Effects of a Silane Coupling Agent on the Tensile Adhesive Strength Between Resin and Titanium

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ABSTRACT: Adhesion of a cured dental opaquer, which masks metallic appearance and color, to sandblasted Ti aided by 3-methacryloy-loxypropyltrimethoxysilane (MPTS) is investigated. The tensile bond strengths of Ti and the opaquer are 43.3 and 45.9 MPa, respectively, when MPTS dissolved in ethanol (6 wt %) and premixed with the opaquer (3 wt %) are applied to the sandblasted Ti surface. Mirror finishing alone and sandblasting alone result in the bond strengths of 1.8 and 21.3 MPa, respectively. After thermal cycling (4 and 60°C for 5000 cycles), the bond strengths of the Ti with sandblasting and the MPTS treatment remain higher than that of the Ti with sandblasting only. Sandblasting and the MPTS treatment effectively promote the adhesion of the opaquer to Ti that rapidly forms an oxide surface layer. The silane-aided adhesion of the opaquer to the sandblasted Ni—Cr, Co—Cr, and Au—Ag—Pd alloys attain adhesive strengths of 33.2, 31.9, and 31.6 MPa, respectively. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2922–2930, 2013

INTRODUCTION

Metal and organic polymer (resin) composites have been widely used as a dental restorative material. For this application, different types of coupling agents are required to enhance adhesion between precious or non-precious metals and the resin. Monomers containing a phosphoric acid, phosphorous acid, or carboxylic acid group have been utilized as the coupling agents for non-precious metals,[1,2] whereas monomers containing a thiol, thione, or disulfide group, which forms a self-assembling unimolecular layer on metals, are known to be effective coupling agents for precious metals.[3–5] Conversely, an organofunctional silane such as 3-methacryloyloxypropyltrimethoxysilane (MPTS) affords the possibility of forming chemical bonds with inorganic and organic substrates and/or between the organofunctional silane molecules.[6] A trimethoxysilylated compound can perform in two types of reactions, hydrolysis and condensation, which occur reversibly with comparable rates,[7] and each trimethoxysilyl group ultimately forms three Si—O bonds by an intermolecular reaction with a substrate bearing OH groups or by the self-condensation of neighboring SiOH groups formed by hydrolysis. OH groups on the surfaces of a wide variety of materials such as glass and porcelain play an important role in the formation of Si—O bonds through fast reactions with SiOCH$_3$ or SiOH groups leading to a hydrophobic layer on the substrate surface.

Recently, Ti and Ti alloys have attracted attention as suitable materials for dental implants based on the biocompatibility and other characteristics of Ti. However, to attain sufficiently strong adhesion between Ti/alloys and a resin, an effective coupling agent has to be selected because solely roughing the metal surface by sandblasting or rubbing with a grit paper results in insufficient adhesion. The tribochemical silica-coating process (Rocatec™), which consists of sandblasting with particular silica-coated alumina sands followed by treatment with a silane priming agent, has been utilized for bonding of a hydrophobic material to Ti. When the Rocatec™ technique is applied to Ti, silicates on the Ti surface can react with the silane priming agent resulting in Si—O bond formation.

The X-ray photoelectron spectroscopy (XPS) of a vapor–deposited metal surface has revealed that the Ti sample was covered by a thin oxide layer containing OH groups as shown in Table I.[8,9] When the reactions of MPTS with OH groups on Ti proceed spontaneously, Si—O—Ti bond formation and hydrolysis of the SiOCH$_3$ group, followed by Si—O—Si linkage formation, occur simultaneously. An intermolecular reaction between the SiOH group with the SiOCH$_3$ group of MPTS may also result in Si—O—Si bond formation on a Ti surface.[7,10] MPTS, which is stable in the presence of water at a pH of 6.5,[7] can form a hydrophobic film by the reaction with the OH group on a Ti

Table I. Oxygen Content and Thickness of the Surface Layer of Vapor Deposited Metals (Quoted from Ref. 8)

Metal	Content (%)		Thickness of surface layer (nm)
	Metal	Oxygen	
Au	100.0	0	–
Ag	91.8	8.2	<5
Cu	34.1	65.9	<5
Ni	29.6	70.4	1.08
Cr	32.1	67.9	1.08
Ti	59.7	40.3	3.70

surface. The formation of a hydrophobic film may promote adhesion between Ti and the resin.

In studies on reactions with metals which have surface OH groups, MPTS was often activated by acid hydrolysis in advance. When the Ti surface was coated with MPTS, an absorption due to the stretching vibration of a Si—OH bond, formed by hydrolysis, diminishes after 10 min and disappear upon heating. The substrate surface was covered by a siloxane film, which was confirmed by the absorptions of a Si—O—Si—O—Si linkage together with an absorption assignable to the carbon–carbon double bond of the methacryloyl group.[11,12]

Atomic force microscopy (AFM) observation indicated a rough surface of Ti, created by grinding, became smoother after treatment with hydrolyzed MPTS (MPTS treatment/hydrolysis) and that the lines generated by grinding disappeared.[11] Therefore, it appears that the MPTS treatment/hydrolysis forms a thin film associated with the reaction of OH groups on the Ti surface and with an intermolecular reaction between neighboring MPTS moieties. Furthermore, silane coupling agents (hydrolyzed) have been utilized to mirror-finished Ti for bonding with segmented poly(ureathane), and it has been confirmed that the reaction of OH groups on the metal surface with the silane compounds enhanced bond strength.[13–15] The reaction of a silane coupling agent with a metal is probably involved the following series of reactions; the formation of a SiOH group by the hydrolysis of a SiOCH$_3$ group → the hydrogen bonding of the SiOH to a OH group on the metal surface →dehydration between the SiOH and the OH to form a Si—O—metal bond → Si—O—Si bond formation by the reaction between neighboring SiOH groups.[13]

Intermolecular condensation between SiOH groups has been reported to occur after the complete hydrolysis of SiOCH$_3$ groups.[16] If the Si—O—Si bond is formed by self-condensation before the reaction with the OH groups on the Ti surface, MPTS would not be efficiently fixed on the surface. The application of MPTS to a metal surface to enhance bonding with a resin has been studied to a limited extent.[17] In dental and related applications, MPTS has been used as a convenient coupling agent to modify the hydrophilicity of a glass or silica filler, otherwise a sufficiently strong interaction between the filler and a matrix resin cannot be attained. If OH groups on a metal surface are allowed to react with MPTS or hydrolyzed MPTS, bet-

ter adhesion between the metal and a resin can be expected as those as glass and silica with a resin.

