UNIVERSIDAD DE SALAMANCA
FACULTAD DE MEDICINA
Departamento de Cirugía

Factors that affect zirconia-resin interface durability and bond strength: an *in vitro* study

Estudio *in vitro* de factores que afectan la durabilidad y eficacia adhesiva de la interfase circona-resina

---

Tesis doctoral

Presentada por **Ana Luísa Gomes** para optar al título de Doctor en Odontologia

Directores:

Dr. Alberto Albaladejo

Dr. Javier Montero

2013

Profesor Dr. D. Clemente Muriel Villoria, Director del Departamento de Cirugía de la Universidad de Salamanca,

CERTIFICA QUE:

El trabajo realizado por Ana Luísa Gomes titulado “Factors that affect zirconia-resin interface durability and bond strength: an *in vitro* study” reúne los requisitos necesarios para su presentación y defensa ante el Tribunal Calificador para poder optar al Grado de Doctor por la Universidad de Salamanca.

Y para que así conste, firmo la presente certificación en Salamanca el 19 de Julio de 2013.

Fdo. Dr. Clemente Muriel Villoria

ACKNOWLEDGMENTS

I would like to express my deepest and sincere friendship and gratitude to my supervisors, *Dr. Alberto Albaladejo* and *Dr. Javier Montero* for their continuous support. Their encouragement and direction have been greatly appreciated and I could not have finished this work without their precious help.

This study was carried out at the *Clínica Odontológica* of the *Facultad de Medicina* from the Salamanca University. *Maria Jose* and *Paco* are thanked for giving me a hand when manufacturing the studies specimens.

A special word of thanks goes to *Prof. João Carlos Ramos* for his constructive criticism and valuable comments, as well as for helping with the laser use in Coimbra University.

I thank *Rita Diz* hers helpfulness lending me a stereoscopic zoom microscope.

Thanks are due to my boss, *Dr. António Alberto Choupina*, for providing me the time and availability to be able to accomplish this thesis.

Julio Afonso is greatly appreciated for helping with excellent diagrams of my studies.

I would like to thank my dear parents, *Ana Maria e Eurico Gomes*, for their support and care that have been the basis for my life, work and career. I own great gratitude to my sister, *Helena Gomes* whose example has been the motive for my dissertation and that I know I can always count with.

I also warmly thank my beloved *Bruno Sousa* for his love and support that has carried me through the years to the final goal.

I appreciate the material donations and technical support received from *Dentsply*, *3M, Kuraray, VOCO, Laboratórios Aragoneses* and *Spanish Pulsed Laser Center (CLPU).*

CONTENTS

LIST OF TABLES 7

LIST OF FIGURES 9

ACRONYMS 11

ABSTRACT 13

RESUMEN 19

I. INTRODUCTION 25

I.1 Different materials used in prosthodontics and their intimate relationship when joining components with different natures (interfacial concept) 25

I.2 Dental ceramics 27

I.2.1 Dental ceramics history 27

I.2.2 Dental ceramics properties 30

I.2.3 Dental ceramics classification 31

I.2.3.1 Chemical content 32

I.2.3.2 Processing method 32

I.2.3.3 Sintering temperature 35

I.2.3.4 Crystalline content 36

I.2.4 Zirconia ceramics *40*

I.3 Adhesion in Dentistry 47

I.3.1 Classical dental ceramics adhesion 47

I.3.2 Crystalline dental ceramics adhesion 48

I.3.2.1 Luting cements mostly used with zirconia ceramics 49

I.4 Surface conditioning to improve resin/zirconia adhesion 51

I.4.1 Grinding 51

I.4.2 Pyrochemical silica coating 52

I.4.3 Tribochemical silica coating 53

I.4.4 Selective Infiltration Etching (SIE) 53

I.4.5 Laser treatment 54

I.4.6 Other surface conditioning methods 58

I.4.6.1 Zirconia coating with nano-structured alumina 58

I.4.6.2 Vapor phase deposition 58

I.5 *In vitro* testing methodology 59

I.5.1 Interfacial degradation by artificial aging 59

I.5.1.1 Chemical degradation 59

I.5.1.2 Thermal degradation 60

I.5.1.3 Mechanical degradation 61

I.5.2 Adhesive strength mechanical assay and microestrutural evaluation 66

II. OBJECTIVES AND JUSTIFICATION 71

Objetivos y Justificación 73

III. ORIGINAL PUBLICATIONS 75

III.1 Gomes AL, Montero J. Zirconia implant abutments: A review. Med Oral Patol Oral Cir Bucal. 2011 Jan 1;16 (1):e50-5 75

III.2 Gomes AL, Oyagüe RC, Lynch CD, Montero J, Albaladejo A. Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. J Dent. 2012; 41:31-41 83

III.4 Gomes AL, Ramos JC, Santos-del Riego SE, Montero J, Albaladejo A. Thermocycling effect on microshear bond strength to zirconia ceramic using Er:YAG and tribochemical silica coating as surface conditioning. 2013. Lasers Med Sci (sent for second review)... 97

IV. DISCUSSION 129

V. CONCLUSIONS 141

Conclusiones... 143

VI. REFERENCES... 145

VII. APPENDICES 169

Appendix I. Original articles quality ratings (JCR 2012) 169

Appendix II. Tesis resumida en Castellano 171

LIST OF TABLES

Table I.1. Dental Ceramics classification by processing laboratorial technique ...…………………………………………………………………………..33

Table I.2. Dental ceramics classification according to firing temperature and respective indications …………………………………………...………………..36

Table I.3. Chemical composition, physical, mechanical and thermal properties of Y-TZP ...…………………………………………………………………………..44

Table I.4. Resume table of relevant articles using zirconia surface conditioning with laser ...…………………………………………………………………………..56

Table I.5. Resume table of relevant articles about zirconia adhesion using different interfacial degradation by artificial aging ...……………………………...………….62

Table I.6. Micro-testing advantages and drawbacks ...……………………..……67

Table III.1.1. Summary of the most relevant studies reviewed ...……………….78

Table III.1.2. Summary of the recent relevant *in vitro* studies ...………………..79

Table III.2.1. Chemical composition and application mode of the materials tested ………...………………………………………………………………………87

Table III.2.2 Mean values of microtensile bond strength recorded in the experimental groups ...…………………………………………………………89

Table III.2.3. Comparison of the distribution of premature failures among the groups tested ...…………………………………………………………………………89

Table III.2.4. Comparison of the failure mode distribution among the groups tested ...………………………………………………………………………………90

Table III.3.1. Study design with the distribution of the samples among the different groups ……………………………………………………………………….122

Table III.3.2. Materials brands, composition and manipulation sequence used in the study ……………………………………………………………………………....123

Table III.3.3. Microshear bond strength mean and ANOVA results …………..125

Table III.3.4. Failure mode distribution in the experimental groups …………..126

Table III.3.5. Type of failures (adhesive *vs* mixed) percentages distribution according to the surface treatment among both BIF and CLE groups ……………….127

LIST OF FIGURES

Fig. I.1. Dental ceramics history summary graphic ...…………………….…..30

Fig. I.2. Zirconia crystal structure transitions with increasing temperatures 40

Fig. I.3. Schematic representation of both micro bond strength evaluation methods used in this study ……………..…………………………………………………..68

Fig. III.2.1. Schematic images of the cutting procedure and the microtensile test ...……………………………………………………………………………88

Fig. III.2.2. Representative SEM images of zirconia debonded surfaces ...……..91

Fig. III.2.3. SEM micrographs of zirconia ceramic surfaces after conditioning treatments ……………………………………………………………………...…92

Fig. III.3.1. SEM images of the zirconia surfaces to assess the failure type of each group ………………………………………………………………………..……119

Fig. III.3.2. SEM images of zirconia after the different surface treatments used ……………………………………………………………………………...121

ACRONYMS

μSBS	Micro-shear Bond Strength test
μTBS	Micro-tensile Bond Strength test
10-MDP	10-methacryloloxydecyl dihydrogenphosphate
3D	Three Dimensional
3-MPS	3-methacryloxypropyl trimethoxysilane
AFM	Atomic Force Microscope
APA	Airborne Particle Abrasion
C	Cubic crystalline zirconia form
CAD/CAM	Computer Aided Design/ Computer Aided Machining
Er: YAG	Erbium-doped Yttrium Aluminium Garnet
FEA	Finite Element Analysis
FPD	Fixed Partial Dentures
HF	Hydrofluoric Acid
ISO	International Standardization Organization
LCTE	Linear Coefficient of Thermal Expansion

