Original Article

Evaluation and comparison of the effect of different surface treatment modifications on the shear bond strength of a resin cement to titanium: An *in vitro* study

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Abstract

The purpose of this study was to evaluate and compare the effect of grit blasting, chemical treatment, and application of alloy primer combinations on the shear bond strength (SBS) of a self-cure resin cement to titanium surface.

Materials and Methods: Fifty cast commercially pure titanium discs (9 mm × 2 mm) were divided into five groups ($n = 10$), which received the following surface treatments: Control group (no surface treatment), group 1 (grit blasting using 110 µm Al_2O_3 particles and application of alloy primer), group 2 (grit blasting using 110 µm Al_2O_3 particles and chemical treatment using 1N HCl), group 3 (chemical treatment using 1N HCl and application of alloy primer), and group 4 (Grit blasting using 110 µm Al_2O_3 particles, chemical treatment using 1N HCl and application of alloy primer). Superbond C and B resin cement was applied to the treated titanium surfaces including controls. SBSs were determined after thermocycling for 5000 cycles. Data (megapascal) were analyzed by ANOVA and Bonferroni test.

Results: Group 4 (grit blasting using 110 µm Al_2O_3 particles, chemical treatment using 1N hydrochloric acid, and application of alloy primer) produced the highest bond strength followed by group 1, group 3, group 2, and the control group which showed the least bond strength.

Conclusion: (1) Air-abrasion with alumina particles increases the micromechanical retention of the resin to titanium. (2) The alloy primer promotes wettability, which increases the adhesive bonding of resin cement to titanium. (3) Chemical treatment using hydrochloric acid effectively pretreats the titanium surface thereby increasing the SBS values.

Key Words: Air-abrasion, hydrochloric acid, primer, resin based cement, shear bond strength, surface treatment, titanium

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INTRODUCTION

Titanium is known as the exotic "space age" metal because of its light weight and high performance in aeronautics. This wonder metal has many advantages as a prosthetic material such as excellent biocompatibility, high strength to weight ratio, low density, sufficient corrosion resistance, and low cost compared to noble alloys and therefore, has gained popularity in dentistry.[1-3] Today titanium and its alloys are used in dental implants, implant frameworks, crowns and bridges, resin bonded bridges, post and core, partial and complete denture frameworks.[4]

Many of these restorations are luted with resin cements. The strength of the cement/metal bond is significantly affected by

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the intimacy of contact between the surfaces of the materials. The intimate contact is optimized when the luting material is capable of flowing into the surface irregularities of the metal surface. Therefore, the properties of the luting cements and metallic substrate surface micro-topography play an important role in preventing debonding of the prostheses.[5]

Many types of surface treatment have been proposed to improve the bond strength of titanium to cement. These treatments include sandblasting, silicoating, acid etching, and use of functional monomers. Studies have shown that the treatments have been effective at increasing bond strength, albeit at varied amounts.[6-8]

Surface treatment of the titanium by sandblasting with AI_2O_3 particles improves the effectiveness of the surface area of the metal and increases the composite resin-metal bond strengths.[9] Chemical etching of titanium using hydrochloric acid, phosphoric acid or sulfuric acid enhances micromechanical bonding by pretreating titanium to make it more receptive to the resin.[10] Chemical bonding of metal to composite resin involves coating the metal with alloy primers or silane coupling agents that contain functional monomers. These functional monomers promote chemical bonding between the cement and the oxides present on the metal surface.[11]

Despite the research, the nature, and the variables affecting titanium-cement junction are still unclear. The current study was concerned with the bonding of resin cement to titanium surface and how we could improve the bond strength at the cement-titanium junction. Previous studies[5,10,12-14] have used individual surface treatments to increase the bond strength at the cement-titanium interface, but there are no studies, which have used a combination of different surface treatments. Hence, the aim of this *in vitro* study was to use different combinations of surface treatment to increase the shear bond strength (SBS) at the cement-titanium interface reducing the chances of failure of the prosthesis.

