Enhanced resin titanium adhesion with silane primers using tribochemical silica-coating

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Experimental silane primers and a urethane dimethacrylate resin were prepared to resin titanium bonding. Commercially pure 2 Ti coupons were pretreated and randomly assigned into groups: group-SM (ESPE Sil™+Multilink® Speed), group-SE (ESPE Sil™+experimental resin), group-AM (1.0 vol% 3-acryloxypropyltrimethoxysilane+Multilink® Speed), group-AE (1.0 vol% 3-acryloxypropyltrimethoxysilane+experimental resin), group-BM (1.0 vol% 3-acryloxypropyltrimethoxysilane+0.5 vol% bis-(1,2-triethoxysilyl)ethane+Multilink® Speed), and group-BE (1.0 vol% 3-acryloxypropyltrimethoxysilane+0.5 vol% bis-(1,2-triethoxysilyl)ethane+experimental resin). Specimens were stored in a desiccator for 24 h, and artificially aged by thermo-cycling (6,000 and 12,000 cycles). According to ANOVA and the Tukey's test ($n=10$, $\alpha=0.05$), the mean enclosed mold shear bond strength after 24 h was highest in group-AE (26.2±4.0 MPa). After 12,000 thermo-cycles, the group-BM exhibited the highest adhesion strength (13.4±3.2 MPa). This study suggests that a silane primer (3-acryloxypropyltrimethoxysilane+0.5 vol% bis-(1,2-triethoxysilyl)ethane) might enhance adhesion strength.

Keywords: 3-acryloxypropyltrimethoxysilane, Adhesion, bis-(1,2 triethoxysilyl)ethane, Titanium, Urethane dimethacrylate

INTRODUCTION

Resin composites are used in dentistry widely as fissure sealants, cavity liners, inlays, onlays, core buildups, cementation of orthodontic brackets, endodontic sealers, root canal posts, and more importantly, luting crown and bridge prostheses¹. Over the time, resin composites have evolved to self-adhesive resin cements but are still based on the Bis-GMA monomer². The present day self-adhesive resin cements have made clinical cementation procedures extremely simple without any pretreatment of the surface—at least in principle. Moreover, their properties such as micromechanical retention, adhesion, and dimensional stability are acceptable³.

All dental restorations are subject to high stresses in the hostile conditions of the oral environment. The difficulty in attaining a sustainable bonding between *e.g.*, a metal restoration and resin composite cement in the mouth is an issue in prosthetic dentistry. The clinical success of adhesive restorations relies on good bonding between the dissimilar surfaces⁴. In dentistry, adhesion may be enhanced with silane coupling agents that chemically connect dissimilar materials: different trialkoxyl silane coupling agents are employed for adhesion between resin composites and indirect restoration surfaces⁵. Among them, functional 3-methacryloxypropyltrimethoxysilane (MPS) can be called a gold

standard due to its ability in forming strong chemical bonding with methacrylate-based resin composite materials. However, its hydrolytic degradation and long-term adhesive strength under oral conditions is a continuous concern and this is why some other reactive silane monomers have been actively studied recently⁶.

Indeed, some silane monomers have been tested in laboratory conditions for long-term adhesion (bond strength^{7,8}). In particular, 3-acryloxypropyltrimethoxysilane (ACPS) and a cross-linking silane, bis-(1,2-triethoxysilyl)ethane (BTSE) have shown promising adhesion promotion in laboratory experiments. A functional silane coupling agent combined with a cross-linker silane might provide hydrolytically more stable and durable bonding⁹.

Over the last decades the properties of titanium (and its alloys) have made it a material of choice in implant dentistry. Titanium is a feasible alternative to noble metal alloys because of its higher biocompatibility, low price, good mechanical properties, chemical inertness, and corrosion resistance¹⁰⁻¹². Despite the many studies on improving the resin Ti adhesion strength, the long-term bonding durability is still a major concern for the researchers. This could impair the performance of this extremely biocompatible high-strength material as a dental prosthesis.

