

Investigation into the Effect of Use of Metal Primer on Adhesion of Heat Cure Acrylic Resin to Cast Titanium: An In Vitro Study

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Abstract The availability of adhesive primers capable of bonding chemically to base metal alloys without well defined passive oxide surface film has been improved significantly over the last decade. Therefore, the purpose of the study was to compare and evaluate the effect of metal primer on adhesion of heat cure acrylic resin to cast titanium. Shear bond strength test was conducted on 80 commercially pure titanium cast metal heat-cure acrylic resin discs treated with different surface treatments. The first group received no surface treatment (group I); the second group was subjected to sandblasting (group II); the third group was treated with bonding agent (alloy primer) (group III) and the fourth was treated with sandblasting and alloy primer (group IV). After the samples were surface treated, acrylic resin was mixed, packed and processed over the test area of cast titanium. Ten specimens of each group were immersed in distilled water for 24 h followed by thermocycling for 20,000 cycles. Shear bond-strength between the heat cure acrylic resin and titanium was evaluated using Instron universal testing machine.

Debonded specimens of all the groups were subjected to SEM analysis. The bond failure (MPa) was analyzed by ANOVA and Duncan's multiple comparison tests. Surface treatment with sandblasting, followed by the application of alloy primer showed maximum shear bond strength before and after thermocycling (24.50 ± 0.59 and 17.39 ± 1.56 MPa respectively). The bond strength values are found to be in decreasing magnitudes as group IV > group III > group II > group I. The following pre-treatment to improve the shear bond strength of heat cure acrylic resin to titanium is recommended in order to attain the maximum bond strength in cast titanium frameworks for various prostheses: sandblasting, cleaning in an ultrasonic bath for 10 min and air drying followed by application of a bonding agent uniformly on the sandblasted cast titanium surface before packing with heat cure acrylic resin.

Keywords Titanium · Heat cure acrylic resin · Surface treatment · Alloy primer

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Introduction

Titanium and its alloys are increasingly being used for dental cast restorations because of their advantages with respect to resin bases, which include low specific gravity, resistance to corrosion, better strength and better biocompatibility [1]. Case reports have described sensitivity reaction to gold and gold alloys and alloys containing cobalt, chromium, molybdenum and nickel [2]. It has been reported that cobalt, chromium and nickel used in denture base alloy may cause not only local oral sensitivity such as gingivitis and stomatitis, but also sensitivity that may result in eczema and dermatitis without mucosal manifestation [3]. Being biocompatible, this disadvantage of base metal

alloys is not seen for titanium and its alloys. Chemical bonding of resin to dental alloys has been improved significantly over the last decade and various bonding methods and techniques for base metal alloys have been developed, such as electrolytic etching [4–6] and chemical etchants [7, 8]. The availability of adhesive primers for base metals capable of bonding chemically to resins has simplified the procedures for surface preparation of base metal alloys without well defined passive oxide surface film [9]. Currently, a variety of vinyl thione coupling agents known as precious metal primers, have been commercially available. A thione–thiol tautomer has been used as a coupling agent between methacrylate base and metal alloy [10]. The choice of the thione tautomer increases the shelf life of the coupling agent and minimizes thiol interference with resin polymerization; since thiol-induced chain transfer during the propagation stage could affect the final conversion in the polymer network [8].

The bond strength of various resins with gold and base metal alloys has been extensively investigated and reported in the dental literature. However, there is a dearth of literature regarding the effect of metal primers containing thione–thiol tautomer on adhesion of heat-cure acrylic resin to cast titanium prostheses like fixed partial denture, metallic denture bases or implant supported prosthesis.

In the absence of any mechanical undercuts or interlocking, it is assumed that surface treatments like sandblasting and the use of alloy primer would affect bonding of resin-cast titanium surface. In addition, the resin-cast titanium interface may also get affected by temperature changes and water absorption. Therefore, it may be possible that the surface treatments, use of alloy primer as well as sandblasting, will influence the bond strength between resin and cast titanium surfaces. Hence, this quantitative and qualitative study was planned to evaluate the efficacy of alloy primer, as well as the effect of other surface treatments and thermocycling on the chemical bonding of heat-cure acrylic resin to cast titanium frameworks.

Materials and Methods

Fabrication of Titanium Samples

Eighty commercially pure (CP) titanium cast metal discs were prepared using a mould of 15 mm length and 2.5 mm width in the center [8]. Wax patterns were prepared by flowing molten casting inlay wax (Schuller-Dental, Germany) into the disc-shaped mould space with the help of a thermostat (Dentaurum). Twelve wax patterns were attached at a time to the runner bar sprue former. It was then fixed to a 9× size crucible former (Titec-Orotig, Verona, Italy) and the wax patterns were sprayed with a



Fig. 1 Sprued wax patterns attached to crucible former

surfactant liquid to reduce the surface tension (Aurofilm, Bego, Germany) and blow dried (Fig. 1). A moistened, asbestos-free ring liner (Kera Vlies, Dentaurum, Germany), 4 mm short at either end of the ring, was attached to the crucible former and the wax patterns were vacuum invested (Multivac 4-Degussa, Germany) using 500 g of magnesia based investment material and 75 ml mixing liquid (Titec-Orotig, Verona, Italy) as per manufacturer's instructions.

