Faculdade de Medicina Dentária
Universidade de Lisboa

Influence of new universal adhesives and zirconia primer application techniques on zirconia repair

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Dissertação orientada pelo

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TABLE OF CONTENTS

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Resumo

Durante a última década, a realização de restaurações protéticas realizadas em cerâmicas de elevada resistência mecânica, como a zircónia, tem tido um aumento exponencial. Este facto parece dever-se a diversos fatores: se por um lado se tem assistido a uma cada vez maior exigência estética por parte dos paciente, por outro, nota-se também uma crescente procura por restaurações isentas de metais. A excelente biocompatibilidade e as elevadas propriedades mecânicas da zircónia têm permitido ir de encontro a estas pretensões.

No entanto, as restaurações em zircónia poderão apresentar ainda algumas limitações. Em diversos estudos em que foi analisada a taxa de sucesso das restaurações em zircónia, foi encontrada uma elevada incidência de *chipping*, em que a cerâmica feldspática de revestimento fratura, separando-se da infraestrutura de zircónia. Quando deparado com este problema, o clínico poderá optar por substituir toda a restauração, ou pela sua reparação. Apesar de algumas limitações que poderão existir sob o ponto de vista estético e mecânico, a reparação intraoral de restaurações deficientes poderá ser uma alternativa viável, por ser um tratamento mais conservador e por ser um procedimento mais fácil e menos oneroso.

Diversas técnicas foram estudadas de forma a permitir a reparação intraoral de restaurações fraturadas.

A aplicação do protocolo de condicionamento tradicionalmente utilizado nas cerâmicas vítreas, revelou-se ineficaz na promoção da adesão à zircónia. Assim, na tentativa de suprir este condicionalismo, tem-se assistido nos últimos tempos ao desenvolvimento de novos cimentos, primers e adesivos. Alguns deles, contendo monómeros de fosfato (MDP), têm apresentado resultados promissores tanto para a cimentação como para a reparação de coroas em zircónia. A sua eficácia foi também comprovada na resistência da adesão ao longo do tempo, pois demonstraram serem de uma forma geral resistentes à hidrólise. Os monómeros MDP, apresentam dois grupos funcionais: um grupo de ácido fosfórico, responsável pela ligação à zircónia; e outro grupo de ácido carboxílico (metacrilato) que pode cofotopolimerizar com a resina composta utilizada na reparação. A recente introdução pelos fabricantes de monómeros MDP em adesivos autocondicionantes, universais, para além de reclamarem bons resultados na adesão ao dente, anunciam ainda a possibilidade de se ligarem também à zircónia.

OBJETIVOS

Estudar a resistência da união estabelecida entre uma resina composta e a zircónia, utilizando como promotor de adesão, um primer de zircónia, com diferentes formas de aplicação, e dois novos adesivos universais, todos à base de monómero MDP.

MATERIAIS E MÉTODOS

Sessenta blocos foram preparados a partir de zircónia tetragonal policristalina estabilizada com ítria (Y-TZP) pré-sinterizada (Lava™ Frame Zirconia - 3M ESPE, Seefeld, Germany). Após a realização da sinterização de acordo com as instruções do fabricante, e da esperada contração na ordem dos 20%, foram obtidos espécimes com dimensões padronizadas de 9,6mm x 9,6mm x 4,8mm. Uma das superfícies de cada espécime foi condicionada mecanicamente com jato de partículas de Al_2O_3 com uma granulometria de 50 µm, durante 15 segundos, a 10 mm de distância e uma pressão de 2,5 Bar. Os 60 espécimes foram divididos aleatoriamente em 6 grupos experimentais (n=10) de acordo com a forma de aplicação do primer ou do adesivo utilizado: 1) Z-Prime™ Plus (Bisco, Schaumburg, USA) – 1 camada sem fotopolimerização (ZPP-1); 2) Z-Prime™ Plus – 1 camada fotopolimerizada (ZPP-1-FP); 3) Z-Prime™ Plus – 2 camadas sem fotopolimerização (ZPP-2); 4) Z-Prime™ Plus – 2 camadas fotopolimerizadas (ZPP-2-FP); 5) All-Bond Universal™ (Bisco, Schaumburg, USA) (ABU); 6) Scotch-Bond Universal™ (3M ESPE, Seefeld, Germany) (SBU). Os adesivos universais foram aplicados numa só camada e fotopolimerizados, de acordo com as instruções dos respetivos fabricantes.

Sobre o primer/adesivo foram aplicados e fotopolimerizados dois incrementos de 1,5 mm de resina compostas (Filtek™ Z250, 3M ESPE, Seefeld, Germany).

Após um período de 48 h em que os espécimes permaneceram numa estufa a 37ºC, em humidade relativa de 100%, foram realizados os ensaios de resistência adesiva a tensões de corte, numa máquina de testes universais (Instrom Ltd., Bucks, HP 12 3SY, England), com uma célula de carga de 1kN e uma velocidade de deslocação de 1 mm/minuto.

As superfícies da fratura foram observadas com um estereomicroscópio (Meiji Techno EMZ-8TR - Meiji Techno Co., Saitama, Japan), com uma ampliação de 20x, para determinar o tipo de falha. As falhas de união foram classificadas como: adesivas, quando a falha ocorreu na interface de adesão entre a zircónia e a resina composta; ou mista, quando existiu a combinação de adesiva e coesiva do compósito.

Os resultados obtidos no ensaio de resistência adesiva foram analisados estatisticamente com ANOVA, seguida de testes *post-hoc* segundo o método de *Student-Newman-Keuls* ($p<0,05$). As falhas registadas foram analisadas com testes não paramétricos segundo *Kruskal-Wallis*, seguido de testes *post-hoc* às classificações segundo o método de LSD ($p<0,05$).

RESULTADOS

Os valores médios de resistência adesiva variaram entre os 19,3 MPa (ZPP-1) e os 34,9 MPa (SBU). Os valores de resistência adesiva obtidos nos grupos SBU, ABU e ZPP-2-FP foram estatisticamente mais elevados que os observados nos restantes três grupos experimentais ($p<0,05$). Não foram observadas diferenças estatisticamente significativas ($p\geq0,05$) entre o SBU, ABU e o ZPP-2-FP. Também não se observaram diferenças estatisticamente significativas ($p\geq0,05$) nas diferentes comparações entre as restantes formas de aplicação do Z-Prime™ Plus (ZPP-1, ZPP-1-LC e ZPP-2).

Os três grupos com valores de resistência adesiva mais baixos, apresentaram 100% de falhas adesivas, enquanto que nos grupos com valores de resistência adesiva estatisticamente mais elevados foram registadas falhas adesivas e mistas. Esta diferença foi estatisticamente significativa ($p<0,05$).

DISCUSSÃO

A reparação intraoral com compósito de restaurações de zircónia fraturadas constitui um enorme desafio para o dentista.

Neste estudo investigou-se a eficácia de dois novos adesivos universais e vários protocolos de aplicação do Z-Prime™ Plus (1 ou 2 camadas; com ou sem fotopolimerização do primer antes da aplicação do compósito reparador).

Como já foi citado, se o clínico seguir as instruções do fabricante, poderá aplicar uma ou duas camadas de Z-Prime™ Plus e optar ou não pela sua fotopolimerização. No entanto, no presente estudo foram encontradas diferenças nos valores de resistência adesiva obtidos com os diferentes protocolos de aplicação.

