UNIVERSIDADE FEDERAL DE PELOTAS
Programa de Pós-Graduação em Odontologia

Dissertação

Desenvolvimento de um método simplificado para obtenção de adesão à zircônia

Aline de Oliveira Ogliari

Pelotas, 2012

ALINE DE OLIVEIRA OGLIARI

DESENVOLVIMENTO DE UM MÉTODO SIMPLIFICADO PARA OBTENÇÃO DE ADESÃO À ZIRCÔNIA

Dissertação apresentada ao Programa de Pós-Graduação da Faculdade de Odontologia da Universidade Federal de Pelotas, como requisito parcial para obtenção do título de Mestre em Odontologia, Área de concentração Dentística.

Orientador: Prof. Dr. Rafael Ratto de Moraes

Co-orientador: Prof. Dr. Fabrício Aulo Ogliari

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Dedicatória

Dedico este trabalho à minha família, minha filha Julia e meu marido Fabrício, por me apoiar e me ajudar em todos os momentos.

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Resumo

OLIVEIRA-OGLIARI, Aline de. **Desenvolvimento de um método simplificado para obtenção de adesão à zircônia.** 2012. 52f. Dissertação (Mestrado) - Programa de Pós-Graduação em Odontologia. Universidade Federal de Pelotas, Pelotas.

O objetivo deste estudo foi desenvolver um método simplificado para obtenção de adesão a uma cerâmica de zircônia estabilizada por ítria. O método foi baseado na deposição de uma camada reativa de sílica na superfície cerâmica seguida por tratamento térmico. O estudo compreendeu seis etapas: (i) preparo de 4 soluções contendo tetraetilortosilicato (TEOS) e tert-butóxido de zircônio (ZTB) diluídos em hexano; (ii) corte e polimento do substrato de zircônia; (iii) tratamento com os precursores orgânicos antes (infiltração, INF) ou depois (cobertura, COA) da sinterização da zircônia; (iv) análise por microscopia eletrônica de varredura e espectroscopia de energia dispersiva (MEV-EDS); (v) análise por espectroscopia confocal μ-Raman; (vi) avaliação de resistência de união ao cisalhamento 24h após preparo e análise de falha. Grupos sem tratamento (controle) e uma referência comercial (Rocatec Plus, 3M ESPE) foram testados. Dados quantitativos foram analisados usando ANOVA e teste *post hoc* de Tukey ($P < 0,05$). Os resultados de MEV mostraram que a superfície da zircônia foi coberta por aglomerados de nanopartículas de sílica, sendo esta composição confirmada por EDS e análise de μ-Raman. Os resultados do teste mecânico mostraram que a maioria dos grupos que receberam cobertura (COA) e infiltração (INF) apresentaram maior resistência de união que o grupo sem tratamento (controle). A maioria dos grupos experimentais foram similares à referência comercial. Falhas do tipo mistas foram predominantes. Em conclusão, o presente estudo introduz um método novo, simples e de baixo custo para promover adesão a cerâmicas de zircônia estabilizada por ítria. Tanto o método de deposição de sílica (se antes ou após sinterização da zircônia) e a concentração de precursores orgânicos de sílica têm impacto significativo na adesão de metacrilatos à cerâmica tratada.

Palavras-chave: Adesão. Cerâmica. Tratamento térmico. Resistência de união ao cisalhamento. MEV-EDS. Cobertura de superfícies. Tratamento de superfície.

Abstract

OLIVEIRA-OGLIARI, Aline de. **Desenvolvimento de um método simplificado para obtenção de adesão à zircônia.** 2012. 52f. Dissertação (Mestrado) - Programa de Pós-Graduação em Odontologia. Universidade Federal de Pelotas, Pelotas.

The aim of this study was to develop a simplified method for bonding to yttria-stabilized zirconia ceramic. The method was based on deposition of a reactive silica layer on the ceramic surface followed by heat treatment. The study comprised six steps: (i) preparation of solutions using four concentrations of tetraethyl orthosilicate (TEOS) and zirconium tert-butoxide (ZTB) diluted in hexane; (ii) cutting and polishing of the zirconia substrate; (iii) organic silica-based treatment before (infiltration, INF) or after (coating, COA) zirconia sintering; (iv) analysis by scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS); (v) μ-Raman confocal spectroscopy analysis; (vi) shear bond strength to zirconia tested after 24-h and failure analysis. An untreated (control) and a commercial reference (Rocatec Plus, 3M ESPE) groups were tested. Quantitative data were analyzed using ANOVA and Tukey's *post hoc* test ($P < 0.05$). SEM micrographs showed that zirconia surface was covered by silica nanoparticle clusters. EDS and μ-Raman analyses confirmed composition of this layer. The bond strength results showed that most groups that received coating (COA) and infiltration (INF) presented higher bonding potential than the untreated (control) group. Almost all experimental groups were similar to commercial reference. Mixed failures were predominant. In conclusion, the present study introduces a novel, simple, and cost-effective method to provide adhesion to yttria-stabilized zirconia ceramic. Both the method of silica deposition (if before or after zirconia sintering) and concentration of organic silica precursors have a significant impact on the adhesion of methacrylates to the treated zirconia.

Keywords**:** Adhesion. Ceramics. Heat treatment. Shear bond strength. SEM-EDS. Surface coating. Surface treatment.

Lista de Abreviaturas e Símbolos

CAD-CAM	Desenho assistido por computador–Manufatura auxiliada por computador
et al.	E colaboradores
$SiCl_4$	Tetraclorosilano
SiO_2	Sílica
$R\text{-}Si(OR')_3$	Representação de um trialcóxi silano
SiOx	Composto siloxano
TBZ	Tert-butóxido de zircônio
TEOS	Ortosilicato de tetraetila
mm	Milímetro
µL	Microlitro
ºC/h	Grau Celsius por hora
ºC	Grau Celsius
h	Hora
ºC/min	Grau Celsius por minuto
EDX	Espectroscopia por energia dispersiva de raios-X
MEV	Microscopia eletrônica de varredura
EDS	Espectroscopia por energia dispersiva
HeNe	Hélio neodímio
nm	Nanômetro
mW	MiliWatt
cm^{-1}	Por centímetro
Si	Silício
O	Oxigênio
s	Segundo
g	Grama
mm/min	Milímetro por minuto
MPa	MegaPascal
x	Vezes
%	Porcento

Sumário

O projeto de pesquisa a seguir é apresentado em sua forma final após qualificação realizada em 15/12/2011 e aprovado pela Banca Examinadora composta pelos Professores Doutores Evandro Piva, Rafael Ratto de Moraes e Sérgio da Silva Cava.

1 Projeto de pesquisa

1.1 Introdução

Cerâmicas policristalinas do tipo zircônia estabilizada com ítria estão sendo cada vez mais utilizadas como biomateriais na odontologia. Estes materiais atendem de forma satisfatória demandas por estética, biocompatibilidade, inércia química e resistência mecânica. Adicionalmente, por meio do uso de tecnologia CAD-CAM, é possível a simplificação das etapas laboratoriais, reduzindo custo, tempo e possibilidade de falhas na confecção de estruturas cerâmicas.

Uma significativa limitação ainda apresentada pelas cerâmicas do tipo zircônia é a falta de união adesiva a cimentos resinosos. Isto pode ser explicado por dois fatores principais: sua estrutura monofásica e homogênea, altamente densa, torna difícil a criação de microrretenções por ataque seletivo da superfície (CHAIYABUTR et al., 2008), e a ausência de silício na sua estrutura, que inviabiliza o estabelecimento da união por meio do uso de organo-silanos. Esta falta de adesão dificulta a utilização destes materiais em preparos com reduzida retenção friccional, como no caso de *inlays, onlays* e coroas em dentes com preparos curto e/ou cônicos (THOMPSON et al., 2011).

Métodos alternativos vêm sendo propostos na tentativa de contornar o problema da adesão à zircônia. Entretanto, uma forma segura, efetiva, prática e com custo viável de aplicação ainda não está disponível. Um destes métodos é a utilização de materiais contendo monômeros fosfatados que, apesar de apresentar bons resultados de adesão iniciais, falham em avaliações de envelhecimento a longo prazo (SMITH et al., 2011; YUN et al., 2010). Outra abordagem é a deposição triboquímica de sílica na superfície da cerâmica (silicatização) que, além de não apresentar resultados consistentes para diferentes materiais resinosos (CHAI; CHU; CHOW, 2010), pode sofrer significativa redução da adesão após envelhecimento (ATTIA; LEHMANN; KERN, 2011). Outros métodos de deposição por vapor de $SiCl_4$ (PIASCIK et al., 2009) e fusão de SiO_2 por plasma (DERAND; MOLIN; KVAM, 2005;

PIASCIK; WOLTER; STONER, 2011) foram propostos; no entanto, são complexos e exigem equipamentos sofisticados.

