The Effects of Different Surface Treatments on the Shear Bond Strength of Composite Resin to Machined Titanium

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THE EFFECTS OF DIFFERENT SURFACE TREATMENTS ON THE SHEAR BOND
STRENGTH OF COMPOSITE RESIN TO MACHINED TITANIUM

by

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ABSTRACT
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Purpose: The purpose of this study was to evaluate the shear bond strength between machined titanium and composite resin using different surface treatments.

Materials and Methods: Titanium (Ti-6Al-4V) specimens were ground with 600 grit SiC paper and randomly divided into 6 groups (n=20/group). Group #1 (Control): samples were sandblasted with 110 µm Al_2O_3 for 10 sec. Group #2 (Rocatec): samples were treated with the Rocatec system following the manufacturer's directions but the silanization step was eliminated. Group #3 (Silano Pen): samples were treated with the Silano Pen system.   Group #4 (H_2SO_4 etched): samples were sandblasted with 110 µm Al_2O_3 for 10 sec and etched with 48% H_2SO_4 for 60 minutes at $60^{o}C$. Group#5 (acid etching + Rocatec): samples received both treatments as described in Groups 4 and 2, respectively. Group #6 (acid etching + Silano Pen): samples received both treatments as described in Groups 4 and 3, respectively. Composite was bonded to the treated titanium surface, half of the specimens from each group (n=10/group) were subjected to thermocycling, and the samples were tested for shear bond strength in a universal testing machine. Representative samples from each group were evaluated with SEM.

Results: Two-way ANOVA revealed that there were significant differences ($p < 0.05$) in bond strength between the six groups of surface treatment and that thermocycling significantly decreased shear bond strength. There was no significant interaction ($p = 0.07$) between surface treatment and thermocycling status. With regard to the effect of surface treatment, a Tukey Post Hoc test showed that groups 3 (Silano Pen) and 6 (Silano Pen + H_2SO_4) showed significantly ($p < 0.05$) greater bond strengths compared to the rest of the groups. There was no significant difference in the bond strength between the four other groups.
Conclusion: 1) Silano Pen is effective in improving the bond strength of titanium to composite resin. 2) The silanization step in the Rocatec system is a critical step and eliminating it may dramatically alter its effectiveness. 3) Combining two surface treatments may not always result in an additive effect. 4) Thermocycling significantly decreased the bond strength regardless of the surface treatment used.

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INTRODUCTION

The use of milled titanium frameworks in implant dentistry has gained popularity in recent years after the huge development in CAD/CAM technology systems. Titanium has many advantages as a prosthesis material, including excellent biocompatibility, high strength to weight ratio, low density, sufficient corrosion resistance, and low cost compared to noble alloys.[1-5] In implant prosthodontics, one is occasionally faced with the need to replace both hard and soft tissues which may necessitate a stable bond between titanium and resin.[6] If there is a separation between these two materials, especially at the junction referred to as the finish line, cracks or crazing in that area may be a nidus for microorganisms and plaque to accumulate, possibly resulting in accompanied staining. Lately, machined titanium frameworks meant for implant supported prostheses have shown bonding problems between the machined surface and acrylic or composite resin.[7] Many different surface treatments have been proposed to improve the strength of this bonded interface. These treatments include sandblasting, silicoating, using functional monomers, acid etching, and many others. Studies have shown the treatments have been effective at increasing bond strength, albeit at varied amounts.[8,9,10]

Many bonding systems are commercially available and each manufacturer touts better bond strength with their system. One of these systems is the Rocatec system by 3M ESPE (Seefeld, Germany). Rocatec was introduced to the German market in 1989 with advantages over the classic silicoater process in the heat-free generation of the silicate layer and its visual monitoring on metal. The manufacturer states that the system is compatible for use with all metals used in dentistry including titanium. Rocatec is a

tribochemical method for silicatizing surfaces. Tribochemistry involves creating chemical bonds by applying mechanical energy. This supply of energy may take the form of rubbing, grinding, or sandblasting. There is no application of heat or light which would normally be the case with chemical reactions.[11] In Rocatec, the surface to be bonded is first cleaned by blasting with 110 μm aluminum oxide (high-purity Al_2O_3, Rocatec Pre), activating the surface and creating a uniform pattern of surface roughness which is ideal for ensuring microretentive anchorage of the resin. This is followed by tribochemical coating of the microblasted surface with silica-modified aluminum oxide (Rocatec Plus or Rocatec Soft). Ceramization of the blasted surface takes place when the grains hit the surface as very high temperatures on a local level are caused by the transfer of impulses and energy, however, macroscopic measurements show no heat formation.[11] The affected surfaces of the substrate and grit on the atomic and molecular ranges are excited to such an extent that a so-called triboplasma forms. The SiO_2 is impregnated into the surface up to a depth of 15 μm and at the same time fused to the surface in islands.[11] Next, the surface is silanized with 3M ESPE Sil to render the surface with a chemical bond between the inorganic silicatized surface and the organic resin to be applied.[11]

Another system that is commercially available is Silano Pen by Bredent (Senden, Germany). The manufacturer claims that the Silano Pen bonding system allows preparation of a chemical-micromechanical bond between acrylate-bases, light-curing or autopolymerizing resins and dental alloys as well as ceramics (including aluminum oxide and zirconium oxide). In this system, the creation of highly stable and durable bonding between metal/ceramic and acrylic is based on the combination of a special gas mixture

with a bonding liquid. The special gas mixture is processed with the firing device known as the Silano Pen. Short firing with the Silano Pen results in fine cleaning and, simultaneously, silicate formation and activation of the surface to be processed. The ensuing application of the bonding agent optimizes the bond between the resulting silicate layer and the acrylic structure.[12]

Other investigations have evaluated the effects of different acid etching solutions on the bond strength of titanium to composite resins. In these investigations it was found that the strongest bond strength was achieved when specimens were etched with 48% H_2SO_4 at $60^{o}C$ for 60 minutes.[10]

The purpose of this study was to evaluate the shear bond strength between machined titanium and composite resin using different surface treatments including treatment with Rocatec, Silano Pen, acid etching with 48% H_2SO_4, and combinations of the three treatments.

LITERATURE REVIEW

The use of titanium in dentistry

Historically, titanium has been widely used in aerospace, aeronautical, and marine applications because of its favorable properties, which include its high strength and rigidity, its low density and weight, its ability to withstand high temperatures, and its corrosion resistance.[13]

The uses of titanium in dentistry have expanded in the last three decades because of the development of new processing techniques such as computer aided machining and electric machining. Today titanium and titanium alloys are used in dental implants, dental implant frameworks, dental crowns, and partial denture frameworks.[14]

Physical and chemical properties

Titanium is abundant in the earth's crust in the form of the oxide rutile. The Kroll process is the method used to refine titanium ore to metallic titanium.[15] In its metallic form at ambient temperature, titanium has a hexagonal, close-packed crystal lattice (α phase), which transforms into a body–centered cubic form (β phase) at 883°C (with a melting point of 1680°C).[16]

The strength and rigidity of titanium are comparable to those of noble and high noble alloys which are commonly used in dentistry.[13,16] Its ductility, when chemically pure, is similar to that of many dental alloys. Titanium can also be alloyed with other metals such as aluminum, vanadium, niobium, and iron and this modifies its mechanical

properties. These physical and mechanical properties make titanium desirable as a material for implants and dental prostheses.

Four grades of commercially pure titanium and three titanium alloys (Ti-6Al-4V, Ti-6Al-4V Extra Low Interstitial, and Ti-Al-Nb) are recognized by the American Society for Testing and Materials (ASTM).[17] Titanium is a highly reactive metal that readily passivates to form a protective oxide layer. This oxide layer is what gives titanium its high corrosion resistance. The low density of titanium makes the fabrication of a high-strength, light-weight prostheses possible.

This highly reactive nature of titanium gives both advantages and disadvantages for its use. Titanium must be melted in a vacuum or under inert gas to prevent oxidation and the incorporation of oxygen can lead to embrittlement of the cast metal.[18] A significant loss of ductility will result with contamination of even low concentrations of atmospheric oxygen. The molten alloy can also react with refractory investment materials, requiring careful selection of compatible materials and/or removal of the surface reacted layer of the metal.

On the other hand, this same reactivity of titanium provides many of titanium's favorable properties. Titanium oxidizes almost instantaneously in air to form a tenacious and stable oxide layer approximately 10 nm thick.[13,18] The oxide layer gives titanium a highly biocompatible surface and a corrosion resistance similar to that of noble metals. Another advantage of the oxide layer is that it allows for bonding of fused porcelains, adhesive polymers, or, in the case of endosseous implants, plasma-sprayed or surface-nucleated apatite coatings.

Titanium has been used in cast dental prostheses since the 1970s and methods to fuse titanium to porcelain have been developed. Unfortunately, two critical factors limit fusing porcelain to titanium: the porcelain fusion temperature must be below 800°C to avoid the α to β phase transition and the coefficient of thermal expansion of the porcelain must match that of the metal.[13,15] These problems led dental clinicians to use veneering composites as an alternative to porcelain. Veneering composites are satisfactorily esthetic and have been developed such that their wear resistance is now similar to tooth structure. This, however, has necessitated the need to increase the bond strength between titanium and composite to create a stable and durable prosthesis.

