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MARIA PAULA GANDOLFI PARANHOS

TRATAMENTOS DE SUPERFÍCIE PARA AUMENTAR A RESISTÊNCIA DE UNIÃO ADESIVA À ZIRCÔNIA

Prof. Dr. Luiz Henrique Burnett Junior
Orientador

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2010

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RESUMO

Foram realizados dois estudos in vitro para avaliar resistência de união de cimentos resinosos à zircônia após diferentes tratamentos de superfície e um estudo in vitro para avaliar a resistência à fadiga de coroas não-retentivas cimentadas adesivamente em pilares de zircônia conforme protocolo adesivo definido pelos estudos de resistência de união.

PRIMEIRO CAPÍTULO

O presente estudo avaliou o efeito de tratamentos de superfície (laser de Nd:YAG, laser de CO_2, jateamento com Al_2O_3 e silicatização) na resistência de união ao cisalhamento (RUC) da zircônia a resina. Blocos de zircônia (Lava, 3M-ESPE) com dimensão de 13x4x2mm foram incluídos em resina acrílica, polidos e aleatoriamente divididos em três grupos que receberam os seguintes tratamentos: nenhum tratamento abrasivo, jateamento com óxido de alumínio (Al_2O_3) (50µm) ou silicatização (CoJet). Cada grupo foi subdividido em três subgrupos que foram tratados com laser de Nd:YAG, laser de CO_2 ou nenhum tratamento com laser. Após os tratamentos de superfície, foi aplicado primer contendo monômero fosfatado e cilindros de cimento resinoso (Panavia F) (n=18) foram confeccionados sobre a superfície da zircônia. Foram também avaliadas a rugosidade superficial e topografia (MEV) após os tratamentos de superfície. De acordo com ANOVA e teste de Tukey (□=0.05), a média de RUC após irradiação com laser de Nd:YAG variou de 14.09 a 16.20MPa e foi estatisticamente superior ao laser de CO_2 (de 6.24 a 10.51MPa) e aos grupos não irradiados com laser (de 4.65 a 8.79MPa). O laser de Nd:YAG criou maior rugosidade superficial na zircônia quando comparado ao laser de CO_2 e aos tratamentos abrasivos. A silicatização aumentou a RUC dos grupos tratados ou não com laser. Micro-fendas foram

encontradas nos especimes tratados com CO_2. Concluiu-se que o pré-tratamento com laser de Nd:YAG, associado a tratamentos abrasivos ou não, criou rugosidade consistente na superfície da zircônia e aumentou significativamente a RUC da zircônia ao cimento resinoso Panavia F. A silicatização pode potencialmente aumentar a resistência de união da zircônia pré-tratada com laser ou apenas com tratamentos abrasivos. Micro-fendas significativas foram encontradas na superfície tratada com laser de CO_2.

SEGUNDO CAPÍTULO

O presente estudo teve como objetico avaliar o efeito de um primer experimental para zirconia na RUC de diferentes cimentos resinosos à zircônia. Neste estudo, 40 blocos de zircônia (Sistema LAVA, 3M-ESPE) com as mesmas dimensões descritas para o primeiro estudo foram incluídos em resina acrílica, polidos e jateados com Al_2O_3. Três diferentes cimentos resinosos (BisCem, Duo-Link, Panavia F) foram usados para construir cilindros de 2.4 mm de diâmetro (n=15) sobre a superfície de zircônia após aplicação de primer para zircônia (Zirconia Prime Plus, Bisco) ou não. O primer foi também usado previamente à confecção de cilindros de resina composta Z100 (3M-ESPE). Além disso, o cimento resinoso Panavia F foi também usado com seu próprio primer para cerâmica (Clearfil Ceramic Primer). A RUC foi realizada após 24h de armazenamento dos especimes em água. Topografia superficial e tipo de falha foram avaliadas sob MEV. De acordo com ANOVA e teste de Tukey (□=0.05), a associação do primer para zircônia e a resina composta Z100 mostrou a mais alta RUC (29.35 MPa) seguido de DuoLink com o mesmo primer (26.68 MPa). Os especimes que não foram tratados com o primer apresentaram os menores valores de RUC (de 5.95 a 9.79 MPa). O modo de falha foi mista para os grupos que foram tratados com o primer e nos grupos que não foram tratados com o primer, as falhas foram predominantemente adesivas. Concluiu-se que o primer para zircônia à base de monômeros organofosfatados e ácido carboxílico aumentaram a resistência de união de diferentes cimentos resinosos, incluindo a resina composta Z100.

TERCEIRO CAPÍTULO

Foram avaliados a resistência à fadiga e o modo de falha de facetas de porcelana e resina composta cimentadas e pilares de zircônia customizados. Vinte e quatro pilares de zircônia padronizados foram fabricados. Usando o sistema CEREC 3, facetas com forma padronizada foram fresadas em cerâmica Vita Mark II ou em resina composta Paradigm MZ100. A superfície interna das restaurações foram condicionadas com ácido hidrofluorídrico e silanizadas (Mark II) ou jateadas e silanizadas (MZ100). A superfície adesiva dos pilares foi jateada, limpa e inserida em um implante ao nível do osso (BLI RC SLActive 10 mm). Todas as facetas (n=24) foram cimentadas adesivamente com primer para zircônia (Z-Prime Plus, Bisco), adesivo (Optibond FL) e resina composta pré-aquecida (Filtek Z100). Foi simulada mastigação isométrica cíclica (5 Hz), iniciando com uma carga de 40N, seguida por estágios de 80, 120, 169, 200, 240 e 280N (20 000 ciclos cada). As amostras foram carregadas até a fratura ou por no máximo 140000 ciclos.Os grupos foram comparados usando a análise de sobrevivência "life table" (Logrank test P=0.05). Os resultados mostraram que os especimes Mark II e MZ100 fraturaram com uma carga média de 216N e 229N (taxa de sobrevivência de 17% e 8%), respectivamente, sem diferença na probabilidade de sobrevivência (p=0.18). Entre as amostras fraturadas, 40% das falhas foram ao nível do pilar para Mark II e 27% para MZ100. Não foram observadas falhas exclusivamente adesivas. Foi concluído que as facetas tipo III Mark II e MZ100 mostraram resistência à fadiga similar quando cimentadas à pilares de zircônia customizados não-retentivos. A resina composta MZ100 apresentou uma maior porcentagem de falhas "reparaveis", mantendo a interface restauração-pilar e o próprio pilar intactos.

Palavras-Chave: Adesão; Laser; Tratamento de superfície; Zircônia; Resistência de união; Resistência à fadiga; CAD/CAM; pilar de implante.

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LISTA DE ABREVIAÇÕES, SIGLAS E SIGNIFICADOS

PUCRS	Pontifícia Universidade Católica do Rio Grande do Sul
Y-TZP	*Yttrium stabilized tetragonal zirconia polycrystals*
MDP	*10-methacryloyloxydecyl dihydrogenphosphate*
Nd:YAG	*Neodymium yttrium-aluminum-Garnet*
CO_2	Dioxido de carbono
CAD/CAM	*Computer-aided design/computer-aided manufacturing*
Al_2O_3	Oxido de aluminio
μm	Micrometro
mm	Milímetro
MEV	Microscopia eletronica de varredura
ANOVA	Análise de variâncial
RUC	Resistência de união ao cisalhamento
MPa	Mega Pascal
N	Newton
Hz	Hertz
α	Nível de significância
P	Valor de probabilidade
et al.	Abreviação de et alii (e outros)

SUMARIO

INTRODUCAO GERAL

O interesse por cerâmicas de óxido de zirconium (zircônia) tem crescido significativamente na última década. Uma das capacidades distintivas desse material é conhecida como "*transformation toughnening*",[1] na qual a cerâmica baseada em Y-TZP (*Yttrium stabilized tetragonal zirconia polycrystals*) resiste à propagação de fendas pela transformação de fases (tetragonal para monoclínica), o que está associado a uma aumento de volume.[2] As propriedades mecânicas resultantes[2,3] combinadas com sua biocomplatibilidade e propriedades ópticas,[1,2,3] tem justificado seu uso como alternativa ao metal em diversas aplicações na Odontologia. Todavia, a zircônia para restaurações dentárias não favorece a cimentação adesiva sendo este fato uma limitação do material. Cimentos convencionais, como cimento de ionômero de vidro, podem fornecer adequada retenção para cimentação de coroas totais e próteses parciais fixas convencionais,[4] muitas vezes há necessidade de se confiar na adesão onde a retenção é escassa ou inexistente, como em caso de facetas parciais e próteses parciais fixas não-retentivas.

A zircônia é uma cerâmica altamente cristalina e devido a ausência de uma fase vítrea, ela tende a resistir aos métodos convencionais de condicionamento ácido.[5,6,7,8] Consequentemente, as pesquisas tem focado no desenvolvimento de estratégias adesivas combinando métodos de asperização e adesão química.

A adesão química à zircônia envolve a utilização de vários elementos de ligação. O uso do silano em combinação com jateamento com óxido de alumínio tem mostrado uma baixa resistência de união,[6,9,10] o que é esperado visto que não existe sílica na composição da zircônia. Por outro lado, a silicatização permite que cerâmicas de alta resistência, à base de alumina e zircônia, se unam à resina pela ligação com os silanos, aumentando os valores de resistência de união.[8,9,11,12,13] A associação dos métodos de asperização (jateamento com óxido de alumínio e silicatização) e *primers* e agentes cimentantes contendo monômeros fosfatados, como o MDP (*10-methacryloyloxydecyl dihydrogenphosphate*) tem mostrado resultados satisfatórios e duradouros.[10,11,14,15,16] Uma nova proposta para adesão química à zircônia consiste no uso de uma mistura de monômeros organofosfato e de àcido carboxilico na forma de primers foto-polimerizáveis.

Inúmeros métodos, além do jateamento com óxido de alumínio e silicatização, tem sido recomendados para criar retenção micromecânica à zircônia, como a criação de retenções positivas pela sinterização de porcelana condicionável.[17,18,19] O uso da irradiação com laser tem sido proposta para o pré-tratamento de cerâmicas. O laser de Nd:YAG (*Neodymium yttrium-aluminum-Garnet*) vem sendo também usado no condicionamento de porcelana [20] e cerâmica à base de alumina [21] e a base de zircônia [22] tornando a superfície da cerâmica com características de retenção micromecânica favoráveis para adesão à resina. O laser de dióxido de carbono (CO_2) vem sendo também amplamente utilizado em Odontologia[23] e mostrado eficácia como pré-tratamento de porcelana e esmalte para melhorar adesão à resina.[24] Não existem dados, no entanto, em relação ao efeito do laser de Nd:YAG e do laser de CO_2 em cerâmicas de Y-TZP.

As cerâmicas de zircônia vem sendo amplamente utilizadas em Implantodontia, tanto em implantes como em pilares. Tal advento se torna também facilitado devido à tecnologia CAD/CAM (*computer-aided design/computer-aided manufacturing*), que possibilita a fresagem de pilares e restaurações customizados, ampliando as aplicações da zircônia para restaurar implantes.

Sabe-se que as restaurações suportadas por implantes são, usualmente, aparafusadas diretamente ao implante ou cimentadas no pilar aparafusado ao implante.[25] No entanto, em casos onde os espaços interdental, interoclusal e buco-lingual são limitados - como na região anterior da mandibula – a chaminé de acesso ao parafuso acaba coincidindo com a incisal do dente, comprometendo a estética. Uma técnica bastante inovadora para esses casos de espaço limitado consiste na confecção de um pilar customizado metalocerâmico não-rententivo restaurado adesivamente com uma faceta tipo III.[26] No entanto, a utilização de um pilar customizado de zircônia tornaria a técnica menos trabalhosa (tecnologia CAD/CAM), com menor custo, com um resultado estético apropriado, facilitando o trabalho conjunto do protético com o dentista. No entanto, uma das grandes limitações em relação à zircônia é sua indicação para preparos e pilares de implantes não-retentivos devido à dificuldade de utilizar um protocolo adesivo de cimentação.

Sendo assim, os objetivos do presente estudo foram:

a) Avaliar o efeito de tratamentos de superfície (laser de Nd:YAG, laser de CO_2, jateamento com Al_2O_3 e silicatização) na resistência de união ao cisalhamento da zircônia à resina (PRIMEIRO CAPÍTULO);

b) Avaliar o efeito de um primer experimental para zircônia, composto por uma mistura de monômeros organofosfato e àcido carboxílico, na resistência de união ao cisalhamento da zircônia à diferentes cimentos resinosos (SEGUNDO CAPÍTULO);

c) Após a determinação do protocolo adesivo mais apropriado para cimentação adesiva à zircônia, avaliar a resistência à fadiga e o modo de falha de facetas “tipo III” de porcelana e resina composta cimentadas em pilares de zircônia customizados e não-retentivos, bem como a influência do material utilizado para confecção das facetas (resina composta ou porcelana) na resistência à fadiga também foi avaliado (TERCEIRO CAPÍTULO);

PRIMEIRO CAPÍTULO

Effect of Nd:YAG laser and CO_2 laser treatment on the resin bond strength to zirconia ceramic

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Effect of Nd:YAG laser and CO_2 laser treatment on the resin bond strength to zirconia ceramic.

AUTHORS

Maria Paula Gandolfi Paranhos, DDS, MS[1]/Luiz Henrique Burnett-Jr, DDS, MS, PhD[2]/Pascal Magne, DMD, PhD[3,1]

[1]PhD Student, Department of Restorative Dentistry, Pontifical Catholic University of Rio Grande do Sul, Porto Alegre-RS, Brazil. Visiting Research Associate, Division of Restorative Sciences, University of Southern California, Los Angeles-California, USA.

[2]Associate Professor, Department of Restorative Dentistry, Pontifical Catholic University of Rio Grande do Sul, Porto Alegre-RS, Brazil.

[3]Tenured Associate Professor, Chair of Esthetic Dentistry, Division of Restorative Sciences, University of Southern California, Los Angeles-CA, USA.

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[1] **Corresponding Author:**

Dr. Pascal Magne
University of Southern California
Division of Restorative Sciences
School of Dentistry, Oral Health Center
3151 S. Hoover St.
Los Angeles, CA 90089-7792
Phone (213) 740-4239
Fax (213) 821-5324
magne@usc.edu

ABSTRACT

Objective: This study evaluated the effect of surface treatments (Nd:YAG laser, CO_2 laser, $Al_2 0_3$ airborne-particle abrasion, and silica-coating) on the zirconia-to-resin shear bond strength (SBS). **Method and Materials:** Eighty-one Lava (3M/ESPE) blocks (13x4x2mm) were embedded in acrylic resin, polished, and randomly divided into three groups which received the following surface treatments: no abrasion, Al_2O_3 airborne-particle abrasion (50µm) or silica-coating (CoJet). Each group was subdivided into three subgroups which were treated with Nd:YAG laser, CO_2 laser or no laser irradiation. Following application of a monomer phosphate-containing primer, cylinders of resin cement (Panavia F) were built (n=18) on the surface. SBS testing was carried out after 24 hours of storage in water. Surface roughness and topography (SEM) after treatments were evaluated. **Results:** According to ANOVA and Tukey test ($\alpha=0.05$), mean SBS after Nd:YAG laser treatment ranged from 14.09 to 16.20MPa and was statistically higher than CO_2 laser (6.24 to 10.51MPa) and no laser treatment (4.65 to 8.79MPa). Nd:YAG laser created more roughness on zirconia when compared to CO_2 laser and abrasion treatments. Silica-coating increased the SBS of lased and non-lased zirconia. Significant microcracks were found on specimens treated with CO_2. **Conclusion:** Nd:YAG laser pre-treatment, whether associated to abrasion methods or not, created consistent roughness on the zirconia surface and significantly increased zirconia SBS to Panavia F. Silica-coating could potentially increase the SBS of lased and non-lased zirconia. Significant microcracks were found on specimens treated with CO_2 laser.

Key-Words: Adhesion; Dental restorative material; Laser; Surface modification; Surface treatment; Zirconia.

INTRODUCTION

The interest for zirconium oxide (zirconia) ceramics has grown significantly in the last decade. A distinctive capability of this material is called “transformation toughening”. Yttrium stabilized tetragonal zirconia polycrystals (Y-TZP) can resist crack propagation by transforming from a tetragonal to a monoclinic phase at the tip of the crack, which is associated with a volume increase.[1] The resulting mechanical properties,[1,2] combined to its biocompatibility and optical properties, have justified its use as a metal-free alternative for a wide array of applications in Dentistry. One of the limitations regarding the use of zirconia ceramic in dental restorations is that it is not originally intended to be adhesively cemented. While conventional cements, such as glass ionomer, might provide adequate retention for conventionally-cemented full-veneer crowns and FPDs,[3] predictable bond to zirconia needs to be achieved in situations where retention of the restoration relies primarily on adhesion, such as partial veneers and resin-bonded FPDs.

Bonding to zirconia is a 20-year old quest initiated by Urano with the bond strength of zirconia ceramic orthodontic brackets.[4] Many researchers have investigated this challenging issue[5-12] because highly crystalline ceramics, due to the absence of a glassy phase, tend to resist conventional etching methods.[5,13-15] Consequently, research has focused on developing other adhesive strategies combining surface roughening and chemical bonding.

