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# Resin Bonding to Silicized Zirconia with Two Isocyanatosilanes and a Cross-linking Silane. Part I: Experimental

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**Abstract** In this study we have investigated the effects of the chain length of hydrolyzable groups in two isocyanato silane coupling agents, 3-isocyanatopropyltrimethoxysilane and 3-isocyanatopropyltriethoxysilane, on the shear bond strength of resin attached to silicized zirconia. In addition, the effects of varying the silane concentration (at 0.1 vol% and 1.0 vol%) with or without the addition of a cross-linking silane (0.05 vol% or 0.5 vol% *bis*-1,2-(triethoxysilyl)ethane) were assessed. It was concluded that the use of the experimental primer of 3-isocyanatopropyltrimethoxysilane at either 0.1 vol% or 1 vol% with cross-linking silane resulted in significantly higher shear bond strengths than the use of primer without the cross-linking silane.

**Keywords** Silane · 3-isocyanatopropyltrimethoxysilane · 3-isocyanatopropyltriethoxysilane · *bis*-1,2-(triethoxysilyl)ethane · 3-methacryloxypropyltrimethoxysilane · Cross-linking · Hydrolyzable group · Zirconia

## 1 Introduction

Zirconia (zirconium dioxide,  $ZrO_2$ ) is used in dentistry and is doped with a small amount of yttria ( $Y_2O_3$ ) tetragonal zirconia polycrystal (Y-TZP). The role of the added yttria is to stabilize the crystal structure transformation during firing at elevated temperatures and to improve the physical properties of zirconia [1]. Yttria-stabilized zirconia is widely used as a dental biomaterial in prosthodontic frameworks because of its

high flexural strength (reported in the literature as 900–1200 MPa) compared with other common ceramic materials such as alumina and base metal alloys such as Co-Cr [2]. Dental zirconia is a dense ceramic biomaterial that has a compression resistance of about 2,000 MPa [3]. Moreover, many investigations on the biocompatibility of yttria-modified zirconia have reported no cytotoxic effects on *in vitro* cell cultures [4] and no adverse *in vivo* tissue reactions in animals [5]. However, the bonding between zirconia and resin cement is relatively weak owing to the extremely inert character of zirconia. Derand et al. [6] reported that the shear bond strength between yttrium-stabilized zirconia and composite, without any pretreatment of the zirconia surface, was only about 1.5 MPa. For samples pretreated with micro pearls of low fusing porcelain and fired at 720 °C and some of them were further treated with silane, the shear bond strengths were 11.3 and 18.4 MPa, respectively, which were much higher than the samples without any treatment. The results revealed that the surface should be pretreated.

It is well understood that functional silane coupling agents have to be activated by hydrolysis before they can react with the substrate, via –OH groups on the substrate surface. Plueddemann and Clark [7, 8] reported that silane coupling agents were effective at significantly promoting adhesion between inorganic substrates such as metals, metal oxides, glass, silicates and organic matrices, including various plastics that are reinforced by fillers, whiskers and fibers. A complex but labile 3D silane film forms during the bonding of the dissimilar matrices to each other. The bonding strength between dental resin-composite cement and zirconia is increased by chemical bonds that form between the silica-coated zirconia and the silane, after the hydrolysis of the silane monomer to form silanol ( $\equiv Si-OH$ ). As a suggested pretreatment procedure, the zirconia surface must be silica-coated [9], because intaglio zirconia

