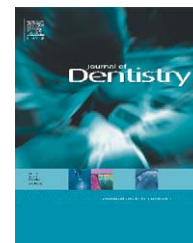


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## Evaluation of five dental silanes on bonding a luting cement onto silica-coated titanium

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### ABSTRACT

**Objectives:** Five commercial dental silanes were evaluated in vitro as adhesion promoters bonding a luting cement to silica-coated titanium surfaces.

**Methods:** Titanium slides ( $n = 20$ ) were cleaned with alumina sand and then silica-coated with a special sand consisting of alumina particles coated with silica. The bonding of a resin composite cement (3 M ESPE, Seefeld, Germany) to silica-coated and silanized titanium was evaluated by using the dental silane (RelyX<sup>TM</sup> Ceramic Primer) that belongs to the RelyX<sup>TM</sup> ARC cementing kit, and their reactions and comparing it to four other dental silanes (Bisco Porcelain Primer<sup>TM</sup>, Cimara<sup>TM</sup>, ESPE Sil<sup>TM</sup>, and Pulpdent<sup>TM</sup> Silane Bond Enhancer). The resin composite cement stubs ( $n = 8$ ) were light-polymerized onto a silanized silica-coated titanium surface. The shear bond strength of the cement stubs was measured after dry storage and thermo-cycling 6000 times between 5 and 55 °C. The silanes and their reactions were chemically monitored by using Fourier transform infrared analysis.

**Results:** Statistical analysis using ANOVA revealed that the brand of silanes and the types of storage condition differ significantly ( $p < 0.005$ ). The highest shear bond strength was obtained with RelyX<sup>TM</sup> ceramic silane in dry conditions ( $19.5 \pm 4.3$  MPa), and after thermo-cycling ( $16.6 \pm 3.5$  MPa). The lowest results were obtained using Pulpdent<sup>TM</sup> Silane Bond Enhancer, in dry conditions ( $7.8 \pm 2.2$  MPa), and after thermocycling ( $5.3 \pm 2.4$  MPa). The analysis showed that silanes had different pH values. Some differences were detected between the silanes and their reactions.

**Conclusions:** Dental silanes provide different bonding strengths and have differences in their pH, solvent system and silane concentration.

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## 1. Introduction

The usual problem encountered clinically is the need for a durable chemical connection between metals, ceramics and veneers, or luting cements.<sup>1,2</sup> Silanes have found an important application as adhesion promoters in composite and coating technology.<sup>3</sup> Silane coupling agents have the general formula R-Y-SiX<sub>3</sub>, where R is an organofunctional group, Y a linker part, and X are hydrolyzable alkoxy groups.<sup>4</sup> The organofunc-

tional group with a carbon-carbon double bond polymerizes with monomers of a resin composite. Hydrolyzed alkoxy groups in, e.g. 3-methacryloyloxypropyltrimethoxysilane turn to reactive silanol groups, ≡Si-OH during hydrolysis reaction at pH 4–5, as shown<sup>4,5</sup> in Fig. 1.

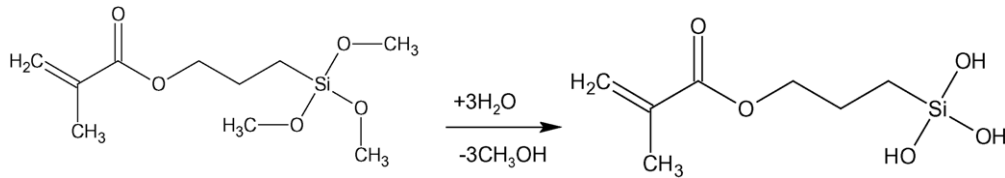
Silanol groups of a silane molecule react on silica surfaces forming covalent bonds.<sup>5</sup> Dental silanes contain typically 1–10 vol.% of 3-methacryloyloxypropyltrimethoxysilane, but the solvent systems vary.<sup>6,7</sup> It must be noted that the

