Novel Organofunctional Silane Coatings on Silica-Coated Ti

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ABSTRACT

This *in vitro* study characterizes a developed novel silane system method to produce coatings on Ti. Hydrophobic coatings are needed in prosthetic dentistry to promote durable adhesion between luting resin cements and coated Ti surfaces. Silane blends may contribute to significantly higher bond strengths than functional silanes alone. We have previously shown that the novel silane system blend with 1.00 vol% of 3-acryloxypropyltrimethoxysilane (ACPS) + 0.30 vol% *bis*-1,2-(triethoxysilyl)ethane (BTSE) produced *in vitro* the highest shear bond strength after artificial aging. The silane primers were prepared of ACPS and BTSE (in four different concentrations) and diluted in acidified ethanol-water solvent. The contact angles, surface free energies and critical surface tensions were assessed and the treated surfaces were analyzed using X-ray photoelectron spectroscopy (XPS) and Atomic force mircoscopy (AFM). A commercially available preactivated dental silane were used as the controls. We may conclude that: 1) the novel silane system was developed and optimized successfully; 2) The surface characterization showed nearly full coverage of silane coatings on titanium surface without compromising the surface roughness; 3) Such hydrophobic coatings on Ti restorations may have huge potential for durable bonding in dentistry.

*Keywords*: AFM, silane, silica-coating, titanium, XPS

1 INTRODUCTION

Titanium (Ti) and its alloys are largely used as biomaterials in dentistry and biomedicine because of their superior biomedical performance and biocompatibility. Ti is extremely reactive to oxygen, and able to instantly forming a biocompatible and extremely thin oxide layer (in a thickness of couple of nanometer) onto Ti surfaces. Various dental applications, such as fixed partial dentures, crowns, and subgingival coated implant fixtures [1-4], utilized Ti as the major materials .

A suitable surface-conditioning, such as sandblasting, is essential for micro-retention, *i.e.* forming micro- and nano-scale pores onto Ti surface, which enables the materials adhesion, *e.g.* penetration of a dental resin composite and osteoblast integration. In particular, silica-coatings add the silicon (Si) content on the Ti surface [5, 6]. Then, applying a silane coupling agent could create chemical bonding between a silica-coated Ti and another substrate, such as a resin composite luting cement, at interface [7, 8]. Such silane concentrations in dentistry are considered entirely harmless and silanes are intrinsically non-toxic [8, 9].

Different trialkoxy silane coupling agents, such as 3-methacryloxypropyltrimethoxysilane (MPS) (Fig. 1), are used to improve chemical adhesion between composite resins and metals, and in prosthetic appliances [8]. Many dental silane studies are concentrated on MPS, due to its methacrylate group at one chain end which is able to form chemical bonding with acrylic based materials [6, 8]. Commercial dental silane coupling agents are usually supplied as 1-2% of their pre-hydrolyzed form (-Si-OH) in 90-95% ethanol, with various formulations [10]. In general, chemical activation of trialkoxy silanes, hydrolysis, proceeds as presented below:

$$R'\text{-Si}(OR)_3 + 3\ H_2O \rightarrow R'\text{-Si}(OH)_3 + 3\ R\text{-OH} \qquad (1)$$
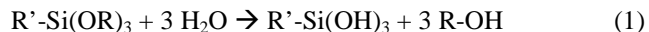
The reaction (1) can be catalyzed - or it may also occur spontaneously - to form labile and acidic silanol groups (Si-OH), which are reactive, able to condense and form *dimers*, and autopolymerize to 3D layers of thin siloxane film (-O-Si-O-). When the silanols are deposited onto the substrate surface, the thin surface oxide layer on Ti with facial hydroxyl group encourage the formation the siloxane-substrate bonds (-Si-O-Ti-) [11, 12]. Such a hydrophobic siloxane layer is usually around tens of molecular layers thick, depending on *e.g.* the silane concentration.

