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Shear bond strength between resin and zirconia with two different silane blends

CHRISTIE YING KEI LUNG[1], EDWIN KUKK[2] & JUKKA PEKKA MATINLINNA[1]

[1]*Dental Materials Science, Faculty of Dentistry, The University of Hong Kong, Hong Kong SAR, PR China, and* [2]*Department of Physics and Astronomy, Faculty of Mathematics and Natural Sciences, University of Turku, Turku, Finland*

Abstract

Objective. To study *in vitro* the effect of two cross-linking silanes, *bis*-1,2-(triethoxysilyl)ethane and *bis*[3-(trimethoxysilyl) propyl]amine, blended with an organofunctional silane coupling agent, (3-acryloxypropyl)trimethoxysilane, on the shear bond strength between resin-composite cement and silicatized zirconia after dry storage and thermocycling. ***Materials and methods.*** Six tested groups of 90 samples of yttria stabilized zirconia were used for sample preparation. The surfaces of the zirconia were silica-coated. 3M ESPE Sil silane was used as a control. Solutions of (3-acryloxypropyl)trimethoxysilane with cross-linking silanes *bis*-1,2-(triethoxysilyl)ethane and *bis*[3-(trimethoxysilyl)propyl]amine were applied onto the surface of silicatized zirconia. 3M ESPE RelyX resin-composite cement was bonded onto the silicatized and silanized zirconia surface and light-cured. Three groups were tested under dry condition and the other three groups were tested for thermocycling. The shear bond strength was measured using a materials testing instrument. Group mean shear bond strengths were analysed by ANOVA at a significant level of $p < 0.05$. The zirconia surface composition was analysed by X-ray Photoelectron Spectroscopy. ***Results.*** The highest shear bond strength was 11.8 ± 3.5 MPa for (3-acryloxypropyl)trimethoxysilane blended with *bis*-1,2-(triethoxysilyl)ethane (dry storage). There was a significant difference between mean shear bond strength values for (3-acryloxypropyl) trimethoxysilane blended with two cross-linking silanes, *bis*-1,2-(triethoxysilyl)ethane and *bis*[3-(trimethoxysilyl)propyl]amine, after thermocycling ($p < 3.9 \times 10^{-8}$). Various surface treatments of zirconia influenced the surface roughness ($p < 4.6 \times 10^{-6}$). The chemical composition analysis showed there was an increase in silicon and oxygen content after sandblasting. ***Conclusions.*** The results suggest that the combination of functional (3-acryloxypropyl)trimethoxysilane with cross-linking *bis* [3-(trimethoxysilyl)propyl]amine showed superior hydrolytic stability than with *bis*-1,2-(triethoxysilyl)ethane.

Key Words: *cross-linking, hydrolytic stability, organofunctional silane, siloxane network, zirconia*

Introduction

Silane coupling agents are widely used synthetic monomers in dentistry to promote adhesion between resin-composite cement and silica-coated ceramics and metal-based alloys restorative materials. A general formula for silane coupling agent is R-$(CH_2)_m$-Si-(OR')$_3$. R is an organofunctional group that reacts with organic matrix, -$(CH_2)_m$- is a linker group, and OR' is an alkoxy group, after hydrolysis to silanol (-Si-OH), that reacts with inorganic substrates. Thus, the silane acts as a bridge to connect the organic and inorganic materials together.

Studies of silane coupling agents on the bonding strength between resin-composite cement and zirconia have been investigated *in vitro* throughout the years because zirconia is a promising dental biomaterial due to its aesthetics, non-toxicity, biocompatibility [1–12] and optimal biomechanical properties [13]. In these studies, the zirconia surface was pre-treated by various methods such as sandblasting [14] or hydrofluoric acid etching [15] or some other chemical approaches [16] before silanization in order to increase the bond strength between resin-composite cement and zirconia. The samples prepared were then tested under dry conditions, water storage and under thermocycling test. They found that the bond strength measured, in most cases for different resin-composite cements and silanes tested, decreased after the water storage or thermocycling

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Correspondence: Christie Ying Kei Lung, Dental Materials Science, Faculty of Dentistry, The University of Hong Kong, Hong, 4/F, Prince Philip Dental Hospital, 34 Hospital Road, Sai Ying Pun, Hong Kong SAR, PR, China. Tel: +852 2859 0380. Fax: +852 2548 9464. E-mail: yklung@graduate.hku.hk

