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Pilot evaluation of resin composite cement adhesion to zirconia using a novel silane system

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Abstract

Objective. In this study, we evaluated the effect of two silane coupling agents and their blends with a cross-linker silane on the bond strength of a dimethacrylate-based resin composite cement to surface-conditioned zirconia. ***Material and Methods.*** A total of 40 planar zirconia specimens were used for 8 test groups. After alumina particle abrasion, followed by tribochemical silica-coating, the specimens were randomly assigned to four silanizations: with 1.0 vol% 3-methacryloyloxypropyltrimethoxysilane or 1.0 vol% 3-mercaptopropyltrimethoxysilane or their blends with 1.0 vol% 1,2-*bis*-(triethoxysilyl)ethane (all in ethanol/water). The resin composite (RelyX™ ARC, 3M ESPE) stubs ($n = 10$/group) were light-polymerized onto zirconia specimens. Four test groups were tested without water storage and 4 thermo-cycled at 6000 cycles (5 ± 1°C to 55 ± 1°C), with a dwelling time of 30 s. The shear bond strength of the cement stubs to zirconia was measured using a universal testing machine at a constant cross-head speed of 1 mm/min. Scanning electron microscopy was employed for imaging the zirconia surface after conditioning and testing. Failure mode was evaluated visually. A surface chemical analysis was carried out with the EDXA system. ***Results.*** The highest shear bond strength was 21.9 ± 8.7 MPa, obtained with a blend of 3-mercaptopropyltrimethoxysilane and 1,2-*bis*-(triethoxysilyl)ethane (dry storage), and 16.0 ± 1.5 MPa, with 3-methacryloyloxypropyltrimethoxysilane (thermo-cycled). Thermo-cycling decreased the bond strengths significantly (ANOVA, $p < 0.01$), and the silanes differed significantly ($p < 0.005$). Some specimens suffered from spontaneous debonding during thermo-cycling. ***Conclusions.*** The luting cement adhesion might be promoted to silica-coated zirconia with 1.0 vol% 3-methacryloyloxypropyltrimethoxysilane and with a blend of 1.0 vol% 3-mercaptopropyltrimethoxysilane and 1.0 vol% 1,2-*bis*-(triethoxysilyl)ethane.

Key Words: *Conditioning, dental cements, dental ceramics, silanization, silica-coating*

Introduction

The intention of keeping tooth preparations to a minimum and of saving dental tissues has led to a growing use of dental ceramics for inlays, onlays, laminates, crowns, and bridges [1]. Zirconia (zirconium dioxide, ZrO_2) is structurally stable when doped [2] with yttria (yttrium trioxide, Y_2O_3) and can stand high masticatory loads in simulated clinical conditions [3]. Stabilized zirconia ceramic is tough; it has a high cohesive strength, adequate flexural properties, and is usually esthetically adequately white in color [4]. High-performance non-etchable zirconia is used in indirect restorations for fixed partial dentures and crowns, substituting metal structures [5]. Zirconia has also been successfully employed in orthopedic joint applications [6].

The clinical application of resin-bonded zirconia in dentistry requires a strong and stable resin composite cement and adhesion. Dual functional silane coupling agents have applications as adhesion promoters for resin composites and coatings [7]. These silanes contain an organofunctional group and three hydrolyzable alkoxy groups (Figure 1A–C). Silanes must undergo hydrolyzation reactions to become activated, often in an acidic ethanol-water solution, where reactive hydrophilic silanols are formed from trialkoxy groups. The organofunctional part, usually the methacrylate group, can polymerize during light-curing with the monomers of a dimethacrylate resin composite system [8]. Silanes mediate adhesion between hydrophobic resin composite and hydrophilic silica-coated surfaces [7,9]. Tribochemical silica-coating carried out using the Rocatec™