After setting of the investment, the crucible former was separated and the ring was placed inside the wax burnout furnace (Type 5640-KAVO EWL, Germany). The invested casting ring was heated in this furnace according to the following schedule-

- (1) 55 °C/min increase in temperature until it reached 150 °C, with a 90 min dwell (holding time);
- (2) 5 °C/min until it reached 250 °C, with a 90 min dwell at this temperature.
- (3) 5 °C/min until it reached 950 °C, with a 60 min dwell time at this temperature.

After reaching the maximum temperature of 950 °C, the casting ring was cooled to 450 °C gradually and casted immediately in a semi-automatic titanium casting machine (Type F-210, Orotig, Italy) (Fig. 2). Once cooled to room temperature, the specimens were devested and sandblasted using 110 µm aluminum oxide powder. All the samples were inspected for internal porosity by taking a radiograph. Samples with internal pores were discarded and a few extra samples were fabricated to bring the sample size to 80 non-defective titanium discs (Fig. 3). To ensure complete removal of the alpha-case layer, the surface of the cast specimens was ground with silicon-carbide abrasive paper (120–600 grit) in sequence. The samples were standardized by holding it to a fixed plane unidirectionally on a horizontal grinding unit and subsequently cleaned in ethanol. All dimensions of the area to be acrylized were controlled by a piece of adhesive tape with circular hole of 5 mm in diameter. Modelling wax (Hindustan Dental Products,



Fig. 2 Titanium casting machine (Titec F 210 M)

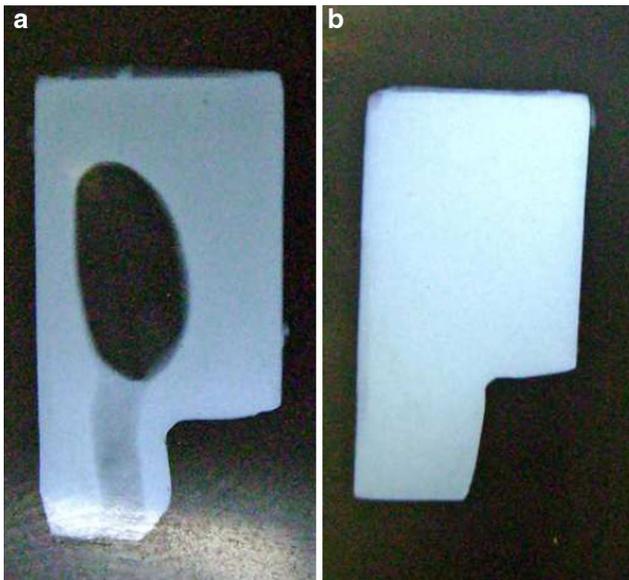


Fig. 3 Radiograph of test specimens with and without porosity

India) was applied to the test area of all the cast specimens in a symmetric cylindrical shape, 1 cm in length and 5 mm diameter. The specimens with the wax patterns were invested in conventional denture flasks with dental stone (Kalabhai, India) and dewaxed (Fig. 4).

Surface Treatment of the Cast Titanium Specimens

All the 80 samples, prior to the application of heat-cure resin were divided into four groups consisting of 20

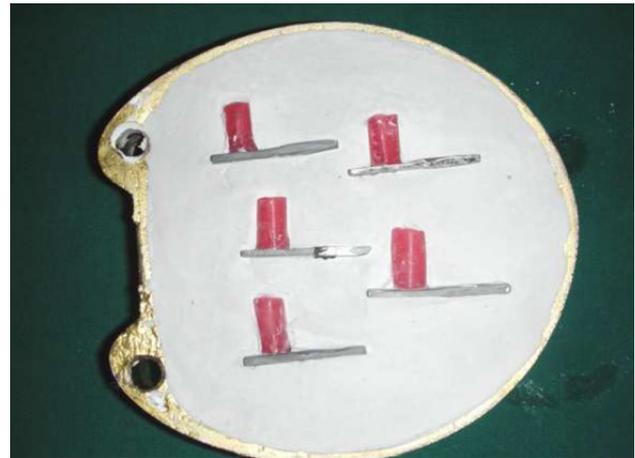


Fig. 4 Flasking of the specimens

specimens each according to the surface treatment they underwent. Standardized sandblasting was done for 40 samples of two groups (group II and IV).

Standardized Sandblasting Procedure

Forty samples were subjected to airborne particle abrasion with aluminum oxide (110 μm) at 4 bar pressure. The distance between the nozzle tip and the specimen surfaces was maintained at 2 cm, perpendicular to the tip, during the sandblasting procedure of 14 s treatment time. These samples were then ultrasonically cleaned in Soniclean ultrasonic cleaner (80T, Transtek systems, Australia) for 10 min each in deionized water and ethanol and air dried to ensure the removal of all residual particles and surface contaminants.

Heat Cure Acrylic Resin Application

After surface treatment of samples, heat-cure acrylic resin (Trevalon, Dentsply, India) was mixed, packed and processed over the test area of cast titanium according to manufacturer's instructions.

Thermocycling the Specimens

Ten specimens of each group were immersed in distilled water for 24 h followed by thermocycling. The specimens were wrapped in a sterile gauge piece and placed in a beaker with ice cubes which was maintained at a temperature of 5 ± 10 °C for 1 min and immediately the specimens were placed in water at 37 °C for a minute, followed by immersion in water maintained at 60 °C for a minute. This procedure was repeated for 20,000 cycles [11]. Thermocycling was done to evaluate the durability of the bond.