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test as compared to bond strengths of dry groups measured. Some samples were even debonded spontaneously during and after water storage and thermocycling. It is suggested that hydrolytic cleavage of siloxane bonds at the interfacial layer occurs, which lowers the bond strength [17]. In order to enhance the hydrolytic stability of the interfacial siloxane layer, the combination of functional silane with non-functional dipodal silane (also called cross-linking silane or bis-silane) would, in principle, increase significantly the bond strength and hydrolytic stability [18]. The action of dipodal silane is to cross-link the silane molecules more effectively by forming extensive three-dimensional siloxane networks and interconnects the functional silane [19]. Therefore, a rigid siloxane network is thought to be formed and, consequently, more energy would be required to break apart the cross-linking network and deteriorate the bonding. Furthermore, the higher the degree of the cross-linking siloxane network is, the more difficult for the water molecules to penetrate into the inner interfacial layer is. As the density of cross-linking (cross-links per unit volume) increases, there is less free volume available to accommodate solvent molecules [20]. Therefore, the hydrolytic cleavage of siloxane bonds from attack of water molecules is minimized. It is possible that in aqueous medium the result would be more stable bonding between the siloxane layer on silica-coated zirconia and resin-composite cement.

An organofunctional silane, (3-Acryloxypropyl)trimethoxysilane (ACPS) and two cross-linking silanes, *bis*-1,2-(triethoxysilyl)ethane (BTSE) and *bis*[3-(trimethoxysilyl)propyl]amine (BTMA) were selected and used in this investigation. The organofunctional silane is currently widely used in many areas such as optimization of performance of holographic grating [21] and UV-nanoimprint lithography [22]. (3-Acryloxypropyl)trimethoxysilane has surprisingly shown significantly higher adhesion promotion *in vitro* in comparison to other silane coupling agent products [23]. The cross-linking silanes are widely used in industry as a protective coating for many metals [24]. In this current study, the shear bond strengths for two groups of ACPS blending with BTSE and BTMA, respectively, were measured under dry and thermocycling conditions to stimulate ageing in oral conditions.

Commercial resin-composite cements such as RelyX Unicem Aplicap resin cement and Panavia contain acidic phosphate ester groups that promote adhesion. These products have been reported to produce durable bonding onto zirconia [25,26]. We have selected RelyX Unicem Aplicap resin-composite cement as our study material because it is clinically very widely used.

The hypotheses of this *in vitro* study were that blending of organofunctional silane with cross-linking silane might result in: (1) an increase in bond strength between resin-composite cement and silica-coated zirconia and (2) no significant decrease in shear bond strength after artificial ageing (thermocycling test).

Materials and methods

The materials used in this study are listed in Table I. An amount of 15 square-shaped zirconia samples with a surface area of ~10 mm × 10 mm were prepared for six study groups with a total of 90 samples. The organofunctional silane used in this study was (3-acryloxypropyl)trimethoxysilane. The two cross-linking silanes used were *bis*-1,2-(triethoxysilyl)ethane and *bis*[3-(trimethoxysilyl)propyl]amine. The molecular structures of the silanes are shown in Figure 1.

Preparation of silica-coated zirconia

The zirconia surfaces of the samples were first polished with 400-grit silicon carbide paper under running water. They were then cleaned for 10 min in deionized water in an ultrasonic bath (Decon Ultrasonics Ltd, Hove, Sussex, UK) and rinsed with 70% ethanol. The samples were allowed to dry in air at room temperature. The surfaces were

Table I. Materials used in this study.

Materials	Manufacturer	Purity/%	Lot. No.
Zirconia (Procera™)	Nobel Biocare, Göteborg, Sweden	N/A.	N/A
(3-acryloxypropyl)trimethoxysilane	Gelest, Morrisville, PA	95.0	5C-6412
bis-1,2-(triethoxysilyl)ethane	Gelest, Morrisville, PA	N/A	5L–7926
bis[3-(trimethoxysilyl)propyl]amine	ABCR, Karlsruhe, Germany	95.0	1,003,242
Rocatec Sand Plus	3M ESPE, Seefeld, Germany	110 μm silica-coated alumina	369,418
Deionized water	Millipore, Bedford, MA	Resistivity 18.2 MΩcm	N/A
Ethanol	Riedel-de Haën, Seelze, Germany	99.8	03,550
RelyX Unicem Aplicap resin cement	3M ESPE, Seefeld, Germany	N/A	363,991
3M ESPE Sil silane	3M ESPE, Seefeld, Germany	<3%	259,583