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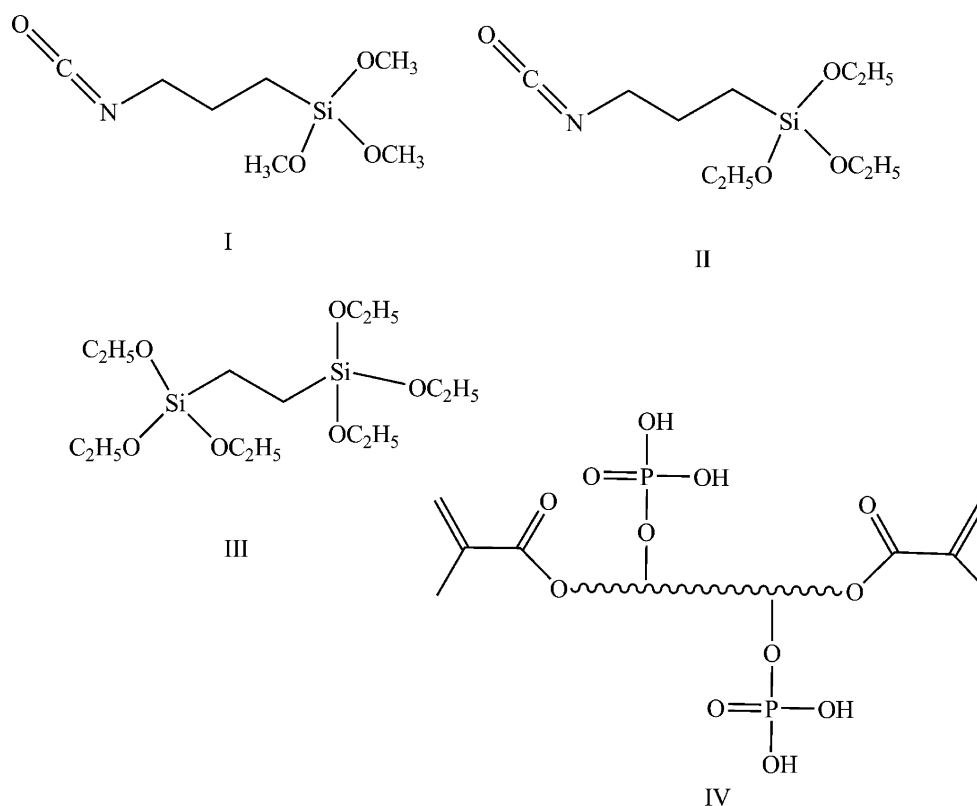
**Table 1** Materials used in this study

Materials	Manufacturer	Purity/%	Lot. No.
Zirconia (Procera™)	Nobel-Biocare, Sweden	N/A	N/A
3-isocyanatopropyltrimethoxysilane	Gelest, USA	95	5I-7514
3-isocyanatopropyltriethoxysilane	Gelest, USA	95	9E-14595
bis-1,2-(triethoxysilyl)ethane	Gelest, USA	N/A	5L-7926
Rocatec Sand Soft	3M ESPE, Germany	30 μm silica-coated alumina	353587
Deionized water	Millipore, Bedford, Massachusetts, USA	Resistivity 18.2 MΩ cm	N/A
Ethanol	Riedel-de Haën, Germany	99.8	03550
Rely X Unicem Aplicap resin cement	3M ESPE, Germany	N/A	363991
3M ESPE Sil-silane	3M ESPE, Germany	< 3% 3-methacryloxypropyltrimethoxysilane	259583

is inert and does not react with silanes. Silica-coating can be performed in dentist's office with a special sand-blasting system using Rocatec Sand Soft (a silica-coated alumina sand with an average particle diameter of 30 μm). This sand-blasting concept is widely used also in dental laboratories and applied in prosthetic dentistry. The technique is based on the principle that silica-coated alumina sand particles become anchored to the substrate surface, be it metal, alloy, amalgam, resin-composite or ceramic material. The sand particles on the surface bond as a very thin ceramic-like coating, which is why this method

is sometimes called ceramic coating; it is more frequently known as silica-coating. Sandblasting also increases the surface roughness of zirconia and thus modifies its topology, which enhances the wetting of the silica-coated surface with silane during silanization [10].

Known applications of 3-isocyanatopropyltriethoxysilane include the functionalization of β-cyclodextrin for cholesterol removal from milk [11] and as a coupling agent for UV-curable epoxyacrylate resin to improve their mechanical properties in protective coatings [12]. Matinlinna et al. [13] demonstrated that isocyanatosilane achieved a significantly



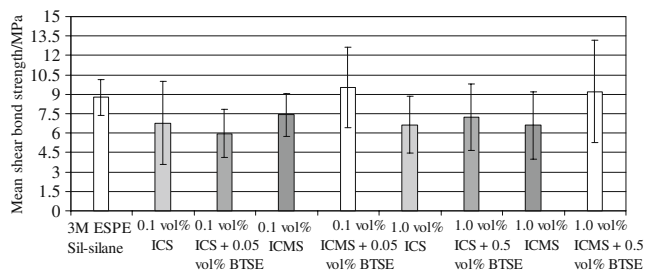
**Fig. 1** The molecular structures of the two isocyanatosilanes, cross-linking silane and reactive monomer in resin-composite. I: 3-isocyanatopropyltrimethoxysilane, II: 3-isocyanatopropyltriethoxysilane, III: bis-1,2-(triethoxysilyl)ethane and IV: reactive monomer in resin-composite

**Table 2** Mean shear bond strength of ICMS and ICS with or without addition of cross-linking silane (BTSE). Key: ICMS: 3-isocyanatopropyltrimethoxysilane, ICS: 3-isocyanatopropyltriethoxysilane, BTSE: *bis*-1,2-(triethoxysilyl)ethane