Some recent *in vitro* studies interestingly showed that acrylate silanes, *e.g.* 3-acryloxypropyltrimethoxysilane (ACPS) (Fig. 1), can provide significantly enhanced adhesion onto silica-coated Ti [13]. ACPS is more reactive than MPS due to the higher reactivity of unprotected acrylate group than methacrylate group, which is more prone to hydrolytic effects [12]. Suitably optimized blends of organofunctional and cross-linker silanes may significantly enhance the mechanical strength, bonding durability and hydrolytic stability *in vitro* of many dental resin composite systems, as suggested [10, 14]. Somel cross-linker silanes, such as *bis*-1,2-(triethoxysilyl)ethane (BTSE) (Fig. 1), are typically employed in such blends to provide corrosion protection applications such as in steel silanization painting [12] and in vulcanized rubber to silanized brass bonding [15]. The cross-linker silane is

usually strongly diluted, blended at the ratio of 1:10 to 1:5 to an organofunctional silane.
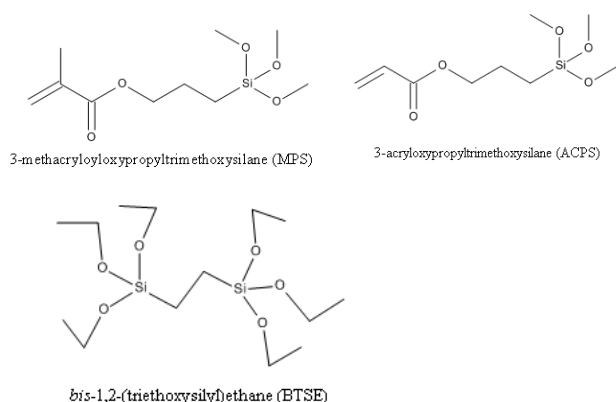

Figure 1: Structures of 3-methacryloxypropyltrimethoxy-silane (MPS, in Cimara™), 3-acryloxypropyltrimethoxy-silane (ACPS), and *bis*-1,2-(triethoxysilyl)ethane (BTSE).

Dental restorations made of Ti or its alloys are subject to hard and humid oral conditions. Thus, a hydrolytically stable and durable bonding might be achieved by preparing a hydrophobic silane coating on such a restoration before cementation. In the current study, four different ratios of ACPS and BTSE were blended (which we call 'a novel silane system'), and applied onto silica-coated Ti substrates. Then, surface characterizations were carried out and surface free energy were calculated according to the contact angles measurement. A commercial dental prehydrolyzed silane coupling agent was used as a control to direct compare with the present hydrophobic novel silane system. Hydrophobic coatings prepared as suggested in this *in vitro* study may be beneficial to promote resin composite adhesion, make it durable and resistant for hydrolytic attacks.

2   MATERIALS AND METHODS

2.1   Preparation of Novel Silane Primers

Acidified ethanol-water were prepared by using 95% ethanol solution with de-ionized (DI) water (milli-Q water, resistivity: 18.6 MΩ cm) with adjusting the pH to 4.5 by 1M CH_3COOH. The solution was allowed to stabilize at room temperature for 24 h. BTSE (Dow Corning Toray Silicone, Tokyo, Japan; 98%) was added into 50.0 mL PE bottles and diluted with the acidified ethanol-water as concentrations of 0.10 vol%, 0.20 vol%, 0.30 vol% and 0.50 vol%. After 23 h of stabilization, a constant amount (1.00 vol%) of ACPS was added in the bottles, respectively. The silane blends were then allowed to activate for an additional hour as described [10, 13]. A dental silane, Cimara™ (VOCO, Cuxhaven, Germany; 3-methacryloxy-propyltrimethoxysilane), was used according to the manufacturer's instructions.