It is noteworthy that bis-phenol A-glycidyl methacrylate (Bis-GMA) based resin cements have also some disadvantages. Among them, the incomplete conversion of double bonds to single bonds, polymerization

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shrinkage, the disputed pseudo-oestrogenic effects, and water sorption should be emphasized. On the contrary, set urethane dimethacrylate (UEDMA) based resins, in general, may have higher flexural strength, elastic modulus and hardness—and they might have the potential to substitute Bis-GMA¹³. The current laboratory study had two aims: on the one hand, to evaluate the effect of some experimental silanes on resin titanium adhesion, and on the other hand, to compare and contrast the adhesive strength of UEDMA resin cement with a widely used dimethacrylate based self-adhesive resin cement (Multilink® Speed) using the enclosed mold shear bond strength testing. The null hypothesis tested was that neither experimental silane primers, nor UEDMA-based resin cement influence the adhesion strength between resin cement to titanium.

MATERIALS AND METHODS

Commercially pure grade 2 Ti sheet (Permascand, Ljungaværk, Sweden; >99%) was cut into 18 coupons, each with the dimensions of 1.0×20×40 mm. The coupons were ground with 600 grit SiC polishing paper under running water for 5 min. The upper half of the Ti coupons was grit-blasted with tribochemical silica-coating, using Rocatec™ Soft (3M ESPE, Seefeld, Germany) powder (particle diameter 30 µm). The treatment of the coupons was carried out with a slowly rotating constant motion, in a jet at 280 kPa. A perpendicular distance of 10±1 mm to the titanium surface was maintained for 10±1 s (all based on manufacturer's recommendation). Next, these coupons were ultrasonically cleansed in 70% ethanol and were randomly assigned into equally size 6 sub-groups, according to the experimental silane primer and resin cement used.

A dental silane coupling agent ESPE Sil™ (3M ESPE)¹⁴ was applied with a primer applicator brush on the silica-coated Ti substrate and allowed to dry 5 min in open air for the groups SM (control) and SE. For the study groups AM and AE, an experimental silane primer containing 1.0 vol% ACPS was applied with a same technique and for the groups BM and BE, a blended experimental silane primer containing 1.0 vol% ACPS+0.5 vol% BTSE were used. The experimental silanes were prepared as presented in literature⁵. Before bonding, a white colored semi-transparent polystyrene enclosed mold (*i.e.*, the mold was not removed but it remained) with an inner diameter of 4.0 mm, 0.5 mm wall thickness, and 4.5 mm of height was placed and kept firmly on the Ti specimen surface, to build up a stub specimen the molds were filled up to the brim and not removed after light curing the specimens. Self-adhesive resin cement, Multilink® Speed (Ivoclar Vivadent, Schaan, Liechtenstein) was mixed and activated according to the manufacturer's instruction and filled into the enclosed molds on the treated titanium substrates for the study groups SM, AM, and BM. Similarly, the experimental resin (70.6 wt% UEDMA+27.4 wt% HPMA) was prepared by following the methodology by Zhang *et al.*¹⁵ and

Fig. 1 Specimens of the study groups seen in a desiccator.

used for the study groups SE, AE, and BE. The light-curing was performed for 40 s from the top of the mold and then from the lateral side for 40 s using a light curing unit (Elipar™ 2500, 3M ESPE, USA). Ten resin stubs were adhered on each Ti coupon (Fig. 1). All the specimens were then kept in a desiccator at room temperature for 24 h for post-polymerization before the next steps.

One-third of the specimens were stored in a desiccator for 24 h before testing to obtain the baseline adhesion strength. One-third of the specimens were artificially aged, *i.e.*, thermo-cycled 6,000 times in distilled water between 5 and 55°C. The dwell time at each temperature was 30 s, with a transfer time of 5 s between the water baths. Similarly, the rest of the one-third of the specimens were thermo-cycled 12,000 times. Each group had ten specimens ($n=10$, $N=180$).

Adhesion strength testing

Specimens were tested for adhesion (enclosed shear bond) strength in a universal testing machine (Model no. 3369 Instron, Canton, USA) with a cross-head speed of 1.0 mm/min. The maximum load (kgf) used and registered prior to debonding was converted to force (in N) and divided by the area of the bonding interface to yield the shear bond strength in MPa.