Considerando que a falta de reatividade da zircônia pode ser contornada pela deposição de uma camada de sílica em sua superfície, justifica-se a busca por métodos mais simples e confiáveis de recobrimento. Surpreendentemente, a simples deposição de precursores orgânicos do tipo $R\text{-}Si(OR')_3$ sobre o substrato de zircônia, seguida por adequada calcinação e condensação da rede de SiOx, ainda não foi descrita na literatura.

1.2 Objetivo

O objetivo do presente estudo é desenvolver um novo método simplificado de adesão à zircônia. Para tal fim, serão depositadas coberturas contendo sílica na superfície de cerâmica odontológica de zircônia estabilizada por ítria, tornando-a suficientemente reativa para obtenção de adesão a metacrilatos.

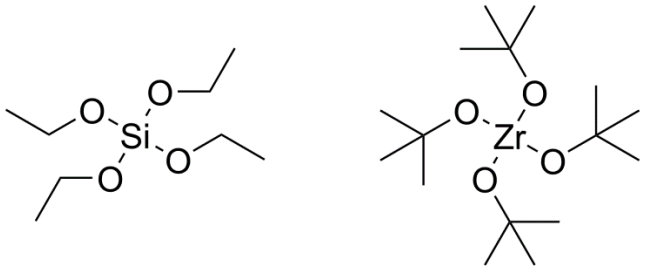
1.3 Metodologia

1.3.1 Preparo das soluções

Serão preparadas quatro soluções utilizando ortosilicato de tetraetila (TEOS) e tert-butóxido de zircônio (TBZ) diluídos em acetona, conforme Tabela 1. As estruturas moleculares dos precursores metálicos são apresentadas na Figura 1.

Tabela 1. Soluções experimentais (% em massa)

Solução	TEOS	TBZ	Acetona
S_1	5	0	95
S_2	3,75	1,25	95
S_3	2,5	2,5	95
S_4	1,25	3,75	95



TEOS TBZ

FIGURA 1. Estrutura molecular dos precursores orgânicos. TEOS: ortosilicato de tetraetila; TBZ: tert-butóxido de zircônio.

1.3.2 Preparo dos substratos de zircônia

Serão utilizados blocos pré-sinterizados de zircônia estabilizada por ítria (Zircon-CAD; Angelus, Londrina, PR, Brasil) medindo 40×19×19mm. Os blocos serão recortados em cortadeira de precisão (ISOMET 1000; Buehler, Lake Bluff, IL, EUA), com disco diamantado, obtendo-se blocos menores com dimensões de 10×9×9mm. As superfícies planas destes blocos serão polidas com lixas de carbeto de silício com granulações de 320, 400, 600 e 1200.

1.3.3 Deposição da cobertura contendo sílica

1.3.3.1 Depósito pré-sinterização

Utilizando como substrato os blocos não sinterizados, serão depositados ~3μL das soluções com os precursores orgânicos na superfície cerâmica com auxílio de uma micropipeta graduada. Os blocos tratados serão sinterizados em um forno mufla, controlado por computador, utilizando o protocolo recomendado pelo fabricante da cerâmica: taxa de aquecimento de 100ºC/h até 1350^{o}C, sendo esta temperatura mantida por 2h.

1.3.3.2 Depósito pós-sinterização

O procedimento realizado será semelhante ao descrito no item 1.3.3.1, exceto pelo fato de que a solução será aplicada após a sinterização da cerâmica, seguida por tratamento térmico com taxa de aquecimento de 10ºC/min com platô de 800ºC por 2h.

1.3.3.3 Controles

Dois grupos controle serão avaliados: sem tratamento superficial da zircônia e com deposição triboquímica de sílica na superfície, utilizando equipamento comercialmente disponível (Rocatec; 3M ESPE, St. Paul, MN, EUA).

1.3.4 Caracterização da cobertura de sílica

1.3.4.1 EDX

Os blocos após tratamento serão avaliados por espectroscopia de fluorescência (EDX-720; Shimadzu, Tóquio, Japão) com o objetivo de caracterizar a composição química da superfície e verificar a presença de sílica.

1.3.4.2 MEV e EDS

A morfologia de superfície da zircônia será analisada por microscopia eletrônica de varredura (SSX-550; Shimadzu). Será realizada microanálise elementar por meio de espectroscopia de energia dispersiva de forma a mapear a deposição dos elementos sobre a superfície da cerâmica.

1.3.4.3 Espectroscopia confocal μ-Raman

Para a avalição da espessura da camada contendo sílica depositada, as amostras tratadas serão avaliadas por meio de espectroscopia confocal μ-Raman (Senterra, Bruker Optics, Ettlingen, Alemanha). As amostras serão avaliadas utilizando os seguintes parâmetros: laser de HeNe com comprimento de onda de 785nm, intensidade de 100mW e resolução espectral de ~3.5cm^{-1}. O mapeamento tridimensional será realizado em profundidade, até ultrapassar totalmente a camada contendo sílica. Serão observados os picos referentes aos estiramentos e deformações da ligação Si-O com absorções na faixa de 100 a 1100cm^{-1}.

1.3.5 Avaliação da adesão à zircônia

1.3.5.1 Resistência de união à zircônia

Todos os grupos, independente do método de deposição de cobertura de sílica, receberão a aplicação de uma camada de organo-silano (Silano, Angelus) e de adesivo sem solvente (Scotchbond; 3M ESPE). Após, matrizes de elastômero (espessura de 0,5mm) com quatro orifícios cilíndricos (diâmetro de 1,5mm) serão posicionadas na superfície dos blocos, seguido de fotoativação do adesivo por 20s. Cilindros de cimento resinoso dual (Relyx ARC; 3M ESPE) serão confeccionados a partir da mistura por 10s das pastas e preenchimento dos orifícios da matriz. As matrizes serão cobertas com tira de poliéster e lâmina de vidro e, sobre o conjunto, será aplicada carga de cimentação de 500g por 3min, seguida de fotoativação do cimento por 40s.

Os corpos-de-prova serão armazenados em água destilada a 37ºC, por 24h, e então submetidos ao teste de resistência de união ao cisalhamento. Um fio de aço inoxidável (diâmetro de 0,2mm) será colocado ao redor do cilindro de cimento e alinhado com a interface de união, sendo o teste de cisalhamento realizado em máquina de ensaios mecânicos (DL500; EMIC, São José dos Pinhais, PR, Brasil), à velocidade de 0,5mm/min. Os valores de resistência de união serão calculados em MPa. Os espécimes fraturados serão observados em lupa estereoscópica, sob aumento de 40×, para determinação dos modos de falha.

1.3.5.2. Ciclagem térmica

Com o objetivo de simular o envelhecimento dos espécimes e avaliar a longevidade da união à zircônia, metade do número de espécimes de cada grupo será submetida à ciclagem térmica. O procedimento será realizado com 5.000 ciclos de imersão alternada por 30s em água a 5^{o}C e 55^{o}C.

1.3.6. Análise estatística

Os dados quantitativos e qualitativos serão submetidos a análises estatísticas apropriadas, com nível de significância de 5%.

1.4 Referências

ATTIA, A., LEHMANN, F., KERN, M. Influence of surface conditioning and cleaning methods on resin bonding to zirconia ceramic. **Dental Materials,** v.27, n.3, p.207-213, 2011.

CHAI, J., CHU, F. C., CHOW, T. W. Effect of surface treatment on shear bond strength of zirconia to human dentin. **Journal of Prosthodontics,** v.20, n.3, p.173-179, 2010.

CHAIYABUTR, Y., MCGOWAN, S., PHILLIPS, K. M., KOIS, J. C., GIORDANO, R. A. The effect of hydrofluoric acid surface treatment and bond strength of a zirconia veneering ceramic. **Journal of Prosthetic Dentistry,** v.100, n.3, p.194-202, 2008.

DERAND, T., MOLIN, M., KVAM, K. Bond strength of composite luting cement to zirconia ceramic surfaces. **Dental Materials,** v.21, n.12, p.1158-1162, 2005.

PIASCIK, J. R., SWIFT, E. J., THOMPSON, J. Y., GREGO, S., STONER, B. R. Surface modification for enhanced silanation of zirconia ceramics. **Dental Materials,** v.25, n.9, p.1116-1121, 2009.

PIASCIK, J. R., WOLTER, S. D., STONER, B. R. Development of a novel surface modification for improved bonding to zirconia. **Dental Materials,** v.27, n.5, p.e99-105, 2011.

SMITH, R. L., VILLANUEVA, C., ROTHROCK, J. K., GARCIA-GODOY, C. E., STONER, B. R., PIASCIK, J. R., THOMPSON, J. Y. Long-term microtensile bond strength of surface modified zirconia. **Dental Materials,** v.27, n.8, p.779-785, 2011.