M	Monoclinic crystalline zirconia form
MTBS	Micro-tensile Bond Strength test
MVD	Molecular Vapor Deposition
Nd: YAG	Neodymium -doped Yttrium Aluminium Garnet
PSZ	Partially Stabilized Zirconia
SEM	Scanning Electronic Microscope
SBS	Shear Bond Strength test
T	Tetragonal crystalline zirconia form
TBS	Tensile Bond Strength test
TC	Thermocycling
TZP	Tetragonal Zirconia Polycrystal
Y- PSZ	Yttrium-oxide Partially Stabilized Zirconia

ABSTRACT

The introduction of zirconia-based ceramics as a restorative material originated great interest and extensive research in the dental community. Zirconia bioceramic presents a wide range of applications given its enhanced biocompatibility and improved physical and optical properties. It is a relatively new and innovative material, and there is still a lot of controversy, from the scientific point of view, about the best method for optimize and promote an effective bonding to substrates used in dentistry. Traditional adhesive chemistry is ineffective on zirconia surface, because it is non-polar and inert. The current approaches for adhesive bonding to zirconia bioceramics is not suitable for all clinical applications, and long-term durability is presently unknown. Due to zirconia inertness, adhesion is difficult to achieve and there are not clear guidelines to the clinicians to follow to get a durable and effective zirconia/resin bond. The objectives of this thesis were: 1) to review the literature on yttrium stabilized zirconia (Y-TZP) ceramics, addressing the state of the art of its recent use as implant abutment; 2) to evaluate the sandblasting particle size effect on the bond strength in the zirconia/resin interface; 3) to investigate the effect of the zirconia surface treatment with tribochemical silica coating and/or Er:YAG irradiation on the zirconia/resin interface bond strength; 4) to assess if the resin cement composition influences its bond strength to zirconia and determine the best type of cement and surface conditioning combination to provide a reliable resin/zirconia bonding and, 5) to evaluate the thermocycling impact on several self-adhesive resin cements bond strength to pretreated zirconia.

A bibliographic review was made in peer-reviewed journals in PubMed/Medline. Initially, a simple search was made with the keywords "zirconia implant abutment" which was lengthened with the sequence: "Dental abutments" [Mesh] AND "Dental Porcelain" [Mesh] AND zirconia. The publication period was the last twenty years, and only articles in English were considered. A review of related articles was also made, selecting the articles considered of interest within the previously chosen manuscripts. These were divided by subtopics: zirconia physical and mechanical properties, precision fit in the implant/abutment interface and finally, bacterial adherence and tissue response to zirconia abutments whose subject was further developed.

The experimental work was conceived to determine some guidelines for improving the zirconia/resin interface. An *in vitro* study was performed to evaluate the factors that affect zirconia/resin interface durability and bond strength.

Two hundred eighty zirconia blocks were used and divided in two experiments: A) forty cylinder-shaped (Ø 19.5 mm × 10.25 mm high) blocks were selected for evaluate the influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia; and B) 240 square-like specimens (measuring 3 x 3 x 1 mm) were used to assess the thermocycling effect on microshear bond strength to zirconia ceramic using Erbium-doped yttrium aluminium garnet (Er:YAG) and tribochemical silica coating as surface conditioning.

In the first study, the zirconia blocks were polished and randomly treated as follows: Group 1 (NT): no treatment; Group 2 (APA-I): airborne particle abrasion (APA) using 25-μm aluminum-oxide (Al_2O_3) particles; Group 3 (APA-II): APA with 50-μm Al_2O_3 particles; and Group 4 (APA-III): APA using 110-μm Al_2O_3 particles. Ceramic blocks were duplicated in composite resin. Samples of each pretreatment group were randomly divided into two subgroups depending on the resin cement used for bonding the composite disks to the treated zirconia surfaces. Subgroup 1 (PAN), which employed a 10-methacryloloxydecyl dihydrogenphosphate (10-MDP) containing luting system (*Panavia 2.0 F*, Kuraray Medical Ltd, Osaka, Japan), and Subgroup 2 (BIF) used a self-adhesive cement (*BiFix SE,*VOCO, Cuxhafen, Germany). After 24h, bonded specimens were cut into 1±0.1mm^2 sticks.

In the second trial, the zirconia samples were polished and randomly assigned in four groups according surface treatment applied as follows: 1) no treatment (NT); 2) silica coating with *Rocatec*™ (*Rocatec*™ *Soft*, 3M Espe, Seefeld, Germany) (ROC); 3) Er:YAG laser irradiation (LAS: 2.940 nm, 200 mJ, 10 Hz) and; 4) laser followed by *Rocatec*™ (LAROC). A small cylinder of a resin cement with 1 mm in diameter and 2 mm in height was bonded to the each ceramic sample Each group was divided into two subgroups according the resin used: A) BIF (*BiFix SE*, VOCO, Cuxhafen, Germany) and B) CLE (*Clearfil SA*, Kuraray Medical Ltd, Osaka, Japan). After 24h, half of the specimens from each subgroup were tested. The other half was stored and thermocycled (5º-55ºC/5000 cycles).

Micro tensile bond strength (µTBS) and micro shear bond strength (µSBS) values were obtained using a universal testing machine (cross-head speed = 0.5mm/min). Failure modes were recorded and the interfacial morphology of the debonded area was observed by scanning electronic microscopy (SEM). Data was analyzed with ANOVA, Student T, chi square tests and linear regressions were performed ($p < 0.05$).

The main results to point out are the following: A) in the first study, despite the sandblasting granulometry, PAN bonded to air-abraded surfaces attained the highest µTBS and frequently showed mixed fractures, BIF recorded no significant differences in μTBS depending on the conditioning method, and registered the highest rates of premature and adhesive failures; and B) in the second experiment, before thermocycling, both cements showed higher μSBS results with ROC and LAROC; after aging, all BIF specimens evidenced severely decreased adhesion with mostly adhesive failures, on the other hand, CLE maintained the initial results in ROC and LAROC groups (performing better with ROC); although the laser treatment creates a rougher surface it did not improve bond strength.

In conclusion: 1) zirconia implant abutments use is well documented in literature with several *in vitro* studies and case reports of their success, they present identical properties to the universally used titanium abutments considering the precision fit and superior characteristics regarding bacterial adherence and biocompatibility, although zirconia abutments have fracture strength values not as good as conventional titanium ones, they are indicated in the anterior sector prosthetic rehabilitation, providing a favorable esthetic and functional addition to implant dentistry; 2) the sandblasting implementation before cementation is determinant to assure good bond strength results in the zirconia/resin interface, regardless of the particles size, however, there is a trend toward a positive correlation between the sandblasting particle granulometry increase and the bond strength at the zirconia/resin interface if a 10-MDP containing cement is used; 3) the adhesive effectiveness is higher if the surface is only conditioned with silica coating (not applying the laser); zirconia Er:YAG etching is not effective in increasing its bond strength to resin; 4) the presence of 10-MDP monomer on the cement composition positively influences the bonding because it is able to enhance chemical adhesion to a zirconia substrate; the application of a cement system that contain 10-MDP, both in the coupling agent and in the resin matrix on a sandblasted or silica

coated substrate may be the key to a successful zirconia/resin bonding; and, 5) the thermocycling impact on the bond strength depends on the materials used; a specific self-adhesive resin cement with 10-MDP in its composition over a zirconia surface pretreated with silica coating (with or without Er:YAG associated) is not influenced by thermocycling.