2.2   Preparation of Titanium Coupon

Planar, commercial pure (cp) grade 2 Ti coupons (Permascand, Ljungaverk, Sweden; 20.0 mm x 40.0 mm x 1.0 mm) were used. The coupons were ground (1200 grit SiC polishing paper) under running water, rinsed and cleansed with DI-water in an ultrasonic bath (Quantrex 90 WT, L&R Manufacturing, Kearny, NJ, USA) for 10 min, and finally degreased with 70% ethanol and acetone. The coupons were then air-abraded first with alumina sand, sonicated with 70% ethanol, and then air-dried at room temperature. One sample was left untreated as a control. Other coupons were further sandblasted by using Rocatec (3M ESPE, Seefeld, Germany) to perform silica-coating.

To simulate a real clinical situation, two drops of the silane primers were brushed onto silica-coated titanium coupons with a new brush for each time by the same operator (one silane coat). All Ti coupons were then gently dried with oil-free compressed air, using the same amount of silane to form the siloxane films. The samples were silanized and allowed to cure at room temperature for 15 min.

2.3   Surface Characterizations

The treated surface of the silanized Ti samples was analyzed by X-ray photoelectron spectroscopy (XPS, Surface Science Instruments, S-probe, Mountain View, CA, USA) with the following operation conditions: a residual pressure: ~10^{-9} mbar; Al anode: 10 kV, 22 mA; a spot size of 250 μm × 1000 μm; the binding energy (BE) scanning range: 0 to 1100 eV (with the pass energy of 150 eV).

Then, the Ti surfaces were analyzed by Atomic Force Microscopy (AFM) imaging (4.0 μm × 4.0 μm) by using a Dimension 3100 microscope (Nanoscoop IV, Veeco Instrument, Santa Barbara, CA, USA) with the following conditions: contact-mode; applied force: below 2 nN; scan rate: ~ 2 Hz, probe: micro-fabricated oxide-sharpened Si_3N_4 cantilevers (Veeco Instruments, Santa Barbara, CA, USA) with a spring constant of 0.06 N m^{-1} and 20 nm probe curvature radius. Surface roughness (R_a) and maximum roughness (R_{max}) were calculated by the provided software. One-way ANOVA ($\alpha = 0.05$) was used to evaluate R_a and R_{max} between specimen groups using a statistical software (SPSS 13.0, USA), and multiple comparisons was tested by using Tukey *post hoc* test.

2.4   Contact Angles Measurements

Sessile drop dynamic contact angle measurements were performed by using a FIBRO 1100 DAT dynamic adsorption tester (FIBRO System AB, Stockholm, Sweden). The contact angles (θ) of four liquids with different surface tensions and polarity were used [16] to evaluate surface free energies (γ_s) and critical surface tensions (γ_c), based on modified Young's equation (Van Oss model [17]) and Zisman Plot, respectively.

3 RESULTS AND DISCUSSION

The XPS analysis suggested that there are differences in the atomic percentage (at%) of Ti samples treated with various novel silane blends (Table 1). After silanization, nearly all silane blends produce results where all titanium has disappeared or diminished, and an increased Si content from the XPS spectra (Fig. 2) were observed, except 1.00 vol% ACPS + 0.20 vol% BTSE. The absence of titanium content from the XPS spectra indicate that the silane systems effectively cover the surface by forming -Si-O-Ti bonds and a cross-linked network covered on titanium surface [18], in which the thin siloxane layers were too thick to allow Ti photoelectrons to escape. In addition, the carbon backbones in ACPS and BTSE may lead to entanglement, which may form effective nodes and increase the cross-linking density [19]. Now, as a careful conclusion, a more constrained network might be formed (Fig. 3).

Table 1: Atomic surface concentrations (at%) of Ti samples after treatment with various silane systems.