MATERIALS AND METHODS

For this study, fifty discs of commercially pure titanium (9 mm in diameter and 2 mm in thickness) were cast, finished and polished. Each disc was embedded in an aluminum mold with polymethyl methacrylate autopolymerizing acrylic resin. All the fifty samples were divided into five different groups before bonding the resin cement to titanium surface. Ten specimens received no surface treatment and acted as a control. Rest of the specimens was divided into four groups ($n = 10$), which were subjected to one of the following surface treatments:

- Group 1 - Grit blasting using 110 μm Al_2O_3 particles, and application of alloy primer (V-primer)
- Group 2 - Grit blasting using 110 μm Al_2O_3 particles, and chemical treatment using 1N hydrochloric acid
- Group 3 - Chemical treatment using 1N hydrochloric acid, and application of alloy primer (V-primer)
- Group 4 - Grit blasting using 110 μm Al_2O_3 particles, chemical treatment using 1N hydrochloric acid, and application of alloy primer (V-primer).

Group 1 specimens were surface treated as follows

Airborne particle abrasion using 110 μm Al_2O_3 particles was performed for 10 s at an angle of 90° under 0.28 megapascal (MPa) air pressure, held at a distance of 10 mm from the specimen surface. Subsequently, all the specimens were cleaned in distilled water for 10 min using an ultrasonic cleaner and air-dried. Alloy primer was applied to the abraded titanium surface with a disposable brush for 15 s and left to dry for 60 s at room temperature.

Group 2 specimens were surface treated as follows

Airborne particle abrasion using 110 μm Al_2O_3 particles was performed for 10 s at an angle of 90° under 0.28 MPa air pressure, held at a distance of 10 mm from the specimen surface. Subsequently, all the specimens were cleaned in distilled water for 10 min using an ultrasonic cleaner and air-dried. The specimens were then immersed in 1N solution of hydrochloric acid for 5 min at room temperature. The specimens were then washed with distilled water for 10 s and air-dried for 5 s.

Group 3 specimens were surface treated as follows

The specimens were cleaned in distilled water for 10 min using an ultrasonic cleaner and air-dried. The specimens were then immersed in 1N solution of hydrochloric acid for 5 min at room temperature. The specimens were then washed with distilled water for 10 s and air-dried for 5 s. Alloy primer was applied to the treated titanium surface with a disposable brush for 15 s and left to dry for 60 s at room temperature.

Group 4 specimens were surface treated as follows

Airborne particle abrasion using 110 μm Al_2O_3 particles was performed for 10 s at an angle of 90° under 0.28 MPa air pressure, held at a distance of 10 mm from the specimen surface. Subsequently, all the specimens were cleaned in distilled water for 10 min using an ultrasonic cleaner and air-dried. The specimens were then immersed in 1N solution of hydrochloric acid for 5 min at room temperature. The specimens were then washed with distilled water for 10 s and air-dried for 5 s. Alloy primer was applied to the treated titanium surface with a disposable brush for 15 s and left to dry for 60 s at room temperature.

Superbond C and B self-cure resin cement were applied to the surface of all the specimens including controls. A custom-made metal split matrix (5 mm internal diameter and 2 mm thickness) was placed on the center of the titanium disc. The purpose of the matrix was to allow the addition of the resin cement at a constant diameter and thickness on the metal substrate. The cement powder was proportioned by weight and mixed with the catalyst and monomer according to the manufacturer's instructions and inserted into the matrix. A glass slab and a weight exerting 500 g were placed on top of the cement to permit overflow of a slight excess of material. The specimens were left undisturbed for 15 min, and the excess cement was removed. All the specimens were stored in distilled water at 37°C for 24 h. All the samples were thermocycled 5000 times in water between 5°C and 55°C. The dwell time at each temperature was 30 s with a transfer time of 15 s between baths.

The specimens were then subjected to shear load of 1kN with a universal testing machine (Model LR 50K; Instron Corp, Lloyd Instruments). A knife-edge chisel apparatus (5 mm blade length) running at a cross-head speed of 0.5 mm/min was used to direct a parallel shearing load at the resin cement/metal interface. SBS values were recorded in MPa).

RESULTS

The SBS values were evaluated, and the mean SBS and standard deviation for each group were calculated [Table 1]. This *in vitro* study rejected the null hypothesis as there was a significant difference in the mean SBS values among all the groups. ANOVA test was performed to compare the mean SBS values among different groups. Highest mean SBS was recorded in group 4 (9.171 ± 0.301 MPa) followed by group 1 (7.593 ± 0.245 MPa), group 3 (6.135 ± 0.546 MPa), group 2 (4.041 ± 0.333 MPa), and control group (2.458 ± 0.367 MPa). The difference in mean SBS among the groups was found to be statistically significant ($P < 0.001$) [Table 2 and Graph 1]. In order to find out among which pair of groups there exist a significant difference, Bonferroni test (*post-hoc* test) was applied [Table 3].