RESUMEN

La introducción de la cerámica de óxido de circonio como un material de restauración propinó un gran interés clínico e investigador en la comunidad odontológica. La circona como biocerámica presenta una amplia gama de aplicaciones dada su alta biocompatibilidad y buenas propiedades físicas y ópticas. Se trata de un material relativamente nuevo y prometedor, aunque sigue generando controversia, desde el punto de vista científico, sobre el mejor método para optimizar y promover su adhesión efectiva a los sustratos utilizados en odontología. Las técnicas de adhesión convencionales resultan ineficaces en la superficie de óxido de circonio, dada su relativa inalterabilidad química (composición molecular no polarizada) y su estructura cristalina pura (sin fase vítrea). Por estas razones, la adhesión (entendida como integración ultraestructural de sustratos a través de una interfase de contacto) es difícil de lograr y, hasta la fecha, no hay directrices claras para que los clínicos puedan garantizar una adhesión duradera y eficaz. Los objetivos de esta tesis fueron: 1) revisar la literatura sobre la circona, con especial enfoque al estado del arte de su reciente uso como pilar del implante; 2) evaluar el efecto del tamaño de partícula de arenado en la fuerza de adhesión en la interfase de circona/resina; 3) investigar el efecto del tratamiento de superficie de la circona con recubrimiento triboquímico de sílice y/o con irradiación de Er: YAG en la fuerza de adhesión de la interfase circona/resina; 4) determinar si la composición de cemento de resina influye en su fuerza de adhesión al óxido de circonio y cuál es la mejor combinación de tipo de cemento y de acondicionamiento de

superficie para proporcionar una adhesión fiable circona/resina; 5) valorar el impacto del termociclado en la fuerza de adhesión de varios cementos de resina auto-adhesivos a circona pretratada.

La revisión bibliográfica se realizó en revistas con revisión por pares en PubMed/Medline. Inicialmente se hizo una búsqueda simple con las palabras clave "pilar de implante de circona", que se alargo con la secuencia: "pilares dentales" [Mesh] AND "Porcelana Dental" [Mesh] AND “circona”. El periodo de publicación fue limitado a los últimos veinte años y sólo se revisaron artículos publicados en inglés. Los resultados de esta búsqueda primaria fueron complementados con los artículos relacionados o mencionados con o por aquellos. Los resultados de la revisión fueron expuestos por subtemas: las propiedades físicas y mecánicas de la circona, el ajuste de precisión en la interfase implante/pilar y, por último, la adhesión bacteriana y la respuesta de los tejidos a los pilares de circona.

Los ensayos experimentales de esta tesis se diseñaron para determinar algunas pautas de actuación para mejorar la interfase de circona/resina. El estudio *in vitro* se llevó a cabo para evaluar los factores que afectan la durabilidad y la resistencia de la adhesión en el interfase circona/resina. Para este estudio se usaron doscientos ochenta bloques de circona y se dividieron en dos experimentos: A) cuarenta bloques en forma de cilindro (Ø 19,5 mm x 10,25 mm de alto) que se seleccionaron para evaluar la influencia de la granulometría de arenado y de la composición de cemento de resina la resistencia de la adhesión de microtensión a circona; y B) 240 especímenes cuadrados (midiendo 3 x 3 x 1 mm) que se utilizaron para evaluar el efecto del termociclado en la fuerza de adhesión al test de micro-cizalla de la circona tratada con laser de Er:YAG y revestimiento triboquímico de sílice como acondicionamiento de la superficie.

En el primer ensayo, los bloques de circona fueron pulidos y separados al azar de la siguiente manera: Grupo 1 (NT): ningún tratamiento; Grupo 2 (APA-I): arenado (APA) usando partículas de óxido de aluminio (Al_2O_3) de 25 micras; en Grupo 3 (APA-II): APA con partículas de Al_2O_3 con 50 micras, y Grupo 4 (APA-III): APA utilizando partículas de Al_2O_3 de 110 micras. Los bloques cerámicos se duplicaron en composite. Las muestras de cada grupo de tratamiento previo fueron divididas aleatoriamente en dos subgrupos en función del cemento de resina utilizado para la unión de los bloques de composite a las superficies de circona tratadas: Subgrupo 1 (PAN), que emplea un sistema de cementado que contiene 10-MDP (*Panavia F 2.0*, Kuraray Medical Ltd, Osaka, Japón), y el Subgrupo 2 (BIF) en el que se utilizó un cemento autoadhesivo (*Bifix SE*, VOCO, Cuxhafen, Alemania). Después de 24 h, las muestras fueron cortadas en micro barras $1 \pm 0.1mm^2$.

En el segundo ensayo las muestras de óxido de circonio fueron pulidas y asignados al azar en cuatro grupos de acuerdo tratamiento de superficie aplicada de la siguiente manera: 1) sin tratamiento (NT); 2) revestimiento de sílice con *Rocatec™* (*Rocatec™ Soft*, 3M Espe, Seefeld, Alemania) (ROC), 3) irradiación con láser de Er:YAG (LAS: 2.940 nm, 200 mJ, 10 Hz) y, 4) láser seguido por *Rocatec™* (LAROC). Un pequeño cilindro de un cemento de resina con 1 mm de diámetro y 2 mm de altura se unió a cada una de las muestras de cerámica. Cada grupo se dividió en dos subgrupos según la resina utilizada: A) BIF (*Bifix SE*, VOCO, Cuxhafen, Alemania) y B) CLE (*Clearfil SA*, Kuraray Medical Ltd, Osaka, Japón). Después de 24 horas, la mitad de las muestras de cada subgrupo se pusieron a prueba. La otra mitad se almacenó y sometió a termociclado (5º-55ºC/5000 ciclos).

Los valores de los tests de resistencia de la adhesión a la microtensión (µTBS) y a la fuerza microcizalla (µSBS) se obtuvieron utilizando una máquina universal de ensayo (velocidad de la cruceta = 0.5mm/min). Los modos de fallo se registraron y la morfología de la zona interfacial desunida se observó por microscopía electrónica de barrido (SEM). Los datos se analizaron estadísticamente con ANOVA, tests de Student, pruebas de chi cuadrado y regresión lineal ($p < 0,05$).

Los principales resultados a señalar son los siguientes: A) en el primer estudio, a pesar de la granulometría de arenado, PAN adherido a superficies arenadas alcanza los valores más altos de µTBS y con frecuencia mostró fracturas mixtas, BIF registró diferencias significativas de la µTBS en función del método de acondicionado, y registró las mayores tasas de fallos prematuros y adhesivos, y B) en el segundo experimento, antes del termociclado, ambos cementos mostraron resultados superiores de µSBS con ROC y LAROC; después del envejecimiento artificial, todos los especímenes BIF evidencian una disminución severa de la adhesión, con fallos principalmente adhesivos. Por otro lado CLE mantiene los valores iniciales en los grupos ROC y LAROC (siendo LAROC mejor que ROC). Evidenciamos que aunque el tratamiento con láser crea una superficie más rugosa, ésta no mejoró la resistencia de la adhesión a la circona.

En conclusión: 1) el uso de pilares circona sobre implantes está bien documentado en la literatura con varios estudios *in vitro* y algunos trabajos clínicos que avalan su indicación, estos pilares de circona tienen un ajuste marginal similar a los pilares de titanio, utilizados universalmente, y ostentan una baja adherencia bacteriana y una alta biocompatibilidad, aunque los pilares de circona tienen valores de resistencia a la fractura inferiores a los de titanio, se indican en la rehabilitación protésica del sector de anterior, proporcionando un resultado estético y funcional superior; 2) la aplicación de arenado antes de la cementación es determinante para asegurar una buena adhesión en la interfase de circona/resina, independientemente del tamaño de las partículas de alumina, sin embargo, hay una tendencia evidente entre el aumento de la granulometría de la partícula del arenado y la resistencia de la unión en la interfase circona/resina si se utiliza un cemento que contiene 10-MDP; 3) la eficacia de adhesivo es mayor si la superficie sólo está condicionado con revestimiento de sílice (sin aplicar el láser), el grabado de circona con laser de Er: YAG no es eficaz en el aumento de su resistencia de la adhesión a la resina; 4) la presencia de monómero de 10-MDP en la composición de cemento influye positivamente en la adhesión una vez que es capaz de mejorar la adhesión química a un sustrato de circona, la aplicación de un sistema de cemento que contiene 10-MDP, tanto en el primer como en la matriz de resina sobre un sustrato recubierto de sílice o arenado puede ser la clave para el éxito de la adhesión circona/resina; 5) el impacto del termociclado en la resistencia de la unión depende de los materiales utilizados, un cemento auto-adhesivo específico, de resina con 10-MDP en su composición, sobre una superficie de circona pretratada con revestimiento de sílice (con o sin Er: YAG asociada) no se afecta por el termociclado.