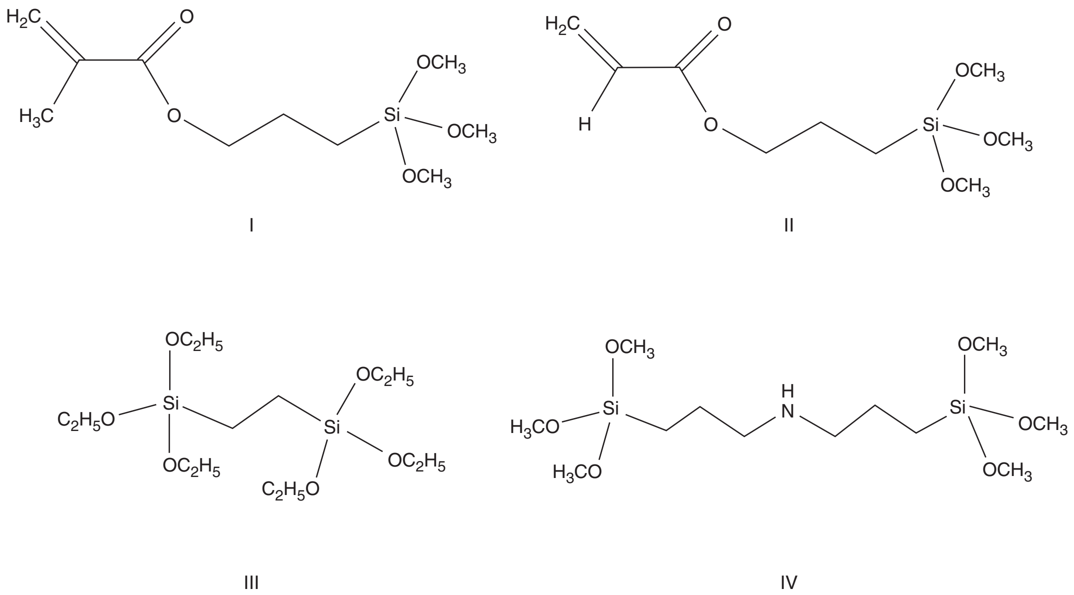


Figure 1. The molecular structures of the two methacrylate silanes and cross-linking silanes. I: 3-methacryloxypropyltrimethoxysilane, II: (3-acryloxypropyl)trimethoxysilane, III: *bis*-1,2-(triethoxysilyl)ethane and IV: *bis*[3-(trimethoxysilyl)propyl]amine.

sandblasted with 3M ESPE Rocatec Sand Plus (110 µm silica-coated alumina) at a constant pressure of 280 kPa for 30 s/cm^2 and at a perpendicular distance of 10 mm. The samples were collected and transferred to a beaker which was filled with 70% ethanol and cleaned ultra-sonically for 10 min and then rinsed with 70% ethanol. The samples were allowed to dry in air at room temperature for 1 h [2,19].

Preparation of experimental silane solution and silanized zirconia surface

The cross-linking silane at a concentration of 0.5 vol% in a solvent mixture of 95 vol% absolute ethanol and 5 vol% deionized water was prepared and its pH was adjusted to 4.5 with 1 M acetic acid. It was allowed to hydrolyse for 23 h. The functional silane coupling agent monomer (3-acryloxypropyl)trimethoxysilane was then added. The final concentration was made up to 1.0 vol%. The experimental silane solution was then allowed to hydrolyse for an additional hour [27].

The experimental silane solution was applied onto the surface of each silica-coated zirconia sample with a new brush each time, and allowed to react and dry for 5 min. 3M ESPE Sil silane was used as a control; it consisted of one functional silane, 3-methacryloxypropyltrimethoxysilane, at a silane content of ~1–2 vol%.

Surface roughness measurement

Five samples of zirconia with different surface treatments were prepared for surface roughness measurement. The details of the sample preparation were shown in Table II. Surface roughness was measured by an electro-mechanical profilometer (Surtronic 3+, Taylor Hobson, Leicester, UK). Five readings were taken at different regions. The surface roughness parameter measured in this study was the average surface roughness, R_a.