Bond Strength Testing

The shear bond-strength between the heat-cure resin and titanium was evaluated in the Instron universal testing machine with two cross heads, upper (movable) and lower (stationary), both mounted on a hydraulic framework connected to a digital recording unit, which recorded the load applied to the resin till separation was affected from the metal surface. A metallic fixture was prepared, especially for testing the specimens according to the universal testing machine. This jig consisted of two main parts:

1. Lower member: rectangular metallic plate of dimension (7 × 5 cm) and thickness of 4 mm. This fitted the lower jaw of the Instron testing machine.
2. Upper member: rectangular metallic plate of dimensions (6 × 5 cm) and thickness 4 cm with the square-shaped gap in the centre (2 × 2 cm). Here, another metallic part which held the specimen was inserted. This was split into two sections with a gap of 2 mm in-between and one surface had a disc shape 1 cm and depth of dimension 1.5 mm, similar to the specimen. These two sections were held tightly with the help of screws and tightened with Allen keys after placing the specimen. The whole unit was placed inside the upper member and tightened with the Allen keys. The upper and lower members of the fixture were joined together with two screws and tightened with Allen keys. The metallic chisel was of dimensions 8 cm length and thickness of 4 mm, with one side bevel. There was a metallic stopper at 5 cm distance from the tip of the chisel (Fig. 5). The lower member of the fixture was held in a wedge-action grip to the lower jaw of the Instron, the chisel was fixed to the upper jaw and was positioned parallel to the interface between the resin and the metal surface was fixed, such that the chisel just touched the resin (passive contact with the resin). Shear bond strength was tested at a crosshead speed of 2 mm/min and load was applied at the interface and was gradually increased till the resin fractured from the metal surface. The fracture loads were recorded in Kilogram-force (Kgf), which was converted to MPa by dividing the loads by the surface area of the built heat-cure acrylic resin surface area. Shear bond strength (MPa) = load at failure (Kgf) × 9.81 (N) surface area (mm²). The values recorded for each sample of four groups were tabulated separately and compared. The results were statistically analyzed using ANOVA and student paired “*t*” test.

Mode of Bond Failure

Fractured test specimens were visually examined for nature of bond failure between resin titanium interface and were classified as adhesive, cohesive and mixed type.

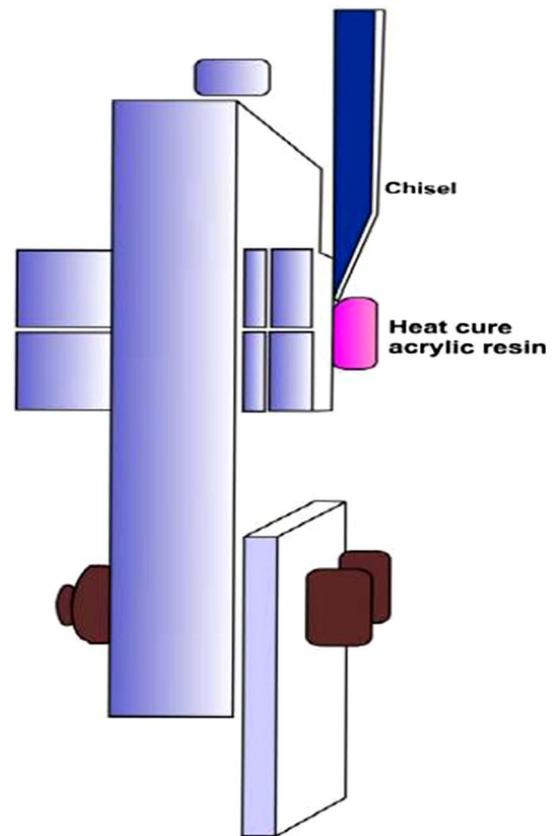


Fig. 5 Dimensions of the chisel used to test the samples



Fig. 6 Scanning electron microscope (JEOL JSM 840A)

Scanning Electron Microscope (SEM)

Two samples from each group were subjected to SEM analysis (Fig. 6). The fractured site was subjected to SEM analysis under 500× magnification with a resolution of 20 μm and the accelerating voltage of 20 kV (Fig. 7). Photomicrographs representing each group and mode of bond failure were prepared (Fig. 8).

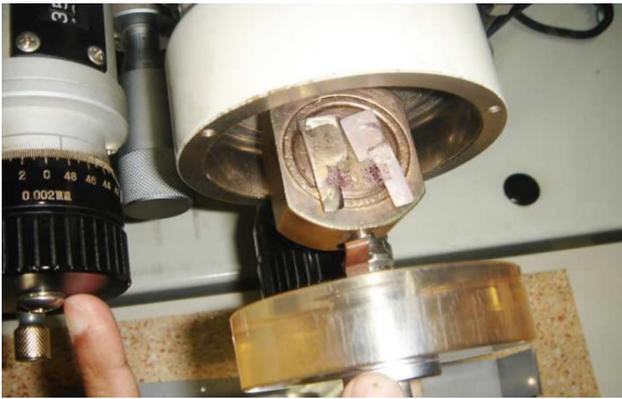


Fig. 7 Gold-plated tested samples mounted on stubs for the scanning electron microscope

Results

The study groups were divided as follows:

Group I: No surface treatment (before and after thermocycling).

Group II: Specimens were treated with only sandblasting (before and after thermocycling).

Group III: Specimens were treated with only alloy primer (before and after thermocycling).

Group IV: Specimens treated with sandblasting and alloy primer (before and after thermocycling).

