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Combined novel bonding method of resin to zirconia ceramic in dentistry: a pilot study

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Short title: A novel resin zirconia bonding method

Abstract

Zirconia is a promising metal-free framework material that can be used to construct all-ceramic resin-bonded restorations in modern minimally invasive dentistry. The lack of a durable bond to zirconia is the major limitation against its widespread use. A technique to promote adhesion to the zirconia surface has thus been actively sought in dental materials research. Selective infiltration etching (SIE) has emerged as a method of conditioning that creates a highly retentive zirconia surface. This *in vitro* pilot study tested a novel adhesion procedure in which two newly engineered silane-based zirconia primers were combined with the SIE method. Zirconia discs were SIE-surface-treated, coated with one of the 2 zirconia primers, and bonded to composite resin discs. Primer activation (hydrolysis) was monitored by Fourier transform infrared (FTIR) spectroscopy. The bilayered specimens were sectioned into microbars and subjected to the microtensile bond strength test. As-sintered zirconia discs served as controls. Surface analysis of zirconia specimens was carried out using photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Zirconia specimens that had been treated with both SIE and primers had a significantly higher (ANOVA) zirconia resin bond strength (40.6 MPa, SD 5.8 MPa) than control specimens (2.6 MPa, SD 3.0 MPa; $p < 0.05$, $F = 13.8$, ANOVA). Controls also exhibited spontaneous failure during sectioning. Additionally, the interfacial failure rate was lower for the specimens subjected to the new combined surface treatment than for controls. The novel combined method of surface treatment method might open new opportunities for enhanced adhesion of resin-bonded zirconia restorations.

Keywords: dental materials; zirconia pretreatment; selective infiltration etching; organophosphate cements; particle abrasion; silane coupling agent; primers; 3-methacryloxypropyltrimethoxysilane.

INTRODUCTION

Resin-bonded zirconia restorations have become an interesting treatment option because they allow the esthetic replacement of missing teeth without the need for extensive preparation of sound abutment teeth [1]. Owing to the characteristic brittleness of all-ceramic frameworks, these restorations are liable to fracture under function. The unique mechanical properties and the high fracture toughness of zirconia make it a considerable framework material for fabrication of metal free all-ceramic restorations [2].

However, zirconia's exceptional chemical inertness, stability, insolubility, corrosion resistance zirconia and dense non-retentive surface prevent the formation of any chemical or actual mechanical bond. To date, the only effective method of bonding to zirconia in dentistry is pretreatment by airborne-particle abrasion, i.e. roughening with alumina particles in a high-pressure jet, followed by the application of resin-composite cements containing 10-methacryloyloxydecyl dihydrogenphosphate (MDP; Figure 1-a) [3]. Even so, the bond strength obtained may not be strong enough to retain resin-bonded zirconia restorations, and concerns remain regarding bond hydrolysis in clinical conditions [4-6]. Zirconia used in dentistry and dental technology typically consists of ca 2-3% of CaO, MgO, CeO₂ or Y₂O₃, which stabilize the crystal structure against the 3-4-% fatal volume expansion when zirconia ingots are fired under controlled conditions during conventional manufacturing. Zirconia also inherently contains traces of hafnia, HfO₂ [7].

Selective infiltration etching (SIE) is a recently introduced type of surface pretreatment for zirconia ceramics [8]. It transfers the visually dense surface of zirconia into a highly retentive surface, prone to establishing nano-mechanical bonding with resin cements through the formation of inter-grain porosities. Crystallographically, zirconia is a highly dynamic ceramic material that undergoes structural transitions in response to external physical stimuli such as pressure and heat [1,7]. The surface grains of zirconia can be further manipulated to result in grain-level splitting, sliding, and re-arrangement. Such changes restructure the surface layers, thereby imparting nano-scale retentive features [9-11]. The method relies on a blend of inorganic oxides acting as a glass infiltration agent, which diffuses at the grain boundary regions on the surface and reacts by controlled heating, thereby resulting in nano-scale surface porosities. After the infiltration agent is melted, cooled, etched and rinsed off, the surface of zirconia becomes highly retentive and readily establishes nano-scale mechanical bonding with the adhesive resin composite cement of choice [12].