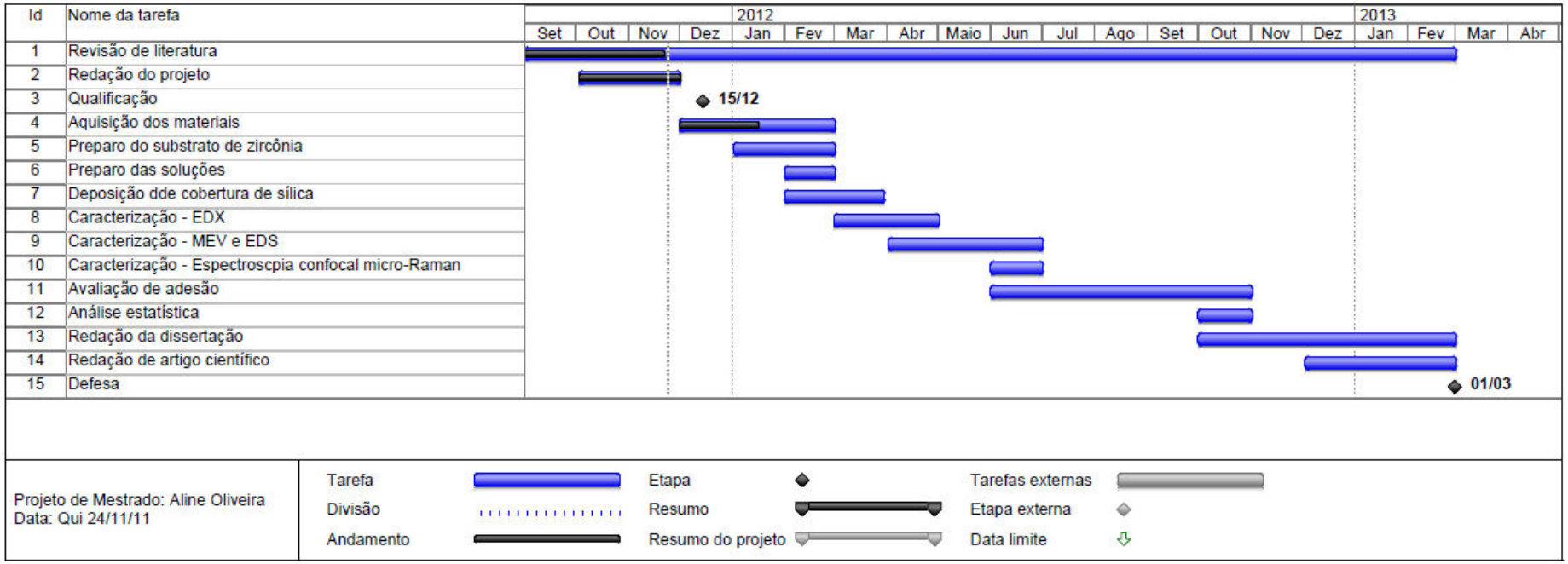
THOMPSON, J. Y., STONER, B. R., PIASCIK, J. R., SMITH, R. Adhesion/cementation to zirconia and other non-silicate ceramics: where are we now? **Dental Materials,** v.27, n.1, p.71-82, 2011.

YUN, J. Y., HA, S. R., LEE, J. B., KIM, S. H. Effect of sandblasting and various metal primers on the shear bond strength of resin cement to Y-TZP ceramic. **Dental Materials,** v.26, n.7, p.650-658, 2010.

1.5 Orçamento

Descrição	Quantidade	Preço unitário, R$	Total, R$
Ortosilicato de tetraetila	250mL	123,00	123,00
Tert-butóxido de zircônio	100mL	147,00	147,00
Acetona	1L	15,00	15,00
Blocos pré-sinterizados de zircônia	10un	120,00	1.200,00
Lixa de carbeto de silício 320	1pct	45,00	45,00
Lixa de carbeto de silício 400	1pct	45,00	45,00
Lixa de carbeto de silício 600	1pct	45,00	45,00
Lixa de carbeto de silício 1200	1pct	185,00	185,00
Micropipeta graduada	1un	597,98	597,98
Ponteiras de 0,5 a 10µL	1pct	28,96	28,96
Deposição triboquímica de sílica	10un	50,00	500,00
Transporte por Sedex	2un	25,00	50,00
Organo-silano	5un	34,60	173,00
Adesivo	5un	108,94	544,70
Elastômero	2un	75,00	75,00
Cimento resinoso dual	5un	145,00	725,00
Tiras de poliéster	2pct	1,40	2,80
Lamínulas de vidro	1cx	75,00	75,00
Pincel aplicador	2cx	11,00	22,00
Espátula	3un	7,22	21,66
Aparelho fotopolimerizador LED	1un	1.545,00	1.545,00
Vidraria de laboratório	-	-	200,00
Material para acondicionamento	-	-	200,00
Material de escritório	-	-	50,00
Material descartável	-	-	150,00
Impressão gráfica	500 un	1,00	500,00
Diária e passagem para congresso	-	-	4.000,00
	TOTAL:		**11.266,10**

1.6 Cronograma



2 Relatório do trabalho de campo

Este trabalho é apresentado de acordo com a estrutura em artigos (nível de descrição 4) prevista no Manual de Normas para Teses, Dissertações e Trabalhos Acadêmicos da Universidade Federal de Pelotas, aprovado pela resolução nº 03 de 22/02/2006 do COCEPE. O artigo apresentado na seção 3 está formatado de acordo com as instruções aos autores do periódico *Dental Materials.*

A única diferença relevante entre o projeto de pesquisa apresentado no item 1 e o artigo a seguir apresentado foi a mudança do método de envelhecimento dos espécimes selecionado. No projeto, a termociclagem foi proposta para avaliar a longevidade da união à zircônia, porém a inconsistência de funcionamento do equipamento foi detectada durante o desenvolvimento da metodologia e, por esta razão, todos os grupos termociclados testados até este momento foram descartados. Optou-se então por armazenagem em água destilada e estufa a 37ºC por um período de 3, 6, 12 meses para futuras análises.

3 Artigo

A simple method for improved bonding to zirconia through silica nanoparticle clusters deposition[¥]

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Short title: A simple method for improved bonding to zirconia

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[¥]Artigo formatado de acordo com as normas do periódico *Dental Materials*.

3.1 Abstract

Objective. The aim of this study was to develop a simplified method for bonding to yttria-stabilized zirconia ceramic.

Methods. The method was based on deposition of a silica nanoparticle clusters layer on the ceramic surface followed by heat treatment. The study comprised six steps: (i) preparation of solutions using four concentrations of tetraethyl orthosilicate (TEOS) and zirconium tert-butoxide (ZTB) diluted in hexane; (ii) cutting and polishing of the zirconia substrate; (iii) organic silica-based treatment before (infiltration, INF) or after (coating, COA) zirconia sintering; (iv) analysis by scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS); (v) μ-Raman confocal spectroscopy analysis; (vi) shear bond strength to zirconia tested after 24-h and failure analysis. An untreated (control) and a commercial reference (Rocatec Plus) groups were tested. Quantitative data were analyzed using ANOVA and Tukey's *post hoc* test ($P < 0.05$).

Results. SEM micrographs showed that zirconia surface was covered by silica nanoparticle clusters. EDS and μ-Raman analyses confirmed the composition of this layer. The bond strength results showed that most groups that received coating (COA) and infiltration (INF) presented higher bonding potential than the untreated (control) group. Almost all experimental groups were similar to commercial reference Rocatec Plus. Mixed failures were predominant.

***Significance*.** Through a simple method, it was possible to promote high adhesion to zirconia.

Keywords: adhesion; ceramics; heat treatment; shear bond strength; SEM-EDS; surface coating; surface treatment.

3.2 Introduction

The use of yttria-stabilized zirconia ceramics is increasing as biomaterials in dentistry. These materials satisfactorily meet demands for aesthetics, biocompatibility, mechanical strength and chemical inertia. Additionally, through the use of CAD-CAM technology, it is possible to simplify the laboratory steps, reducing cost, time and possibility of failures when processing ceramic structures.

A significant shortcoming of zirconia ceramics is their lack of adhesive bonding to resin cements. This can be explained by two main factors: the homogeneous and single-phase structure of zirconia is highly dense and hard to attack for creation of selective micro-retentions [1], and the absence of silicon in the zirconia structure hinders the establishment of chemical bonds mediated by organo-silanes. This lack of adhesion limits the use of zirconia ceramics in preparations with reduced frictional retention as in the case of inlays and onlays, or crowns and bridges in teeth with short or conical abutments [2].