DISCUSSION

The results of this study concluded that the highest mean SBS was recorded in group 4 (9.171 ± 0.301 MPa) followed by group 1 (7.593 ± 0.245 MPa), group 3 (6.135 ± 0.546 MPa), group 2 (4.041 ± 0.333 MPa), and control group (2.458 ± 0.367 MPa).

The group 4 specimens, which were abraded with 110 μm Al_2O_3 particles followed by chemical treatment using 1N HCl acid and application of alloy primer produced the highest SBS values. Air-abrasion with 110 μm Al_2O_3 particles created a rough surface, which increased the surface area for bonding.[9] Chemical treatment of the abraded Ti surface was done using 1N HCl acid after sandblasting. 1N HCl acid can be used to treat the titanium surface as negligible amount of chloride can be detected which would interfere with the bonding. This effectively decontaminated the titanium surface and removed the smear layer.[10]

Alloy primer (V-primer) was then applied to the chemically etched surfaces. Alloy primer promotes the diffusion of the functional monomers into the micro- and nano-scale cavities

Table 1: Mean SBS values for different groups

Group	Mean	SD
Control	2.458	0.367
Group 1	7.593	0.245
Group 2	4.041	0.333
Group 3	6.135	0.546
Group 4	9.171	0.301

SD: Standard deviation, SBS: Shear bond strength

Table 2: ANOVA test for different groups

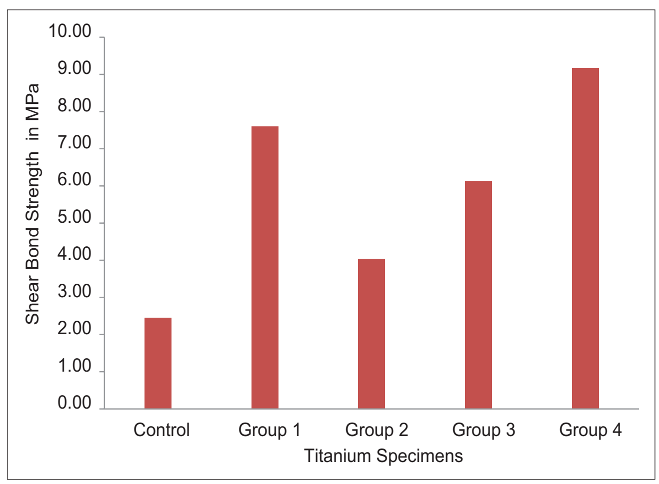
Group	Mean	SD	ANOVA
Control	2.458	0.367	F=520.886
Group 1	7.593	0.245	P<0.001
Group 2	4.041	0.333	
Group 3	6.135	0.546	
Group 4	9.171	0.301	

SD: Standard deviation

Table 3: Bonferroni test for different groups

Group (I)	Group (J)	Mean difference (I–J)	*P*
Control	Group 1	−5.135	<0.001*
	Group 2	−1.583	<0.001*
	Group 3	−3.677	<0.001*
	Group 4	−6.713	<0.001*
Group 1	Group 2	3.552	<0.001*
	Group 3	1.459	<0.001*
	Group 4	−1.578	<0.001*
Group 2	Group 3	−2.093	<0.001*
	Group 4	−5.129	<0.001*
Group 3	Group 4	−3.036	<0.001*

*P<0.001: Highly significant



Graph 1: Comparison of mean shear bond strength between all the groups

created by sandblasting and acid etching thereby decreasing the contact angle for bonding between resin cement and titanium.[15] When the alloy primer comes in contact with the residual alumina particles, there results in an increase in the bond strength of the alloy primer to the residual alumina particles and ultimately the treated titanium surface thereby increasing the bond strength of the cements.[16] Therefore, in this present study, it was observed that a combination of all these surface treatment produced the best bond strength. The results observed in this group are in agreement with a similar study, which concluded that combined use of sandblasting, application of etchant, and primer had a synergistic effect on titanium bonding.[15]