I. INTRODUCTION

I.1 Different materials used in prosthodontics and their intimate relationship when joining components with different natures (interfacial concept)

Research in dental materials is increasingly directed towards the no metal restoration to improve the prostheses esthetics. The aim is a bio-identical restoration that mimetizes the natural tooth optical metamerism. A soft tissues natural look can be achieved considering the gingival thickness and the restorative material. Nowadays, together with acrylics, metals and resins, dental ceramics are a fundamental restoration material.

In the search for the ultimate restorative material, all-ceramic systems were considered as the best option (Kelly 1997). Ceramics are materials with unique mechanical behavior: they have very high compression resistance but are also brittle (ceramics can fracture without elastic deformation due to their low flexural strength) (Kelly *et al.,* 1996). When esthetic is compromised – a subjective concept, influenced by socio cultural tendencies – dental ceramics are commonly used. Today, talking about dental esthetic is talking about all-ceramic restorations. These help to preserve the natural soft tissues color, because there is no change in the gingival pigmentation if the material color is similar to the teeth (Denry *et al.,* 2008).

In areas such as dentistry, the conceptualization of these esthetic objectives involves the connection of organic and inorganic materials. However, the different materials nature counteract the interfacial connection because there is no chemical interaction between the surfaces (Casucci *et al.*, 2009). Changing the contact surfaces, as well as looking for bonding agents that make both surfaces compatibles, may solve this problem.

In prosthodontics, the adhesion concept was not really important before the metal free restorations and the conservative dentistry emergence. The longevity of fixed dental prostheses can be particularly affected by the cementation mode, whose primary function is to establish a reliable retention, a durable seal of the space between the teeth and the restoration, and to provide adequate optical properties.

Since the end of the 1990's, the introduction of zirconia-based ceramics as a restorative material originated great interest and extensive research in the dental community. Zirconia bioceramic presents a wide range of applications given its enhanced biocompatibility and improved physical and optical properties (Koutayas *et al.*, 2009).

The next section provides the framing of the study carried out, based in a literature review.

.

I.2 Dental ceramics

The word “ceramic” can be traced back to the Greek term “keramos” which in Sanskrit means “burn earth”. The American Ceramic Society has defined ceramic as inorganic, non metallic materials, which are typically crystalline in nature, and are formed between metallic and non metallic elements such as: aluminium and oxygen (Alumina - Al_2O_3), calcium and oxygen (Calcia - CaO) or silicon and nitrogen (Nitride - Si_3N_4) (Sukumaran *et al.*, 2006).

Ceramics usually have crystalline structure, with regular and periodic arrangement of the component atoms and may exhibit ionic or covalent bonding. Ceramics can be classified into four categories: (1) silicates, (2) oxides, (3) non-oxides, and (4) glass. Silicate ceramics are characterized by an amorphous glass phase and can have a porous structure. The main component is SiO_2 with small additions of crystalline Al_2O_3, MgO, ZrO_2 and/or other oxides. Dental porcelain falls into this category (Anusavice 2003). Oxide ceramics contain a principal crystalline phase (Al_2O_3, MgO, ZrO_2) with either no glass phase or a small amount of a glass phase. Non-oxide ceramics are impractical for use in dentistry because of high processing temperatures, complex processing methods, and unaesthetic color and opacity. Glass-ceramics are partially crystallized glasses, which occur by nucleation and growth of crystals in the glass matrix (Anusavice 2003).

Ceramics can be very strong under compression, but they are also extremely brittle, when submitted to tension can catastrophically fail after minor flexure.

I.2.1 Dental ceramics history

After decades of efforts, Europeans mastered the porcelain manufacturing technique. By the 1720’s the use of feldspar to replace lime (calcium oxide) and high firing temperatures were crucial developments in the fine European porcelain, which became comparable to the Chinese one. Porcelain is a high quality ceramic, with low porosity, harder with excellent properties and superficial look. The optical requisites demanded that only the finest and purest components are to be used in its production. Feldspathic dental ceramics were adapted from this porcelain simultaneously with their development.

Approximately in 1774, Alexis Duchateau, a Parisian apothecary, with the assistance of Nicholas Dubois de Chemant made the first porcelain denture at the Guerhard Porcelain factory, replacing the stained and malodorous ivory prosthesis of Duchateau (Kelly *et al.,* 1996). In 1791, Dubois de Chemant patented, in Britain, his idea and, in 1792, he began selling his wares.

In the second half of the XVIII century, Pierre Fauchard and others attempted to use porcelain in dentistry, but their efforts were largely unsuccessful. In 1808, G. Fonzi, an Italian dentist invented the “terrometallic” porcelain tooth that used a platinum pin or frame to be held in place. Planteau, a French dentist, introduced porcelain teeth to the United States of America in 1817, and Peale, an artist in Philadelphia, developed a baking process for them in 1822 (Anusavice 2003). Stockton began its commercial production in 1825. In 1844, the S.S. White Company was founded, and this led to design refinement and mass production of porcelain denture teeth.

Dr. Charles Land introduced the first successful fused feldspathic porcelain inlay and crowns to dentistry in 1886 (Kelly *et al.,* 1996). Land described a technique for fabricating ceramic crowns using a platinum foil, as a substructure, with high controlled heat of a gas furnace. These crowns exhibited excellent aesthetics, but the low flexural strength of porcelain resulted in a high failure incidence. This was the first crown with esthetical aspirations for unitary use.

Dental ceramics production was highly impelled after in the late 1950's, when Weinstein and Weinstein presented the metal-ceramic crown. They patented the feldspathic porcelain formulation that allowed the control of the sintering temperature and thermal expansion, as well as the components that could be used to produce alloys that bonded chemically to and were compatible with feldspathic porcelains (Weinstein *et al.,* 1962; Weinstein *et al.,* 1962; Luthardt *et al.,* 1999).

In 1963, Vita Zahnfabrik, introduced the first commercial porcelain products which were known for their esthetic properties. Significant improvement in the fracture resistance of porcelain crowns was introduced by McLean and Hughes, who developed the alumina reinforced feldspathic core in 1965 (McLean *et al.*, 1965). The material consisted of a feldspathic glass containing 45-50% Al_2O_3 (McLean 1967). The alumina ceramic was strengthened by dispersion of a crystalline phase in the glassy matrix (Craig *et al.*, 2002).

An important development in dental ceramic was registered in 1993, when *Procera All Ceram* was invented in Sweden. This material is a nucleus of highly sintered alumina (99,9%) covered by a feldspathic porcelain veneer, to achieve acceptable aesthetics.

All ceramic crowns fulfill the esthetics expectations of both professionals and patients. Since the 1960's, investigation developed new products with the aim of harder, and stronger restorations with better marginal accuracy. Recently, there have been developments in both dental ceramic materials and fabrication techniques (Kelly 1997). For example, higher strength substructure materials such as lithium-disilicate, alumina, and zirconia have been used. Additionally, fabrication techniques such as slip-casting and copy milling techniques have been improved. Esthetic demand in dentistry influenced ceramic popularity as choice material used in crowns, veneers, inlays and onlays.

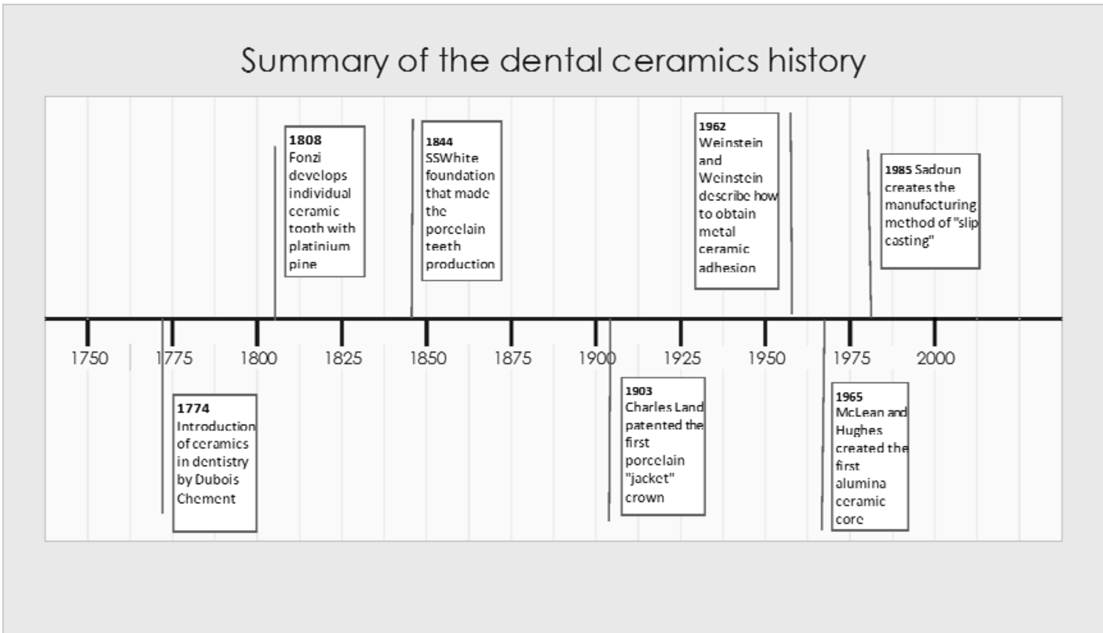

Fig. 1. Dental ceramics history summary graphic.