Surface treatment of titanium

Many surface treatments have been proposed to increase the bond strength between titanium and composite or acrylic resins. These surface treatments are classified as roughening of the surface to provide micromechanical retention, chemical bonding between the restorative material and titanium, or treatments that combine both a roughening and a chemical bonding component.[19]

The micromechanical retention surface treatment involves air abrasion with alumina particles (sandblasting). This creates surface defects in the metal surface which result in an increase in surface roughness and surface area.[20] Studies have demonstrated that air abrasion can be an effective surface treatment to enhance the bond strength between composite and metal.[19,20]

Using scanning electron microscopy (SEM), Giachetti et al.[21] made a morphological analysis of titanium surfaces sandblasted with different sizes of alumina

particles (50 μm vs. 150 μm). Their results showed that the group surface treated with 50

μm alumina particles appeared irregular and rough, and the group treated with 150 μm

particles presented larger and deeper cavities where the resin penetrated completely as

opposed to the 50 μm group. Kern and Thompson[22] evaluated the surface morphology of

titanium after sandblasting with 110 μm alumina particles. The authors concluded that

while most of the alumina was firmly embedded into the surface of titanium, any loose

alumina particles should be removed through ultrasonic cleaning prior to the application

of resins with chemically active monomers because these loose particles may weaken the

interfacial resin bond.

Chemical bonding of metal to composite resins involves coating the metal with

primers that contain what are called functional monomers. Theses functional monomers

create chemical adhesion between the resin restorative material and the metal. Studies

have shown that the bond of metal to composites can be enhanced by the use of metal

primers.[23-26]

Surface treatments may also comprise both a roughening component and a

chemical component in an effort to combine the two treatments to achieve a better bond.

One problem with the use of resins is the gap that can occur between the resin and the

metal surface. This marginal gap usually contributes to a weaker bond. Factors that

participate in creating this gap are polymerization shrinkage and the different coefficient

of thermal expansion between the resin and the metal.[27] Many bonding systems have

been developed by different manufacturers to help with this problem. Some of these

systems include: Rocatec, Silicoater (Heraeus Kulzer, Wherheim, Germany), and Kevloc

bonding systems (Heraeus Kulzer, Wherheim, Germany). Studies have shown that these

treatments, which are based on silica coating/silanization, are effective in increasing the bond between resins and metals.[22,27-29]

The Rocatec system is one of the commercially available systems that combine silica coating and silanization. Rocatec involves sandblasting with silica-coated alumina particles that become embedded in the metal surface upon impact to form a ceramic-like surface referred to as a "tribochemical coating." The silica-coated alumina particles hit the alloy surface with a theoretically calculated speed of 200 m/s. This creates spot heating up to 1000°C, which may reach the melting point of the alloy. The melted surface layer is usually limited to 1 or 2 μm and high energy is released to form the silicate layer by trapping the particles on the metal surface.[29]

The alloy is treated in three steps in the Rocatec system, as mentioned above.[11] In the first step, Rocatec Pre is used in the form of blasting with 110 μm aluminum oxide to create a uniform, rough surface that appears as a matte finish. Next, Rocatec Plus is applied and creates a chemically reactive surface. A multitude of reactive groups on this surface create an environment of bonding groups for the silane coupling agent "ESPE Sil". This organic adhesive mediator contains suitable methacrylate groups necessary for binding to resin material. Silanes are also successfully used to bond ceramic filler particles to the resin matrix of composite resin material. Metal surfaces, however, lack the suitable bonding sites, such as Si-OH and Al-OH groups that are important for the silane bonding agents to be effective, thus the Rocatec Plus step is needed.[30]

Watanabe et al.[20] evaluated the effect of sandblasting and silicoating on the bond strength of composite resin to cast titanium. The product Silicoater from Heraeus Kulzer also claims to produce a "tribochemical coating" and was the silicoater used in this study.

It was found that the Silicoater technique and sandblasting with coarser alumina particles (250 μm vs. 50 μm) significantly improved the shear bond strength of composite resin to cast titanium. May et al.[31] showed that when titanium is pretreated with 110 μm alumina followed by a silicoating material, a 60 % increase in the shear bond strength between titanium and poly(methyl methacrylate) (PMMA) resulted.

In another study, May et al.[32] investigated the bond strength of chemically pure grade 2 titanium that was treated with Rocatec to PMMA. The purpose was to evaluate if the Rocatec pre-treatment would enhance the bond between the two prosthetic materials. Significant differences in shear bond strengths were found when test specimens were treated with the Rocatec bonding material. The mean shear bond strength was 23.8 MPa for the Rocatec group and 16.1 MPa for the untreated titanium group, representing an increase of 68 % in shear bond strength.

Mukai et al.[30] studied the effect of sandblasting on the bond strengths of composite resin to two alloys with the Silicoating technique. Ni-Cr and Ag-Pd alloys were sandblasted with 37 μm or 250 μm alumina particles. They found that after sandblasting with 37 μm alumina particles, the bond strength improved from 9.5 MPa (polished surface) to 19.5 MPa. Similar bond strengths were observed when 250 μm particles were used. The resin-alloy bond strengths were found to improve remarkably after sandblasting regardless of whether the specimens were stored dry or thermocycled 10,000 times.

Cobb et al.[19] investigated the effects of four techniques of metal surface treatment and the use of silane on the bond strength between resin and a noble metal alloy. Alloy disks received one of the following treatments: roughening with a diamond bur,

sandblasting with 50 μm alumina particles, sandblasting with 27 μm alumina particles, or sandblasting with a tribochemical silica (CoJet-Sand). Half of the specimens in each group were silanized prior to the bonding procedure with a composite resin material. The specimens were subjected to thermocycling (300,000 cycles between 5 and 55°C) before shear bond strength testing. The results revealed that sandblasting with CoJet-Sand and using silane resulted in a significantly greater resin-to-metal bond strength compared to the other metal surface treatments. The bond strength was similar for all other particle abrasive treatments regardless of the use of silane. Thus, using silane significantly improved bond strength only for the alloy surfaces treated with the CoJet-Sand system.

Kern and Thompson[22] investigated the effect of long term water storage combined with thermocycling at regular intervals on the durability of the bond strength of adhesive systems to pure titanium. The adhesive systems that were investigated in this study included two silica-coating systems (Rocatec and Silicoater) and two adhesive resins. They found that the bond strength of Bis-GMA composite resin material to sandblasted titanium was significantly lower than when the silica-coating bonding systems were used. On the sandblasted titanium, the additional use of silane resulted in an insignificant increase in bond strength that decreased over storage time to the same level as the sandblasted-only titanium. The bond strength of Bis-GMA composite resin to titanium was 2 to 2.5 times higher when the chemo-mechanical bonding systems were used. The authors concluded that by using chemo-mechanical bonding systems, the resin bond to titanium was durable over 150 days, even after being stored in water and thermocycled 37,500 times.

Vojvodic et al.[27] evaluated the bond strength values achieved by using the Kevloc technique (an improved bonding system over Silicoater) on Ag-Pd and Co-Cr alloys and compared it to those obtained by the Silicoater technique. Shear bond testing was performed after artificial aging of the specimens. No marginal gap was seen for either system. The Kevloc technique resulted in better results than the Silicoater regardless of the alloy used. A reduction in bond strength and a cohesive type of failure between the opaque and the resin occurred after thermocycling.

Vallittu and Kurunmaki[28] evaluated the push-out bond strengths of fiber-reinforced composite to titanium with various surface treatment methods. The specimens were either left untreated, sandblasted with 110 μm aluminum oxide, pyrolytically silica-coated (Silicoater) and silanized, tribochemically silica-coated (Rocatec) and silanized, or tribochemically silica-coated (Rocatec) and left unsilanized. Half of the specimens were thermocycled 12,000 cycles (5-55°C) and the other half were stored dry for one week. They found that the pyrolytically silica-coated titanium (Silicoater) gave the highest bond strengths (30 MPa). Tribochemical silica-coating with a silane treatment gave slightly lower bond strengths (27 MPa) but was found to be higher than that obtained with aluminum oxide sandblasting (13 MPa). The group with no surface treatment was found to have the lowest bond strength (7 MPa). The authors observed that a trend of an increase in bond strength after thermocycling. It was expected that a reduction of the bond strength values would be found. Their findings are contrary to most other studies.

Taira et al.[25] investigated the effects of three metal primers on bond strength durability when used with titanium and two luting agents. Metal Primer II contains a refined methacrylate with a thiophosphate acid moiety (MEPS).[33] Cesead II Opaque

Primer and Alloy Primer have MDP (10-methacryloyloxydecyl dihydrogen phosphate) as its functional monomer. Studies have shown that primers containing MDP enhance the adhesion between resin and base metal alloys.[24,34] In this study, a shear bond test was performed after 24 hours of water storage and after 10,000 cycles of thermocycling (4-60°C). The authors concluded that bond strengths were decreased overall by thermocycling and that primer and luting agent combinations resulted in an increase in bond strengths. It was concluded that all three metal primers were comparable in the bonding of titanium.

Matsumura et al.[26] investigated the effects of acidic primers (Cesead Opaque Primer, Super-Bond liquid, Acryl Bond, and MR Bond) on the bond between stainless steel and two different auto-polymerizing methacrylate resins. Stainless steel disks were air particle abraded with 50 μm alumina followed by the application of the primers. Shear bond strength was evaluated before and after thermocycling (20,000 cycles; 4-60°C). Bond strengths of the two resins varied from 21.0 to 46.0 MPa before thermocycling, and ranged from 0 to 11.9 MPa after thermocycling. Shear bond strength of Metal Primer before thermocycling was 38.4 MPa. After thermocycling, the bond strength was reduced to 3.9 MPa. The results show that thermocycling significantly reduced the bond strengths and that the primers were effective in increasing the bond strengths.[26]

Yanagida et al.[33] evaluated the adhesive performance of eight metal conditioners (Acryl Bond, All-Bond 2 Primer B, Alloy Primer, Cesead II Opaque Primer, Eye Sight Opaque Primer, Meta Fast Bonding Liner, Metal Primer II, and MR Bond) and a surface modification technique (Siloc) in bonding composite resin material to titanium alloy.