Airborne particle abrasion alone slightly roughens the zirconia surface[13] but does not always provide reliable resin bond strength.[8,16] Combination of this procedure to chemical bonding using a silane coupling agent also yields to limited results[8,13,16] unless tribochemical silica-coating is used.[6,15,17] Increased bond strength values could be obtained after silica-coating high-strength alumina-based and zirconia-based ceramics.[6,15-18] Another recommended protocol has been the association of airborne-particle abrasion (aluminum oxide or silica-coating) and luting agents containing phosphate ester monomer 10-methacryloyloxydecyl dihydrogenphosphate (MDP).[6-8,19,20]

Because chemical bonding is susceptible to hydrolytic degradation[8,21] there has been a continuous interest in forming micromechanical interlocking to zirconia. A pioneering and successful approach was first developed by Sadoun and Asmussen in 1994,[22] who sintered fine-grained refractory powder at the intaglio surface of alumina-based ceramic, creating a positive retention. Using the same principle, new techniques to create resin micromechanical interlocking to zirconia have been recently developed.[10,23]

An additional innovative treatment for the development of surface roughness is the use of laser etching, which, unlike the above-mentioned techniques, features the possibility of being performed chairside. Solid or gas state laser devices have become increasingly popular in dentistry. Solid state Neodymium yttrium-aluminum-Garnet (Nd:YAG) laser has shown to be effective for tooth hypersensitivity,[24] removal of carious tissue,[25] sealing enamel pits and fissures,[26] tooth bleaching,[27] and disinfection of dental tissues.[28] Li et al. introduced the use of Nd:YAG laser on feldspathic porcelain before adhesive cementation and found bond strength values similar to hydrofluoric acid etching.[29] Other authors have evaluated the effect of Nd:YAG laser radiation on high-strength alumina-based ceramics and reported that the treated surfaces showed a micromechanical retention pattern more favorable for resin bonding.[30,31] Gas state laser, such as carbon dioxide (CO_2), is another device used in dentistry for soft tissue and periodontal surgery with significant post-surgical benefits.[32] CO_2 laser etching also enhanced osseo-integration of zirconia bioceramic implants,[33] adhesion of orthodontics brackets to feldspathic porcelain,[34] as well as the bonding of composite resin to human enamel.[35] There is no data, however, regarding the effect of Nd:YAG and CO_2 laser on Y-TZP ceramics.

The purpose of this study was to evaluate the effect of various chairside treatments such as Nd:YAG laser, CO_2 laser, Al_20_3 airborne-particle abrasion, and silica-coating on the zirconia-to-resin shear bond strength (SBS). The null-hypothesis considered was that Nd:YAG laser and CO_2 laser, as well as airborne-particle abrasion and silica-coating would not influence the SBS of Y-TZP to resin cement.

METHOD AND MATERIALS

Eighty-one blocks (13x4x2 mm) of high-purity zirconium-oxide ceramic (LAVA; 3M/ESPE, Saint Paul, Minnesota, USA) were fabricated. The specimens were embedded in acrylic resin (Palapress; Heraeus Kulzer, Hanau, Germany) and polished with 400-, 600-, 800- and 1500-grit silicon carbide paper under water cooling. The blocks were randomly divided into three groups according to the type of surface abrasion treatment (27 blocks per treatment). In the first group, airborne-particle abrasion was applied using 50 µm aluminum oxide (Al_2O_3) particles (RondoFlex 2013; Kavo, Biberach, Germany) under a pressure of 46-55 psi using a fine airborne particle-abrasion unit (Kavo RONDOFlex Plus 360; Kavo) for 15 seconds at a distance of 10 mm perpendicularly to the surface. In the second group, silica-coated sand (CoJet Sand, 3M ESPE, Seefeld, Germany) was blasted to the surface using the same parameters (pressure, distance) and device as in the first group. The third group did not receive any abrasion treatment.

Each group was divided into three subgroups of nine blocks, which received either Nd:YAG laser treatment, CO_2 laser treatment, or no laser treatment. The Nd:YAG laser (λ=1064 nm)(Sunlase 400, Sunrise Technologies International Inc., Fremont, California, USA) was delivered using a 320 µm diameter optical fiber perpendicular to the surface, scanning the ceramic in a contact mode. The laser parameters used were 100 mJ, 20 Hz (pulse per second), 2 W with an energy density of 124.40 J/cm^2.[30,31] The CO_2 laser (λ =10600 nm) (Lutronic Spectra DENTA, GPT Inc., Fairfield, Nebraska, USA) was delivered by 1 mm optical fiber perpendicular to the ceramic, scanning the surface in a non-contact continuous mode, 1 mm distant from the surface. The laser parameters used were 5 J, 1 Hz (pulse per second), 5 W with an energy density of 63694.27 J/cm^2. The ceramic threshold was determined varying the energy (mJ) and frequency (Hz) to find the minimum CO_2 laser energy density required to physically modify the ceramic surface.[36]

The surface of each block was then cleaned with 40% phosphoric acid (K-Etchant Gel; Kuraray, Kurashiki, Okayama, Japan) for 5 seconds, water rinsed for 15 seconds, and immersed in an ultrasonic bath for 2 minutes. Following air-drying, a MDP-containing primer (Clearfil Ceramic Primer; Kuraray) was applied onto the surface and left to dry for 5 minutes. Equal amounts of luting cement (Panavia F 2.0; Kuraray) A and B pastes were mixed for 20 seconds and inserted in a plastic mold (Ultradent Jig; Ultradent Products, South Jordan, Utah, USA) with a bubble-free application system (Composite-Gun and n^{o}. 1916 Tubes and plugs; KerrHawe SA, Bioggio, Switzerland). The resin cylinder was light polymerized for 20 seconds at 800 mW/cm^{2} (Rembrandt Allegro LED Curing Light; Den-Mat, Santa Maria, California, USA). The cement surface was protected with an oxygen barrier (Oxiguard II; Kuraray) for 3 minutes as per the manufacturer instructions. Two resin cement cylinders were built onto each ceramic block, resulting in 18 specimens per subgroup. The materials used are presented in Table 1 and the experimental groups in Table 2.

Samples were stored in distilled water for 24 hours before shear bond testing (Shear Bond Tester; Bisco Inc., Schaumburg, Illinois, USA) with a ramp load of 43.8-kg-force per minute. To convert the load values (Kg) to megapascals (MPa), failure load was converted to Newtons (N) and was divided by the bonding area (mm^{2}). The failure mode (cohesive, adhesive, or mixed failure) was assessed by examination of the debonded surfaces with a stereomicroscope (MZ12.5; Leica Microsystems, Wetzlar, Germany) at X8 magnification.

One specimen of each group was randomly selected for surface roughness measurement and topographical analysis. For surface roughness (Ra - µm) (Surftest SJ 201 Profilometer, Mitutoyo Co, Kawasaki, Japan), ten spaced measurements were recorded for each specimen of each group (cut-off length of 2.5 mm). For topographical analysis, specimens were sputter coated with carbon powder (Kinney Vacuum KSE-2A-M Evaporator; Kinney Vacuum Co., Boston, Massachusetts, USA) and observed under a scanning electron microscope (SEM) (JSM-6610LV Scanning Electron Microscope; JEOL USA Inc., Peabody, Massachusetts, USA) at an accelerating voltage of 15 kV.

Bond strength data obtained from the nine experimental groups were analyzed with a two-way analysis of variance (ANOVA) (abrasion methods and laser treatments). The mean surface roughness (Ra) values of each group were submitted to one-way ANOVA. The Tukey HSD post hoc test was used to detect pairwise differences among experimental groups. All statistical testing was performed at a preset alpha of 0.05.

RESULTS

According to ANOVA, the two main factors (abrasion methods and laser treatments), and their interaction were significant ($P<0.001$) (Table 3). The values of shear bond are illustrated in Fig. 1. Nd:YAG laser groups presented the highest mean SBS and surface roughness values (Fig. 1 and Table 4). The association of CO_2 laser with Al_2O_3 yielded the lowest SBS values equivalent to the control group (4.65 MPa and 6.24 MPa, respectively). The failure mode was predominantly mixed (Table 5 and Fig. 2).

In the SEM micrographs, the non-treated zirconia surface was characterized by the total absence of undercuts and a moderate roughness created by the cutting device (Fig. 3A and Table 4). After airborne particle abrasion with 50 µm Al_2O_3 particles, the surface appeared coarsened, with a uniform presence of irregularities and shallow pits (Fig. 3B). Tribochemical silica-coating generated a surface similar to that of Al_2O_3 airborne-particle abrasion, although characterized by a finer texture (Fig. 3C). On the other hand, the Nd:YAG laser-treated zirconia surface exhibited typical blister-like globules with voids surrounded by a flat and porous layer with openings of various diameters (Fig. 4A). This exact same characteristic aspect was obtained when preceding laser application by abrasion methods (Figs. 4B-4C). High magnification revealed numerous micro-cracks within the perimeter of each globule (Fig. 4D). CO_2 laser-treated specimens, alike non-treated ones, featured a smooth non-retentive surface. Clearly defined cracks, however, were present throughout the entire surface, which also appeared to be slightly striated by the laser path (Fig. 5A). The same pattern was found with abrasion pre-treatments without changes in surface roughness values (Figs. 5B-5C and Table 5). Cracks were found to be much wider than those generated by Nd:YAG laser (Fig. 5D, compared to Fig. 4D).

DISCUSSION

This study evaluated the effect of laser treatments and abrasion methods on the bond strength of a zirconia ceramic to a resin cement. The present findings suggest rejecting the null hypotheses since the resin-ceramic bond strength was significantly affected by the various surface treatments.

The usual limitation of using SBS testing is the irregular distribution of stresses in the adhesive interface, which may generate cohesive failures in the base materials (such as dentin or porcelain), possibly leading to misinterpretation of the real bond strength results.[11,15,37] The base material in this study (zirconia), however, does not present such drawback, which was confirmed by the absence of cohesive failures (Table 5).[38]

Different strategies have been proposed to obtain a reliable resin-zirconia bond. Because irregularities generated during fabrication/milling of the ceramic do not produce reliable bond strength values,[5,23,39] it seems necessary to further increase the surface roughness.[7] Surface roughening by Al_2O_3 airborne-particle abrasion has been proposed[15,16,23,40-42] because of its potential for increasing surface energy, surface area for bonding, and wettability.[15,16] Studies have evaluated the effect of grinding and airborne-particle abrasion on the microstructure, biaxial flexural strength and reliability zirconia ceramics and it was concluded that airborne-particle abrasion may provide a powerful technique for strengthening Y-TZP in clinical practice due to transformation toughening (tetragonal to monoclinic phase).[40,43] On the other hand, it is considered that flaws and microcracks created by this abrasion method can act as stress concentration sites, possibly weakening the ceramic in the long-term.[10] In the present study, after 50 µm Al_2O_3 airborne-particle abrasion (as stated by the manufacturer not to compromise the strength of this ceramic), the surface appeared slightly rougher (0.315 Ra when compared to 0.233 Ra on polished zirconia) (Table 4) with uniform presence of irregularities and shallow pits, but no microcracks could be detected under SEM (Figs. 3B and 3C).[41]

Silica blasted surfaces revealed a thin and micro-retentive layer (Fig. 3C). The resulting improvement in resin bond strength is not only explained by the acquired roughness but also because the silica-coating process allows chemical coupling through the use of silane.[6,15,17] Without silica-coating, silanes are not able to promote chemical coupling between the resin composite cement and pure zirconia.[5,8,40,44,45]

The use of phosphate monomers, such as MDP, is another way of promoting chemical bonding and has shown to improve the resin bond strength to zirconia.[7-9,18-20,40,43] The primer used in this study (Clearfil Ceramic Primer) has silane molecules (3-methacryloxypropil trimethoxy silane) mixed with phosphate monomers (10-MDP) which improves surface wettability and form cross-linkages with methacrylate groups of the resin cement as well as siloxane bonds with the hydroxyl groups of the ceramic surface.[9,40,43] The MDP/silane combination seems to provide the advantage of forming hydrothermally stable bonds between silica-coated zirconia and the resin cement.[8,19,20]

In the present study, all groups were treated with a MDP/silane primer and MDP-containing resin cement. A higher SBS was evident after Al_2O_3 particle abrasion (8.79 MPa) or Cojet Sand (7.56 MPa) when compared to non-abraded zirconia (4.65 MPa) (Fig. 1). The roughness created by abrasion methods played a significant role in the resin cement adhesion by nearly doubling the bond obtained by chemical coupling alone, as in the case of Al_2O_3. Other studies comparing Al_2O_3 and silica-coating, however, found better bond strength after silica-coating zirconia-based ceramics.[15-18,30,31,44] The adequacy of the sole chemical bond between MDP to zirconium oxides could not be supported by the present study because the non-abraded zirconia presented the lowest SBS values (Fig. 1). It was confirmed that without particle abrasion as a pretreatment, no beneficial effect could be attributed to the phosphate monomer alone.[38] On the other hand, other studies showed that MDP-containing cement presented the highest bond strength values when compared to MDP-free cements[7,10] independently of the zirconia surface treatment (no treatment, airborne-particle abrasion and silica-coating).[39,41,43] The use of different primers and resin cements would have been valuable for understanding MDP benefits but this was beyond the scope of this investigation.

Innovative concepts in creating micro-retention on zirconia include the development of positive retentions rather than negative ones.[5,10,22,23] However, all of these treatments must be performed in the laboratory, precluding the possibility of being performed chairside after try-in, immediately before cementation. The present results show that Nd:YAG laser treatment produces a surface with typical blister-like globules with voids surrounded by a flat and porous layer with openings of various diameters (Fig. 4A,B,C). Some authors found similar but mild and more uniform alterations on high-strength alumina-based ceramics when using the same laser source.[30,31] Those studies used the same laser parameters (100 mJ, 20 Hz, 2 W), yet in a non-contact mode. In addition, graphite powder initiator was used by those authors to increase the energy absorption since alumina-based ceramics do not absorb the 1064 nm wavelength emitted by the Nd:YAG laser.[30,31] Zirconia ceramic could absorb the laser energy in a contact mode without requiring any initiator in the present study.

SEM images (Figs. 4A-4C) and surface roughness results (Table 4) showed that the Nd:YAG laser irradiated surface was favorable to mechanical retention between ceramic and resin cement. This assumption was confirmed by the SBS results, since the Nd:YAG laser treated groups presented the highest values (14.09 MPa), regardless of the type of abrasion pre-treatment (Al_2O_3 – 16.20 MPa; Cojet Sand – 15.21 MPa), when compared to non-laser treated and CO_2 laser treated groups. The present findings are in agreement with other studies showing higher bond strength values after Nd:YAG laser treatment when compared to airborne-particle abrasion and silica-coating of high-strength alumina-based ceramics (In-Ceram Zirconia and In-Ceram Alumina, Vita Zahnfabrik, Seefeld, Germany).[30,31] Alike non-laser treated samples, pretreatment by Al_2O_3 particle-abrasion enhanced the SBS of Nd:YAG laser treated specimens

(Fig. 1). This can be explained by the irregularities of the residual spaces left between the laser impacts.

High magnification SEM micrographs of Nd:YAG laser treated specimens revealed micro-cracks within the perimeter of each globule (Fig. 4D), which was not observed by other authors.[30,31] During Nd:YAG laser application, fusing and melting of the most superficial ceramic layer are followed by solidification to a smooth blister-like surface.[31] This suggests that the increase in the temperature may have overcome the melting temperature of Lava (around 2700^{o}C according to the manufacturer). When melting, the surface is expanding and immediately contracts during re-solidification. This temperature-induced stress could explain cracking of the ceramic surface. Further investigation should be carried out to evaluate the effect of controlled cooling and various cooling rates on laser treated ceramic surfaces in order to limit the development of re-solidification cracks. An additional challenge lays in the fact that Nd:YAG laser treated surfaces were characterized by a carbonized layer with a silver pigmentation. This might be a limitation for esthetic applications, and further investigation would be required to determine the influence of the laser-treated area on the optical characteristics of a fully layered restoration.

CO_2 laser has been used previously to etch zirconia bioceramic implants (in order to enhance their osseo-integration)[33] and to improve adhesion of orthodontics metal brackets to feldspathic porcelain.[34] There is no previous study, however, using CO_2 laser to modify zirconia ceramic surface with the purpose of increasing its bond strength to resin cement. The present attempt proved unsuccessful. When compared to the Nd:YAG laser treated groups, CO_2 laser treated groups presented lower SBS results (Fig. 1). The amount and pattern of surface roughness created by Nd:YAG laser explains this difference. Micrographs of CO_2 laser treated specimens displayed a smooth non-retentive surface and clearly defined cracks throughout the entire surface. Akova et al. (2005) reported that with 2 W of energy, CO_2 laser-irradiated feldspathic porcelain surface exhibited conchoidal irregularities that are believed to provide mechanical retention between resin composite and porcelain.[34] Since CO_2 laser has not been used on zirconia for surface roughening, a pilot study was previously performed to define the parameters that were able to alter the ceramic surface. The ceramic threshold using CO_2 laser was defined as 5 W. Unlike Nd:YAG, this laser was applied in a non-contact mode due to the configuration of the device, which did not allow predictable application of the laser in contact mode.