The result is tabulated in Tables 1, 2, 3 and 4. It was observed that the chemically treated specimens with sandblasting showed the maximum bond strength values which is primarily due to the use of alloy primer as well as activation of the surface energy. There was a significant difference in the shear bond strength of the titanium-resin system at 1 % level of significance before ($F = 513.2638$) and after thermocycling ($F = 2,241.6608$). Four groups differed significantly with respect to shear bond strength at 1 % level of significance. Group IV had a significantly higher shear bond strength compared to other groups. F value being significant, analysis was done using the Duncan's multiple comparison tests. Table 3 indicates superior bond strength of acrylic-cast titanium surface than surface treatments given to group III, group II and group I in that order. Table 5 shows that group I had only adhesive failure whereas group II, III and IV had more of mixed type of failure. Graph 1 depicts the mean and standard deviation of shear bond strength (MPa) of heat cure acrylic resin with cast titanium after different surface treatments and Graph 2 shows the mode of bond failure and the failure rates in each of the groups tested.

Discussion

Recent improvement in the casting technology has made it possible to accurately fabricate prostheses made from commercially pure titanium (Cp Ti), thus expanding the use of this metal in clinical prosthodontics. Titanium has many advantages as a dental prosthetic material including excellent biocompatibility, good mechanical property and low density. However there is absence of chemical bonding of resin which affects the metal–resin interface. Microscopically, a space is present between the metal framework and resinous part of the denture. Bonding of resin to dental alloys has been significantly improved over the last decade and various bonding techniques for base metal alloys have been developed. Several chemical methods that enhance the bonding of resin veneers to cast alloys have been introduced, such as adhesive heat cure opaque resin, silicoater system, silane coupling agents and adhesive metal primer. Significant differences in shear bond strength were demonstrated when test specimens were treated with Rocatec bonding material. May et al. [12] in the quest of superior adhesion system for titanium demonstrated that application of primer containing either carboxylic, phosphoric or orthophosphoric acid derived monomers resulted in increased bond strengths. Many recent studies have observed that the use of metal primers increases bond strength between metals and heat-cured resins. The shear bond strength of the acrylic resin to base metal alloys is significantly higher than the shear bond strength to noble metals and titanium or its alloys [6, 13].

During late 1980s, an alternative approach was introduced by Kojima [14] who synthesized [6-(4-vinylbenzine-*n*-propyl-1, 3, 5-triazine-4-dithione)] (VBATDT), a thione–thiol tautomer, to be used as a coupling agent between methacrylate-based monomers and noble metal alloys. Since there are no reports regarding the effect of MDP[10,-methacrylic-decyl dihydrogen phosphate]-VBATDT containing alloy primer on the shear bond strength of resin with cast titanium, this study was conducted to evaluate and compare the shear bond strength of heat cure acrylic resin to titanium with surface treatments like sandblasting. It is believed that surface texture of the metal influences the mechanical integrity of metal–resin system. Specimens of two groups were sandblasted (group II and group IV). The purpose of sandblasting the bonding surface was to increase the surface area for bonding and decreasing the surface tension. May et al. [15] reported that there is remarkable improvement in the shear bond strength in the resin-alloy after sandblasting. However, Kim et al. [13] concluded from their study that if appropriate choice of

