The effect of silica-coating by sol-gel process on resin-zirconia bonding

Christie Ying Kei LUNG¹, Edwin KUKK² and Jukka Pekka MATINLINNA¹

¹Dental Materials Science, Faculty of Dentistry, The University of Hong Kong, Hong Kong SAR, P.R. China

²Department of Physics and Astronomy, Faculty of Mathematics and Natural Sciences, University of Turku, Finland

Corresponding author, Christie Ying Kei LUNG; E-mail: yklung@graduate.hku.hk

The effect of silica-coating by sol-gel process on the bond strength of resin composite to zirconia was evaluated and compared against the sandblasting method. Four groups of zirconia samples were silica-coated by sol-gel process under varied reagent ratios of ethanol, water, ammonia and tetraethyl orthosilicate and for different deposition times. One control group of zirconia samples were treated with sandblasting. Within each of these five groups, one subgroup of samples was kept in dry storage while another subgroup was aged by thermocycling for 6,000 times. Besides shear bond testing, the surface topography and surface elemental composition of silica-coated zirconia samples were also examined using scanning electron microscopy and X-ray photoelectron spectroscopy. Comparison of silica coating methods revealed significant differences in bond strength among the Dry groups ($p < 0.001$) and Thermocycled groups ($p < 0.001$). Comparison of sol-gel deposition times also revealed significant differences in bond strength among the Dry groups ($p < 0.01$) and Thermocycled groups ($p < 0.001$). Highest bond strengths were obtained after 141-h deposition: Dry (7.97 ± 3.72 MPa); Thermocycled (2.33 ± 0.79 MPa). It was concluded that silica-coating of zirconia by sol-gel process resulted in weaker resin bonding than by sandblasting.

Keywords: Sol-gel processing, Resin composite, Zirconia, Bond strength, Silica-coating

INTRODUCTION

Yttria-stabilized tetragonal zirconia is widely used in dentistry as the material of choice for endodontic posts, implant abutments, single crowns, dental bridges, and dental subgingival implants¹. However, because of the inertness of zirconia, the bonding of dental resin composites to zirconia is inherently weak. To promote the adhesion of resin composites to zirconia in dental restorations^{2,3}, surface conditioning of zirconia is typically sandblasting with silica-coated alumina particles followed by application of silane coupling agent.

In dental laboratories, surface conditioning by sandblasting is carried out by blasting the substrate surface with silica-coated alumina particles forcibly propelled out of a nozzle under compressed air onto the surface⁴. Upon impact, the particles transfer their kinetic energy to the substrate surface. The energy absorbed by the substrate surface causes the latter to melt microscopically, allowing some silica-coated alumina particles to be incorporated within the substrate surface^{5,6}. Finally, the silica-coated surface is primed by a silane coupling agent and the dental restoration cemented using a resin composite.

Other zirconia surface conditioning methods studied include chemical etching, laser irradiation, selective infiltration etching and chemical vapour deposition⁷⁻⁹. All these methods were developed in order to enhance resin-zirconia bonding. In this study, another surface conditioning method of zirconia by sol-gel process is introduced. The applications for sol-gel-derived products are numerous, ranging from fabrication of integrated sensor systems, fiber optics, lasers, non-linear optical

switching devices, and solid nanoparticles for drug delivery to thin-film coatings for dental implants and solar cells¹⁰⁻¹².

In dentistry, the sol-gel process has several advantages over the sandblasting method. Sandblasting potentially introduces surface defects or flaws. These surface irregularities generate compressive stresses on the surface layer, which adversely affect the long-term clinical performance of dental ceramics¹³. Another advantage is cost-related. Sol-gel processing requires less working space and less expensive equipment and chemical reagents as compared to the large and expensive sandblasting unit and silica-coated alumina sand particles used.

The purpose of this study was to evaluate the effects of different surface treatments for zirconia, sol-gel processing *versus* sandblasting, on the bond strength of resin composites bonded to zirconia. The null hypothesis was that different surface treatments and aging by thermocycling would have no influence on the shear bond strength of resin composites to zirconia. After sol-gel processing and sandblasting, surface elemental composition and surface topography of zirconia samples were also examined using X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) respectively.

MATERIALS AND METHODS

The materials used in this study are listed in Table 1. To simulate clinical conditions, materials used in clinical dentistry were employed in this study.

