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ORIGINAL ARTICLE

Effect of the cross-linking silane concentration in a novel silane system on bonding resin-composite cement

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Abstract

Objective. Four experimental blends of an organo-functional silane monomer with a non-functional cross-linking silane monomer (a novel silane system) were evaluated as adhesion promoters in an experiment in which a resin-composite cement was bonded to silica-coated titanium. ***Material and Methods.*** 3-Acryloyloxypropyltrimethoxysilane (as constant 1.0 vol%) was blended with 1,2-*bis*-(triethoxysilyl)ethane, where its concentration was 0.1, 0.2, 0.3, or 0.5 vol%. Titanium slides ($n = 20$) were grit-blasted, silica-coated, and silanized with four experimental silane solutions, with a pre-activated silane Cimara™ (VOCO, Germany) as control. After silanization, resin-composite cement stubs (Bifix™ QM; VOCO, Germany) were photo-polymerized. The shear bond strength was measured after dry storage (24 h) or after thermo-cycling (6000 cycles between 5°C and 55°C). The resin stub failure mode was determined. ***Results.*** Statistical analysis (ANOVA) showed that type of storage ($p < 0.05$) and concentration of cross-linker silane ($p < 0.005$) both significantly affected the shear bond strength. The highest shear bond strength was obtained with a blend of 1.0 vol% 3-acryloyloxypropyltrimethoxysilane + 0.3 vol% 1,2-*bis*-(triethoxysilyl)ethane, 15.9 MPa (standard deviation SD 3.4 MPa) for both the thermo-cycled group and after dry storage (24 h), 14.3 MPa (SD 4.1 MPa) ($n = 8$/group). The lowest values were obtained with Cimara™ silane 7.3 MPa (SD 2.2 MPa) in dry storage and 7.9 MPa (SD 2.0 MPa) obtained with 1.0 vol% 3-acryloyloxypropyltrimethoxysilane + 0.1 vol% 1,2-*bis*-(triethoxysilyl)ethane. The failure type was mainly cohesive. ***Conclusion.*** A novel silane system with an optimal concentration of the cross-linking silane may produce significantly higher shear bond strength between silica-coated titanium and resin-composite cement compared to a pre-activated silane product.

Key Words: *Adhesion promotion, resin-composites, silane bonding, silane coupling agents*

Introduction

In dentistry, adhesion between essentially dissimilar materials is promoted by using activated silane coupling agents [1]. Before veneering or cementing, silica-coating [2] combined with silanization of metals such as titanium and metal alloys [3,4] and zirconia [5] is a required conditioning pretreatment method. Silane coupling agents are hybrid inorganic-organo-functional trialkoxysilane monomers, with three chemically labile hydrolyzable alkoxy groups and an organo-functional polymerizable group, which can co-polymerize with the double-bond containing monomers in the resin-composite system. Silane monomers are usually activated in an alcohol-water medium with a catalyst before their use as adhesion promoters. Activated silanes hydrolyze, i.e. turn to intermediary silanols and condense to form an interfacial siloxane film [6]. However, silane-aided bonding with its hydrolytic stability and longevity under humid oral conditions is a continuing concern in clinical dentistry [7,8].

Some novel hydrophobic silane monomers may enhance the flexural properties of dental resin composites [9]. Blends of cross-linking and organo-functional silanes (Figure 1) have the well-known property of significantly enhancing the mechanical strength of bonding between matrices, and thus the hydrolytic stability of many resin-composite systems in technology. Non-functional cross-linking silanes are often employed in blends; for example, the relatively widely used and studied