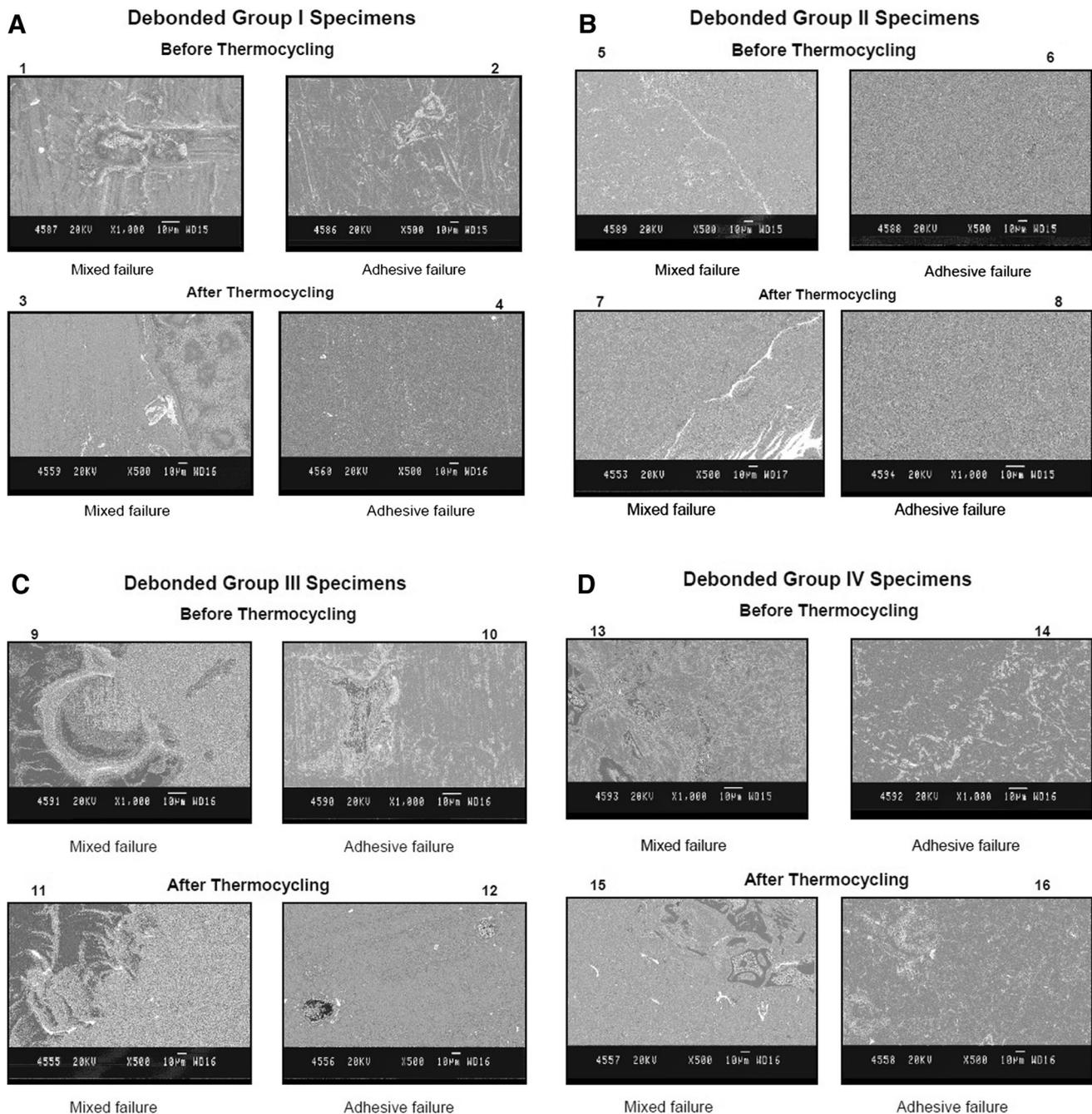


Fig. 8 a–d SEM photomicrograph for debonded samples: debonded group I specimens before and after thermocycling, **b** debonded group II specimens before and after thermocycling, **c** debonded group III

specimens before and after thermocycling, **d** debonded group IV specimens before and after thermocycling

metal primers was made, it is possible to eliminate the need for surface preparation of the metal framework before heat-cure resin application. In this study alloy primer, a variety of vinyl-thione coupling agent was used to enhance the adhesion between titanium and heat cure acrylic resin with the principle ingredients acetone, MDP [10-methacryloyldecyl dihydrogen phosphate] and VBATDT [6-(4-vinylbenzene-*n*-prophyl-1,3,5-triazine-4-dithione)] a thione–thiol

tautomer. The coupling mechanism of this monomer comprises of two stages:

- (i) Transformation of thione ($-C=S$) to thiol ($-C-S-H$) groups on metal surface (M) and subsequently primary bond formation ($-C-S-M$) and
- (ii) Co-polymerization of vinyl groups with the methacrylate-based resin monomer.

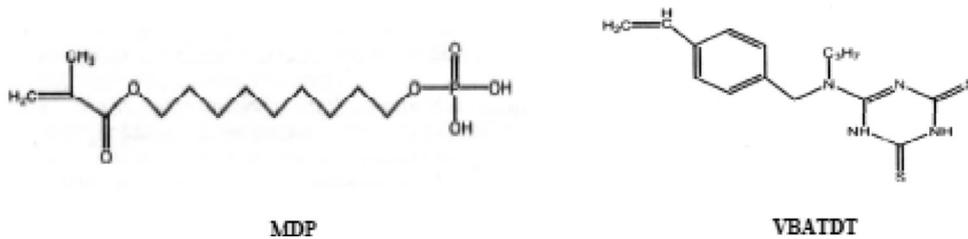


Table 1 Mean, standard deviation, standard error, coefficient of variation, minimum and maximum of shear bond strength (MPa) of heat cure acrylic resin with cast titanium after different surface treatment

Group	Thermo-cycling	Mean	SD	SE	CV	Minimum	Maximum
I	Before	2.81	0.37	0.12	13.06	2.29	3.46
	After	2.25	0.30	0.09	13.13	1.85	2.94
II	Before	9.83	0.68	0.21	6.90	9.00	11.14
	After	8.89	0.32	0.10	3.58	8.48	9.44
III	Before	18.49	0.82	0.26	4.46	17.03	19.66
	After	15.14	1.00	0.31	6.57	13.56	17.07
IV	Before	24.50	0.59	0.19	2.41	23.78	25.49
	After	17.39	1.56	0.49	8.97	13.28	18.80

Table 2 Statistical analysis (one-way ANOVA) for shear bond strength of heat cure acrylic resin with cast titanium of the four groups

Variable	SV	DF	SS	MSS	F value	p value	Significant
Before	Between groups	3	2728.63	909.54	2241.6608	0.0000	S*
	Within groups	36	14.61	0.41			
	Total	39	2743.24				
After	Between groups	3	1390.07	463.36	513.2638	0.0000	S*
	Within groups	36	32.50	0.90			
	Total	39	1422.57				
Difference	Between groups	3	271.71	90.57	115.9423	0.0000	S*
	Within groups	36	28.12	0.78			
	Total	39	299.83				

* Significant at 1 % level of significance ($p < 0.01$)

Table 3 Duncans's multiple comparison test for the shear strength of heat cure acrylic resin with titanium specimens of the four groups before and after thermocycling