Alternative methods have been proposed to address the possibility of bonding to zirconia. A safe, practical, and cost-effective application is, however, not yet available. One of the proposed methods is the use of phosphate monomers-containing materials that, despite showing good initial adhesion results, might present unreliable long-term results [3-5]. Another approach is the tribochemical deposition of silica on the surface; this method has been reported to not provide consistent results for different resin materials [6], and suffer from significant reduction in bonding ability after aging [7]. Methods such as vapor deposition of $SiCl_4$ [8] and SiO_2 fusion by plasma treatment [9,10] have also been proposed but are costly, complex, and require sophisticated equipment.

The lack of reactivity of zirconia can be addressed by depositing a silica layer on its surface; therefore, the search for simple and reliable silica-coating methods is justified. Surprisingly, the simple deposition of organic alkoxy R-Si(OR')$_3$ precursors on the zirconia substrate, followed by appropriate calcination and condensation of SiOx network, has not been described in the literature.

The aim of this study was to develop a novel and simple method to obtain adhesion to yttria-stabilized zirconia using organic Si precursors in a convenient process. The hypothesis tested was that deposition of a silica layer on the zirconia surface would make it sufficiently reactive to bond to methacrylate-based materials.

3.3 Materials and methods

Four solutions were prepared using tetraethyl orthosilicate (TEOS) and zirconium tert-butoxide (ZTB) diluted in hexane, as shown in Table 1. The molecular structures of the metallic precursors are shown in Figure 1. Mixtures of silica and zirconia precursors were tested in order to increase the compatibility of the surface coating with the ceramic substrate.

Pre-sintered blocks of yttria-stabilized zirconia (Zircon-CAD; Angelus, Londrina, PR, Brazil) measuring 40×19×19 mm were used. The blocks were cut with a diamond saw into smaller blocks with dimensions of 10×9×9 mm. The flat surfaces of these specimens were sequentially polished with 320, 400, 600, and 1200 SiC papers. The silica-coating process was tested either before of after fully sintering of the zirconia ceramic.

Non-sintered specimens (groups labeled as INF) were immersed for 5 min into the formulated solutions in order to allow maximum infiltration of the organic precursors into the ceramic, as observed in a pilot study. The blocks were then sintered in a computer-controlled muffle furnace (FEZ-1600/4; INTI, São Carlos, SP, Brazil) using the protocol recommended by the ceramic manufacturer: heating rate of 100°C/h until 1350°C and keeping this temperature for 2 h. Non-impregnated samples (groups labeled as COA) were sintered before coating with ~100 µL of the prepared solutions with organic precursors with the aid of a graduated micropipette; additional heat treatment was applied at a heating rate rate of 10ºC/min until 800ºC, which was maintained for 2 h for condensation of the SiOx network. A control group (untreated zirconia) and a commercial reference of tribochemical silica deposition (Rocatec Plus; 3M ESPE, St. Paul, MN, USA) were also tested.

The surface morphology of zirconia was analyzed by scanning electron microscopy (SEM – SSX-550; Shimadzu, Tokyo, Japan) linked with an x-ray energy dispersive spectroscopy (EDS) for surface elemental microanalysis. This analysis was corroborated by confocal μ-Raman spectroscopy (Senterra, Bruker Optics, Ettlingen, Germany) when the samples was evaluated in a HeNe laser with a 785 nm wavelength, 100 mW intensity, and ~3.5 cm^{-1} spectral resolution. Peaks were observed related to the stretching and deformation of the Si-O bonds with absorptions in the range between 250 and 1100 cm^{-1}.

All groups, regardless of the method of silica coating, including the control group, received a layer of organo-silane (Silano, Angelus) and solvent-free adhesive (Scotchbond, 3M ESPE). After, elastomer molds (thickness 0.5 mm) with four cylindrical orifices (diameter 1.5 mm) were placed on the surface of the blocks, followed by photopolymerization of the adhesive for 20 s using a LED curing unit (Radii-Cal; SDI, Bayswater, Australia) with 1200 mW/cm^2 irradiance. The orifices were filled with dual-cured resin cement (RelyX ARC; 3M ESPE), a polyester strip and glass slide were placed onto the molds, and the cement was light-cured for 40 s. For each group, 10 resin cement cylinders were built up on the ceramic surfaces.

The samples were stored in distilled water at 37ºC for 24 h and then tested for shear bond strength. A stainless steel wire (diameter 0.2 mm) was placed around the cylinder, aligned with bonding interface, and the shear test performed on a universal testing machine (DL500; EMIC, São José dos Pinhais, PR, Brazil) at a crosshead speed of 0.5 mm/min until failure. Bond strength values were calculated in MPa. The fractured specimens were observed in a light microscope, under a 40× magnification, and failures were classified as mixed (remnants of the cement left on

the ceramic) or adhesive (interfacial debonding). Data were analyzed using one-way ANOVA and Tukey's as *post hoc* test at a 5% significance level.

3.4 Results

Figure 2 depicts SEM micrographs of the untreated ceramic, the ceramic treated with Rocatec Plus, and zirconia surfaces subjected to the experimental coatings using the solution with highest content of silica precursors (100:00). The control surface (Fig. 2a and 2b) presented a highly homogeneous and dense appearance with grooves left by the polishing process. The surface treated with Rocatec Plus (Fig. 2c and 2d) showed a pattern of particle deposition heterogeneously dispersed and apparently poorly bonded to the substrate. In the group COA (Fig. 2e and 2f), the surface was entirely covered by silica particles; in the group INF (Fig. 2g and 2h), the surface coating had some irregularity and voids.

Figure 3 shows that densely agglomerated silica nanoparticle clusters, approximately 140 nm to 300 nm in size, were deposited on the surface of zirconia when the experimental silica coating method is used. In the EDS analysis, it was possible to confirm that the coating of the groups with the identified nanoagglomerates was composed exclusively by silica. Figure 4 shows SEM micrographs comparing the methods COA (Fig. 4a and 4b) and INF (Fig. 4c and 4d) for the solution with the lowest content of silica precursors (25:75). The coating had a typical profile of phase separation between the silica and zirconia precursors, with the silica dispersed as nanoparticle coated by a layer composed of zirconia with characteristics of a brittle material. Figure 5 shows results for the μ-Raman analysis, indicating differences in intensity for peaks at 642 cm^{-1} and 464 cm^{-1} related to the presence of silica on the surface.

Results for the bond strength test are shown in Table 2; the power of the statistical test was 1. The control group showed the lowest bond strength values; yet, this group had somewhat unexpected high bond strength values. The groups COA

100:00, COA 50:50, INF 50:50, and Rocatec Plus had significantly higher bond strength than the control group ($P < 0.001$). With exception of the groups INF 75:25 and INF 25:75, all the other groups showed similar bond strength to the commercial reference Rocatec Plus ($P \geq 0.079$).

3.5 Discussion

The clean characteristic of the zirconia surface (as observed in the SEM analysis) associated with its low of reactivity has been reported as the main responsible for the lack of adhesion to resin materials [11,12]. In the present study, however, evidence of bonding was observed on untreated zirconia, which is likely a result of the polishing scratches left on the surface allowing mechanical keying of the adhesive. This result is corroborated by a previous investigation [13]. The characteristics observed on the surface treated with Rocatec Plus are also in line with previous studies [6,11]. The experimental treatment tested using the COA method, in contrast with Rocatec Plus, was able to uniformly coat the zirconia with silica nanoclusters. These agglomerates, formed by particles 140 nm to 300 nm in size, determined a significant increase in the surface area of the ceramic. Assuming a perfectly spherical shape for the silica particles, it is possible to obtain a theoretical increase of approximately 57% of the surface area available for adhesion without the need for mechanical abrasion of the surface.

The profile of silica nanoparticle agglomerates deposited on the zirconia by the experimental COA method is comparable to the profile obtained in studies where hexamethyldisilazane was deposited by plasma on polymeric substrates of polyethylene naphthalate [14], or when using spray drying [15]. When the INF method was tested, the deposition of silica on the zirconia surface was not homogeneous, indicating a higher technique sensitivity of the INF compared with the COA method. In addition, when the content of silica precursors on the solution was low and the COA method was used, phase separation on the coating was observed, possibly due to a thermal incompatibility between the organometallic precursors during heating due to their different condensation rates. The same phase-separation

effect was not observed for the INF method; our hypothesis for that is a possible role of ZTB acting as a ligand, allowing better wetting of TEOS adjacent to the non-sintered zirconia.

The μ-Raman analysis was conducted in an endeavor to investigate the thickness and in-depth homogeneity of the silica layer. A reduction in the intensity of peaks at 642 cm^{-1} and 464 cm^{-1} related to the presence of silica [16] was observed for the control when compared to COA 100:00. The analysis was conducted up to 10 μm deep into the coating layer, without to identification any significant differences in silica concentration. This result indicates that the coating had a thickness above 10 μm; further investigation is required to assess the actual thickness of the silica-coating deposited on zirconia by the methods proposed in this study.