Resin-composite cement bonding to zirconia samples for thermocycling

RelyX Unicem Applicap resin-composite cement (3M ESPE, Seefeld, Germany) was activated according to manufacturer's instructions and transferred to a high-frequency mixing unit (Silamat, Ivoclar Vivadent, Schaan, Liechtenstein) for mixing for 15 s. The resin-composite cement was transferred to a cylindrical polyethylene mould with a diameter of 3.7 mm and height of 4.0 mm. The resin-composite cement stub, with an average height of 3.0 mm, was light cured for 40 s using a light-curing unit (Elipar 2500 Halogen Curing Light, 3M ESPE), from the top and at the contact area between the resin-composite cement and silicatized and silanized zirconia. The wavelength ranged from 400–500 nm, with the light intensity of 1300 mW/cm^2. The mould was carefully removed after curing process. The samples were kept in a desiccator. Other samples were tested under a thermocycling regime. The regime was set at 6000 cycles between two water baths (filled with deionized water) at temperatures of 5°C and 55°C.

Shear bond strength testing and failure type analysis

The zirconia sample with the light-cured resin-composite stub was positioned on the materials testing

Table II. Various treatments on zirconia surfaces for XPS analysis.

Sample	Surface treatment conditions
1	(i) Polishing, (ii) Rinsing
2	(i) Polishing, (ii) Rinsing, (iii) Sandblasting, (iv) Rinsing
3	(i) Polishing, (ii) Rinsing, (iii) Sandblasting, (iv) Silanized with 3M ESPE Sil silane primer, (v) Rinsing
4	(i) Polishing, (ii) Rinsing, (iii) Sandblasting, (iv) Silanized with 1 vol% ACPS + 0.5 vol% BTSE, (v) Rinsing
5	(i) Polishing, (ii) Rinsing, (iii) Sandblasting, (iv) Silanized with 1 vol% ACPS + 0.5 vol% BTMA, (v) Rinsing

All sample surfaces were polished with 400-grit silicon carbide paper. After polishing and sandblasting, all samples were rinsed in 70% ethanol in the ultra-sonic bath for 10 min and air-dried. Samples 2–5 were sand-blasted (30 s/cm^2) using Rocatec Plus sand (110-μm silica-coated alumina) on the surface of zirconia at pressure of 280 kPa.
ACPS, (3-acryloxypropyl)trimethoxysilane; BTSE, *bis*-1,2-(triethoxysilyl)ethane; BTMA, *bis*[3-(trimethoxysilyl)propyl]amine.

instrument (Instron LTD, Model 1185, Norwood, MA). A load of 1000 N was applied at a cross-head speed of 1.0 mm/min [28] until failure occurred. The shear bond strength, δ, was calculated by the formula: $\delta = F/A$, where F is the force at failure and A is the cross-sectional area of the stub.

The modes of failure of the tested groups were assessed visually by light microscopy and classified according to the amount of resin stub remaining on the zirconia surface after bond strength measurement. When 1/3 or less of the resin stub remained, the failure type was classified as ‘adhesive’ and when the amount remaining was >1/3 but <2/3, it was classified as ‘mixed’. When the amount remaining was ≥2/3, it was classified as ‘cohesive’ failure [29].

Statistical analysis

Analysis ToolPak in Microsoft Office Excel 2003 (Microsoft Corporation) was used for the statistical analysis of the collected data. The mean shear bond strengths of tested groups were analysed by one-way analysis of variance (ANOVA). A p-value < 0.05 was taken as being statistically significant.

X-ray photoelectron spectroscopy (XPS)

Five samples of zirconia with different surface treatments were prepared for XPS analysis. The details of the sample preparation are shown in Table II.

The chemical composition of the surfaces of the samples was examined by XPS using a Perkin-Elmer PHI 5400 spectrometer that had a mean radius of 140 mm and was equipped with a resistive anode detector. The ionization source was Mg Kα radiation (hν = 1253.6 eV) from a twin-anode x-ray tube. Broad-range survey scans were performed to determine atomic concentrations, at a pass energy of 89.45 eV and an entrance slit width of 4 mm. The base pressure in the chamber was maintained at $\sim 8 \times 10^{-15}$ MPa and the x-ray tube was operated at 200 W. The peak composition and energy positions were then determined using the least-squares curve-fitting technique in Igor Pro analysis environment with SPANCF macro package [30].