I.2.2 Dental ceramics properties

Dental ceramics present properties set that makes them desirable as restorative materials (Álvarez-Fernandez *et al.*, 2003):

- Biocompatibility;
- Excellent optical characteristics such as translucency, transparency, color, brightness, high reflection and texture, which implies a variety of options to mimetizes natural teeth;
- Durability and time stability, due to high chemical stability in the oral environment;
- Compatibility with other material like metals and resins;

- Low thermal conductivity and elastic modulus similar to hard dental tissues;
- Radiopacity that allows the marginal accuracy evaluation and secondary caries diagnosis;
- Hardness and high abrasion resistance;
- Mechanical strength;
- Easy production process and reasonable cost (Álvarez-Fernandez *et al.*, 2003).

I.2.3 Dental ceramics classification

Dental ceramics are defined as inorganic materials predominantly formed by no-metallic elements, produced by firing several mineral at high temperature and which final structure is partial or totally crystalline (Denry *et al.*, 2010). Most dental ceramics have a mixed structure with an amorphous glass matrix (with an atomically architecture disorganized without fixed angles or distances) where we find bigger or smaller mineral particles immersed (these particles have the atoms structured in a regular and periodic way with ionic or covalent connections) (Shenoy *et al.*, 2010). The crystalline phase improves the mechanical properties of the material. It can be said that the glass phase is responsible for the esthetics and the crystalline for the strength.

In the last decades, dental ceramics manufacturing methods had a big development directed towards the mechanical properties improvement, esthetic optimization and long term *in vivo* performance. To provide a better understanding of dental ceramics, their classification can be made based on several criteria, like chemistry, processing method, sintering temperature or crystalline content.

I.2.3.1 Chemical content

Chemically ceramics can be grouped in (Fons-Font *et al.,* 2001; Álvarez-Fernandez *et al.,* 2003; Díaz-Romeral Bautista *et al.,* 2008):

- Feldspathic ceramics:
  - Classic or traditional: used in veneering ceramic or metal cores.
  - Reinforced or high resistant: leucite (K_2O-Al_2O_3-$4SiO_2$) crystals or lithium-disilicate is used to strengthen feldspathic ceramic.
- Alumina ceramic:

  Aluminous porcelain is composed of a glass matrix phase and at least 35 vol % of alumina. An aluminous core is stronger than feldspathic porcelain, the alumina particles are stronger than glass and more effective at preventing crack propagation than quartz (van Noort 2002).

  - Classic
  - Reinforced or high resistance
- Zirconia ceramic

I.2.3.2 Processing method

Dental ceramics are produced using thermal processes, which involve high temperatures, like sinterization and ceramization. Processing method can be divided by (Álvarez-Fernandez *et al.,* 2003; Martinéz-Rus *et al.,* 2007): pressing, powder condensation, casting, or machining (Table 1). Ceramics having similar composition may be produced by different laboratory techniques, and each forming method results in a different distribution of flaws, opportunity for translucency depth and fit accuracy.

Table 1. Dental Ceramics classification by processing laboratorial technique.

Classification by processing method	**Presentation**	**Technique**
Powder condensation	Powder + Liquid	Mixing the component, build up by hand and fire in vacuum
Pressing	Pre fabricated ceramic ingots	Lost wax
Casting	Porous substrate + infiltrated glass	Slip casting
Machining	Pre fabricated ceramic ingots	CAD/CAM

- **Powder condensation**

This is a traditional method of forming ceramic prostheses that involve applying a moist porcelain powder with an artist's brush and removing excess moisture to compact the powder particles. The porcelain is further compacted by viscous flow of the glass component during firing under vacuum. The crystalline particles that strengthen the material on a microscopic scale are not connected to each other but separated by glassy regions. A large amount of residual porosity and the discontinuous nature of the crystalline phase lead to relatively low strength. Ceramics fabricated by powder condensation have greater translucency than can be achieved using other methods (Anthonson *et al.,* 2001), so these materials are usually applied as the esthetic veneer layers on stronger cores and frameworks.

- **Hot Pressing**

The lost wax method is used to fabricate molds for pressable dental ceramics. A restoration wax pattern is lined in a phosphate-bonded investment material. Following the burn out procedure, a glass-ceramic prefabricated ingot is pressed into the mould at a temperature of 1050°C in a custom furnace. An example of the material used is leucite-reinforced feldspathic porcelains strengthened by incorporating leucite (K_2O-Al_2O_3-$4SiO_2$) crystals, approximately 45% volume, in the glass matrix (Isgro *et al.,* 2003). The microstructure is similar to powder/liquid porcelain however, pressable ceramics do not contain much porosity and can have a higher crystalline content. The ingots are manufactured from non-porous glass by applying a heat treatment that transforms some of the glass into crystals (Griggs 2007). Contrary to expected, the higher crystalline content and lack of porosity do not lead to increase fracture resistance or decrease strength variability (Tinschert *et al.,* 2000).

- **Slip Casting**

A slip is a low viscosity slurry or mixture of ceramic powder particles suspended in a fluid (usually water). Slip casting involves forming a negative replica of the desired framework geometry and pouring the slip into the mold. This is made from a material (usually gypsum) that extracts some water from the slip into the walls of the mold through capillary action, and some of the powder particles become compacted against the gypsum walls forming a thin layer that is to become the framework. The remaining slurry is discarded, and the framework can be removed from the mold after partial sintering. This fired porous core is later glass infiltrated, a process by which molten lanthanum glass is drawn into the pores by capillary action at high temperatures. Materials processed this way exhibit less porosity, fewer defects from processing, greater strength and higher toughness than conventional feldspathic porcelains (Probster *et al.,* 1992) because the strengthening crystalline particles form a continuous network throughout the framework. This glass-infiltrated core is later veneered with a feldspathic ceramic for final restoration. The use of this method in dentistry has been limited to the series of *In-Ceram*®, Vita Zahnfabrik.

- **Computer Aided Design-Computer Aided Machining (CAD-CAM)**

Dental CAD-CAM systems have been available for 20 years. Recently, the increasing use of polycrystalline alumina and zirconia as framework materials and the expanding popularity of computerized methods seem to be mutually accelerating trends.

Like pressable ceramics, CAD-CAM ceramics are available as prefabricated ingots that can be machined or milled by computer-controlled tools. Glass infiltrated CAD-CAM ingots have similar composition to slip cast ceramics, but starting with a porous ingot eliminates the complicated steps of slip casting. After milling, the porosity is eliminated by molten glass infiltration.

In the case of pre-sintered ceramics, the ingots are porous, which enables a fast milling. The disadvantage of this called "Green Milling" method is the need for subsequent sintering treatment to eliminate the porosity. The computer software must calculate and compensate the shrinkage that occurs during sintering to achieve a good fit accuracy.

Densely sintered ceramics are available in non-porous ingots, which are more difficult to mill, "Hard Machining", but they do not require any further sintering.

I.2.3.3 Sintering temperature

According to the firing temperature, dental ceramics can be divided into high-fusing (1300°C), medium fusing (1101-1300°C), low fusing (850-1100°C), and ultra-low fusing (<850°C) ceramics (Anusavice 2003). This classification was employed intensively with earlier dental ceramic compositions, which contained three major ingredients: quartz, feldspar, and clay (or kaolin) (Craig *et al.*, 2002). The fusion temperature is dictated by the relative amount of these three ingredients. Table 2 presents the classification criteria and the main applications of different dental ceramics.

