

Issued as:

Matinlinna JP, Lassila LV Enhanced resin-composite bonding to zirconia framework after pretreatment with selected silane monomers, *Dental Materials*, 2011, v. 27(3) p. 273-280

**Enhanced Resin-Composite Bonding to Zirconia Framework
after Pretreatment with Selected Silane Monomers**

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Abstract

Objective. To evaluate the effect of five experimental silane monomer primers *in vitro* on the shear bond strength of a phosphate ester resin-composite cement bonded to silicized zirconia framework.

Methods. A total of 144 planar zirconia (Procera AllZircon) specimens were subjected to tribochemical silica-treatment, randomly divided into 12 sub-groups (n=12), and silanized with 1.0% (v/v) activated solutions of 3-acryloxypropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, styrylethyltrimethoxysilane, and 3-isocyanatopropyltriethoxysilane, which had been prepared in 95% ethanol (pH 4.5). A ready-to-use 3-methacryloxypropyltrimethoxysilane (RelyX™ Ceramic Primer) was used as the control. One resin-composite cement (RelyX™ Unicem) stub was bonded to silicized and silanized zirconia using polyethylene molds. Half of the specimen groups were dry-tested (without aging) and half were thermo-cycled at 6000 cycles between 5 °C and 55 °C, with a constant dwelling time of 30 s. The shear bond strength of the cement stubs bonded to zirconia was measured using a universal testing machine using a constant cross-head speed of 1 mm/min. The silane primer activation was evaluated using Fourier-transform infrared spectroscopy.

Results. In dry conditions, the highest shear bond strength was 11.7 (SD 2.3) MPa, obtained with 3-acryloxypropyltrimethoxysilane and after thermo-cycling 17.6 (4.1) MPa, both. Thermo-cycling increased the bond strengths significantly (ANOVA, $p < 0.001$) and varied with the type of silane (ANOVA, $p < 0.001$).

Significance. Silanization with five experimental silane primers *in vitro* produced significantly greater shear bond strengths than the ready-to-use control silane.

Keywords: Primers, Resin bonding, Silica-coating, Shear bond strength, Silanization, Zirconia, Conditioning

1. Introduction

Biocompatible yttrium-stabilized tetragonal zirconia (ZrO_2) is structurally stable and stiff as a framework material. It has no known adverse tissue reactions, and serves at high simulated masticatory loads [1]. However, the reliable and durable clinical cementing of CAD/CAM-zirconia is still a clinical concern [2]. Pretreatment methods that modify the surface texture or chemistry to enhance durable adhesion have thus been investigated and suggested [3-7]. Some special resin composite cements have also been developed. These cements contain acidic phosphate ester groups, for example, as in 10-methacryloyloxydecyl dihydrogenphosphate (MDP) that is employed in Panavia™ (Kuraray, Osaka, Japan) [8] or other multifunctional molecules with methacrylate and phosphoric ester groups, for example, utilized in RelyX™ Unicem (3M ESPE, Seefeld, Germany) [5]. Both of these products have demonstrated durable bonding [9,10].

Silane coupling agents find wide use in silanization of fillers in resin-composite. Dual functional silane monomers can be used as coupling agents to promote adhesion between dissimilar matrices for composites and coatings, such as silica-coated materials in dentistry, because of their organofunctional group which polymerize with the monomers of resin composite and three hydrolyzable alkoxy groups which bond with silica and silica-coated surfaces [11]. An essential role of chemically activated silanes in dentistry is to mediate adhesion between dissimilar materials, hydrophobic resin composite and hydrophilic silica-coated surfaces. Experimental silane monomer primers have been evaluated in resin zirconia bonding

and they have exhibited a significant rise in the micro tensile bond strength [4,7]. However, intaglio zirconia is ineffective for silanization. In a widely used pretreatment method, tribochemical silica-coating in the Rocatec™ system, silica-coated alumina particles are blasted onto the zirconia surface to pretreat it [12,13].