Sample and silanization	Atomic Concentration (%)					
	C (1s)	O (1s)	N (1s)	Ti (2p3)	Si (2s)	Ca (2p)
Unsilanized Ti (Control)	49.6	35.6	5.1	5.2	2.4	1.9
Vol.% of BTSE 0.10 %	64.4	25.1	1.4	0.6	7.4	1.1
Vol.% of BTSE 0.20 %	53.9	32.1	4.6	4.5	2.8	1.8
Vol.% of BTSE 0.30 %	59.3	28.4	0.0	0.3	11.8	0.2
Vol.% of BTSE 0.50 %	61.3	27.4	0.0	0.0	11.1	0.2
Cimara™ (control)	61.8	26.4	1.4	1.1	9.1	0.3

The AFM images of titanium samples show the changes of surface roughness due to silanization (Fig. 4). It may be seen clearly from the figures that the non-treated titanium samples have irregular roughened surfaces, and the silanized titanium surface is smoother. Table 2 shows the average surface roughness (R_a) and maximum surface roughness (R_{max}) determined by AFM. In general, silanized surface yield a smaller R_a and R_{max} than the unsilanized, however, this is not significantly identified ($p > 0.05$) from the one-way ANOVA and Tukey *post hoc* tests.

Table 2: Surface roughnesses (R_a and R_{max}) of various Ti samples measured using AFM (4.0 μm x 4.0 μm).

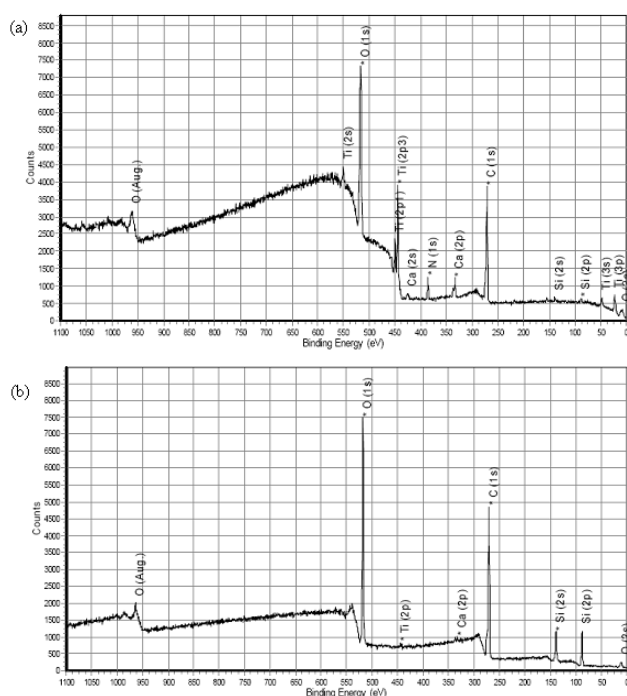| Sample	R_a (μm)	R_{max} (μm)
Unsilanized Ti (Control)	0.045 ± 0.016	0.375 ± 0.028
Vol % of BTSE 0.10 %	0.062 ± 0.007	0.508 ± 0.123
Vol % of BTSE 0.20 %	0.054 ± 0.022	0.403 ± 0.016
Vol % of BTSE 0.30 %	0.041 ± 0.019	0.374 ± 0.253
Vol % of BTSE 0.50 %	0.045 ± 0.025	0.377 ± 0.134
Cimara™ (control)	0.035 ± 0.015	0.288 ± 0.073
p-value, 1-way ANOVA (between groups)	0.539	0.573

Figure 2: Representative XPS spectra of (a) an unsilanized Ti control coupon and (b) a silanized Ti sample (1.00 vol% ACPS + 0.30 vol% BTSE).