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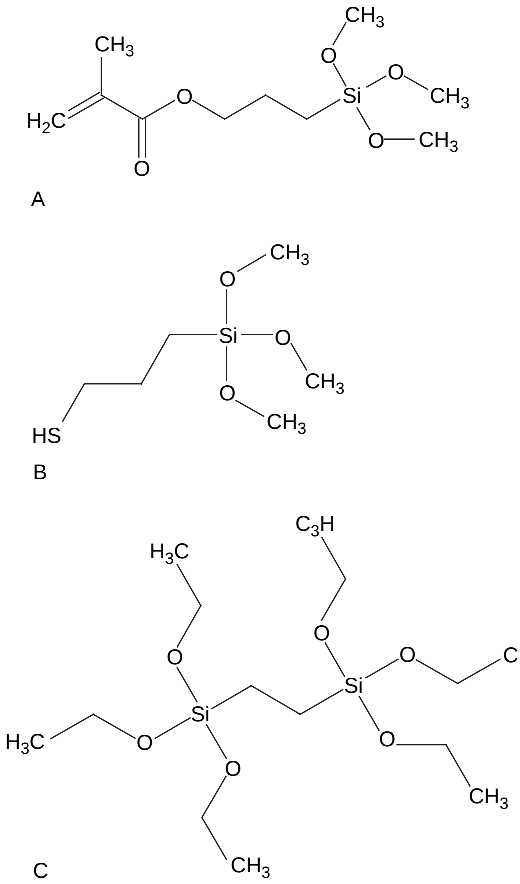

Figure 1. Molecular structures for the silanes in this study: A. 3-Methacryloyloxypropyltrimethoxysilane. B. 3-Mercaptopropyltrimethoxysilane. C. 1,2-*bis*-(Triethoxysilyl)ethane.

system (3M ESPE, Seefeld, Germany) is a conventional conditioning technique for dental laboratories. It employs alumina (corundum, Al_2O_3) particles coated with colloidal silicon dioxide [10]. These particles are blasted onto the metallic (or resin composite) surface prior to bonding with a resin composite cement [10]. The indications of the RelyX™ ARC resin composite cement (applied in this pilot study) are: all ceramic and porcelain crowns, inlays, onlays, bridges, and fixed partial dentures [11]. The bond strengths of various adhesive systems to some zirconia ceramics have been evaluated and reported [12,13].

Some other luting cements indicated for zirconia contain, for example, methacrylated phosphoric ester groups in RelyX™ Unicem with (3M ESPE, Seefeld, Germany) [14] or organophosphate groups in 10-methacryloyloxydecyldihydrogenphosphate (MDP) in Panavia™ F (Kuraray Medical, Okayama, Japan) [3]. Both adhesion systems can provide reliable adhesion as evaluated [12]. Some zirconia ceramics can be conditioned with alumina particles that are less in diameter than 50 μm and with the Rocatec™ system without any weakening of the flexural properties [15].

Combinations of cross-linker silanes (Figure 1C) and organofunctional silanes significantly enhance bonding, mechanical strength, and hydrolytic stability in many industrial resin composite systems [16]. These silane blends improve the wet adhesion. A cross-liner silane such as *bis*-1,2-(triethoxysilyl) ethane provides excellent protection for corrosion before the final painting application [17,18]. Nevertheless, the literature does not give exact information on which functional silane best fits the commercial resin composite cements. Moreover, essential information is lacking on the shear bond strengths of resin composite cements to alumina particle abraded and silica-coated and silanized zirconia. Without silica-coating, or applying only pure alumina particle abrasion, silanes cannot promote the adhesion of a resin composite cement onto zirconia (or to alumina ceramics), since the =Al-O-Si= bond linkage that is formed in the siloxane film at the zirconia-resin composite interface is not durable for hydrolytic effects in oral conditions [1].

The aim of this pilot study was to evaluate the adhesion promotion properties of two trialkoxy silanes, 3-methacryloyloxypropyltrimethoxysilane and a structurally similar 3-mercaptopropyltrimethoxysilane (Figure 1A–B), and also their blends with 1,2-*bis*-(triethoxysilyl)ethane. Some recent reports about silanized silica-coated titanium support the use of such silane blends [19]. Specific organofunctional groups, such as mercapto (thiol group – SH), may in some cases improve compatibility of the silane molecule at the interface and hence enhance the adhesion [16].