The bond strengths of various commercially available adhesive systems to zirconia vary in magnitude [5,14]. Inert zirconia itself is not amenable to silane-based methods of adhesion promotion [3-5], but it can be pretreated using the Rocatec™ system, which cleanses the surface from eventual impurities and creates a highly microretentive surface and leaves a surface with a partial silicon dioxide coverage [15] without any weakening in its flexural properties [16]. After this pretreatment step, immediate silanization (silane application) can promote bonding to resin composite [11]. Furthermore, the rationale behind applying experimental silane primers is that the presence of specific organofunctional groups, such as an aromatic reactive styryl [17], isocyanato [18], glycidoxo (epoxy), and acrylate [19,20] in certain types of silane monomers may improve the spatial compatibility of the silane molecule. This steric improvement may also increase reactivity of silane monomers (enable polymerization reactions) with methacrylate, acrylate and styryl with their vinylic C=C groups with phosphate ester groups in resin composite. Adhesion would be promoted by formed covalent bonds and a 3D siloxane bond system. The resin-composite cement used is acidic (with an initial pH value 2), due to its phosphate groups, as its chemical character, however it is not known or reported that this feature would inhibit chemical reactions of the silane in this study. In contrary,

silanes need an acidic environment to catalyze their necessary hydrolysis (activation) and enable them for polymerization [11].

This study tested the hypothesis that silane monomers with such functional groups as isocyanato, styryl, glycidoxy methacrylate and acrylate in experimental primers significantly enhance bonding, presented as shear bond strength, between an acidic resin composite and silica-coated zirconia compared to a clinically available control silane.

2. Materials and methods

All experimental materials of this study are listed in Table 1; throughout the laboratory work all manufacturers' instructions were followed and by only one operator. The zirconia specimens and resin-composite cement stubs were prepared in a standardized way. First, 144 planar zirconia specimens (surface area, 10 mm x 10 mm; thickness, 3 mm) were embedded in acrylic denture resin blocks to leave one surface free. The surface was kept carefully intact and clean from any acrylic resin remains (visual check). Uniform abrasion pretreatment with RocatecTM Plus sand (with a grain diameter of 110 µm) was performed with an operational pressure of 300 kPa at a perpendicular position approximately 10 mm away, for 60 s with slow rotation of the exposed surface of ca. 1.0 cm². The specimens were cleaned in ethanol for 10 min in an ultrasonic bath, air dried, and protected from dust. The

specimens were divided randomly into two storage-type groups: (a) to be kept dry and (b) to be thermo-cycled, equaling to 12 test groups.

2.1. Activated trialkoxysilanes and silanization

All experimental silane primers were prepared at 1.0% (v/v) in a standard solution of 95.0% (v/v) ethanol and deionized (milli-Q) water that had been adjusted to pH 4.5 with 1 M acetic acid, a procedure further-developed by the authors. The silane primers were allowed to stabilize for 24 h and were then activated for 1 h at room temperature [4,7,18-20]. The two groups of silica-coated zirconia samples were each assigned randomly to 5 sub-groups for silanization. Each silane primer coating was applied with a new, clean brush. The silane was allowed to dry and react for 3 min, and then gently dried with oil-free compressed air.

2.2. Fourier-transform infrared spectroscopic analysis

Hydrolysis of each silane monomer was observed analytically up to 60 min using reflectance-absorbance Fourier-transform infrared spectroscopy (Spectrum One spectrometer; Perkin-Elmer, Beaconsfield, UK) to detect molecular bending, vibration, wagging, and rocking of functional groups [21]. The surface analysis of a silane primer film layer was conducted throughout the spectral range 3800–600 cm^{-1} with a specular reflectance monolayer and grazing angle accessory in which the primer film was placed against a cleaned, planar, inert Ge crystal [18,19].

2.3 Bonding of the resin composite cement and testing

One RelyX™ Unicem cement stub was carefully prepared and bonded to each silica-coated silanized zirconia specimen using polyethylene molds (diameter, 3.6 mm; height, 5.0 mm). The cement was carefully packed against the substrate and the stubs were light-polymerized for 40 s (light-intensity, 470-520 mW/cm²; wavelength, 490 nm) from the top of the stub and also from two lateral directions at the contact area of resin-composite stub to zirconia. The mould was gently removed and the specimens in the dry group were kept in a desiccator for about 2 h before shear bond strength testing. Specimens in the other groups were subjected to thermo-cycling in de-ionized water for 6000 cycles between 5°C and 55°C. The dwelling time at each temperature was 30 s, and the transfer time was 2 s (ISO Standard 10477)[22]. Each study group had 12 specimens (n=12).

The bond strength of the 12 test groups after dry storage and thermo-cycling with 6000 cycles were assessed by applying shear bond strength testing. Zirconia specimens were mounted in a jig of the universal testing machine (Lloyd LRX; Lloyd Instruments, Fareham, UK) and shear force was applied at a crosshead speed of 1.0 mm/min to the adhesive interface until failure occurred.

After debonding, the failure type was assessed and classified according to the failure origin by using an optical microscope, with a magnification of 100x.. “Interfacial failure” (also called adhesive failure in literature) was assigned as to have occurred across the zirconia-resin interface, resulting in exposure of the zirconia surface and with less than 33% of resin-composite remaining, and “mixed failure” with more than 33% but less than 66%, whereas “cohesive failure” occurred within

the resin composite with more than 66% composite remaining on the zirconia surface.