Apesar de existirem algumas diferenças na forma de preparação dos espécimes, diversos autores obtiveram um valor médio de resistência adesiva ao corte semelhante ao obtido com ZPP-2-LC no presente estudo. A aplicação de duas camadas de primer antes da sua polimerização parece permitir uma melhor difusão e infiltração no substrato.

Teoricamente, quando se opta por não fotopolimerizar o Z-Prime™ Plus de forma independente, poderia esperar-se que existisse a copolimerização do primer com o primeiro incremento de resina reparadora. No entanto, se tal tivesse ocorrido, não deveriam ter existido as diferenças observadas entre ZPP-2 e ZPP-2-LC.

Outro objetivo do estudo foi determinar a eficácia de dois novos adesivos universais autocondicionantes (ABU e SBU) na promoção da adesão à zircónia. A inexistência de diferenças estatisticamente significativas entre os valores de resistência adesiva ao corte obtidos nos grupos ZPP-2-LC, ABU e SBU, parece indicar que estes novos adesivos universais com monómeros MDP são eficazes na promoção da adesão de resina composta à zircónia.

Os resultados da análise estatística do tipo de falha estão de acordo com os resultados observados na análise da resistência adesiva ao corte.

Uma das limitações deste estudo foi o facto de não terem sido estudadas as alterações prévias que podem surgir na superfície da zircónia quando esta é exposta ao meio oral. Estudos anteriores provaram que o envelhecimento artificial da zircónia antes da reparação ou cimentação provoca uma diminuição da resistência adesiva em cerca de 40%. Por outro lado, reconhecendo a susceptibilidade da adesão a factores mecânicos, químicos e térmicos, outra limitação deste trabalho pode ser o facto de os espécimes reparados não terem sido sujeitos a termociclagem ou cargas cíclicas. Será necessário desenvolver estudos complementares para avaliar a durabilidade das ligações químicas entre zircónia e os primers/adesivos em diferentes condições.

CONCLUSÃO

Os dois novos adesivos universais mostraram-se eficazes na promoção da adesão entre o compósito e a zircónia. O Z-Prime™ Plus deverá ser aplicado em duas camadas, seguido de fotopolimerização, de forma a promover valores de resistência adesiva semelhantes aos novos adesivos universais.

ABSTRACT

INTRODUCTION

The protocol traditionally used for bonding composite resin to feldspathic ceramic is not effective to promote adhesion to Zirconia. In the last years, different methods have been studied to achieve that purpose.

The development of new primers and adhesives containing phosphate monomers (MDP), have shown promising results.

OBJECTIVES

To investigate the influence of a zirconia primer, with different application protocols, and two new universal adhesives, all containing MDP, on the shear bond strength between resin composite and zirconia.

MATERIALS AND METHODS

60 zirconia Y-TZP blocks (Lava™ Frame Zirconia - 3M ESPE, Seefeld, Germany) with standardized dimensions (9.6mm x 9.6mm x 4.8mm) were mechanically conditioned with 50 µm Al_2O_3 airborne particle abrasion and randomly divided into six experimental groups (n=10) according to the application protocol of the primer or the adhesives used: 1) Z-Prime™ Plus (ZPP) (Bisco, Schaumburg, USA) – 1 coat without light-curing (ZPP-1); 2) ZPP – 1 coat light-cured (ZPP-1-LC); 3) ZPP – 2 coats without light-curing (ZPP-2); 4) ZPP – 2 coats light-cured (ZPP-2-LC); 5) All-Bond Universal™ (Bisco, Schaumburg, USA) (ABU); 6) Scotch-Bond Universal™ (3M ESPE, Seefeld, Germany) (SBU).

Universal adhesives were coated to the zirconia specimen surface according to the manufacturer´s recommendations. Two 1.5 mm increments of composite (Filtek™ Z250) were inserted and light-cured, over the primer/adhesive. After 48 h stored in distilled water at 37 °C, shear bond strength test (1mm/min) was performed.

Failure mode determination was performed with a stereomicroscope (20x) Meiji Techno EMZ-8TR (Meiji Techno Co., Saitama, Japan), and classified as adhesive or mixed failure.

SBS data were analyzed using 1-way ANOVA, followed by Student-Newman-Keuls post-hoc tests ($p<0.05$). Kruskal-Wallis, followed by LSD method post-hoc tests was used to analyze failure data.

RESULTS

The mean SBS values ranged from 19,3 MPa (ZPP-1 - 1 coat no light-cured) to 34,9 MPa (SBU). SBU, ABU and ZPP-2-LC groups achieved statistically higher SBS mean values than the other three experimental groups ($p<0.05$). No statisticallly significant differences ($p\geq0.05$) were found between SBU, ABU and ZPP-2-LC or comparing ZPP-1, ZPP-1-LC and ZPP-2 application protocol.

The three groups with the lowest SBS values registered 100% of adhesive failures. Groups with highest SBS values registered adhesives and mixed failures.

CONCLUSION

The two new universal adhesives were effective in promoting adhesion between composite and zirconia. Z-Prime™ Plus should be applied in two coats, followed by light-curing, to promote SBS similar to the new universal adhesives.

Palavras-chave

Primer para zircónia; Reparação da zircónia; Adesivo universal; Resistência adesiva a tensões de corte; Monómero de fosfato

Keywords

Zirconia primer; Zirconia repair; Universal adhesive; SBS; Phosphate monomer.

INTRODUCTION

In the last decade, the increase application of zirconia in dentistry is related to the high demand for metal-free and esthetic restorations, excellent biocompatibility and impaired mechanical properties (Josset *et al.* 1999; Piconi and Maccauro 1999; Scarano *et al.* 2003; Scarano *et al.* 2004)

Zirconia is a polymorphic material that can switch between 3 phases: monoclinic, tetragonal and cubic. Zirconia in monoclinic (m) form is stable below 1170 ºC. Between 1170°C and 2370°C, the material transforms to tetragonal phase (t), and then to a cubic (c) structure above 2370°C, to its melting point at 2716°C. Transformation phases are martensitic, involving change of crystal structure (Chevalier *et al.* 2007). This transformation during cooling is associated with volume expansion of about 2,5%, from cubic to tetragonal phase, and of 3-5%, from tetragonal to monoclinic phase. Consequently, high stress is induced in pure zirconia (Kelly and Denry 2008). Oxides such as Y_2O_3 or MgO are added to achieve stabilized zirconia (Y-TZP) in the t phase at room temperature (Piconi and Maccauro 1999).

Due to its mechanical properties, zirconia has indication to be used in fixed dental prosthesis (FDP), mainly in the molar region, with high functional demands (Piconi and Maccauro 1999; Luthy *et al.* 2005; Sailer *et al.* 2006; Örtorp *et al.* 2009).

However, this dense sintered ceramic is also more opaque. To overcome this esthetic problem, it is used as an infrastructure with a layered veneering esthetic ceramic (Della Bona and Kelly 2008; Saito *et al.* 2010).

Many studies designed to evaluate the clinical performance of zirconia restorations have shown a success rate that ranged between 73.9% and 100%, after 2 to 5 years in function (Sailer *et al.* 2006; Denry and Kelly 2008; Sailer *et al.* 2009; Triwatana *et al.* 2012). However, a high incidence of chipping that could affect up to 25% of total FPDs was observed (Sailer *et al.* 2007; Triwatana *et al.* 2012).

The interface between core and veneer is one of the weakest points of Y-TZP (Della Bona and Kelly 2008; Triwatana *et al.* 2012).

These fractures can be intra-orally repaired and different repair techniques, involving mechanical and chemical treatments, are available. Increasing zirconia roughness not only implies a higher surface area for micromechanical retention but can also increase the surface energy and so, the wettability and the adhesion (Della-Bona 2005; Amaral *et al.* 2006; Thompson *et al.* 2011).