The lower firing temperature the lower the tendency to fracture and to originate micro flaws, because there is less contraction during cooling; nevertheless the better properties are achieved when firing temperature is very high (Poujade *et al.*, 2004). Recently, the classification was extended with the dental ceramics processed in very low temperature, even at room temperature.

Table 2. Dental ceramics classification according to firing temperature and respective indications.

Classification	**Firing temperature**	**Indications**
High fusing	1300-1370ºC	Industrial production tooth
Medium fusing	1101-1300ºC	Jacket crowns cores
Low fusing	850-1100ºC	Esthetical veneering aluminous or metal cores
Very low fusing	<850ºC	Gold or titanium veneering. Small rectifications like contact point, oclusal anatomy, angles and details. Glazing.
Room temperature		Chair side processing avoiding the laboratorial technician

I.2.3.4 Crystalline content

Nowadays dental ceramics classification by crystalline/glass content is one of the most accurate for understanding and handling of this material.

The glass phase is a binding matrix that keeps together the set and gives the ceramic translucency. The crystalline phase or charge consists in crystals that improve the mechanical properties and affect the ceramic optical behavior (opalescence, color and opacity). Its influence depends on type, size and the percentage they appear. Generally high esthetic porcelains are predominately vitreous, and the high strength ceramics are very crystalline.

The dental ceramics evolution was conducted in the way of increasing the crystalline phase to improve the mechanical properties and refine optical characteristics:

- **Glass based systems** (mainly silica)

  Glass-based systems are made from materials that contain mainly silica that contains various amounts of alumina. These materials were the first used in dentistry to make porcelain dentures. Mechanical properties are low, with flexural strength from 60-70 MPa, thus they tend to be employed as veneer materials for metal or ceramic frameworks as well as for laminate veneers.

- **Glass based systems with fillers** (usually crystalline, typically leucite or a different high-fusing glass)

  This category has a large range of glass-crystalline ratios and crystal types. The glass composition is basically the same as the glass-based systems the difference is that varying amounts of different types of crystals (leucite, lithium-disilicate) have either been added or grown in the glassy matrix. This category can be divided into three groups:

- *Low to moderate leucite-containing feldspathic glass* - these materials has been called “feldspathic porcelains” by default, the glass phase is based on aluminosilicate glass.
- *High leucite-containing (approximately 50%) glass* - again, the glassy phase is based on an aluminosilicate glass. These materials have been developed in powder/liquid, machinable and pressable forms.
- *Lithium-disilicate glass ceramic* - this is a glass ceramic (introduced by Ivoclar *IPS Empress*®, now called *IPS e.max*®) where the aluminosilicate glass has lithium oxide added.

Flexural strength for leucite reinforced ceramic has been reported to be 120 MPa (Isgro *et al.,* 2003). Conventional feldspathic porcelains designed for metal ceramic restorations contain 12 to 25% volume leucite and have a flexural strength in the range of 60 MPa. The increase in strength has been achieved through a heat treatment that enhances the formation of a highly crystallized microstructure and resists crack propagation under stress (Isgro *et al.,* 2003). Also, large pore formation can be avoided due to the better distribution of the crystalline phase within the glass matrix (Isgro *et al.,* 2003). The final restoration can use either a leucite-reinforced core material alone or a 2-layer all-ceramic crown veneered with low fusing porcelain (Isgro *et al.,* 2003).

- **Crystalline-based systems with glass fillers**

Glass-infiltrated, partially sintered alumina was introduced in 1988 and marketed under the name *In-Ceram*. The system was developed as an alternative to conventional metal ceramics and had great clinical success. Examples of materials that have used this technique are *In-Ceram Alumina, In-Ceram Spinell, In-Ceram Zirconia* (Vita Zahnfabrik, Bad Säckingen, Germany). Infiltrated ceramics are made through the process called slip-casting above described. The limited application of those ceramics is probably because the fabrication method requires a complicated series of steps, which provide a challenge to achieve accurate fit and may result in internal defects that weaken the material from incomplete glass infiltration (Griggs 2007). To simplify the slip casting technique glass infiltrated CAD-CAM ingots are available.

- **Polycrystalline solids**

Solid sintered, monophase ceramics are materials that are formed by directly sintering crystals together without any intervening matrix, forming a dense, air-free, glass-free, polycrystalline structure. Special processing techniques in combination with polycrystalline oxide ceramics has made it possible to fabricate fixed partial dentures (FPD) frameworks with a flexural strength and fracture toughness that are considerably higher than those of feldspathic, leucite or lithium disilicate ceramics that have been previously used.

There are several different processing techniques that allow the fabrication of either solid sintered alumina or zirconia frameworks. The esthetic and functional form are achieved by the use of conventional feldspathic dental ceramics.

I.2.4 Zirconia ceramics

Zirconium oxide (ZrO_2) known as zirconia is a white crystalline oxide from the transition metal Zirconium (Zr). Pure zirconia is not spontaneous in nature but is founded in minerals: Badeleyte (ZrO_2) and Zircon ($ZrSiO_4$) which contain a percentage of zirconia (80-90%) with traces of TiO_2 and Fe_2O_3.

Zirconia is a polymorphic crystal - it presents a different crystal structure at different temperatures with no change in chemistry (Figure 2). Zirconia has three crystalline forms:

1) Cubic (C) - prismatic form with square section, stable at temperatures above 2370º C until melting temperature (2680º C) with moderate mechanical properties;
2) Tetragonal (T) - prismatic form with rectangular section, stable between 1170-1370º C and with improved properties when compared with form C.
3) Monoclinic (M) - irregular prismatic form with tetragonal section, stable under 1170º C with low mechanical properties.

Orthorombic ⟷ Monoclinic ⟷ (1170ºC) Tetragonal ⟷ (2370ºC) Cubic ⟷ (2680ºC) Liquid

Fig. 2. Zirconia crystal structure transitions with increasing temperatures.

Each crystal in M phase is 4.4% bigger in volume than T form this implies a volume increase of 3-5% in the transformation T-M, which occurs during cooling (for example after sinterization). This T-M transformation causes internal stress and fragmentation that, if not controlled, are capable of causing the material collapse (Piconi *et al.,* 1999; Vagkopoulou *et al.,* 2009).

In 1929, Ruff *et al* (Ruff *et al.,* 1929) described the zirconia stabilization in the cubic phase at room temperature with the addition of small amounts of CaO, making it possible to use zirconia as an engineering material. The addition of stabilizing oxides like CaO, MgO, CeO_2 and Y_2O_3 to the pure zirconia allows the creation of multiphase materials known as Partially Stabilized Zirconia (PSZ). At room temperature, PSZ generically consists in a primarily C zirconia phase with T and M precipitates in minor phase (Piconi *et al.,* 1999).

Garvie *et al,* in 1975 (Garvie *et al.*, 1975) found three similarities between PSZ and steel that allowed them to do the parallelism between both materials and call PSZ "the ceramic steel": 1) presence of three allotropes; 2) martensilic transformation and 3) metastable phases. Also both materials have similar properties concerning the elasticity modulus and thermal expansion coefficient (Kelly *et al.*, 2008).

T-M transformation in PSZ can occur to enhance zirconia ceramics strength and hardness (Garvie *et al.*, 1975). In their study, Garvie *et al* observed that finely dispersed, in the C matrix, metastable T precipitates can turn into M when the matrix pressure over them decreases, for example, during crack propagation. The hardness is improved, because there is a T-M transformation where the energy of the crack evolution is dispersed in the own transformation and in overcoming the volume expansion compressive stress. An excess of energy is now necessary for the crack to continue to propagate, thus increasing PSZ's resistance to fracture. This mechanism known as transformation toughening is considered the basis of zirconia strength. However, it is noteworthy that it does not prevent the fracture progress it only makes it harder (Kosmac *et al.,* 1999; Luthardt *et al.,* 1999; Piconi *et al.,* 1999; Kohal *et al.,* 2004; Raigrodski 2004).

PSZ can be obtained in the system ZrO_2-Y_2O_3, with this combination it is possible to produce porcelain that, at room temperature, only presents T phase called tetragonal zirconia polycrystal (TZP). TZP contains approximately 2-3% mol of Y_2O_3 and are completely constituted by nanometric tetragonal zirconia grains. The tetragonal fraction present, at room temperature, depends on the grain size, the ytria content and the grade of constrain exerted on them by the matrix. The mechanical properties of these materials depend on such factors (Lange 1982).