Table 1 Materials used in this study

Material	Manufacturer	Composition	Lot No.
Zirconia (Lava™)	3M ESPE	Yttria-stabilized zirconia	NA
Sil Silane	3M ESPE	<3% 3-methacryloxypropyltrimethoxysilane	259583
Poly(methyl methacrylate) resin	Ivoclar Vivadent AG	Monomer: methyl methacrylate and tetramethylene dimethacrylate Polymer powder: poly(methyl methacrylate), plasticizer, pigments, and catalyst	N69980
Tetraethyl orthosilicate	Sigma-Aldrich	98% tetraethyl orthosilicate	131903
Rocatec Sand Plus	3M ESPE	110 µm silica-coated alumina	369418
Deionized water	Millipore	18.2 MΩcm resistivity	NA
Ethanol	Riedel-de Haën	99.8% ethanol	03550
Ammonia	Sigma-Aldrich	28–30% aqueous ammonia solution	221228
RelyX Unicem Aplicap	3M ESPE	Powder: silanized fillers, initiator, pigments Liquid: methacrylate monomers containing phosphoric acid groups, initiator, stabilizers	363991

Polishing of zirconia surfaces

Zirconia blocks (Lava, 3M ESPE, Seefeld, Germany) of 16×15×3 mm³ dimensions were pressed into cylinder-shaped plastic molds filled with a poly(methyl methacrylate) resin (ProBase Cold, Ivoclar Vivadent AG, Schaan, Liechtenstein).

The surfaces of zirconia samples were polished with 400-grit silicon carbide papers under running deionized water. After ultrasonic cleaning in 70% ethanol (Decon Laboratories Ltd., Hove, East Sussex, UK) for 10 min, they were rinsed with 70% ethanol and allowed to dry in air at room temperature.

Silica-coating of zirconia by sol-gel process

The sol-gel solvent mixture was prepared at room temperature using tetraethyl orthosilicate (TEOS; 98%, Sigma-Aldrich, USA), absolute ethanol (99.8%, Riedel-de Haën, Seelze, Germany), deionized water, and ammonia catalyst (28–30%, Sigma-Aldrich).

Tetraethyl orthosilicate was added to a mixture of ethanol and deionized water, and then aqueous ammonia solution was added. Zirconia samples were immersed in the solvent mixture. The solution was slowly stirred. After the sol-gel deposition process, silica-coated zirconia samples were allowed to dry at room temperature, followed by rinsing with 70% ethanol and drying at room temperature. Four test groups of silica-coated zirconia samples by sol-gel process were thus prepared: Groups I to IV according to reagent ratios and deposition times (Table 2).

Silica-coating of zirconia by sandblasting

For control, a group of zirconia samples (Group V, Table 2) were silica-coated by sandblasting. Sandblasting was performed using Rocatec Sand Plus (110 µm of silica-

coated alumina particles; 3M ESPE) at a constant pressure of 280 kPa for 30 s/cm² and at a perpendicular distance of 10 mm, according to standard procedure in dental laboratories¹⁴.

Sandblasted zirconia samples were then ultrasonically cleaned in 70% ethanol for 10 min. After rinsing with 70% ethanol, they were allowed to air-dry at room temperature.

Bonding of resin composite to silica-coated and silanized zirconia surfaces

Using a new fine brush for each application, one primer coating of Sil Silane (3M ESPE) solution was applied on silica-coated zirconia surfaces. 3M ESPE Sil Silane was a pre-hydrolyzed silane product consisting of 3-methacryloxypropyltrimethoxysilane¹⁵. The coating was allowed to dry and react for 5 min.

RelyX Unicem Aplicap resin composite (3M ESPE) was activated and mixed according to manufacturer's instruction. The resin composite was filled into a polyethylene mold of 3.7 mm diameter and 4.0 mm height, which was placed on the silica-coated and primed zirconia surface. After resin composite was light-cured for 40 s (Lunar Curing Light, Benlioglu Dental Inc., Ankara, Turkey), the mold was removed by being lifted up carefully.