The hypothesis in this pilot study was that silane blends ('a novel silane system') promote adhesion better than the functional silanes alone.

Material and methods

Zirconia and conditioning

All materials are listed in Table I. The planar-shaped zirconia specimens (total 40), with a surface area of 10 × 10 mm and a thickness of 5 mm, were embedded in cylindrical acrylic resin blocks, ensuring that one surface of the zirconia surface remained uncovered. Forty ceramic samples were divided randomly into eight experimental study groups: in each study group, cement stubs $n = 10$, i.e. two stubs on one zirconia specimen. Four different silane solutions were evaluated (Table IIA) for RelyX™ ARC luting cement (see below).

Alumina particle abrasion was first performed using 50-μm grain-sized aluminum trioxide powder at an operation pressure of 300 kPa from a perpendicular distance of approximately 10 mm for 2 × 15 s with slowly rotating motion for the exposed surface of each specimen. Abrasion was carried out uniformly across the specimen surface to prevent the formation of areas of increased localized stress. The samples were then cleaned for 10 min in an

Table I. Materials used in this study. The information is based on the manufacturers' up-dated use of instruction booklets

Trade name	Description and composition	Manufacturer	Purity (%)	Batch no.
Procera® AllZircon	Zirconium dioxide	Nobel Biocare, Göteborg, Sweden	N/A	N/A
RelyX™ ARC	Adhesive resin cement paste, shade A3, Bis-GMA, TEGDMA, Silane-treated ceramic and silica fillers, functionalized DMA	3M ESPE, St. Paul, Minn., USA	N/A	20041012
Z-6030	3-Methacryloyloxypropyltrimethoxysilane	Dow Corning Toray Silicone, Tokyo, Japan	98	VN02011454
RMS 820	1,2-bis-(Triethoxysilyl)ethane	Dow Corning Toray Silicone, Tokyo, Japan	98	0000635513
SH 6062	3-Mercaptopropyltrimethoxysilane	Dow Corning Toray Silicone, Tokyo, Japan	98	0002027204
Ethanolum anhydricum	Ethanol	Primalco, Helsinki, Finland	99.5	030305
Acetic acid	Acetic acid	Merck, Darmstadt, Germany	100	K12716063
Adper™ Scotchbond	Bis-GMA, 2-hydroxyethylmethacrylate	3M ESPE, St. Paul, Minn., USA	N/A	5CM1X7
Korox™ Sand	Alumina sand, 50 μm	BEGO, Bremen, Germany	99.6	401221
Rocatec™ Sand	Silica-coated alumina sand, 110 μm	3M ESPE, Seefeld, Germany	N/A	498

ultrasonic bath (Quantrex 90 WT, L&R Manufacturing, Lahti, Finland) in water-free ethanol. The samples were dried in compressed oil-free air and kept in a desiccator before the next, immediate steps. The specimens were silica-coated with Rocatec® Plus sand at 300 kPa, from a distance of 10 mm for 3 × 15 s (cf. Table I). The samples were again cleaned in an ultrasonic bath, dried as described above, and then stored briefly in a desiccator prior to silanization.

Silanes, silane blends, and silanization

A standard solution of 95.0 vol% ethanol and de-ionized water (milli-Q water) was prepared and allowed to stabilize for 24 h before use in diluting the silanes. The pH was adjusted at 4.5 with 1 M acetic acid. Next, 1.0 vol% solutions of 3-methacryloyloxypropyltrimethoxysilane and 3-mercaptopropyltrimethoxysilane in the standard ethanol/water solution were prepared in 50-ml polyethylene bottles. Both were allowed to hydrolyze for 1 h at room temperature before use [19,20].

Preparation of silane blends: 1.0 vol% 1,2-*bis*-(triethoxysilyl)ethane in the standard ethanol/water solution was first allowed to activate for 23 h. The organofunctional silane was then added (1.0 vol%) and the silane blend (yielding 1.0 vol% + 1.0 vol%) was allowed to activate in 50-μm polyethylene bottles for an additional 1 h. In the final silane blends, 1,2-*bis*-(triethoxysilyl)ethane was therefore activated for 24 h and the organofunctional silane for 1 h.