Traditionally, feldspathic ceramics are conditioned with hydrofluoric acid and the chemical adhesion to resin composite is promoted by silanization. However, due to zirconia glass-free structure, hydrofluoric etching is not effective and the lack of silica turns impossible the chemical adhesion to Bis-GMA based resin composite (Kern and Wegner 1998; Özcan and Vallittu 2003).

Other methods such as grinding, aluminum oxide airborne particle abrasion, selective infiltration etching (SIE), laser etching, and surface fluorination have been proposed for surface conditioning (Kosmac *et al.* 1999; Özcan and Vallittu 2003; Curtis *et al.* 2006; Papanagiotou *et al.* 2006; Aboushelib *et al.* 2008; Karakoca and Yılmaz 2009; Cavalcanti *et al.* 2009; Akin *et al.* 2011; Usumez *et al.* 2012; Subaşı and İnan 2012; Piascik *et al.* 2012). Tribochemical silica coating has been also proposed as a method to embedded the zirconia surface with silica that allows the silanization and the chemical bond between zirconia and resin based luting cements and adhesives (Piconi and Maccauro 1999; Özcan and Vallittu 2003; Amaral *et al.* 2006; Senyilmaz *et al.* 2007).

Since Kern et al, 1998, proved adhesion efficacy and aging stability of cements containing MDP monomers to sandblasted zirconia, many studies have been published and results showed high bond strength, even after thermocycling, indicating that MDP monomer promotes a water-resistant chemical bond to the metal oxides of Y-PSZ (Kern and Wegner 1998; Luthy *et al.* 2006; Aboushelib *et al.* 2009; Kim *et al.* 2011; D'Amario *et al.* 2010).

MDP monomer contains two functional groups. It has a phosphoric acid group that is responsible for bonding to zirconia through hydroxyl groups. The other is a carboxylic acid group (methacrylate) that can be light-cured and will bond to composite resin (Table 1). Bond strength with MDP monomer is stable over time because it is resistant to hydrolysis (Ural *et al.* 2011; Piascik *et al.* 2012).

There are many primers with MDP monomer, nevertheless Z-Prime™ Plus seems to be the most effective in the available studies (Magne *et al.* 2010; Lee *et al.* 2011; Perdigão *et al.* 2012; Piascik *et al.* 2012; Chen *et al.* 2012; Barragan *et al.* 2012). However, manufacturer instructions about the clinical protocol of this commercial primer are not very clear (BISCO 2010). Manufacturer claims that it can be applied either in one or two coats, and it is not very precise about light curing.

Although this ambiguity may explain the different protocol used in the different studies, with different results, there is not any study that compare different protocol for ZPP application.

Recently, new universal self-etch adhesives, whose manufacturer claims that also bond to zirconia, incorporate this molecule in its composition. However, there are no independent studies to corroborate this statement.

The aim of the present investigation was to analyze the influence of a zirconia primer, with different application protocols, and two new universal adhesives, all containing MDP monomer, on the shear bond strength between resin composite and zirconia.

	Polymeryzation Group	Spacer Group	Acid Group
MDP	CH2=C(CH3)COO-	(CH2)10	-O-P(=O)(OH)2

Table 1 - Molecular structure of MDP monomer.

Methods and Materials

Specimens Fabrication

Sixty Yttria-stabilized tetragonal zirconia polycristals (Y-TZP) blocks were prepared from green-stage zirconia (Table 2). After finishing and polishing under running water with decreasing grain sandpaper (220, 400 and 600 grit), specimens were cleaned with distilled water to remove any remains and dried with air blast.

Specimens were then sintered according to the manufacturer instructions. After approximately 20% shrinkage, the final dimensions of zirconia blocks were 9.6mm x 9.6mm x 4.8mm.

Material	Trade Name	Abbrev	Manufacturer	Composition
Zirconia Ceramic	*Lava™ Frame Zirconia*	ZR	3M ESPE, Seefeld, Germany	Yttrium partially stabilized with tetragonal polycrystalline structure (3Y TZP)
Zirconia Primer	*Z-Prime Plus*	ZPP	Bisco, Schaumburg, USA	Organophosphate monomer (MDP) Carboxylic acid monomer (BPDM) HEMA Ethanol
Universal Adhesive	*All-Bond Universal*	ABU	Bisco, Schaumburg, USA	Organophosphate monomer (MDP) BisGMA HEMA Ethanol Water Initiators
Universal Adhesive	*Scotch-bond Universal*	SBU	3M ESPE, Seefeld, Germany	Organophosphate monomer (MDP) Dimethacrylate resins (BisGMA, etc) HEMA Vitrebond Copolymer Filler Ethanol Water Initiators Silane
Composite	*Filtek Z250*	Z250	3M ESPE, Seefeld, Germany	BisEMA BisGMA TEGDMA UDMA Zirconium Silica Pigments

Table 2 - Materials used for specimen preparation.

SURFACE TREATMENT

One surface of each block was mechanically conditioned with 50 µm Al_2O_3 airborne particle abrasion, performed perpendicularly to the zirconia surface with 2.5 bar pressure for 15 seconds at 10 mm distance. After air abrasion, zirconia blocks were placed in an ultrasonic bath with ethanol for 5 min, cleaned with water-spray and dried with oil-free air blast.

BONDING PROCEDURE

Pretreated zirconia blocks were randomly divided into six experimental groups (n=10) according to several adhesive and primer application protocol used (Figure 1 and Table 3).

Figure 1 - Primer and Adhesives used in the study (Z-Prime™ Plus, All-Bond Universal™ and Scotch-Bond Universal™).

To customize and define the area for primer/adhesive application, transparent stickers with round-shaped orifices (3 mm in diameter) were positioned on the airblasted surface of the ceramic block.

Each adhesive was applied according to the manufacturer´s recommendations, with a new and clean disposable brush. Each primer/adhesive coat applied was scrubed in for 20 sec and a gentle stream of air was directed over the liquid for about 5 sec to allow the complete evaporation of the solvent (Figure 2).

		Layers	LightCured
Group 1	ZPP	1	✗
Group 2	ZPP	1	✓
Group 3	ZPP	2	✗
Group 4	ZPP	2	✓
Group 5	ABU	1	✓
Group 6	SBU	1	✓

Table 3 – Experimental groups according to adhesive and primer application protocol (n=10) (ZPP - Z-Prime™ Plus; ABU - All-Bond Universal™; SBU - Scotch-Bond Universal™).

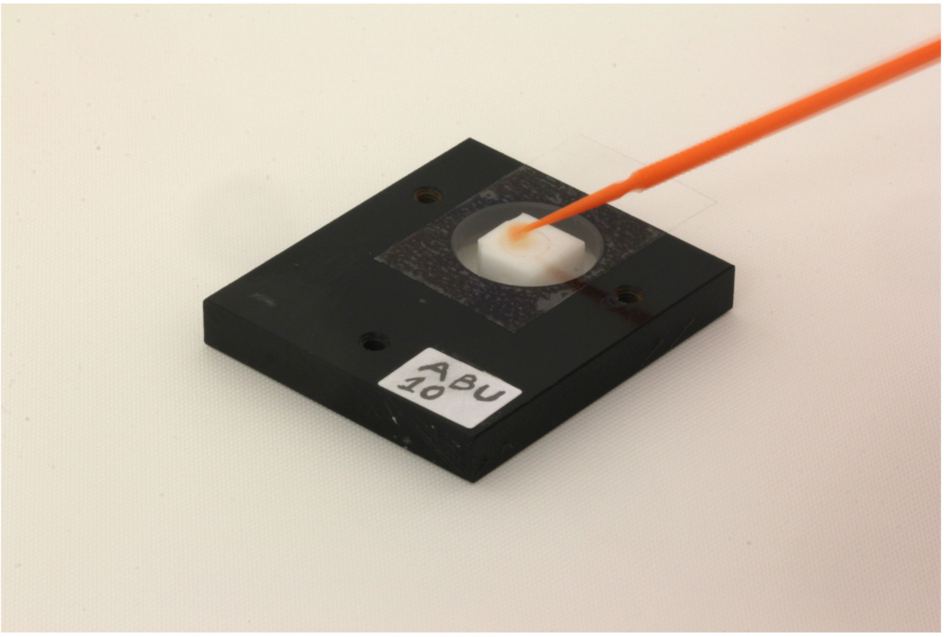

Figure 2 - Adhesive application.