Silane	Mean shear bond strength $\pm$ SD/MPa	Coefficient of variation	Cohesive failure/%	Mixed failure/%	Adhesive failure/%
ICS (0.1 vol%)	6.8 $\pm$ 3.2	47.3	0	13.3	86.7
ICS (1.0 vol%)	6.6 $\pm$ 2.2	33.0	0	0	100
ICS (0.1 vol %) + BTSE (0.05 vol%)	6.0 $\pm$ 1.9	31.5	6.7	20	73.3
ICS (1.0 vol %) + BTSE (0.5 vol%)	7.2 $\pm$ 3.1	43.1	13.3	23.3	73.3
ICMS (0.1 vol%)	7.4 $\pm$ 1.7	22.5	6.7	13.3	80
ICMS (1.0 vol%)	6.6 $\pm$ 2.6	39.2	0	13.3	86.7
ICMS (0.1 vol %) + BTSE (0.05 vol%)	9.5 $\pm$ 2.6	26.9	6.7	20	73.3
ICMS (1.0 vol %) + BTSE (0.5 vol%)	9.2 $\pm$ 3.9	42.8	6.7	20	73.3
3M ESPE silane	8.8 $\pm$ 1.4	16.0	6.7	13.3	80

higher shear bond strength specifically the adhesion between silicized titanium and an experimental resin based on *bis*-phenol-A-diglycidyl dimethacrylate (*bis*-GMA), than 3-methacryloxypropyltrimethoxysilane. It should be emphasized that water is always present in the interface of the silane (siloxane) film and silicized zirconia surface under ambient humidity [8]. Water molecules can penetrate freely into the siloxane network and form hydrogen bonds among the polar functional groups. This process results in a reduction in thermal stability and polymer plasticization [14]. The amount of water adsorbed varies with the relative humidity of the environment.

The aim of this study, as an extension of some previous work [13], was to investigate the effects of varying hydrolyzable groups of isocyanatosilanes and silane concentrations, as well as the effect of adding a cross-linking silane, on the shear bond strength of a modern resin-composite attached to silicized zirconia. The specimens were stored and tested in dry conditions under ambient humidity at room temperature to investigate the initial bond strength. The hypothesis of this *in vitro* study was that differences in bond shear strength would result from different alkoxy group types and by blending the functional silane.

**Fig. 2** Mean shear bond strengths of silicized and silanized zirconia of control group and at two different concentrations of ICS and ICMS with cross-linking silane added. Key: ICS = 3-isocyanatopropyltriethoxysilane, BTSE = *bis*-1,2-(triethoxysilyl)ethane, ICMS = 3-isocyanatopropyltrimethoxysilane

## 2 Materials and Methods

The materials used in this study are listed in Table 1. A square-shaped zirconia specimen with a surface area of about 10 mm $\times$ 10 mm was embedded in cylinder-shaped plastic mold filled with PMMA acrylic resin. 15 specimens were prepared for each study group with a total of 135 specimens for 9 study groups. The two isocyanatosilanes in this study were 3-isocyanatopropyltrimethoxysilane and 3-isocyanatopropyltriethoxysilane. The cross-linking silane used was *bis*-1,2-(triethoxysilyl)ethane. The molecular structures of the silanes and the reactive monomer present in the resin-composite cement are shown in Fig. 1.

### 2.1 Preparation of Silica-coated Zirconia

The surfaces of the zirconia specimens were first polished with 400-grit silicon carbide paper under running water. They were then cleaned ultrasonically (Decon Ultrasonics Ltd, Hove Sussex, England) for 10 min in deionized water and rinsed with 70% ethanol. After the specimens were allowed to dry at room temperature, their surfaces were sandblasted with 3M ESPE Rocatec Sand Soft (particle size, 30  $\mu$ m) at a constant pressure of 280 kPa for 30 s/cm<sup>2</sup> and at a perpendicular distance of 10 mm. The specimens were transferred to a beaker filled with 70% ethanol and cleaned ultra-sonically for 10 min and then rinsed with 70% ethanol. The specimens were allowed to air-dry at room temperature for 1 h. All specimens were prepared by one operator.