The silica-coated zirconia samples were assigned randomly to eight subgroups for silanization. One silane coating was applied, each time with a new, clean brush onto the zirconia substrate. The silane was allowed to dry and to react for 3 min, and then gently air-blasted dry with an oil-free air stream [21].

Bonding of the resin composite cement and testing

Two RelyX™ ARC cement stubs were carefully bonded to one silica-coated silanized zirconia specimen using polyethylene molds with an inner diameter of 3.6 mm and a height of 5 mm. The cement was carefully packed against the substrate with a composite-filling instrument. The cement stubs were light-polymerized using a light intensity of 470–520 mW/cm^2 for 40 s (emission max. 490 nm). Polyethylene molds were gently removed from the test specimens. While dry samples (4 groups) were kept in a desiccator for 1 h prior to shear bond strength testing, the other four groups were subjected to thermo-cycling for 6000 cycles at between 5°C and 55°C in de-ionized water. Dwelling time at each temperature was 30 s, and the transfer time from one bath to the other was 2 s (ISO Standard 10477).

Table IIA. Tested zirconia groups in 'dry conditions'. Key: ZMP = silanization with 1.0 vol% 3-methacryloyloxypropyltrimethoxysilane in acidified ethanol/water, ZMBS = 1.0 vol% 3-methacryloyloxypropyltrimethoxysilane + 1.0 vol% 1,2-*bis*-(triethoxysilyl)ethane in acidified ethanol/water, ZME = 1.0 vol% 3-mercaptopropyltrimethoxysilane in acidified ethanol/water, ZMEBS = 1.0 vol% 3-mercaptopropyltrimethoxysilane + 1.0 vol% 1,2-*bis*-(triethoxysilyl)ethane in acidified ethanol/water. Silane abbreviations: MPS = 3-methacryloyloxypropyltrimethoxysilane, BTSE = 1,2-*bis*-(triethoxysilyl)ethane, MEPS = 3-mercaptopropyltrimethoxysilane

Sample code	Silane	n/group	Shear bond strength (MPa)	Standard deviation (MPa)
ZMP	MPS	10	19.0	3.3
ZMBS	MPS + BTSE	10	6.7	4.7
ZME	MEPS	10	9.8	9.8
ZMEBS	MEPS + BTSE	10	21.9	8.7

Zirconia specimens were mounted in a jig of the universal testing machine (Lloyd LRX; Lloyd Instruments, Fareham, UK) and the shear force was applied to the adhesive interface until fracture occurred. The specimens were loaded at a cross-head speed of 1.0 mm/min and the stress-strain curve was analyzed with Nexygen 2.0 software (Lloyd LRX).

Statistical analysis

Statistical analysis for the data was performed using SPSS 11.0 (Statistical Package for Statistical Science, Chicago, Ill., USA). The means of each group were analyzed by two-way analysis of variance (ANOVA), with shear bond strength as the dependent variable and the silane types and specimen storage types as the independent factors. *Post hoc* comparisons were made using Tukey's test, and p-values <0.05 were considered to be statistically significant.

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDXA)

The impact of the surface conditioning after alumina particle abrasion and silica-coating and the failure area of the shear bond strength tested thermo-cycled samples were evaluated employing scanning electron microscopy (SEM) (JSM 5500; Jeol, Tokyo, Japan). The zirconia samples were first mounted on aluminum sample-holder stubs and sputtered with gold (BAL-TEC SCD 050; Balzers, Liechtenstein). The SEM analysis was then performed at a working distance of 20 mm and an operating voltage of 17 kV in the backscatter electron mode. The images were captured using the software in the SEM system. Magnifications of 1400 and 35 were chosen for visual observation. A standardless EDXA analysis (PRISM 2000; Princeton Gamma-Tech, Princeton, N.J., USA) was carried out in vacuum with the accelerating voltage of 20 kV. A lithium-drifted silicon detector with 30 mm^2 active area was employed to collect the X-ray spectra. The analysis ($n=5$/group) was made of 1.14×0.84 mm^2 areas, with a working distance of 20 mm. Position-tagged spectrometry mode (PTS) was applied to analyze the element distribution on the conditioned zirconia surface. To obtain the proportions of Si, Al, and Zr, carbon and oxygen were de-convoluted from the spectra and the results.