It has been reported that the bond formation between poly-(hyphone) (methyl methacrylate) (PMMA) and Ti was promoted by MPTS in the presence of propylamine as a catalyst.[18] The essential use of an amine catalyst, which simultaneously accelerates the hydrolysis and self-condensation of MPTS,[19] suggests that MPTS is less reactive with metals than glass or silica. While OH groups on an oxide layer act as active sites for the reaction with hydrolyzed MPTS,[11–15] there might be an insufficient quantity of OH groups on the metal surface for the reaction with MPTS. To solve this problem, sandblasting was applied; the sandblasting of non-precious metals could effectively increase the surface area and the number of OH groups. To the best of our knowledge, the application of MPST to enhance adhesion with sandblaste metals has not been reported.

This study deals with the enhanced adhesion of a dental opaquer, which is used to mask or eliminate the appearance of metallic color fulfilling the aesthetic requirements of dental restoration, with sandblasted Ti and metal alloys using MPTS dissolved in ethanol or premixed with the opaquer in the absence of a catalyst. Furthermore, vinyltrimethoxysilane (VTMS) and tetramethoxysilane (TEMS) containing a trimethoxysilyl group were also used without hydrolysis as references. In general, MPTS without and with activation by hydrolysis has been applied to siloxane and metal-bearing OH groups, respectively. However, MPTS was used without activation (hydrolysis) unless otherwise noted in the present article.

EXPERIMENTAL

Materials

Commercial MPTS (Momentive Performance Materials), VTMS (Tokyo Chemical Industry), and TEMS (Tokyo Chemical Industry) were used as received. The opaquer used in this study was TWiNY IvO (Yamamoto Precious Metal), which consists of urethane dimethacrylate (55 wt %, 1,6-bis(methacryoyloxy-2-ethoxy-carbonylamino)-2,4,4-trimethylhexane, UDMA, Mitsubishi Rayon), triethyleneglycoldimethacrylate (2 wt %, 1,8-dimethacryloyloxy-3,6-dioxaoctane, TEGDMA, Shin-Nakamura Chemical), camphorquinone (2 wt % based on UDMA, Tokyo Chemical Industry), and *N,N*-dimethylaminoethyl methacrylate (1 wt % based on UDMA, Wako Pure Chemical Industries) as an initiating system for photocuring, titanium oxide (2 wt % based on UDMA) as an opalizer, and two kinds of spherical silica fillers with a mean particle size of 15 nm (7 wt %, Nissan Chemical Industries) and with a mean particle size of 100 nm (32.5 wt %, Tatsumori Ltd) treated with MPTS. The opalizer was used as received. The opaquer was a pseudo-homogeneous paste after blending and defoaming. A commercial composite cement (Panavia F2.0, Kuraray Medical) was used in the attachment of a stainless steel rod for strength measurements. The compositions and suppliers of Ti, Co-Cr alloy, Ni-Cr alloy, Au-Ag-Pd alloy, and Au alloy are shown in Table II.

A 12-mm diameter quartz disk (Fused quartz, Ustron) was used as a silica specimen.

Table II. Metal and Alloys Used as Adherends

Metal or alloy	Components (wt %)	Code	Manufacturer or supplier
Ti	Ti 99.0, other 1.0	JIS 4 grade	Shinsho Corporation
Ni-Cr alloy	Ni 65.0, Cr 22.5, Mo 9.5, Nb 1.5, Si 1.0, Fe 0.5, Ce 0.5	Wiron 99	BEGO
Co-Cr alloy	Co 61.0, Cr 26.0, Mo 6.0, W 5.0, Si 1.0, Fe 0.5, Ce 0.5	Wirobond C	BEGO
Au-Ag-Pd alloy	Au 12.0, Ag 49.5, Pd 20.0, Cu 16.85, other 1.65	Para Z12-n	Yamamoto Precious Metal
Au alloy	Au 83.0, Ag 12.0, Cu 5.0	YP-Gold type I-n	Yamamoto Precious Metal

Specimen Preparation

Each Ti/alloy disk (6 mm in diameter and 5 mm in thickness) was embedded in a cured UDMA resin ensuring that one surface of the disk remained uncovered. The exposed surface of each metal disk was sanded with a #600-grit silicon carbide abrasive paper and subsequently sandblasted using a 50 μm grain alumina at 0.3 MPa air pressure (Jet mill 3, Morita). The distance between the orifice and the metal surface was approximately 20 mm. Finishing by a #1000-grit silicon carbide abrasive paper was performed without sandblasting. For mirror finishing, the metal disk was ground with a #2000-grit silicon carbide paper, followed by suspension containing 1 μm diamond grains (Aquadia Liquid, Maruto) for 1 min. The quartz disks were polished to mirror-finished, washed, and dried. Each specimen was subjected to cleaning by distilled water in an ultrasonic bath for 10 min, washed with Solmix AP-7 (ethanol (85.5 $\pm$ 1%), 2-propanol (<5.0%), and 1-propanol (9.6 $\pm$ 0.5%)) (Nippon Alcohol Hanbai Company), and air-dried.