Even though a mild non-retentive striation was found after laser treatment, the results showed higher SBS values for CO_2 laser-treated group (7.92 MPa) when compared to the non-treated group (4.65 MPa). The same pattern was found for CO_2 laser-treated group preceded by Cojet Sand (10.61 MPa) when compared to the Cojet Sand treated group only (7.56 MPa). The surface roughness values were slightly higher in the CO_2 laser treated groups when compared to the non-lased groups. Silica-coating also enhanced the performance of CO_2 laser probably due to the chemical bond with the silane.[15-18] Inversely, the group treated with CO_2 laser preceded by Al_2O_3 abrasion presented lower SBS values (6.24 MPa) when compared to Al_2O_3 treated group only (8.79 MPa). SEM micrographs showed that the cracks resulting from CO_2 laser treatment were found to be much wider and numerous than those generated by Nd:YAG laser (Fig. 5D, compared to Fig. 4D). The high energy (5 W) that was required by CO_2 laser might have induced extreme temperatures and related cooling stresses that could be responsible for these cracks. Lower energies were tested during the pilot study, but no modification of the ceramic surface could be observed. For feldspathic porcelain[34] and enamel,[35] however, 2 W were enough to promote surface alterations. In addition, the beam used for CO_2 laser delivered more energy because of its thickness (1 mm in diameter) compared to Nd:YAG laser optic fiber (320 µm). This also accounts for the difficulty to generate a fine retentive pattern with the CO_2 laser device.

The failure mode of all treated specimens was predominantly mixed. There were no cohesive failures of zirconia (Table 5). For the Nd:YAG laser treated groups, there was a high percentage of mixed failures (67% to 86%), which corroborates with previous studies using this laser.[30,31] The Al_2O_3 + CO_2 laser group was the only one that presented a high percentage of pure adhesive failures without cement residues (60%), which was associated to the lowest SBS found in the CO_2 laser treated group (6.24 MPa). Adhesive failures are common with low bond strength values.[43]

Artificial aging methods, such as fatigue, thermo-cycling and long-term water storage were not performed to evaluate the hydrolytic degradation, stability, and durability of the resin-zirconia bond and this may be considered one of the limitations of the present study. It can be predicted that long-term water storage and thermo-cycling may significantly affect the bond strength of resin-based luting agents to zirconia.[7,8,19,46,47] Further investigation should consider this issue and also evaluate the mechanical properties and phase changes of zirconia after the proposed treatments. The use of MDP-free primer/cements would also be valuable to assess their real benefit when using mechanical retention methods to improve resin to zirconia bond strength.

A new array of applications could result from a reliable adhesion between zirconia and resin cements. Machinable zirconia custom abutments combined to novel design porcelain veneers, as proposed by Magne et al.,[48] would benefit from this adhesion and are currently under investigation. Bonded metal-free FPDs, zirconia brackets, and endodontic posts would also take advantage of this research.

CONCLUSIONS

Within the limitations of this study it was possible to conclude that Nd:YAG laser creates roughness on zirconia and increases its resin bond strength, whether preceded by abrasion methods or not. Silica-coating could potentially increase the SBS of lased and non-lased zirconia. Significant microcracks were found on specimens treated with CO_2 which contra-indicates its use.

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FIGURE LEGENDS

Figure 1. Mean SBS values of experimental groups.

Figure 2. Representative optical microscope view (magnification x7) of the mixed failure mode, which was predominant in all groups. (A – Control; B – CO_2 Laser; C – Nd:YAG Laser).

Figure 3. Representative SEM micrograph (magnification x100) of non-treated zirconia (A), Al_2O_3 airborne-particle abrasion (B), and Cojet Sand (C).

Figure 4. Representative SEM micrograph (magnification x100) of zirconia after Nd:YAG laser (A), Al_2O_3 + Nd:YAG Laser (B), and Cojet Sand + Nd:YAG Laser (C). High magnification (x250) of "globule" (D).

Figure 5. Representative SEM micrograph (magnification x100) of zirconia after CO_2 laser (A), Al_2O_3 + CO_2 laser (B), and Cojet Sand + CO_2 laser (C). High magnification (x250) of cracks (D).

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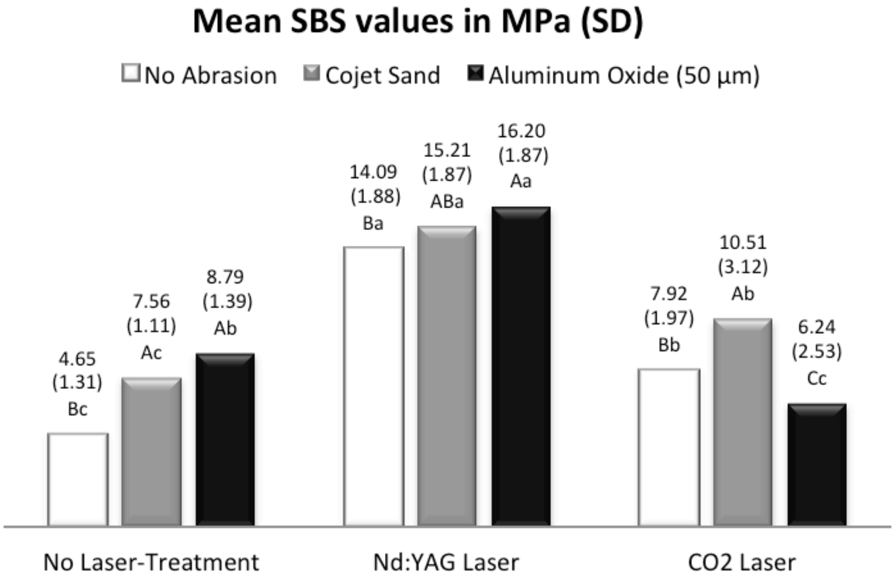
FIGURES



Values of groups having similar superscript letters were not statistically different for $p < 0 .05$ (uppercase letters refers to abrasion treatment; lowercase letters refers to laser treatment).

Figure 1

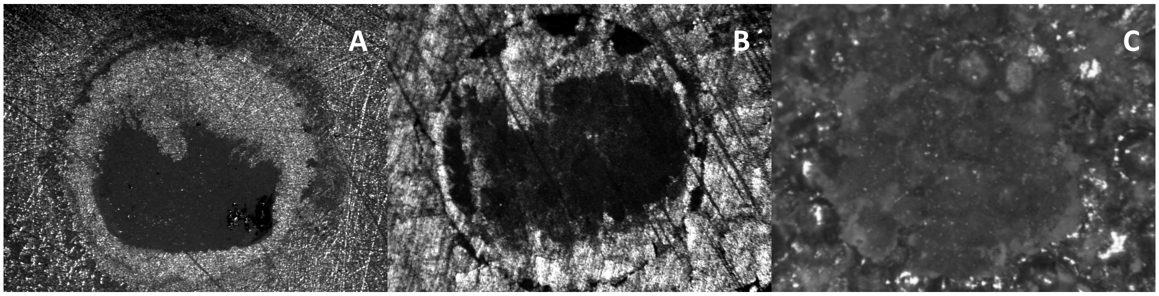


Figure 2 (A/B/C)

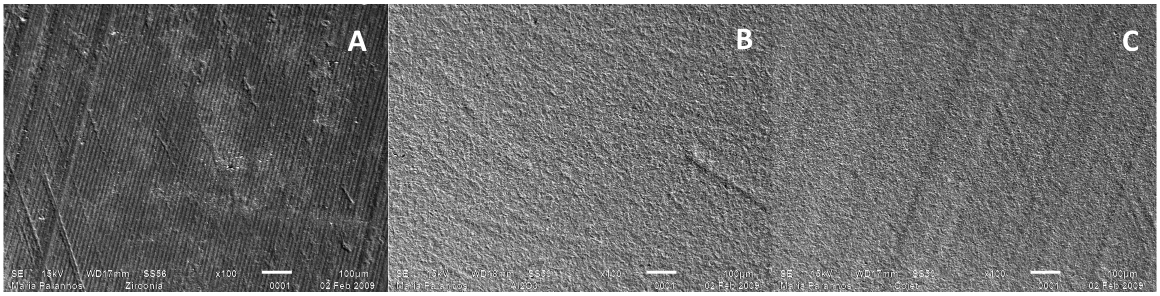


Figure 3 (A/B/C)

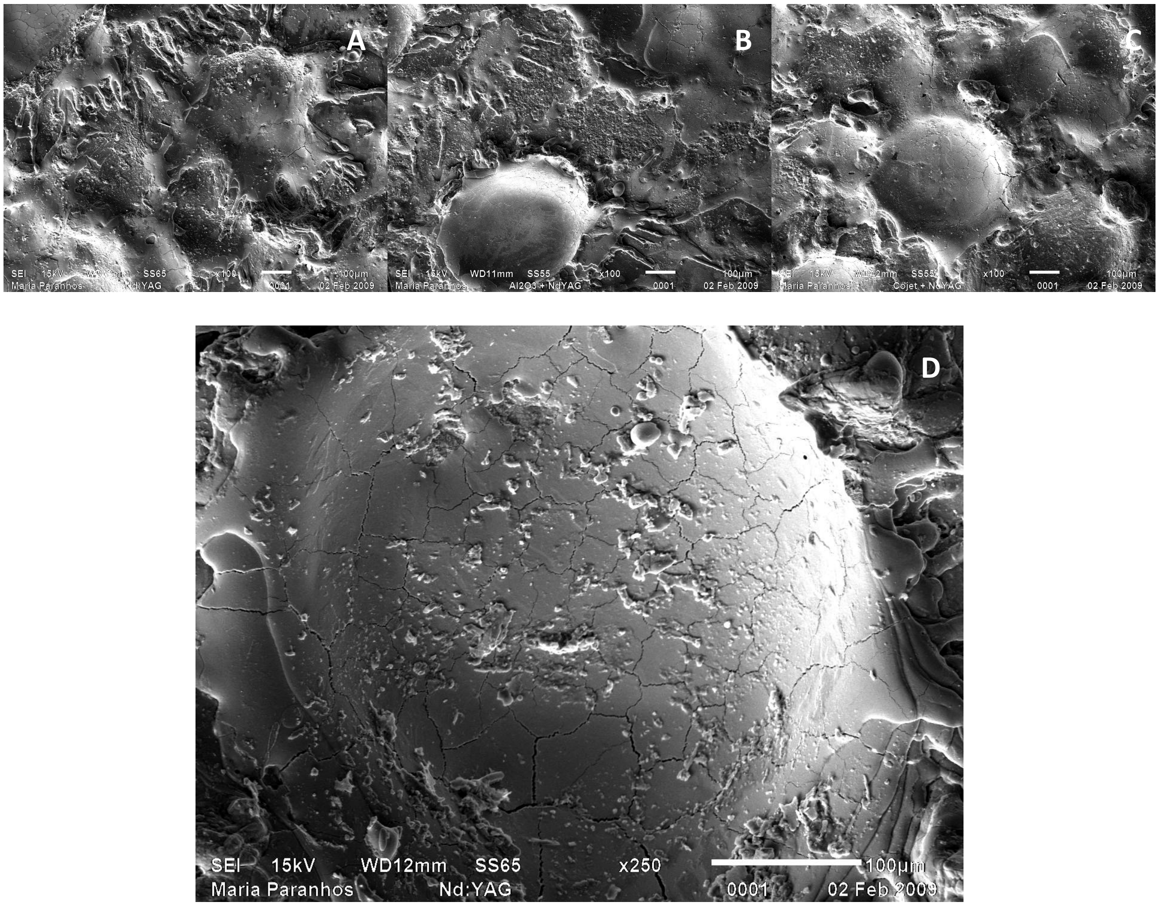


Figure 4 (A/B/C/D)

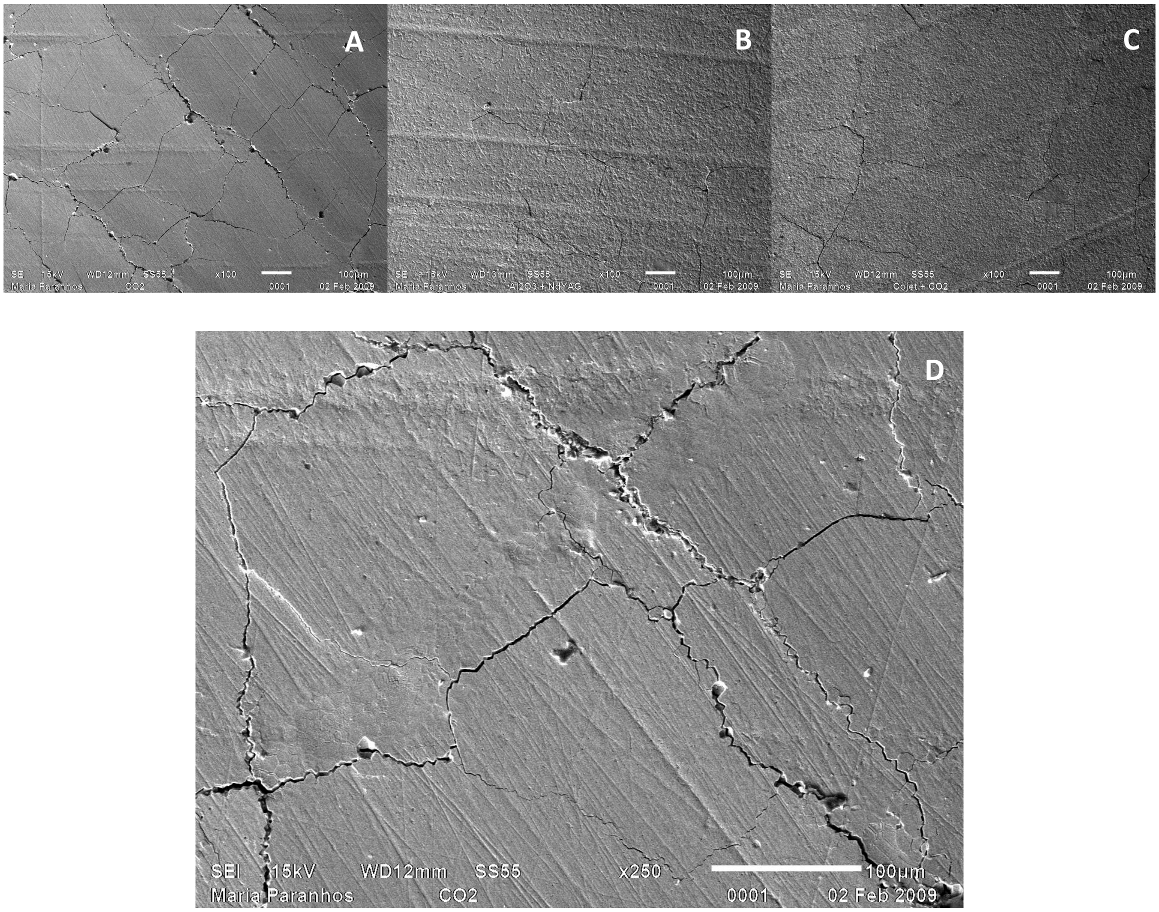


Figure 5 (A/B/C/D)

TABLES

Table 1 Materials used and their characteristics

System	Component	Batch Number	Main Composition*	Manufacturer
Panavia F 2.0	Paste A	00059A/00330A	BPEDMA/MDP/DMA/silica/barium sulfate/dibenzoylperoxide	Kuraray, Kurashiki, Okayama, Japan
	Paste B	00059A/00330A	*N*,*N*-diethanol-*p*-toluidine/silica sodiumfluoride	
	Oxyguard II	00586A	Polyethyleneglycol/glycerine/sodium benzenesulfinate cont. gel	
Clearfil Ceramic Primer		00006C	3-methacryloxypropil trimethoxy silane/MDP/Ethanol	
K-Etchant Gel		00431A	Phosphoric Acid	
Lava Ceramic Block			ZrO_2 (94%), Y_2O_3 (3%), HF (3%) Tetragonal polycrystalline zirconium partially stabilized with yttrium (3 mol-%)	3M-ESPE, St Paul, MN, USA

**Information provided by the manufacturer: BPEDMA: bisphenol-A-polyethoxy dimethacrylate; DMA: aliphatic dimethacrylate; MDP: 10-methacryloxydecyl dihydrogen phosphate.*

Table 2 Experimental Groups

Group	Surface Treatments				Silane/Primer and Luting Cement
	50 µm Al_2O_3 Airborne Particle Abrasion	**Cojet Sand Silica-Coating**	**Nd:YAG Laser Treatment**	**CO_2 Laser Treatment**	
Control	-	-	-	-	**Clearfil Ceramic Primer and Panavia F 2.0**
Nd:YAG	-	-	✓	-	
CO_2	-	-	-	✓	
Al_2O_3	✓	-	-	-	
Al_2O_3 + Nd:YAG	✓	-	✓	-	
Al_2O_3 + CO_2	✓	-	-	✓	
Cojet Sand	-	✓	-	-	
Cojet Sand + Nd:YAG	-	✓	✓	-	
Cojet Sand + CO_2	-	✓	-	✓	

Table 3 Two-way ANOVA for Abrasion and Laser

Source	*Df*	Sum of Squares	Mean Square	F	*p**
Abrasion	2	137.604	68.802	16.512	<0.001
Laser	2	2094.841	1047.421	251.374	<0.001
Abrasion x Laser	4	231.864	57.966	13.911	<0.001

**p<.05 indicates statistically significant differences.*

Table 4 **Surface Roughness**

Groups	Mean (Ra)
Nd:YAG Laser	11.991^{A}
Cojet Sand + Nd:YAG Laser	11.286^{A}
Al_2O_3 + Nd:YAG Laser	8.522^{B}
CO_2 Laser	0.799^{C}
Al_2O_3 + CO_2 Laser	0.658^{C}
Cojet Sand + CO_2 Laser	0.639^{C}
Al_2O_3	0.315^{C}
Cojet Sand	0.305^{C}
No Treatment (Control)	0.233^{C}

Table 5 **Percentage of Failure Mode after Shear Testing**

Failure Mode	Control	Al_2O_3	Cojet Sand	Nd:YAG	Al_2O_3 + Nd:YAG	Cojet Sand + Nd:YAG	CO_2	Al_2O_3 + CO_2	Cojet Sand + CO_2
Cohesive	0%	0%	0%	0%	0%	0%	0%	0%	0%
Adhesive	50%	33%	0%	11%	17%	33%	33%	60%	33%
Mixed	50%	67%	100%	89%	83%	67%	67%	40%	67%

SEGUNDO CAPÍTULO

New zirconia primer improves bond strength of resin-based cements

CARTA DE ACEITE – DENTAL MATERIALS*

*Artigo em anexo

From: Ron Sakaguchi <sakaguch@ohsu.edu>
Date: December 9, 2009 6:17:41 AM PST
To: magne@usc.edu
Subject: Your Submission DEMA-D-09-00309R1

Ms. Ref. No.: DEMA-D-09-00309R1
Title: New zirconia primer improves bond strength of resin-based cements
Dental Materials

Dear Pascal,

I am pleased to confirm that your paper "New zirconia primer improves bond strength of resin-based cements" has been accepted for publication in Dental Materials.