Light microscopy analysis for the failure mode

A light microscopy analysis (WILD M38; Leica, Heerbrugg, Switzerland) was carried out after the shear bond testing to examine visually the cement stub contact areas (thermo-cycled samples) to zirconia surfaces. A magnification of 40 was employed to estimate the failure modes: adhesive or cohesive.

Results

The results of the shear bond strength test for the zirconia study groups are presented in Figure 2 and Table IIA, B. While ANOVA revealed significant influence of silane type ($p<0.005$) and sample storage ($p<0.01$) on the shear bond strength values, no interaction between silane type and storage conditions was found ($p<0.240$). *Post hoc* comparisons were made using Tukey's HSD test for the type of silane, when strength was the dependent variable.

The highest shear bond strength was obtained in dry storage conditions, 21.9 ± 8.7 MPa, with a blend of 3-mercaptopropyltrimethoxysilane and 1,2-*bis*-(triethoxysilyl)ethane and the lowest with a blend of 3-methacryloyloxypropyltrimethoxysilane and 1,2-*bis*-(triethoxysilyl)ethane, 6.7 ± 4.7 MPa. After thermo-cycling, the shear bond results were calculated for non-debonded sample populations: the highest thermo-cycled shear bond strength value, 16.0 ± 1.5 MPa, was obtained using 3-methacryloyloxypropyltrimethoxysilane. The lowest value, 1.0 ± 0.0 MPa, was obtained with a blend of 3-methacryloyloxypropyltrimethoxysilane and 1,2-*bis*-(triethoxysilyl)ethane. Some debonding occurred during thermo-cycling as presented in the Table IIB.

The SEM imaging analysis of the zirconia surfaces, with a magnification of 1400 or 35, suggested visible differences between non-treated samples (Figure 3A), alumina sand-blasted surface (Figure 3B) and alumina sand-blasting followed by silica-coating (Figure 3C). Zirconia that had been conditioned successively with both abrasion techniques and then silanized suggested a partially cohesive failure for all thermo-cycled cement stub samples according to the light microscopy analysis. As an example, silanized with 3-methacryloyloxypropyltrimethoxysilane, a tested zirconia-cement stub joint surface is presented (Figure 3D). According to the EDXA analysis, the silica-coated zirconia surface contained silicon 4.0 wt% and 10.9% as atomic concentration (Table III).

Discussion

Zirconia substrates were first pretreated with air abrasion, then cleaned ultrasonically before silica-coating; after silica-coating, they were cleaned again ultrasonically, since this protocol has been shown to remove loose particles and impurities [13]. In principle, the chosen protocol should not weaken the flexural properties of zirconia ceramics, as has been observed for another commercial zirconia product [3]. Roughening a surface with abrasion