After surface preparation, a piece of adhesive tape with a 3-mm diameter circular hole was positioned on each disk to define a bonding area. The opened area was covered by pouring an ethanolic solution of MPTS (1 μL) and dried for 2 h in atmosphere at 25°C. After air-drying, the surface to be tested for adhesion was coated with the opaquer, which was cured by the irradiation of visible light (400–600 nm) for 3 min (α-Light II, Morita). When MPTS was premixed with the opaquer, the opened area was directly coated with this mixture and cured. Ethanol solutions of VTMS and TEMS with a molar concentration similar to that of the MPTS solution were spread on the metal surface and dried.

For bond strength measurement, a stainless steel rod (5 mm in diameter and 15 mm in length) was bonded to the metal disk using the composite resin cement under 10 N. The assembly of the specimen is shown in Figure 1. The bonded specimen was stored in distilled water for 1 day at 37°C, and then subjected to thermal cycling for 5000 times in water at 4 and 60°C for 1 min dwell time per each immersion. The adhesion of the composite resin cement to the cured opaquer was sufficiently strong to accomplish the bond strength measurement.

Measurements

Surface areas of the metal specimens were measured by laser scanning microscopy (LSM700, Carl Zeiss). The topology and roughness of the whole surface of the metal specimens were also examined by laser scanning microscopy. The roughness parameter RS_a in μm was obtained as the arithmetic mean deviation of all profile height values;[20,21]

$$RS_c = \frac{1}{N_x \cdot N_y} \cdot \sum_{i=1}^{N_i} \cdot \sum_{j=1}^{N_j} z(x_i, y_i)$$

$$RS_a = \frac{1}{N_x \cdot N_y} \cdot \sum_{i=1}^{N_i} \cdot \sum_{j=1}^{N_j} \cdot [z(x_i, y_i) - RS_c]$$

where RS_c denotes the mean height of all surface height values. N_x and N_y refer to the numbers of pixels in X- and Y- directions. The mean and standard deviation were calculated for each adherend for three replications.

The tensile bond strength was measured by a universal testing machine (Ez-Graph, Shimadzu) at a crosshead speed of 0.5 mm/min. The mean and standard deviation were calculated for each adherend for five replications. Cohesive and interfacial failures are defined as a fracture in the opaquer layer and that at the interface, respectively, when the opaquer and the adherend were debonded during the tensile bond strength measurement. Actually, both cohesive and interfacial failures contribute to the
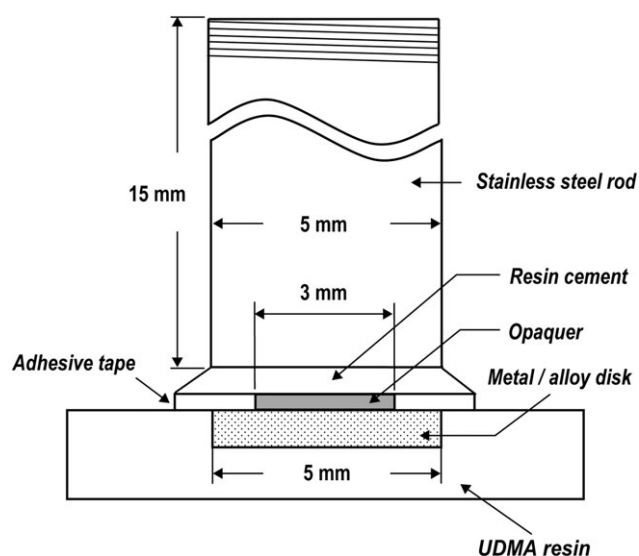

Figure 1. Assembly of the specimen for tensile bond strength measurement of the opaquer and a metal as adherend.

Table III. Tensile Bond Strength After Each Finishing Surface and with/Without MPTS Treatment

Finishing method	RS_a (μm)	Tensile bond strength (MPa)		
		None[a]	MPTS (6 wt %)[b] ethanol solution	MPTS (3 wt %)[c] premixed with the opaquer
Sandblasting (Ti)	0.701 ± 0.009	21.3 ± 2.6	43.3 ± 4.6	45.9 ± 6.2
#1000-grit paper finishing (Ti)	0.672 ± 0.033	21.9 ± 11.9	33.6 ± 7.8	29.6 ± 8.7
Mirror finishing (Ti)	0.051 ± 0.003	1.8 ± 0.5	29.7 ± 3.6	26.7 ± 10.5
Mirror finishing (Quartz)	0.040 ± 0.002	2.1 ± 2.0	23.4 ± 5.1	8.9 ± 1.2

[a] An opaquer (0.3 mg) without the addition of MPTS was applied to each surface.
[b] An ethanol solution (1 μL) of MPTS was applied to each surface. Then, the opaquer (0.3 mg) without the addition of MPTS was applied on the surface treated with the MPTS.
[c] A premixture (0.3 mg) with the opaquer and MPTS was applied to each surface.

fracture of most of the samples examined. The mode of debonding was visually determined by naked eyes. The Vickers hardness of the cured opaquer was measured using a Mitsutoyo HV-113. A load of 200 g was applied using a pyramid-shaped diamond indenter according to JIS and ISO.[22,23]

RESULTS AND DISCUSSION

Effects of MPTS and Ti Surface Roughness

Ti specimens with different RS_a values resulting from sandblasting, #1000-grit-paper finishing, and mirror finishing were submitted for the bonding experiment; the results are shown in Table III. As expected, the surface roughness decreased in a following order: sandblasting > #1000-grit-paper finishing > mirror finishing. The considerable difference in bond strength between the sandblasted- and mirror-finished Ti specimens without the MPTS treatment (21.3 and 1.8 MPa, respectively) conformed to the highest and the lowest RS_a values, respectively, indicating the contribution of the surface roughness to the bond strength by interlocking.