Shear bond strengths were determined both before and after thermocycling (20,000 cycles; 4-60°C) for evaluation of the durability of the bonds. It was concluded that the Siloc-treated group exhibited the greatest post-thermocycling bond strength (26.8 MPa) followed by the Alloy Primer and Cesead II-treated groups (22.2 and 19.2 MPa, respectively) and then the Metal Primer II-treated group (13.2 MPa). There was a 50% reduction in the bond strength of Metal Primer II with thermocycling. It was suggested that the hydrophobic phosphate functional monomer (MDP) of Cesead II Primer and Alloy Primer was superior to the MEPS monomer of Metal Primer II for bonding titanium alloy.

Bulbul and Kesim[35] evaluated the effect of 3 metal primers on the shear bond strength of 3 acrylic resins to 3 different types of alloys. The alloys were a Co-Cr alloy, a titanium alloy, and a noble metal alloy (Au-Ag-Pt). The primers were Alloy Primer which contains 6-(4-vinylbenzyl-n-propyl) amino-1,3,5-triazine-2,4-dithione (VBATDT) and MDP, Meta Fast which contains 4-methacryloxyethyl trimellitate anhydride (4-META), and Metal Primer which contains MDP. Four groups of specimens were evaluated per alloy and resin, with three groups bonded with the three different primers and the fourth group bonded without a primer to act as the control group. After thermocycling, the authors found that the shear bond strength values varied according to the type of metal and primer used. Among the metals tested, it was observed that the Co-Cr alloy showed the highest shear bond strength and the noble metal alloy showed the lowest shear bond strength. This study suggested that primers should be selected depending on the type of metal alloy used. They recommended the use of Metal Primer for base metal alloys, Meta Fast for titanium alloys, and Alloy Primer with noble alloys.

The author states that the primers that include MDP monomer demonstrate better bond strength to Co-Cr than the primer containing 4-META monomer. Additionally, it was thought mercapto groups in the VBATDT monomer react chemically with noble metals and produce a chemical bond at the metal–resin interface.

Lim et al.[36] compared the shear bond strength and mode of failure of a PMMA denture base resin to commercially pure titanium, Ti-6Al-4V alloy, and a cobalt-chromium alloy using a metal surface conditioner. The surface conditioner used in this study was Alloy Primer, which contains VDATDT and MDP. The shear bond strength of the heat-cured denture base resin was significantly higher in the group treated with the metal conditioner. The authors found no significant differences between the types of metal used. Without the primer, only adhesive failures were observed, but when Alloy Primer was used, the CP titanium and the Ti-6Al-4V alloy specimens showed mixed failure modes while only one adhesive failure was observed in the Co-Cr alloy group. The shear bond strength of the conditioned groups ranged between 16-18 N and the unconditioned specimens ranged between 2-4 N. The authors conclude that the conditioner containing VBATDT had a significantly positive effect on the bond between the PMMA denture base and the metal alloys.

Koizumi et al.[9] evaluated the bond strength of two acrylic resin adhesives joined to titanium-aluminum-niobium (Ti-Al-Nb) alloy primed with two metal conditioners. Six combinations of two resin adhesives (Super Bond C&B and Multi Bond) and three surface conditions (Alloy Primer, M.L. Primer, and an unprimed control) were tested for shear bond strength both before and after 20,000 thermal cycles. Super Bond C&B resin exhibited greater bond strength than Multi Bond resin. Both the Alloy Primer with a

hydrophobic phosphate and the M.L. Primer with phosphonoacetate effectively improved the 24-hour bond strength of Multi-Bond resin as well as the post-thermocycling bond strength of Super Bond C&B resin.

Oyafusu et al.[37] evaluated the shear bond strength of two indirect composite resins (Artglass and Targis) to cast titanium and a gold alloy. Twenty specimens of each metal were prepared and the composite resin was bonded to them according to the manufacturer's directions. The specimens were sandblasted with 250 μm aluminum oxide before the application of the resin. Opaque, dentin, and enamel composite was applied. The specimens were thermocycled for 3,000 cycles. They found that the gold alloy presented a significantly greater shear bond strength for both composites compared to the cast titanium (18.44 and 9.81 MPa, respectively).

Lim et al.[38] demonstrated similar shear bond strengths when composite resin was bonded to titanium treated by sandblasting versus a commercially available acidic fluoride gel. For different titanium alloys, the bond strengths with sandblasting ranged from 14.28 MPa to 17.66 MPa, and for the fluoride gel, it ranged between 14.52 to 19.34 MPa. Prolonged fluoride treatment time from 5 minutes to 20 minutes did not increase bond strength. The author suggested this technique to avoid the contamination of alumina particles or distortion of prostheses by sandblasting.

Lee et al.[39] evaluated the shear bond strength of composite resin to commercially pure titanium and a Ti-6Al-4V alloy after different surface treatments. The surface treatments included sandblasting, using a metal conditioner, tin coating, and silicoating (Rocatec). For the commercially pure titanium, it was found that the metal conditioner treated group achieved the highest bond strength of 27.26 MPa, followed by the other

treatments in this order: the silicoated group (19.51 MPa), the tin coated group (14.68 MPa), and the sandblasted group (14.39 MPa). For the Ti-6Al-4V alloy, the silicoated group performed the best with 24.93 MPa shear bond strength followed by the other groups in the following order: the metal conditioner group (20.65 MPa), the sandblasted group (19.10 MPa), and the tin coated group (18.93 MPa). All methods of surface treatment passed the requirement of ISO 10477 (> 5 MPa), which is the specification for polymer-based crown and bridge materials. The type of metal conditioner used was not mentioned in this study.

Behr et al.[40] compared the shear bond strength between veneering composites and titanium (CP grade 1), a cobalt chromium alloy, and a high-noble alloy. The metals were pretreated by silicoating (Rocatec), applying functional monomers, or by using an experimental titanium dioxide coating system. Results showed that regardless of the type of metal and surface treatment, the lowest shear bond strengths were found after thermocycling. For titanium, the shear bond strength of the silica coating and the functional monomers systems did not differ statistically. However, the titanium dioxide coating method possessed significantly higher bond strength values compared to the other methods. The authors concluded that for the high-noble alloy, the silicoating method is recommended, while the functional monomers are recommended for the cobalt-chromium alloy. They state that both bonding concepts can be used successfully with titanium. The experimental titanium coating method seems to be the most alloy independent concept. It reached the highest shear bond strength and was still reliable after thermocycling and long term water storage.

Fernandes et al.[41] evaluated 4 indirect composite and adhesive systems employing different methods of metal treatment to enhance bonding to Ti-6Al-4V alloy. The composite systems included Ceramage, Gradia, Synfony, and Solidix. For each system, the manufacturers' instructions in preparing the metal surface were followed. After the bonding was accomplished, the specimens were subjected to different times of water storage and the microtensile bond strengths were determined. Significant variations in the bond strengths were observed between the different systems. All the systems showed high initial bond strength. Water aging had an adverse effect on the bond strength of Ceramage and Solidix, but it did not affect Gradia and Synfony. Ceramage and Solidix exhibited failures at the opaque-titanium interface, which is often the weak link of metal-composite bonding. For Gradia and Synfony, this interface was not affected by water storage.

Tanaka et al.[42] reported that metal surface modification by coating with TiN significantly improves the bond strength between a Au-Pd-Ag alloy and resin composite material. When they observed the surface of treated specimens with the use of an SEM and electron probe microanalyzer, the TiN coating filled the microgap between metal and veneering composite resin. The TiN coating group was significantly stronger than non-coated groups with a metal conditioner for one of the two resin composites examined.

Janda et al.[12] evaluated the shear bond strength of three alloys after surface treatment with either Rocatec, Silano Pen, or an experimental spark erosion technique. The three metals were a high-noble alloy, a Co-Cr alloy, and pure titanium. Half of the specimens in each group were thermocycled for 5,000 cycles. After 24 hours, the spark erosion generated significantly higher shear bond strength values on Ti than Rocatec and

Silano Pen. The numbers were as follows: 21.8, 18.4, and 16.4 MPa, respectively. After

thermocycling, the shear bond strength was as follows: spark eroded 16.9 MPa, Silano

Pen 11.1 MPa, and Rocatec 12.2 MPa. The Silano Pen performed significantly better

with the base metal alloy (Co-Cr) than either spark erosion or Rocatec. Its performance

on the gold alloy and titanium was similar to both of the other bonding systems. No

significant differences were observed among all the bonding systems on the high-noble

alloy.

Ban et al.[10] compared the effects of acid etching titanium on the bonding strength

to veneering composite resins. Different types of acids and different acid etching times

were investigated. They also bonded five different types of composites. Specimens

etched in 48% H_2SO_4 at 60°C for 60 min had the greatest bond strength to the five types

of composite resin evaluated before and after 10,000 and 20,000 thermal cycles.[10]

The purpose of this study was to evaluate the shear bond strength between

machined titanium and composite resin using different surface treatments including

treatment with Rocatec, Silano Pen, acid etching with 48% H_2SO_4, and combinations of

the three treatments.

MATERIALS AND METHODS

Sample fabrication

A long rod of Ti-6Al-4V was cut into 120 samples in the shape of a cylinder (dimensions: 12 mm in diameter and 18 mm in length). The bonding surface of each cylinder was ground with water-lubricated, 600 grit silicon-carbide paper. Figure 1 shows samples after they were ground with 600 grit silicon-carbide paper.

Figure 1. Samples after grinding with 600 grit silicon-carbide paper.

The 120 samples were divided into 6 different groups with each receiving a different surface treatment before bonding the composite to the specimen. Figure 2 shows the samples after they were divided into their respective groups.

Figure 2. Samples divided into their respective groups.

Surface treatment groups

Each of the six groups received a different surface treatment as follows:

- Group #1 (Control): samples were sandblasted with 110 µm Al_2O_3 for 10 sec at a

pressure of 4 bar. To standardize the sandblasting distance, an acrylic jig was used to

hold the specimen and the sandblasting tip at a certain distance as shown in Figure 3.