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**Fig. 1 – Silane reactions during activation: a hydrophobic silane (in this case, 3-methacryloyloxypropyltrimethoxysilane) with its methoxy groups turns to a hydrophilic adhesion promoter with the characteristic silanols.**

application of silane coupling agent may also be followed by certain chemical primers in some clinical protocols.<sup>8</sup>

A conditioning system, based on extra-oral tribochemical silica-coating, Rocatec<sup>®</sup> (ESPE, Seefeld, Germany), was introduced as early as 1989.<sup>9</sup> The system enhances the bond strength between such systems as composite-to-metal, composite-to-ceramic, and composite-to-composite.<sup>10</sup> Application of 3-methacryloyloxypropyltrimethoxysilane provides a covalent bonding between a silica-coated substrate and composite resins.<sup>9</sup> Some evaluation results stress the importance of silanization in conjunction with silica-coating in clinical use, since without silanization the bond strengths produced would be less than 65%.<sup>7,9,11</sup>

Chair-side versions, such as CoJet<sup>®</sup> (ESPE, Seefeld, Germany) for the dentist's office are employed to repair fractured ceramics<sup>12,13</sup> and pre-treat or repair amalgams, alloys or metals.<sup>14,15</sup> Recent studies conclude that tribochemical silica-coating improves the adhesion of resin composite cements to ceramics, such as alumina and zirconia.<sup>1</sup>

RelyX<sup>™</sup> ARC resin composite cement is cured both chemically and by light-activation. Such cements are used for the cementing of metal crowns, bridges, onlays, inlays and Maryland bridges. Modern dental cements typically employ a dimethacrylate monomer system, such as based on Bis-GMA and TEGDMA.<sup>16</sup> The cements contain carbon-carbon double bonds that react with the methacrylate groups in 3-methacryloyloxypropyltrimethoxysilane, forming covalent bonds.<sup>6,17</sup>

The authors have been asked frequently, not only by clinicians but also by dental technicians, whether any dental silane would be applicable for clinical use with any cementing kit. The question has not been evaluated or discussed in literature previously. Silica-coated and silanized titanium has been studied previously.<sup>15,18</sup> Titanium is a widely used biomaterial in dentistry, not only in crowns but also as CAD/CAM partial-denture substructure fixed with implants.<sup>19</sup> Such substructures are veneered and crowns are cemented with a suitable resin composite.

One available cementing kit with its silane was arbitrarily selected for the current evaluation and four other silanes were compared with the original silane by measuring the shear bond strength. The hypothesis in this evaluation was that all five dental silanes show equal bonding properties.

## 2. Materials and methods

### 2.1. Titanium specimen preparation

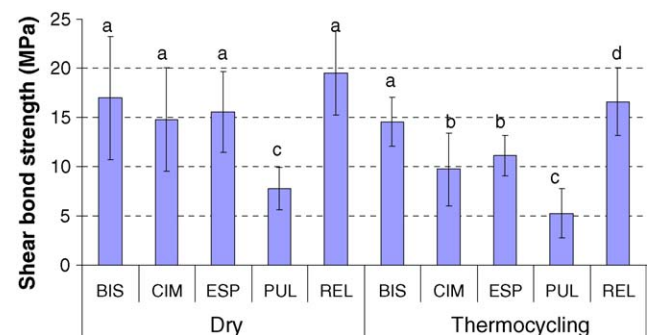
The materials used in this study are presented in Tables 1 and 2. Commercial pure grade 2 titanium (with a thickness of

1 mm) was cut into 20 mm × 40 mm slides ( $n = 20$ ). The upper half of the surface (10 mm × 40 mm) was first cleaned and abraded by grit-blasting using 50 μm particle-sized alumina in a jet at 300 kPa set 10 mm perpendicular from the titanium surface for 10 s. The other half of the slide was left intact. The slides were cleaned ultrasonically in ethanol for 10 min prior to tribochemical silica-coating with Rocatec<sup>®</sup> Plus abrasive, a 110 μm particle-sized alumina, chemically surface modified with colloidal silicon dioxide. The silica-coating was carried out on the abraded parts of the slides with a slow horizontal rotating motion of the handpiece, also in a jet at 300 kPa set 10 mm perpendicular from the titanium surface for 15 s.