The zirconia substrate was not sandblasted as it is typically done in other studies [17-19] in order to enhance the observation sensitivity of the potential effects of the proposed treatments. Thus, variables related to the three-dimensional morphology of the substrate were reduced. The need for previous sandblasting in the commercial reference group might be considered a shortcoming of such a treatment, as it has been reported that airborne-particle abrasion could affect the long-term reliability of oxide ceramics [20]. Another factor considered in this study was the application of an organosilane methacrylate even in the control group. Although chemical coupling is not expected, the silane could improve the wettability of resin components on the substrate.

The experimental treatment tested here, especially by the COA method, was able to impart adhesion of methacrylates to zirconia. The bonding ability is explained by incorporation of silica on the surface, allowing substantial increase in the surface area and subsequent silanization. Another result observed was that good adhesion

occurred between the layer of agglomerated silica nanoparticle and zirconia substrate. Although the interaction is mainly physical and the occurrence of covalent bonds at the zirconia-silica interface is not expected, it is possible to consider the establishment of secondary bonds such as van der Waals forces; considering the nanostructured characteristic of the silica layer, this interaction is enhanced by the large contact area available.

It is worth mentioning that all COA groups showed similar bond strength values to Rocatec Plus, which is one of the most used and studied methods in the literature for the establishment of adhesion to zirconia [7,21,22]. The method INF generally had lower bonding potential as compared with the COA method, the INF method also showing higher variability. This result might be explained by the less homogeneous surface coating observed in the SEM analysis. Application of the organometallic precursor solutions before zirconia sintering (INF method) could theoretically improve the retention of the coating, with better physical entanglement of the silica layer and zirconia. The INF method, however, appears to be more sensitive to errors during processing, leaving untreated areas or areas treated inconsistently.

The use of yttria-stabilized zirconia in dentistry has become an excellent alternative for obtaining prostheses relatively easy to build and with good reliability of structural integrity. The good performance of zirconia restorations has been demonstrated in clinical studies [23-25]. However, the challenge of adhesively bonding to zirconia limits its use. In this study, a simple and reliable alternative for obtaining adhesion to zirconia was presented. The reagents used are extremely safe, non-toxic, and cost-effective. The application technique used is also convenient as it demands the same clinical and laboratory step unemployed in the processing of

oxide ceramics. To exemplify, the furnace time and temperature used for sintering the veneering ceramic or glazing it could be used for the COA method, while the sintering cycle of zirconia itself could be used for the INF method.

There are still points to be clarified in this technology, such as the durability of adhesion obtained. At present a study is being conducted using accelerated aging of bonded interfaces to investigate the stability of the adhesion. Another characteristic that could not be determined in this study and should be further evaluated is the thickness of the deposited silica layer. This information is of great importance since it might interfere with the adaptation of the ceramic structure on the abutment teeth. It is expected that the thickness of the silica coating might be controlled by the concentration of organometallic precursors used in the treatment solution. Other techniques such as spin-coating and dip-coating, despite showing great efficiency in the control of film thickness, would be difficult to reproduce in the laboratory and clinical application. Another question concerning the technology here presented is whether the INF method could significantly affect the structural integrity and sintering cycle of zirconia. From a structural point of view, the INF method is quite audacious as it could alter the environmental conditions that the zirconia is subjected. Studies evaluating the dynamic and static mechanical resistance should be performed for further investment in this treatment approach. That notwithstanding, the COA method seems to better address the problem of yielding adhesion potential to zirconia ceramic.

3.6 Conclusion

The present study introduces a novel, simple, and cost-effective method to provide adhesion to yttria-stabilized zirconia ceramic. Both the method of silica deposition (before or after zirconia sintering) and concentration of organic silica precursors have a significant impact on the adhesion of methacrylates to the treated zirconia.

Acknowledgments

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3.7 References

[1] Chaiyabutr Y, McGowan S, Phillips KM, Kois JC, Giordano RA. The effect of hydrofluoric acid surface treatment and bond strength of a zirconia veneering ceramic. J Prosthet Dent 2008;100(3):194-202.

[2] Thompson JY, Stoner BR, Piascik JR, Smith R. Adhesion/cementation to zirconia and other non-silicate ceramics: where are we now? Dent Mater 2011;27(1):71-82.

[3] Smith RL, Villanueva C, Rothrock JK, Garcia-Godoy CE, Stoner BR, Piascik JR, et al. Long-term microtensile bond strength of surface modified zirconia. Dent Mater 2011;27(8):779-85.

[4] Yun JY, Ha SR, Lee JB, Kim SH. Effect of sandblasting and various metal primers on the shear bond strength of resin cement to Y-TZP ceramic. Dent Mater 2010;26(7):650-8.

[5] Moraes RR, Guimaraes GZ, Oliveira AS, Faot F, Cava SS. Impact of acidic monomer type and concentration on the adhesive performance of dental zirconia primers. Int J Adhes Adhes 2012;39:49-53.

[6] Chai J, Chu FC, Chow TW. Effect of surface treatment on shear bond strength of zirconia to human dentin. J Prosthodont 2010;20(3):173-9.

[7] Attia A, Lehmann F, Kern M. Influence of surface conditioning and cleaning methods on resin bonding to zirconia ceramic. Dent Mater;27(3):207-13.

[8] Piascik JR, Swift EJ, Thompson JY, Grego S, Stoner BR. Surface modification for enhanced silanation of zirconia ceramics. Dent Mater 2009;25(9):1116-21.

[9] Derand T, Molin M, Kvam K. Bond strength of composite luting cement to zirconia ceramic surfaces. Dent Mater 2005;21(12):1158-62.

[10] Piascik JR, Wolter SD, Stoner BR. Development of a novel surface modification for improved bonding to zirconia. Dent Mater 2011;27(5):e99-105.

[11] Matinlinna JP, Lassila LV, Vallittu PK. Pilot evaluation of resin composite cement adhesion to zirconia using a novel silane system. Acta Odontol Scand 2007;65(1):44-51.

[12] Ozcan M, Vallittu PK. Effect of surface conditioning methods on the bond strength of luting cement to ceramics. Dent Mater 2003;19(8):725-31.

[13] Akyil MS, Uzun IH, Bayindir F. Bond strength of resin cement to yttrium-stabilized tetragonal zirconia ceramic treated with air abrasion, silica coating, and laser irradiation. Photomed Laser Surg 2010;28(6):801-8.

[14] Petersen J, Bardon J, Dinia A, Ruch D, Gherardi N. Organosilicon coatings deposited in atmospheric pressure Townsend discharge for gas barrier purpose: effect of substrate temperature on structure and properties. ACS Appl Mater Interfaces doi:10.1021/am3015229.

[15] Oguri T, Tamaki Y, Hotta Y, Miyazaki T. Effects of a convenient silica-coating treatment on shear bond strengths of porcelain veneers on zirconia-based ceramics. Dent Mater J 2012;31(5):788-96.

[16] Kirkpatrick RJ, Yarger JL, McMillan PF, Yu P, Cong XD. Raman spectroscopy of C-S-H, tobermorite, and jennite. Advn Cem Based Materials 1997;5(3-4):93-99.

[17] Akin H, Ozkurt Z, Kirmali O, Kazazoglu E, Ozdemir AK. Shear bond strength of resin cement to zirconia ceramic after aluminum oxide sandblasting and various laser treatments. Photomed Laser Surg 2011;29(12):797-802.

[18] Bhargava S, Doi H, Kondo R, Aoki H, Hanawa T, Kasugai S. Effect of sandblasting on the mechanical properties of Y-TZP zirconia. Biomed Mater Eng 2012;22(6):383-98.

[19] Gomes AL, Castillo-Oyague R, Lynch CD, Montero J, Albaladejo A. Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. J Dent doi:10.1016/j.jdent.2012.09.013.

[20] Zhang Y, Lawn BR, Malament KA, Van Thompson P, Rekow ED. Damage accumulation and fatigue life of particle-abraded ceramics. Int J Prosthodont 2006;19(5):442-8.

[21] Amaral R, Ozcan M, Bottino MA, Valandro LF. Microtensile bond strength of a resin cement to glass infiltrated zirconia-reinforced ceramic: the effect of surface conditioning. Dent Mater 2006;22(3):283-90.

[22] Fonseca RG, Martins SB, de Oliveira Abi-Rached F, Dos Santos Cruz CA. Effect of different airborne-particle abrasion/bonding agent combinations on the bond strength of a resin cement to a base metal alloy. J Prosthet Dent 2012;108(5):316-23.