Smaller differences in bond strength were observed among the Ti samples treated with an ethanol solution of MPTS after sandblasting (43.3 MPa), #1000-grit-paper finishing (33.6 MPa), and mirror finishing (29.7 MPa) (Table III); the MPTS treatment enhanced the bond strengths in a considerable extent. As MPST promoted the enhancement of the bonding of mirror-finished Ti to the opaquer from 1.8 to 29.7 MPa, even the mirror finishing could increase the quantity of OH groups on the Ti surface, which react with MPTS. When MPTS premixed with the opaquer was used instead of the ethanol solution, similar bond strengths were obtained as shown in Table III. The MPTS mixed with the opaquer, which has a similar enhancement effect for the bond strength, is particularly interesting because a liquid coupling agent was not required.

The opaquer containing two types of the fillers (the mean particle sizes = 15 and 100 nm) attained fluidity suitable for pseudo-homogenous and thin coating on the metal surface before curing. In this study, the opaquer of the same composition was employed after various surface treatments; difference in the bond strength should be ascribed to the surface treatment of Ti. The Vickers hardness and the tensile strength of the cured opaquer were 32 Hv and 106 MPa, respectively, indicating that the opaquer is sufficiently hard and tough after curing. The highest bond strength in

Table III (45.9 MPa) is lower than the tensile strength of the opaquer (106 MPa) because of a fracture caused by interfacial failure as mentioned later. Therefore, one of the most important factors for strong bonding between the opaquer and the metal seems to be the efficient priming of MPTS.

An increase in the roughness of the Ti surface by sandblasting could cause an increase in the surface area leading to an increase in the number of OH groups, because Ti instantaneously forms an oxide surface layer (Table I).[8,9] Figure 2 shows the surface topology of the Ti specimens with sandblasting only, sandblasting with the MPTS treatment, #1000-grit-paper finishing, and mirror finishing. Lines originating from grinding with a grit paper appeared on the specimen finished with a #1000-grit-paper. Sandblasting and grinding with a #1000-grit-paper apparently increased the surface area to different extents, and the mirror finishing did not increase the surface area (Table IV). Although no remarkable change was observed for the morphology of the Ti surface after the MPTS treatment as shown in Figure 2, the surface area and the RS_a value deceased after the MPTS treatment, which is consistent with the formation of a uniform and smooth film on the Ti surface after silanization using MPTS, as observed by AFM.[11]

Although the mirror-finished Ti without the MPTS treatment exhibited bond strength considerably lower (1.8 MPa) than that observed for the #1000-grit-paper-finished Ti (21.9 MPa), the MPTS- treated mirror-finished Ti attained bond strength at a level only slightly less than that of the #1000-grit-paper-finished specimen. It appeared that the contribution of the interlocking effect is much less significant for the mirror-finished Ti than for the #1000-grit-paper-finished specimen and that the application of MPTS results in the similar increase of the bond strength irrespective of the surface area and the RS_a value.

Figure 3 indicates that the treatment with a small amount of MPTS in ethanol or with a mixture with the opaquer yielded bond strength as high as approximately 40 MPa, and a further increase in the amount of MPTS tended to reduce the bond strength. When 1 μL of 30 wt % MPTS in ethanol, which is not shown in Figure 3, was applied, the bond strength decreased to 22.1 MPa. These findings suggest that a sufficient amount of MPTS exists for the reaction with the OH groups on the Ti surface, which is 1 μL of a 5% solution.

Intact MPTS could hydrogen-bond to the surface layer produced by the reaction of MPTS with the OH groups on the Ti
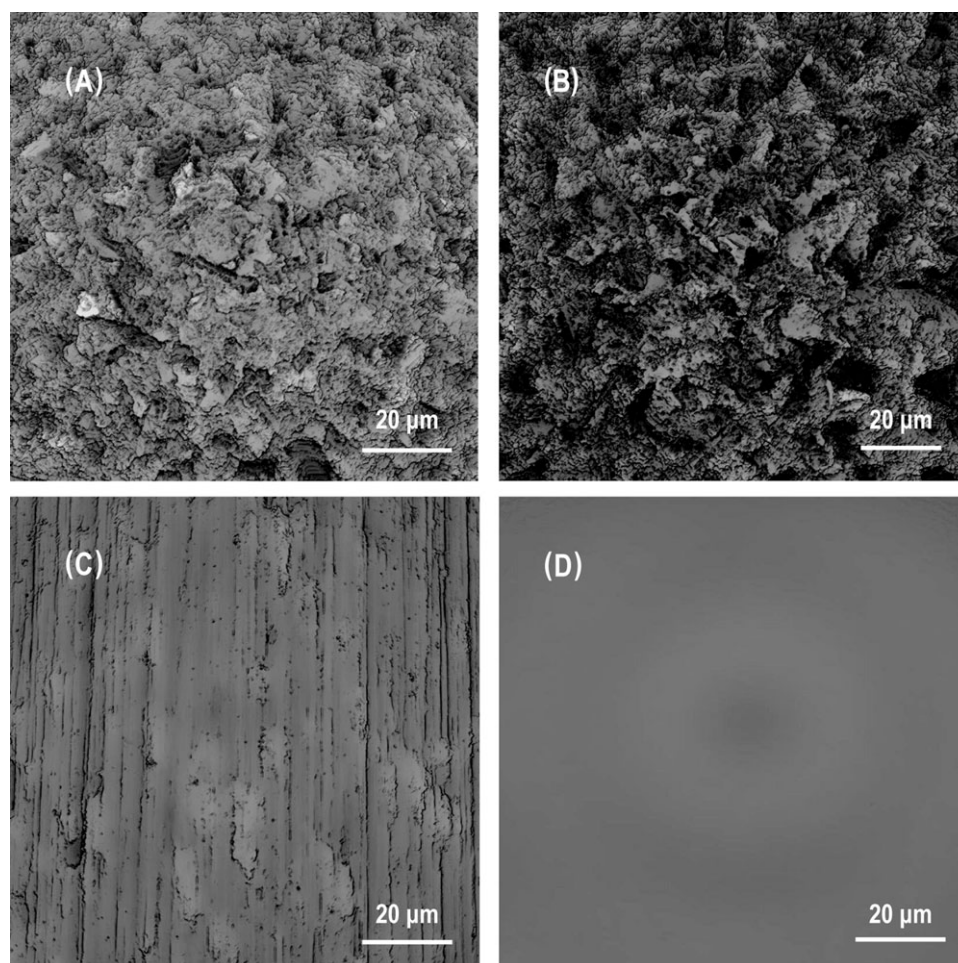
Figure 2. Laser scanning microscopic images of Ti disks after sandblasting only (A), sandblasting/MPTS treatment (B), #1000-grit paper finishing (C), and mirror finishing (D).