### 2.2 Preparation of Silane Solution and Silanized Zirconia

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 stabilize for at least 24 h at about 7 °C (in a refrigerator) before use. The preparation procedure for the silane solution has been

**Table 3** ANOVA: single-factor analysis of 0.1 vol% ICMS with cross-linking silane. Key for Tables 3, 4, 5, 6, 7, 8, and 9: ICS = 3-isocyanatopropyltriethoxysilane, ICMS = 3-isocyanatopropyltrimethoxysilane, BTSE = bis-1,2-(triethoxysilyl)ethane

Silane	Count	Sum	Average	Variance		
0.1 vol% ICMS	15	111.19	7.412667	2.79895		
0.1 vol% ICMS + 0.05 vol% BTSE	15	142.82	9.521333	6.577584		
Source of variation	SS	df	MS	<i>F</i>	<i>P</i> -value	<i>F</i> crit
Between groups	33.34856	1	33.34856	7.113197	0.012572	4.195982
Within groups	131.2715	28	4.688267			
Total	164.62	29				

**Table 4** ANOVA: single factor analysis of 1.0 vol% ICMS with cross-linking silane

Silane	Count	Sum	Average	Variance		
1.0 vol% ICMS	15	98.8	6.586667	6.663952		
1.0 vol% ICMS and 0.5 vol% BTSE	15	138.1	9.206667	15.5591		
Source of variation	SS	df	MS	<i>F</i>	<i>P</i> -value	<i>F</i> crit
Between groups	51.483	1	51.483	4.633298	0.040122	4.195982
Within groups	311.1227	28	11.11152			
Total	362.6057	29				

**Table 5** ANOVA: single-factor analysis of 0.1 vol% ICS with cross-linking silane

Silane	Count	Sum	Average	Variance		
0.1 vol% ICS	15	101.79	6.786	10.32104		
0.1 vol% ICS + 0.05 vol% BTSE	15	89.54	5.969333	3.540592		
Source of variation	SS	df	MS	<i>F</i>	<i>P</i> -value	<i>F</i> crit
Between groups	5.002083	1	5.002083	0.721716	0.402787	4.195982
Within groups	194.0629	28	6.930816			
Total	199.0649	29				

**Table 6** ANOVA: single-factor analysis of 1.0 vol% ICS with cross-linking silane

Silane	Count	Sum	Average	Variance		
0.1 vol% ICS	15	99.6	6.64	4.810229		
0.1 vol% ICS + 0.05 vol% BTSE	15	108.24	7.216	9.659997		
Source of variation	SS	df	MS	<i>F</i>	<i>P</i> -value	<i>F</i> crit
Between groups	2.48832	1	2.48832	0.343923	0.562272	4.195982
Within groups	202.5832	28	7.235113			
Total	205.0715	29				

**Table 7** ANOVA: single-factor analysis of control silane, 0.1 vol%, 1.0 vol% of ICS and ICMS

Silane	Count	Sum	Average	Variance		
3M ESPE silane	15	131.37	8.758	1.965531		
0.1 vol% ICS	15	91.96	6.130667	7.994607		
0.1 vol% ICMS	15	111.19	7.412667	2.79895		
1.0 vol% ICS	15	99.6	6.64	4.810229		
1.0 vol% ICMS	15	98.8	6.586667	6.663952		
Source of variation	SS	df	MS	<i>F</i>	<i>P</i> -value	<i>F</i> crit
Between groups	63.91929	4	15.97982	3.297084	0.015574	2.502659
Within groups	339.2658	70	4.846654			
Total	403.185	74				

described elsewhere [15]. Concentrations of 0.1 vol% and 1.0 vol% of 3-isocyanatopropyltrimethoxysilane and 3-isocyanatopropyltriethoxysilane in the solvent mixture were prepared in a 25 mL volumetric glass flask. The silane primers were allowed to hydrolyze for 1 h at room temperature [16].

The cross-linking silane at concentrations of 0.05 vol% and 0.5 vol% in the solvent mixture were separately allowed to hydrolyze for 23 h. The two functional silane coupling agent monomers were then added, corresponding to a final functional silane concentration of 0.1 vol% and 1.0 vol%. The silane primer was then allowed to hydrolyze for 1 additional hr [17].

The silane solution was applied onto the surface of each zirconia specimen with a new fine brush each time, and allowed to react and dry for 5 min on the zirconia surface. 3M ESPE Silsilane was used as a control; this is commonly used in the dental clinic and is a pre-hydrolysed silane product that has one functional silane, 3-methacryloxypropyltrimethoxysilane, at a silane content of about 1 vol% to 2 vol%.

### 2.3 Procedure to Bond Resin Cement to Silica-coated and Silanized Zirconia

RelyX resin cement (a so-called universal dental resin-composite cement) from 3M ESPE was activated according to manufacturer's instructions and transferred to a high-frequency mixing unit (Silamat, Ivoclar Vivadent, Schaan, Liechtenstein) for 15 s. The resin-composite cement was

transferred to a cylindrical polyethylene mold with a diameter of 3.7 mm and height of 4.0 mm, which was held firmly in place on the surface of the zirconia. The resin-composite cement stub, with an average height of 4.0 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 and silicized and silanized zirconia. The wavelength ranged from 400 nm to 500 nm and the light intensity was 1,300 mW/cm<sup>2</sup>. The mold was carefully removed by pressing the stub gently with an instrument while the mold was lifted upwards. The specimens were kept in a desiccator for 24 h before shear bond strength testing.