Zirconia properties depend on its granular metastable microstructure. Concerning the long-term stability, the low temperature degradation (LTD) phenomenon has to be considered - a progressive and spontaneous transformation from T to M (Piconi *et al.*, 1999; Ban 2008; Vagkopoulou *et al.*, 2009) that is followed by mechanical properties degradation.

Swab (Swab 1991) resumed the main steps of LTD on TZP:

1) The temperature range between 200-300º C is the most critical;
2) The LTD effects are the strength, toughness and density reduction as well as the increasing of M phase content;
3) The material degradation is due to the T-M transformations taking place with micro- and macro- cracking of the material;
4) The T-M transformation begins superficially and progresses into the material bulk;
5) Reducing the grain size and/or increasing the stabilizing oxide concentration reduces the transformation rate;
6) The presence of water or vapor enhances the transformation T-M (Swab 1991).

Surface degradation during LTD involves roughening, increasing wear and micro-cracking, grains pullout and possible premature failure of the material (Chevalier 2006). Although LTD has been shown to be indirectly associated with a series of the femoral head prostheses failures in 2001, and despite a well established definition of the conditions for which LTD is susceptible to occur, there seems to be no clear relationship between LTD and failure predictability when zirconia is used as bioceramic (Chevalier 2006; Denry *et al.*, 2008).

Yttrium-oxide partially stabilized zirconia (Y-PSZ) exhibits exceptional fundamental properties of great interest to biomedical appliances such as high strength, hardness, fracture toughness, wear resistance, low thermal conductivity, good frictional and non-magnetic behavior, modulus of elasticity similar to steel, corrosion resistance to acids and alkalis and coefficient of thermal expansion similar to iron (Vagkopoulou *et al.*, 2009) (Table 3).

Zirconia cores have a radiopacity comparable to metal, which allows, via X-ray, a rigorous marginal integrity evaluation, the observation of cement excesses and secondary caries diagnosis (Raigrodski 2004).

Zirconia can be milled in two main ways by CAD-CAM. First a core or framework increased in volume can be designed and milled from a homogeneous pre-sintered zirconia block (Sundh *et al.*, 2005). The framework suffers a linear contraction in the range of 20-25% during sintering until the desired dimension is achieved. This process known as green milling, not only reduces the working time but also diminishes the cutting instruments wear (Piwowarczyk *et al.*, 2005). On the other hand, Y-TZP cores can be milled, directly from a totally sintered zirconia block to the final dimensions, by a method called hard machining. However, this method can compromise the material microstructure and strength (Luthardt *et al.*, 2002; Luthardt *et al.*, 2004).

Table 3. Chemical composition, physical, mechanical and thermal properties of Y-TZP by(Vagkopoulou *et al.*, 2009)

Property	**Y-TZP**
Chemical composition (wt%)	
Al_2O_3	<0.5
Other oxides	<0.5
Physical properties	
Bulk Density (g/cm^3)	6.05
Grain size (μm)	0.2
Monoclinic phase (%)	<1
Porosity (%)	<0.1
Mechanical Properties	
Flexural strength(4 points) (MPa)	1666
Elastic modulus (GPa)	201
Vickers Hardness (HV)	1270
Fracture toughness ($Kgf/mm^{2/3}$)	16.8
Fracture toughness ($MPa\ m^{-1}$)	7-10
Compressive strength (MPa)	4900
Impact strength (MPa)	137
Thermal properties	
Thermal expansion coefficient ($x\ 10^{-6}/^oC$)	$11x\ 10^{-6}\ K^{-1}$
Thermal Conductivity (W/ mºK)	2
Specific Heat (J/kgºK)	500

The spectrum of the contemporary clinical applications of zirconia includes the fabrication of veneers, full and partial coverage crowns or FPDs, posts and/or cores, implants and implants abutments. In addition, different zirconia-based auxiliary components such as cutting burs and surgical drills, extracoronal attachments, and orthodontic brackets are also available as commercial dental products (Koutayas *et al.*, 2009).

I.3 Adhesion in Dentistry

Adhesion is defined as the phenomenon in which of two surfaces that are held together by chemical or physical forces, or both, often with the aid of an adhesive (ISO/TR 11405: 1993). Adhesion implies a contact between adherent and adhesive by physical and chemical interactions. The adhesion condition involves several mechanisms, compatibles and that can be observed simultaneously:

1. Mechanical adhesion depends on the adhesive penetration in the adherent micro or macroscopic irregularities.
2. Chemical adhesion based in forces present in chemical bonds between the adherent and the adhesive. These can be primary and strong (ionic and covalent) or secondary or weak (Van der Waal's forces, Hydrogen bond, London dispersion forces).

In Prosthodontics, a strong adhesion provides high retention, improves marginal adaptation and prevents the micro infiltration, increases the fracture strength of the restored tooth and its restoration (Blatz *et al.,* 2003). This kind of bonding is based on micro-mechanical interconnections and chemical adhesion of the adhesive to the ceramics surface, which requires the creation of roughness and adequate cleaning to ensure surface activation. Mechanical surface treatments such as sandblasting with alumina particles, abrasion with rotating tools, or chemical treatments such as acid etching and/or combinations of these are commonly accepted.

I.3.1 Classical dental ceramics adhesion

The adhesion to glass ceramics containing silica is a predictable process with lasting results when using the following protocol. Etching with hydrofluoric acid (HF) can achieve a favorable surface for bonding in the glass ceramics (Sorensen *et al.*, 1991;

Blatz *et al.*, 2003). When the silica-based ceramics are treated with HF, the glass matrix is dissolved and may be rinsed, thereby obtaining a microscopically porous and micro-retentive surface with high energy. The acid treatment also increases the density of hydroxyl groups (-OH) on the surface, which increases the connections between the surfaces with silica and the silanes (Matinlinna *et al.*, 2007).

The silanes are bifunctional molecules that bond to the silica dioxide (SiO_2) through the -OH groups of the surface of the ceramics. On the other hand, they have a functional group that co-polymerize with organic matrix resins. The silanization also increases the wettability of the ceramic surface. Thus, we see that the bonding with the ceramic occurs by a condensation reaction between the silanol group (Si-OH) of the ceramic surface and the silanol groups of the hydrolyzed silane molecule, creating siloxanes joints (Si-O-Si), with a water molecule as subproduct. The bonding occurs with the resin by the polymerization by an addiction reaction between methacrylate groups to the organic portion of the silane during the curing reaction of the resin used in the cementing (Söderholm *et al.*, 1993).

Mechanical engraving methods are not recommended because they can damage the ceramic and diminish its physical properties.

I.3.2 Crystalline dental ceramics adhesion

The composition and mechanical properties of alumina and zirconia crystalline ceramics differ substantially from those of classical ceramics. The lack of silica makes the acid etching with HF useless and also removes the possibility of chemical bonding between silica-silane necessary for silanization, thus requiring the implementation of new techniques to achieve strong and durable adhesion (Kern *et al.*, 1998). Bonding to zirconia has become a topic of interest. Traditional adhesive chemistry is ineffective on zirconia surface, as it is non-polar and inert. The currently approaches for adhesive bonding to zirconia bioceramics is not suitable for all clinical applications, and long term durability is currently unknown (Blatz *et al.*, 2004).

I.3.2.1 Luting cements mostly used with zirconia ceramics

Generally, the cements function is to establish a reliable retention between the indirect restorations inner surface and tooth structure irregularities, protecting the remaining tooth structure, providing a durable margins seal from oral fluid and/or bacteria micro-infiltration and adequate optical properties (Burke 2005).

Resin cements are active luting materials capable of bonding with enamel, dentin and indirect restorations surfaces. The difficulty associated with the use of resin cements lies in the application technique (Burke 2005). The use of resin cements requires a bonding procedure, in which becomes necessary the application of a series of complicated bonding procedures to the dental substrate as to restoration surface (ceramic, composite, etc.). These cements application technique is critical, susceptible to factors related to the material and the operator that can lead to the occurrence of postoperative sensitivity and restorative treatment failure (Ferracane *et al.*, 2011).