The silica-coated titanium slides were again cleaned ultrasonically in ethanol for 10 min, and randomly distributed to 10 study groups: 5 thermocycled and 5 'dry' groups, with two slides in each group, were labeled as BIS, CIM, ESP, PUL and REL (cf. Table 1 and Fig. 2). Each silane was applied by brushing one coat on the silica-coated surface and it was allowed to react for 2 min prior to the bonding procedure.<sup>9,10</sup>

### 2.2. Bonding procedure

A constant amount of RelyX<sup>™</sup> ARC cement, one squeezed portion was dispensed onto a mixing pad, spread and mixed with a plastic spatula for 10 s before being transferred with the spatula to a polyethylene mold. The cement was applied to polyethylene molds (2 mm diameter and 4 mm height) as stubs. Four stubs were evenly placed on the upper horizontal borders of the Ti slide. The resin stubs were light-polymerized (Optilux 501, SDS Kerr, Danbury, USA) for 40 s, with an



**Fig. 2 – The shear bond strength results according to the storage condition. Key: 'Dry' – testing without water storage; 'Thermocycling' – thermal aging between 5 and 55 °C for 6000 cycles. Abbreviations: BIS, CIM, ESP, PUL and REL—see Table 1. According to t-test, groups labeled with a, b, c or d do not differ significantly.**

**Table 1 – Dental silanes used in the study and the test groups**

| Name                           | Code for test groups | Manufacturer                         | Indication                            | Effective silane and concentration | Solution and concentration (%) | pH  | Batch number |
|--------------------------------|----------------------|--------------------------------------|---------------------------------------|------------------------------------|--------------------------------|-----|--------------|
| Bisco™ Porcelain Primer        | BIS                  | Bisco, Schaumburg, IL, USA           | Porcelain, composite                  | 'Silane with methacrylate 1–10%'   | Ethanol, 30–70; acetone, 30–70 | 4.5 | 0300007596   |
| Cimara™                        | CIM                  | VOCO, Cuxhaven, Germany              | Direct repair of ceramic restorations | MPS, 3%                            | Isopropanol, 95                | 5.5 | 28578        |
| ESPE™ Sil                      | ESP                  | ESPE Dental, Seefeld, Germany        | Metals, ceramics, composites          | 'A silane', N/A                    | Ethanol, >90                   | 5.5 | 199624       |
| Pulpdent™ Silane Bond Enhancer | PUL                  | Germany Pulpdent, Watertown, MN, USA | Porcelain, composites                 | Silane, 1–3%                       | Ethanol, 92.6; acetone, 7.4    | 6.0 | 020201       |
| RelyX™ Ceramic Primer          | REL                  | 3M ESPE, St. Paul, MN, USA           | Ceramics                              | 'A silane', <1%                    | Ethanol, 70–80; water, 30–20   | 4.0 | 5WJ          |

The information is based on the available manufacturers' updated use of instructions. The presented pH values were determined by a chemical strip analysis during this study. N/A, not available.

intensity of 590 mW cm<sup>-2</sup>. The molds were removed gently by pressing the cured resin stub to the substrate with an instrument.

The silanization and bonding was performed by the same operator and the cement handling was employed in accordance with the manufacturer's instructions. Each study group included eight resin stubs.

### 2.3. The sample aging and shear bond test

One half of the titanium slides with the resin stubs were subjected to thermo-cycling for 6000 cycles at temperatures alternating between 5 and 55 °C, with a standard immersion time of 30 s (Heto CBN 18–30 baths, Allerø, Denmark). One half, the 'dry samples', were kept 1 h in a desiccator prior to testing. Shear bond tests for the stubs were carried out with a universal material testing machine (LRX<sup>®</sup>, Lloyd Instrument, Fareham, UK) with Nexygen<sup>®</sup> software, using a constant crosshead speed of 1.0 mm min<sup>-1</sup>.