surface.[24] However, MPTS bound to the surface layer by hydrogen bonding could not enhance the bond strength.[25] A decrease of the shear bond strength in the presence of an excess amount of trimethoxysilyl coupling agent was also observed, when segmented poly(urethane) was adhered to Ti treated with hydrogen peroxide.[15] The decrease in the bond strength at a MPTS concentration over 10 wt % (Figure 3) would be caused by the unreacted or insufficiently reacted MPTS. The flexural bond strength of a methyl methacrylate (MMA)/PMMA resin containing 2–6 mol % of MPTS bonded to a Co-Cr alloy decreased, when the MPTS content in the resin was increased to 20 or 30

mol %.[26] As shown in Figure 3, when the premixed MPTS was used for the surface treatment of Ti, the bond strength was lower than that observed for Ti treated with the MPTS in ethanol except for the maximum bond strength.

When a MPTS ethanol solution is used, MPTS covers the surface of Ti and reacts with the OH groups on the Ti surface after the vaporization of ethanol prior to adhesion to the opaquer. In contrast, a limited amount of MPTS in a paste with the opaquer undergoes reactions with the OH groups to form Si—O—Ti bonds and efficiently participates in curing with the

Table IV. Ti Surface Area After Different Treatments Estimated by Laser Scanning Microscopy

Surface treatment	Surface area[a] (μm^2)	Relative surface area[b]	RS_a (μm)
Sandblasting (Ti)	0.05875 ± 0.00161	3.59	0.701 ± 0.009
Sandblasting + MPTS treatment (Ti)	0.05610 ± 0.00547	3.42	0.672 ± 0.033
#1000-grit paper finishing (Ti)	0.01891 ± 0.00040	1.16	0.193 ± 0.018
Mirror finishing (Ti)	0.01630 ± 0.00001	1.00	0.051 ± 0.003
Mirror finishing (Quartz)	0.01631 ± 0.00001	1.00	0.040 ± 0.002

[a]Surface area of field of vision.
[b]Relative to field of vision (128 μm x 128 μm = 0.01638 μm^2).
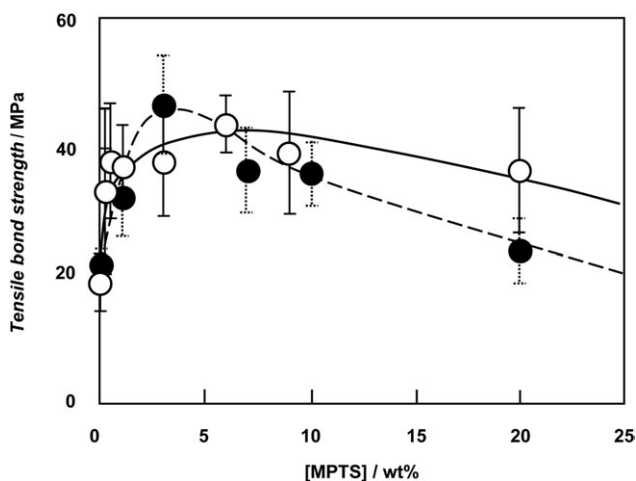
Figure 3. Effect of MPTS concentration in ethanol (○) and mixture with the opaquer (●) on tensile bond strength between Ti adherend and the opaquer.

dimethacrylate derivatives. Since the composition of the opaquer was the same for the MPTS/opaquer mixed paste treatment and for the MPTS ethanol solution treatment, followed by the opaquer covering, with any MPTS concentrations, the effect of the size and content of the filler on the bond strength would be negligible for the apparent enhanced bond with the MPTS. The difference in the bond strength shown in Figure 3 suggests that a smaller amount of MPTS in the mixture with the opaquer efficiently reacts with the Ti surface in comparison to that of MPTS in an ethanol solution.