[23] Pelaez J, Cogolludo PG, Serrano B, Lozano JF, Suarez MJ. A prospective evaluation of zirconia posterior fixed dental prostheses: three-year clinical results. J Prosthet Dent 2012;107(6):373-9.

[24] Pelaez J, Cogolludo PG, Serrano B, Serrano JF, Suarez MJ. A four-year prospective clinical evaluation of zirconia and metal-ceramic posterior fixed dental prostheses. Int J Prosthodont 2012;25(5):451-8.

[25] Poggio CE, Dosoli R, Ercoli C. A retrospective analysis of 102 zirconia single crowns with knife-edge margins. J Prosthet Dent 2012;107(5):316-21.

3.8 Tables and Figures

Table 1 - Experimental solutions (mL)

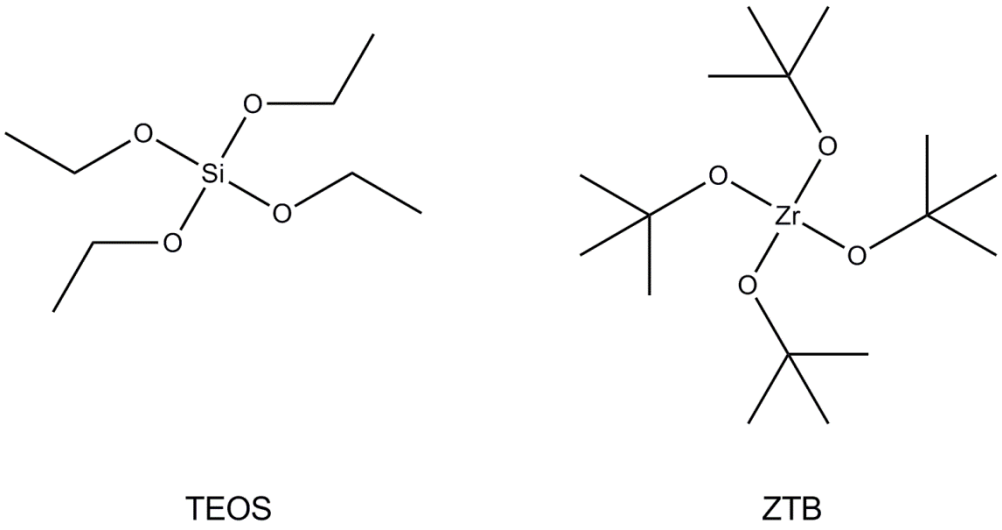
Solution	TEOS	ZTB	Hexane
100:00	2.5	0	50
75:25	1.875	0.625	50
50:50	1.25	1.25	50
25:75	0.625	1.875	50

Table 2. Means (standard deviations) for shear bond strength (SBS), n=10

Group*	SBS (MPa)	Coefficient of variation (%)	Adhesive failures (%)	Premature failures
Control	14.0 (8.0)[d]	57	0	1
COA 100:00	36.7 (6.3)[a]	17	10	0
COA 75:25	24.6 (5.6)[bcd]	23	33	1
COA 50:50	33.8 (6.4)[ab]	19	67	1
COA 25:75	23.7 (8.5)[bcd]	36	20	0
INF 100:00	23.2 (10.6)[bcd]	46	0	1
INF 75:25	15.4 (5.2)[d]	33	40	0
INF 50:50	29.1 (6.0)[abc]	21	70	0
INF 25:75	20.3 (2.0)[cd]	10	70	0
Rocatec Plus	33.3 (9.0)[ab]	27	40	0

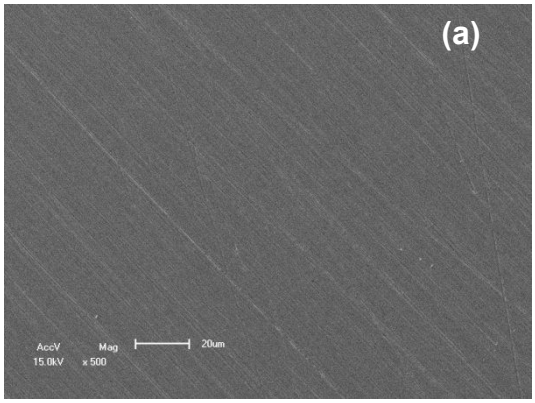
Distinct letters indicate significant differences between groups.

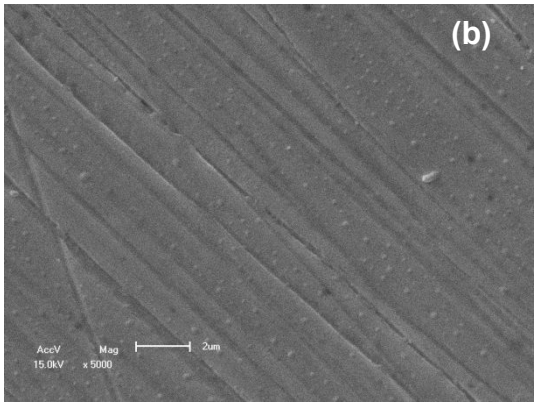
*Groups labeled as COA: experimental silica coating was carried out after zirconia sintering; Groups labeled as INF: experimental silica coating was carried out before zirconia sintering.



TEOS ZTB

Fig. 1 - Molecular structure of the organic precursors tested. TEOS: tetraethyl orthosilicate; ZTB: zirconium tert-butoxide.


(a)
AccV Mag 20um
15.0kV x 500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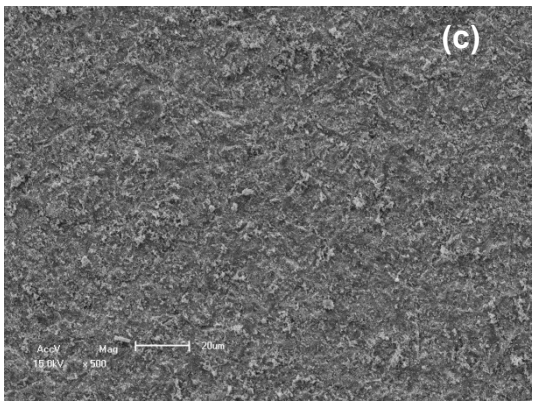
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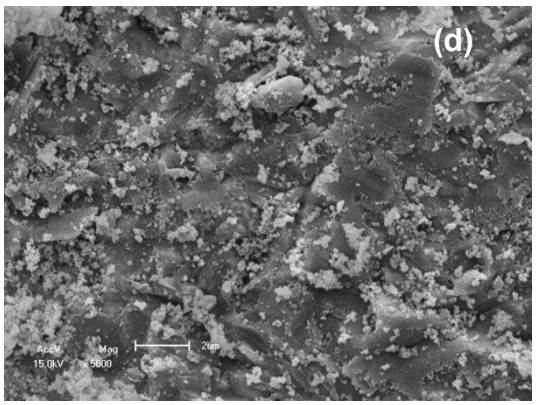
(d)
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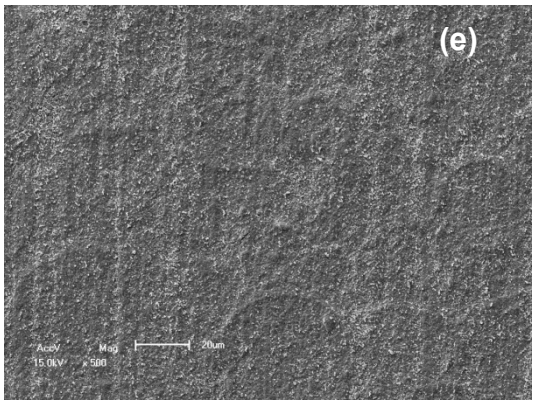
15.0kV x 5000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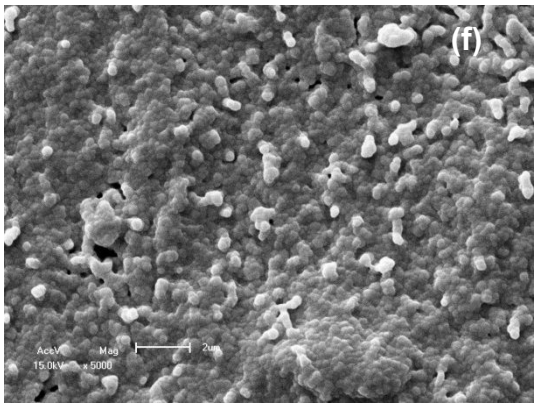
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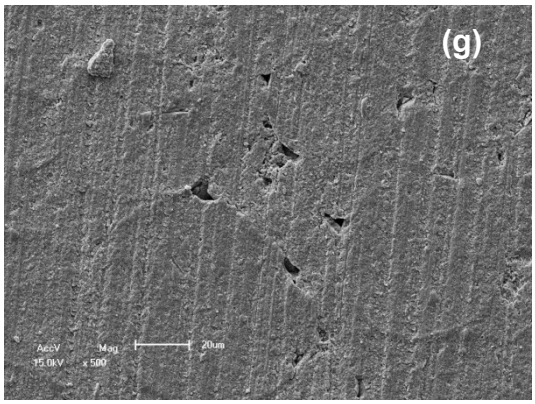
(g)
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15.0kV x 500