Figure 1 illustrates the entire process of preparing the silica-coated (by sol-gel process or sandblasting) and silanized zirconia samples for shear bond strength measurement. Ten test groups of bonded samples were thus prepared: Groups I–V Dry and Groups I–V Thermocycled. Each test group consisted of 15 resin composite stubs for shear bond strength measurement. For the Dry samples of Groups I–V, they were kept in a desiccator at room temperature for 24 h prior to shear

Table 2 Test groups I–V according to silica-coating method (sol-gel process or sandblasting) and according to reagent ratios and deposition times for sol-gel process

Group	Surface treatment conditions	TEOS:Ethanol: Ammonia: H ₂ O ratio (mL)	Deposition time (h)
I	Polishing, rinsing (70% ethanol), sol-gel process, rinsing (70% ethanol)	10:100:1:20	24
II	Polishing, rinsing (70% ethanol), sol-gel process, rinsing (70% ethanol)	20:100:1:20	48
III	Polishing, rinsing (70% ethanol), sol-gel process, rinsing (70% ethanol)	5:100:2:35	72
IV	Polishing, rinsing (70% ethanol), sol-gel process, rinsing (70% ethanol)	5:100:1:15	141
V	Polishing, rinsing (70% ethanol), sandblasting, rinsing (70% ethanol)	—	—

Fig. 1 Schematic illustration of bonding resin composites to silica-coated and silanized zirconia surfaces for shear bond strength testing using the sol-gel process or sandblasting method.

bond strength testing. For the thermocycled samples of Groups I–V, they were thermocycled 6,000 times using a custom-made thermocycling unit (Dental Materials Science Laboratory, University of Hong Kong, Hong Kong) between $5.0 \pm 0.5^\circ\text{C}$ and $55.0 \pm 0.5^\circ\text{C}$ with a dwell time of 20 s in each deionized water bath.

Shear bond strength measurement

Shear bond strengths (SBSs) of zirconia samples were measured using a universal testing machine (Model 1185, Instron, Norwood, MA, USA). A load of 1,000

N was applied at a crosshead speed of 1.0 mm/min until fracture occurred. SBS was calculated using the maximum fracture load divided by the circular area of resin stub¹⁵.

After SBS testing, failure mode of each sample was assessed using a light microscope (NZ6, Leica, Wetzlar, Germany). Failure modes were classified as follows: 'adhesive failure' when less than 33% of resin composite remained on substrate surface; 'mixed failure' when more than 33% but less than 66% of resin composite remained on substrate surface; and 'cohesive failure'

when the remaining amount was more than 66%¹⁴⁾.

Statistical analysis of shear bond strengths

Mean SBSs of resin composite to zirconia by sol-gel process using different deposition times and according to different surface conditioning methods were analyzed by one-way analysis of variance (ANOVA). Mean SBS was the dependent variable. Independent variables were namely: sol-gel deposition time, surface conditioning method (sol-gel process *versus* sandblasting), and storage condition (dry *versus* thermocycled). Inter-group comparisons of mean SBSs were performed using *post-hoc* Tukey's test. Significance level for all comparisons was set at $p < 0.05$.

Surface topography analysis

Surface topographies of zirconia samples after silica-coating by sol-gel process and sandblasting were analyzed by SEM (XL30CP, Philips Electron Optics, Eindhoven, The Netherlands) at 10 kV operating voltage.

After SBS testing, representative zirconia samples were also analyzed by SEM (S-3400N, Hitachi, Tokyo, Japan) at 15 kV operating voltage.

XPS analysis

The surface elemental compositions of five zirconia samples with surface treatments by sol-gel process and sandblasting (Table 2) were examined by XPS using a spectrometer (Perkin-Elmer PHI 5400, Waltham, MA, USA) with MgK α radiation ($h\nu = 1253.6$ eV). Wide survey scans were performed to determine atomic concentrations. Chamber base pressure was about 8×10^{-8} Pa and X-ray tube was operated at 200 W. Peak composition and energy positions were determined using the least-squares curve-fitting technique with SPANCF macro package¹⁶⁾.

RESULTS

Shear bond strength

Table 3 shows the SBSs of resin composites to zirconia

silica-coated by the sol-gel process or by sandblasting. Statistical analysis revealed that there were significant differences among different sol-gel deposition times within the Dry group ($p < 0.01$) and within the Thermocycled group ($p < 0.001$).

When comparison was made between the two surface conditioning methods of sol-gel processing *versus* sandblasting, significant differences were also found within the Dry group ($p < 0.001$) and within the Thermocycled group ($p < 0.001$).

On the effect of aging by thermocycling, the mean SBSs of all test groups were significantly decreased after thermocycling. Some zirconia samples of Groups I–IV even debonded during thermocycling.