As shown in Table 3, in the groups 1 and 2, one coat of Z-Prime™ Plus (ZPP) was applied; in the groups 3 and 4, two coats of ZPP were applied; in the groups 5 and 6, one coat of All-Bond Universal™ (ABU) and Scotchbond Universal™, respectively, was applied.

In groups 2, 4, 5 and 6 the primer or adhesive used was light cured (LC) for10 seconds with a Ortholux LED Curing Light (3M Unitek, 82171 Puchheim, Germany, nº de série: 939830000776).

After bonding, two 1.5 mm increments of composite Filtek™ Z250 Universal Dental Restorative (3M ESPE, Seefeld, Germany) were applied and light-cured for 20 seconds each (Figure 3, 4 e 5).

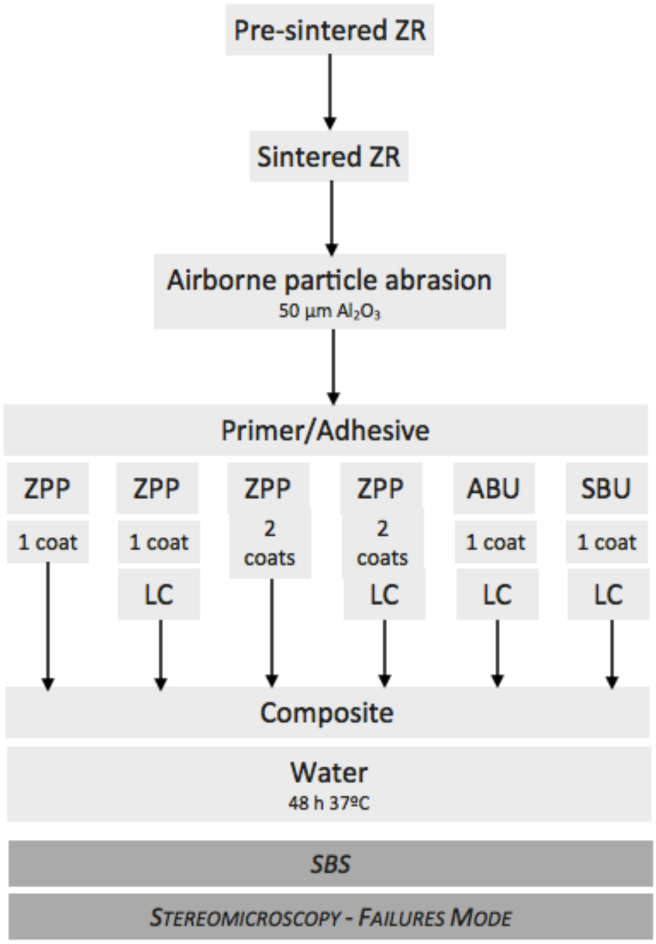

Figure 3 – Experimental design protocol (ZPP - Z-Prime™ Plus; ABU - All-Bond Universal™; SBU - Scotch-Bond Universal™; LC - Light-cured; SBS - Shear Bond Strength)

STORAGE CONDITIONS

Specimens were stored in distilled water at 37°C for 48 h, before testing the resin composite shear bond strength to zirconia (Figura 6).

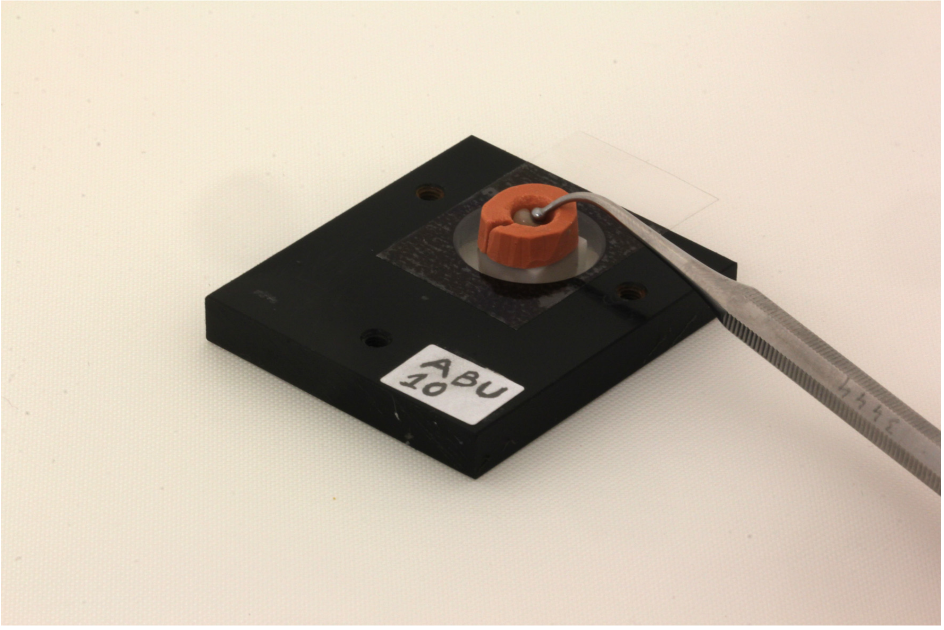

Figure 4 - Silicon mold placed for first Z250 composite layer.

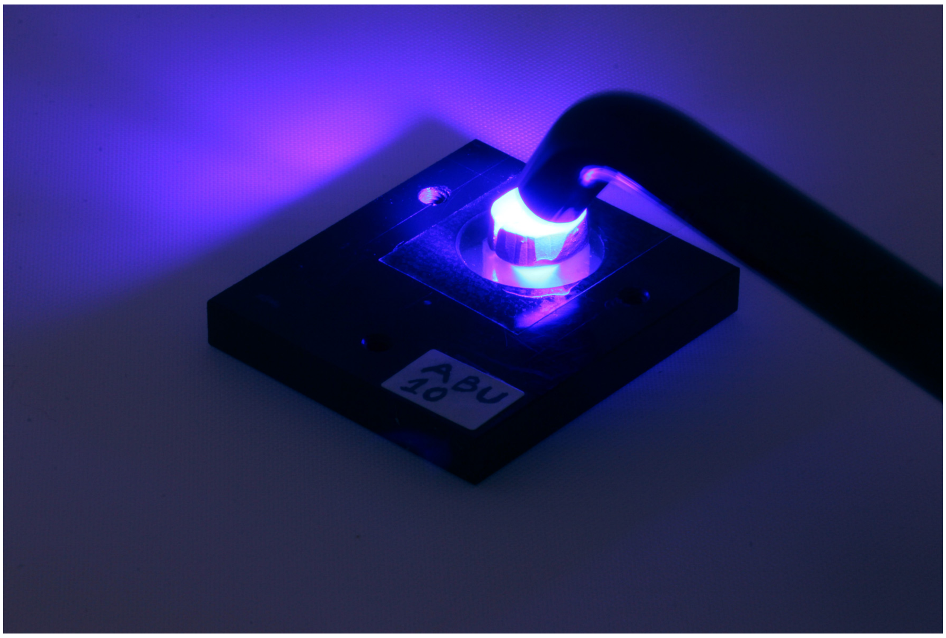

Figure 5 - Light-curing of the second 1,5 mm Z250 composite layer.