Silanes have numerous technical applications because they form covalent bonds between dissimilar matrices without reacting directly with the inert surface of zirconia [13]. 3-Methacryloxypropyltrimethoxysilane (Figure 1-b) is a silane monomer that is widely used in dentistry for promote e.g. the bonding of resin cement to glassy materials. Other reactive functional silane monomers have been recently evaluated in bonding resin-composites to metals [14,15], and to silica-coated zirconia [16]. The aim of this pilot study was to evaluate the zirconia-resin micro-tensile bond strength to zirconia after it had been conditioned with the SIE technique and then treated with one of two newly engineered zirconia primers. In this study dry test conditions were used. The surface

analysis of SIE-treated zirconia and chemical analysis to monitor the activation of the primers were carried out. The hypothesis was that the combined adhesion promotion method would significantly enhance bonding *in vitro*.

MATERIALS AND METHODS

Zirconia disc preparation

Sintered zirconia discs (radius 19.5 mm; thickness 3 mm), donated by the manufacturer (Procera Zirconia, NobelBiocare, Göteborg, Sweden) were randomly allocated to 2 groups (n = 18 each). One group was used as ‘as-sintered’ controls, which were polished with SiC abrasive paper (600 grit) for 5 min (and finally rinsed with de-ionized water and dried in air), and the other was subjected to SIE. The surface of the SIE-treated zirconia discs was coated with a uniform, even layer of an experimental infiltration glass powder that had a low melting temperature. The chemical composition of the glass powder was (in wt%) Si 30.0, Ti 13.0, Al 8.0, K 3.0, Rb and Mg 1.0, and balance O₂ is 44.0 [8]. The coated disc specimens were heated at a constant 750 °C in an electrical oven (Austromat 3001; Dekema Dental-Keramikofen, Freilassing, Germany) for 2 min and then allowed to cool to room temperature. The infiltration agent was dissolved away with 5 vol% hydrofluoric acid (IPS Etching Gel; Ivoclar Vivadent, Schaan, Liechtenstein) for 15 min, and the discs were briefly steam cleaned and dried with oil-free compressed air. All discs were then kept before the next steps in a desiccator for 24 h.

Experimental zirconia primers

Two new zirconia primers were prepared for investigation: the first (labelled AM) contained 3-methacryloxypropyltrimethoxysilane monomer and the other (labelled AN) contained 3-(N-allylamino)propyltrimethoxysilane monomer. Both monomers were used as such, without re-distillation. A solution of 95 vol% ethanol (Absolutt alcohol; 99%, Arcus, Oslo, Norway) and 5 vol% de-ionized water (milli-Q water system) was prepared and allowed to stabilize for 24 h at +4 °C. After the solution's pH was adjusted to 4.5 with 1 mol/l CH₃COOH (Merck, *pro analysi*; Darmstadt, Germany), it was used to make a 1.0 vol% solution of each of the silane monomers in a 50 ml polyethylene bottles by adding the appropriate amount of the silane monomer (Table 1, Figures 1-b- and 1-d). After a gentle manual shaking, the two silane preparations were allowed to activate for 1 h at room temperature [14].

Activation analysis of zirconia primers

Silane monomer activation was followed the period of one hour, at 15 min intervals, using Fourier transform infrared (FTIR) spectroscopy. Because silanes absorb infrared light between 4000 and 600 cm⁻¹ [17], the surface analysis of each silane solution layer was conducted throughout the spectral range of 3800 to 600 cm⁻¹ with a Reflectance-Absorbance Fourier Transform Infrared (RA-FTIR) Perkin Elmer Spectrum One spectrometer (Perkin-Elmer, Beaconsfield, UK), equipped with a specular reflectance monolayer/grazing angle accessory in which the experimental silane solution to be

studied was spread as a layer onto a planar and polished Ge crystal (which is inert to the solution) [18].

Chemical analysis of the zirconia surface

X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical changes on the surface of the zirconia specimens to a depth of 1 to 3 nm. For this step, a Perkin-Elmer PHI 5400 ESCA Spectrometer (Perkin-Elmer, Eden Prairie, MN, USA) with a monochromated Al K_α X-ray source ($h\nu = 1486.6$ eV) was operated at 14.4 kV and 300 W. The specimens were mounted with a double-sided adhesive carbon tape onto a holder and placed in an ultra-high vacuum at 10^{-8} mbar. XPS analysis was made at different spots over a diameter of 1 mm. The take-off angle was 45° and the electron analyzer pass energy in the XPS high-resolution scans was 35.75 eV. A survey spectrum of each specimen was recorded and atomic concentrations of Zr, O, P, Al, Si, Y, Na and F were then calculated [19].