The stress-strain curve was analyzed with Nexygen 2.0 software (Lloyd Instruments, Fareham, UK). Statistical analysis was performed using SPSS version 11.0 (Statistical Package for Statistical Science, Chicago, IL, USA). The means of each group were analyzed by two-way analysis of variance (ANOVA), with shear bond strength as the dependent variable, and silane type and specimen storage type as independent variables. p values of less than 0.05 were considered to be statistically significant in all tests. Multiple comparisons of different surface silanizations were analyzed using Tukey HSD test. Statistical comparison of differences between the storage type of each test group was carried out using t test.

2.4. Scanning electron microscopy analysis

The impact of the surface conditioning after silica-coating, and also the failure area of the shear bond strength tested, of the thermo-cycled samples was evaluated by a scanning electron microscopy, SEM (JSM 5500, Jeol, Tokyo, Japan), study. The zirconia specimens were first mounted on aluminum sample-holder stubs and sputtered with gold (BAL-TEC SCD 050, Balzers AG, Balzers, Liechtenstein). The SEM analysis was then performed with 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 28 and 200 were chosen for a visual observation and to be compared with observations obtained using optical microscopy.

3. Results

All experimental silanes tested resulted in greater shear bond strengths than the control, *i.e.* initial values, with thermo-cycled samples achieving greater shear bond strengths than dry-stored specimens (Table 2a, 2b). While ANOVA revealed a significant influence of the silane type ($p < 0.0001$), and specimen storage ($p < 0.001$) on the shear bond strength values, interaction between silane type and storage conditions was not found ($p < 0.201$). Tukey's *post hoc* test for silane type, with strength as the dependent variable, showed that the highest shear bond strength was obtained for 3-acryloxypropyltrimethoxysilane in both dry and thermo-cycled storage conditions, 11.7 (SD 2.3) MPa and 16.0 (2.5) MPa, respectively. The lowest values were found for the control in both dry and thermo-cycled storage conditions 4.5 (1.3) MPa and 6.5 (2.6) MPa, respectively. The lowest values for an experimental silane primer were 6.8 (2.1) MPa after dry storage and 8.5 (1.6) MPa after thermo-cycling. The visually assessed failure mode after thermo-cycling varied among silane treatment groups (Table 2c). No specimens showed spontaneous debonding, and all exhibited different types of failure, except the group treated with 3-isocyanatopropyltriethoxysilane, which showed interfacial failure only.

Fourier-transform infrared spectroscopy analysis of the experimental silane primers revealed that ethoxy and methoxy groups had reacted and hydrolyzed (releasing C_2H_5OH and CH_3OH , respectively) to yield silanol $\equiv Si-OH$ groups (Fig 2). During activation of the zirconia primers, there were signal changes at the wave number region ranging from 1000 to 1200 cm^{-1} . This finding indicated that the labile $-O-CH_3$ ($-O-C_2H_5$) alkoxy groups had turned into reactive silanol groups. Three

spectra are presented (Fig. 2).^{18,19} The spectra also suggested intensive and complex $\equiv\text{Si-OH}$ and $\equiv\text{Si-O-Si}\equiv$ signals for the control, and the same signals, but with somewhat reduced intensity, for the silane monomers with acrylate and styryl functionalities. The spectra suggest that all the silane primers and control had been converted to silanol oligomers during the first 15 min, but definitely during 60 min.

4. Discussion

There is active on-going discussion around the role of silica-coating on zirconia. One concern is the thickness of the framework: for zirconia restorations with walls thicker than 2 mm, it has been found that silica-coating itself does not weaken flexural strength [23]. Zirconia specimens can be successfully cleaned ultrasonically to remove all loose sand and debris [1], and airborne particle abrasion methods can be used to dramatically enlarge the surface area and thereby enable micromechanical retention [6,13]. As a potential shortcoming, such methods might contribute to flaws that occur after treatment, which can contribute to fracture and thus failure [24]. Nevertheless, there is a general consensus that air-borne particle abrasion and corresponding silica-coating are acceptable pretreatment methods in resin zirconia bonding to promote durable bonding of the framework [5,13-15].