### 2.4 Shear Bond Strength Testing

The zirconia specimen with the light-cured resin-composite stub was mounted on the materials testing instrument (Instron LTD, Model 1185, Norwood, MA). A load of 1,000 N was applied at a cross-head speed of 1.0 mm/min [15] until failure occurred. The shear bond strength 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.

### 2.5 Failure Type Analysis

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. When 1/3 or less

**Table 8** ANOVA: single-factor analysis of 0.1 vol% and 1.0 vol% of ICS

Silane	Count	Sum	Average	Variance		
0.1 vol% ICS	15	101.79	6.786	10.32104		
1.0 vol% ICS	15	99.6	6.64	4.810229		
Source of variation	SS	df	MS	<i>F</i>	<i>P</i> -value	<i>F</i> crit
Between groups	0.15987	1	0.15987	0.021131	0.885464	4.195982
Within groups	211.8378	28	7.565634			
Total	211.9976	29				

**Table 9** ANOVA: single-factor analysis of 0.1 vol% and 1.0 vol% of ICMS

Groups	Count	Sum	Average	Variance		
0.1 vol% ICMS	15	111.19	7.412667	2.79895		
1.0 vol% ICMS	15	98.8	6.586667	6.663952		
Source of variation	SS	df	MS	F	P-value	F crit
Between groups	5.11707	1	5.11707	1.081501	0.307259	4.195982
Within groups	132.4806	28	4.731451			
Total	137.5977	29				

of the resin stub remained, the failure type was assigned as ‘adhesive’ and when the amount remaining was  $>1/3$  but  $<2/3$ , it was classified as ‘mixed’. When the amount remaining was  $\geq 2/3$ , it was classified as ‘cohesive’ failure [18].

## 2.6 Scanning Electron Microscopy (SEM)

SEM (XL30CP, Philips Electron Optics, Eindhoven, The Netherlands) analysis of the polished and silica-coated zirconia surfaces and resin bonding to zirconia after shear bond test was performed. The operational voltage was 10 kV. The vacuum pressure for measurement was  $3.5 \times 10^{-5}$  Pa. Tungsten filament was used for electron beam generation. The secondary electron detector was used for detecting the secondary electron signals.

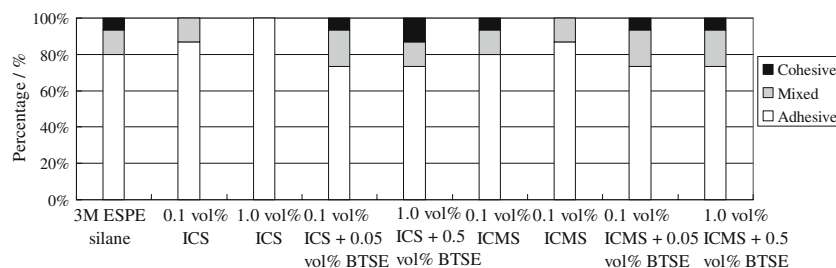
## 2.7 Statistical Analysis

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 analyzed by ANOVA with mean shear bond strength as the dependent variable and concentration, type of silane and addition of cross-linking silane as independent variables. A  $p$  value  $< 0.05$  was taken as being statistically significant.

## 3 Results and Discussion

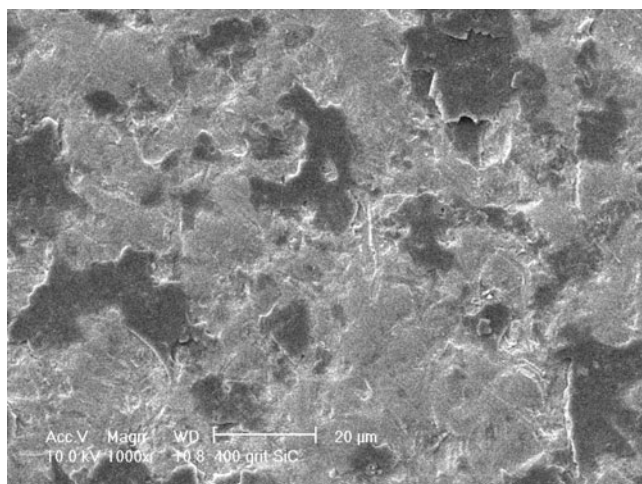
The results for all mean shear bond strengths measured for 3-isocyanatopropyltrimethoxysilane and 3-