Bonding procedure

The bonding surface of the SIE-treated zirconia discs was coated with 1 primer coat, which was applied with a new, clean micro-brush (that are used in clinical dentistry) and allowed to dry and react for a conventional time of 3 min. Control specimens were also primer-coated. Already-prepared, pre-aged, resin-composite discs (Tetric EvoCeram; A3.5, IvoclarVivadent, Schaan, Liechtenstein) were coated with a freshly mixed resin cement (Panavia F 2.0; Kuraray, Tokyo, Japan) and placed on top of the primer-coated

zirconia specimens under a fixed load of 20 N. Excess cement was wiped off from the vertical sides, then an air barrier gel (Kuraray, Tokyo, Japan) was coated around the margins of the double layered specimens to prevent the formation of an oxygen inhibition layer. After 24 h of room storage the specimens were cut into 6 mm long microbars (1 x 1 mm in cross section) using a precision cutting device (Isomet 1000; Buehler, Lake Bluff, IL, USA) and a diamond-coated saw (Diamond Wafering Blade, No-11-4276; Buehler) under water cooling (Figure 2).

Microtensile bond strength testing [20] was conducted by applying axial load to the resin-to-zirconia interface at a constant speed in a universal testing machine (Instron 6022; Instron Corp, High Wycombe, England). The load cell (100 N) and crosshead speed (0.5 mm/min) were frequently calibrated during the measurement process (Millitron; Feinpruf Perthen, Gottingen, Germany). Fractured microbars were ultrasonically cleaned, dried, gold sputter coated, and examined by scanning electron microscopy, (XL20; Philips, Eindhoven, The Netherlands). The failure type analysis was analyzed by SEM and classified as either a) adhesive or b) cohesive.

Statistical analysis

Two-way analysis of variance (ANOVA) within groups (2 different experimental primers) and between groups (2 zirconia surfaces: surface treated + primed, and primer-treated only) was used to analyze the data ($\alpha = 0.05$, $F = 13.8$). The Bonferroni *post hoc* test was used for pair-wise comparisons (SPSS 10.0; SPSS Inc, Chicago, IL, USA).

RESULTS

This study revealed a significant difference in between the as-sintered control specimens and SIE-treated samples ($p < 0.0001$), the 2 tested experimental zirconia primers ($p < 0.0001$), and the interaction between the surface treatment and the primers ($p < 0.000$, Table 1). One third of as-sintered specimens demonstrated spontaneous failure during cutting or testing which resulted in the high standard deviation observed (2.7 MPa, SD 3.0 MPa) in MTBS values. SIE-treated specimens did not fail at cutting and had significantly higher MTBS values (40.6 MPa, SD 5.8 MPa). Scanning electron microscopy revealed that SIE resulted in the creation of a highly retentive surface (Figure 3). SEM examination of tested microbars revealed adhesive interfacial failure for the primed control specimens, but predominantly cohesive failure for selectively etched and primed specimens (Figure 3). According to the FTIR spectra, during activation of the zirconia primers for 60 min there were signal changes at regions ca. 1000 to 1200 cm^{-1} , which indicated that the labile $-\text{O}-\text{CH}_3$ groups had been converted to reactive $-\text{Si}-\text{OH}$ groups (Figures 1 c and 1 e) and volatile methanol had been released. XPS analysis was able to detect differences in the chemical composition of the outer 1 to 2 nm surface layer of control and SIE-treated zirconia (Table 2).

DISCUSSION

Because of the continuous debate regarding the use of shear bond strength (SBS) testing and whether the obtained value truly represents the measured bond strength, MTBS tests are nowadays used more and more in adhesion studies in dental materials research [21]. The cohesive failures usually observed in shear bond strength tests are

understood to be related to the inhomogeneous stress distribution around the edge of the loaded sample discs, which also falsely implicates stronger shear bond strength. On the contrary, MBTS testing has gained popularity, as it subjects the bonded interface to axial tension so that failure is expected in the weakest structure. Moreover, the relatively small cross-section of the microbars in MTBS test reduces the chance of incorporating structural defects in the bonded area that would affect the bond strength result [22].

The spontaneous failure for 16.5% of the samples, low bond strength, and the interfacial failure observed for the as-sintered specimens (*i.e.* successfully tested) directly imply that the establishment of a chemical bond with zirconia is not successful when using only the MDP-containing resin-composite is applied. This conclusion agrees with those of some published key studies [23-25]. In addition, degradation of the established bond is expected under the influence of water presence and fatigue [26]. Such low performance would be highly suggestive of debonding failure of resin-bonded zirconia restorations, especially in the absence of mechanical retention. Creating a durable and long-lasting adhesion to non-silica based ceramics (alumina and zirconia) is thus a real clinical challenge [27].