The experimental silane primers used in this study were activated by hydrolysis, in this case catalyzed by acetic acid over a time that is shown to be sufficient, following a procedure supported by the literature [4,18-20]. Numerous studies have concluded that silanes alone do not provide reliable chemical covalent bonding with zirconia due to the inertness of zirconia [3,5,9,14]. After thermo-cycling, all the shear bond strength values were increased, apparently owing to post-

polymerization accelerated by dwelling period at the relatively high temperature, at 55 °C. All the bonding strength values exceeded the 5-MPa minimum set by the International Organization for Standardization [21]. Nevertheless, one should preferably have a closer look at the changes in the shear bond strength value (growth/increase) in this study after thermo-cycling when the bond values produced using experimental primers are compared to the control specimen group (normalization), and after thermo-cycling. In this case it can be observed that experimental 3-glycidoxypropyltrimethoxysilane may produce a growth of 171%, and 3-acryloxypropyltrimethoxy 146 % in the shear bond strength values, respectively. Even 3-isocyanatopropyltriethoxysilane is suggesting a significant enhancement of 31% for the shear bond strength even though its observed adhesion failure mode was interfacial (Table 2a).

There is now found an interesting discrepancy between the experimental 3-methacryloxypropyltrimethoxysilane-based primer and the control silane, because both bear very much chemical similarity, *e.g.* silane compound, solvent, pH [11]. They should in principle have relatively similar performance. However, the adhesion promotion performance of the experimental primer was significantly better, *viz.* it produced 109% higher shear bond results after thermo-cycling, and also a significant rise in shear bond strength value after dry storage, 129%, was observed. The control silane is a prehydrolyzed clinical product, which means that it consists of polymerized silane aggregates (oligomers) which may have lost the initial reactivity regardless its reported relatively long suggested self life (often 2-3 years). In general it should be noted that there are significant chemical differences between

commercially available silane products and their bonding properties in clinical dentistry [26]. Styrylethyltrimethoxysilane, a reactive aromatic silane (cf. Fig. 1b) was evaluated previously as a dual silanization reagent in combination with other silane monomers for experimental nanocomposites: the results suggested that high biaxial flexural strength values were obtained using it for filler silanization [17]. At the moment, 3-glycidoxypropyltrimethoxysilane (an epoxy type silane) is used as coupling agent for epoxy composites employed in electronic chip encapsulation and to prepare epoxy-containing hybrid organic-inorganic materials.

Silanization of the silica-coated zirconia surfaces with all of the silane primers resulted in statistically greater shear bond strengths than the control. As a comparison to figure out the magnitude of the obtained shear bond strength values, they agree with some bond strength values in clinical dentistry published in the literature: *e.g.* between resin-composite bonding to enamel (18-22 MPa) and resin-composite cement bonding to enamel for orthodontic brackets (18-20 MPa) [27]. 3-Isocyanatopropyltriethoxysilane led to statistically equally low bonding strength as the control silane, which has approximately the same low silane concentration as the experimental primers in this study, but has another silane compound, viz. 3-methacryloxypropyltrimethoxysilane. This is somewhat surprising to observe because treatment of a silica-coated Ti surface with experimental 3-isocyanatopropyltriethoxysilane primer has been shown to promote adhesion significantly more than compared to 3-methacryloxypropyltrimethoxysilane [18]. However, it is essential to note that all-ceramic surfaces and silica-coated metal surfaces are not equivalent or comparable as such.

Chemically probably the most reactive silane monomer in this study, 3-glycidoxypropyltrimethoxysilane which yielded the highest shear bond values for thermo-cycled specimens. This is supported by some other studies of the authors [19, 20, 28]. The observed failure mode was mainly interfacial (adhesive) for this silane, whereas both styrylethyltrimethoxysilane and 3-glycidoxypropyltrimethoxysilane exhibited 50% interfacial failure, 3-acryloxypropyltrimethoxysilane and 58%, control 50% and 3-methacryloxypropyltrimethoxysilane 42% cohesive failure. For an unknown reason, control was not observed to exhibit a mixed failure (Table 2c). It is noteworthy that siloxane films on the substrates cannot be detected by SEM imaging. SEM images (Fig. 3a-b) are of a tested thermo-cycled specimen, silanized with 3-glycidoxypropyltrimethoxysilane and demonstrating a cohesive failure type. Good bonding and contact to the zirconia in this case are apparent.