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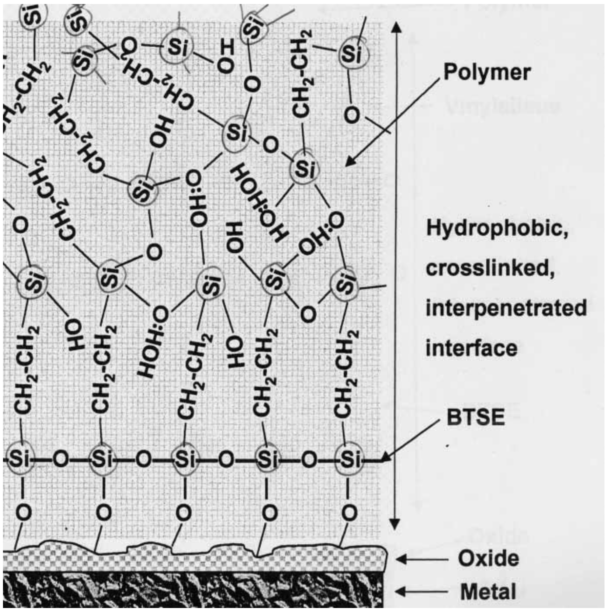

Figure 1. Interpenetrating polymer network, IPN, is assumed to exist between a silica-coated and silanized substrate and the resin composite. In this illustration, the interface consists of an activated functional silane and non-functional silane BTSE (1,2-*bis*-(triethoxysilyl)ethane) blend that has interpenetrated the polymer matrix (=grey background). Courtesy: Professor Wim van Ooij, University of Cincinnati, USA, 2002.

bis-1,2-(triethoxysilyl)ethane (Figure 2) contains only hydrolyzable alkoxygroups, viz. ethoxy groups. Some carefully selected silane blends containing *bis*-1,2-(triethoxysilyl)ethane are used in applications where steel sheets are silanized and then painted for corrosion protection [10]. In bonding vulcanized rubber to silanized brass in tire production, a cross-linking silane is usually combined in a 1:10 to 1:5 ratio with an organo-functional silane [11,12]. It has been suggested that an interpenetrating polymer network, IPN (cf. Figure 1), is formed between the cross-linked siloxane film and resin-composite matrix [13]. Cross-linker silanes in silane blends are known to promote adhesion by strengthening the 3D siloxane film structure through extensive cross-linking and interpenetration, which interconnects the functional organo-silanes [10].

For dental applications, a novel silane system consisting of a functional silane monomer + a cross-linking silane monomer was evaluated recently [14,15], and it was observed that silane blends might enhance the adhesion significantly *in vitro*. Some less studied organo-functional silane monomers, such as fluoroalkyl silanes [9], phenyl silanes [16], and reactive organo-silane monomers, such as isocyanato silane [17] and acrylate-functionalized silane [14,15,18], demonstrate a significant improvement in the adhesion promotion *in vitro*.

