., Tokyo, Japan). The bonding area was surrounded by an acrylic ring (inner diameter: 6 mm; height: 2 mm). The acrylic mold was filled with the Ceramage Duo Body resin (Shofu Inc., Kyoto, Japan) that was subsequently light cured for 150 s.

Shear bond strength test

The bonded specimens were left exposed to the atmosphere for 30 min, and then immersed in distilled water at 37 °C for 24 h. The shear bond strength of 24 specimens (three groups of eight specimens each) was tested (designated as thermocycle 0), and the remaining 48 specimens (two sets of three groups) were subjected to 50,000 or 100,000 thermocycles. Each thermocycle comprised sequential 1-min immersion into water baths held at 4 °C and 60 °C.

The cycled specimens were embedded in an acrylic mold and fitted to a shear testing jig (No. ISO/TR11405, Wago Ind., Nagasaki, Japan) used to apply a shearing load parallel to the bonded interface. The shear bond strengths were determined using a universal testing machine (AGS-10kNG, Shimadzu Corp., Kyoto, Japan) at a cross-head speed of 0.5 mm/min.

Failure mode observation

After shear testing, the cpTi and resin composite surfaces of debonded specimens were observed by optical microscopy (SMZ-10, Nikon Corp., Tokyo, Japan) at a magnification of 20 × to determine the type of bond failure (adhesive failure at the resin composite—cpTi interface (A), cohesive failure within the resin composite (C), or mixed-mode of these failures (A/C)).

Statistical analysis

The mean bond strengths and corresponding standard deviations (SDs) were calculated for each test group of eight specimens. The homoscedasticity assumption was assessed using Levene's test, and all data were compared using a non-parametric Steel—Dwass test at a statistical significance level of 0.05. Statistical analysis was carried out using the JMP Pro software system (ver. 11, SAS Institute Japan Ltd., Tokyo, Japan).

Results

The mean shear bond strengths, SDs, and failure modes obtained for each sample group are listed in Table 2, which shows that the mean bond strengths ranged from 0.5 to 25.7 MPa. Prior to thermocycling, no significant differences were observed between the no-ETCH, ETCH10, and ETCH30 groups, and all specimens exhibited complete cohesive failure. After 100,000 thermocycles, the bond strength decreased from 25.7 to 0.5 MPa for no-ETCH samples, the failure mode of which shifted from complete cohesive failure to complete adhesive failure.

On the other hand, no significant changes in the bond strength were observed for the ETCH10 (23.6 MPa) and ETCH30 (24.3 MPa) samples, and their failure modes shifted to mixed failure after 100,000 thermocycles. After 50,000 or 100,000 thermocycles, the ETCH10 and ETCH30 samples exhibited significantly higher bond strengths than no-ETCH ones. The difference between ETCH10 and ETCH30 was not statistically significant irrespective of the number of thermocycles.

Discussion

The obtained results revealed that alumina abrasion followed by ETCH application significantly improved the durability of the resin—cpTi bond strength, and the null hypothesis was therefore rejected.

Since thermal stresses originate from differences between thermal expansion coefficients of the employed substrate materials, resin-to-metal bonds are much more sensitive to thermocycling than metal-to-metal ones.[4,8] Previously, we reported that, although chemical etching with ammonium hydrogen fluoride or sodium hydrogen fluoride significantly improved the strength of resin—cpTi bonding, a significant decrease in the bond strength was observed after 10,000 thermocycles.[8] As we performed thermocycling ten times longer than the previous study (100,000 cycles) and the ETCH10 and ETCH30 samples maintained their bond strengths (23.6 and 24.3 MPa, respectively), we concluded that the developed etching method was superior to those reported previously.

Upon ETCH application, the color of the cpTi surface changed to dark gray as in the case of using ammonium hydrogen fluoride or sodium hydrogen fluoride. Since cpTi surfaces are covered with a passive film of TiO_2 under atmospheric conditions, TDTF is thought to react with the surface of the TiO_2 layer. The adsorption of fluoride on TiO_2 involves an exchange reaction between F^- and surface

Table 2 Shear bond strengths and failure modes.

Group Name	Mean (SD) of bond strength (MPa)[a]			Failure mode (number of specimens)[b]		
	Thermocycle 0	50,000 cycles	100,000 cycles	Thermocycle 0	50,000 cycles	100,000 cycles
no-ETCH	25.7 (3.0)^a	19.3 (1.4)^b	0.5 (0.9)	C (8)	A/C (8)	A (8)
ETCH10	23.6 (1.6)^a	24.9 (2.6)^a	20.0 (3.5)^{a,b}	C (8)	C (8)	A/C (8)
ETCH30	24.3 (1.8)^a	25.7 (3.4)^a	23.0 (3.4)^{a,b}	C (8)	C (8)	A/C (8)

[a] Same letters indicate no significant differences ($p > 0.05$).
[b] A: adhesive failure at resin composite-cpTi interface; C: cohesive failure within resin composite; A/C: mixed failure of A and C.

hydroxyl groups ($\equiv$Ti-OH + F^- → Ti-F + OH^-). The added fluoride may facilitate anatase crystal growth, and the surface fluorination of TiO_2 produces mobile free OH radicals.[9] We speculate that these mechanisms are responsible for the excellent bonding durability when TDTF is applied to cpTi. Therefore, further investigations (e.g., X-ray photoelectron spectroscopy analysis and scanning electron microscopy observation) are required to verify the bonding mechanisms and to reveal the aging process of the bonded interface during the thermocycling.

According to the manufacturer's protocol for veneering resin composite on metal frameworks, air abrasion and the primer containing 6-methacryloyloxyhexyl phosphonoacetate (6-MHPA) were applied to all samples. Phosphoric monomers, such as 6-MHPA or 10-methacryloyloxydecyl dihydrogen phosphate (MDP), are known to promote bonding to the surface of air-abraded titanium.[10] However, both the present and previous findings indicate that no durable bonding can be obtained using only primers containing a phosphoric monomer without etching.[4,6,8] Thus, although ETCH contains a phosphoric monomer and TDTF, we suggest that TDTF plays a significant role in maximizing the bonding durability.

Considering these findings, the combined use of air abrasion and ETCH treatment can inhibit the delamination of veneered resin composites from titanium frameworks and the debonding of resin-bonded fixed partial dentures. However, care should be taken to protect the skin and eyes when using etching agents, which should never be applied directly to the oral cavity.

Within the limitations of the present study, it is concluded that the durability of the cpTi—resin bond strength is significantly improved by the application of an etching agent containing TDTF for 10—30 s after air abrasion.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

None.

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