SHEAR BOND STRENGTH TEST

After a 48 h period in distilled water at 37ºC, specimens were included in a single plane lap shear bond strength device and tested in an universal testing machine Instron model 4502 (Instrom Ltd., Bucks, HP 12 3SY, England) (ISO-11405, 2003.). Shear bond strength (SBS) was determined with a 1kN load cell and a crosshead speed of 1 mm/min. (Figura 7).

Figura 6 - Specimens were stored in distilled water for 48 h at 37ºC.

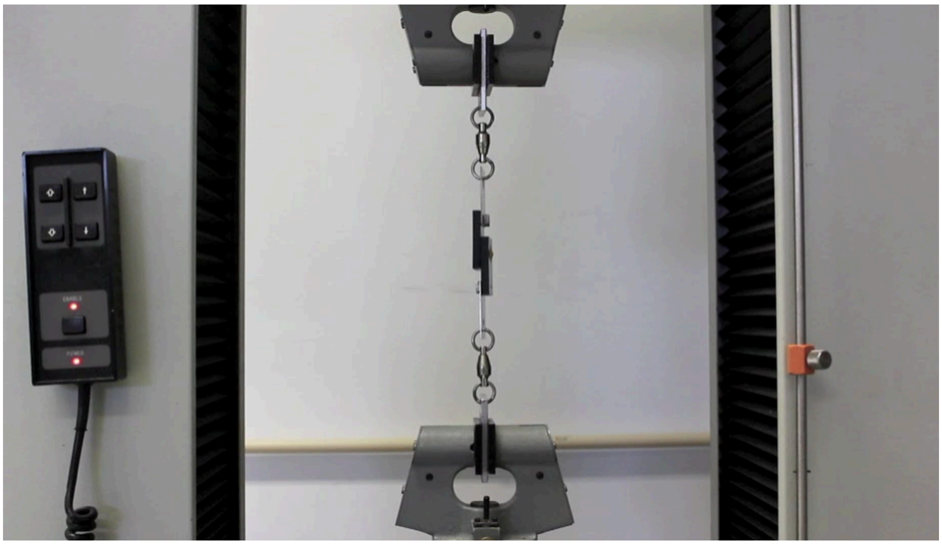

Figura 7 - SBS test in an universal testing machine Instron model 4502
(Instrom Ltd., Bucks, HP 12 3SY, England)

ESTEREOMICROSCOPY (EM) – FAILURE MODE

Failure mode analysis was performed using a stereomicroscope Meiji Techno EMZ-8TR serial nº 411479 (Meiji Techno Co., Saitama, Japan) with a 20x magnification (Figura 8). The failure was classified as: adhesive, if the failure occurred at the adhesive interface; or mixed, when a combination of adhesive and cohesive in composite was observed.

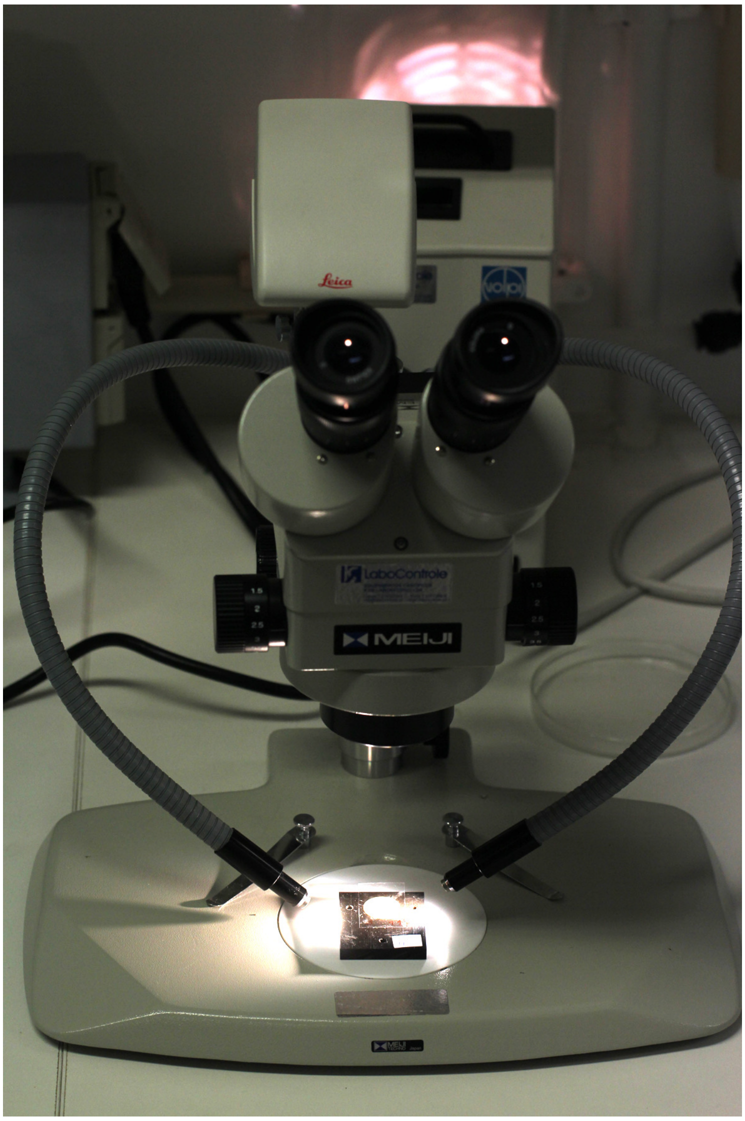

Figura 8 - Stereomicroscope Meiji Techno EMZ-8TR, and specimen observation (Meiji Techno Co., Saitama, Japan).

STATISTIC ANALYSIS

Data was statistically analyzed using SPSS Statistics 20 (SPSS Inc., Chicago, IL, USA). SBS data was submitted to one-way ANOVA, followed by Student-Newman-Keuls (SNK) post-hoc tests, ($p<0.05$). Kruskal-Wallis and Fisher's Least Significant Difference (LSD) post-hoc tests were used to analyze failure mode data ($p<0.05$).

RESULTS

The results of the SBS test are summarized in Table 4, where the mean, standard deviation, minimum and maximum values of the six groups are registered. The mean SBS values ranged from 19.3 MPa, in Z-Prime™ Plus – 1 coat no light-cured group, to 34.9 MPa, in Scotchbond Universal™ Adhesive specimens.

		SBS (MPa)	SD (MPa)	Min (MPa)	Max (MPa)
Group 1	ZPP 1	19,28	8,14	11,29	37,25
Group 2	ZPP 1 LC	21,38	6,70	14,67	34,96
Group 3	ZPP 2	21,54	7,55	13,65	39,09
Group 4	ZPP 2 LC	31,68	8,45	14,83	42,61
Group 5	ABU	30,66	7,81	20,91	44,14
Group 6	SBU	34,93	5,41	25,22	43,94

Table 4 - SBS data according to the experimental group

(mean, standard deviation, minimum and maximum values).