An MPTS molecule was shown to be fixed on the substrate in a perpendicular or parallel orientation.[24,25] The perpendicular orientation results in Si—O—Ti bond formation by the reaction of the $Si(OH)_3$ group with the OH groups on the surface. The Si—O—Ti bond formation and the hydrogen bonding of the carbonyl group in MPTS with the surface OH group render the orientation parallel to the surface. The perpendicular or parallel orientation would depend on the MPTS and OH concentrations. When MPTS is perpendicularly oriented, based on a space-filling projection, each $Si(OH)_3$ group is estimated to occupy 0.24 nm^2 irrespective of the moiety bound to the Si atom, while an MPTS molecule in the parallel orientation can occupy 0.55 nm^2.[24] However, the area occupied by an MPTS molecule seems to be variable between 0.24 and 1.11 nm^2, depending on the orientation of MPTS, the substrate, and the estimation method.[25,27,28]

In this study, 1 μL of an MPTS ethanol solution (for example 6 wt %) was placed on the Ti surface, and 1.6×10^{13} molecules of MPTS were deposited on the whole surface. If each molecule of MPTS covers the surface perpendicularly and occupies 0.24 nm^2, which is the smallest estimate, the unimolecular layer formed by MPTS can cover 3.9×10^{12} nm^2 of the surface. Since the surface area of the flat and smooth 3-mm diameter disk is 7×10^{12} nm^2, which will increase by sandblasting as shown in Table IV, MPST could hypothetically cover almost the whole disk surface.

The quantity of OH groups on the mirror-polished Ti surface has been estimated to be 285 nm^{-2},[9] and the OH concentration

on TiO_2 as the main ingredient of the surface oxide layer of Ti was obtained as 4.4 nm^{-2}.[27] The difference in the OH concentration is ascribed to the presence of active and inactive OH groups in the surface oxide layer. The surface of the 3-mm diameter flat and smooth Ti disk (7.0×10^{12} nm^2) is expected to contain 3.0×10^{13}–2.0×10^{15} OH groups. The quantity of OH groups on the Ti surface may increase after sandblasting. The OH group density on the silica surface, which depends on various factors, has been estimated to be typically 4.9[29] and 8.20 nm^{-2}.[30] Based on these values, it can be noted that the OH density on the Ti surface is not very largely different from that on the silica surface.

As shown in Table III, the bond between the opaquer and quartz promoted by an ethanol solution of MPTS was as large as that between the opaquer and Ti under the conditions of similar RS_a value and surface area. The Ti surface area and the quantity of OH groups should increase for efficient bond formation between MPTS and the OH group. The increase in the surface area of Ti could not be as large as that of the surface area of an agglomerated silica filler; for example, 20 m^2/g.[31] The bond strength between the mirror finished quartz and the opaquer was enhanced only slightly using the MPTS premixed with the opaquer unlikely to the ethanol solution. The effect of MPTS might be diminished by a lower wettability of the quartz by the opaquer than ethanol.

An increase in the MPTS concentration did not affect the bond strength over 5% as already shown in Figure 3. However, the methacryloyl moiety of MPTS fixed on the Ti surface may be copolymerized with the dimethacrylate compounds (UDMA and TEGDMA) in the opaquer. Since the MPTS layer forms Si—O—Ti covalent bonds to the Ti surface, the linkage between Ti and the opaquer, formed by interpenetration and copolymerization, could strengthen the Ti-opaquer bond.[32] The $SiOCH_3$ and SiOH groups incorporated in the cured opaquer, may be involved in further reactions with MPTS and reaction products of MPTS.[7]

VTMS, as a less effective coupling agent than MPTS, promoted the adhesion of the opaquer and Ti (Table V), where the $Si(OCH_3)_3$ group is expected to react similarly with the OH group. The bond between Bis-GMA (bisphenol-A-glycidyl methacrylate)/TEGDMA resin and a glass plate is promoted more effectively by MPTS than VTMS.[33] The lower reactivity of VTMS as a trimethoxysilyl compound can be attributed to deterioration by fast dimerization or oligomerization than Si—O—Si bond formation and to the higher feasibility of hydrolysis than MPTS.[7,27,33] Furthermore, the possibility that VTMS copolymerizes with conjugated methacrylate and dimethacrylate compounds should almost be ruled out because VTMS as a non-conjugated vinyl monomer would be much less reactive than conjugated vinyl monomers. On the other hand, TEMS without a vinyl group is not copolymerizable. As shown in Table V, the bond strength increases in the following order; MPTS > VTMS > TEMS in accordance with the copolymerization reactivity. The contribution of the copolymerization to the bond strength can be observed in the difference in the bond

Table V. Tensile Bond Strength of Ti and Opaquer Using Trimethoxysilyl Coupling Agents Before and After Thermal Cycling

Coupling agent		Tensile bond strength (MPa)	
Compound	Molar amount (mol)	Before thermal cycling	After thermal cycling
None[a]	–	21.3 ± 2.6	16.5 ± 4.6
MPTS (6 wt %)[b]	1.94×10^{-10}	43.3 ± 4.6	27.9 ± 3.8
MPTS (3 wt %)[c]	3.63×10^{-8}	45.9 ± 6.2	34.7 ± 7.7
VTMS (5.1 wt %)[b]	2.75×10^{-10}	38.5 ± 7.2	26.6 ± 5.4
TEMS (3.7 wt %)[b]	1.94×10^{-10}	22.9 ± 7.8	19.7 ± 5.6

[a]An opaquer (0.3 mg) without the addition of MPTS was applied after sandblasting.
[b]An ethanol solution (1 μl) of each coupling agent was applied after sandblasting. Then, the opaquer (0.3 mg) without the addition of MPTS was applied on the surface treated with the MPTS.
[c]A premixture (0.3 mg) with the opaquer and MPTS was applied after sandblasting.

strength between the MPTS and TEMS treated specimens or between the VTMS and TEMS treated specimens.