	Groups	I	II	III	IV
Shear bond strength in MPa Before thermocycling	Mean	2.8110 ± 0.37	9.8.320 ± 0.68	18.4860 ± 0.82	24.4980 ± 0.59
	I	–			
	II	0.0001*	–		
	III	0.0001*	0.0001*	–	
	IV	0.0001*	0.0001*	0.0001*	–
Shear bond strength in MPa After thermocycling	Mean	2.2485 ± 0.30	8.8876 ± 0.32	15.1440 ± 1.00	17.3890 ± 1.56
	I	–			
	II	0.0001*	–		
	III	0.0001*	0.0001*	–	
	IV	0.0001*	0.0001*	0.0001*	–

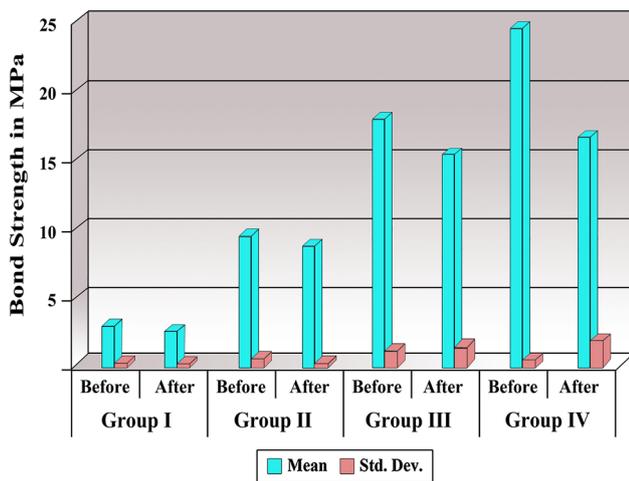
Table 4 Statistical pair wise comparison by student paired “*t*” test of difference in mean shear bond strength values of heat cure acrylic resin with cast titanium specimens of four test groups before and after thermocycling

Groups	Mean difference	SE	<i>t</i>	<i>p</i> value	Remark
I	0.5625	0.1007	5.59	0.0003	S
II	0.9444	0.2116	4.46	0.0016	S
III	3.3424	0.215	15.54	0.0000	S
IV	7.1094	0.4597	15.97	0.0000	S

Table 5 The mode of failure and their failure rates in each Group

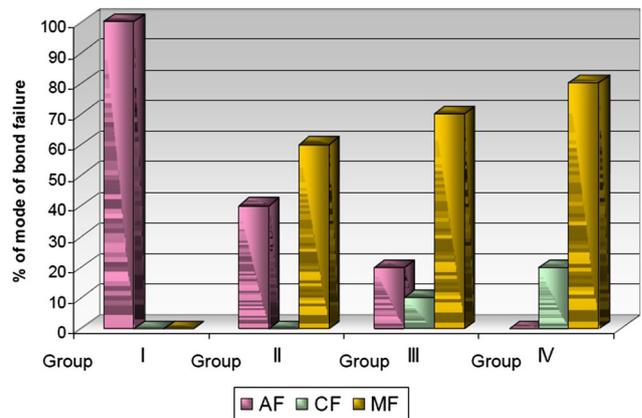
Group	AF	%	CF	%	MF	%	Total
I	10	100.00	0	0.00	0	0.00	10
II	4	40.00	0	0.00	6	60.00	10
III	2	20.00	1	10.00	7	70.00	10
IV	0	0.00	2	20.00	8	80.00	10
Total	16	40.00	3	7.50	21	52.50	40

AF adhesive, MF mixed failure, CF cohesive failure



Graph 1 Mean and standard deviation of shear bond strength (MPa) of heat cure acrylic resin with cast titanium for each group, before and after thermocycling

It was observed that the chemically treated specimens with sandblasting showed the maximum bond strength values, primarily due to the use of alloy primer as well as activation of the surface energy due to roughening of the surface. This may be attributed to the principal constituent i.e., MDP which is said to react with the oxide film produced on the titanium surface which contributed to increased bond strength and durability as speculated by Taire et al. [16]. The untreated titanium surface showed the lowest bond strength being a surface that produces a weak, porous, non-protective and non-adherent oxide layer, unsuitable for resin bonding. When titanium discs were



Graph 2 Mode of bond failure and the failure rates in each of the groups tested

treated with alloy primer (group III and group IV), the mean strength values were significantly greater when compared with the non-primed specimens. The thione tautomer increased the shelf-life of the coupling agent and minimized thiol interferences with resin polymerization, since thiol-induced chain transfer reactions during the propagation stage could affect the final conversion in the polymer.

According to Silikas et al. [10] surface-enhanced Raman scattering spectroscopic analysis (SERS) confirmed thione to thiol transformation of VBATDT in an aqueous colloidal gold solution, but failed to confirm the existence of a primary bond. Yoshida et al. [17] stated that MDP and VBATDT, having a hydrogen phosphate group, yielded higher bond strength than primer containing 4-META (4-methacryloyloxyethyl trimellitate anhydride) which are carboxylic acid groups. Student paired *t* test was performed to compare the mean of shear bond strength values before and after thermocycling of the four groups as shown in Table 4. The results obtained in this study were consistent with other studies [18, 19].

The use of water bath has been an accepted method of simulating thermal changes and the effect of moisture. Although in majority of studies, it was observed that post-thermocycling bond strengths were lesser than before performing the procedure, one study was not consistent with this finding [20]. The authors used a chemical etchant prior to bonding agent application and found enhanced bond strength more so after thermocycling.