Failure mode

According to the SEM micrographs in Fig. 2, all representative zirconia samples showed adhesive failure mode for both the sol-gel process and sandblasting treatment method.

Mode of failure assessment for all zirconia samples in all test groups was adhesive failure.

Surface topography

Figures 3(a)–(d) are the SEM micrographs that illustrate the surface topographies of silica-coated zirconia surfaces by sol-gel process. For deposition times of 24 h and 48 h, there was non-uniform distribution of silica particles deposited in multiple layers on the zirconia surface (Figs. 3(a) and (b)). As the deposition time increased, there was more uniform distribution of the silica particles deposited on the zirconia surface (Figs. 3(c) and (d)).

Figure 3(e) shows that after sandblasting, silica-coated alumina particles deposited on the zirconia surface were finely distributed.

Figure 3(f) shows the surface topography of polished zirconia surface without any surface treatment by the sol-gel process or by sandblasting.

Surface elemental composition

Table 4 shows the elemental compositions of silica-

Table 3 Mean shear bond strengths of resin composite to zirconia by sol-gel processing at different deposition times and by sandblasting

Group	Silica coating method	Deposition Time (h)	Mean SBS $\pm$ SD (MPa)		Debonded during thermocycling (%)
			Dry	Thermocycled	
I	Sol-gel process	24	5.49 ^A _{a,b} $\pm$ 1.94	0.06 ^B _d $\pm$ 0	86.7
II	Sol-gel process	48	4.59 ^A _a $\pm$ 0.96	0.06 ^B _d $\pm$ 0.02	75.0
III	Sol-gel process	72	6.48 ^A _{a,b} $\pm$ 3.22	1.94 ^B _e $\pm$ 0.47	46.7
IV	Sol-gel process	141	7.97 ^A _b $\pm$ 3.72	2.33 ^B _e $\pm$ 0.79	66.7
V	Sandblasting	—	13.54 ^A _c $\pm$ 1.67	10.43 ^B _f $\pm$ 2.42	0

Different capital letters in the same row mean that groups are significantly different ($p < 0.05$).

Different lowercase letters in the same column mean that groups are significantly different ($p < 0.05$).

Fig. 2 SEM micrographs (25×) which show resin composite remaining on Dry zirconia samples after SBS testing.
(a) 24-h deposition; (b) 48-h deposition; (c) 72-h deposition; (d) 141-h deposition; and (e) sandblasting.

coated zirconia surfaces, after sol-gel processing or sandblasting, as examined by XPS. For samples 1–4 after the sol-gel process, only elemental C, Si, and O were detected on the surface layer. For sample 5 after sandblasting, elemental C, O, Zr, Si, and Al were detected. Si and Al contents in Group V samples were due to the use of silica-coated alumina particles during sandblasting. Further comparison between the two silica-coating methods revealed that Si content in sample 1–4 was higher than in sample 5.

DISCUSSION

In this study, the effect of silica-coating on zirconia by sol-gel process on the shear bond strength of resin composites to zirconia was evaluated. It was found that bond strength increased with deposition time for both dry and thermocycled samples. However, in routine clinical practice, it is quite impractical to implement such long sol-gel deposition times.

Fig. 3 SEM micrographs (500×) of: (a–d) Silica-coating of zirconia by sol-gel process after deposition of 24 h (a), 48 h (b), 72 h (c), 141 h (d); (e) Silica-coating by sandblasting; and (f) Polished zirconia surface without surface conditioning.

Table 4 XPS elemental compositions of zirconia surfaces after sol-gel processing and sandblasting

Sample	Silica coating method	Atomic concentration (%)				
		Zr3d	O1s	Si2p	C1s	Al2p
1	Sol-gel process		54.0	26.9	19.1	
2	Sol-gel process		62.4	28.6	9.0	
3	Sol-gel process		38.6	20.4	41.0	
4	Sol-gel process		54.9	27.4	17.7	
5	Sandblasting	7.2	44.0	9.9	31.0	7.9

Effect of aging by thermocycling

Thermocycling is a common artificial aging method used in dental research to test bond durability, where the bonding interface is exposed to the combined effects of hydrolytic degradation and thermal stress. In the present study, all samples from Groups I–V showed significant decrease in shear bond strength after thermocycling. In particular, samples with 24 h and 48 h of sol-gel deposition showed near-zero bond strength after thermocycling.