The high bond strength achieved by treatment with SIE and the tested primers could be attributed to two interacting mechanisms, namely nano-mechanical and chemical. First, the physical features created by SIE (as seen on SEM images) resulted in a highly retentive surface that the zirconia primers were able to penetrate and wet; the primers were also able to chemically react with the elemental silicon present on the surface. Nevertheless, the zirconia had a low percentage of silicon after SIE-treatment compared with a relatively high Si-content for as-sintered zirconia, owing to polishing

with SiC abrasive paper followed by insufficient cleaning. Although this ‘extra’ silicon was eliminated during priming and etching, the remaining Si on the SIE-treated discs could have reacted with the silane-based primers. Indeed, silicon was found in substantial amounts after the application of either zirconia primer (Table 2; Figure 1 f-g). The presence of primer-silicon might offer protection against micro-leakage and hydrolysis, and would thus protect the bonded surface from the deteriorating effect of the oral environment. Consequently, the applied resin cement can penetrate and interlock with surface inter-grain porosities and finally chemically react (polymerize) with the zirconia primer. All these events apparently resulted in high zirconia-resin bond strength.

The registered FTIR spectra suggested that all the silane monomers had been activated, and had formed silanol oligomers during the 60 min. After the priming step, the silicon content was notably higher. It is noteworthy that silanes do not need 100% hydrolysis to be active coupling agents and only partial hydrolysis is sufficient [28]. Minute amounts of methanol are released during hydrolysis and evaporate immediately.

The primer AM (with 3-Methacryloxypropyltrimethoxysilane) achieved significantly higher bond strengths than primer AN (with 3-(*N*-allylamino)propyltrimethoxy), showing that the 3-methacryloxypropyltrimethoxysilane is more reactive and more prone to form bonds to pretreated zirconia. The methacrylate group in that primer can also react with the organophosphate group (MDP) present in the resin cement (Panavia F 2.0) again resulting in higher MTBS values [19]. 3-(*N*-allylamino)propyltrimethoxysilane is an amino-functional silane containing a secondary amino group (*cf.* Figure 1 d) and is often applied when coupling to polyesters but in particular to acrylic coatings [29]. It was selected for this study because aminosilanes form an interesting reactive group of

coupling agents with potential bonding properties not yet studied in dental materials science. 3-(N-allylamino)propyltrimethoxysilane in primer AN is thought to chemically react between the vinyl C=C bonds in the monomers of the resin cement. The reaction mechanism deserves further studies. The high proportion of nitrogen (N) found in the XPS analysis is attributed to the amino-functionality in this silane. The nitrogen present in control specimens before treatment thus demonstrates adsorbed ambient nitrogen. The Table 2 also suggests a decrease of atomic percent for Zr and Y (i.e. elements present in the bulk of un-primed zirconia) after priming which is a good indication of the presence of both primers on the treated zirconia surface.

Once the resin infiltrates the 3-dimensional inter-grain porosities, it becomes structurally integrated with the surface and higher forces are required to disrupt the formed bonding (Table 1). The newly etched retentive surface, with silicon as a trace element, is thought to require special primers to fully penetrate into the created porosities, establish adequate wetting of the surface, react with it, and finally polymerize with the cement, without inducing damaging polymerization contraction stresses. Activated (hydrolyzed) silanes can easily wet the zirconia and chemically bond with silica content and monomers of an organic phase [28]. It is widely accepted that the use of MDP-containing adhesives after air abrasion with alumina particles is considered ‘the gold standard’ for bonding to non-silica based ceramics and is used in many studies [16, 23-25]. Air abrasion with particles was left outside the scope of this pilot study which aimed to test SIE combined with priming as a new surface pretreatment. The hypothesis was accepted: the combined adhesion promotion method significantly enhanced bonding *in vitro*.

In the immediate future, further study is needed to optimize the performance of the two tested zirconia primers. Moreover, artificial aging tests by water storage and/or controlled thermo-cycling [5, 14-16, 26] are needed to assess the spontaneous debonding rate and to simulate the clinical situation.

CONCLUSION

The combination of selective infiltration etching (SIE) and the use of chemically reactive zirconia primers in this *in vitro* pilot study resulted in a strong zirconia resin-bond strength in dry storage conditions. The 3-methacryloxypropyltrimethoxysilane primer was more effective in yielding higher resin to zirconia bond strength than that of 3-(N-allylamino)propyltrimethoxy primer. This pretreatment technique might give opportunities for resin bonded zirconia restorations.