 The samples were steam cleaned for 5 sec, air-dried for 10 sec, and treated with Meta

Fast (Sun Medical Co, Ltd, Shiga, Japan).

Figure 3. A specimen being sandblasted using the acrylic jig.

- Group #2 (Rocatec): samples were treated with the Rocatec system following the manufacturer's directions as follows: the surface to be bonded was first cleaned by blasting with 110 μm aluminum oxide (Rocatec Pre). Subsequently, the samples were blasted with silica-modified aluminum oxide (Rocatec Plus). The typical third step of applying 3M ESPE Sil as recommended by the manufacturer was replaced with applying Meta Fast to test the effects of eliminating this step on the Rocatec system.

- Group#3 (Silano Pen): samples were treated with the Silano Pen system following the manufacturer's directions as follows: the surface to be coated was sandblasted with Al_2O_3 (grain size 110 to 150 µm) at a pressure of 3 to 4 bar and then cleaned with water- and oil-free compressed air. The metal surface was evenly heated with the flame for 5 seconds per cm^2. Once the fired surface cooled down (below 50ºC),

the bonding agent was applied in accordance with the manufacturer's instructions and

allowed to dry in air for approximately 3 minutes. Figure 4 displays the Silano Pen Kit.
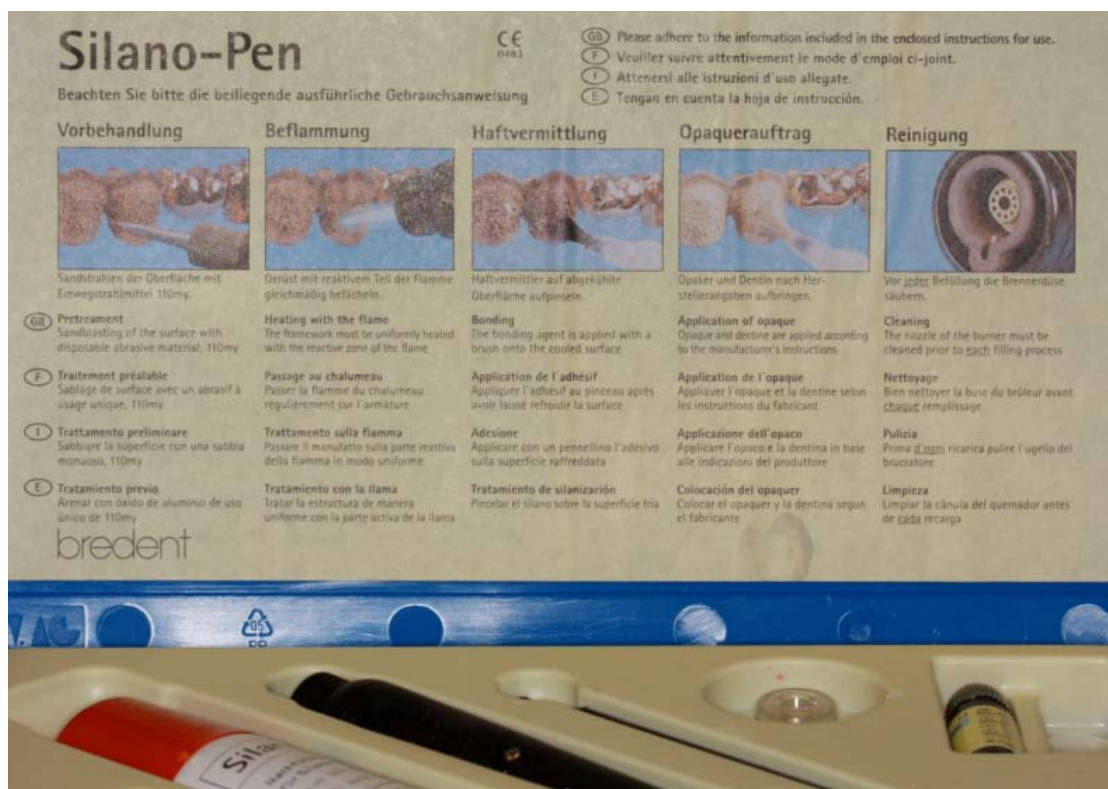

Figure 4. The Silano Pen Kit.

- Group#4 (H_2SO_4 etched): samples were sandblasted with 110 µm Al_2O_3 for 10

sec at a pressure of 4 bar. The samples were etched with 48% H_2SO_4 for 60 minutes at

60^oC by submerging up to 2 mm of the bonding surface end of the cylinders in the acid.

Figure 5 shows the samples being acid etched.

Figure 5. Specimens being acid etched.

 After etching, specimens were rinsed thoroughly with distilled water and air-dried at room temperature.

- Group#5 (acid etching + Rocatec): samples received both treatments as described in Groups 4 and 2, respectively.

- Group#6 (acid etching + Silano Pen): samples received both treatments as described in Groups 4 and 3, respectively.

Meta Fast was used as the bonding agent for all of the groups except groups #3 and 6. Each group consisted of 20 samples. The materials used in this study are listed in Table 1.

Table 1. Materials used in this study

Material	Lot Number	Manufacturer/Supplier
Ti-6Al-4V		ThyssenKrupp Materials North America (www.onlinemetals.com, Seattle, WA, USA)
Meta Fast Liner	TS1A	Sun Medical Co., Ltd., Shiga, Japan
Silano Pen	59	Bredent GmbH, Senden, Germany
Gradia GUM shade	1006111	GC Corp., Aichi, Japan

Rocatec system
    Rocatec-Pre
    Rocatec-Plus
	
	0031
	276
		3M ESPE, Seefeld, Germany

H_2SO_4 48%		
Al_2O_3 110µm Cobra	1583-1005	Renfert, Hilzingen, Germany

The application of composite

A master sample 21 mm in length was used to fabricate a putty mold to standardize the length of the composite. The specimens were inserted in that mold flush with one end, and because the specimens were only 18 mm in length, 3 mm of composite was able to be built up. Figure 6 illustrates these steps.
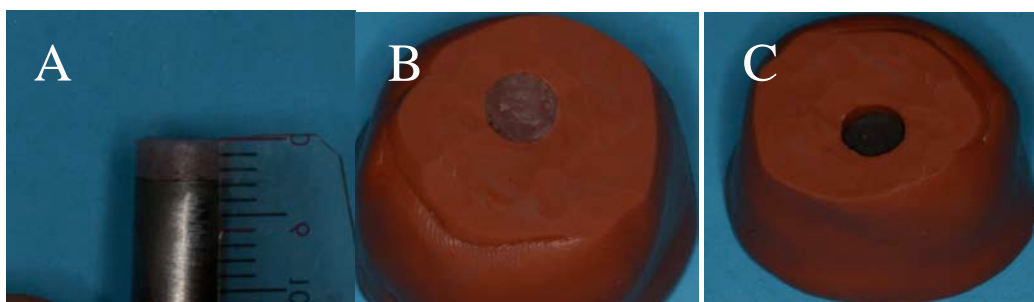

Figure 6. Composite application, A: The master sample; B: Putty around the master

sample; C: The space available for composite when a specimen is inserted.

After Meta Fast was applied to the specimens, the composite (Gradia) was added in two 1.5 mm increments. Each increment was cured for 20 sec with the light

perpendicular to the surface, followed by light-curing along the margin from all directions for 1 min. Gradia Gum shade #23 and a LED light-curing unit (LEDemetron II, Kerr Corporation, CT, USA) were used. The intensity of the light-curing unit was measured after every five specimens using a radiometer (Optilux Radiometer, Kerr Corporation, CT, USA) to ensure the light output was 700-800 mW/cm^2.

Thermocycling

Half of the specimens from each group (n=10/group) were subjected to thermocycling to observe its effect on the shear bond strength of the different groups. The samples were thermocycled 5,000 times in water between 5 and 55°C. The dwell time at each temperature was 30 seconds with a transfer time of 15 seconds between baths. The parameters of thermocycling were chosen according to the estimation that 5,000 thermocycles represents the situation during 5 years in the oral cavity.[36,37] Figure 7 displays the thermocycling apparatus. After thermocycling, the specimens were tempered to room temperature in a water bath prior to measuring shear bond strength.

Figure 7. The Thermocycling apparatus.