Results

The mean shear bond strength values of (3-acryloxypropyl)trimethoxysilane (ACPS) blended with two cross-linking silanes are tabulated in Table III. ANOVA analysis revealed there is no significant difference in the mean shear bond strength values between the control silane and ACPS blending with the two cross-linking silanes, *bis*-1,2-(triethoxysilyl) ethane (BTSE) and *bis*[3-(trimethoxysilyl)propyl] amine (BTMA), in dry condition ($p > 0.13$). There is also no significant difference of ACPS blended with two cross-linking silanes tested in dry condition ($p > 0.09$). However, there is a significant difference between the three tested groups after 6000 thermocycles ($p < 3.8 \times 10^{-8}$). There is also a significant difference for the thermocycling groups for ACPS blending with BTSE and BTMA ($p < 3.9 \times 10^{-8}$). Significant difference is found for the shear bond strength of ACPS blending with BTSE between the dry and thermocycling test groups ($p < 4.9 \times 10^{-6}$). Significant differences were also found for the shear bond strength of ACPS blending with BTMA between the dry and thermocycling test groups ($p < 0.004$). For the control group, there is no significant difference in shear bond strength between the dry group and thermocycling group ($p < 0.08$).

Analysis of failure mode (Table III) showed the adhesive mode was predominant for control silane groups after dry storage and thermocycling. Some samples of the tested groups of ACPS blending with BTSE exhibited cohesive failures (20% and 40% for dry and thermocycling). For tested groups of ACPS blending with BTMA, the predominant mode was adhesive failures.

The surface roughness of zirconia surfaces after various treatment measured were tabulated in Table IV. There was a significant difference in surface roughness between polishing and polishing with sandblasting ($p < 4.6 \times 10^{-6}$). No significant

Table III. Mean shear bond strength of ACPS with addition of cross-linking silanes BTSE and BTMA under dry storage and after thermocycling.

	Mean shear bond strength ± SD (MPa)					
Silane	Dry	Thermocycling (6000 cycles)	Debonding (%)	Adhesive (%)	Mixed (%)	Cohesive (%)
3M ESPE Sil	10.3 ± 1.7	—	0	80.0	13.3	6.7
	—	10.5 ± 2.4	0	93.3	6.7	0.0
ACPS+BTSE	11.8 ± 3.5	—	0	66.7	13.3	20.0
	—	5.8 ± 2.2	0	53.3	6.7	40.0
ACPS+BTMA	9.8 ± 2.8	—	0	73.3	6.7	20.0
	—	13.9 ± 4.2	0	93.3	6.7	0.0

ACPS, (3-acryloxypropyl)trimethoxysilane; BTSE, *bis*-1,2-(triethoxysilyl)ethane; BTMA, *bis*[3-(trimethoxysilyl)propyl]amine. [ACPS] = 0.1 vol%, [BTSE] = [BTMA] = 0.05 vol%.

difference was found between samples 2, 3 and 4 ($p < 0.25$). There was significant difference between samples 2, 3, 4 and 5 ($p < 0.001$).

The chemical composition and atomic concentration of the five samples were tabulated in Table V, which showed variation of atomic concentration of Si, Zr, C, O and Al after different surface treatments. The Si content on the zirconia surface was increased after sandblasting. Al was also detected after sandblasting.

Discussion

Thermocycling and water storage are the popular methods used in dental research for ageing artificially the specimens and thereby testing the durability of adhesion. Thermocycling combines the hydrolytic effect and thermal stresses that may simulate the natural process of ageing of the bonded interface [31]. Therefore, thermocycling is used in this study to test the hydrolytic stability and the thermal stress on resin-composite cement bonding to silica-coated and silanized zirconia.

The addition of cross-linking silane with organofunctional silane is to enhance the bond strength between resin-composite cement and silicatized zirconia. In this study, the shear bond strength of the (3-acryloxypropyl)trimethoxysilane (ACPS) blending with *bis*-1,2-(triethoxysilyl)ethane (BTSE) was decreased significantly after thermocycling, whereas the shear bond strength of ACPS blending with *bis* [3-(trimethoxysilyl)propyl]amine (BTMA) increased after thermocycling. For the control 3M ESPE Sil silane, there was no significant difference in shear bond strength between the dry groups and the thermocycling groups. As widely discussed, shear bond strength testing bears some uncertainty due to the method itself [32]. However, we decided to carry out adhesive testing by using it, due to its universal use.