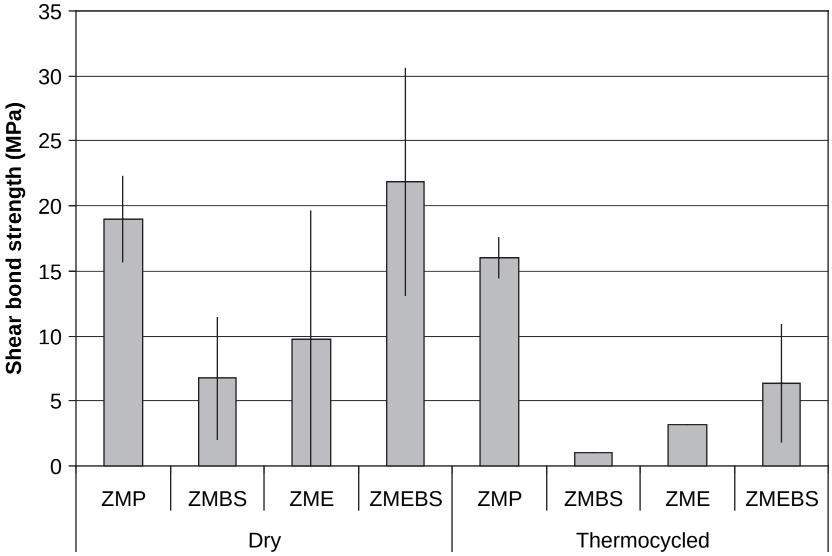

Figure 2. The measured shear bond strengths in two storage conditions ('dry' = without thermo-cycling or water storage; 'Thermo-cycled' = after thermo-cycling). Key to the silanizations: ZMP = 1.0 vol% 3-methacryloyloxypropyltrimethoxysilane in acidified ethanol/water, ZMBS = 1.0 vol% 3-methacryloyloxypropyltrimethoxysilane + 1.0 vol% 1,2-*bis*-(triethoxysilyl)ethane in acidified ethanol/water, ZME = 1.0 vol% 3-mercaptopropyltrimethoxysilane in acidified ethanol/water, ZMEBS = 1.0 vol% 3-mercaptopropyltrimethoxysilane + 1.0 vol% 1,2-*bis*-(triethoxysilyl)ethane in acidified ethanol/water. Silanes: MPS = 3-methacryloyloxypropyltrimethoxysilane, BTSE = 1,2-*bis*-(triethoxysilyl)ethane, MEPS = 3-mercaptopropyltrimethoxysilane.

enlarges the surface area and enables micromechanical retention [22]. SEM images showed visible changes in the topography: the effective rough surface area was clearly increased. However, the siloxane films cannot be directly detected, since the film is too thin, about 10–50 nm [17].

The experimental silanes were hydrolyzed following a procedure presented in the literature [20,23]. 3-Methacryloyloxypropyltrimethoxysilane is a widely employed adhesion promotion reagent between silica-coated surfaces and methacrylated polymeric materials [8]. However, some studies show that the silanes alone do not provide a reliable bonding with zirconia or alumina ceramic surfaces [1,12,13,24–26]. In this study, the blend of 3-mercaptopropyltrimethoxysilane and 1,2-*bis*-(triethoxysilyl)ethane provided the highest shear bond results for 'dry samples' (Table IIA). It might be concluded that the mercapto group (—SH) (Figure 1B) had some chemical interaction between the resin composite cement and silica-rich zirconia surface. On the other hand, the methacrylate group (Figure 1A) promoted adhesion without activated cross-linker silane molecules, demonstrating relatively high shear bond strength values (Figure 2). When the same silane was blended with the cross-linker silane, the values obtained were inferior against the hypothesis. Dry tests (without water storage) cannot predict much in terms of clinical behavior but are often recommended to be carried out and presented in publications.

However, though half of the thermo-cycled cement stubs debonded spontaneously for 3-methacryloyloxypropyltrimethoxysilane, the shear bond strength values were still relatively high. The obtained shear bond strength level as such *might be* clinically relevant for further investigations, since it equals with some composite cement bonding to enamel for orthodontic brackets, 18–20 MPa, or composite bonding to enamel, 18–22 MPa, using some resin composite systems [27]. Nevertheless, different test centers unfortunately use different bond strength methods, providing a large variation in the strength values.

The best shear bond results after thermo-cycling obtained with 3-methacryloyloxypropyltrimethoxysilane might suggest also that the wet strength of the siloxane film with its $\equiv$Si–O–Si$\equiv$ bonds at the cement–zirconia interface was durable (Table IIB). According to one of the latest silane theories, silane blends somehow modify the outermost inorganic

Table IIB. Thermo-cycled zirconia groups after thermo-cycling 6000 × between 5 and 55°C. For abbreviations, see Table IIA