isocyanatopropyltriethoxysilane with and without the addition of the cross-linking silane (*bis*-1,2-(triethoxysilyl)ethane) in dry conditions are summarized in Table 2 and Fig. 2. ANOVA analysis (Tables 3, 4, 5, 6, 7, 8, and 9) revealed that there were no significant differences in the mean shear bond strengths between 0.1 vol% and 1.0 vol% concentrations of 3-isocyanatopropyltrimethoxysilane ( $p=0.307$ ) and 3-isocyanatopropyltriethoxysilane ( $p=0.885$ ). There were also no significant differences in the mean shear bond strengths between 3-isocyanatopropyltrimethoxysilane and 3-isocyanatopropyltriethoxysilane at concentrations of 0.1 vol% ( $p=0.205$ ) and 1.0 vol% ( $p=0.952$ ). However, there were significant differences between the control group, 0.1 vol% and 1.0 vol% for 3-isocyanatopropyltrimethoxysilane ( $p<0.02$ ) and for 3-isocyanatopropyltriethoxysilane ( $p<0.04$ ). There were significant differences in shear bond strengths after cross-linking silane had been added, both for 0.1 vol% 3-isocyanatopropyltrimethoxysilane ( $p<0.01$ ) and 1.0 vol% 3-isocyanatopropyltrimethoxysilane ( $p<0.04$ ). In contrast, there were no significant differences in mean shear bond strengths after cross-linking silane had been added to 3-isocyanatopropyltriethoxysilane at 0.1 vol% ( $p=0.403$ ) or 1.0 vol% ( $p=0.562$ ). There was no significant difference between the control group and 3-isocyanatopropyltrimethoxysilane at 0.1 vol% ( $p=0.320$ ) or 1.0 vol% ( $p=0.681$ ) with cross-linking silane added, but there were significant differences between the control group and 3-isocyanatopropyltriethoxysilane at 0.1 vol% ( $p<8 \times 10^{-5}$ ) or 1.0 vol% ( $p<0.009$ ) with cross-linking silane added. There was also a significant difference between the control group, 0.1 vol% and



**Fig. 3** Percentage modes of failure of nine tested groups. Key: ICS = 3-isocyanatopropyltriethoxysilane, BTSE = *bis*-1,2-(triethoxysilyl)ethane, ICMS = 3-isocyanatopropyltrimethoxysilane



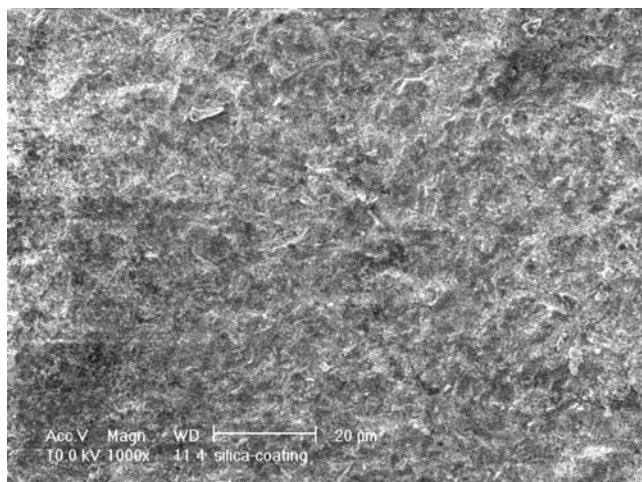


**Fig. 4** Zirconia surface by polishing (SEM image, magnification 1,000×)

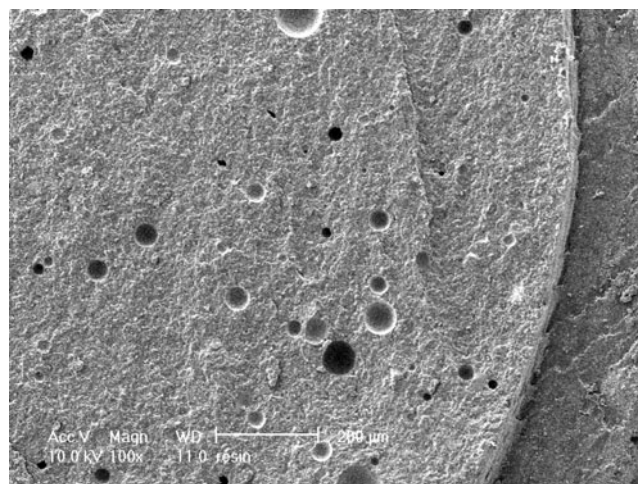
1.0 vol% 3-isocyanatopropyltriethoxysilane and 3-isocyanatopropyltrimethoxysilane ( $p < 0.02$ ). The failure mode assessment is presented in Table 2. A bar-chart diagram summarizing the results of the failure mode assessment is shown in Fig. 3.