Thank you for submitting your work to this journal.

With kind regards,

David Watts
Receiving Office/Editor
Dental Materials

Title:

New zirconia primer improves bond strength of resin-based cements.

Authors:

Pascal Magne[1], Maria P. G. Paranhos[1,2], Luiz H. Burnett-Jr[2]

[1]Division of Primary Oral Health Care, University of Southern California, Los Angeles, USA

[2]Department of Restorative Dentistry, Pontifical Catholic University of Rio Grande do Sul, Porto Alegre, Brazil

Short Title: Bonding to Zirconia

Corresponding Author:

Dr. Pascal Magne
University of Southern California
Division of Primary Oral Health Care
School of Dentistry, Oral Health Center
3151 S. Hoover St.
Los Angeles, CA 90089-7792
Phone (213) 740-4239
Fax (213) 821-5324
magne@usc.edu

ABSTRACT

Objective. Various chemical interactions can be used to develop ceramic-resin bonding and specific approaches are available for zirconia ceramics. This study evaluated the effect of a new experimental primer, a mixture of organophosphate and carboxylic acid monomers, on the zirconia-to-resin shear bond strength (SBS).

Methods. Forty Y-PSZ blocks (15x4x2mm) were embedded in an acrylic resin base, polished, Al_2O_3-sandblasted and randomly divided into eight groups. Three different resin-based luting agents (BisCem, Duo-Link, Panavia F) were used to build 2.4mm-diameter cylinders (n=15) onto the zirconia surface with and without the new experimental zirconia primer. The new primer was also tested with Z100 composite resin cylinders. In addition, Panavia was used with its own primer (Clearfil Ceramic Primer). SBS testing was carried out after 24 hours of storage in water. Scanning Electron Microscopy (SEM) was used to evaluate the zirconia surface topography and failure mode.

Results. According to ANOVA and Tukey test ($\alpha=0.05$), the association of the experimental primer with the restorative composite resin Z100 yielded the highest SBS (29.35 MPa) followed by DuoLink with the new primer (26.68 MPa). The groups that did not receive the experimental primer presented the lowest SBS values (from 5.95 to 9.79 MPa). The failure mode was adhesive for the non-primed specimens and predominantly mixed in the primed groups.

Significance. The use of the new zirconia experimental primer based on organophosphate/carboxylic acid monomers increased the bond strength of different resin-based luting agents including Z100 restorative material.

Key-Words: Bond Strength; Shear Test; Surface Conditioning Methods; Airborne-Particle Abrasion; Resin Luting Material; Zirconia Ceramics.

INTRODUCTION

There has been a significant growth of interest for zirconiumoxide (zirconia) ceramics in recent times, with amajor impact in the field of prosthodontics and implant dentistry. Due to its mechanical properties [1‑3], biocompatibility, and optical properties, zirconia has been elected as a metal-free alternative. “Transformation toughening” is a distinctive capability of Yttrium stabilized tetragonal zirconia polycrystals (Y-TZP), through which it can resist crack propagation by transforming from a tetragonal to amonoclinic phase [1,3]. One of the major limitations regarding the use of zirconia is the difficulty to adhere to this material. Zirconia FDPs and full-veneer crowns have been successfully used when cemented with conventional cements, such as glass ionomer [4]. A reliable bond to zirconia, however, needs to be achieved when retention of the restoration relies primarily on adhesion, as in partial veneers and resin-bonded FPDs.

The search for a predictable bond to zirconia started in the 80s where the bond strength of ceramic brackets was evaluated by Urano [5]. The main challenge besides in the fact that highly crystalline ceramics resist conventional etching techniques (absence of a glassy phase) [6‑9]. Classic surface roughening methods (airborne-particle abrasion) can only produce a mild coarsening of the zirconia surface [6] and reliable resin bond strength may not be always achieved [8,10]. As a result, a large body of literature has been produced and innovative adhesive strategies combining new surface roughening procedures [11,12], laser treatments [13,14], and chemical bonding have been developed [10,15‑20].

Chemical bonding to zirconia ceramics involves the use of various couplers. The use of a silane coupling agent in combination with aluminum oxide sandblasting presents low bond strength [6,8,15], which is expected given the absence of silica in the substrate. On the other hand, tribochemical silica coating allows high-strength alumina-based and zirconia-based ceramics to be chemically more reactive to resin through silane coupling agents yielding increased resin bond strength values [8,9,19,21,22]. The association of airborne-particle abrasion (aluminum oxide or silica-coating) and primer/luting agents containing phosphate ester monomer 10-methacryloyloxydecyl dihydrogenphosphate (MDP) [10,15,16,19,20] and zirconate coupler agent [17,18] has also been suggested. The presence of other acidic monomers such as 4-methacryloxyethyl trimellitic anhydride (4-META), and thiophosphoric acid methacrylate (MEPS) permits additional chemical bond with zirconium/metal oxides [23]. A new approach is to use a mixture of organophosphate and carboxylic acid monomers in form of a light-polymerizable priming agent.

The purpose of this study was to evaluate the effect of a Z-Prime Plus (Bisco, Schaumburg, IL) (organophostphate/carboxylic acid monomers) on the zirconia SBS to different types of resin-based luting agents which include: Duolink (Bisco), a conventional dual-cured resin-based luting cement; Panavia F 2.0 (Kuraray), a MDP containing dual-cured resin cement; BisCem (Bisco), a self-adhesive resin cement which contains phosphate monomer other than MDP; and Z100 (3M-ESPE), a restorative composite resin with higher filler content (85 wt%). The null-hypothesis considered was that the use of the new zirconia primer would not influence the SBS of Y-TZP to resin-based luting agents.

MATERIAL AND METHODS

Forty blocks (15 x 4 x 2 mm) of high-purity zirconium-oxide ceramic (LAVA; 3M-ESPE, Saint Paul, MN) were produced. The specimens were embedded in an acrylic resin base (Palapress; Heraeus Kulzer, Hanau, Germany) and polished with 400-, 600-, 800- and 1500-grit silicon carbide paper under water cooling. All groups received airborne-particle abrasion with 50 µm aluminum oxide (Al_2O_3) particles (RondoFlex 2013; Kavo, Biberach, Germany) under a pressure of 46-55 psi using a fine airborne particle-abrasion unit (Kavo RONDOFlex Plus 360; Kavo) for 15 seconds at a distance of 10 mm perpendicularly to the surface. The blocks were randomly assigned to eight groups according to primer and resin luting agent used (Table 1). The characteristics of the materials are presented in Table 2. << Insert Tables 1 and 2 >>

The surface of each block was cleaned with 40% phosphoric acid (K-Etchant Gel; Kuraray, Kurashiki, Okayama, Japan) for 5 seconds, water rinsed for 15 seconds, and immersed in an ultrasonic bath for 2 minutes. Fiften blocks did not receive further surface treatment (No Primer - NP). Following air-drying, twenty blocks received two even coats of Experimental Zirconia Primer (ZrP) (Bisco Inc., Schaumburg, IL) that were applied onto the surface, gently air-dried for 10 seconds and light polymerized for 20 seconds at 800 mW/cm^2 (Rembrandt Allegro LED Curing Light; Den-Mat, Santa Maria, CA). MDP-contaning primer (Clearfil Ceramic Primer - CCP) was applied onto the surface of the five remaining blocks and left to dry for 5 minutes. Four different luting materials were used in this study and applied according to their manufacturer’s recommendations (Table 2). For Panavia F 2.0 (Kuraray), equal amounts of pre-heated A and B pastes were mixed for 20 seconds and inserted in a plastic mold (Ultradent Jig; Ultradent Products, South Jordan, UT) with a bubble-free application system (Composite-Gun and no. 1916 Tubes and plugs; KerrHawe SA, Bioggio, Switzerland). The resin cement cylinder was light polymerized for 20 seconds. The cement surface was then protected with an oxygen barrier (Oxiguard II; Kuraray) for 3 minutes. BisCem and Duo-Link resin cements were applied into the plastic mold (Ultradent Jig) using the auto-mixing tips provided in their respective kit and light polymerized for 40 seconds. The restorative composite resin Z100 (3M-ESPE) was inserted into the plastic mold (Ultradent Jig) in two increments of approximately 1.8 mm using a spatula and each increment was light polymerized for 20 seconds. Three resin cylinders (diameter: 2.4 mm) were built onto each ceramic block (length: 15 mm, width: 4 mm, thickness: 2 mm), 3.5 mm apart, resulting in 15 specimens per group.

After 24 hours stored in distilled water, samples were submitted to SBS testing (Shear Bond Tester; Bisco Inc., Schaumburg, IL) with a ramp load of 43.8-kg-force per minute. The failure mode was assessed by examination with a stereomicroscope (MZ12.5; Leica Microsystems, Wetzlar, Germany) at X8 magnification. Failures were classified as adhesive if the fracture site was located entirely between the resin/cement and zirconia surfaces, mixed if the fracture site continued into the resin/cement and cohesive if the fracture occurred exclusively within the resin/cement. Three specimens of each group were randomly selected for surface topography and further failure mode analysis which was observed by a scanning electron microscope (SEM) (JSM-6610LV Scanning Electron Microscope; JEOL USA Inc., Peabody, MA) at an accelerating voltage of 15 kV after sputter coating with gold powder (Cressington Sputter Coater 108; Ted Pella Inc., Redding, CA).

Bond strength data obtained from the eight groups were analyzed with a one-way analysis of variance (ANOVA). The Tukey HSD post hoc test was used to detect pairwise differences among experimental groups. All statistical testing was performed at a preset alpha of 0.05 (Statistix for Windows v.8, Fort Lauderdale, FL).

RESULTS

According to ANOVA, the difference among the experimental groups was significant ($P<0.001$)(Table 3). << Insert Table 3 >> The SBS values are illustrated in Fig. 1. The groups where the experimental zirconia primer (ZrP-groups) was used presented the highest mean bond strength values (Table 4). The association of the experimental primer with the Z100 restorative composite resin yielded the highest SBS (29.35 MPa) followed by the combination of this primer with Duo-Link (26.68 MPa). The groups that did not receive the experimental primer (NP-groups) and the group treated with the MDP-containing primer (CCP-group) presented the lowest mean bond strength values (Figure 1). << Insert Figure 1 >>

The SEM micrograph of a sample partially primed with the experimental zirconia primer (Fig. 2) reveals the untreated zirconia surface (characterized by a uniform presence of irregularities and shallow pits created by the Al_2O_3 particles), in contrast with the primed surface, uniformly smooth as if it was resin-coated. << Insert Figure 2 >> The failure mode (Table 4) was adhesive for all NP-groups (Fig. 3) and predominantly mixed for the CPP-group and ZrP-groups (Fig. 4). << Insert Table 4 and Figures 3 and 4 >>

DISCUSSION

This study evaluated the effect of an experimental primer on the bond strength of a zirconia ceramic to four different resin-based luting materials. In accordance with the results, the null-hypothesis was rejected since the resin-zirconia bond strength was significantly affected by the application of the new primer (Table 3).

Considering that zirconia is a tough material and extremely difficult to be sectioned, the SBS test method was chosen for this study. Being a resistant and hard material gives zirconia the advantage of not failing cohesively when submitted to shear forces [24] (Table 4). In this way, the irregular distribution of stresses in the adhesive interface and consequent misinterpretation of the real bond strength results, which is the most common concern regarding shear bond testing, was eliminated [9,25]. It has also been demonstrated that microtensile and SBS methods present similar results on high-strength ceramics, but the shear methodology is significantly simpler and results in exclusively adhesive failures [24].

The original roughness produced by the milling during fabrication is not sufficient to promote adhesion and it seems important to mention that not only cleaning, but roughening and activating the surface are important to achieve durable resin bond to densely sintered zirconia ceramic [10,26,27]. Al_2O_3 airborne-particle abrasion has been widely used on zirconia [9,15,16,26,28–30]. In the present study, standardization of the ceramic surfaces was carried out using this abrasion technique, since it has proven to increase the surface energy, surface area for bonding, and wettability [9,15]. It has been demonstrated that, besides increasing surface roughness of Y-TZP ceramics, air abrasion also leads to the transformation from tetragonal to monoclinic phase. This phase transformation is usually accompanied by an increased flexural strength [30–34]. On the other hand, the presence of this monoclinic phase layer created by air abrasion may contain microcracks and flaws that could compromise the long-term stability and reliability of this ceramic [10,31,32,34]. The lack of clinical information regarding this issue may be one of the reasons why some zirconia ceramic manufacturers do not recommend air abrasion before cementation. The manufacturer of the ceramic used in the present study does not contraindicate air abrasion and clearly states no reduction in strength when using aluminum oxide particles up to 50_m. Tribochemical silica coating has also been recommended on zirconia as a roughening procedure [9,21,22,26,29] and presents good immediate results especially when combined to silanes, associating the micromechanical with the chemical retention via siloxane bonds [9,21,35]. Siloxane bonds may, however, be sensitive to hydrolytic degradation, affecting the stability of the adhesive interface [24,35–37]. Additionally, it has been shown that even after tribochemical silica coating, zirconia surface remains too silicon-poor for long-lasting adhesion and that the Zr–O–Si bonds are not durable [37]. When focusing on the topographical modification of zirconia, however, similar surface roughness can be created with Al_2O_3 airborne-particle abrasion and silica-coating methods [20,30,35].

Hence, the aforementioned roughening methods alone are not capable of producing reliable bond between zirconia and resin luting agents [23,35,38]. The same can be said about chemical surface treatments with primers/silanes [23,39]. Therefore, a combination of both pretreatment methods (chemical modification of the coarsened zirconia surface) is recommended to try achieving higher bond strength. As mentioned before, the chemical bond strategies involve the use of adhesive monomers that are present in some luting agents and zirconia/metal primers (such as MDP, 4-META, MEPS, and zirconate coupler). These acidic monomers can react with the oxide groups on zirconia ceramic surface similar to the surface reaction between silane coupling agents and silica-based ceramics [18,23,35,40]. The new primer used in this study includes a mixture of organophosphate and carboxylic acid monomers. Like silanes, organophosphate monomers have an organofunctional part, most often a methacrylate group that can be co-polymerized with the monomers of a composite resin system [37]. The phosphate monomers also contain phosphoric acid groups that can develop the bond with the metal oxides in the substrate. The other monomers in ZrP, such as the carboxylic acid monomer, are cooperating in the development of the bond.

The use of the ZrP had a positive influence on SBS regardless of the luting agent used. This feature indicates that the ZrP is chemically compatible with all tested resin-based luting agents, giving the possibility of a wide range of applications. The ZrP also presents the advantage of being a light polymerizable primer, which allows the controlled application and visual inspection of the primed area. After applying the ZrP, the surface looked uniformly smooth as if it was resin-coated (Fig. 2A or B). This may be due to the presence of two light curing acidic monomers in ZrP, which also increases the affinity of resin to zirconia.

Highest values in this experiment were obtained either with Z100 or Duo-Link, both associated to the ZrP (29.35 and 26.68MPa, respectively). They presented predominantly mixed failures (Table 4). The use of pre-heated Z100 restorative composite resin as a luting agent features the benefit of being a solely light-cured material, which has increased color stability, optimal physic-chemical properties and radiopacity. The working time is quasi unlimited with this material and allows the controlled removal of excesses as it becomes less viscous after cooling [41]. The excellent SBS obtained with ZrP and Z100 also suggests that the new primer could be used for intraoral repair of chipped/failed restorations with exposed zirconia substructure. Duo-Link was used in order to match the ZrP with a conventional resin luting agent from the same manufacturer. The resin parts of both Z100 and Duo-Link are mainly composed by methacrylate-based monomers, such as Bis-GMA, which interacts directly with the organofunctional part of the ZrP (i.e. methacrylate groups).