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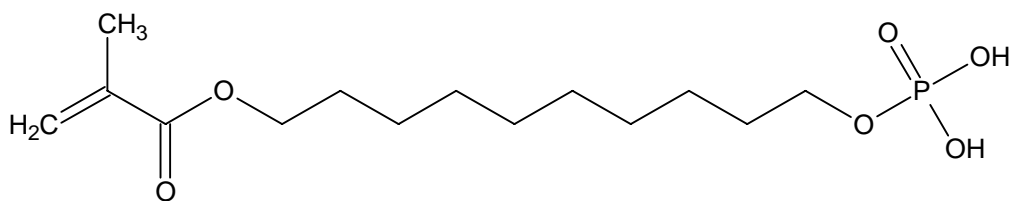
Table 1. Composition of the zirconia primers (1 vol% in concentration) and measured microtensile bond strength (MPa) of the test groups. (MTBS = microtensile bond strength).

Surface treatment	Zirconia primer	Functional silane monomer	Purity (%)	Manufacturer of the silane monomer	Bond strength MTBS (MPa)	Std. deviation (MPa)
SIE	AM	3-Methacryloxypropyl-trimethoxysilane	>95	Gelest, Morrisville, PA, USA	40.6	5.8
As-sintered					2.6	3.1
SIE	AN	3-(<i>N</i> -allylamino)propyl-trimethoxysilane	95	Gelest, Morrisville, PA, USA	32.6	2.5
As-sintered					2.9	3.1

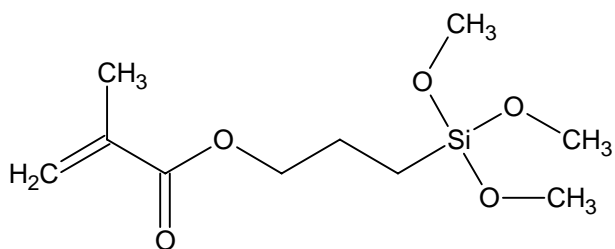
Table 2. XPS analysis of different zirconia specimens, results are expressed as atomic concentrations (at%). Carbon (C) was omitted from the results.

Element	As-sintered zirconia	SIE treated zirconia	SIE treatment + zirconia primer AM	SIE treatment + zirconia primer AN
N	11.7	0.0	0.0	14.0
O	61.1	52.4	63.2	56.3
F	0.0	15.1	10.6	0.0
Na	0.0	3.2	0.0	0.0
Al	0.0	0.0	0.0	0.0
Si	4.2	4.9	20.3	28.4
P	1.8	0.0	0.0	0.0
Y	2.2	2.0	0.0	0.0
Zr	19.0	22.4	5.9	1.3
	100.0	100.0	100.0	100.0