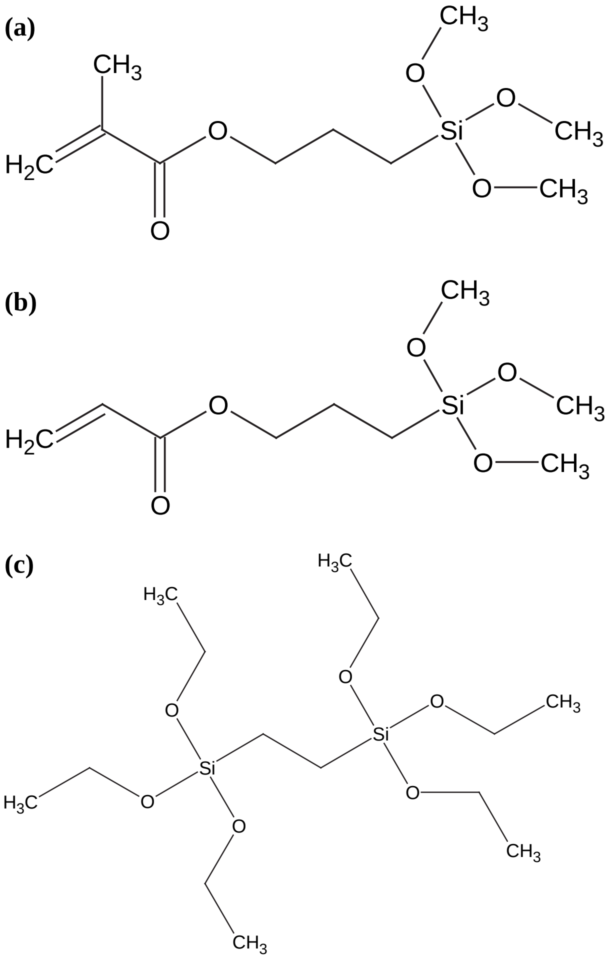

Figure 2. Silane monomer molecules. (a) 3-Methacryloyloxypropyltrimethoxysilane (in the control silane), (b) 3-Acryloyloxypropyltrimethoxysilane, and (c) 1,2-*bis*-(Triethoxysilyl)ethane. Silane molecules (b) and (c) belong to a novel silane system.

There is no exact or even general information in the literature about an optimal concentration of silane blends for given resin systems and substrates. For the present study, a chemically reactive 3-acryloyloxypropyltrimethoxysilane and *bis*-1,2-(triethoxysilyl) ethane blends were selected on the basis of encouraging previously reported findings [14,15, 18]: one activation time, 24 h, was selected for the cross-linking silane [14], but its concentration was now systematically varied. Titanium was used as the substrate material, since it is easily silica-coated and it generates wide interest in dentistry. Bifix QM™ is a radiopaque *bis*-GMA-based dual-cured resin-composite cement. It is cured both chemically and by light-induced activation. Such cements are used for the luting of pretreated metal bridges, crowns, pins, facades, inlays, and onlays.

The hypothesis was that there is an optimal concentration in the range 0.1, 0.2, 0.3, or 0.5 vol% for the cross-linking silane in dilute silane blends. Moreover, it was assumed that the optimal blend can enhance the resin-composite bonding to silanized and silica-coated titanium significantly above a pre-activated ready-to-use available silane in clinical use (control).

Table I. Materials used in this study (N/A = not available).

Material	Abbreviation or trade name	Manufacturer	Purity (%)	Batch no.
Titanium	Ti	Permascand, Ljungaverk, Sweden	>99	AS TM B26589
Pre-hydrolyzed dental silane Cimara	CIM	VOCO, Cuxhaven, Germany	N/A	510418
Universal dual-curing composite luting cement	Bifix QM	VOCO, Cuxhaven, Germany	N/A	600429
Ethanolum Anhydricum	Ethanol	Primalco, Helsinki, Finland	99	030305
Acetic acid		Merck, Darmstadt, Germany	100	K12716063
3-Acryloyloxypropyl-trimethoxysilane monomer	ACPS	Dow Corning Toray Silicone, Tokyo, Japan	98	VN02011454
1,2-*bis*-(triethoxysilyl)ethane monomer	BTSE	Dow Corning Toray Silicone, Tokyo, Japan	98	0000635513
Korox 50 Alumina Sand		BEGO, Bremen, Germany	99.6	1013283
Rocatec Plus abrasive sand		3M ESPE, Seefeld, Germany	>95	305

Material and methods

Experimental silane coupling agent blends

The materials in this evaluation are listed in Table I. Four experimental silane solutions were prepared in a standard ethanol-water (95:5) solution, using deionized milli-Q water. The pH was adjusted to 4.5 with acetic acid and the solution was allowed to stabilize at room temperature for 24 h. The cross-linking silane monomer, 1,2-*bis*-(triethoxysilyl) ethane, was added to 4 different 50 ml polyethylene bottles and diluted with the acidified ethanol-water solvent to form 0.1 vol%, 0.2 vol%, 0.3 vol%, and 0.5 vol% concentrations. These were then allowed to activate for 23 h. Next, a constant amount of 3-acryloyloxypropyltrimethoxysilane monomer (corresponding 1.0 vol%) was added to each of the bottles, after which the bottles were filled up to the gauge level with the solvent. The silane blends were allowed to activate for an additional hour.