In contrast, the lowest SBS value was observed for NP-DuoLink (5.95MPa). This conventional resin luting agent is not supposed to have chemical interaction with zirconia. Nevertheless, this material was studied on non-primed zirconia to serve as a control for the ZrP-DuoLink group and to compare this phosphate monomers-free cement to BisCem and Panavia F. The residual bond strength found in the NP-DuoLink group could be explained by the presence of undercuts created by airborne-particle abrasion that may have led to a slight microretention [42]. The SEM micrograph of the Al_2O_3 airborne-particle abraded zirconia was characterized by a uniform presence of irregularities and shallow pits [35,36], which supports this finding. However, a stable and long-term bond is not achieved when using conventional resin luting agents on zirconia [16,36,42]. The combination of ZrP with the self-adhesive resin cement, BisCem, yielded lower SBS mean values (21.89MPa) when compared to conventional resin luting agents (ZrPZ100 and ZrP-DuoLink), but higher SBS when compared to ZrP-Panavia (14.96MPa). BisCem is amodified version of composite resin with acidic monomers and nonsilanized glass ionomer powder. The benefits of conventional and adhesive luting techniques have been combined in this category of cements [28,43]. However, when acidic monomers of self-etching adhesives are incorporated into dental adhesives at high concentrations, the adhesive becomes more hydrophilic and absorbs more water. Water sorption by polymers causes plasticization and lowers mechanical properties of the material, such as the modulus of elasticity [44]. It can be assumed that the presence of acidic monomers in this cement may have contributed for a decrease in the modulus of elasticity elasticity and consequent decrease in the SBS values. Also, these acidic monomers may be a weak link between ZrP and the methacrylate groups of this material. Adhesive cements were meant to be applied directly on the substrate,with no adhesive layer in-between, since this category of cements is thought to interact with the inorganic material present on the substrate. This assumption was proved by the relative bonding ability of BisCem to non-primed zirconia (9.79MPa), that presented higher, but not statistically significant, SBS among NP-Panavia and NP-DuoLink groups. These finding are in accordance to other studies that found better long-term performance of self-adhesives resin cements when compared to conventional resin cements after air abrasion [45].

Clearfil Ceramic Primer (CCP) was the other primer used in this study, together with Panavia F. The use of CCP or NP with Panavia yielded statistically similar SBS mean values (8.74 and 6.78MPa, respectively). This primer has a silane molecule (3-methacryloxypropil trimethoxy silane) mixed with a phosphate monomer (10-MDP). MDP is also present in Panavia F and the phosphate ester group of this monomer bonds chemically to aluminum and zirconium oxides [15,20,23,35,36,46]. According to the literature, the presence of MDP in the resin luting agent creates stable bond strength to airborne-particle abraded zirconia before and after thermo-cycling [10,15,26,36,42]. The slightly higher value found in the CCP-Panavia when compared to NP-Panavia (also evidenced by the presence of mixed failures in the CCP-Panavia groups) [16] could be explained by the presence of a silane molecule mixed with MDP. In this case, the silane coupler agent would have the property of increasing the wettability of the ceramic surface for the resin luting cement, thus improving the ability of the ceramic to adhere to resin cements [18]. The formation of siloxane bonds in this situation was improbable since no silica was present on the zirconia surface [15,37,46–48]. Based on these results, it could be assumed that the use of an MDP-containing primer may not be essential when using a MDP-containing luting agent. Inversely, according to Blatz et al. [16], an adhesive functional monomer is not necessary in the resin luting agent if it is contained in the primer.

Many other innovative attempts have been developed to increase the resin-zirconia bond strength. Modification of the zirconia surface by sintering a porous ceramic layer on the milled zirconia allowing resin infiltration (NobelBond; Nobel Biocare AB, Goteborg, Sweden) [12], transformation of zirconia into an etchable substrate by the selective infiltration technique [11], the use of Nd:YAG laser to create microporosities [14]; ultra-thin silica-like seed layers with conventional silane [38], and others. However, their long-term efficacy is currently unknown. The driving force is to establish stable and durable resin bond without damaging and weakening the overall clinical performance of zirconia restorations. The use of new primers/luting agents may have a significant contribution to achieve this outcome.

Improved marginal adaptation, prevention of microleakage, increased fracture strength, and increased retention in situations where mechanical retention does not exist constitute the benefits of a stable and durable resin bond to zirconia. The fatigue resistance of machinable zirconia custom abutments combined to novel design porcelain veneers, as proposed by Magne et al. [49], would also profit from this adhesion and is already under investigation. Bonded metal-free FPDs, zirconia brackets, and endodontic posts would also take advantage of this research. The association of this new primer with the aforementioned innovative micromechanical approaches, rather than focusing on airborne-particle abrasion only, would also be valuable.

Artificial aging methods, such as thermo-cycling and long-term water storage were not performed to evaluate the durability, stability, and hydrolytic degradation of the resin-ceramic bond. This may be considered one of the limitations of the present study as it can be projected that long-term water storage and thermo-cycling may significantly affect the bond strength of resin-based luting agents to zirconia [16,26], especially MDP-free cements [10,15,36,42]. Further investigation should consider those issues to confirm the stability of the SBS claimed by the manufacturer (28.7MPa versus 28.3MPa after accelerated ageing in boiling water for 72 h).

CONCLUSIONS

Within the limitations of this study it was possible to conclude that the new zirconia experimental primer based on organophosphate/carboxylic acid monomers increases the resin bond strength of LAVA to resin-based luting agents.

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CAPTIONS

Figure 1. Mean SBS values and SD of experimental groups. Values of groups having similar superscript letters were not statistically different for $p < 0.05$.

Figure 2. Representative SEM micrographs (magnification X600) of the sandblasted zirconia surface treated with the experimental primer (A), the transition between the primed and non-primed surface (B), and the non-primed surface (C).

Figure 3. Representative SEM micrographs (magnification X37) of the adhesive failure mode of non-primed groups. NP-BisCem (A), NP-DuoLink (B), and NP-Panavia (C).

Figure 4. Representative SEM micrographs (magnification X37 and X250) of the mixed failure mode of the experimental primer treated groups. ZrP-BisCem (A), ZrP-BisCem - X250 (B), ZrP-DuoLink (C), ZrP-Panavia (D) and ZrP-Z100 (E).

TABLES

Table 1	Experimental Groups						
	Primer			Luting Material			
Groups	No Primer	Experim. Primer	Clearfil C. Primer	BisCem	DuoLink	Panavia F	Z100
NP-BisCem	■			■			
NP-DuoLink	■				■		
NP-Panavia	■					■	
ZrP-BisCem		■		■			
ZrP-DuoLink		■			■		
ZrP-Panavia		■				■	
ZrP-Z100		■					■
CCP-Panavia			■			■	

Table 2	**Materials used and their characteristics**			
System	**Component**	**Batch Number**	**Main Composition***	**Manufacturer**
Experimental Zirconia Primer		REF 586-191-C	Organophosphate monomer/Carboxylic Acid monomer/other monomers	Bisco Inc., Schaumburg, IL, USA
Duo-Link Dual-Cured Composite Luting Cement	Base	0900000998	Bis-GMA/TEGDMA/UDMA/glass fillers	
	Catalyst		Bis-GMA/TEGDMA/glass fillers	
BisCem Dual-Cured Self-Adhesive Resin Cement		0800013337	Bis (Hydroxyethyl methacrylate) phosphate/TEGDMA/dental glass	
Panavia F 2.0 Dual-Cured Resin Based Cement	Paste A	00335A	BPEDMA/MDP/DMA/silica/barium sulfate/dibenzoylperoxide	Kuraray, Kurashiki, Okayama, Japan
	Paste B	00117A	*N*,*N*-diethanol-*p*-toluidine/silica sodiumfluoride	
	Oxyguard II	00586A	Polyethyleneglycol/glycerine/sodium benzenesulfinate cont. gel	
Clearfil Ceramic Primer		00006C	3-methacryloxypropil trimethoxy silane/MDP/Ethanol	
K-Etchant Gel		00431A	Phosphoric Acid	
Z100 Restorative Composite Resin		8RE	Bis-GMA/TEGDMA/zirconia/silica	3M-ESPE, St Paul, MN, USA
Lava Ceramic Block		-	ZrO_2 (94%), Y_2O_3 (3%), HF (3%) Tetragonal polycrystalline zirconium partially stabilized with yttrium (3 mol-%)	

**Information provided by the manufacturer: BPEDMA: bisphenol-A-polyethoxy dimethacrylate; DMA: aliphatic dimethacrylate; MDP: 10-methacryloxydecyl dihydrogen phosphate.*

Table 3	**One-way ANOVA for experimental groups**				
Source	***Df***	**Sum of Squares**	**Mean Square**	**F**	***p****
Groups	6	8267.0	1377.83	76.9	<0.001
Error	98	1756.0	17.92		
Total	104	10022.9			

**p<0.05 indicates statistically significant differences.*

Table 4	Percentage of Failure Mode after Shear Testing							
Failure Mode	**NP-BisCem**	**NP-DuoLink**	**NP-Panavia**	**CPP-Panavia**	**ZrP-BisCem**	**ZrP-DuoLink**	**ZrP-Panavia**	**ZrP-Z100**
Cohesive	0%	0%	0%	0%	0%	0%	0%	0%
Adhesive	100%	100%	100%	33%	7%	0%	0%	0%
Mixed	0%	0%	0%	67%	93%	100%	100%	100%

FIGURES

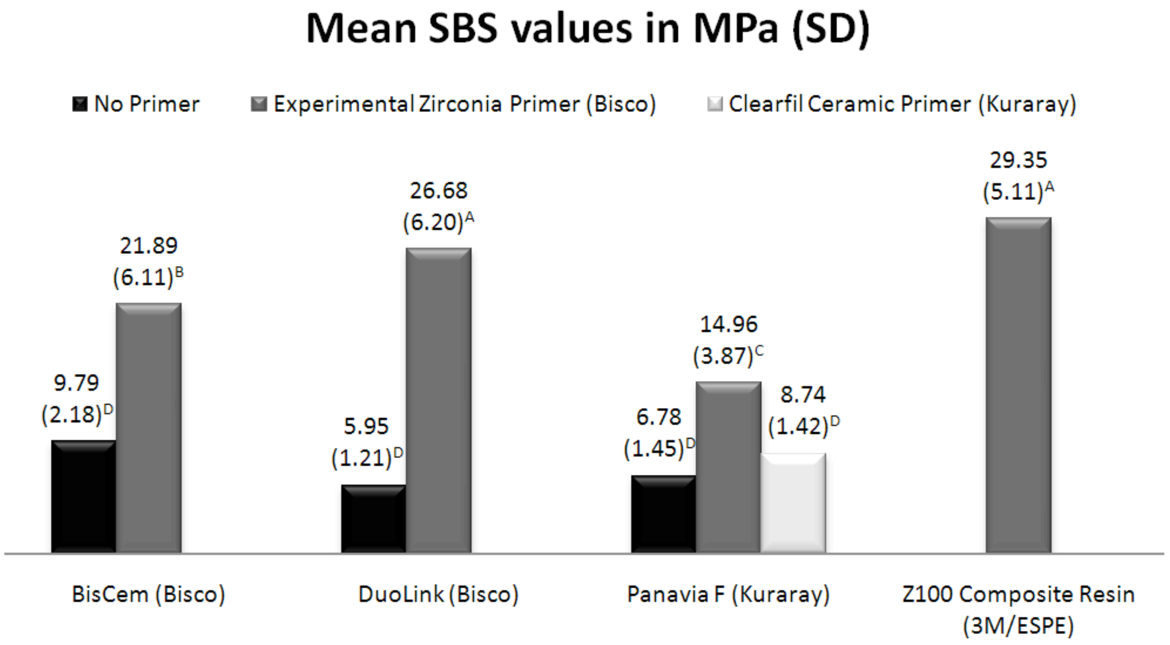

Fig. 1

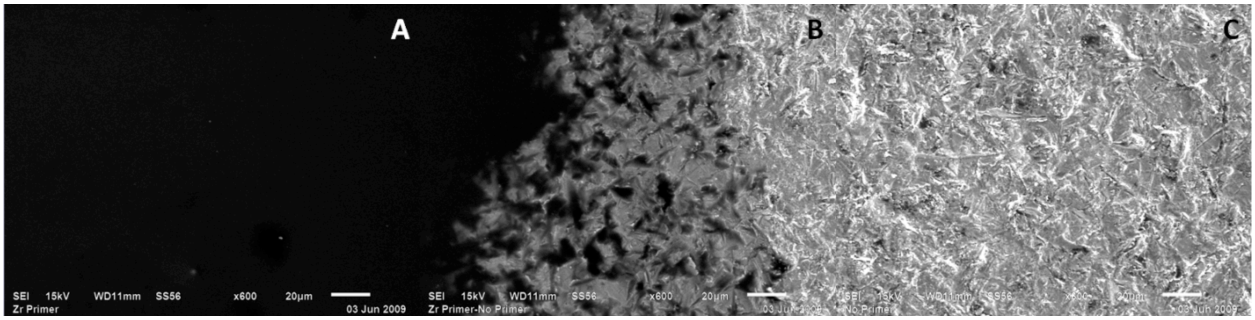
A
B
C
SEI 15kV WD11mm SS56 x600 20µm
Zr Primer
03 Jun 2009
SEI 15kV WD11mm SS56 x600 20µm
Zr Primer-No Primer
03 Jun 2009
SEI 15kV WD11mm SS56 x600 20µm
No Primer
03 Jun 2009

Fig. 2

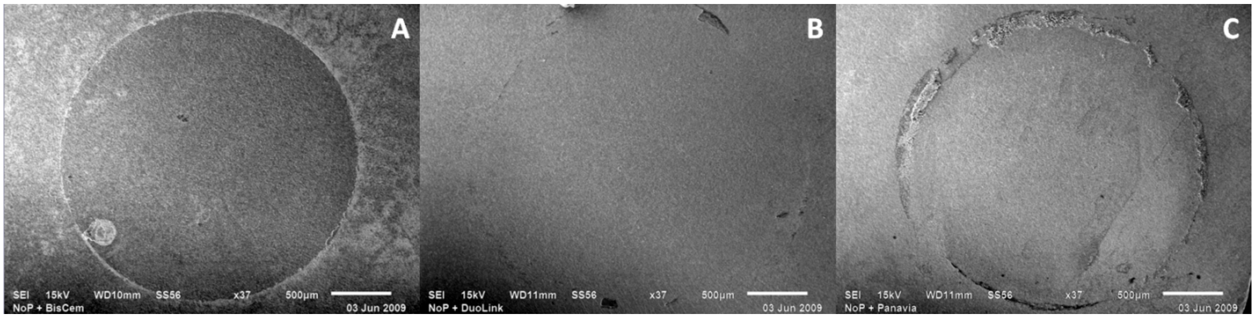
A
SEI 15kV WD10mm SS56 x37 500μm
NoP + BisCem 03 Jun 2009
B
SEI 15kV WD11mm SS56 x37 500μm
NoP + DuoLink 03 Jun 2009
C
SEI 15kV WD11mm SS56 x37 500μm
NoP + Panavia 03 Jun 2009

Fig. 3

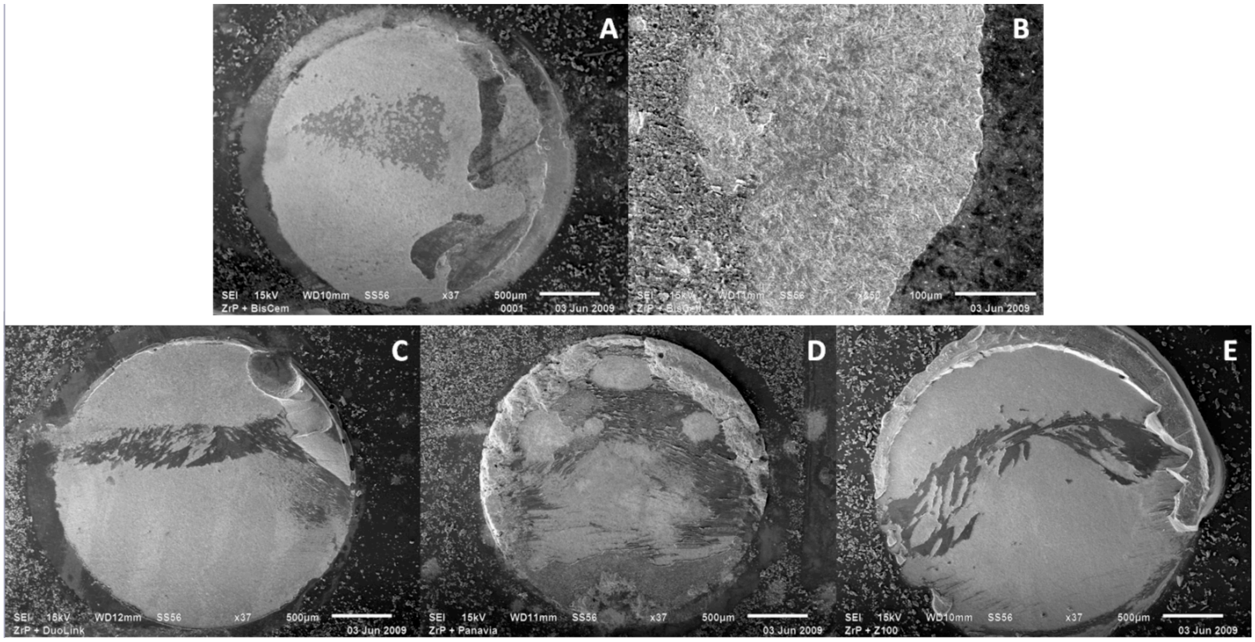
A
SEI 15kV WD10mm SS56 x37 500µm
ZrP + BisCem 0001 03 Jun 2009
B
SEI 15kV WD11mm SS56 x250 100µm
ZrP + BisCem 03 Jun 2009
C
SEI 15kV WD12mm SS56 x37 500µm
ZrP + DuoLink 03 Jun 2009
D
SEI 15kV WD11mm SS56 x37 500µm
ZrP + Panavia 03 Jun 2009
E
SEI 15kV WD10mm SS56 x37 500µm
ZrP + Z100 03 Jun 2009

Fig. 4

TERCEIRO CAPITULO

Fatigue resistance and failure mode of novel-design anterior single-tooth implant restorations: influence of material selection for type III veneers bonded to zirconia abutments

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FATIGUE RESISTANCE AND FAILURE MODE OF NOVEL-DESIGN ANTERIOR SINGLE-TOOTH IMPLANT RESTORATIONS – INFLUENCE OF MATERIAL SELECTION FOR TYPE III VENEERS BONDED TO ZIRCONIA ABUTMENTS

Running title: Non-retentive veneers bonded to customized zirconia implant abutments

Pascal Magne[a], Maria Paula Gandolfi Paranhos[b], Luiz Henrique Burnett Junior[c], Michel Magne[d], Urs Christoph Belser[e]

[a]Tenured Associate Professor, The Don & Sybil Harrington Foundation Chair of Esthetic Dentistry, Division of Restorative Sciences, School of Dentistry, University of Southern California.