Nevertheless, bond strength results based on shear bond strength testing are often criticized. The typical failure mode during shear bond strength testing is a sliding or in-plane shear mode in which the cracked surfaces slide over one another in a direction perpendicular to the leading edge of the crack [5,13,18-20,29]. This is, however, also the typical mode during which the adhesive such as a silane primer, exhibits increased resistance to fracture. Hence, bonding and adhesion studies are being performed more frequently using microtensile bond strength testing [3,4,7], which can be described as testing under a tensile (“opening”) mode, where the loading is normal to the crack. Given that a limitation of both microtensile and shear bond strength testing is unintentional antiplane shear mode (or tearing), the

measurement of fracture toughness has been suggested [29, 30]. Still, shear bond strength testing may be considered relevant in providing an initial idea of whether adhesion has been chemically promoted or not using various silane monomers in experimental primers, though the relevance for presenting the dry-storage results might remain disputable. Nevertheless, the authors feel it is important to report also them [5].

It is noteworthy that, for unknown reasons, silane treatment has not been observed to strengthen the porcelain matrix and its flexural strength [31]. This question should be investigated for silica-coated zirconia as well. As the next step for the authors, the effect of concentration of the three functional silanes evaluated here merits further study, on bond strength (*e.g.* shear bond strength) after long-term water storage. Thus the hydrolytic stability of the silane film between silica-coated zirconia and resin composite cement should be assessed. The authors summarize that silane coupling agents exhibit a unknown and huge potential in biomaterials science, let alone silane compounds (organic silicon derivatives) have no intrinsic toxicity [32].

The hypotheses of this study was met: a significant bond strength enhancement may take place using some less usual silane monomers in experimental primers.

5. Conclusion

Silanization with four experimental silane primers produced significantly greater shear bond strengths after artificial aging than a ready-to-use control silane. 3-

acryloxypropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane or styrylethyltrimethoxysilane may enhance the bonding of organophosphate resin to silica-coated zirconia significantly and merits further investigations.

Acknowledgements

The authors wish to thank Dr. Barry Arkles (Gelest Inc., Tullytown, PA, USA) for donating the silane monomers and Dr. Trevor Lane (The University of Hong Kong) for proofreading the manuscript.

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Table 1 Materials used in this study.

Brand	Description	Manufacturer	Purity (%)	Batch
Procera AllZircon	Zirconium dioxide (zirconia)	Nobel Biocare, Göteborg, Sweden	N/A	N/A
Rocatec Plus	Sand, silica-coated alumina (diameter 110 µm)	3M ESPE, Seefeld, Germany	N/A	260762
RelyX Unicem	Adhesive resin cement paste, shade A2, bis-GMA, TEGDMA, silane treated ceramic and silica fillers, functionalized DMA	3M ESPE, Seefeld, Germany	N/A	259571
RelyX Ceramic Primer	Dilute 3-methacryloxypropyltrimethoxysilane in organic solvent	3M ESPE, St. Paul, MN, USA	N/A	6XJ
Z-6030	3-Methacryloxypropyltrimethoxysilane	Dow Corning Toray Silicone, Tokyo, Japan	98	VN02011454
SIA0200.0	3-Acryloxypropyltrimethoxysilane	Gelest, Morrisville, PA, USA	95	5C-6412
SIS6990.0	Strylethyltrimethoxysilane	Gelest, Morrisville, PA, USA	92	7D-10467-5
SII6455.0	3-Isocyanatopropyltriethoxysilane	ABCR, Karlsruhe, Germany	95	9E-14595
SIG5840.0	3-Isocyanatopropyltriethoxysilane	Gelest, Morrisville, PA, USA	98	N/A
Ethanolum Anhydricum	Ethanol	Arcus, Oslo, Norway	99.5	030305
Acetic acid	Acetic acid	Merck, Darmstadt, Germany	100	K12716063

Table 2a Tested zirconia specimens with cements stubs (n = 12). Key: MPS = 1.0 vol% 3-methacryloxypropyltrimethoxysilane, ACPS = 1.0 vol% 3-acryloxypropyltrimethoxysilane, STYRX = 1.0 vol% styrylethyltrimethoxysilane; ABCR, Germany), ICS = 1.0 vol% 3-isocyanatopropyltriethoxysilane, GPS = 1.0% glycidoxypropyltrimethoxysilane, and Control: RelyX Ceramic Primer, 3M ESPE, USA.

Silane	Shear bond strength + standard deviation (dry storage)/MPa	Change to Control/%	Shear bond strength + standard deviation (thermo-cycled)/MPa	Change to Control/%
MPS	10.3 (3.4)	129	13.6 (4.9)	109
ACPS	11.7 (2.3)	146	16.0 (2.5)	146
STYRX	10.3 (3.0)	128	14.9 (4.3)	129
ICS	6.8 (2.1)	51	8.5 (1.6)	31
GPS	7.8 (1.0)	73	17.6 (4.1)	171
Control	4.5 (1.3)	-	6.5 (2.6)	-

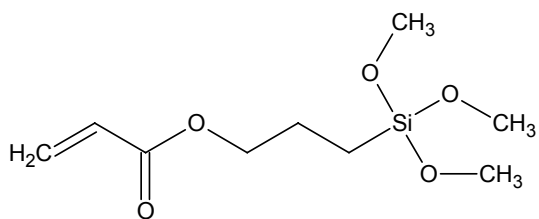
Table 2b Statistical analysis: tests of between-subjects effects. Results of two-way ANOVA for the shear bond strength of the experimental silane primers. Dependent variable: strength.