### 2.4. Statistical analysis

The data for all the groups were analyzed statistically with SPSS 11.0 (Statistical Package for Statistical Science Inc., Chicago, IL, USA) software. Two-way factorial analysis of variance (ANOVA), followed by Tukey post hoc tests, was carried out and the dependent variable (shear bond strength) was explained by two independent factors, silane and storage conditions. The level of statistical significance was set at  $\alpha = 0.05$ . t-Test was employed to evaluate obtained values that were numerically close to each other.

### 2.5. Fourier transform infrared spectroscopy

A Fourier transform infrared spectrophotometer (Perkin-Elmer Spectrum One, Perkin-Elmer, Beaconsfield, UK) was utilized at a resolution of 2 cm<sup>-1</sup> by taking 32 scans for the follow-up of the silane reaction. Silane reaction to form a siloxane film was followed up with an attenuated total reflectance (ATR) device (Perkin-Elmer, Beaconsfield, UK), equipped with an inert ZnSe crystal, by applying two drops of fresh, unopened silane onto the ATR device and left there to evaporate to simulate the silane application in clinical conditions. The observation points for spectra were at time = 0 and 5 min.

### 2.6. pH Determination

The pH values were measured with pH-indicator strips, by applying two drops of silane onto the strip paper. The wet strip was visually compared with a pH-indicator chart. Three pH parallel measurements of each silane were made to verify the final color of the pH-indicator strip. No differences were observed, and the pH values were transferred as such in the data.

## 3. Results

Statistical analysis using ANOVA revealed that the brand of silanes and the types of storage condition differed statistically

**Table 2 – Other materials used in this study**

| Trade name                  | Description and composition   | Manufacturer                   | Purity (%) | Batch number |
|-----------------------------|---|--------------------------------|------------|--------------|
| RelyX™ ARC                  | Adhesive resin cement paste, shade A3, Bis-GMA, TEGDMA, Silane treated ceramic and silica fillers, functionalized DMA | 3M ESPE, St. Paul, MN, USA     | N/A        | 20041012     |
| Adper™ Scotchbond 1X7       | Bis-GMA, 2-hydroxyethylmethacrylate   | 3M ESPE, St. Paul, MN, USA     | N/A        | 5CM          |
| Commercially pure titanium  | Metallic planar Ti coupon, commercially pure grade 2  | Permascand, Ljungaverk, Sweden | 99.70      | AS TMB26589  |
| Korox™ Sand                 | Alumina sand, 50 µm   | BEGO, Bremen, Germany          | 99.6       | 1013283      |
| Rocatec™ Sand               | Silica-coated alumina sand, 110 µm  | 3M ESPE, Seefeld, Germany      | N/A        | 305          |
| Spezialindikator pH 2.0–9.0 | Non-bleeding pH-indicator strips  | Merck, Darmstadt, Germany      | –          | OO 127274    |

The information is based on the available manufacturers' up-dated use of instructions.

significantly ( $p < 0.005$ ). There was no interaction between silane and storage conditions ( $p = 0.725$ ). The results are presented in Fig. 2 which carries superscripts (a to d) to indicate that the groups do not differ statistically (t-test).

The highest shearbond values were obtained with RelyX™ Ceramic silane for samples in dry conditions ( $19.5 \pm 4.3$  MPa) and for thermo-cycled samples ( $16.6 \pm 3.5$  MPa). The lowest values were obtained with Pulpdent™ Silane Bond Enhancer (Pulpdent, Watertown, USA), in dry conditions ( $7.8 \pm 2.2$  MPa), and after thermo-cycling ( $5.3 \pm 2.4$  MPa).