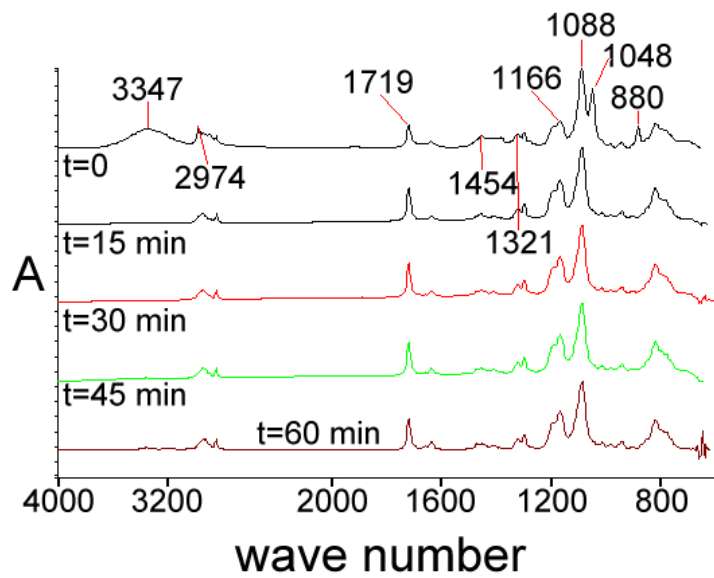
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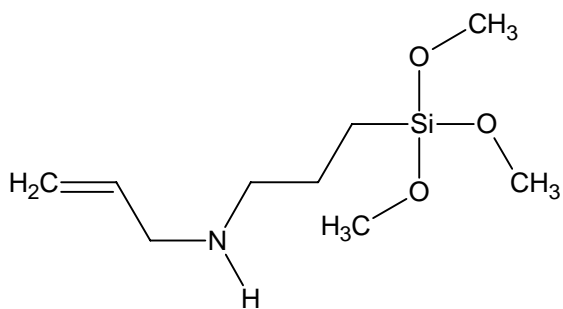
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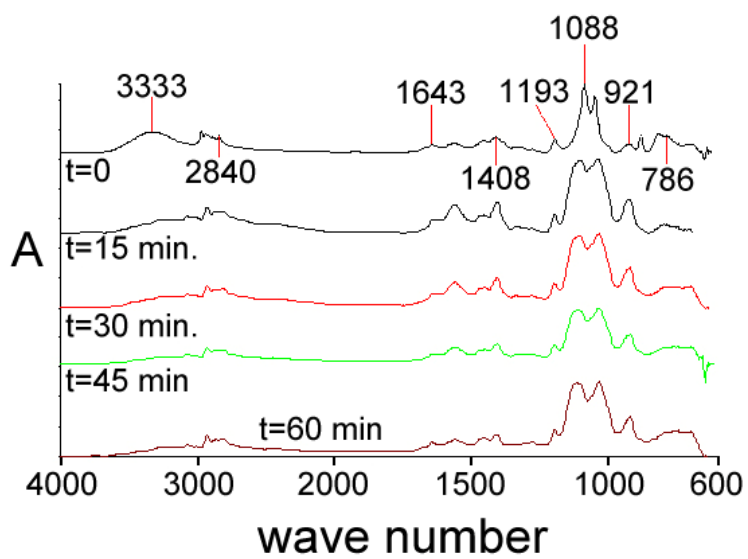