Source	Sum of Squares	df	Mean Square	F	Significance
Corrected Model	2293.153 a	11	208.486	23.174	0.000
Storage	683.662	1	683.662	75.998	0.000
Silane	1330.303	5	266.061	29.576	0.000
Storage * Silane	268.924	5	53.785	5.979	0.000
Error	1214.432	135	8.996		
Total	20416.781	147			

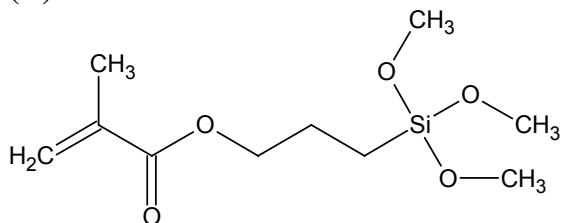
a. R Squared = 0.654 (Adjusted Squared = 0.626)

Table 2c Failure mode analysis after thermo-cycling, 6000 x between 5-55 °C. Key: See Table 2a.

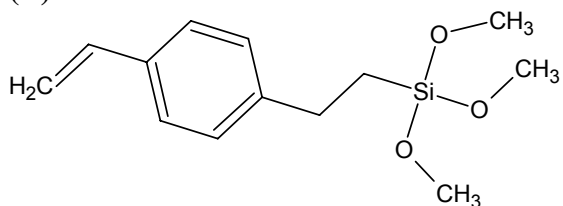
Silane	Spontaneous debonding	Cohesive failure	Mixed failure	Interfacial failure
Control	0	6	0	6
MPS	0	5	3	4
ACPS	0	3	2	7
STYRX	0	3	3	6
GPS	0	4	2	6
ICS	0	0	0	12



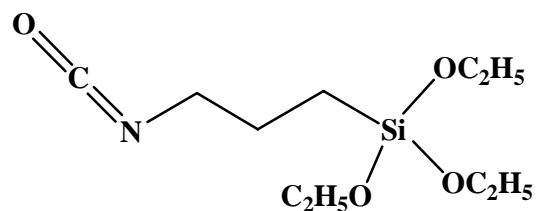
(A)



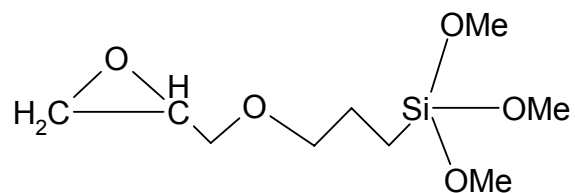
(B)



(C)



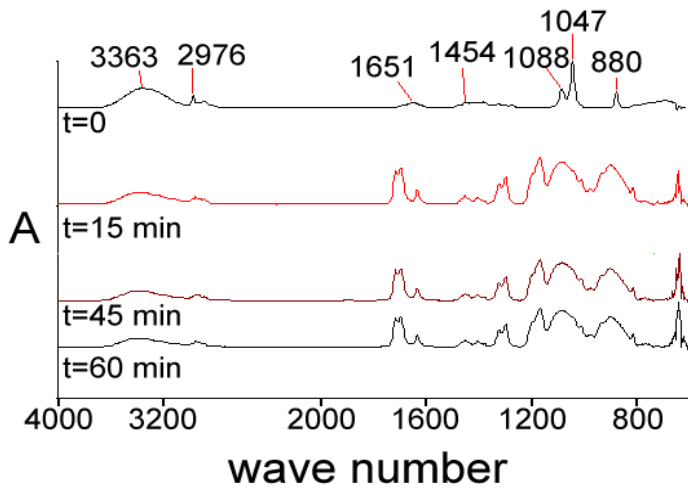
(D)