ANOVA and SNK post-hoc tests showed that SBU, ABU and ZPP-2-LC SBS values were statistically higher than those observed in the other 3 experimental groups ($p<0,05$) (Table 5). No statistical differences were observed between SBU, ABU and ZPP-2-LC, or between ZPP-1, ZPP-1-LC and ZPP-2 ($p\geq0.05$)(Figure 8).

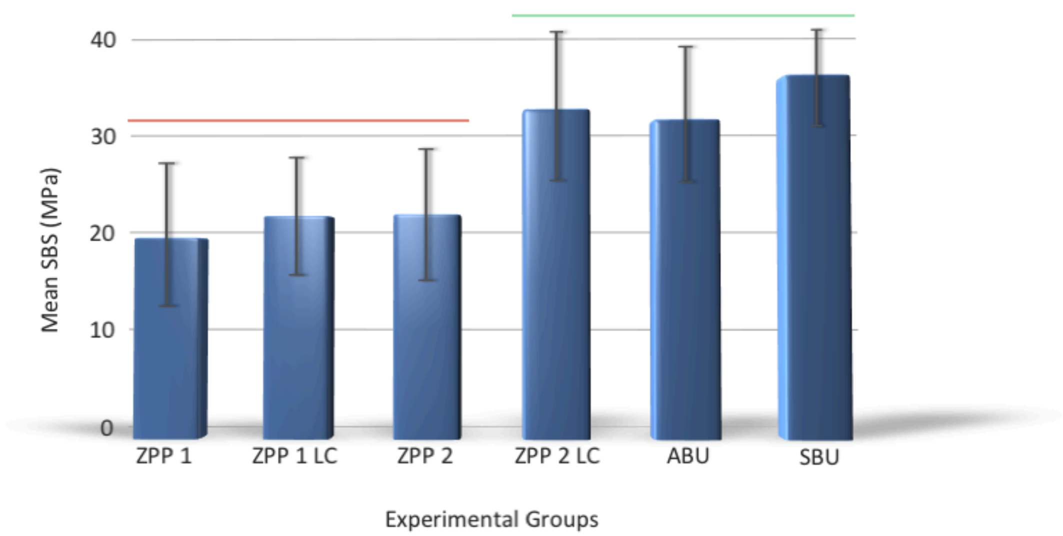

Figure 8 - Mean SBS values for the six groups. ($p<0,05$)

(There are no statistically significant differences ($p<0,05$) between bars under same line).

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2181,524	5	436,305	7,933	0,001
Within Groups	2969,861	54	54,997		
Total	5151,385	59			

Table 5 - One-way ANOVA for experimental groups.

After Estereomicroscopy analyse of zirconia and resin surfaces the failure mode were qualified and registered in Figure 9.

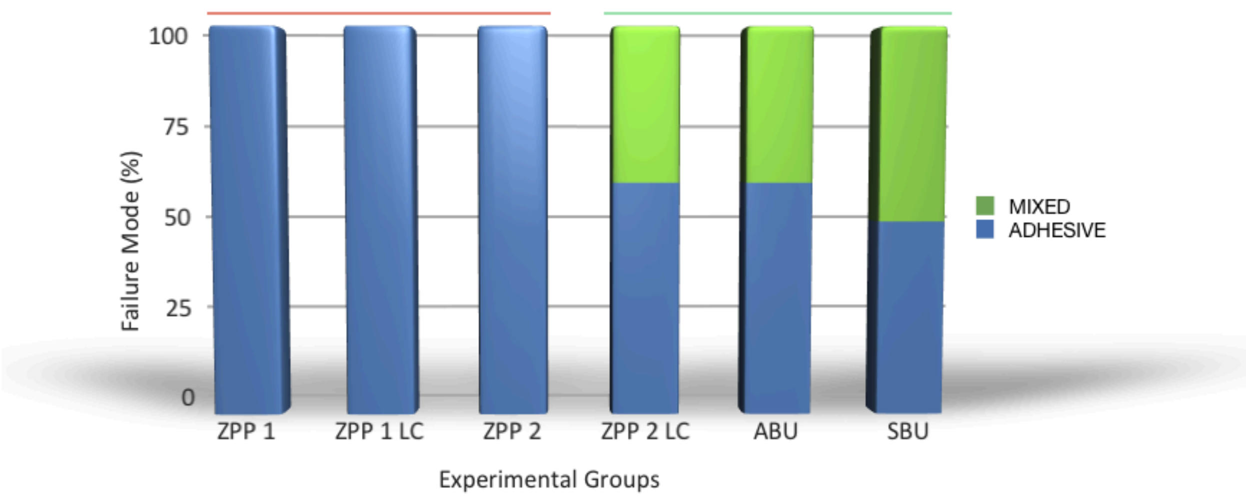

Figure 9 - Failure Mode distribution for the six experimental groups (There are no statistically significant differences ($p<0,05$) between bars under same line).

The three groups with the lowest SBS values registered 100% of adhesive failures. Groups with highest SBS values registered adhesives and mixed failures. Kruskal-Wallis test revealed a statistically significant ($p=0.005$) influence of the bonding protocol on the failure mode. Again, no statistical differences were observed between SBU, ABU and ZPP-2-LC, or between ZPP-1, ZPP-1-LC and ZPP-2 ($p\geq0.05$).

DISCUSSION

Intraoral repair of fractured veneered zirconia restorations with composite resin is an important challenge for a dentist.

In the present study, the effectiveness of two new universal adhesives and several Z-Prime™ Plus applications protocols (1 or 2 primer coats; with or without primer light curing before resin composite application) to promote adhesion to zirconia, was investigated.

Despite, some authors claim that SBS test is an inappropriate test to assess the quality of resin bonded to ceramic, since cohesive failure occurs in the ceramic base and not at the adhesive interface (Della Bona and van Noort 1995; Garcia and D'Alpino 2002; Behr *et al.* 2011), this kind of test was used in the present investigation to evaluate adhesion between Y-TZP and resin. Y-TZP is a strong and fracture-resistant (Piconi and Maccauro 1999) ceramic that can withstand cohesive forces during shear tests, allowing SBS test to be used with this material, without interfering or changing bonding strength in the adhesive interface (De Munck *et al.* 2005). In the present study, no cohesive failures were found in the ceramic. Only adhesive and mixed failures were observed, clearly demonstrating that only adhesive performance was measured, without misinterpretation (Khoroushi and Motamedi 2007; Valandro *et al.* 2008).

In previous studies, mechanical conditioning of zirconia surface has proved to be an important factor to create microretentions and improve adhesion (Kern and Wegner 1998; Amaral *et al.* 2006). Particle sizes between 50 and 110 µm, at pressures from 1.5 to 2.5 bars, have shown effective to that purpose (Lee *et al.* 2011; Hallmann *et al.* 2012). So, in the present study, zirconia surface was conditioned with 50 µm Al_2O_3 airborne particle abrasion, at 2.5 bars.

However, microretentions by itself have not proved sufficient to achieve clinically acceptable bond, therefore different adhesive systems have been launched in the market in order to establish chemical union to zirconia (Cavalcanti *et al.* 2009; Thompson *et al.* 2011; Chen and Suh 2012).

As previously stated, according to the manufacturer instructions, clinician may use one or two coats of Z-Prime™ Plus and may choose light curing or not. However, in the present study differences were found by changing the application protocol.