The SEM analysis of the images of the polished zirconia surface (Fig. 4) and the silica-coating zirconia surface (Fig. 5) showed some differences. It can be seen clearly from Fig. 5, that the silica-coated alumina particles were finely divided depositing on the polished zirconia surface. Figure 6 showed silica-coated zirconia surface and silanized with 0.1 vol% ICMS and with light-cured RelyX resin cement residue after shear bond test.

This study of the chain length of the hydrolyzable groups of two isocyanatosilanes on the shear bond strength of silicized zirconia revealed that the rate of hydrolysis is slower the more bulkier the hydrolyzable alkoxy group is. The hydrolysis of the



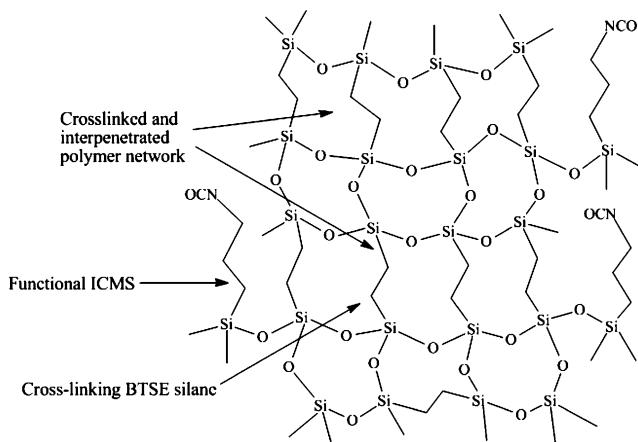
**Fig. 5** Silica-coated zirconia surface (SEM image, magnification 1,000×)



**Fig. 6** RelyX resin cement residue left on the zirconia surface after shear bond test (SEM image, magnification 100×)

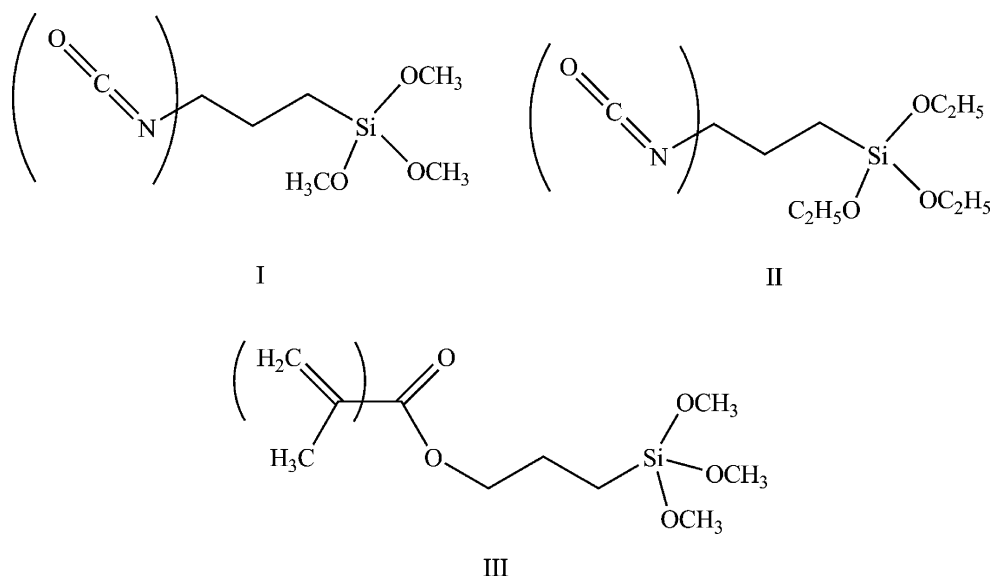
silane takes place by a bimolecular nucleophilic substitution ( $S_N2$ ) reaction at the silicon atom [19], in which there is nucleophilic backside attack of the central silicon atom in the silane backbone. A new bond is formed between the nucleophile and the silicon, while a bond is broken between the leaving group (alcohol) and silicon. The rate of hydrolysis for 3-isocyanatopropyltrimethoxysilane is thus faster than for 3-isocyanatopropyltriethoxysilane, because methoxy groups hydrolyze at a rate that is approximately 10 times that of ethoxy groups. Therefore, the mean shear bond strength value for the former is greater than for the latter, although the difference is statistically insignificant.