Scanning electron microscope (SEM) observations

Representative specimens from each specimen group were analyzed for the surface morphological changes (at 1,000× and 2,000×) with a scanning electron microscope (JEOL JSM 5900LV SEM, Tokyo, Japan) operated at 10 kV, in vacuum.

Failure mode analysis

A light-stereomicroscope (Nikon SM2-10, Tokyo, Japan)

was used at a magnification of 30× to assess and estimate the failure mode. Adhesive, mixed or cohesive failure modes were assigned, according to proportion of resin composite cement (or resin) remained on the Ti surface. When ≤33% resin cement remained on Ti substrate, it was considered adhesive failure; when ≥34% but ≤66%, mixed failure mode, whereas ≥67% and ≤100% was considered cohesive failure¹⁶⁾.

Statistical analysis

Data were analyzed by SPSS software version 21.0 (SPSS®, Chicago, IL, USA) utilizing two-factor analysis of variance (ANOVA) to determine significant differences between the two independent variables (*i.e.*, materials and storage conditions) at 0.05 level of significance. If there was significant interaction between them, one-factor ANOVA and the *post hoc* Tukey's test were used to analyze the differences between the shear bond strength values within each variable.

RESULTS

Table 1 displays the enclosed mold shear bond strength (adhesion strength) values. Significant differences ($p < 0.05$) were observed in the mean adhesion strength values of the baseline, 6,000 thermo-cycles, and 12,000

thermo-cycles groups. The highest mean shear bond strength was observed in group-AE with 24 h dry storage (26.2 ± 4.0 MPa). The lowest mean shear bond strength value was observed in group-SE that underwent 12,000 thermo-cycles (2.2 ± 0.2 MPa). No spontaneous de-bonding was observed during the artificial water aging. Two-way ANOVA results showed a significant effect of storage conditions on the adhesion strength values. However, no statistical difference was observed between the groups SM and AM, SE and AE, SE and BE, and on the other hand, between the groups AE and BE.

Further, Table 1 explains the percentage change in the adhesion strength values due to the artificial aging in thermo-cycling. After 12,000 thermo-cycles, an 88 to 90% reduction in the adhesion strength values was observed in SE, AE, and BE. On the other hand, a decrease of 13 to 30 % in the adhesion strength values was observed in the groups SM and AM. Group-BM showed a sharp increase in the adhesion strength values after 6,000 thermo-cycles. However, a declining trend was observed in group-BM after 12,000 cycles.

The failure mode analysis is explained in Table 2. After 24 h dry storage, mixed and cohesive failure modes were observed in the groups SE, AE, and BE. However, after thermo-cycling, none of the specimens showed mixed or cohesive failure modes.

Table 1 Mean (standard deviation) of enclosed mold shear bond strength recorded in tested groups and their corresponding change in adhesion (enclosed mold shear bond) strength in percentage (%)

Group	Shear bond strength (SD) (MPa)			
	24 h dry storage	6,000 thermo-cycles	12,000 thermo-cycles	Change (%)
SM	15.4 (3.00) ^{A,B} _a			0
		13.4 (3.0) ^F _{a,b}		-12.8
			12.6 (2.9) ^{I,J} _b	-18.5
SE	22.8 (5.1) ^{C,D}			0
		2.7 (0.4) ^G _e		-88.6
			2.2 (0.2) _e	-90.1
AM	16.3 (4.4) ^{A,E} _d			0
		14.0 (4.8) ^F _{d,e}		-14.6
			11.9 (2.8) ^{I,K} _e	-27.4
AE	26.2 (4.0) ^C			0
		3.0 (0.7) ^{G,H} _f		-88.5
			2.8 (0.7) ^L _f	-89.2
BM	17.0 (3.6) ^{B,E}			0
		23.8 (3.1)		+40.1
			13.4 (3.2) ^{J,K}	-21.0
BE	22.7 (4.3) ^D			0
		3.4 (0.6) ^H _g		-84.8
			2.8 (0.4) ^L _g	-87.8

Key: SD=standard deviation

Different superscript uppercase letters demonstrate insignificant differences between the material groups. Different subscript lowercase letters demonstrate the insignificant differences between the aging groups.