Even though there are some differences in specimen’s preparation among studies, the mean SBS value obtained with ZPP 2LC, was similar to those described by other authors (Griffin *et al.* 2010; Magne *et al.* 2010). Application of multiple layers of adhesive before curing seems to allow more time for adhesive diffusion and infiltration in the substrate (Ma *et al.* 2012; Lafuente 2012).

Theoretically, it might be thought that Z-Prime™ Plus copolymerized with the first resin increment. However, if that occurred, statistically differences between ZPP-2 and ZPP-2-LC groups should not happen. More studies should be done to try understand why Z-Prime™ Plus did not copolymerize with the first 1.5 mm composite increment, since Z250™ manufacturer recommends the application of 2.5 mm thick composite increments.

Another objective of this study was to determine the effectiveness of two new self-etch universal adhesives (ABU and SBU) in promoting adhesion to zirconia.

No differences were found between groups ZPP-2-LC, ABU and SBU SBS values, indicating that the application of MDP-containing universal adhesives, are effective to promote adhesion to zirconia.

In vitro studies, few that exist with these new universal self-adhesives already have shown good adhesive stability to teeth, specially to dentin (Yoshida *et al.* 2012; Perdigão *et al.* 2012; Thalacker *et al.* 2012; Salz and Bock 2012) This can be a great improvement, particularly during adhesive cementation of zirconia crowns. As so, clinicians may use the same product, MDP-containing self-adhesive, to prepare the tooth and to prepare zirconia surface.

Results of the statistical analysis on the failure mode data were in accordance with the results observed in SBS analysis. Failure mode was only adhesive within groups with lowest SBS value (ZPP-1, ZPP-1-LC, ZPP-2).

One of the limitations of this research was the fact that some changes that may occur on the surface of zirconia when it is exposed to the oral environment have not been studied. It has been proved that artificial aging of zirconia followed by surface conditioning with Z-Prime™ Plus or Cojet™ and cementation with a MDP-containing resin cement, registered a decrease of strength of adhesion in about 40% (Perdigão *et al.* 2012)

On the other hand, knowing how susceptible adhesion is to mechanical, chemical and thermal factors, the fact that thermocycles and mechanical load were not performed could be another limitation of this work. (Thompson *et al.* 2011; Schmitt *et al.* 2011; Lafuente 2012)

Further research is needed to evaluate the durability of chemical bond between zirconia and resin composite under different circumstances.

CONCLUSION

Bond strength between zirconia ceramic and resin is affected by the zirconia primer application protocol and new universal MDP containing adhesives can be effectively used to promote bond between resin composite and zirconia.

Z-Prime™ Plus must be placed in two coats, followed by light cure, in order to achieve higher resin composite bond strength to zirconia.

References

1. Aboushelib M, Ghoniem M, Mirmohammadi H, Salameh Z (2009). General principles for achieving adequate bond to allceramic Restorations. *J Dent O Hyg* 1(3)**:** 36-41.
2. Aboushelib M, Matinlinna J, Salameh Z, Ounsi H (2008). Innovations in bonding to zirconia-based materials: Part I. *Dent Mater* 24(9)**:** 1268-1272.
3. Akin H, Tugut F, Emine Akin G, Guney U, Mutaf B (2011). Effect of Er:YAG laser application on the shear bond strength and microleakage between resin cements and Y-TZP ceramics. *Lasers Med Sci* 27(2)**:** 333-338.
4. Amaral R, Özcan M, Bottino MA, Valandro LF (2006). Microtensile bond strength of a resin cement to glass infiltrated zirconia-reinforced ceramic: The effect of surface conditioning. *Dent Mater* 22(3)**:** 283-290.
5. Barragan G, Frois J, Chasqueira A, Arantes-Oliveira S, Portugal J (2012). Influence of Chemical and Mechanical Surface Conditioning on Zirconia Repair. *J Dent Res* 91(Special Issue c)**:** Abstract 148.
6. Behr M, Proff P, Kolbeck C, Langrieger S, Kunze J, Handel G, Rosentritt M (2011). The bond strength of the resin-to-zirconia interface using different bonding concepts. *J Mechan Behav Biomed Mater* 4(1)**:** 2-8.
7. BISCO. 2010. *Z-Prime Plus - Instructions for use* [Online]. Available: http://www.bisco.com/instructions/IN-178R3_English.pdf.
8. Cavalcanti AN, Foxton RM, Watson TF, Oliveira MT, Giannini M, Marchi GM (2009). Bond Strength of Resin Cements to a Zirconia Ceramic with Different Surface Treatments. *Oper Dent* 34(3)**:** 280-287.
9. Chen L, Suh BI (2012). Bonding of Resin Materials to All-Ceramics: A Review. *Curr Res Dent* 3(1)**:** 7-17.
10. Chen L, Suh BI, Brown DT, Chen X (2012). Bonding of primed zirconia ceramics: Evidence of chemical bonding and improved bond strengths. *American Journal of Dentistry* 25(2)**:** 103-108.
11. Chevalier J, Gremillard L, Deville S (2007). Low-Temperature Degradation of Zirconia and Implications for Biomedical Implants. *Ann Rev Mater Res* 37(1)**:** 1-32.
12. Curtis AR, Wright AJ, Fleming GJP (2006). The influence of surface modification techniques on the performance of a Y-TZP dental ceramic. *J*

Dent 34(3): 195-206.

13. D'Amario M, Campidoglio M, Morresi A, Luciani L, Marchetti E, Baldi M (2010). Effect of thermocycling on the bond strength between dual-cured resin cements and zirconium oxide ceramics. *J Oral Sci* 52(3): 425-430.
14. De Munck J, Van Landuyt K, Peumans M, Poitevin A, Lambrechts P, Braem M, Van Meerbeek B (2005). A Critical Review of the Durability of Adhesion to Tooth Tissue: Methods and Results. *J Dent Res* 84(2): 118-132.
15. Della Bona A, Kelly J (2008). The clinical success of all-ceramic restorations. *J Am Dent Assoc* 139 Suppl8S-13S.
16. Della Bona A, van Noort R (1995). Shear vs. Tensile Bond Strength of Resin Composite Bonded to Ceramic. *J Dent Res* 74(9): 1591-1596.
17. Della-Bona A (2005). Characterizing ceramics and the interfacial adhesion to resin: II- the relationship of surface treatment, bond strength, interfacial toughness and fractography. *J Appl Oral Sci* 13(2): 101-9.
18. Denry I, Kelly J (2008). State of the art of zirconia for dental applications. *Dent Mater* 24(3): 299-307.
19. Garcia F, D'Alpino P (2002). Mechanical Tests for Laboratory evaluation of resin7dentin bonding. *Rev Fac Odont Bauru* 10(3): 118-127.
20. Griffin J, Suh BI, Chen L (2010). Surface Treatments for Zirconia Bonding: A Clinical Perspective. *J Can Dent Rest et Prost* Winter: 23-29.
21. Hallmann L, Ulmer P, Reusser E, Hämmerle CHF (2012). Effect of blasting pressure, abrasive particle size and grade on phase transformation and morphological change of dental zirconia surface. *Surf Coat Techn* 206(19-20): 4293-4302.
22. Josset Y, OumÕHamed Z, Zarrinpour A, Lorenzato M, Adnet J, Laurent-Maquin D (1999). In vitro reactions of human osteoblasts in culture with zirconia and alumina ceramics. *J Biomed Mater Res* 47:481-493.
23. Karakoca S, Yılmaz H (2009). Influence of surface treatments on surface roughness, phase transformation, and biaxial flexural strength of Y-TZP ceramics. *J Biomed Mat Res* Part B: Applied Biomaterials 91B(2): 930-937.
24. Kelly J, Denry I (2008). Stabilized zirconia as a structural ceramic: An overview. *Dent Mater* 24(3): 289-298.
25. Kern M, Wegner SM (1998). Bonding to zirconia ceramic: adhesion methods and their durability. *Dent Mater* 14(1): 64-71.