Effect of Thermal Cycling and Drying Time
Table V shows the bond strengths before and after thermal cycling. The bond strength between the opaquer and the sandblasted Ti without the MPTS treatment was 21.3 MPa before thermal cycling and lowered to 16.5 MPa after thermal cycling. The opaquer layer was fractured by cohesive failure, and interfacial failure occurred by tearing the opaquer layer from the adherend at the interface. Hence, debonding by cohesive and interfacial failures suggest sufficient or insufficient adhesion, respectively, from the viewpoint of adhesion. Therefore, the bond aided by the silane coupling agents after sandblasting would be cleaved primarily by cohesive failure before thermal cycling, although the contribution of cohesive failure for the bonds aided with VTMS and TEMS were less than that with MPTS. However, the contribution of cohesive failure decreased and the contribution of interfacial failure increased after thermal cycling irrespective of the silane coupling agents. The tensile bond strengths in Table III are less than that of the cured opaquer itself because of the contribution of interfacial failure.

The bond strengths to the roughened surface with the MPTS treatment (43.3 and 45.9 MPa) were reduced to 27.9 and 34.7 MPa, respectively, after thermal cycling. Debonding by cohesive failure was observed not only before thermal cycling but also after thermal cycling, indicating that the MPTS treatment improved the resistance of the bond to be attacked by moisture. It is noteworthy that the bond strength of the Ti with sandblasting, followed by the MPTS treatment, after thermal cycling (27.9 and 34.7 MPa) is similar to that of a MMA/PMMA resin and the mirror-finished Ti treated with 0.1 mol % of 10-methacryloyloxydecyldihydrogenphosphate (MDP) in acetone (37.9 and 38.7 MPa depending on the initiator system for curing).[34] As MDP has been employed for use with non-precious metals, it is expected that MPTS accomplished a sufficiently strong bond between Ti and the opaquer for practical use.

Although the VTMS treatment of the sandblasted Ti promoted the bond strength from 21.4 to 38.5 MPa before thermal cycling, the bond strength was reduced to 26.6 MPa by thermal cycling, which is similar to the MPTS treatment, because of the improved resistance to moisture in comparison to the specimen

without the silane treatment after thermal cycling (16.5 MPa). These findings are consistent with the effects of a silica filler with and without the MPTS treatment for the UDMA/TEGDMA resin.[35] Although thermal cycling slightly reduced the flexural strength, the strength of the resin containing the filler without the silane treatment was considerably decreased by thermal cycling. The treatment with TEMS slightly enhanced the bond strength before and after thermal cycling, indicating the promotion of the adhesion to limited extents.

The Ti disk was heated for different times after the MPST treatment before placing the opaquer stub. As shown in Figure 4, the bond strength remained almost constant irrespective of the heating time and temperature. These results are likely to a constant bond strength between the MPTS-treated silicate and the composite resin irrespective of drying time (1 and 7 min) associated with fast reaction.[36] Then, it can be deduced that the reaction of the sandblasted-Ti surface with MPTS is as fast as the reaction of MPTS with silica.

The effectiveness of MPTS has already been demonstrated by the difference in bond strength between sandblasting only (21.3 MPa) and sandblasting with the MPTS treatment (43.3 and 45.9
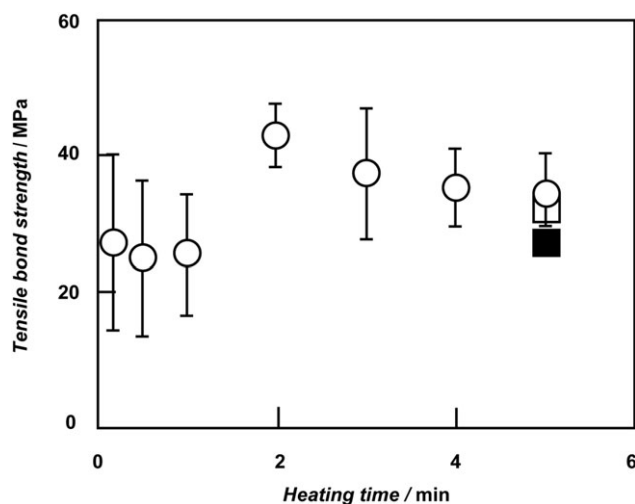

Figure 4. Dependence of tensile bond strength between Ti and the opaque on heating time of MPTS (6 wt % ethanol solution) treated Ti adherend at 25 (○), 37 (□), and 110 °C (■).

Table VI. Effects of MPTS on Tensile Bond Strength of Sandblasted Alloy and Opaquer

	Tensile bond strength (MPa)		
Alloy[a]	None[b]	MPTS (6 wt %)[c] ethanol solution	MPTS (3 wt %)[d] premixed with the opaquer
Ni-Cr	22.6 ± 4.1	31.2 ± 8.6	33.2 ± 4.4
Co-Cr	27.0 ± 6.0	34.6 ± 9.0	31.9 ± 4.9
Au-Ag-Pd	24.5 ± 5.4	27.9 ± 8.4	31.6 ± 12.6
Au	13.6 ± 2.7	14.7 ± 3.9	11.0 ± 5.0

[a]Compositions are given in Table I.
[b]An opaquer (0.3 mg) without the addition of MPTS was applied to each metal after sandblasting.
[c]An ethanol solution (1 μL) of MPTS was applied to each metal after sandblasting. Then, the opaquer (0.3 mg) without the addition of MPTS was applied on the surface treated with the MPTS.
[d]A premixture (0.3 mg) with the opaquer and MPTS was applied to each metal after sandblasting.

MPa) (Table III). As alumina grains used for sandblasting would remain on the Ti surface,[37,38] the amount of residual alumina has been studied using different sizes of alumina grains. When the grain size was 50 μm in diameter, the surface consisted of 42% alumina residues and 58% Ti.[39,40] The adhesion of alumina to Bis-GMA resin[41] and the organic polymer[42] has been reported to be enhanced with the MPTS treatment/hydrolysis as evaluated by the shear bond strength; it is suggested that the enhanced bond of Ti to the opaquer sandblasting and the MPTS treatment involves the contribution of alumina. However, the bond strength of the mirror-finished Ti without sandblasting was increased by the MPTS treatment from 1.8 to 29.7 MPa, which is similarly to the extent of the increase from 21.3 to 43.3 MPa by sandblasting and the MPTS treatment (Table III). Therefore, the influence of alumina residues from 50-μm diameter grains to the enhanced bond strength by the MPTS treatment can be ruled out in this study. Furthermore, the ultrasonic cleaning (10 min) of the sandblasted Ti should remove loose surface particles without relevant change in composition.