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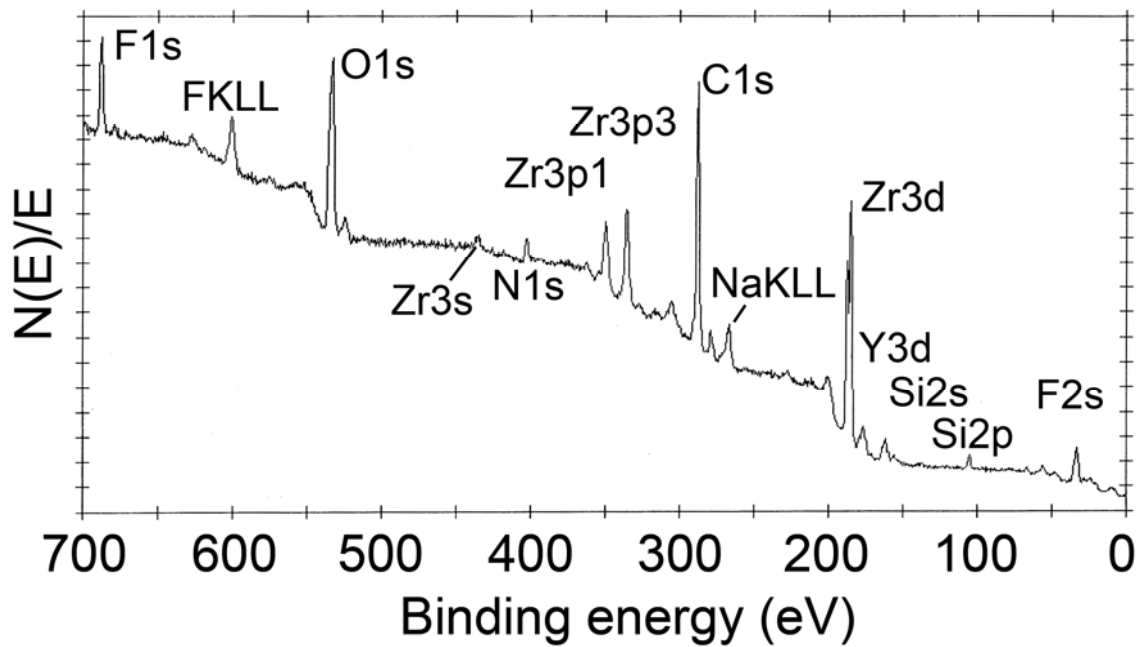
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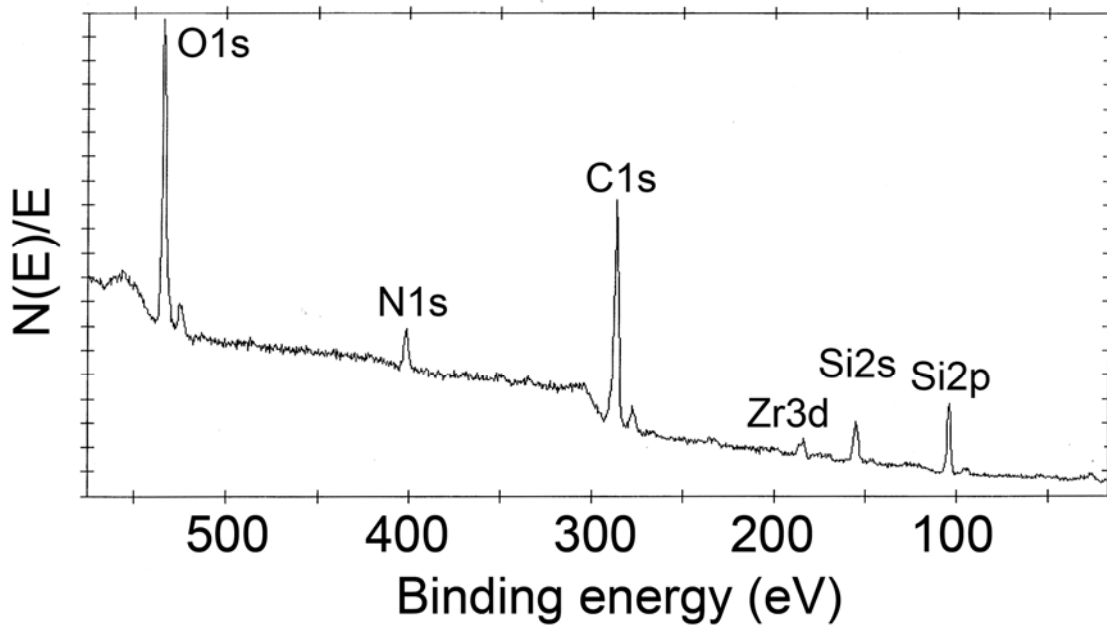
d)