Table 2 Number of failure and mode of failure after shear testing

Storage condition	Study groups																	
	SM			SE			AM			AE			BM			BE		
	A	M	C	A	M	C	A	M	C	A	M	C	A	M	C	A	M	C
24 h dry storage	10	0	0	6	2	2	10	0	0	4	5	1	10	0	0	0	8	2
6,000 thermo-cycles	10	0	0	10	0	0	10	0	0	10	0	0	5	4	1	10	0	0
12,000 thermo-cycles	10	0	0	10	0	0	10	0	0	10	0	0	10	0	0	10	0	0

Key: A=adhesive failure, M=mixed failure, C=cohesive failure

DISCUSSION

In this laboratory study, the specimens were prepared in an enclosed mold (made of polystyrene) to avoid any flaws possibly caused by the removal of the molds. The rationale behind was not to affect adhesion of resin (experimental or commercially available) to Ti during removing the mold^{17,18}. Artificial aging *via* thermo-cycling significantly affected the adhesion strength in the groups studied (Table 1). This deteriorating effect of thermo-cycling could be attributed to the thermal stresses generated during thermo-cycling, *i.e.*, from 5 to 55°C¹⁹. The thermal cycles used induced mechanical stresses due to the differences in the coefficients of the thermal expansion that results in adhesion failure at the resin-Ti interface. On the other hand, a sharp increase in adhesion strength after 6,000 cycles was observed in the group-BM. This could be attributed to release of stresses generated during the polymerization contraction of resin composite²⁰. Moreover, the cross-linking silane (BTSE) together with the functional silane (ACPS) might improve bonding by forming a 3D siloxane film that contributed to bonding between the dissimilar materials. Regardless of the increase in adhesion strength values in group-BM, a sharp decline in the adhesion strength values in all other experimental groups is in accordance with some previous studies^{1,10,21,22}. Nevertheless, thermo-cycling is a widely used and accepted rapid, accelerated aging method used in laboratories, in addition to the shear bond strength test, regardless of their undisputable limitations²⁰.

The experimental silanes showed promising results with Multilink® Speed resin composite cement in both baseline and thermo-cycled study groups. However, the adhesive strength of the experimental resin groups was markedly affected in the thermo-cycled study groups. This was without causing any spontaneous debonding of the specimens. After 12,000 thermo-cycles, the shear bond strength values in the groups SE, AE, and BE were reduced down to 88 to 90% of the corresponding values of the 24 h dry storage (baseline) groups (Table 1). Regardless of the lower mean shear bond strength values in the experimental resin study groups, both using 1.0 vol% ACPS and the blend of 1.0 vol% ACPS+0.5 vol% BTSE, were found to be hydrolytically stable in

Multilink® Speed resin cement groups. Not all the silane primers used in this study could exceed the critical limit of adhesion strength *i.e.*, minimum 5 MPa set by a ISO Standard 10477 Amendment⁶ when used in combination with the UEDMA-based experimental resin cement in the artificially aged groups. Therefore, it would not perhaps be wrong to say that the UEDMA/HPMA resin system was hydrolytically unstable.