Shear bond testing

Samples were tested for shear bond strength in a universal testing machine (Model 55R1114; Instron Corp, Canton, Mass) with a cross head speed of 1 mm/min. The maximum load (kgf) obtained prior to debonding was converted to Newtons and divided by the area of the bonding interface to yield shear bond strength in MPa. Figure 8 shows a specimen being tested with the universal testing machine.
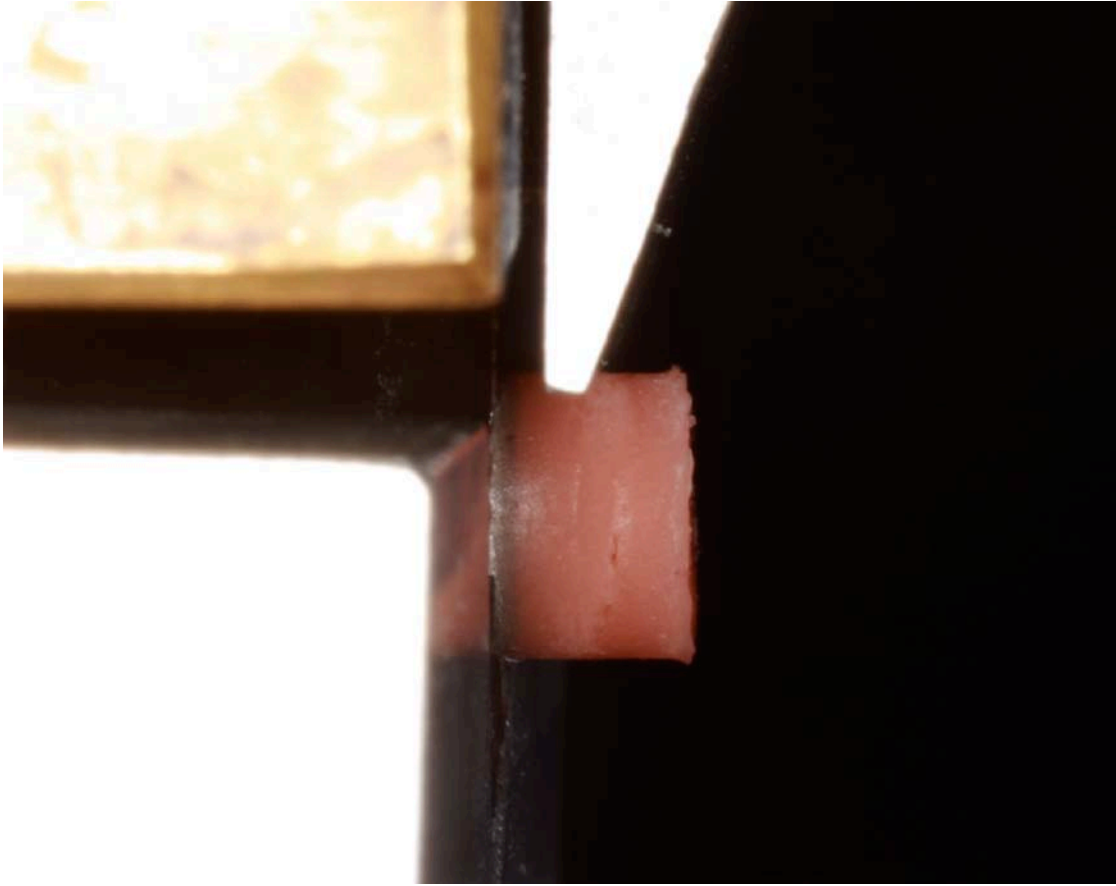
Figure 8. A specimen being tested with the universal testing machine.

Statistical analysis

Shear bond strength was examined with two-way ANOVA with surface

preparation and thermocycling status as factors. SPSS Statistics 17.0 (SPSS Inc.,

Chicago, IL, USA) was used for the analysis with significance set at $p < 0.05$.

Scanning electron microscope (SEM) evaluation

Representative samples from each group were submitted for SEM (JSM-35; JEOL

Ltd., Tokyo, Japan) evaluation to qualitatively analyze the surface to be bonded after the

various surface treatments. Magnifications of 15, 100, 300, and 500X were used for each

sample. Figure 9 displays the SEM that was used.

Figure 9. The JEOL scanning electron microscope.

RESULTS

Shear bond strength

Table 2 displays the shear bond strength values. Two-way ANOVA revealed that there were significant differences ($p < 0.05$) in bond strength between the six groups of surface treatment. It also revealed a significant difference ($p < 0.05$) between the thermocycled groups and the non-thermocycled groups, with the latter having greater bond strength. Overall, the mean bond strength for the non-thermocycled groups was 8.08 ± 3.64 MPa and for the thermocycled groups the mean bond strength was 6.29 ± 3.29 MPa, showing that thermocycling significantly reduced bond strengths in this study. There was no significant interaction ($p = 0.07$) between surface treatment and thermocycling status. With regard to the effect of surface treatment, a Tukey Post Hoc test showed that groups 3 (Silano Pen) and 6 (Silano Pen + H_2SO_4) showed significantly ($p < 0.05$) greater bond strengths compared to the rest of the groups. There was no significant difference in the bond strength between the four other groups.

Table 2. Shear bond strengths of the different surface treatment groups.

Group	Shear Bond Strength (MPa)		
	Non-thermocycled group	Thermocycled Group	All Specimens
1	5.78 ± 0.95	5.03 ± 0.86	5.39 ± 0.96
2	6.42 ± 1.89	3.56 ± 0.69	4.99 ± 2.02
3	11.55 ± 2.77	11.48 ± 1.53	11.52 ± 2.17
4	6.34 ± 1.68	5.29 ± 1.51	5.82 ± 1.65
5	6.09 ± 1.73	3.30 ± 0.49	4.76 ± 1.91
6	12.62 ± 4.03	9.89 ± 1.16	11.26 ± 3.21

SEM evaluation

SEM micrographs of the titanium after the various surface treatments are shown in Figures 10-17. Compared to the titanium surface ground with 600 grit SiC, the blasted surface and the Rocatec and Silano Pen groups presented with much greater surface roughness.
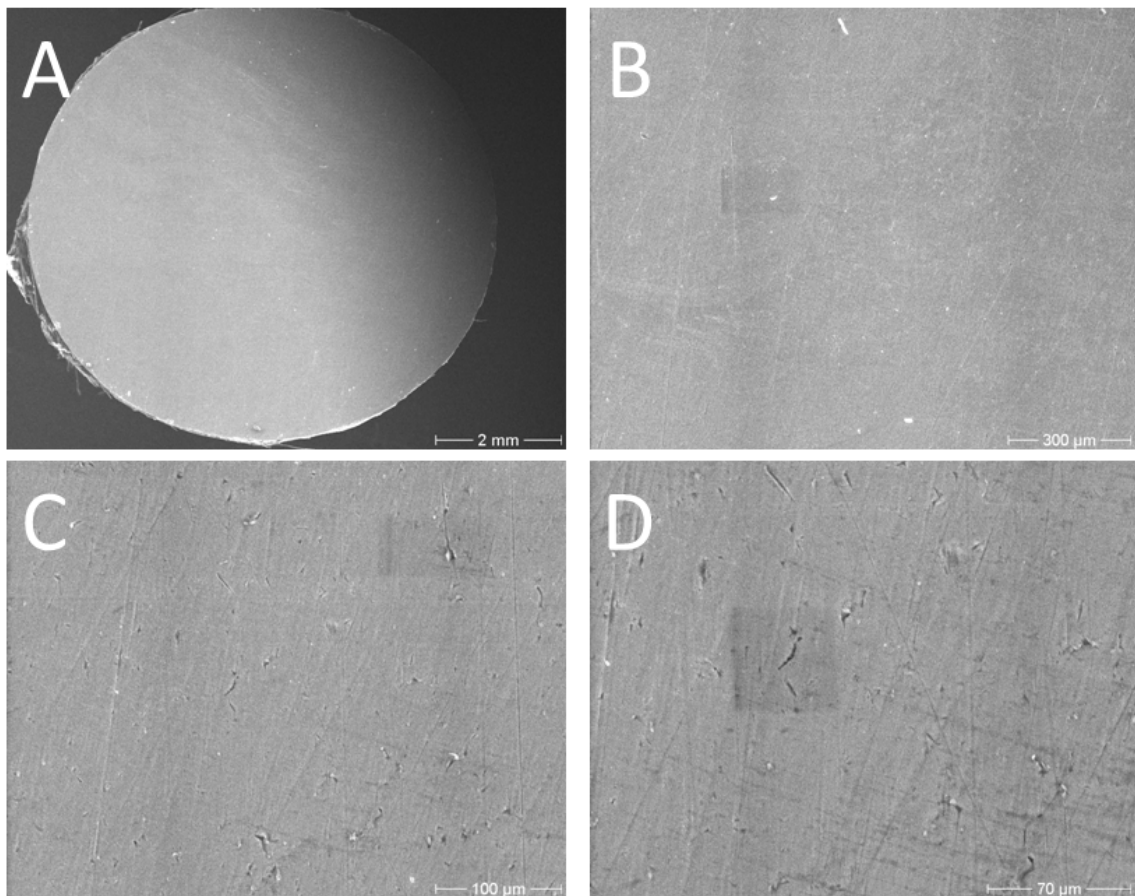

Figure 10. Titanium surface ground with the 600 grit SiC viewed with SEM under A:

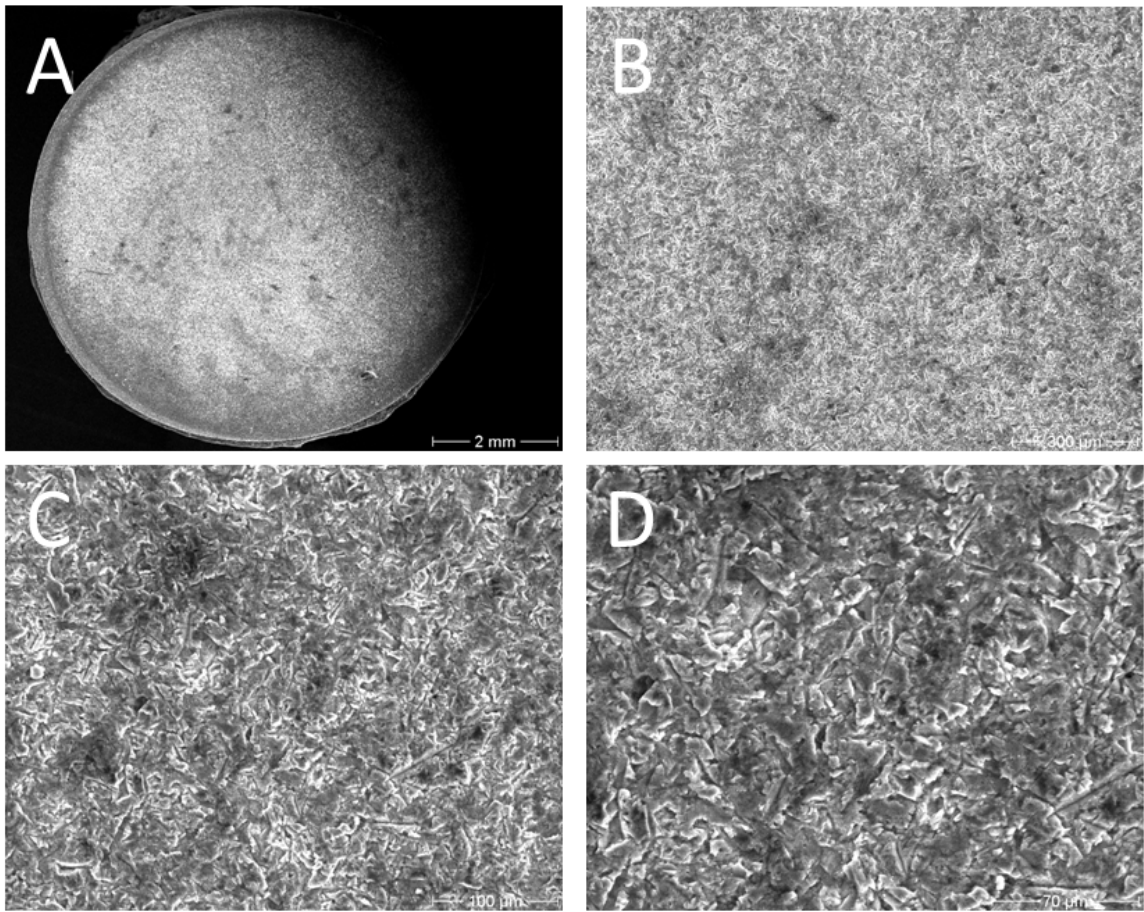15X, B: 100X, C: 300X, and D: 500X magnifications.