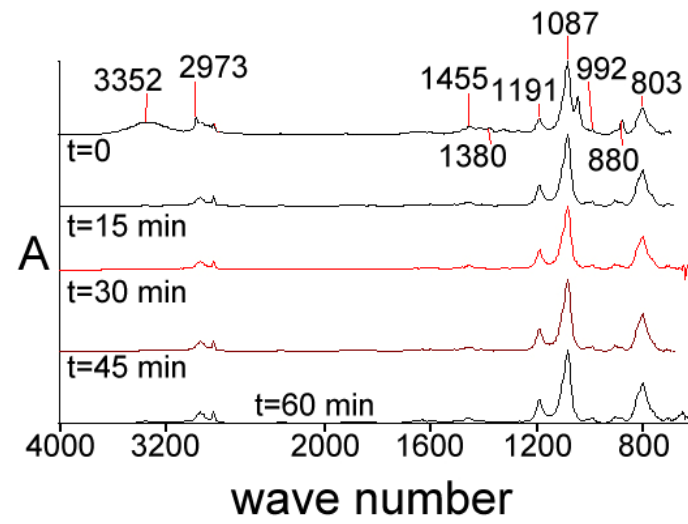
(E)

Fig. 1 Structures of silane monomers used in the experimental primers:

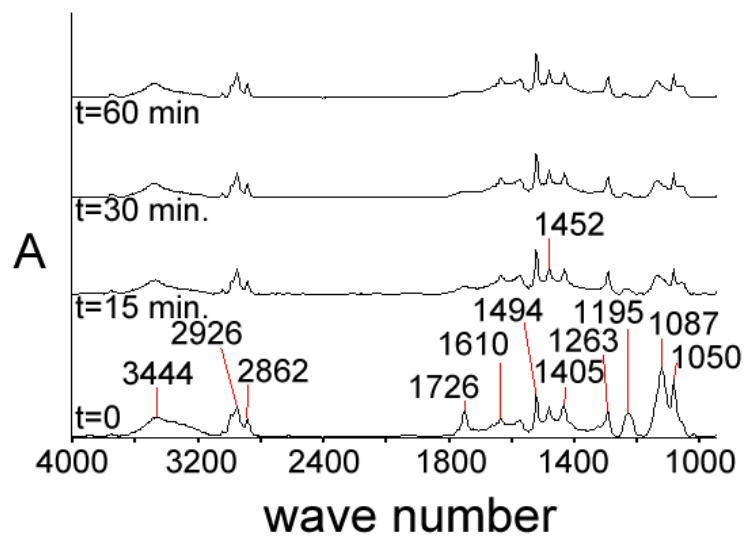
(A) 3-Acryloxypropyltrimethoxysilane, (B) 3-Methacryloxypropyltrimethoxysilane (also present in the control), (C) Styrylethyltrimethoxysilane, (D) 3-Isocyanatopropyltriethoxysilane, (E) 3-Glycidoxypropyltrimethoxysilane.



(A)



(B)



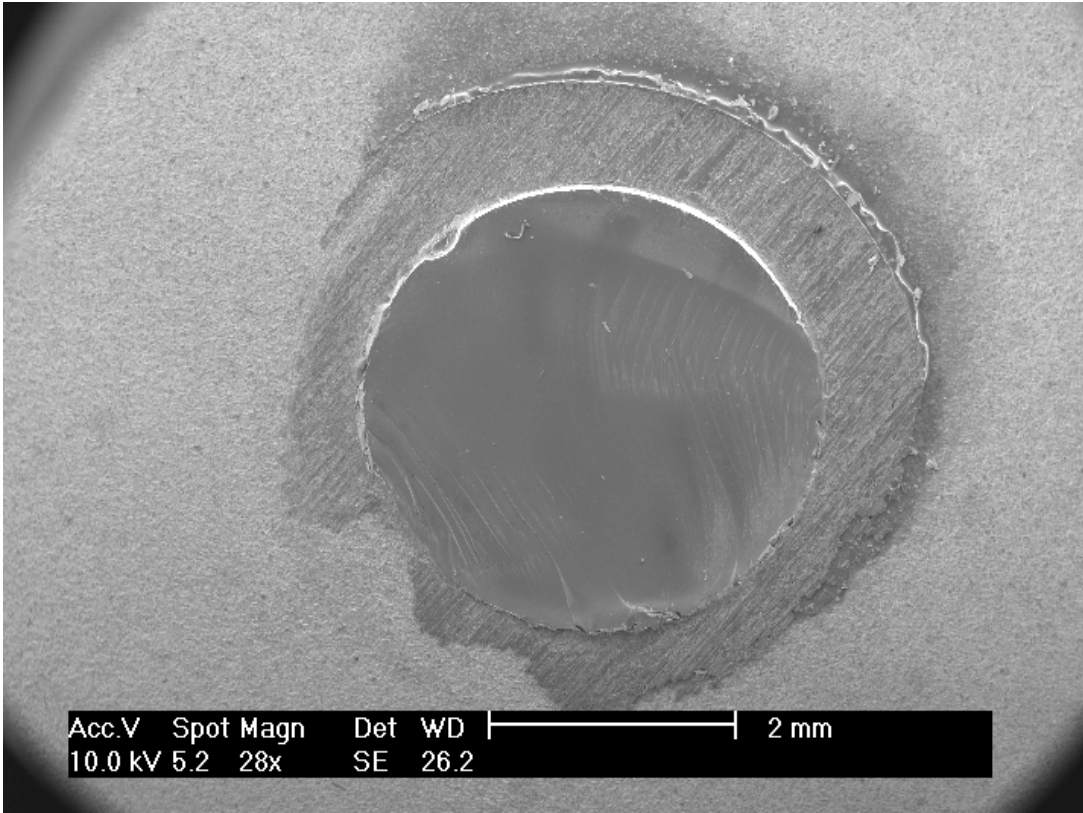
(C)