26. Khoroushi M, Motamedi S (2007). Shear Bond Strength of Composite-Resin to Porcelain: Effect of Thermocycling. *J Dent Tehran Univ Med Sci* 4(1)**:** 21-26.
27. Kim M-J, Kim YK, Kim K-H, Kwon T-Y (2011). Shear bond strengths of various luting cements to zirconia ceramic: Surface chemical aspects. *J Dent* 39(11)**:** 795-803.
28. Kosmac T, Oblak C, Jevnikar P, Funduk N, Marion L (1999). The effect of surface grinding and sandblasting on flexural strength and reliability of Y-TZP zirconia ceramic. *Dent Mater* 15426-433.
29. Lafuente D (2012). Effect of Layers of Bonding System on Dentin Bond Strength. *J Dent Res* 91(Spec Iss B)**:** 1304.
30. Lee J-H, Kim H-S, Pae A, Woo Y-H (2011). Influence of sandblasting and primer on shear bond strength of resin cement to zirconia. *J Kor Acad Prosthod* 49(1)**:** 49.
31. Luthy H, Filser F, Loeffel O, Schumacher M, Gauckler L, Hammerle C (2005). Strength and reliability of four-unit all-ceramic posterior bridges. *Dent Mater* 21(10)**:** 930-937.
32. Luthy H, Loeffel O, Hammerle C (2006). Effect of thermocycling on bond strength of luting cements to zirconia ceramic. *Dent Mater* 22(2)**:** 195-200.
33. Ma L, Zhou J-f, Jing Q, Zhao J-z, Wan K (2012). Multiple Coatings can Improve the Bond Durability of One-step Self-etching Adhesive to Primary Dentin. *Chin Med Sci J* 27(2)**:** 106-111.
34. Magne P, Paranhos MPG, Burnett LH (2010). New zirconia primer improves bond strength of resin-based cements. *Dent Mater* 26(4)**:** 345-352.
35. Örtorp A, Kihl ML, Carlsson GE (2009). A 3-year retrospective and clinical follow-up study of zirconia single crowns performed in a private practice. *J Dent* 37(9)**:** 731-736.
36. Özcan M, Vallittu PK (2003). Effect of surface conditioning methods on the bond strength of luting cement to ceramics. *Dent Mater* 19(8)**:** 725-731.
37. Papanagiotou HP, Morgano SM, Giordano RA, Pober R (2006). In vitro evaluation of low-temperature aging effects and finishing procedures on the flexural strength and structural stability of Y-TZP dental ceramics. *J Prosthet Dent* 96(3)**:** 154-164.
38. Perdigão J, Fernandes SD, Pinto AM, Oliveira FA (2012). Effect of Artificial Aging and Surface Treatment on Bond Strengths to Dental Zirconia. *Oper Dent*

37(5): 1-9.

39. Perdigão J, Sezinando A, Monteiro P (2012). Laboratory bonding ability of a multi-purpose dentin adhesive. *Am J Dent* 25(3): 153-158.
40. Piascik JR, Swift EJ, Braswell K, Stoner BR (2012). Surface fluorination of zirconia: Adhesive bond strength comparison to commercial primers. *Dent Mater* 28(6): 604-608.
41. Piconi C, Maccauro G (1999). Zirconia as a ceramic biomaterial. *Biomaterials* 20(1): 1-25.
42. Sailer I, Fehér A, Filser F, Lüthy H, Gauckler L, Schärer P, Hämmerle C (2006). Prospective clinical study of zirconia posterior fixed partial dentures: 3-year follow-up. *Quint Int* 37(9): 685-693.
43. Sailer I, Gottnerb J, Kanelb S, Hammerle C (2009). Randomized controlled clinical trial of zirconia-ceramic and metal-ceramic posterior fixed dental prostheses: a 3-year follow-up. *Int J Prosthodont* 22(6): 553-560.
44. Sailer I, Pjetursson BE, Zwahlen M, Hämmerle CHF (2007). A systematic review of the survival and complication rates of all-ceramic and metal-ceramic reconstructions after an observation period of at least 3 years. Part II: fixed dental prostheses. *Clin Oral Impl Res* 1886-96.
45. Saito A, Komine F, Blatz M, Matsumura H (2010). A comparison of bond strength of layered veneering porcelains to zirconia and metal. *J Prosthet Dent* 104(4): 247-257.
46. Salz U, Bock T (2012). Relationship Between Operator Skill and Shear-Bond-Strengths of One-Component Self-Etch Adhesives. *J Dent Res* 91(Special Issue C): Abstract 105.
47. Scarano A, DiCarlo F, Quaranta M, Piattelli A (2003). Bone response to zirconia ceramic implants: an experimental study in rabbits. *J Oral Implantol* 298-12.
48. Scarano A, Piattelli M, Caputi S, Favero G, Piattelli A (2004). Bacterial adhesion on commercially pure titanium and zirconium oxide disks: an in vivo human study. *J Periodontol* 75292–6.
49. Schmitt J, Wichmann M, Karl M, Göllner M, Lohbauer U, Holst S (2011). Surface Characteristics of Zirconia-Based Posterior Restorations: Clinical and Scanning Electron Microscopic Analysis. *J Can Dent Assoc* 77(b31): 1-6.
50. Senyilmaz DP, Palin WM, Shortall ACC, Burke FJT (2007). The Effect of

Surface Preparation and Luting Agent on Bond Strength to a Zirconium-based Ceramic. *Oper Dent* 32(6)**:** 623-630.

51. Subaşı MG, İnan Ö (2012). Evaluation of the topographical surface changes and roughness of zirconia after different surface treatments. *Lasers Med Sci.*
52. Thalacker C, Loll H, Zerguine R, Van Vliet F (2012). Shear Bond Strength of Self Etch Adhesives to Primary Teeth. *J Ades Dent* 91(Special Issue C)**:** Abstract 108.
53. Thompson JY, Stoner BR, Piascik JR, Smith R (2011). Adhesion/cementation to zirconia and other non-silicate ceramics: Where are we now? *Dent Mater* 27(1)**:** 71-82.
54. Triwatana P, Nagaviroj N, Tulapornchai C (2012). Clinical performance and failures of zirconia-based fixed partial dentures: a review literature. *J Advan Prosthodont* 4(2)**:** 76.
55. Ural Ç, Külünk T, Külünk Ş, Kurt M, Baba S (2011). Determination of Resin Bond Strength to Zirconia Ceramic Surface Using Different Primers. *Acta Odontol Scand* 69(1)**:** 48-53.
56. Usumez A, Hamdemirci N, Koroglu BY, Simsek I, Parlar O, Sari T (2012). Bond strength of resin cement to zirconia ceramic with different surface treatments. *Lasers Med Sci.*
57. Valandro L, Ozcan M, Amaral R, Vanderlei A, Bottino M (2008). Effect of testing methods on the bond strength of resin to zirconia-alumina ceramic: microtensile versus shear test. *Dent Mater J* 27(6)**:** 849-855.
58. Yoshida Y, Yoshihara K, Nagaoka N, Hayakawa S, Torii Y, Ogawa T, Osaka A, Meerbeek BV (2012). Self-assembled Nano-layering at the Adhesive Interface. *J Dent Res* 91(4)**:** 376-381.