According to the SEM micrographs (Fig. 2), there was no marked difference observed between the surface morphology of the different study groups except, loosely connected grit particles which can be seen in Figs. 2A and C. Thus, the higher adhesion (bond) strength achieved in different test groups could not fully be attributed to the surface morphology. The shear bond strength values of the experimental unfilled resin were higher in the baseline groups. However, thermo-cycling had a deteriorating effect on the adhesion strength values in the artificially aged groups. This said, these numerically lower values could be also attributed to water sorption of the UEDMA-based experimental resin²³, and thereby causing a damaging effect at the siloxane interface at the silica-coated and silanized Ti surface. The 27.4 wt% diluent monomer of HPMA was the constituent part of the experimental resin together with 70.6 wt% UEDMA (in addition, there was a catalyst and inhibitor to achieve polymerization). After polymerization, it is possible that the lower content of the linear polymer (HPMA) occupies the vacant space in the cross-linking UEDMA polymer. It is noteworthy that the experimental resin used was unfilled. Now, this fact may cause the H₂O molecules to be absorbed. On the other hand, Multilink® Speed consists of Bis-GMA, a rigid monomer with the presence of 75 wt% glass fillers of silicon dioxide. The strong intra-molecular hydrogen bonding of the hydroxyl groups (–OH) on the Bis-GMA molecular backbone with the rigid aromatic rings in its structure, make this material strong enough to resist water uptake. The mean enclosed mold adhesion strength values of the thermo-cycled groups achieved with the experimental silanes in combination with Multilink® Speed might justify this claim (Table 1).

Table 2 presents the failure mode analysis data on the tested specimens, whereas predominant adhesive failure mode can be seen in Figs. 3B and C. In the current

Fig. 2 Representative SEM images of Ti surfaces treated with different silanes at $\times 2,000$. A: The surface treated with Rocatec® Soft followed by ESPE Sil® primer application; B: The surface treated with Rocatec® Soft followed by 1.0 vol% ACPS experimental primer application; and C: The surface treated with Rocatec® Soft followed by blend of 1.0 vol% ACPS and 0.5 vol% BTSE experimental primer.

Fig. 3 Stereomicroscopy images of the specimens. A: Cohesive failure in BE group after 24 h dry storage; B: Adhesive failure in AM group after 6,000 thermo-cycles; and C: Adhesive failure in BE group after 12,000 thermo-cycles.

study it was observed that the mode of resin composite specimen failure during adhesion (enclosed mold shear bond) testing is time and material dependent. The resin composite cement used at the lower adhesion strength values may be showing the cohesive mode of failure (because of the low strength of the material) and the other resin composite cement may have adhesive mode of failure (because of the high strength of the material). Hence, the idea of failure mode analysis cannot always be truly supportive and such results should be regarded with some caution. Application of enclosed mold adhesion strength testing in lieu of shear bond strength testing may have affected these results, but how, would need more laboratory studies to give an explanation.

The hypothesis could be verified partially: Experimental UEDMA based resin cement improved the adhesion strength in dry storage condition only. In the near future studies, addition of fillers in the UEDMA-based resin would be interesting to investigate. Moreover, a diluent hydrophobic monomer instead of hydrophilic HPMA monomer might be worth evaluating for long-term artificial aging.

CONCLUSIONS

The following conclusions could be drawn from this laboratory study:

1. The experimental blended silane primer consisting of a blend of 1.0 vol% 3-acryloxypropyltrimethoxysilane and 0.5 vol% bis-(1,2-triethoxysilyl)ethane produced higher adhesion strength values after thermo-cycling.
2. An experimental urethane dimethacrylate-based resin cement might be an option to Bis-GMA-based resins.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