Figure 11. Titanium surface blasted with Al_2O_3 viewed with SEM under A: 15X, B: 100X, C: 300X, and D: 500X magnifications.
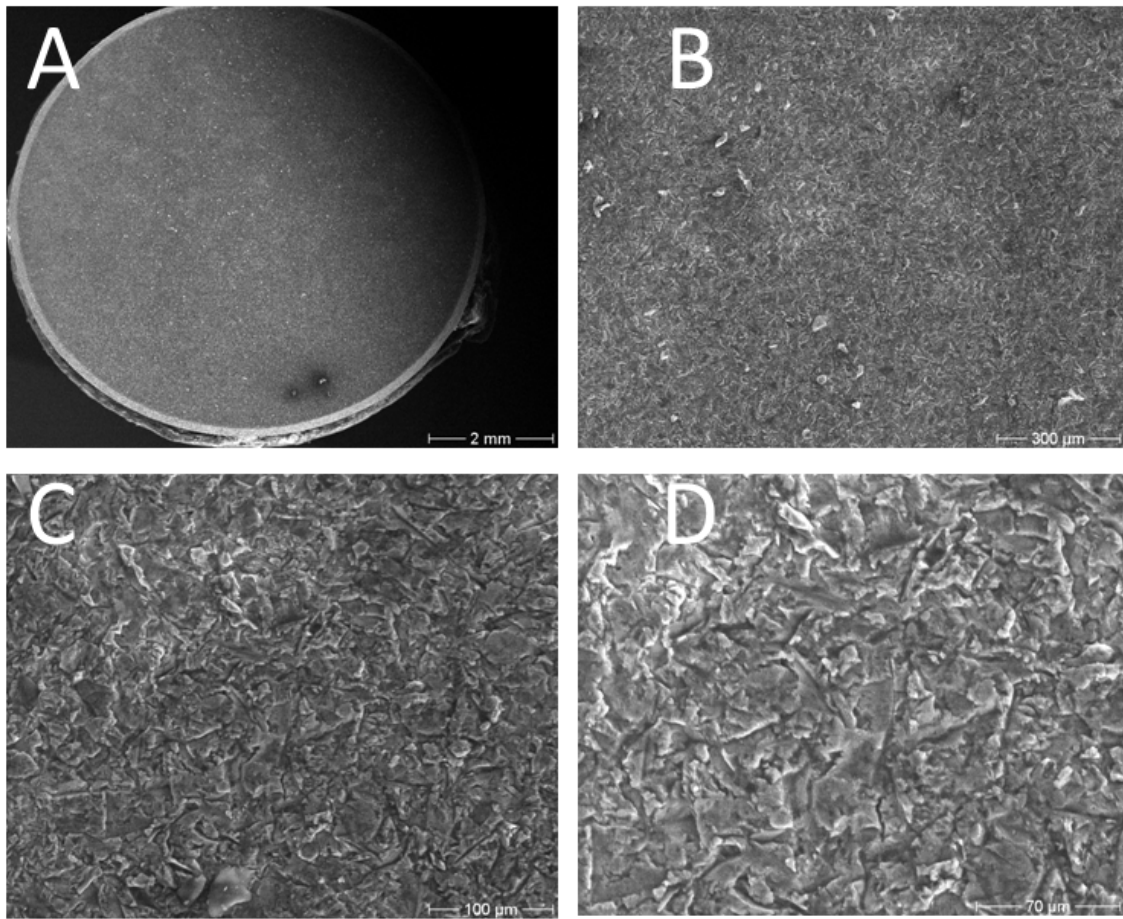
Figure 12. The Blasted titanium surface after treatment with Meta Fast viewed with

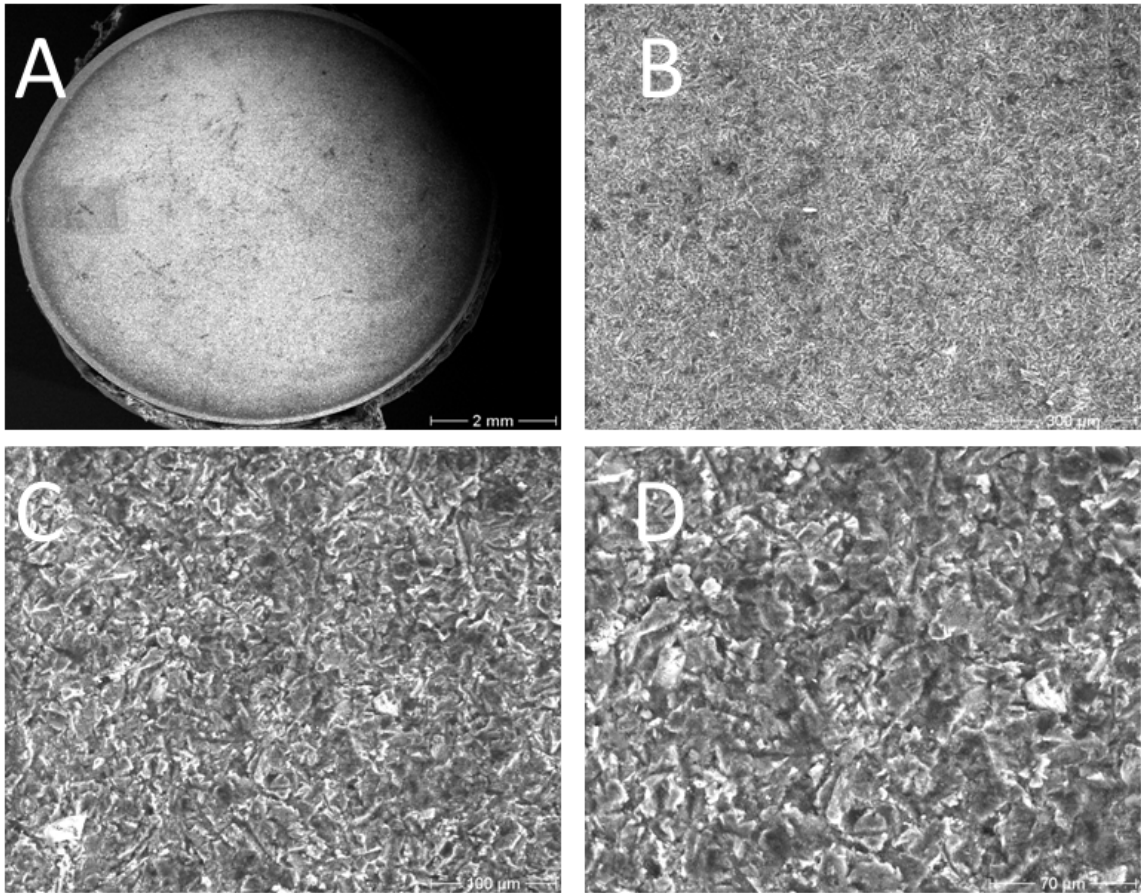SEM under A: 15X, B: 100X, C: 300X, and D: 500X magnifications.

Figure 13. Titanium surface treated with Rocatec viewed with SEM under A: 15X, B: 100X, C: 300X, and D: 500X magnifications.

Figure 14. Titanium surface treated with H_2SO_4 and Rocatec viewed with SEM under

A: 15X, B: 100X, C: 300X, and D: 500X magnifications.