[b]Assistant Professor, Division of Restorative Sciences, School of Dentistry, University of Southern California; and Department of Restorative Dentistry, School of Dentistry, Pontifical Catholic University of Rio Grande do Sul, Brazil.

[c]Associate Professor, Department of Restorative Dentistry, School of Dentistry, Pontifical Catholic University of Rio Grande do Sul, Brazil.

[d]Michel Magne 901 Dental Laboratory, Marina del Rey, CA.

[e]Professor and Chairman, Department of Prosthodontics, School of Dental Medicine, University of Geneva, Switzerland.

Address for correspondence:
Dr. Pascal Magne
UNIVERSITY OF SOUTHERN CALIFORNIA
Division of Restorative Sciences
School of Dentistry
3151 S. Hoover St
Los Angeles, CA 90089-7792
Phone (213) 740-4239
Fax (213) 821-5324
magne@usc.edu

ABSTRACT

Objectives: This study assessed the fatigue resistance and failure mode of type III porcelain and composite resin veneers bonded to custom zirconia implant abutments.

Material and Methods: Twenty-four standardized zirconia implant abutments were fabricated. Using the CEREC3 machine, type III veneers of standardized shape were milled in ceramic Vita Mark II or in composite resin Paradigm MZ100. The intaglio surfaces of the restorations were hydrofluoric acid etched and silanated (Mark II) or airborne-particle abraded and silanated (MZ100). The fitting surface of the abutments was airborne-particle abraded, cleaned, and inserted into a bone level implant (BLI RC SLActive 10 mm). All veneers (n=24) were adhesively luted with a zirconia primer (Z-Prime Plus), adhesive resin (Optibond FL) and a preheated light curing composite resin (Filtek Z100). Cyclic isometric chewing (5 Hz) was simulated, starting with a load of 40 N, followed by stages of 80, 120, 160, 200, 240 and 280 N (20 000 cycles each). Samples were loaded until fracture or to a maximum of 140 000 cycles. Groups were compared using the life table survival analysis (Logrank test at P=.05).

Results: Mark II and MZ100 specimens fractured at an average load of 216 N and 229 N (survival rate of 17 % and 8 %), respectively, with no difference in survival probability (P=.18). Amongst the fractured samples, 40 % of the failures were at the abutment level for Mark II and 27 % for MZ100. No exclusive adhesive failures were observed.

Conclusions: Type III Mark II and Paradigm MZ100 veneers showed similar fatigue resistance when bonded to custom non-retentive zirconia implant abutments. MZ100 presented a higher percentage of “friendly” failures, i.e. maintaining the restoration-abutment adhesive interface and the abutment itself intact.

Key-Words: Zirconia ceramic, Dental implant, Surface treatment, Fatigue resistance, Implant abutment, Adhesion.

INTRODUCTION

Implant restorations are usually connected directly to implants with screws or can be cemented to abutments, themselves attached to implants with screws (Chee & Jivraj 2006). In presence of limited interdental, buccal or interocclusal space, especially in the anterior segment of the mouth, it can be challenging to restore small-diameter implants. A solely screw-retained porcelain-fused-to-metal (PFM) or porcelain-fused-to-zirconia restoration may represent an appropriate solution. Screw-retained restorations, however, present several disadvantages such as the increased risk for porcelain fracture and microcracks (Zarone et al. 2007) and the potential of leakage of bacterial contaminants around traditional light-cured composites obturating the screw-access channel. A major problem arises when the screw-access channel interferes with the incisal edge. A cemented crown over a screw-retained custom abutment can potentially resolve most aforementioned issues but requires retention and resistance form for cementation as well as increased restorative space. A new esthetic solution for single-tooth replacement was proposed to address the dilemmas of limited restorative space and insufficient retention and resistance form of the abutment (e.g. lateral mandibular incisor sites), especially when a superior esthetic result is expected (Magne et al. 2008). It consists of a non-retentive screw-retained custom metal-ceramic abutment and a separate porcelain veneer, also fabricated with feldspathic porcelain, using the refractory die technique (Fig 1). This innovative approach is applicable to any clinical situation featuring severely reduced spatial architecture and mismatching implant/crown axes and corresponds to the translational application of novel design (type III) porcelain veneers and adhesive restorative principles (Andreasen et al. 1992, Walls 1995, Magne et al. 2000) in the implant realm. The traditional principles of retention and resistance form of the abutment are substituted by the strong and reliable porcelain-to-porcelain adhesive approach (hydrofluoric acid etching and silanization) (Magne & Cascione 2006, Magne et al. 2008).

The technique is not only suitable in the anterior dentition but also in posterior teeth with limited interocclusal space (onlay-type restoration). The novel-design restoration ultimately allows generating a restoration with advantages similar to those of a cemented restoration (absence of a screw-access channel); yet providing optimal esthetics despite extremely limited restorative space.

In the recent years, metal-free abutments have been increasingly used due to the development of CAD/CAM technology and zirconium oxide ceramic systems with improved biocompatibility, as well as optical and mechanical properties (Garvie et al. 1975, Pittayachawan et al. 2007, Denry & Kelly 2008). One of the major limitations regarding the use of zirconia is the difficulty to adhere to this material. Recently, a new zirconia primer was introduced to the market with highly promising results in shear bond testing (Magne et al. 2010), opening a new window of opportunities, including its association with the novel-design restorative technique (type III veneer and custom zirconia abutment) in order to improve the esthetics and possibly the mechanical properties of this assembly (Fig. 2). It is not known, however, whether the association of a non-retentive abutment and this new adhesion strategy to zirconia will withstand repeated mechanical loading in a moist environment.

The aim of the present study was to assess *in vitro* the fatigue resistance and failure mode of type III veneers bonded to non-retentive custom zirconia implant abutments. The influence of material selection (porcelain vs. composite resin type III veneer) was also evaluated. The null-hypothesis considered was that the abutment-restoration adhesive interface would not fail before the abutment itself and that the restorative material (porcelain vs. composite resin) would not have an influence of the fatigue resistance and failure mode of the assembly.

MATERIAL AND METHODS

Twenty-four bone level implants (BLI 4.1 mm-diameter, 10 mm-length, RC SLActive; Straumann, Basel, Switzerland) were embedded in acrylic denture resin (Palapress; Heraeus Kulzer, Armonk, NY) simulating the bone.

A master custom abutment was fabricated using a wax-up sleeve and additional wax to shape the abutment to a design simulating the natural emergence profile of a lateral maxillary incisor and a type III veneer preparation. Using the etkon CAD/CAM system (Straumann), the master abutment was scanned and replicated in zirconia dioxide ceramic. Twenty-four identical screw-retained custom abutments were produced (one per implant).

Type III veneers were fabricated using the Cerec 3 CAD/CAM system (Sirona Dental Systems GmbH, Bensheim, Germany). An optical impression of the master abutment with the access channel filled with wax was taken. All abutments were fitted with the same standardized veneer from the Cerec database (left maxillary incisor, Lee Culp Youth database). Using the Design Tools of the Cerec Software (version 3.03, Sirona Dental Systems, Charlotte, NC) set in Master Mode, the anatomical restoration was positioned in order to generate a 6 mm-thick restoration with a 3 mm scalloped buccal margin for a total veneer height of 9 mm (Fig. 3).

All restorations were milled in Endo mode with the sprue located at the distal surface. Twelve veneers were milled in composite resin (Paradigm MZ100; 3M/ESPE, Saint Paul, MN) and another twelve in feldspathic porcelain (Mark II; Vident, Brea, CA). The ceramic veneers were initially polished using the intra-oral dialite porcelain adjustment polishing kit (Brasseler, Savannah, GA) and the composite resin veneers were polished using the Q-Polishing System (Kit ref. 4477; Komet, Schaumburg, IL) and silicon carbide-impregnated polishing brushes (Occlubrush; Kerr-Hawe, Bioggio, Switzerland). The pre-cementation assembly is presented in figure 4A.

The abutment adhesion area was delimited with wax to protect its outer surface (Fig. 4B) and sandblasted with aluminum oxide 50 µm at 0.2 MPa for 5 s at a distance of 10 mm, perpendicular to the surface, followed by rinsing with water/air spray for 5 s. The wax was then removed and additional cleaning was performed using 35 % phosphoric acid (Ultra-Etch; Ultradent, South Jordan, Utah) with a gentle brushing motion for 1 min, followed by rinsing with water/air spray for 20 s, and immersion in distilled water in an ultrasonic bath for 2.5 min.

Surface conditioning of the porcelain veneers included airborne-particle abrasion with 50 µm aluminum oxide at 0.2 MPa, followed by etching with 9 % hydrofluoric acid (Porcelain Etch; Ultradent) for 90 s, and rinsing with water for 20 s. Post-etching cleaning was performed using 35 % phosphoric acid (Ultra-Etch; Ultradent) with a gentle brushing motion for 1 min, followed by rinsing with water for 20 s. After final cleaning by immersion in distilled water in an ultrasonic bath for 2.5 min and oil-free air drying, intaglio surfaces were silanated (Silane; Ultradent) and dried at 212 F for 1 min. The same protocol was applied for the composite resin restorations except the hydrofluoric etching step.

The custom zirconia abutment was inserted into the bone level implants and 35 N cm of torque was applied to the abutment screw. Teflon tape was used to cover the abutment screw and fill part of the access-channel. Following air-drying, 2 coats of Z-Prime Plus (Bisco Inc., Schaumburg, IL) were applied to the adhesion area with a micro brush, gently air dried for 10 s to evaporate the solvent, and light-cured for 20 s. A pre-heated restorative composite resin (Filtek Z100; 3M-ESPE, preheated for 5 min in Calset; Addent, Danbury, CT) was used for the adhesive luting of the veneer to the abutment. A small amount of pre-heated composite resin was applied onto the abutment, and adapted with a spatula. After applying one layer of bonding agent (Optibond FL; Kerr, Orange, CA) on the veneer, it was carefully positioned onto the zirconia abutment with gentle pressure. After removal of the composite resin excess, the buccal and lingual surfaces were light-polymerized for 60 s (20 s per surface, for 3 times with Allegro; Den-Mat, Santa Maria, CA). All margins were covered with an air-blocking barrier (K-Y Jelly; Personal Products Company, Skillman, NJ) for the final polmerization cycle. The specimens were cleaned with water/air spray for 5 s and stored in distilled water for 24 h before testing.

Masticatory forces were simulated with an artificial mouth using closed-loop servo-hydraulics (Mini Bionix II; MTS Systems, Eden Prairie, MN) (Fig. 5). The chewing cycle was simulated by an isometric contraction (load control) applied through a flat surface (made from composite resin Z100; 3M-ESPE) at a palatal angle of 30 degrees according to norm ISO 14801 (dynamic fatigue test for osseous implants) with the flat surface contacting ¾ of the incisal edge width of the veneer (Fig. 2). The load chamber was filled with saline solution to submerge the sample during testing. Cyclic load was applied at a frequency of 5 Hz, starting with a load of 40 N, followed by stages of 80, 120, 160, 200, 240, and 280 N, a maximum of 20 000 cycles each. Samples were loaded until fracture or to a maximum of 140 000 cycles. The number of endured cycles and failure mode were recorded. The specimens were evaluated by transillumination (Microlux; Addent, Danbury, CT) and optical microscope (Leica MZ 125; Leica Microsystems, Wetzlar, Germany) at 10:1 magnification (2-examiner agreement). A visual distinction was made between cohesive fractures of the abutment or implant, cohesive fracture of the veneer, adhesive failure of the veneer/abutment interface, or mixed failure (adhesive and cohesive). This difference was easily perceived since the color of the resin materials and zirconia abutments was strongly distinctive. This evaluation was essentially qualitative and no surface area was measured.

The fatigue resistance of the two groups was compared using the life table survival analysis. At each time interval (defined by each load step), the number of specimens starting the interval intact and the number of specimens fracturing during the interval were counted, allowing the calculation of survival probability at each interval. The influence of veneer material on the fracture strength (load step at which failure occurred) were analyzed by using the Logrank test at a significance level of .05.

RESULTS

The fatigue resistance values and survival rates of type III veneers bonded to custom non-retentive zirconia abutments are presented in Table 1 and Figure 6. MKII veneers fractured at an average load of 216 N and two specimens withstood all 140 000 loading cycles (survival=17 %) without damage; with MZ100, the average fracture load was 229 N and the survival rate was 8 % (1 specimen without damage). No difference in survival probability was observed between the two veneering materials (P=.18). The failure modes are presented in Table 2 and Figure 7. Amongst the fractured specimens, 40 % of the failures were in the abutment for Mark II and 27 % for Paradigm MZ100. All other failures were mixed and no solely adhesive failures were observed. Mixed failures were predominantly adhesive with Mark II, while the opposite was observed with Paradigm MZ100 (predominantly cohesive with large fragments of composite resin restoration left on the abutment).

DISCUSSION

The aim of the present study was to assess the fatigue resistance and failure mode of type III veneers bonded to non-retentive custom zirconia implant abutments and the effect of veneer material selection. The null hypothesis can be only rejected in part. The fatigue resistance of the assembly was not influenced by veneer material selection but failure modes were slightly different. While the adhesive interface demonstrated partial failure, the bond was strong enough to induce abutment fractures.

The experimental protocol of this study is based on norm ISO 14801. Some specific elements, however, were designed to adapt to the load configuration of an incisor and prevent local damage at the load point. A flat composite resin surface was used as an antagonist instead of stainless steel as suggested in other similar fatigue studies (Magne & Knezevic 2009). The flexibility and wear of the antagonist allowed more realistic simulation of anterior tooth contact through a wear facet included in the incisal edge of the restoration. The large and uniform contact surface prevented localized and intense point loads which could exceed the compressive limit of the restorative materials and generate surface damage and powder-like debris by crushing (Hertzian cone-cracks) (Kelly 1999). This mechanism was confirmed in pilot tests using smaller contact areas and in which delamination and cohesive failure of the incisal edge was observed. Another modification from norm ISO 14801 is the “staircase” load protocol used in this study. It was originally introduced by Fennis et al. (2004) and later used in several studies (Kujis et al. 2006, Magne & Knezevic 2009a/b/c). It represents a reasonable balance between the simple load-to-failure test and more sophisticated and time-consuming fatigue tests. In the load-to-failure test, the specimen is forced to fail under displacement control of the load apparatus, providing useful data under extreme conditions but limited clinical relevance. The present study design covers a wide range of clinically relevant situations. The first part of the test lies inside the range of realistic bite forces in the anterior region, namely up to 100 N (Ferrario et al. 2004). The second part comprises the range of loads that may be encountered in bruxism, trauma (high extrinsic loads) or intrinsic masticatory accidents (under chewing loads but delivered to small area due to a hard foreign body like a stone or seed, for example).

Because both abutment and restoration were fabricated with CAD/CAM technology, many confounding variables could be avoided, such as the dental technologist skills and mechanical properties (absence of man-made defects), as well as other steps involved in the fabrication process. Cerec 3 is also characterized by its ability to control the restoration thickness and anatomy. It also allowed the standardization of the internal fit of the veneers. The cementation process was the only confounding variable left in this experiment.