Heikkinen et al. [2] reported that the mean shear bond strengths measured between resin-composite cement and silicatized and silanized zirconia after thermocycling were decreased. They suggested that the difference in linear coefficient of thermal expansion (LCTE) of resin-composite cement and zirconia ceramic may cause thermal stress at the interface between resin-composite cement and zirconia which leads to failure of the bond during thermocycling. On the other hand, they pointed out that post-curing may increase the bond strength during thermocycling, but it was not observed in their results.

RelyX Unicem Aplicap resin-composite cement without any silane treatment was not selected as a control in this study because it has been reported that the acidic phosphate ester monomer has some degree of bonding to zirconia without any surface pre-treatment. The reported values were ~4 MPa in dry

Table IV. Mean surface average roughness, R_a, measurement of zirconia surfaces with various treatments.

Sample	Mean R_a (μm ± SD)
1	0.90 ± 0.07^a
2	1.36 ± 0.1^b
3	1.26 ± 0.07^b
4	1.28 ± 0.1^b
5	1.58 ± 0.17^c

Different letters (a,b, and c) mean that the groups are significantly different ($p < 0.05$).

Table V. Atomic concentrations of zirconia surface before and after sandblasting and silanization.

	Atomic concentration (%)				
Sample	Si	Zr	C	O	Al
1	4.3	6.0	71.8	18.0	0.0
2	10.2	6.0	35.9	39.7	8.3
3	9.2	6.2	37.7	39.0	7.9
4	11.5	5.5	32.1	42.7	8.2
5	11.0	4.4	40.4	36.8	7.5

condition which was decreased to 3.7 MPa after 24 h water immersion and 1.4 MPa after thermocycling for 1000 cycles [3].

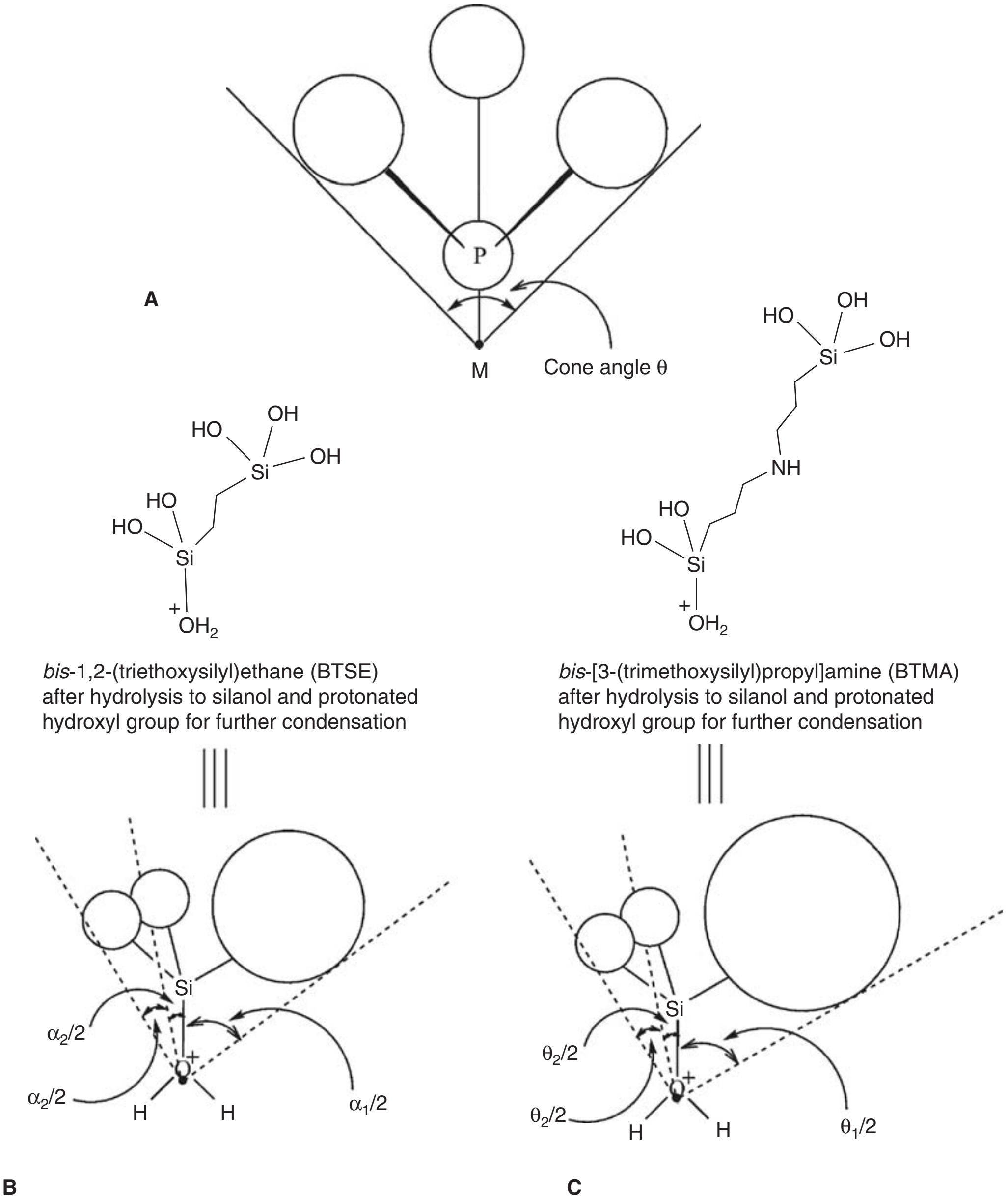
The hydrolytic stability of the resin-composite cement bonding to silica-coated zirconia was affected by which cross-linking silanes are blended with ACPS. An alternative approach is now proposed to explain the results.