Figure 15. Titanium surface treated with Silano Pen viewed with SEM under A: 15X,

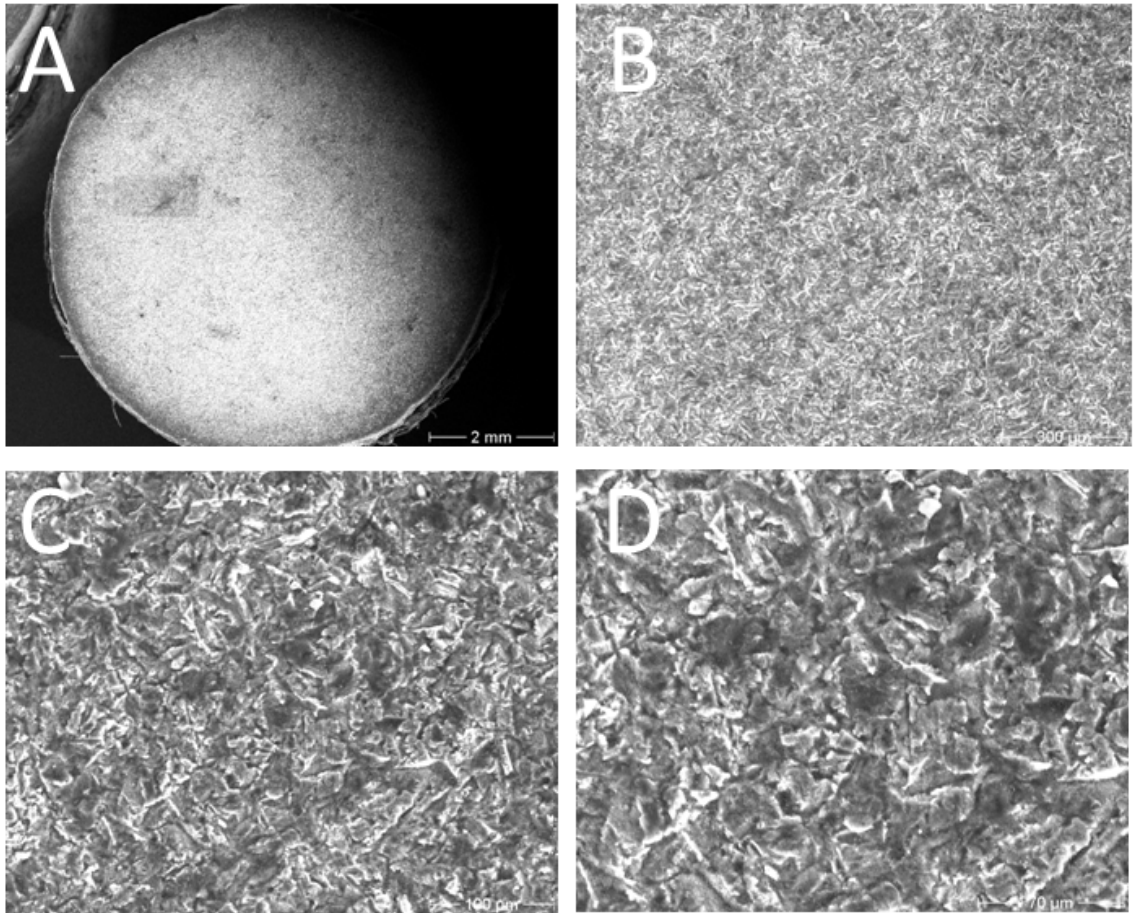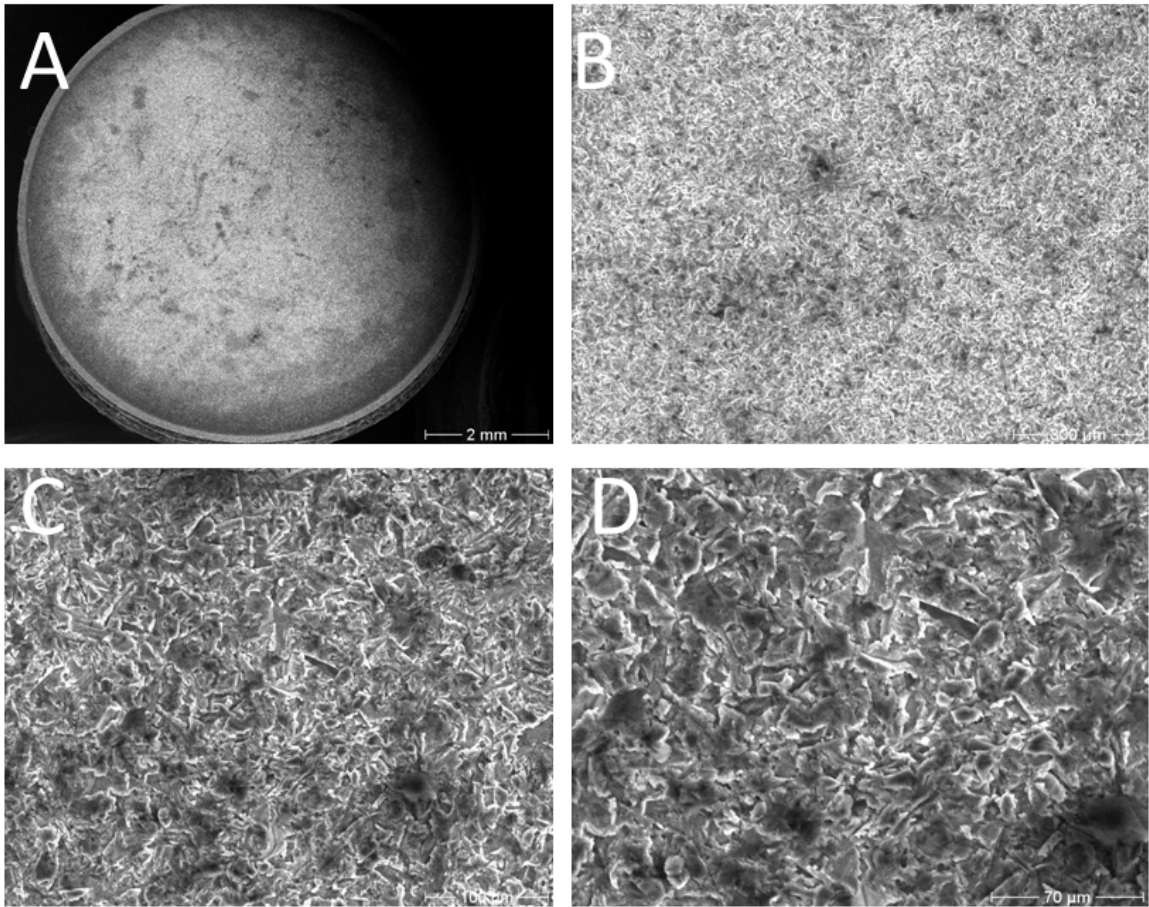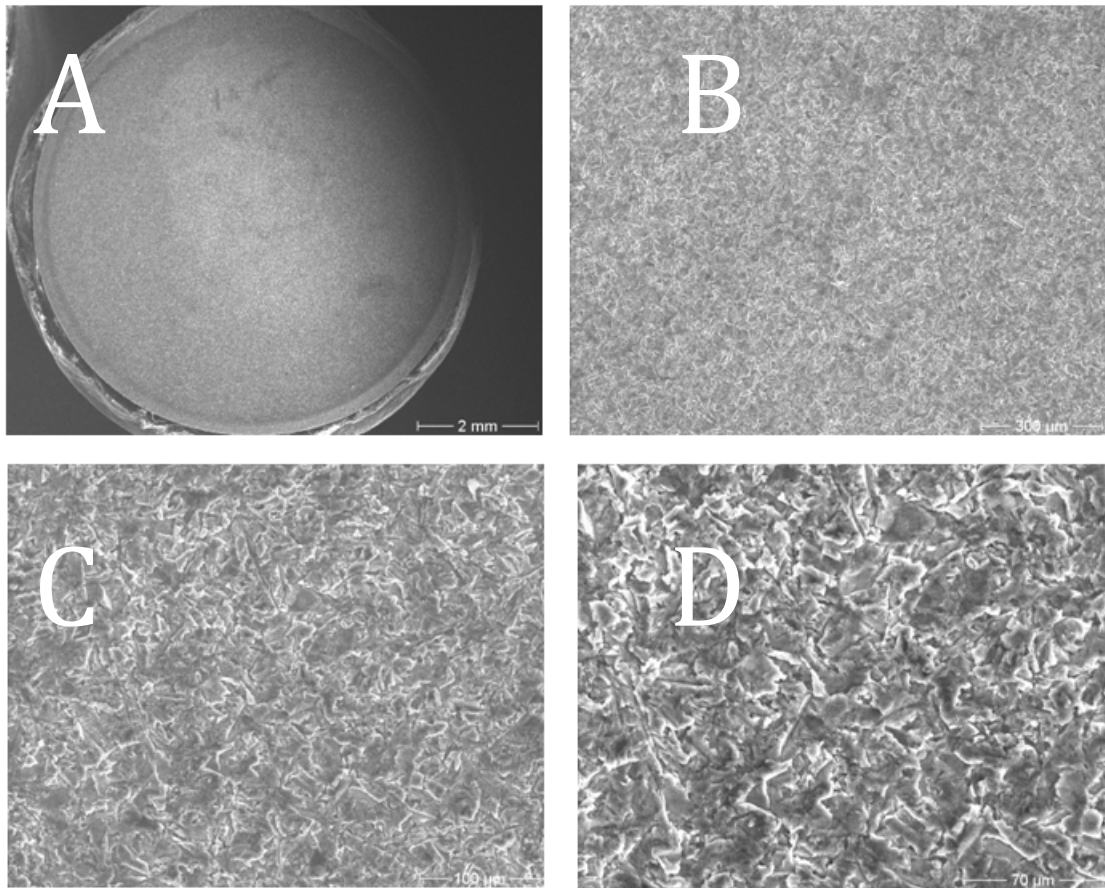B: 100X, C: 300X, and D: 500X magnifications.