Silica-coated titanium

C.p. grade 2 titanium with a thickness of 1 mm was cut into ($n = 20$) 20 mm × 40 mm coupons. Half of the surface (ca. 10 mm × 40 mm) was first cleaned and grit-blasted for 15 s using 50 μm particle-sized alumina in a jet at 300 kPa set 10 mm perpendicular from the titanium surface. The other half of the coupon was left intact. The coupons were cleaned ultrasonically in ethanol for 10 min prior to tribochemical silica-coating with Rocatec® Plus abrasive, a 110 μm particle-sized alumina, surface-modified with silicon dioxide. The silica coating was carried out uniformly only on the previously grit-blasted surface part of the coupons with a slow horizontal rotating motion of the hand-piece, in a jet at 300 kPa that was set 10 mm perpendicular from the titanium surface, for 15 s [14,17].

The silica-coated titanium coupons were again cleaned ultrasonically in ethanol for 10 min and randomly distributed to 10 study groups, i.e. 5 groups for "dry" and 5 for thermo-cycling, with two coupons in each group. They were labelled CIM, CA1, CA2, GA3, and GA5 (cf. Tables II and III).

Silanization and bonding procedure

Silanization was carried out by brushing one coat of experimental silane solution on to the silica-coated Ti substrate with a fine brush; a new brush was used for each silane. The silane was allowed to dry for 5 min. A constant amount of Bifix QM™ resin composite, one squeezed portion, was dispensed on to 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 as stubs with a diameter of 3.6 mm and height of 4 mm. Four stubs were evenly placed along the upper conditioned long edge of the Ti coupon. The lower part of the coupon was reserved to fasten the Ti coupon in the universal testing machine. The resin-composite stubs were photo-polymerized (Optilux 501; SDS Kerr, Danbury, USA) for 40 s, with an intensity of approximately 590 mW cm^{-2}. The molds were removed gently by pressing the cured resin-composite stub to the substrate with an instrument. Each study group consisted of 8 resin-composite stubs. Silanization, resin-composite cement handling, and bonding were carried out in accordance with the manufacturer's instructions and by the same operator.

Sample storage and shear bond testing

Half of the titanium coupons were subjected to thermo-cycling for 6000 cycles at temperatures between 5°C and 55°C, with a standard dwell time of 30 s and a transfer time of 2 s (Heto CBN 18–30 baths; Allerø, Denmark). The samples were then kept in a water bath (37°C) prior to testing. Shear bond strength tests of the stubs were carried out with a universal material testing machine (LRX®; Lloyd Instruments, Fareham, UK) at a constant cross-head speed of 1.0 mm min^{-1} until fracture occurred. Shear bond strengths were calculated by dividing the highest fracture force (in N) by the area of the resin stub (diameter 3.6 mm) and recorded (in MPa) using Nexygen® software (Lloyd Instruments, Fareham, UK). The non-thermo-cycled ("dry group") test group was kept in dry storage for 24 h before shear bond strength was measured.

Table II. Results. Test groups, shear bond strength results (dry storage and thermo-cycled), standard deviations, and the percentage of the spontaneous de-bonding of resin-composite cement stubs. Key: CIM = Cimara silane (control), GA1-GA5 = groups where experimental silane blends were used, MPS = 3-Methacryloyloxypropyltrimethoxysilane, ACPS = 3-Acryloyloxypropyltrimethoxysilane, BTSE = 1,2-*bis*-(triethoxysilyl)ethane. The concentration of ACPS is constant (1 vol%).