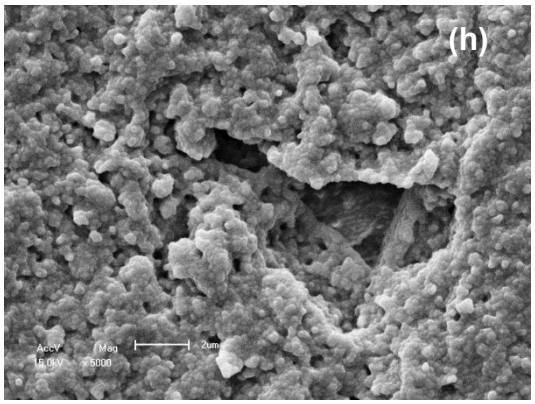
(h)
AccV Mag 2um
15.0kV x 5000

Fig. 2 - SEM micrographs showing treated and untreated zirconia surfaces in low (500×, left hand side) and high (5000×, right hand side) magnifications. The control surface was clean, with grooves owing to the polishing procedure (a,b). The surface treatead with Rocatec Plus had a rough particle deposition. In (e) and (f), the surface was entirely covered by silica nanoparticle clusters (group COA 100:00), while in (g) and (h) the formation of nanoparticle clusters covering the zirconia surface had some irregularity and voids (group INF 100:00).

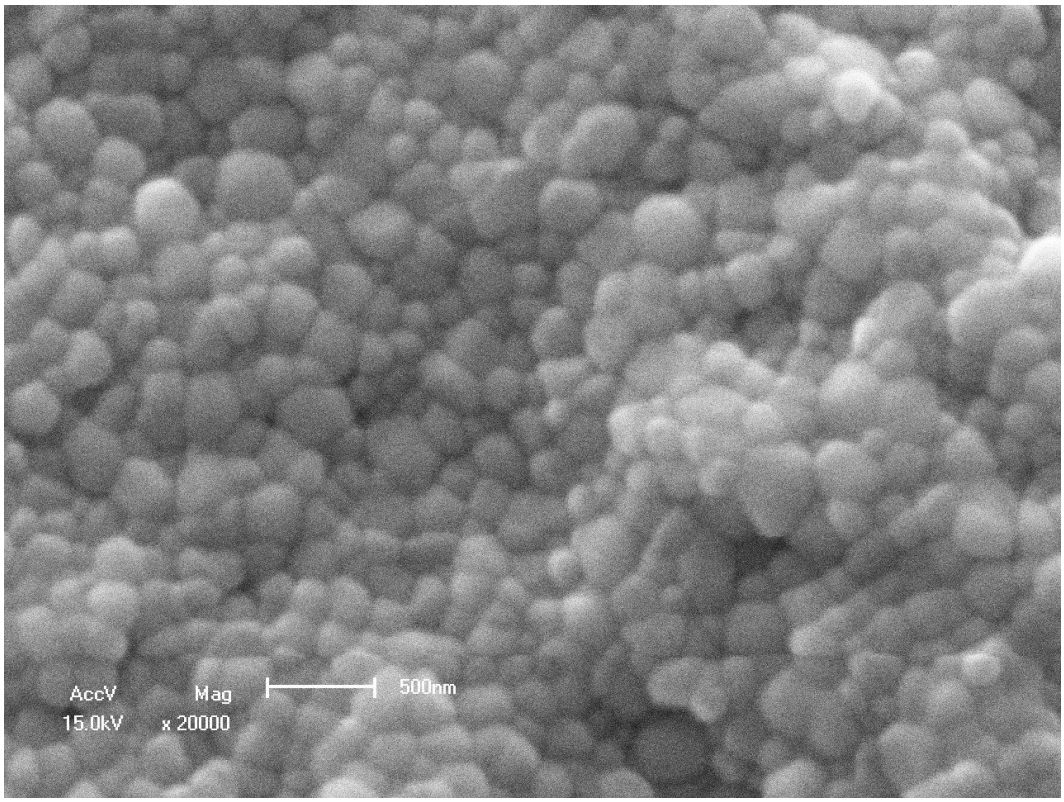

Fig. 3 - SEM micrograph of a treated zirconia surface (group COA 50:50) observed at a 20,000× magnification. Densely clustered nanoparticles are observed; the silica composition was confirmed by the EDS analysis.

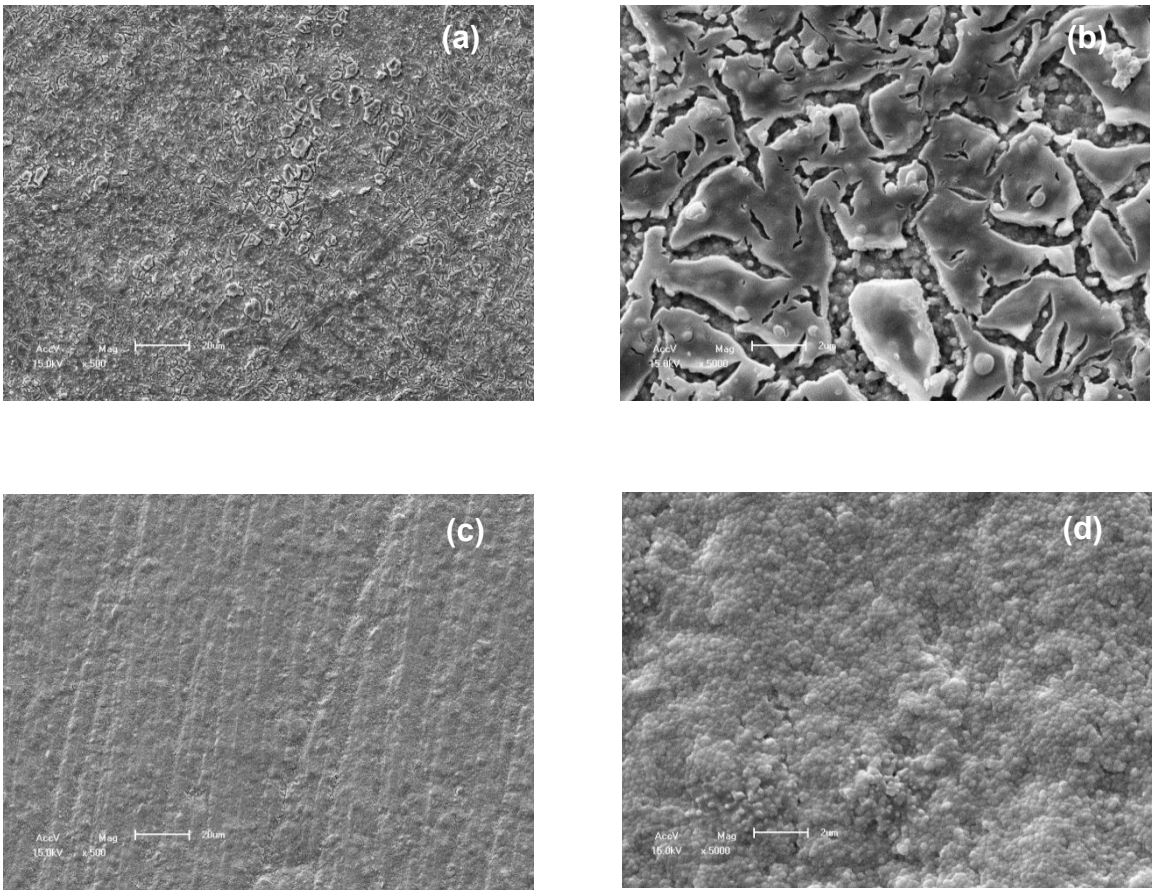

Fig. 4 - SEM micrographs comparing the COA (a, b) and INF (c, d) methods for the solution with the lowest content of silica precursors (25:75). In (a) and (b), the coating had a typical profile of phase separation between the silica and zirconia precursors, with the silica dispersed as nanoparticles coated by a layer composed of zirconia with characteristics of a brittle material. The same was not observed in (c) and (d).