Silane solutions were analyzed by using infrared spectroscopic analysis system for fresh silane and for silane which was allowed to dry for 5 min. The results showed some differences between the five silanes. They are shown in Fig. 3. As can be seen on the B-spectra, all the silanes had formed siloxane bonds (–Si–O–Si–O–) seen between 1250 and 1100  $\text{cm}^{-1}$ . Methoxy groups (–O–CH<sub>3</sub>) in spectra labeled A have disappeared. Water and ethanol (or isopropanol) have vanished at 3600–3000  $\text{cm}^{-1}$ , in some B-spectra signal are still seen but they indicate silanols ( $\equiv\text{Si–OH}$ ). Typical (harmless) noise coming from the atmospheric CO<sub>2</sub> can be observed at 2400–1900  $\text{cm}^{-1}$ . The carbonyl peak ( $>\text{C}=\text{O}$ ) can be seen at 1720  $\text{cm}^{-1}$ . Other silanes than Pulpdent™ revealed strong carbonyl peaks. Qualitatively, it might be estimated that strong siloxane signals suggest a strong siloxane bonding.

The five silanes had varying pH values as shown in Table 1. The silane that yielded the highest shear bond results had a pH of 4.0, while the silane that yielded the lowest shear bond value had a pH of 6.0.

#### 4. Discussion

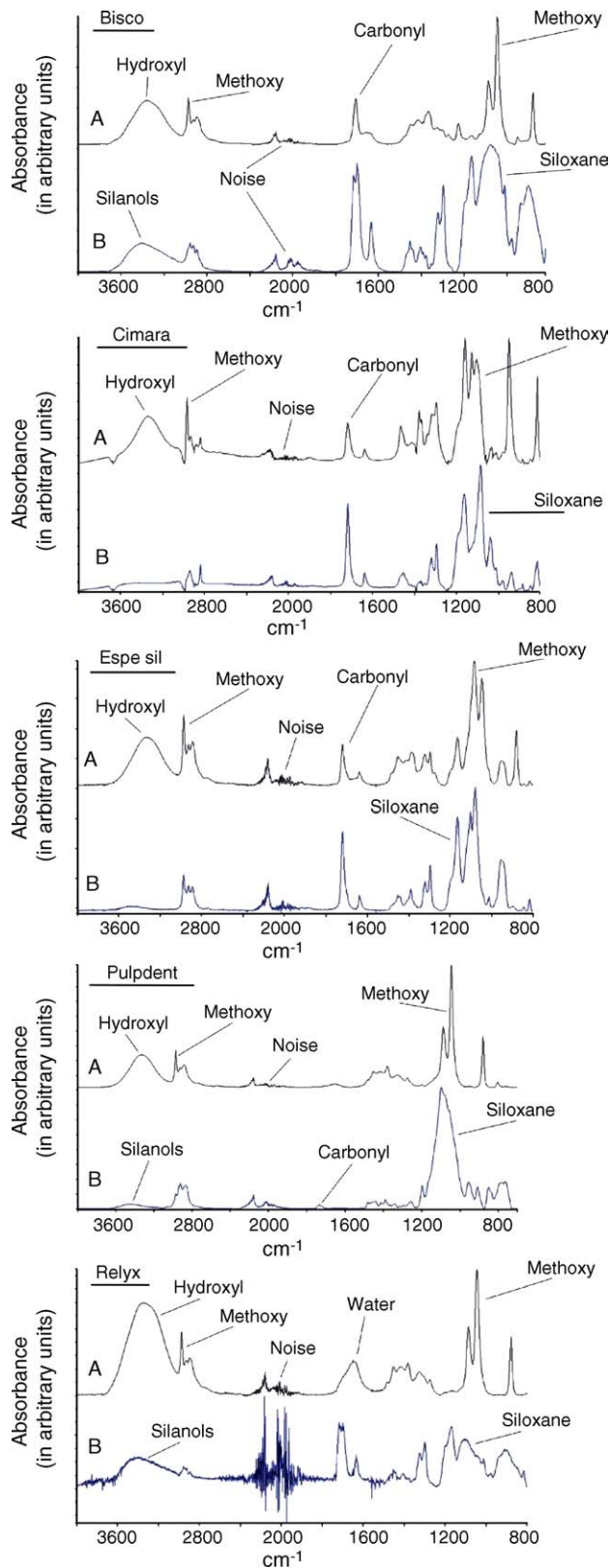
The titanium samples were cleaned ultrasonically twice prior to the bonding procedure: after the cleaning abrasion and after the silica-coating.<sup>20</sup> It has been observed that ultrasonic cleaning of grit-blasted alloy surfaces that were subsequently silica-coated and silanized might improve resin bonding as loose particles were removed.<sup>15</sup> Some recent studies suggest Si 19% atomic concentration, and Ti 59% atomic concentration on Ti surface after a Rocatec™-treatment.<sup>18</sup>