Adhesion to Co-Cr, Ni-Cr, and Au-Ag-Pd Alloys

Some other non-precious metals, as well as Ti, tend to instantaneously form a thin oxide layer, which can be seen from the oxygen content of vapor-deposited metal surfaces analyzed by XPS (Table I).[8] TiO_2, Cr_2O_3, NiO_2, and CuO were detected on Ti, Cr, Ni, and Cu surfaces, respectively, and the presence of active OH groups in the respective oxide layers was highly expected. Table VI shows the effects of the MPTS treatment on the bond strength between the alloy adherends and the opaquer, showing that MPTS effectively enhanced the bond strength of the Co-Cr and Ni-Cr alloys as well as the Au-Ag-Pd alloy containing Cu. The tensile bond strengths of MMA/PMMA resin to the Co-Cr and Ni-Cr alloys treated with MDP have been reported to be 32.9 and 41.1 MPa after 2000 thermal cyclings,[34] respectively, while the bond strength of the respective alloys and the opaquer after sandblasting followed by treatment with an MPTS ethanol solution were 31.2 and 34.6 MPa before thermal cycling (Table VI). Although these two sets of values were obtained after and before thermal cycling, the bond strengths shown in Table VI indicate that MPTS can promote the bond between the alloys and the opaquer to a considerable extent.

All metal and alloys examined except for the Au alloy, showed similar bond strength after sandblasting without the MPTS treatment due to the contribution of the interlocking of the opaquer and the roughened surface. However, after sandblasting and the subsequent MPTS treatment, the alloys exhibited enhanced bond strengths, whereas the Au alloy with and without the MPTS-treatment exhibited low bond strength. These findings suggest that the presence of a sufficient number of OH groups on the metal/alloy surface after sandblasting is one of the most important requirements for the promotion of the MPTS-aided adhesion to the opaquer. As expected, the Co-Cr and Ni-Cr alloys exhibited enhanced bond strengths with sandblasting and the MPTS treatment because of the oxygen content on the surface layer (Tables I and II). Recently, XPS analysis has revealed that the surface oxide layer of Co-Cr alloy is richer in OH groups than that of Ti.[9] However, the bond strengths of the Co-Cr and Ni-Cr alloys are slightly less than that of Ti despite of a significantly large amount of OH groups on the surfaces of the alloys than those on the Ti surface (The bond strengths of the sandblasting metal surfaces, Tables III and VI). FT-IR studies revealed that, for the Co-Cr alloy, the MPTS treatment/hydrolysis forms Si—O—Cr and Si—O—Co bonds as well as the Si—O—Si—O—Si bond and that the Si—O peak is weaker than the similarly treated Ti.[11]

The bond strength of the Au-Ag-Pd alloy treated with MPTS was similar to that of the MPTS- treated Co-Cr and Ni-Cr alloys. However, Table I shows that the oxygen and OH contents on the Au and Ag surfaces are significantly lower than those on the Ti, Co, Ni, and Cr surfaces.[8] The bond strength of the Au-Ag-Pd alloy containing 16.85% of Cu (Table II) after sandblasting and the MPTS treatment is accounted for by the contributions of the Cu_2O and CuO as the surface layer. The ineffectiveness of MPTS on the bond strength of the Au alloy is ascribed to the absence of a sufficient quantity of OH groups; the contribution of surface roughness associated with sandblasting could attain a bond strength of 13.6 MPa for the alloy without the MPTS treatment. Debonding between the alloys and the opaquer would occur through both of cohesive and interfacial failures except for the Au alloy, while the bond between the Au alloy and the opaquer should be fractured by interfacial failure only.

CONCLUSIONS

Ti as an adherend was found to strongly bond to a dental opaquer after sandblasting and treatment with MPTS without preliminary hydrolysis. The tensile bond strength reached 43.3 or 45.9 MPa when the Ti surface was treated with MPTS dissolved in ethanol or premixed with the opaquer in contrast to those of only sandblasted and mirror-finished Ti (21.3 and 1.8 MPa, respectively). After thermal cycling at 4 and 60°C for 5000 cycles, the strength was reduced from 43.3 to 27.9 MPa, which is still higher than the corresponding value for Ti without the MPTS treatment (16.5 MPa). The bond strength between the sandblasted Ti, treated with the premixed MPTS, and the opaquer was lowered by thermal cycling from 45.9 to 34.7 MPa. The $SiOCH_3$ groups of MPTS and SiOH groups derived are expected to participate in Si—O—Ti and Si—O—Si bond formations. It is feasible that the methacryloyl group of MPTS copolymerizes with the dimethacrylate monomers in the opaquer to strengthen the adhesion. Thus, the reactions between OH groups on the Ti surface and MPTS that proceed after sandblasting are associated with the enhanced bond strength and with the improved resistance to moisture. The adhesion of the opaquer to the Ni-Cr, Co-Cr, and Au-Ag-Pd alloys is also promoted by the MPTS treatment after sandblasting. VTMS consisting of vinyl and trimethoxysilyl groups, enhanced the bond strength of Ti to the opaquer before and after thermal cycling to a lesser extent than MPTS. TEMS without the vinyl group promoted the bond between the Ti and the opaquer to a lesser extent than VTMS.

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