e)



f)



g)

Figure 1. Monomeric molecule structures and FTIR spectra of the functional silane activation reactions. (Key: In c) and e): A = absorbance in arbitrary units, ‘wave number’ as cm^{-1}). a) 10-methacryloyloxydecyldihydrogenphosphate (MDP), b) 3-methacryloxypropyltrimethoxysilane (primer AM), c) Hydrolysis of 3-methacryloxypropyltrimethoxysilane, d) 3-(N-allylamino)propyltrimethoxysilane (primer AN), e) Hydrolysis of 3-(N-allylamino)propyltrimethoxysilane. F) XPS survey spectrum of SIE-treated zirconia and g) of SIE-treated + zirconia primer treated specimen.

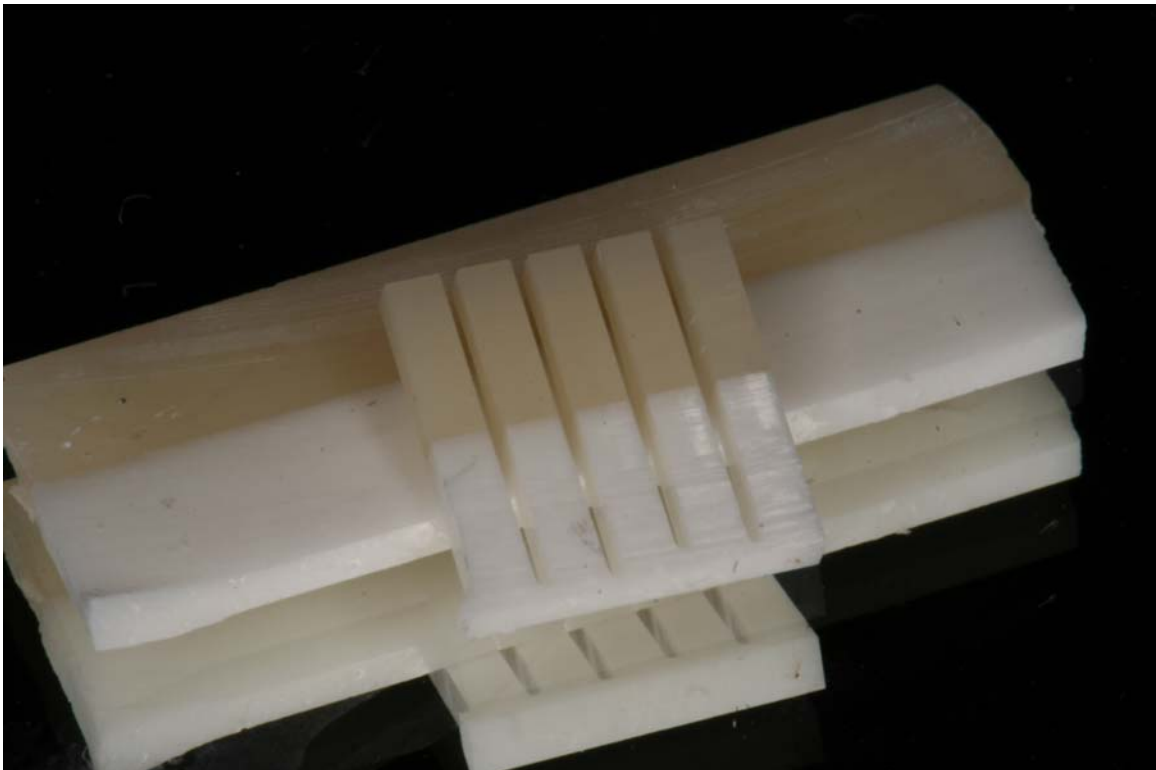
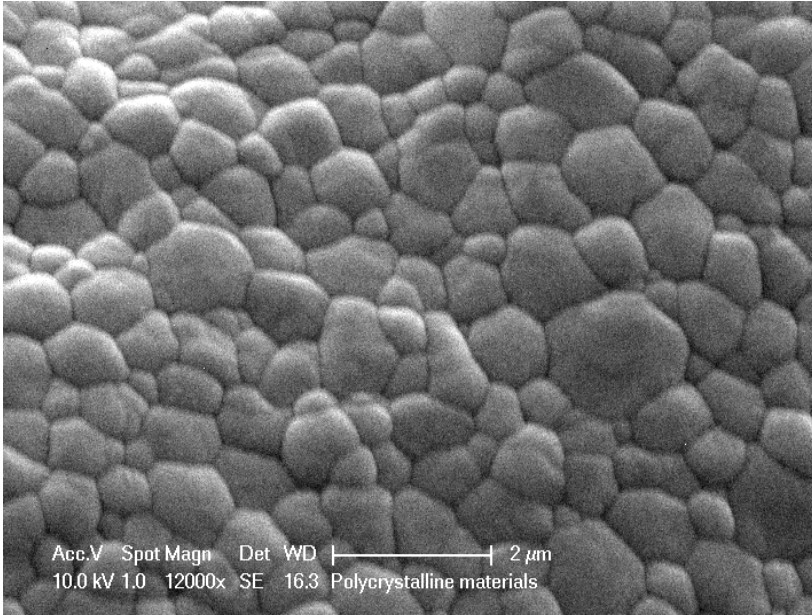
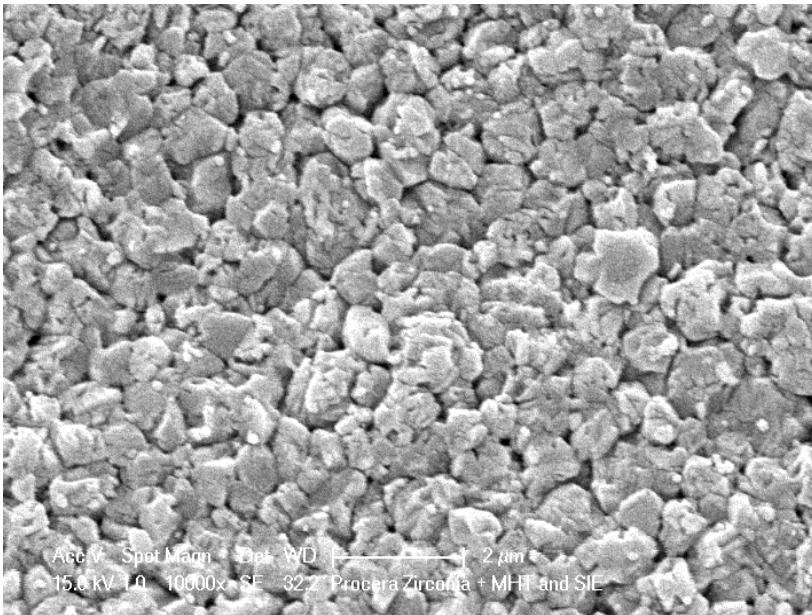


Figure 2. Bi-layered specimens were cut in 1 direction to reveal 1 mm thick slabs which were cut in a perpendicular direction giving independent microbars.



a)



b)

Figure 3. SEM images, 10000x, demonstrating the original zirconia surface, and b) the inter-grain spaces created by SIE surface treatment (NB The magnifications are not exactly the same).