Figure 16. Titanium surface treated with Silano Pen and its bonding agent viewed with

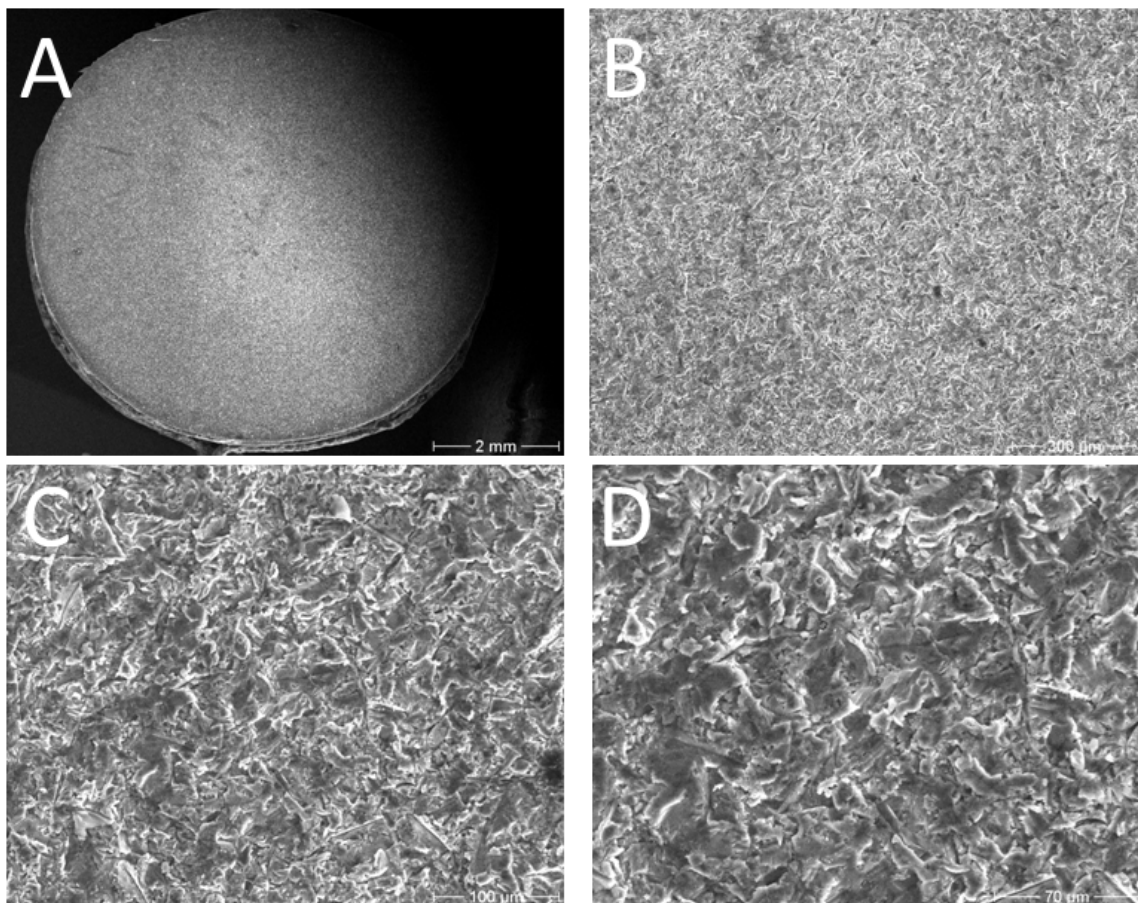SEM under A: 15X, B: 100X, C: 300X, and D: 500X magnifications.

Figure 17. Titanium surface treated with Silano Pen and H_2SO_4 viewed with SEM under A: 15X, B: 100X, C: 300X, and D: 500X magnifications.

DISCUSSION

Many surface treatments have been proposed in the literature to increase the bond strength between metal and resin. These treatments include surface roughening to provide micromechanical retention, chemical bonding between the restorative material and titanium, or treatments that combine both a roughening and a chemical component.

The effects of sandblasting or air-particle abrasion on the bond strength between resin and titanium have been demonstrated in the literature. Both Giachetti et al. and Kern and Thompson showed an increase in the bond strength after sandblasting.[21,22] The SEM evaluation in the current study showed sandblasting increased surface roughness of the titanium compared to the 600 grit SiC ground group, which would allow greater micromechanical bonding. For bond strength determination, however, a comparative group comprised of a ground titanium surface without sandblasting was not established because this would not be commonly performed clinically. Yet, sandblasting alone was able to achieve similar bond strengths to three other surface treatment groups as discussed below.

Systems that are based on silica coating and silanization have been thoroughly studied in the literature. Most authors showed significantly improved bond strengths by using these systems, which include the Silicoater, Rocatec, and the Kevloc bonding system.[19,21,22,27,30-32] May et al. reported increases of 68% in shear bond strength with the Rocatec system as compared to the untreated group.[32] Vallittu and Kurunmaki reported achieving a greater bond strength by eliminating the silanization step in the Rocatec system.[28] Their results are controversial as they go against the manufacturer's recommendations. The current study does not confirm the results of Vallittu and

Kurunmaki since the overall bond strength of group 2 (Rocatec without the silanization step) had a comparable overall mean bond strength to that of the control/sandblasted group (4.99 vs. 5.39 MPa, respectively). Dental laboratories sometimes substitute this silanization step with other bonding agents; based upon this study, that practice is not recommended.

Silano Pen is a relatively easy system to use, but it is not well documented in the literature as only one study by Janda et al. reported the use of Silano Pen. Janda et al. bonded resin to grade 1 cp Ti with Silano Pen and reported shear bond strengths of 18.4 MPa and 11.1 MPa before and after thermocycling, respectively.[12] The reduction in bond strength was significant. Also, these bond strengths were statistically similar to the same group but treated with Rocatec. In the present investigation, however, the Silano Pen group and the Silano Pen + H_2SO_4 group performed significantly better than the rest of the groups. A mean shear bond strength of 11.55 MPa (Silano Pen) and 12.62 MPa (H_2SO_4 + Silano Pen) were achieved before thermocycling. After thermocycling, the mean bond strength was 11.48 MPa (Silano Pen) and 9.89 MPa (H_2SO_4+ Silano Pen), which is consistent with the drop in bond strength after thermocycling observed by Janda et al.[12]

Ban et al. used different types of acid treatments to improve the bond strength between titanium and composite resins.[10] They reported achieving the strongest bond strength by etching the titanium with 48% H_2SO_4 at 60°C for 60 minutes. In this investigation, this treatment did not significantly improve the bond strength as compared to the control group. Also investigated was to see if combining this treatment with Silano

Pen and the Rocatec systems would have an additive effect on the bond strength, but no significant improvement was observed, deeming this extra step unnecessary.

Thermocycling significantly decreased the bond strength in the groups studied. This negative effect of thermocycling is in accordance with most of the other studies.[10,12,19,22,27,30,37,40,41] Accounting for all groups, thermocycling reduced the shear bond strength from 8.08 MPa to 6.29 MPa, a decrease of 22%. Individually, the Rocatec groups were the most affected with decreases in shear bond strength of 44-46%. This may reflect some incompatibility between the Rocatec blasted particles and the Meta Fast bonding agent that is further deteriorated by thermocycling. The Silano Pen group (3) was the least affected by thermocycling with a decrease in bond strength of less than 1%.

Based upon the recommendation of Bulbul and Kesim[35], Meta Fast is suggested as a bonding agent for titanium. In their study, Bulbul and Kesim evaluated the effect of 3 metal primers on the shear bond strength of 3 acrylic resins to 3 different types of alloys. The alloys were a Co-Cr alloy, a titanium alloy, and a noble metal alloy (Au-Ag-Pt). The primers were Alloy Primer which contains VBATDT and MDP, Meta Fast which contains 4-META, and Metal Primer which contains MDP. They suggested that primers should be selected depending on the type of metal alloy used with Metal Primer for base metal alloys, Meta Fast for titanium alloys, and Alloy Primer with noble alloys. Additionally, Meta Fast was chosen for this study because the application of it is rather easy as it only requires one step. Many options exist as to choice of bonding agent, and perhaps Meta Fast might not be the best bonding agent available, but it was not in the scope of this investigation to compare available bonding agents.

Nevertheless, the bond strengths that were achieved in this investigation with Meta Fast are low compared to the results that were reported by other investigators who have used other metal primers.[26,33] Yanagida et al.[33] evaluated the adhesive performance of cast titanium to composite resin by using eight metal conditioners including Meta Fast. They were able to achieve shear bond strengths of 22.2 MPa with a metal conditioner called Alloy Primer which contains the hydrophobic phosphate functional monomer MDP. MDP monomer contains three differently functioning components: methacryloyl, decyl and dihydrogen phosphate groups. Of these, the methacryloyl group copolymerizes with the matrix monomers of the composite while the dihydrogen phosphate group chemically bonds to the metal oxides on the titanium.[33] As mentioned above, different metal primers, especially primers that contain MDP as the functional monomer, could have performed better in comparison with Meta Fast.

The SEM evaluations of the titanium surface after treatment with Rocatec, H_2SO_4 and Rocatec, Silano Pen, and Silano Pen with H_2SO_4 reveal no discernable differences. Thus, the superior bond strength that was achieved in the groups that had Silano Pen as part of the surface treatment could not be attributed to the surface topography. The superior bond strength may possibly be attributed to the use of the silane agent that is supplied in the Silano Pen kit. Only the groups that had Silano Pen as part of the surface treatment used this silane agent, whereas all the other groups were bonded with Meta Fast. This again emphasizes the importance of the silanization step in the Rocatec system that was eliminated in this study. Not having a Rocatec group without eliminating the silanization step is another limitation of this study as direct comparisons could have been made.

Other limitations of the study may include that it is an in vitro study and conditions that may affect the bond strength in vivo were not all tested. For example, the effects of fluctuating pH, as would be observed in the oral cavity, were not evaluated in this study. Similarly, apart from thermal stresses induced by the thermocycling, the titanium/resin interface will be subject to repeated cycles of stress during normal function. Also, with regard to testing methodology, it may be that specimen geometry combined with shear bond testing parameters used may not accurately reflect the stress state observed in an actual prosthesis during function.

CONCLUSIONS

Within the limitations of this investigation the following conclusions may be drawn:

1. Silano Pen is a relatively easy and effective system to be used with titanium to improve the bond strength of titanium to composite resin.

2. The silanization step in the Rocatec system is a critical step and eliminating it may dramatically affect the effectiveness of this system.

3. Combining two surface treatments will not always result in an additive effect.

4. Thermocycling significantly decreased the bond strength regardless of the surface treatment used.

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