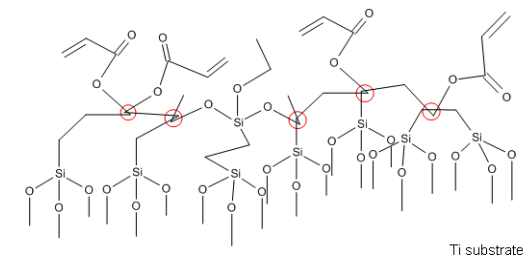
Figure 3: Illustration of entanglement in the novel silane system. The red circles denote the possible entanglement.
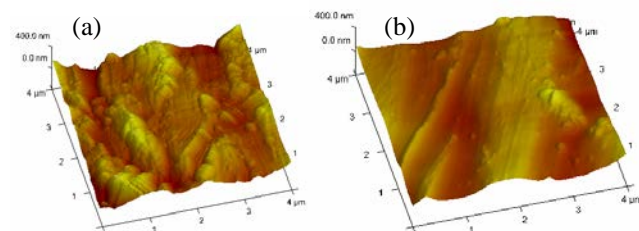

Figure 4: AFM images (4.0 μm × 4.0 μm) of various treated Ti surfaces: (a) control Ti without silanization, (b) silanized with 1.00 vol% ACPS + 0.30 vol% BTSE.

It appears that the combined treatment, *i.e.* applying sandblasting and silanization by a novel silane system (APCS + BTSE), gives a good and effective silane coating on the original roughened Ti surface without compromising the surface roughness. Such a matrix consisting of a roughened surface and a silane coating, is not only essential but also a key factor for successful adhesion of resin to titanium surface.

Table 3 shows the contact angles (θ) and surface free energies (γ_s) of various silane treated Ti surfaces with respect to various selected solvents. All the novel system treated surfaces have higher contact angles and lower surface free energies than the control Ti sample and using the control silane. Fig. 5 shows the Zisman plot and all data can form a linear relationship, especially for the novel silane blends that regression correlation factor $r^2 > 0.95$. By setting $\cos\theta = 1$, critical surface tension (γ_c) could be found and all novel silane blends has lower than controlled Ti, whilst Cimara[TM] has the highest γ_c value. All these data proved the novel silane treated surface become more hydrophobic than the controls. 1.00 vol % ACPS + 0.30 vol% BTSE has the lowest γ_s, concurrent with the highest shear bond strength (SBS) presented previously [20].

Table 3: Average contact angles and surface free energies (Υ_s) of various specimens by various treatments.

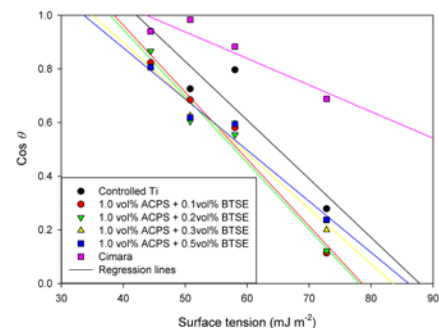| Sample	Average contact angle ($\theta/\ ^{\circ}$)				γ_s (mJ m^{-2})
	DI-Water	Diiodo-methane	Form-amide	1-bromo-naphtha-lene	
Unsilanized Ti (Control)	73.8	43.5	37.2	19.8	43.17
1.00 vol % ACPS+ 0.10 vol% BTSE	83.5	46.8	54.5	34.5	38.50
1.00 vol % ACPS+ 0.20 vol% BTSE	83.0	52.8	56.3	30.0	37.77
1.00 vol % ACPS+ 0.30 vol% BTSE	78.5	51.3	57.3	36.0	37.34
1.00 vol % ACPS+ 0.50 vol% BTSE	76.3	51.8	53.5	36.3	37.64
Cimara[TM] (control)	46.5	10.5	28.0	20.0	49.77

Figure 5: Zisman plot of contact angles (cos θ).

4 CONCLUSION

Finally, we may conclude that: 1) The novel silane system (ACPS + BTSE) was developed and optimized successfully; 2) The surface characterization showed nearly full coverage of silane coatings on titanium surface without compromising the surface roughness; 3) Such hydrophobic coatings may have huge potential for durable restoration bonding in dentistry.

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