With average fracture loads of 216 N and 229 N (Mark II and Paradigm MZ100, respectively) and acceptable survival rates within realistic bite forces, it appears that both experimental groups provided appropriate performance. The absence of difference in survival probability between the two veneering materials is in alignment with their similar flexural strength (150 MPa for Mark II and 160 MPa for Paradigm MZ100). The same trend is observed when considering a subset of data without fractured abutments or survived specimens, with average fracture loads of 200 N and 230 N (Mark II and Paradigm MZ100, respectively). The restoration failure modes, however, differed markedly. Mark II demonstrated mixed failure with majority of adhesive failure and small restoration fragments left on the abutment while the opposite was observed with Paradigm MZ100 (predominantly cohesive with large fragments of composite resin restoration left on the abutment). This difference might be correlated to the substantial disparity in the elastic modulus of those two materials (34 GPa for Mark II and 13 GPa for Paradigm MZ100). With its increased deformation under load, Paradigm MZ100 is more likely to absorb the stress and protect the restoration-abutment adhesive interface and the abutment itself. This was confirmed by the fact that only 27 % of the failures were in the abutment for Paradigm MZ100 (vs. 40 % for Mark II).

No solely adhesive failures were observed in this fatigue study despite the fact that very limited micromechanical retention was generated. This emphasizes the successful performance of the adhesive interface (resin-zirconia bond), which allowed to maintain the restoration-abutment cohesiveness. As a result a significant amount of abutment fractures was observed (Table 2). Different strategies have been proposed to obtain a reliable resin-zirconia bond. Micromechanical approaches are usually emphasized (development of microretentions and microporosities) along with chemical coupling (use of silicoating as well as various silane/MDP solutions and cements) (Kern & Wegner 1998, Bottino et al. 2005, Kim et al. 2005, Spohr et al. 2008, Heikkinen et al. 2009, Phark et al. 2009). Creating mechanical retentions or porosities in a high-strength material such as zirconia, however, appears particularly challenging and irregularities generated during fabrication/milling of the ceramic do not produce reliable bonding (Derand et al. 2005, Wolfart et al. 2007, Phark et al. 2009). Another innovative approach is the selective infiltration (SIE) technique (Aboushelib et al. 2008, Aboushelib et al. 2009), in which the surface of zirconia is transformed into an etchable substrate. In combination with silanization, SIE produces strong resin-zirconia bonding. However, there are not chairside methods currently available and proven to enhance micromechanical bonding to zirconia. Only the use of Al_2O_3 airborne-particle abrasion was considered in the present study. Besides increasing surface roughness of Y-TZP ceramics, air abrasion induces phase transformation and increased flexural strength (Kosmac et al. 2000, Guazzato et al. 2005, Wang et al. 2008, Karakoca & Yilmaz 2009). Claims that microcracks and flaws created by air-abrasion that could compromise the long-term stability and reliability of the zirconia surface (Kosmac et al. 2000, Guazzato et al. 2005, Wolfart et al. 2008, Karakoca & Yilmaz 2009) cannot be supported by the present work. In fact, there were no observations of cohesive damage to the air-abraded surface and all abutment failures occurred at the cervical level, which was not air-abraded. The primer used in this study (Z-Prime Plus) includes a mixture of organophosphate and carboxylic acid monomers. Organophosphate monomers have an organofunctional part, most often a methacrylate group that can be co-polymerized with the monomers of a composite resin system (Piascik et al. 2009) and phosphoric acid groups that can develop the bond with the metal oxides in the substrate. The use of the Z-Prime Plus had a positive influence on shear bond strength regardless of the luting agent used. However, the highest bond strength values are obtained with Filtek Z100 (Magne et al. 2010), which features the benefit of being a solely light-cured material (unlimited working time, increased color stability, optimal physico-chemical properties and radioopacity). As it becomes less viscous after cooling, this composite resin stabilizes the veneer and allows controlled excess removal (Magne & Knezevic 2009c).

Significant clinical implications can be drawn from the present study, which should simplify the work of the surgeon, the restorative dentist and the ceramist. Because of the substitution of “retention and resistance form" of the abutment by adhesive principles, the spatial relationship between the implant and its coronal restoration becomes secondary. The surgeon can benefit from having a broader choice during the determination of optimal fixture axis (allowing for a more "bone-driven" placement) and the design of secondary zirconia components by the ceramist becomes possible even in cases of severely reduced mesio-distal or occlusal clearances. In addition, any crown-root angle (CRA) can be simulated. There is a wide variation in the CRA of natural teeth themselves (Bryant et al. 1984, Van Loenen et al. 2005, Knosel et al. 2009). A type III veneer bonded to a custom abutment would allow the replacement of teeth with extreme CRA even when placing the implant in the original root position. Finally, the abutment design and optical properties allow for the definition of less subgingival margins, which in turn facilitate the final delivery (less risk of excess cement) and esthetic outcome (e.g. in case of thin labial peri-implant mucosa).

While it is difficult to draw direct correlation with the clinical performance of those novel-design single-tooth implant restorations, the present study provides a baseline for the optimization of the abutment material/design, adhesive strategies and other translational applications (e.g. the posterior dentition).

Within the limitations of the present study, it was possible to conclude that type III porcelain Mark II and composite resin Paradigm MZ100 veneers showed similar fatigue resistance when bonded to customized non-retentive zirconia abutments. Paradigm MZ100 presented a higher percentage of "friendly" failures, protecting the restoration-abutment adhesive interface and the abutment itself.

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Table 1. Fatigue resistance of type III veneers (porcelain vs composite resin) bonded to custom zirconia abutments.

Veneer Material	Specimen	Failure Load (N)	Cycles	Failure Mode
Porcelain (Mark II)	01	240	119,874	Mixed*
	02	240	105,500	Abutment
	03	200	98,104	Mixed
	04	240	102,480	Abutment
	05	160	67,480	Mixed
	06	160	60,318	Mixed
	07	240	101,366	Abutment
	08	240	103,369	Mixed
	09	280	140,000	No Failure
	10	280	140,000	No Failure
	11	240	118,909	Abutment
	12	200	88,321	Mixed
Composite Resin (Paradigm MZ100)	01	200	81,048	Abutment
	02	200	89,406	Mixed
	03	160	73,780	Mixed
	04	280	121,908	Mixed
	05	200	98,953	Mixed
	06	240	103,711	Mixed
	07	240	102,001	Abutment
	08	240	102,169	Mixed
	09	280	127,569	Mixed
	10	280	140,000	No Failure
	11	240	103,763	Mixed
	12	240	103,125	Abutment

*Mixed Failure: Adhesive and Cohesive in the veneer (material still bonded to the abutment)

Table 2. Failure mode of fractured specimens.

	Mixed*	Abutment
Mark II	60%	40%
Paradigm MZ100	73%	27%

*Mixed Failure: adhesive (at the interface) and cohesive in the veneer (veneer material still bonded to the abutment)

Figure 1. Novel-design single implant restoration on left maxillary lateral incisor (A) combining a screw-retained gold abutment customized with porcelain (attached to laboratory analogue) and a type III porcelain veneer generated by the refractory die technique (B, C).

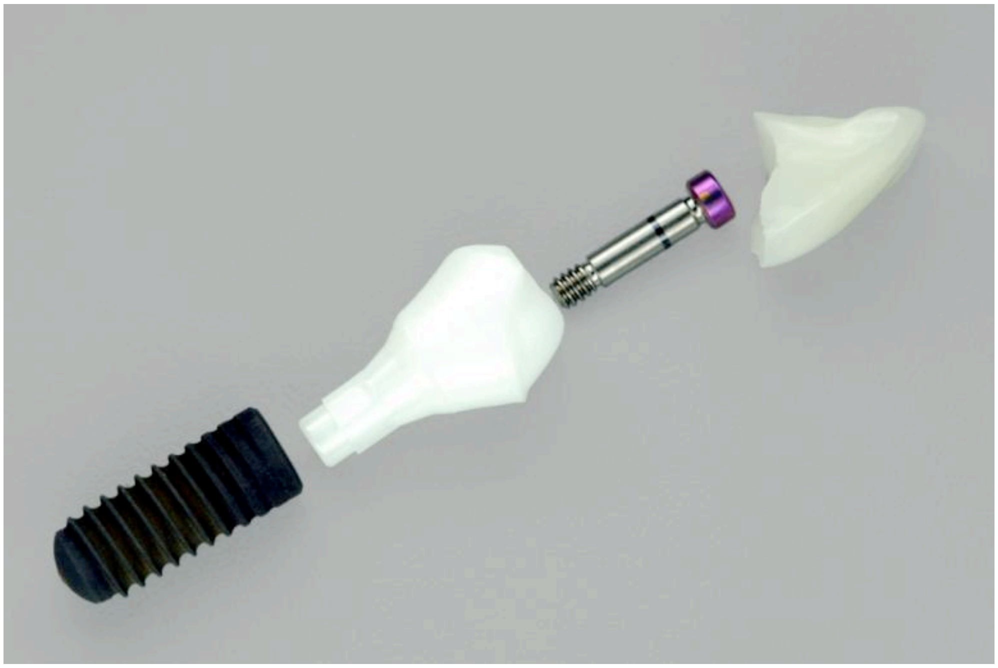

Figure 2. Novel-design single implant restoration combining a screw-retained zirconia CAD/CAM abutment and a type III CAD/CAM veneer.

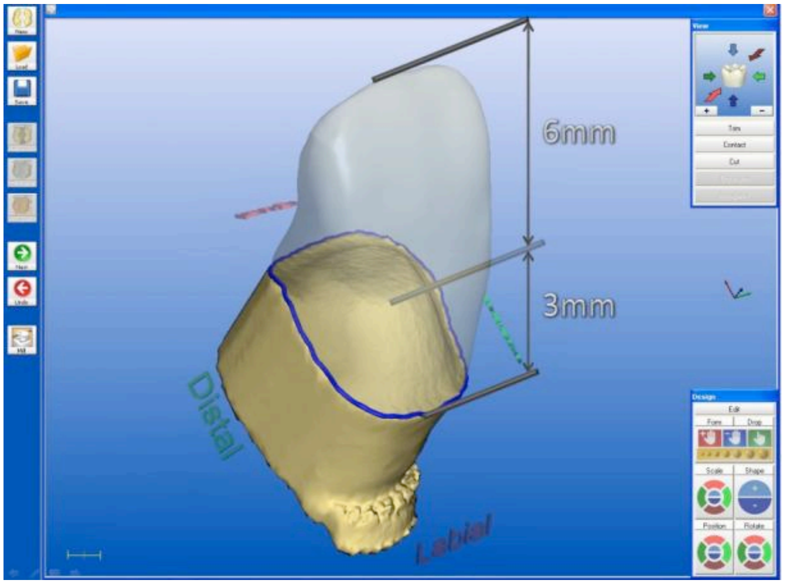

Figure 3. View of restoration design in Cerec Software.

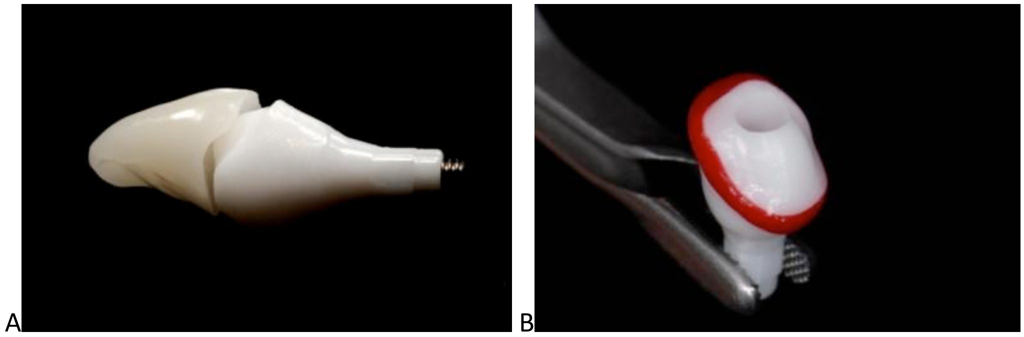

Figure 4. View of abutment and porcelain restoration (A) and abutment with wax protecting the outer surface before airborne particle abrasion of the adhesion area (B).

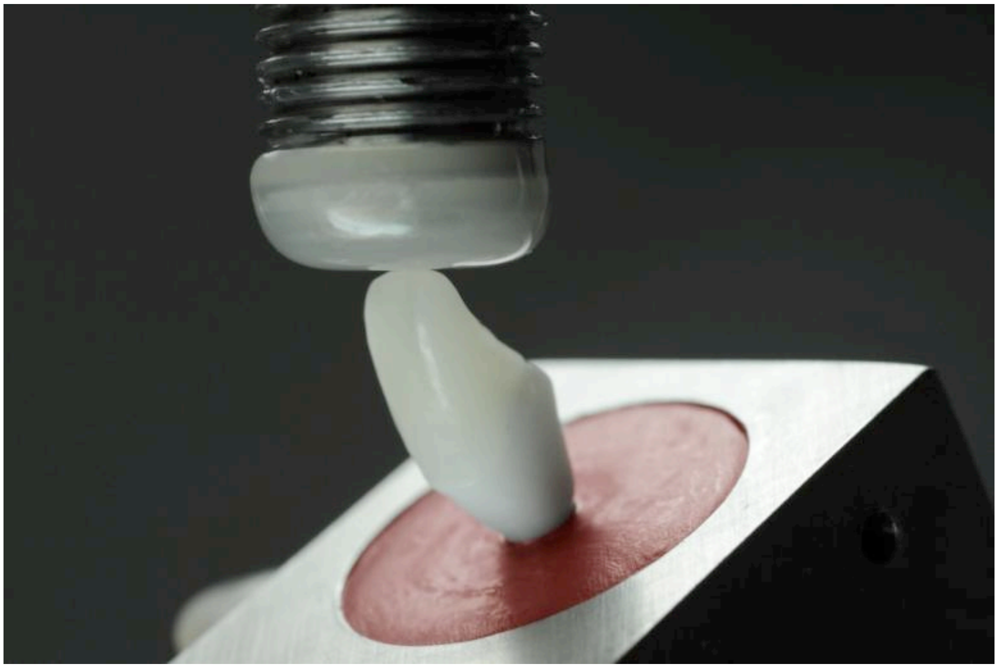

Figure 5. View of the implant/abutment/veneer under load application (modified ISO 14801). The assembly was completely immersed in saline solution during testing (not shown).

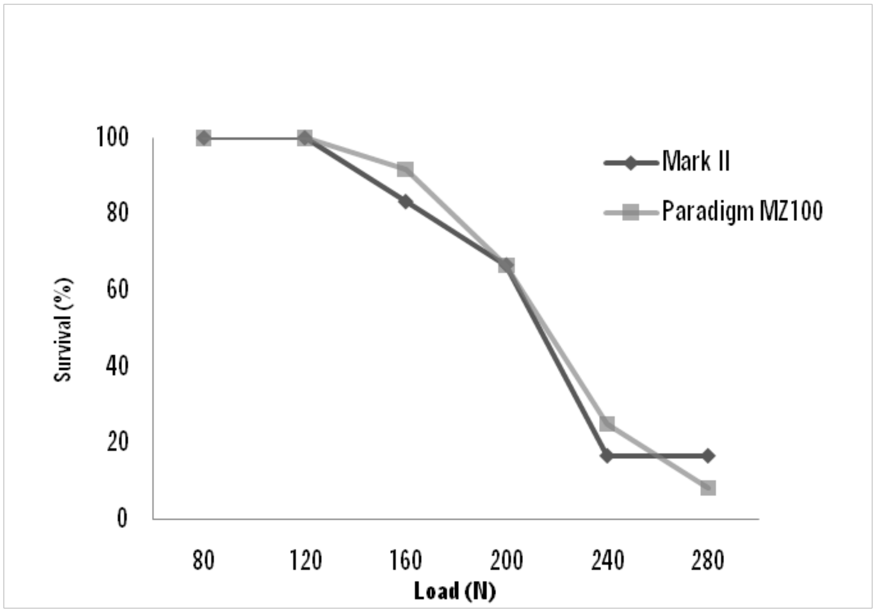

Figure 6. Survival rate of the type III veneers bonded to custom non-retentive zirconia abutments.

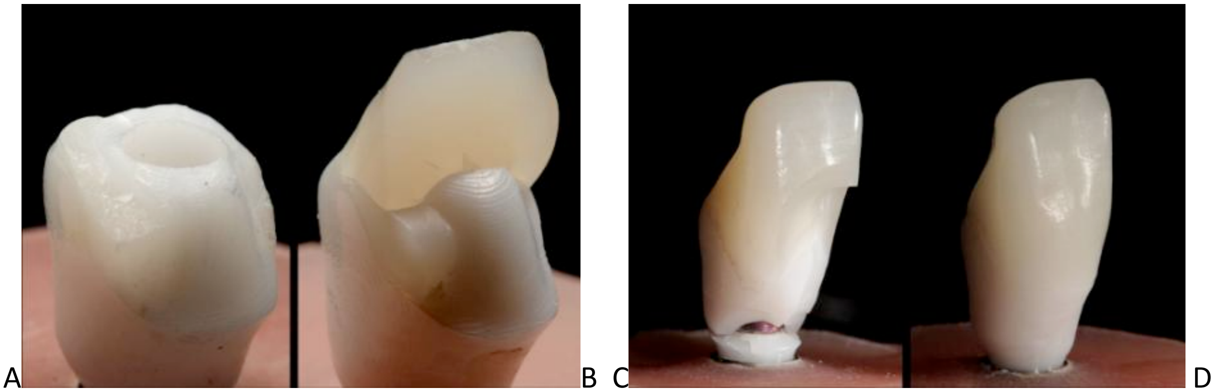

Figure 7. Examples of typal failure modes. (A) porcelain Mark II, mixed failure with majority of adhesive failure and small restoration fragments left on abutment. (B) Paradigm MZ100, mixed failure with large restoration fragments still attached to abutment. (C) Typal abutment fracture with secondary delamination of the restoration (observed with both Mark II and Paradigm MZ100). (D) Intact survived Mark II specimen.