Tanaka et al. and Matsumura et al. [4, 21] have shown that the thermocycling procedure is considered to be a satisfactory indicator to the effect of accelerated water ageing and is expected to fatigue the metal/acrylic joint. Studies have shown that there is a reduction in shear bond strength after thermocycling. Thermocycling causes a significant drop in shear bond strength of the metal and denture tooth resin bond and there is accelerated diffusion of

water into the adhesive interface at 60 °C which may reduce the bond strength after thermocycling [22].

SEM Results and Bond Failures

SEM analysis of the metal surface indicated that the dark areas were heat cure acrylic resin, while the light regions were titanium (Fig. 8). The bonding layer consisted of both morphologically and chemically distinct materials; most likely an admixture of titanium particles and heat cure acrylic resin. Figure 8a shows that a majority of the surface reaction layer was removed by grinding. Ultrasonic cleaning with deionized water and ethanol ensured the removal of all residual particles and surface contaminants. The shear bond strength of group I specimens was least amongst the four groups as there were no surface treatments. This finding concurs with those reported by May et al. [12]. Figure 8b shows that air borne abrasion likely improves the bond strength by removing loosely attached furrows, overlaps and flakes of metal created during grinding procedures. Ultrasonic cleaning of the sandblasted specimens resulted in a slight decrease in the alumina, which removes loose powder particles from the surface. The embedded alumina particles might also play an important role in the bonding mechanism when resin is intended to bond directly to sandblasted titanium. The shear bond strength of these specimens was marginally greater than group I. These results are consistent with those reported by Kern and Thompson [18, 19]. Taira et al. [20] concluded that sandblasting results in removal of the debris as well as metal oxide layer, however due to the reactivity of titanium, even though the oxide layer is removed from the surface, immediate reoxidation of titanium takes place. The surface, covered with a thin, stable oxide film, is essential for strong bonding in combination with heat cure acrylic monomer. Group III specimens had more of mixed than adhesive failures both before and after thermocycling. Figure 8c shows that alloy primer improves the bond strength by getting incorporated into the loosely attached furrows, overlaps and flakes of metal forming a chemical bond with the resin.

Using Fourier-transform infrared micro spectroscopy (FTIR) mapping, Silikas et al. [14] studied the mechanism of bonding of alloy primer. They reported that the primer shows the presence of VBATDT in the amorphous alloy primer film phase along with MDP and VBATDT predominant at the dispersed phase regions. The fact that the dispersed crystalline phase was always wetted by the amorphous phase implied miscibility between VBATDT and MDP monomers. The amphiphilic nature of both these monomers along with the high spreading pressure and H-bonding capacity of acetone led to the formation of homogeneous and thin film, thus enhancing the bonding mechanism. Group IV showed

more mixed failures and even few cohesive failures, both before as well as after thermocycling. Kern and Thompson [19] reported that there are both morphological and compositional changes which occur through sandblasting and coating procedures. Figure 8d shows that after air-borne abrasion and primer treatment, the bond strength improved due to deposition of chemically active monomers such as VBATDT and MDP in the micromechanical roughened surfaces of titanium. Group-IV SEM examination of the debonded titanium surfaces demonstrated sporadic resin remnants on the surface of titanium resulting in mixed failure. The alloy primer appeared to be incorporated well within the surface of the metal and evenly penetrated by the resin. This group produced significantly greatest bond strength values amongst the tested groups due to the enhancement of metal wettability when the primer is applied over the sandblasted surface.

Summary and Conclusion

Within the limitations of this investigation and for the materials used in this study, the following conclusions were drawn:

- (1) No surface treatment (group I) on the titanium surfaces with heat cure acrylic resin has the least shear bond strength resulting in adhesive failure (100 %).
- (2) Surface treatment using air borne-particle abrasion (group II) significantly enhanced the bond strength, resulting in more mixed bond failure (60 %) than adhesive bond failure (40 %).
- (3) The use of bonding agent significantly improved the titanium-heat cure acrylic resin bond strength (group III) with both cohesive and mixed failure but more of mixed failure (70 %).
- (4) Group IV which was treated with sandblasting and bonding agent (Alloy Primer) had more of mixed failure (80 %) than cohesive failure and gave the maximum bond strength than group III and group II.
- (5) The shear bond strength values before and after thermocycling were found to be in decreasing magnitudes as group IV > group III > group II > group I, indicating that bond strength might have been more as compared to fracture of heat cure acrylic resin. The highest bond strength values were for group IV before and after thermocycling (24.50 ± 0.59 MPa and 17.39 ± 1.56 MPa) respectively. The shear bond strength values for group III before and after thermocycling were (18.49 ± 0.82 MPa and 15.14 ± 1.00 MPa), followed by group II (9.83 ± 0.69 and 8.89 ± 0.68 MPa) and group I (2.81 ± 0.37 MPa and 2.25 ± 0.30 MPa) respectively.

- (6) Thermocycling simulating the oral temperature changes and environment resulted in reduction of shear bond strength.

Based on the findings and conclusions of the study, the following pretreatment procedures to improve the shear bond strength of heat cure acrylic resin to titanium are recommended in order to attain the maximum bond strength in cast titanium frameworks for various prostheses.

- (1) Surface grinding and finishing using titanium finishing burs.
- (2) Sandblasting, cleaning in an ultrasonic bath for 10 min and air drying.
- (3) Application of a bonding agent uniformly on the sandblasted cast titanium surface before packing.