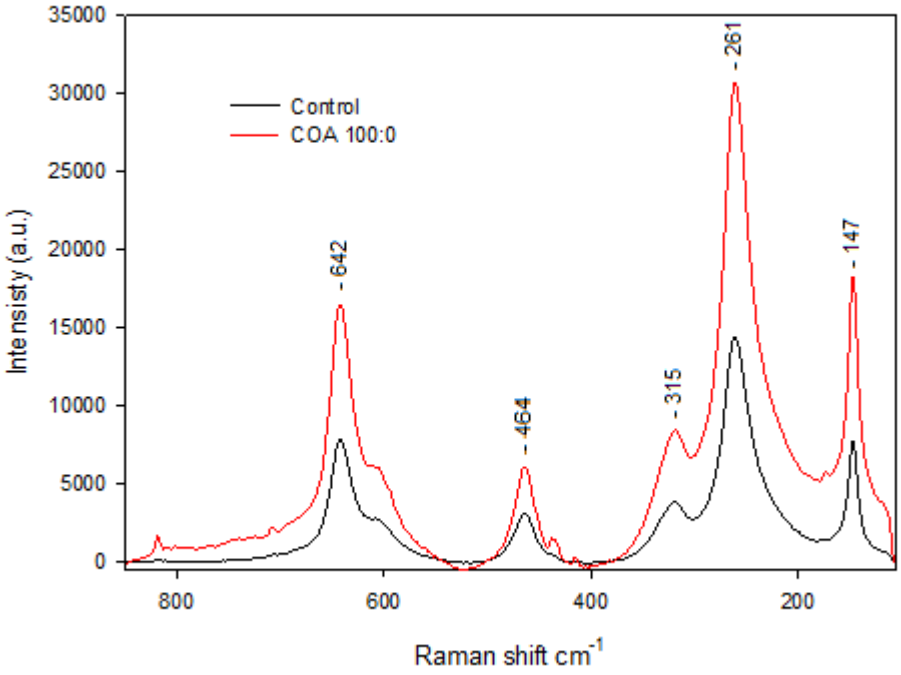

Fig. 5 - μ-Raman spectra of the control group and a silica-coating group (COA 100:00). Differences in intensity for peaks at 642 cm^{-1} and 464 cm^{-1} related to the presence of SiO_2 were observed.

4 Conclusão

O presente estudo introduziu um novo e simples método para propiciar união adesiva de materiais baseados em metacrilatos a cerâmicas de zircônia estabilizada por ítria.

Referências

AKIN, H., OZKURT, Z., KIRMALI, O., KAZAZOGLU, E., OZDEMIR, A. K. Shear bond strength of resin cement to zirconia ceramic after aluminum oxide sandblasting and various laser treatments. **Photomedicine and Laser Surgery,** v.29, n.12, p.797-802, 2011.

AKYIL, M. S., UZUN, I. H., BAYINDIR, F. Bond strength of resin cement to yttrium-stabilized tetragonal zirconia ceramic treated with air abrasion, silica coating, and laser irradiation. **Photomedicine and Laser Surgery,** v.28, n.6, p.801-808, 2010.

AMARAL, R., OZCAN, M., BOTTINO, M. A., VALANDRO, L. F. Microtensile bond strength of a resin cement to glass infiltrated zirconia-reinforced ceramic: the effect of surface conditioning. **Dental Materials,** v.22, n.3, p.283-290, 2006.

ATTIA, A., LEHMANN, F., KERN, M. Influence of surface conditioning and cleaning methods on resin bonding to zirconia ceramic. **Dental Materials,** v.27, n.3, p.207-213, 2011.

BHARGAVA, S., DOI, H., KONDO, R., AOKI, H., HANAWA, T., KASUGAI, S. Effect of sandblasting on the mechanical properties of Y-TZP zirconia. **Bio-Medical Materials and Engineering,** v.22, n.6, p.383-398, 2012.

CHAI, J., CHU, F. C., CHOW, T. W. Effect of surface treatment on shear bond strength of zirconia to human dentin. **Journal of Prosthodontics,** v.20, n.3, p.173-179, 2010.

CHAIYABUTR, Y., MCGOWAN, S., PHILLIPS, K. M., KOIS, J. C., GIORDANO, R. A. The effect of hydrofluoric acid surface treatment and bond strength of a zirconia veneering ceramic. **Journal of Prosthetic Dentistry,** v.100, n.3, p.194-202, 2008.

DERAND, T., MOLIN, M., KVAM, K. Bond strength of composite luting cement to zirconia ceramic surfaces. **Dental Materials,** v.21, n.12, p.1158-1162, 2005.

FONSECA, R. G., MARTINS, S. B., DE OLIVEIRA ABI-RACHED, F., DOS SANTOS CRUZ, C. A. Effect of different airborne-particle abrasion/bonding agent combinations on the bond strength of a resin cement to a base metal alloy. **Journal of Prosthetic Dentistry,** v.108, n.5, p.316-323, 2012.

GOMES, A. L., CASTILLO-OYAGUE, R., LYNCH, C. D., MONTERO, J., ALBALADEJO, A. Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. **Journal of Dentistry**, doi: 10.1016/j.jdent.2012.09.013.

KIRKPATRICK, R. J., YARGER, J. L., MCMILLAN, P. F., YU, P., CONG, X. D. Raman spectroscopy of C-S-H, tobermorite, and jennite. **Advanced Cement Based Materials,** v.5, n.3-4, p.93-99, 1997.

MATINLINNA, J. P., LASSILA, L. V., VALLITTU, P. K. Pilot evaluation of resin composite cement adhesion to zirconia using a novel silane system. **Acta Odontologica Scandinavica,** v.65, n.1, p.44-51, 2007.

MORAES, R. R., GUIMARÃ£ES, G. Z., OLIVEIRA, A. S., FAOT, F., CAVA, S. R. S. Impact of acidic monomer type and concentration on the adhesive performance of dental zirconia primers. **International Journal of Adhesion and Adhesives,** v.39, n.0, p.49-53, 2012.

OGURI, T., TAMAKI, Y., HOTTA, Y., MIYAZAKI, T. Effects of a convenient silica-coating treatment on shear bond strengths of porcelain veneers on zirconia-based ceramics. **Dental Materials Journal,** v.31, n.5, p.788-796, 2012.

OZCAN, M., VALLITTU, P. K. Effect of surface conditioning methods on the bond strength of luting cement to ceramics. **Dental Materials,** v.19, n.8, p.725-731, 2003.

PELAEZ, J., COGOLLUDO, P. G., SERRANO, B., LOZANO, J. F., SUAREZ, M. J. A prospective evaluation of zirconia posterior fixed dental prostheses: three-year clinical results. **Journal of Prosthetic Dentistry,** v.107, n.6, p.373-379, 2012.

PELAEZ, J., COGOLLUDO, P. G., SERRANO, B., SERRANO, J. F., SUAREZ, M. J. A four-year prospective clinical evaluation of zirconia and metal-ceramic posterior fixed dental prostheses. **International Journal of Prosthodontics,** v.25, n.5, p.451-458, 2012.

PETERSEN, J., BARDON, J., DINIA, A., RUCH, D., GHERARDI, N. Organosilicon coatings deposited in atmospheric pressure Townsend discharge for gas barrier purpose: effect of substrate temperature on structure and properties. **ACS Applied Materials Interfaces,** doi:10.1021/am3015229.

PIASCIK, J. R., SWIFT, E. J., THOMPSON, J. Y., GREGO, S., STONER, B. R. Surface modification for enhanced silanation of zirconia ceramics. **Dental Materials,** v.25, n.9, p.1116-1121, 2009.

PIASCIK, J. R., WOLTER, S. D., STONER, B. R. Development of a novel surface modification for improved bonding to zirconia. **Dental Materials,** v.27, n.5, p.e99-105, 2011.

POGGIO, C. E., DOSOLI, R., ERCOLI, C. A retrospective analysis of 102 zirconia single crowns with knife-edge margins. **Journal of Prosthetic Dentistry,** v.107, n.5, p.316-321, 2012.

SMITH, R. L., VILLANUEVA, C., ROTHROCK, J. K., GARCIA-GODOY, C. E., STONER, B. R., PIASCIK, J. R., THOMPSON, J. Y. Long-term microtensile bond strength of surface modified zirconia. **Dental Materials,** v.27, n.8, p.779-785, 2012.

THOMPSON, J. Y., STONER, B. R., PIASCIK, J. R., SMITH, R. Adhesion/cementation to zirconia and other non-silicate ceramics: where are we now? **Dental Materials,** v.27, n.1, p.71-82, 2011.

YUN, J. Y., HA, S. R., LEE, J. B., KIM, S. H. Effect of sandblasting and various metal primers on the shear bond strength of resin cement to Y-TZP ceramic. **Dental Materials,** v.26, n.7, p.650-658, 2010.

ZHANG, Y., LAWN, B. R., MALAMENT, K. A., VAN THOMPSON, P., REKOW, E. D. Damage accumulation and fatigue life of particle-abraded ceramics. **International Journal of Prosthodontics,** v.19, n.5, p.442-448, 2006.