Group	Silanes	Concentration (vol%)	Shear bond strength (dry storage) (MPa)	Standard deviation (MPa)	Shear bond strength (thermo-cycled) (MPa)	Standard deviation (MPa)	De-bonding during thermo-cycling (%)
CIM	MPS (Cimara)	Ca. 1.0	7.3	2.2	8.5	2.6	0
GA1	ACPS+BTSE	1.1	11.8	4.4	7.9	2.0	0
GA2	ACPS+BTSE	1.2	12.9	3.6	11.5	3.0	0
GA3	ACPS+BTSE	1.3	14.3	4.1	15.9	3.4	0
GA5	ACPS+BTSE	1.5	11.6	5.5	9.0	3.6	0

Statistical analysis of the results

The shear bond data for all sample groups were statistically analyzed using the analysis of variance, ANOVA (SPSS, Chicago, Ill., USA). The dependent variable, shear bond strength, was explained by the independent variables, type of functional silane, with or without the cross-linker silane, and hydrolysis time. Multiple comparisons were performed with Tukey's test and Levene's test of equality of error variances. Statistical significance was set at $\alpha = 0.05$.

Fracture ranking and analysis

A visual evaluation of the thermo-cycled samples after testing was carried out. Each tested fractured stub area on the titanium slide was evaluated visually by being given a score in the following relative scale: 0 = no resin-composite cement left, 1 = <1/3 cement left, 2 = >1/3 but <2/3 cement left, or 3 = >2/3 cement left. The results are presented in Table III. Non-parametric statistical tests were used for analysis of fracture ranking. Statistical analysis, Kruskal-Wallis ANOVA, was employed and the statistical significance was set at $\alpha = 0.05$.

Results

ANOVA revealed that mean shear bond strength varied significantly with the cross-linking silane concentration ($p < 0.005$) and with type of storage ($p < 0.05$, F = 4.478). No spontaneous de-bonding occurred during the thermo-cycling. The shear bond results are presented in Table II.

The fracture analysis employing ANOVA revealed that the use of cross-liner silane affected the shear bond strength significantly ($p < 0.002$), but storage type was not significant ($p = 0.252$). The failure was scored mainly as "0" for the study groups CIM and GA3, and as "1" or "2" for groups GA1, GA2, GA4, and GA5. On the other hand, the failure type for group GA3 did not differ significantly from any of the other groups (Table III).

Discussion

3-Acryloyloxypropyltrimethoxysilane and 1,2-*bis*-(triethoxysilyl)ethane blends have been evaluated as adhesion promoters for a dental resin-composite cement. The bonding of such resin-based cements to titanium (or in general to metal, ceramics, composites) requires a silica-coating followed by silanization [3,4,8]. Organo-functional silane monomers should be hydrolyzed sufficiently, usually for 1 h or less [8], thus 1 h was thought to be sufficient for the experimental silanes used in this study. Since silicatization was performed in the same manner and Ti coupons were designated to study groups randomly, it was not expected that there would be significant differences due to the silica content on titanium surfaces or to operator factor. The Bifix™ QM resin-composite stubs were not post-polymerized *in vacuo*, since the idea was to simulate the clinical cementing procedure at the dentist's office. As controls, a pre-activated silane (Cimara™) was selected because it belongs to the same product family as Bifix™ QM and is thus assumed to be used in clinical work.

Table III. Failure types and the amount of tested resin-composite cement stubs, classified according to failure types ($n = 8$ stubs/group). Failure mode: Type 0 = no resin-composite cement left; Type 1 = <1/3 cement left; Type 2 = >1/3 but <2/3 cement left; Type 3 = >2/3 cement left on the substrate. Key: "dry" = dry storage, "tc" = thermo-cycled. The percentage of each failure mode type in an experimental group is indicated in parentheses (e.g. 50.0%). CIM = Cimara silane (control), GA1-GA5 = groups where experimental silane blends were used.