Implications of Findings of This Study

- (1) When fabricating or repairing removable partial dentures involving resin-metal bond, laboratory procedures, such as removal of surface contaminants by steam cleaning and/or ultrasonic cleaning followed by air drying should be completed before creating resin-metal bond.
- (2) Sandblasting by controlled application of 110 μm alumina air abrasive to titanium frameworks prior to processing with heat cure acrylic resin, will increase the shear bond strength by more than three times over the non-air abraded and unprimed titanium surface.
- (3) It is recommended that the applications of an adhesive primer along with sandblasting are essential to obtain a strong bond between heat cure acrylic resin and commercially pure titanium.
- (4) The magnitudes of shear bond strengths of specimens of different groups obtained in this study are pertaining to the materials and methods used in fabrication of test samples, variables and methodology used for testing. However, the bond strength values may vary if these parameters and/or methodology are altered.

Limitations and Further Scope of the Study

- (1) Only one brand of metal primer was tested; the findings related to this product may not be extrapolated to other resin bonding agents.
- (2) Porosity and air entrapment between titanium and heat cure acrylic resin interface might have affected the shear bond strength in the specimens of same group.

- (3) In this study specimens of standard dimensions were immersed in distilled water. However the oral cavity is bathed with saliva, which is not chemically similar to distilled water.

References

1. Parr GR, Gardner LK, Toth RW (1985) Titanium: the mystery metal of implant dentistry and dental material aspects. *J Prosthet Dent* 54:410–413
2. Shah KM, Agrawal MR, Chougule SA, Mistry JD (2013) Oral lichenoid reaction due to nickel alloy contact hypersensitivity. *BMJ Case Rep* 8. doi:10.1136/bcr-2013-009754
3. Kononen M, Odont D, Rintanen J, Waltimo A, Kempainen P (1995) Titanium framework removable partial denture used for patient allergic to other metals: a clinical report and literature review. *J Prosthet Dent* 73:4–7
4. Tanaka T, Atsuta M, Nakabayashi N, Masuhara E (1998) Surface treatment of gold alloys for adhesion. *J Prosthet Dent* 60:271–279
5. Livaditis GJ, Thompson VP (1982) Etched casting: an improved retentive mechanism for resin bonded retainers. *J Prosthet Dent* 47:52–58
6. Bulbul M, Kesim B (2010) The effect of primers on shear bond strength of acrylic resins to different types of metals. *J Prosthet Dent* 103(5):303–308
7. Sedberry D, Burgess J, Schwartz R (1992) Tensile bond strengths of three chemical and one electrolytic etching systems for a base metal alloy. *J Prosthet Dent* 68(4):606–610
8. Matsuda Y, Yanagida H, Ide T, Matsumura H, Tanoue N (2010) Bond strength of poly (methyl methacrylate) denture base material to cast titanium and cobalt–chromium alloy. *J Adhes Dent* 12(3):223–229
9. Fonseca RG, de Almeida JG, Haneda IG, Adabo GL (2009) Effect of metal primers on bond strength of resin cements to base metals. *J Prosthet Dent* 101(4):262–268
10. Silikas N, Wincott PL, Vaughan D, Watts DC, Eliades G (2007) Surface characterization of precious alloys treated with thione metal primers. *Dent Mater* 23(6):665–673
11. Kim JY, Pfeiffer P, Niedermeier W (2003) Effect of laboratory procedures and thermocycling on the shear bond strength of resin-metal bonding systems. *J Prosthet Dent* 90:184–189
12. May KB, Fox J, Razzoog ME, Lang BR (1995) Silane to enhance the bond between polymethyl methacrylate and titanium. *J Prosthet Dent* 73:428–431
13. Kim S, Vang M, Yang H et al (2009) Effect of adhesive primers on bonding strength of heat cure denture base resin to cast titanium and cobalt-chromium alloy. *J Adv Prosthodont* 1(1):41–46
14. Matsumura H, Taira Y, Atsuta M (1999) Adhesive bonding of noble metal alloys with a triazine dithiol derivative primer and an adhesive resin. *J Oral Rehabil* 26(11):877–882
15. May KB, Van Putten MC, Bow DA, Lang B (1997) 4-META polymethyl methacrylate shear bond strength to titanium. *Oper Dent* 22:37–40
16. Matsumura H, Tanoue N, Yanagida H, Atsuta M, Koike M, Yoneyama T (1998) Influence of surface oxidation of titanium on adhesion. *J Dent* 26(1):69–73
17. Yoshida K, Kamada K, Atsuta M (1999) Adhesive primers bonding cobalt chromium alloy to resin. *J Oral Rehab* 26:475–478

18. Kern M, Thompson V (1993) Sandblasting and silica-coating of dental alloys: volume loss, morphology and changes in the surface composition. *Dent Mater* 9:155–161
19. Kern M, Thompson VP (1994) Effects of sandblasting and silica-coating procedures on pure titanium. *J Dent* 22:300–306
20. Taira Y, Yanagida H, Matsumura H, Atsuta M (2004) Effects of a metal etchant and two primers on resin bonding durability to titanium. *Eur J Oral Sci* 112(1):95–100
21. Matsumura H, Yoshida K, Tanaka T, Atsuta M (1990) Adhesive bonding of titanium with a titanate coupler and 4-META/MMA-TBB opaque resin. *J Dent Res* 69:1614–1616
22. Ohkubo C, Watanabe I, Hosoi T, Okabe T (2000) Shear bond strengths of polymethyl methacrylate to cast titanium and cobalt-chromium frameworks using five metal primers. *J Prosthet Dent* 83(1):50–57