Failure mode analysis indicated adhesive failure in both dry and thermocycled samples of Groups I–V. In other words, interfacial failure occurred between the resin composite and silica-coated layer on zirconia. Some samples from Groups I–IV even debonded during thermocycling. Therefore, it was apparent that resin-zirconia bonding was adversely affected by thermal fatigue and hydrolytic degradation during thermocycling.

Effect of silica-coating by sandblasting

For the sandblasting process, tribochemical coating process is the mechanism by which silica particles are deposited on the zirconia surface. Tribochemistry involves creating chemical bonds by applying mechanical energy. During sandblasting, chemical reactions are initiated by frictional energy and shearing forces between the lubricant (silica-coated alumina particles) and the substrate surface (zirconia) under boundary lubrication conditions¹⁷.

In the present study, the two sources of tribochemistry were: (1) chemical reactions induced by mechanical impact; and (2) chemical reactions induced by frictional heat generated between the silica-coated alumina particles and zirconia surface¹⁸. First, mechanical impact caused the interatomic bonds of surface atoms to stretch, hence reducing the activation barrier of interfacial reactions¹⁹. Secondly, frictional heat caused the surface temperature to rise and reach the maximum temperature, called the ‘flash temperature’. Rise to the maximum temperature also increased the rate of chemical reactions between the silica-coated alumina particles and zirconia surface²⁰.

Effect of silica-coating by sol-gel process

For the sol-gel process, the formation of a silica network involves two steps: hydrolysis and polycondensation of tetraethyl orthosilicate²¹. Tetraethyl orthosilicate undergoes hydrolysis to form silanols. Two silanol molecules condense to form a siloxane linkage, which then undergoes polycondensation to form a silica network.

Silica particles chemically react with the zirconia surface, through the interaction of hydroxyl groups of silica particles with the surface hydroxyl groups of zirconia, to form a silica layer on the zirconia surface. Besides, hydrolyzed tetraethyl orthosilicate may also condense on the zirconia surface first and then build up to form a silica layer on it.

Effect of silane coupling agents

Silane coupling agents, such as 3M ESPE Sil Silane, are

used to promote adhesion of resin composites to dental restorative materials⁹. They contain two different functional groups: $>C=C<$ vinyl double bond and $-OR$ group. The former can react with the functional groups of resin composites consisting of $>C=C<$ bonds. The latter forms $-OH$ after hydrolysis, which then reacts chemically with the silica-coated zirconia surface.

In the present study, the statistically significant difference in SBS between the two silica coating methods was largely due to the mechanism of silica deposition on the zirconia surface. With sandblasting, a silica layer was formed on the zirconia surface after the surface was blasted with silica-coated alumina particles, followed by deposition of silica particles on the surface. For the sol-gel process, a silica layer was formed on the zirconia surface by the hydrolysis of tetraethyl orthosilicate to form silanols. Condensation of silanols then resulted in the formation and deposition of silica particles on the zirconia surface.

After silica-coating zirconia by both methods, a silane coupling agent was applied. The silane coupling agent formed silanols after hydrolysis, which then reacted with the surface hydroxyl groups of the silica layer on zirconia surface to form siloxane linkages ($-O-Si-O-$) after condensation. Finally, resin composite was bonded to the silica-coated and silanized zirconia surface by light-curing. During polymerization, the $>C=C<$ bonds in the composite resin reacted with the $>C=C<$ bonds in the silane coupling agent to form $-C-C-$ single bonds.

Given the explanation above, it became clear that difference in SBS between the sandblasting treatment and sol-gel process stemmed from the difference in adhesion between the silica layer and the zirconia surface, since the bonding mechanism was the same between the resin composite and the silane primer coating in both methods.

Future work

Our aim was to develop a novel zirconia surface conditioning method to improve the adhesion of resin composites to zirconia. This method must be cost-effective, energy-saving, and easy in implementation to both dentists and dental technicians. Further studies would be carried out to investigate the silica-coating of zirconia by sol-gel process with optimized modifications as well as by other surface conditioning methods.

CONCLUSIONS

Within the limitations of the current study, the following conclusions were drawn:

1. The null hypothesis was rejected. Two factors significantly affected the shear bond strength of resin composite to zirconia: silica coating method of zirconia (sol-gel process or sandblasting) and aging effect of thermocycling.
2. Shear bond strength increased with sol-gel deposition time, but it is impractical in clinical practice for long deposition times.

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