The functional hydrophobic silanes are first to be activated by hydrolysis at low pH, acid catalysed to increase the rate of hydrolysis, before coupling with the inorganic substrate surface. It undergoes a bimolecular nucleophilic substitution (S_N2) reaction which involves the protonation of alkoxy group and then backside attack of the water molecule on the silicon atom to finally give the product intermediate labile hydrophilic silanols ($\equiv$SiOH) [33]. After hydrolysis, the hydroxyl group in silanol is protonated and then attacked by of another silanol molecule to form siloxane dimer [34]. Successive condensation of the silanol molecules forms a hydrophobic three-dimensional siloxane ($\equiv$Si-O-Si$\equiv$) network. Chambers et al. [35] studied the electronic and steric (molecular size) effects on the acid-catalysed hydrolysis of silane. They found that the steric effect was the critical factor that affects the rate of hydrolysis. Therefore, the larger the size alkoxy groups are, the slower the rate of reaction is. It would be more clearly illustrated by using the ‘cone angle’ concept which was introduced by Tolman [36] to explain the steric effect of phosphorus ligands in substitution reaction of organometallic compounds. Nevertheless, a ‘cone angle’ is a measure of the steric effect exerted by the functional or non-functional groups. The cone angle θ is the angle of the cone apex (the metal atom, M) of a cylindrical cone at a distance from the phosphorous atom, i.e. the bond length of M-P bond (Figure 2A) [37]. Based on this concept with some modification, the cone angles as defined for cross-linking silanes, BTSE and BTMA, in Figures 2B and C for unsymmetrical groups [38], increase from smaller size of 2-(trihydroxysilyl)ethyl [$(HO)_3SiC_2H_4$—] group in BTSE to larger size of 3-(3-(trihydroxylsilyl)propylamino)propyl [$(HO)_3SiC_3H_6NHC_3H_6$—] group around the silicon atom in BTMA. With increasing the cone angle, there is an increase in congestion when the incoming second hydrolysed BTMA molecule attack from the back to the central silicon in BTMA during condensation. Therefore, the rate of condensation for BTMA is slower than that of BTSE. As a result, the cross-linking of siloxane network formed from BTMA with ACPS is less extensive than that for BTSE with ACPS after 24 h of hydrolysis and activation.