Fig. 2 Fourier-transform infrared spectra of some silane monomers in the experimental primers and activation reactions within 1 h (Key: 'A' = absorbance (in arbitrary units), 'wave number' as cm^{-1}):

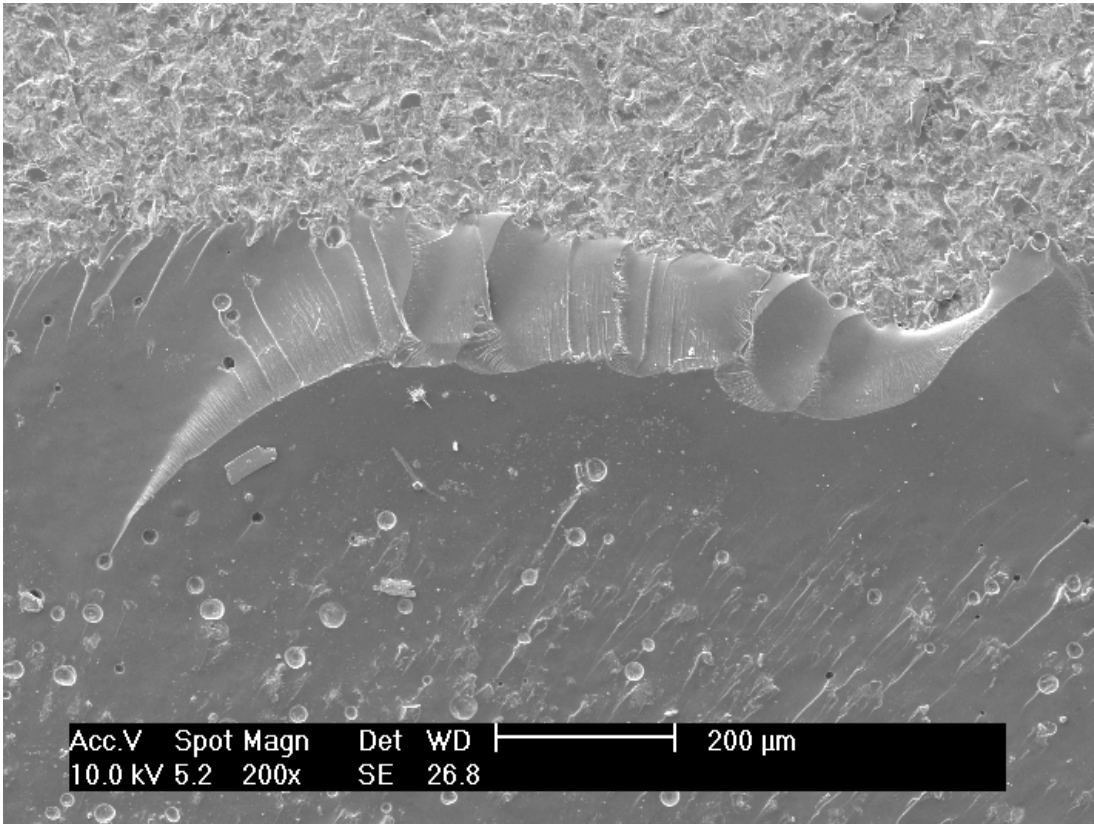
(A) The control silane,

(B) Styrylethyltrimethoxysilane,

(C) 3-Acryloxypropyltrimethoxysilane.



a)



b)

Fig. 3 SEM images of zirconia specimens after thermal aging (thermo-cycling) showing the cohesive failure (fracture) mode. Images of a zirconia specimen silanized with 3-glycidoxypropyltrimethoxysilane.