REFERENCES

- 1) Matinlinna JP, Lassila LV, Vallittu PK. The effect of five silane coupling agents on the bond strength of a luting cement to a silica-coated titanium. *Dent Mater* 2007; 23: 1173-1180.
- 2) Ferracane JL. Resin composite -state of the art. *Dent Mater* 2011; 27: 29-38.
- 3) Radovic I, Monticelli F, Goracci C, Vulicevic ZR, Ferrari M. Self-adhesive resin cements: a literature review. *J Adhes Dent* 2008; 10: 251-258.
- 4) Lung CYK, Matinlinna JP. Aspects of silane coupling agents and surface conditioning in dentistry: An overview. *Dent Mater* 2012; 28: 467-477.
- 5) Zaghloul H, Elkassas DW, Haridy MF. Effect of incorporation of silane in the bonding agent on the repair potential of machinable esthetic blocks. *Eur J Dent* 2014; 8: 44-52.
- 6) Matinlinna JP, Özcan M, Lassila L, Kalk W, Vallittu PK. Effect of the cross-linking silane concentration in a novel silane system on bonding resin-composite cement. *Acta Odontol Scand* 2008; 66: 250-255.
- 7) Matinlinna JP, Lassila LV, Vallittu PK. The effect of a novel silane blend system on resin bond strength to silica-coated Ti substrate. *J Dent* 2006; 34: 436-443.
- 8) Matinlinna JP, Lassila LV. Experimental novel silane system in adhesion promotion between dental resin and pretreated titanium. Part II. Effect of long term water storage. *Silicon* 2010; 2: 79-85.
- 9) Durgesh BH, Al Hijji S, Al Kheraif AA, Ramakrishnaiah R, Basavarajappa S, Al Sharawy M, Matinlinna JP. A novel silane system as a primer for orthodontic bonding —a pilot study. *Int J Adhes Adhes* 2015; 62: 101-106.
- 10) Matinlinna JP, Lassila LV, Kangasniemi I, Yli-Urpo A, Vallittu PK. Shear bond strength of Bis-GMA resin and methacrylated dendrimer resins on silanized titanium substrate. *Dent Mater* 2005; 21: 287-296.
- 11) Özcan M, Hämmerle C. Titanium as a reconstruction and implant material in dentistry: advantages and pitfalls. *Materials* 2012; 5: 1528-1545.
- 12) Mallineni SK, Nuvvula, S, Matinlinna JP, Yiu CKY, King NM. Biocompatibility of various dental materials of contemporary dentistry: A narrative insight. *J Investig Clin Dent* 2013; 4: 9-19.
- 13) Gajewski VE, Pfeifer CS, Fróes-Salgado NR, Boaro LC, Braga RR. Monomers used in resin composites: degree of conversion, mechanical properties and water sorption/solubility. *Braz Dent J* 2012; 23: 508-514.
- 14) Matinlinna JP, Lassila LVJ, Vallittu PK. Evaluation of five dental silanes on bonding a luting cement onto silica-coated titanium. *J Dent* 2006; 34: 721-726.
- 15) Zhang M, Matinlinna JP, Botelho MG, Säilynoja ES. Comprehensive properties of a novel fiber reinforced composite with a UEDMA-based resin matrix. *Odontology* 2014; 102: 176-183.
- 16) Almilhatti HJ, Neppelenbroek KH, Vergani CE, Machado AL, Pavarina AC, Giampaolo ET. Adhesive bonding of resin composite to various titanium surfaces using different metal conditioners and a surface modification system. *J Appl Oral Sci* 2013; 21: 590-596.
- 17) Cheetham JJ, Palamara JE, Tyas MJ, Burrow MF. A comparison of the micro-shear bond strength and failure mode of non-enclosed and mold-enclosed luting cements bonded to metal. *Dent Mater J* 2013; 32: 896-905.
- 18) Cheetham JJ, Palamara JE, Tyas MJ, Burrow MF. A comparison of the shear bond strength and failure mode to metals of unsupported and supported luting cement specimens. *J Adhes Dent* 2014; 16: 251-260.
- 19) Wattanawongpitak N, Yoshikawa T, Burrow MF, Tagami J. The effect of thermal stress on bonding durability of resin composite adaptation to the cavity wall. *Dent Mater J* 2007; 26: 445-450.
- 20) Korkmaz Y, Gurgan S, Firat E, Nathanson D. Effect of adhesives and thermocycling on the shear bond strength of a nano-composite to coronal and root dentin. *Oper Dent* 2010; 35: 522-529.
- 21) Behr M, Rosentritt M, Groger G, Handel G. Adhesive bond of veneering composites on various metal surfaces using silicoating, titanium-coating or functional monomers. *J Dent* 2003; 31: 33-42.
- 22) Fernandes CA, Ribeiro JC, Larson BS, Bonfante EA, Silva NR, Suzuki M, Thompson VP, Coelho PG. Microtensile bond strength of resin-based composites to Ti-6Al-4V. *Dent Mater* 2009; 25: 655-661.
- 23) Toledano M, Osorio R, Osorio E, Fuentes V, Prati C, Garcia-Godoy F. Sorption and solubility of resin-based restorative dental materials. *J Dent* 2003; 31: 43-50.