During the thermocycling (6000 cycles), the water molecules apparently penetrate into the interphase siloxane layer between the resin-composite cement and silica-coated zirconia. The siloxane bond (-Si-O-Si-) network formed between BTSE and ACPS is attacked by the water molecules which results in the cleavage of siloxane bonds. On the other hand, further condensation of BTMA proceeds in the presence of water molecules. This results in an increase of cross-linking of siloxane network. As a result, the shear bond strength measured for the tested groups of ACPS blended with BTSE is decreased after thermocycling, whereas for ACPS blended with BTMA is increased after thermocycling. The control, 3M ESPE Sil silane is commonly used in the dental clinic. It is a pre-hydrolysed silane product of 3-methacryloxypropyltrimethoxysilane (MPS) which undergoes a series of hydrolysis and condensation reactions after the packaging for a period of time before use during clinical practice [39]. Having said this, a portion of MPS monomers is oligomerized during the storage. A cross-linking network is formed that the penetration of water molecules during thermocycling into the interfacial siloxane network is less accessible. This may explain there is no significant difference in shear bond strength between the tested control groups under dry storage and thermocycling test. However, different commercial silanes produce varying bonding strengths in simulated *in vitro* tests [40].

As discussed above, the cross-linking of ACPS blended with BTSE was decreasing during thermocycling. It is apparent that the difference in linear coefficient of thermal expansion between resin-composite cement and silica-coated zirconia developed thermal stress which further weakened the bonding at the interface. On the other hand, the cross-linking of ACPS blended with BTMA was increasing during thermocycling, which suppressed the thermal stress developed at the interface. Therefore, there is no decrease of bond strength after thermocycling. For the control group, the bonding interface has been extensively cross-linked because the silane was pre-hydrolysed and this might compensate the thermal stress. Thus, there is no decrease of bond strength as in the case of ACPS blended with BTMA.

Various surface treatments significantly affect the surface roughness of zirconia. The surface roughness, R_a, is increased after sandblasting (Table IV). The zirconia surface is bombarded with high energy silica-coated alumina particles which resulted in formation of pores and hillocks. A more irregular surface is produced. There is significant difference in surface roughness between the control silane and ACPS blending with the two cross-linking silanes, *bis*-1,2-(triethoxysilyl)ethane (BTSE) and *bis*[3-(trimethoxysilyl)propyl]amine (BTMA). However, no significant difference is found in shear bond strength values between these groups. The bond strength between the resin cement and zirconia depends on the surface treatment of zirconia, the nature of the silane primer and the resin cement used. In this study,



bis-1,2-(triethoxysilyl)ethane (BTSE) after hydrolysis to silanol and protonated hydroxyl group for further condensation

bis-[3-(trimethoxysilyl)propyl]amine (BTMA) after hydrolysis to silanol and protonated hydroxyl group for further condensation

Figure 2. (A) The cones angle θ for three symmetrical groups; (B) The cone angles for *bis*[3-(trimethoxysilyl)propyl]amine (BTMA) with unsymmetrical functional and non-functional groups defined by silicon-oxygen axis and the outmost van der Waals contact between substituent groups and (C) for *bis*-1,2-(triethoxysilyl)ethane (BTSE) after hydrolysis as the sum of half angles. Note: half angle $\theta_1/2 > \alpha_1/2$.

the variation of silane formulation does not show any significant difference in bond strength ($p > 0.13$).

From Table IV it can be seen that only Si, Zr, C and O are detected in sample 1. Si and C derive from polishing the zirconia surface with silicon carbide (SiC) paper. For samples 2, 3, 4 and 5, there is an observed increase in atomic concentrations of Si, which has its origin from the sandblasting as there are small variations in Si content between samples 2 and 3–5 after silanization. The Al detected also apparently comes from sandblasting for samples 2–5. The results support the idea that the Si content on the zirconia is increased after sandblasting. In the near future, it may be worth optimizing the functional silane to cross-linking silane ratio.

Conclusions

The hydrolytic stability of the bond formed between resin-composite cement and silicatized zirconia using ACPS blended with cross-linking BTSE and BTMA silanes was investigated and assessed. It was observed that the bond was weakened using cross-linking BTSE silane and that the cross-linking BTMA silane is more effective than BTSE to enhance the hydrolytic stability of the interfacial siloxane layer between the resin-composite cement and zirconia surface. It is also suggested that the molecular size of the cross-linking silane has a pronounced effect on the hydrolytic stability of resin-zirconia bonding. In the near future, the effect of more cycles in thermocycling should be studied to find out the long-term effect of hydrolytic stability and thermal stresses on the bonding between resin-composite cement and silica-coated and silanized zirconia. Moreover, the hydrolytic stability of resin-composite cement bonded to silica-coated and silanized zirconia after long-term water storage merits further study.

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