Sample code	Silane	n/group	Spontaneous debonding (%)	Shear bond strength (MPa)	Standard deviation (MPa)
ZMP	MPS	10	50	16.0	1.5
ZMBS	MPS+BTSE	10	60	1.0	0.0
ZME	MEPS	10	80	3.2	0.0
ZMEBS	MEPS+BTSE	10	21.9	6.3	4.5

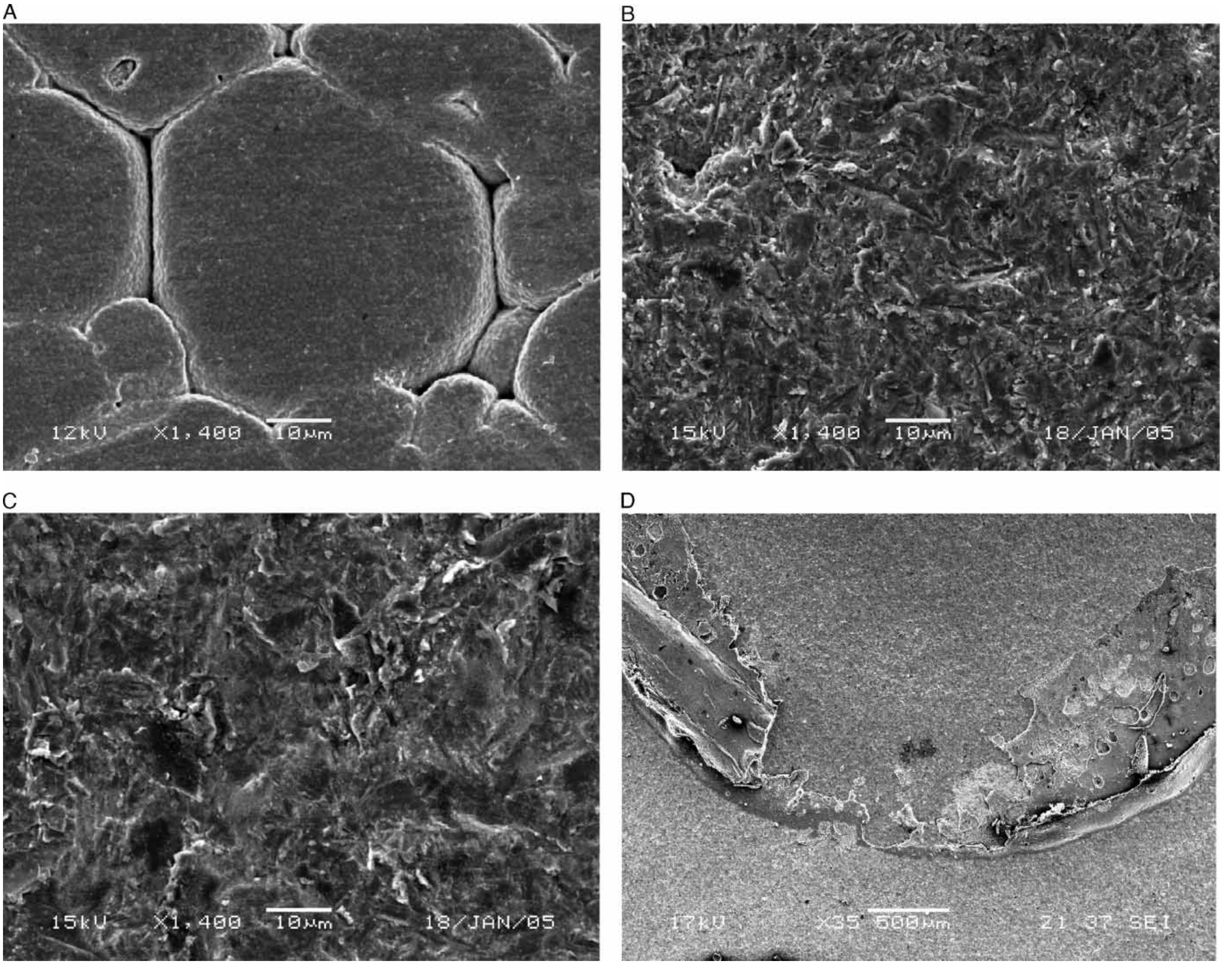

Figure 3. A. Zirconia surface before conditioning (SEM image: magnification 1400 ×). B. Zirconia surface conditioned with alumina sand (SEM image: magnification 1400 ×). C. Zirconia surface after alumina sand blasting, followed by silica-coating with the Rocatec™ system (SEM image: magnification 1400 ×). D. The contact area of the RelyX™ ARC luting cement stub to zirconia, silanized with 3-methacryloylxypropyltrimethoxysilane. After thermo-cycling and shear bond testing, remains of the luting cement can be observed (SEM image: magnification 35 ×).

oxide layer of the substrate, thereby enhancing the adhesion [28].

During thermo-cycling, samples treated with 3-mercaptopropyltrimethoxysilane demonstrated spontaneous debonding (80% cement stubs failed), which might imply that the mercapto group alone did not interact chemically for a hydrolytically stable siloxane bonding. The standard deviations varied in all test groups (cf. Table IIA, B), sometimes due to the operator factor, but since all the experiments were performed carefully by one person, reasons might be, for example, in the concentration of the silane and its blends. There is no information that the mercapto group would decompose in the used solvent system. Bonding between the mercapto group and the silica-coated zirconia surface has been susceptible for hydrolytic shocks. It might be useful to conduct optimization work for 3-methacryloyloxypropyltrimethoxysilane and the 3-mercaptopropyltrimethoxysilane + 1,2-*bis*-(triethoxysilyl)ethane blend in the near future.

Table III. Chemical analysis of the conditioned zirconia surfaces using EDXA

Element	Weight-% atoms on the surface	Atomic concentration (%) on the surface
Si	4.0	10.9
Al	6.2	15.2
Zr	89.8	73.9