DISCUSSÃO GERAL

O presente estudo avaliou, primeiramente, a resistência de união ao cisalhamento da cerâmica de zircônia (Y-TZP) S diferentes cimentos resinosos, após variados tratamentos de superfície. Após determinação do protocolo adesivo que proporcionou o maior valor de resistência de união e, simultaneamente, a maior previsibilidade de aplicação, foi realizada a avaliação da resistência à fadiga de pilares de zircônia não-retentivos restaurados adesivamente com facetas de resina composta ou porcelana.

A zircônia é um material muito resistente, duro e difícil de ser seccionado. Por isso, falhas coesivas em zircônia raramente ocorrem quando esta cerâmica é submetida as forças de cisalhamento.[27] Dessa forma, a distribuição irregular de estresse na interface adesiva e a consequente falha na interpretação dos resultados de resistência de união (uma das principais desvantagens em relação ao ensaio de cisalhamento) podem ser evitados.[19,28] Além disso, tem sido demonstrado que os ensaios de microtração e cisalhamento apresentam resultados similares quando testadas cerâmicas de alta-resistência. No entanto, o ensaio de cisalhamento é siginificativamente mais simples e resulta em não-coesivas.[24]

Quando se trata de cerâmicas de alta resistência, como a zircônia, tem sido reportado que a aspereza criada durante o processo de fresagem parece não ser suficiente para promover a adesão a esse material. Há necessidade de ativar a superfície com métodos de abrasão e adesão química.[10,26,27]

No primeiro capítulo deste estudo, o foco foi a utilização de métodos de asperização de superfície (jateamento com Al_2O_3, silicatização, laser de Nd:YAG e laser de CO_2) com o objetivo de criar microretenções na superfície da cerâmica e, consequentemente, aumentar sua resistência de união ao cimento resinoso testado. De acordo com os resultados obtidos, os diferentes tratamentos de superfície afetaram significativamente a RUC zircônia-resina. Foi observado que os métodos convencionais de asperização de superfície (jateamento com Al_2O_3 – 8.79 MPa, silicatização – 7.65 MPa) aumentaram significativamente os valores de RUC quando comparados a zircônia apenas polida (4.65 MPa). (Fig. 1)

O jateamento da zircônia com Al_2O_3 tem sido proposto [8,9,18,29,30,31] devido ao seu potencial de aumentar a energia de superfície, a área superficial para adesão e a molhabilidade.[8,9] Alguns estudos mostram que o jateamento pode causar fendas e rachaduras na zircônia, enfraquecendo a cerâmica com o passar do tempo.[17] Por outro lado, tem sido reportado que o jateamento pode ser uma técnica eficaz para o aumento da resistência da cerâmica Y-TZP devido a transformação de fases (fase tetragonal para monoclínica).[29,32] No presente estudo, não foram observadas fendas na zircônia após jateamento com Al_2O_3.

A silicatização foi capaz de criar uma camada microretentiva na zircônia no presente estudo. No entanto, o aumento nos valores de RUC quando comparado ao grupo controle pode ter sido causado também pela união química entre a sílica depositada na superfície e o silano presente no primer (Clearfil Ceramic Primer contem moléculas de silano misturadas com 10-MDP) usado para condicionar a superfície.[8,11,13] Sabe-se que o silano não e capaz de promover uma união quimica entre o cimento resinoso e a zircônia se esta não for silicatizada.[5,10,29,31,33] Considerando que no presente estudo todos os grupos foram igualmente tratados com o primer contendo silano e MDP, combinação responsável por formar união hidrotermicamente estável entre superfície da zircônia silicatizada e cimento resinoso,[10,15,16] não foi possível avaliar a contribuição unicamente química do MDP para a adesão a este material. No presente estudo, o grupo que não foi tratado por nenhum método de asperização de superfície apresentou os mais baixos valores de RUC.[27] Alguns estudos mostram, entretanto, que cimentos contendo MDP apresentam os mais altos valores de RU quando comparados com cimentos sem MDP na composição [14,34] independentemente de pré-tratamentos para asperização de superfícies.[30,31,34] O uso de diferentes primers e cimentos facilitaria o entendimento em relação aos beneficios do MDP.

O tratamento inovador proposto pelo presente trabalho foi a utilização de diferentes lasers (Nd:YAG e CO_2) para criação de microretenções na zircônia. Os resultados mostraram que a irradiação com laser de Nd:YAG criou glóbulos na superfície da zircônia combinados com porosidades de diferentes tamanhos (MEV) (Figs. 4A-4C), o que aumentou os valores de rugosidade superficial e também os valores de resistência de união independente do pré-tratamento abrasivo utilizado (jateamento ou silicatização). Resultado também reportado em outros estudos para cerâmicas de alta resistência à base de alumina e zirconia.[13,14] No entanto, a fusão e a resolidificacão devido a alta temperatura e imediato resfriamento causado pela irradiação com laser Nd:YAG, pode ter sido responsável pelas micro-rachaduras observadas na superfície da zircônia. Estudos futuros avaliando as modificacões estruturais e consequente impacto da irradiação com laser de Nd:YAG nas propriedades da zircônia devem ser realizados. Além disso, as superfícies tratadas com esse laser apresentam uma camada acinzentada, caracteristica de carbonização. Isso pode ser uma limitação do uso dessa técnica, principalmente em relação a áreas estéticas.

Os resultados obtidos com o laser de CO_2 não foram satisfatórios tanto em relação à rugosidade superficial quanto aos valores de resistência de união. Os valores de RUC foram sutilmente mais altos que os grupos não tratados com laser e mais baixos que os grupos tratados com o laser de Nd:YAG. Além disso, inúmeras e visíveis rachaduras foram encontradas na superfície da zircônia após aplicação deste laser, provavelmente devido a alta temperatura causada pela alta potência (5W). A combinação de todos estes fatores leva a contra-indicar o uso deste laser nestes parâmetros em cerâmicas Y-TZP.

O tipo de falha predominante foi a falha mista (Tabela 5) e não foram observadas falhas coesivas em zircônia. A maior porcentagem de falhas puramente adesivas foi encontrada no grupo tratado com jateamento e laser de CO_2, o que esta também associado aos mais baixos valores de RUC encontrados nestes grupos.

No segundo capítulo deste estudo, o foco foi a avaliação do efeito de um primer para zircônia (Z-Prime Plus) na RUC dessa cerâmica a diferentes cimentos resinosos. Dessa forma, todos os especimes receberam o mesmo pré-tratamento de superfície com Al_2O_3 e pôde-se comparar o efeito dos diferentes cimentos e primer na adesão, principalmente, química à zircônia.

As estratégias de adesão química à zircônia envolvem o uso de monômeros adesivos que estão presentes em alguns cimentos resinosos/primers (como o MDP, 4-

META, MEPS e “ziconate coupler”). Os monômeros acídicos podem reagir com a superfície da zircônia similarmente à reação entre silanos e cerâmicas à base de sílica.[30,35,36,37] O novo primer apresentado por este estudo contém uma mistura de monômeros organofosfatos e ácido carboxílico. Assim como os silanos, os monômeros organofosfatos tem um parte organofuncional, mais comumente o grupo metracrilato, que pode ser co-polimerizado com os monômeros presentes na resina.[38] Os monômeros fosfatados também contém grupos de ácido fosfórico com capacidade de desenvolver uma união com os óxidos metálicos presentes no substrato. O outro monômero presente no primer para zircônia, monômeros de ácido carboxílico, cooperam no desenvolvimento da adesão.

De acordo com os resultados, o uso do primer para zircônia, no presente estudo, teve uma influência positiva nos valores de RUC, independentemente do cimento resinoso usado. Isto indica que este primer parece quimicamente compatível com todos os agentes cimentantes testados, abrindo um enorme leque de aplicações. Este primer também tem a vantagem de ser fotopolimerizável, o que permite o controle da aplicação e inspeção da área onde ele foi aplicado. A superfície se torna uniforme a brilhante após a aplicação deste primer como se estivesse sido coberta por adesivo (Fig. 2A ou B – SEGUNDO CAPITULO).

Os grupos tratados com o primer para zircônia e restaurados com a resina composta Z100 ou com o cimento resinoso dual Duo-Link apresentaram os mais altos valores de RUC (29.35 e 26.68 MPa, respectivamente). A grande vantagem de usar a resina composta Z100 pré-aquecida como agente cimentante, dá-se ao fato de ser um material exclusivalmente fotopolimerizável, o que lhe confere uma maior estabilidade de cor, propriedades físico-quimicas otimizadas e radiopacidade. Além disso, o tempo de trabalho é aumentado e possibilita um controle maior durante a remoção dos excessos porque a resina se torna menos viscosa após o resfriamento.[43] Ambos cimentos resinosos, Z100 e Duo-Link, possuem Bis-GMA na composição, o qual interage diretamente com a parte organofuncional do primer para zircônia (grupo metacrilato).

O valor mais baixo de RUC foi observado no grupo Duo-Link, sem a utilização prévia do primer para zircônia (5.95 MPa). Resultado relativamente previsível visto que este cimento não possuiu monômeros fosfatados capazes de se ligar quimicamente à zircônia. Os cimentos auto-adesivos também apresentaram valores de RUC relativamente baixos quando aplicados diretamente sobre a zircônia, sem a aplicação prévia do primer para zircônia.

O Clearfil Ceramic Primer foi apenas utilizado em combinação com o Panavia F. Entretanto, a RUC desse cimento com ou sem a utilização prévia do seu respectivo primer, não foi significativamente alterada (8.74 e 6.78 MPa, respectivamente). Pode ser especulado que o uso do primer contendo MDP, como e o caso do Clearfil Ceramic Primer, pode não ser essencial quando um cimento contendo o mesmo MDP for usado. Inversamente, alguns autores reportam que não há necessidade de se usar um cimento contendo MDP, se o primer utilizado apresenta esse monômero na composição.[15]

Tendo em vista os resultados obtidos nos dois estudos de resistência de união, onde diferentes tratamentos de superfície e diferentes cimentos/primers foram utilizados, foi determinado que o novo primer para zircônia associado à resina composta Z100 seria o protocolo mais adequado para restaurar adesivamente a zircônia no estudo subsequente. Além de ter oferecido o melhor resultado de resistência de união, essa técnica demonstrou não causar danos e enfraquecimento à cerâmica de zircônia.

No entanto, métodos de envelhecimento da adesão, como termociclagem e armazenagem em água, para avaliar a durabilidade, estabilidade e degradação hidrolítica da adesão cerâmica-resina não foram realizados e isso pode ser considerado uma das limitações do presente estudo. Sabe-se que os métodos de envelhecimento podem afetar significativamente a resistência de união de cimentos resinosos a zircônia.[15,39]

Sendo assim, após definido o protocolo adesivo mais apropriado para cimentação adesiva da zircônia, foi realizado um terceiro estudo que envolveu a avaliação da resistência à fadiga e do modo de falha de facetas "tipo III" de porcelana e resina composta cimentadas sobre pilares de zircônia customizados não-retentivos.

O protocolo experimental utilizado teve como referência a norma ISO 14801. Contudo, algumas modificações foram realizadas, como a utilização de uma superfície plana de resina composta como antagonista, em vez de aço inoxidável, para prevenir danos no local de aplicação da carga.[40] Além disso, foi usado o protocolo de aplicação de carga em degraus.[40,41,42,43,44] Este protocolo representa um equilíbrio entre o teste de carga para fratura e os ensaios de fadiga mais demorados e mais sofisticados. Além disso, o desenho dessa metodologia engloba uma ampla variação de situações clínicas relevantes. A primeira parte do teste simula as forças de mordida mais realísticas na região anterior, até 100N.[45] A segunda parte do estudo engloba uma variação de cargas que pode ser encontrada em pacientes com bruxismo, em casos de trauma (cargas extrínsecas) ou acidentes mastigatórios intrínsecos.

Ambos pilares e facetas (resina composta e porcelana) usados neste estudo foram fabricados pela tecnologia CAD/CAM, conferindo uma ótima padronização em relação à forma, espessura e adaptação.

Os resultados mostraram uma média de carga de fratura de 216N e 229N (Mark II-porcelana e Paradigm MZ100-resina composta, respectivamente) e taxa de sobrevivência aceitável e realística quanto às forças mastigatórias para ambos materiais usados. A ausência de diferença na probabilidade de sobrevivência entre os dois materiais testados está de acordo com a resistência flexural similar de ambos (150 MPa para Mark II e 160 MPa para Paradigm MZ100).

O tipo de falha, no entanto, diferiu drasticamente entre os materiais. Mark II demonstrou falha mista, sendo que a maior parte foi falha adesiva com pequenos fragmentos da restauração ainda aderidos ao pilar. O oposto ocorreu com a MZ100, onde a maior parte foi falha coesiva com fragmentos grandes de resina composta ainda aderido ao pilar. Essa diferença pode estar correlacionada com a disparidade no módulo de elasticidade destes materiais (34 GPa para Mark II e 13 GPa para Paradigm MZ100). Com sua deformação aumentada quando submetida a carga, é mais provável que a MZ100 absorva o estresse e proteja a interface restauração-pilar e o próprio pilar. Isso foi confirmado pelo fato de apenas 27% das falhas terem ocorrido no pilar para o grupo Paradigm MZ100, enquanto 40% das falhas foram em pilar para Mark II.

Não foram observadas falhas exclusivamente adesivas neste ensaio de fadiga, apesar da retenção micromecânica quase inexistente. Tal achado enfatiza o sucesso da interface adesiva (resina-zircônia), que permitiu a manutenção da coesividade entre o pilar e a restauração. Como resultado, uma quantidade significativa de fraturas no pilar foi observada (Tabela 2 – TERCEIRO CAPITULO). O protocolo adesivo aqui usado foi exatamente o protocolo determinado pelos estudos de resistência de união (SEGUNDO CAPÍTULO) com o primer para zircônia que contém organofosfatos e acido carboxílico na sua composição (Z-Prime Plus, Bisco).

Inúmeras implicações clínicas podem ser delineadas a partir do presente estudo, o que simplificaria tanto o trabalho do dentista quanto o trabalho do protético/ceramista. Devido a substituição da “forma de resistência e retenção” do pilar por princípios adesivos, a relação espacial entre o implante e a restauração coronária se torna secundária. O cirurgião pode se beneficiar por ter uma maior possibilidade de escolha durante a determinação do eixo de fixação do implante e o uso dos componentes secúndarios em zircônia, pelo ceramista, se torna possível até nos casos de redução do espaço mesio-distal e inter-oclusal. Além disso, o ângulo formado pela raiz-coroa (CRA) pode ser simulado. Sabe-se que mesmo na dentição natural, existe uma enorme variação entre o CRA.[46,47,48] O uso de facetas tipo III adesivamente cimentadas à pilares customizados permitiria o reposicionamento dos dentes com extrema CRA, quando o implante for colocado na posição original da raiz. Finalmente, o formato do pilar a as propriedades ópticas permitiriam a colocação de margens mais supragengivais, o que falicitaria a cimentação da restauração final melhorando o resultado clínico (ex. nos casos de mucosa labial peri-implantar fina).

CONCLUSÕES

Respeitando as limitações do presente estudo, foi possível concluir que:

PRIMEIRO CAPÍTULO

1. A irradiação com laser de Nd:YAG aumenta a rugosidade superficial da zircônia Y-TZP e aumenta sua resistência de união ao Panavia F, pré-asperizando ou não a superfície com Al_2O_3 ou silicatização.

2. A silicatização como pré-tratamento aumenta a resistência de união da zircônia Y-TZP ao Panavia F, inclusive nos grupos tratados com laser de Nd:YAG e laser de CO_2.

3. Rachaduras significativas são encontradas após tratamento da zircônia Y-TZP com laser de CO_2 o que contra-indica seu uso nestes parâmetros para o condicionamento de superfície.

SEGUNDO CAPÍTULO

1. O novo primer para zircônia (Z-Prime Plus), a base de monômeros organofosfatados e ácido carboxilico, aumenta a resistência de união da cerâmica Y-TZP a cimentos resinosos.

TERCEIRO CAPÍTULO

1. Facetas tipo III de porcelana Mark II e de resina composta MZ100 mostraram resistência à fadiga similar quando cimentadas a pilares de zircônia sobre implantescustomizados não-retentivos.

2. A resina composta paradigm MZ100 apresentou uma maior porcentagem de falhas reparaveis, mantendo a interface restauração-pilar e o próprio pilar intactos.

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