The SBS values for group 1 specimens were not as good as group 4 specimens but better than the other groups. In this group, the specimens were abraded with 110 μm Al_2O_3 particles followed by the application of the alloy primer. If HCl was used, it would have etched the abraded titanium surface, creating more surface roughness and, therefore, better bonding. This could be the reason why the bond strength of group 1 specimens was lower than group 4 specimens. The results observed in this group are in agreement with similar studies, which concluded that sandblasting and primer application significantly improved the SBS of the resin cement to titanium.[17-21]

The SBS values for group 3 specimens were better than group 2 and control group but less when compared to group 1 and group 4. In Group 3, the specimens were treated with 1N HCl acid followed by the application of the alloy primer. As the specimens were not abraded with alumina particles, the surface roughness created by only acid etching was not sufficient to increase the bond strength. Bond strength also increases when the alloy primer comes in contact with the residual alumina particles. The results observed are in agreement with a similar study, which concluded that chemical etchant improved the resin bonding durability to titanium in combination with the primer compared to the untreated Ti surface.[22,10]

The SBS values for group 2 specimens were much less compared to group 4, group 1, and group 3. The specimens in this group underwent air-abrasion with alumina particles followed by chemical treatment using 1N HCl acid. Although this group had a combination of mechanical, as well as chemical treatment, it still showed poor bond strength. This signifies the role of alloy primer in achieving good bond strength.

The control group did not undergo any of these surface treatments. Therefore, the SBS observed was the least. The results are in agreement with other researches, which concluded that a strong and durable bond between titanium and cement can be improved by surface treating the metal surface.[6,14,18,20,22,23]

According to ISO 10477 requirements, the SBS at the interface between resin-based materials and substrate should be >5 MPa.[24] In the present study, group 2 and the control group showed mean SBS values lower than 5 MPa. Therefore, surface treatment is essential for achieving the desired bond strength.

The luting composite used in this study, Superbond C and B, includes 4-META as the functional monomer and has been reported to yield high bond strengths between resin-based materials and base metal alloys.[11] The resin structure has a micro hardness and flexural modulus substantially lower than other composite resin cements. Because of its low modulus of elasticity, the Superbond cement displays high plastic deformation and simply changes shape. This resilience gives Superbond a significant advantage over traditional adhesive cements.[25] Light cured cement was not used in this study as curing the cement through titanium, where it is intended to be used clinically, would be very difficult. Dual cured cement was also not recommended in this study for the fact that, it could get cured both chemically, as well as by light. The bond strength of self-cured resin cement is more when compared to dual-cured resin cement. Moreover, the bond strength of chemically activated dual-cured resin cement is much lesser compared to light and chemically activated dual-cured resin cement.[26]

The significant improvement in the SBS of titanium disks was because of the combined effect of all the surface treatments. Therefore, from this study, it can be concluded that a combination of all the surface treatment, both mechanical and chemical, produces a stronger and more durable bond between the resin cement and titanium.

However, there are certain limitations of the study. SBS is not the only factor that may influence the durability of resin-metal bonds. Careful interpretation of the clinical implication of these results is suggested. Thermal cycling of specimens accelerates the diffusion of water between the resin and metal or ceramic, decreases the bond strength, but represents a limited simulation of the intraoral situation. Therefore, the specimens should be subjected to long-term storage under simulated oral conditions and fatigue loading for evaluation of their performance during clinical service.

Combined mechano-chemical treatments of commercially pure titanium can be employed in day-to-day clinical practice, which proves to be beneficial in enhancing the adhesion of resin luting cements, thereby improving the retention and longevity of the prosthesis.

CONCLUSION

Within the limitations of this *in vitro* study, the following conclusions were drawn:

- Air-abrasion with alumina particles provided greater surface area for bonding and increased the micromechanical retention of the resin to titanium
- Chemical treatment using hydrochloric acid effectively etched the titanium surface and considerably removed the smear layer, which led to increase in the SBS values
- The alloy primer promoted a significant increase in the adhesive bonding of resin cement to titanium
- Highest SBS values were yielded by group 4 specimens (combination of grit blasting, chemical treatment, and alloy primer application) followed by group 1 specimens (grit blasting and alloy primer application). The SBS values for these groups were more than 5 MPa, which satisfied the ISO requirements
- Lowest SBS values were yielded by the control group (no surface treatment) followed by group 2 (grit blasting and chemical treatment). The SBS values for these groups were <5 MPa, and hence not suitable for clinical situations.

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