Silica content is a very important factor, since silica is needed for formation of the hydrolytically stable $\equiv Si-O-Si \equiv$ linkage at the interface. According to the elemental distribution analysis of a silica-coated zirconia surface, it still contains 73.9% of zirconium, 10.9% of silicon, and 15.2% of aluminum when expressed as atomic concentrations. This corresponds with some previous studies [29]. In the near future, it might useful to evaluate the effects of a longer silica-coating time and a long period of water storage (at 37°C).

Contrary to the hypothesis, only one silane blend, 3-mercaptopropyltrimethoxysilane and 1,2-*bis*-(triethoxysilyl)ethane provided results that exceeded 5 MPa, a standard limit set by the International Organization for Standardization (ISO) [30].

Some of the shear bond results obtained might have a high standard deviation, but only 10% of the cement stubs had debonded spontaneously when zirconia was silanized with 3-mercaptopropyltrimethoxysilane + 1,2-*bis*-(triethoxysilyl)ethane blend. It might thus be interesting to carry out further optimization work on the 'novel silane system' with silica-coated zirconia. In addition, the effect of surface condition methods applied in this pilot study on the flexural properties of Procera® AllZircon will be carried out in the near future. This might be justifiable clinically, since particle size in the conditioning method may have a significant effect on the flexural properties.

Conclusions

In summary, the hypothesis in this *in vitro* pilot evaluation, 'silane blends perform better than the functional silanes alone' for silica-coated zirconia ceramics and the resin composite cement, was partially met. The main conclusions, bearing in mind the limitations, can be presented:

1. Thermo-cycling decreased the bond strength values significantly for the RelyX™ ARC luting cement stubs to silica-coated and silanized zirconia ceramics.
2. Silanizations with 1.0 vol% 3-methacryloyloxypropyltrimethoxysilane and with a blend of 1.0 vol% 3-mercaptopropyltrimethoxysilane and 1.0 vol% 1,2-*bis*-(triethoxysilyl)ethane produced promising bond strengths after thermocycling.
3. Silanization with 3-mercaptopropyltrimethoxysilane alone, or with a blend of 3-methacryloyloxypropyltrimethoxysilane and 1,2-*bis*-(triethoxysilyl)ethane did not provide hydrolytically durable bonding.

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