The addition of a cross-linking silane to form a blend with a functional silane enhanced the bonding of resin to zirconia. This was statistically significant for the tested groups for 3-isocyanatopropyltrimethoxysilane (0.1 vol% ( $p < 0.01$ ) and 1 vol% ( $p < 0.04$ )) but it was



**Fig. 7** Incorporation of a cross-linking silane with an organofunctional silane forming an interpenetrating cross-linking polymeric network. Key: ICMS = 3-isocyanatopropyltrimethoxysilane, BTSE = *bis*-1,2-(triethoxysilyl)ethane





**Fig. 8** The organofunctional groups in I: 3-isocyanatopropyltrimethoxysilane and II: 3-isocyanatopropyltriethoxysilane is  $-NCO$ , and in III: 3-methacryloxypropyltrimethoxysilane is  $>C=C<$ . Organofunctional groups are highlighted in brackets

statistically insignificant for the tested groups of 3-isocyanatopropyltriethoxysilane (0.1 vol% ( $p=0.403$ ) and 1.0 vol% ( $p=0.562$ )). Incorporation of a cross-linking silane with an organofunctional silane supposedly forms an interpenetrating cross-linking polymeric network with the siloxane film (Fig. 7) [20], which is understood to increase the interlocking nature of the whole network, such that a larger force is required to break it (Tables 3, 4, 5, and 6).

The two silane concentrations of 0.1 vol% and 1.0 vol% revealed a higher shear bond strength for the lower concentration, although the result was statistically insignificant, *viz.*  $p=0.307$  for 3-isocyanatopropyltrimethoxysilane and  $p=0.885$  for 3-isocyanatopropyltriethoxysilane. Park and Jang [21] have suggested that physisorbed silane layers formed on the chemisorbed layer because of an excess amount of unreacted (unhydrolyzed) silane at a relatively high concentration. This layer can be thought to act as a lubricant or deformable layer. Therefore, fracture and failure will tend to occur in this region through the slippage of physisorbed silane layers. According to Table 2, the proportion of failures for 0.1 vol% 3-isocyanatopropyltriethoxysilane and 3-isocyanatopropyltrimethoxysilane showing the adhesive mode of failure is lower than for 1.0 vol% (*c.f.* Fig. 4). This observation is in agreement with the findings of Park and Jang [21], who concluded that fracture occurs at the interface between the resin cement and zirconia (adhesive type of failure) at higher silane concentrations and within the resin cement (cohesive failure) at lower concentrations (Tables 8 and 9).

The shear bond strength measured for the control group silanized with 3-methacryloxypropyltrimethoxysilane (control) was higher than the 3-isocyanatopropyltriethoxysilane and 3-isocyanatopropyltrimethoxysilane groups. This effect may be

largely because of the organofunctional groups of the silane, which are prone to react with functional groups in RelyX Unicem resin composite cement (see Fig. 1). The organofunctional group in 3-methacryloxypropyltrimethoxysilane is  $>C=C<$ , whereas in 3-isocyanatopropyltriethoxysilane and 3-isocyanatopropyltrimethoxysilane it is  $-NCO$  (Fig. 8), with the carbon–carbon double bond being more reactive than  $-NCO$  towards the functional group in RelyX Unicem resin (Table 7). This property will be discussed in more detail in the second paper related to this study see, “Part II: Mechanistic Approach”.

Finally, the standard deviation varied between different test groups. A low standard deviation for the control group might be explained by the fact that the silane used in this study was prehydrolyzed. Furthermore, the arbitrary character of sand-blasting the zirconia surface during silica-coating cannot be easily assessed.

The effect of short-term and long-term water storage of the specimens, *i.e.* the silicized zirconia silanized with two isocyanato silanes, will be carried out in the near future to assess the different hydrolytic effects on silane-aided bonding, again using the two isocyanate silanes alone and in blends with a cross-linking silane.

#### 4 Conclusions

In this *in vitro* study carried out under ambient conditions, the following conclusions might be drawn:

1. The effect of differing sizes of hydrolyzable alkoxy groups in two silanes on the bonding of resin to zirconia was statistically insignificant.

2. The addition of cross-linking silane to a functional silane enhanced the bonding strength between resin and zirconia for the tested groups of 3-isocyanatopropyltrimethoxysilane but not for 3-isocyanatopropyltriethoxysilane.
3. The shear bond strength was higher for 3-methacryloxypropyltrimethoxysilane (control) than for 3-isocyanatopropyltriethoxysilane and 3-isocyanatopropyltrimethoxysilane.

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