The tested samples after dry storage gave interesting results: only one silane (Pulpdent™) differed statistically from the other silanes. In general, the silanes seemed to

maintain their hydrolytic stability relatively well (Fig. 2). Only the shear bond values obtained with Cimara™ and ESPE™ Sil became significantly lower after thermo-cycling. This might suggest that they are more prone to hydrolytic degradation. Cimara™ has a silane concentration of 3%, but the silane concentration of ESPE™ Sil is unknown. On the other hand, silane concentration for the 'best' silane, RelyX™ is less than 1 vol.%, and the 'next best' silane Bisco™ has a concentration somewhere between 1 and 10 vol.%.<sup>6</sup> Exact silane concentrations remain somewhat unclear (Table 1). No conclusions can be made based on the reported silane concentration. It is known that a low silane concentration keeps the silane in such a balance that the silane monomers do not polymerize: the shelf-life can be a couple of years.<sup>21</sup> The amount of water in the silane solvent systems varied: the 'best' silane (RelyX™) contains ca. 20–30% water, while the water-free Pulpdent™ and Bisco™ have an ethanol-acetone solvent system. Cimara™ is based on 95% iso-propanol.

The dilute silane solution has the highest stability at pH 4–5.<sup>22</sup> The pH values for two silanes were within this limit, while three silanes had somewhat higher pH values. The lowest shear bond strength might be attributed to the highest pH (6.0), for Pulpdent™ (Table 1). Nevertheless, it must be kept in mind that Pulpdent™, RelyX™ and Bisco™ are not purely indicated for silica-coated surfaces, but rather for etched porcelain (Table 1) which both are chemically typical inorganic surfaces. According to the results after thermo-cycling, the silanes with the lowest pH values (RelyX™ and Bisco™) contributed to the highest shear bond strength values.

According to Fig. 3, some FTIR signals overlapped and remain unexplained in this context, but are not deemed to be relevant to the bond formation. The FTIR analysis results confirmed the formation of bonding siloxane bonds for all the silanes. The silane that gave the highest shear bond result (RelyX™) and the silane that gave the second best results (Bisco™), seemed to have qualitatively more non-reacted silanols left. The question remains, whether the other three silanes were to some extent more polymerized. This cannot be directly interpreted from the FTIR spectra. Interestingly, Pulpdent™ did not have a carbonyl signal and it suggests that it does not contain 3-methacryloyloxypropyltrimethoxysilane: carbonyl signals can namely be attributed to the methacrylate group in silane molecule.<sup>21</sup>



**Fig. 3 – The Fourier transform infrared spectra of the five dental silanes. A, immediately after application (time = 0 min); B, after 5 min drying time. X-axis: wavenumber in  $\text{cm}^{-1}$ ; Y-axis: absorbance in arbitrary units.**

A chemical analysis might reveal the actual silane (silicon) content in and this information might provide some insight into the possible correlation between silane concentration and shear bond strength. This evaluation is the next research topic in the near future.

## 5. Conclusion

The hypothesis set by the authors could not be verified: all five dental silanes did not promote equal bonding. The observations in this evaluation can be summarized: thermo-cycling weakened the shear bond strength obtained with two silanes. Dental silanes with lower pH values (4.0 and 4.5) seemed to provide somewhat stronger bonding than those with a higher pH (5.5 and 6.0). It can be concluded that these results do not suggest that any silane could be used for bonding a resin composite cement to silica-coated titanium.

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