Failure mode	CIM dry	CIM tc	GA1 dry	GA1 tc	GA2 dry	GA2 tc	GA3 dry	GA3 tc	GA5 dry	GA5 tc
Type 0	5 (62.5%)	5 (62.5%)	2 (25.0%)	0	1 (12.5%)	0	1 (12.5%)	4 (50.0%)	3 (37.5%)	2 (25.0%)
Type 1	3 (37.5%)	3 (37.5%)	3 (37.5%)	5 (62.5%)	6 (75.0%)	5 (62.5%)	6 (75.0%)	2 (25.0%)	4 (50.0%)	1 (12.5%)
Type 2	0	0	3 (37.5%)	3 (37.5%)	1 (12.5%)	3 (37.5%)	1 (12.5%)	2 (25.0%)	1 (12.5%)	5 (62.5%)
Type 3	0	0	0	0	0	0	0	0	0	0

Thermo-cycling is a widely accepted laboratory method for testing resin-bonded restorations of prosthetic materials, despite its limitations [19]. It can be seen from Table III that all the shear bond strength values exceeded the critical threshold of 5 MPa set by ISO Standard 10477 Amendment [20]. The 10 test sample groups did not demonstrate large standard deviations (cf. Table II). For the samples kept in dry conditions, the addition of 1,2-*bis*-(triethoxysilyl)ethane, with a constant volume of 3-acryloyloxypropyltrimethoxysilane, significantly enhanced the adhesion. A maximum is indicated for the dry sample results, namely the shear bond strength obtained with 0.3 vol% 1,2-*bis*-(triethoxysilyl)ethane + 1 vol% 3-acryloyloxypropyltrimethoxysilane blend. This supports the notion that in silane blends the cross-linking silane concentration should be relatively small, and always smaller than the concentration of the reactive functional silane monomer [10–12].

It is remarkable that the temperature change during thermo-cycling, 5°C to 55°C, did not cause the resin-composite stubs to de-bond spontaneously from the titanium substrates. Again, a maximum shear bond strength value is observed, at the same silane blend concentration as for the "dry group" samples. There was also an increase in the shear bond value for the control silane. Under both storage conditions, the control silane remained the weakest adhesion enhancing agent. Some hydrolytic degradation processes at the adhesive siloxane interface may have taken place for sample groups GA1, GA2, and GA5, i.e. in all other study groups than the optimal and control groups, since their shear bond values were lower.

After thermo-cycling, the failure type analysis suggests a relatively uniform distribution between the failure types for blend GA3: half of the cement stubs suffer from cohesive failure. However, interestingly, the GA5 group attained the highest score for the cohesive failure type, but not the highest shear bond strength. It was noticed that the control silane (CIM) indicated an adhesive failure for 2/3 of the tested resin-composite stubs. The cross-linker silane plays a significant role, according to the ANOVA [14,15,18].

In general, it can be concluded that a durable covalent bonding and hydrolytically stable siloxane film has been created between the matrices using the novel silane system. The highest shear bond strength level might be clinically interesting, since making a literature comparison, it is comparable with resin-composite bonding to dentin using hydroxyethylmethacrylate (HEMA) and glutaraldehyde (11–17 MPa) and with resin-composite bonding to enamel using some bonding systems (10–12 MPa) [21]. There are no published data on the shear bond strengths in technical applications using such silane blends. This makes comparisons difficult and does not allow clinical relevance to be evaluated.

It should be noted that in the silane blends the functional silane concentration was between 10 times and twice as great as in the functional 3-acryloyloxypropyltrimethoxysilane alone in the experimental silane blends. For comparison, it has to be kept in mind that ready-to-use silanes in dentistry have a concentration typically between 0.5 and 5 vol% [8].

In the near future, the effect of the pH level and the silane drying time would be interesting to evaluate for 3-acryloyloxypropyltrimethoxysilane and its blends with the cross-linking silane. Moreover, longer water storage periods (at 37°C) or testing the effect of boiling water could be carried out.

Conclusions

This study is a first *in vitro* evaluation of the novel silane system and the concentration effect of the cross-linking silane in dental materials science. Some conclusions can be drawn based on these preliminary results:

- No spontaneous de-bonding was observed during the thermo-cycling.
- Novel silane blends exhibited superior performance to the ready-to-use control silane. Thermo-cycling enhanced shear bond strength significantly.
- The hypotheses are thereby verified: there is an optimal cross-linking silane concentration for the experimental novel silane system blend.

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