Adhesive cements have been developed in order to combine the easy handling and self adhesion of conventional cements with the resin cements superior mechanical, adhesive and esthetic properties. Self-adhesive cements application is summarized as a clinical single step: after mixing base and catalyst pastes, the material is applied directly to the surfaces that will be bonded (Proença 2010).

There is a notable problem with chemical bonding a resin to Y-TZP as it is an inert, non-reactive and complex surface with Zr atoms on the surface. In contemporary dental research literature, there can be found several studies suggesting that the use of a phosphate monomer containing luting resin which provides higher bonding strength values to zirconia than conventional luting cements (Atsu *et al.,* 2006; Lüthy *et al.*, 2006; Wolfart *et al.,* 2007; Shahin *et al.,* 2010).

I.4 Surface conditioning to improve resin/zirconia adhesion

In order to achieve good adhesion, the key requirement is that the substrate surface is clean, dry and degreased. The surface conditioning is a set of procedures that aim to increase the surface energy of the substrate to improve its affinity to the adhesive agent. It is intended that the surface energy of the substrate is greater than the cohesive forces of the molecules of the adhesive agent so that the wettability is as high as possible.

Because of the difficulty in creating mechanical and chemical bonding in zirconia, alternative methods have been explored to bond zirconia using resin cements. In the following sections will be described some important techniques used in the conditioning of the surface of the zirconia used in dentistry.

I.4.1 Grinding

Surface grinding is commonly used for roughening the zirconia surface. In dental laboratories, the usual procedure is blasting surfaces with alumina particles (Al_2O_3) with an average size of 50 µm under a pressure of 380 kPa for about 10-15 s at a perpendicular distance of 10 mm from the holder (Blatz *et al.,* 2003). Some alumina particles can become embedded in the surface during blasting. Thus, an alumina coated onto the substrate is formed after blasting. The amount of alumina increases with increasing blasting pressure (Darvell *et al.,* 1995). After silanization = Al-O-Si ≡ links can form, however, they are hydrolytically unstable (Lung *et al.,* 2012).

Other methods can be used for surface grinding: grinding using abrasive paper or wheels (SiC or Al_2O_3) and grinding using a diamond bur (Dérand *et al.,* 2000). These grinding methods are easy to apply in a dental environment. However, research has concluded that these techniques, using traditional resin cements, have no significant effect on increasing the bond strength of zirconia to resin cements (Kern *et al.*, 1998; Dérand *et al.*, 2000; Wegner *et al.*, 2000; Piwowarczyk *et al.*, 2005; Atsu *et al.*, 2006; Blatz *et al.*, 2007).

I.4.2 Pyrochemical silica coating

This process makes a pyrochemical and thermal silica coating application to the surface searching for obtain a durable covalent bonding ≡Si-O-Si≡. The implementation systems of this method are the *Silicoater*® *Classical*, the *Silicoater*® *MD* and *Siloc*® (Heraus-Kulzer, Wehnheim, Germany) (Matinlinna *et al.*, 2007). *Silicoater*® system is composed by a serialization where the substrate, after blasting, passes through a flame. A silane solution is injected into the flame and a series of pyrochemical reactions occur, resulting in a silica coating on the surface (Matinlinna *et al.*, 2007). The gas is lit and the silane decomposed in the flame, coating the material with a layer of SiO_x-C that bond adhesively to the surface of the material (Janda *et al.*, 2003). After cooling, to room temperature, a layer of silane is applied on the newly formed silica layer and allow it to proceed with adhesion (Kolodney *et al.*, 1992).

Silicoater® has been successful in improving the bond strength of resin cement to metals and decreasing the bond degeneration after thermocycling (Peutzfeldt *et al.*, 1988; Hummel *et al.*, 1994). Nevertheless, it was expensive and too complex to be commercially viable for standard dental applications.

Recent innovations in pyrolytical silica coating, the *PyrosilPen-Technology* (PyrosilPen, SurA Instruments, Jena, Germany) have made it easier to use for chair-side applications (Janda *et al.*, 2003). Only two studies were found about this technology application on ceramics (Janda *et al.*, 2003; Rüttermann *et al.*, 2008) so, further investigation is required before it can be used as an acceptable method to enhance bonding of zirconia to resin cements (Thompsom *et al.*, 2011).

I.4.3 Tribochemical silica coating

The basic principles of the tribochemistry are the chemical and physicochemical changes of the matter during the application of mechanical energy (Fischer 1988). The *Rocatec*™ and *CoJet*™ (3M ESPE, Seefeld, Germany) systems using silica-coated alumina particles and compressed air for blasting the substrate surface. The impact of particles on the substrate results in kinetic energy transfer. The energy absorbed by the substrate surface cause its microscopic fusion, momentarily the surface temperature increases to 1200 °C. The particles of silica-coated alumina penetrate the surface and become embedded in the substrate surface, leaving it partially silica coated. This surface can be subsequently primed by silanization, after which adhesive cement may be used.

The tribochemical silica coating is achieved using both the *Rocatec*™ *Soft* (with Al_2O_3-SiO_2 particles of 30 µm) or *Rocatec*™ *Plus* (with Al_2O_3-SiO_2 particles of 110 µm) blasting with a pressure of 280 kPa for 13 s/cm^2 at a perpendicular distance of 10 mm (Lung *et al.*, 2010).

I.4.4 Selective Infiltration Etching (SIE)

With this surface conditioning method, the surface of the zirconia is coated with a thin layer of a glass conditioning agent that is heated to a temperature above the glass transition temperature. The molten glass infiltrates the limits of the zirconia micro-granular structure exerting capillary forces and surface tension. Finally, it is removed by an acid bath after cooling to room temperature, which creates a new 3D (Three Dimensional) network of inter-granular porosity that allows nano-mechanical interlocking of the resin cement (Aboushelib *et al.*, 2007; Aboushelib *et al.*, 2010). It was observed that the combination of SIE with the use of silanes significantly improves the resin zirconia adhesion (Aboushelib *et al.,* 2008; Aboushelib *et al.,* 2011). Casucci *et al* (Casucci *et al.*, 2009) confirmed, with an Atomic Force Microscope (AFM) work, that the surface roughness of zirconia after SIE is significantly greater when compared to airborne particle abrasion (APA) or HF etching (Casucci *et al.,* 2009).

I.4.5 Laser treatment

The use of lasers in dentistry has been developed since its introduction in 1962. Several researches have been carried out on a different wavelength laser effect on dental tissues and materials, as they become available (Wigdor *et al.,* 1993; Visuri *et al.*, 1996). Laser light has specific properties, it travels in a specific wavelength (it is monochromatic) in a predictable pattern (is coherent) and parallel (collimated) (Kutsch 1993). Lasers and target surfaces interact in four ways. When a laser hits the surface can be reflected, absorbed, dissipated through the target or transmitted into the target (Kutsch 1993). During laser application light energy is converted into heat and energy absorption on the target surface causes vaporization. This process is called ablation or photo-ablation by vaporization (Lee *et al.,* 2007; Cardoso *et al.,* 2008; Tachibana *et al.,* 2008).

According to literature there is no optimum wavelength for all applications. Each wavelength has distinct treatment advantages and offers various options (Kutsch 1993). During the mid 1990s, researchers assessed the safety and values of using the Er:YAG for preparation of hard tissues (Burkes *et al.,* 1992; Paghdiwala *et al.,* 1993). This laser operates at the wavelength of 2940 nm in a pulse mode one of its distinctive features (Bertrand *et al.,* 2005). In the referred studies, it was seen that this wavelength (when used with water) would ablate solid tooth structure without thermal damage. If this laser is used without irrigation, then typical microcracks and other thermal damage would appear. The mechanism of action for hard dental tissues laser ablation with Er:YAG is based on the expansion of interstitially trapped water within the mineral substrate that causes a massive volume expansion, causing the surrounding material to be exploded away (van As 2004). A feature of erbium lasers is a popping sound (photo-acoustic effect) when interacting with hard tissues. This popping sound is a very quick shock wave that is created when laser energy dissipates explosively (Walsh 2003).

Lasers were proposed to modify the surfaces of materials in a relatively safe and easy way (Gökçe *et al.*, 2007; Spohr *et al.*, 2008; Cavalcanti *et al.*, 2009; Ersu *et al.*, 2009). One of the most used lasers in research, as well as in clinical practice is the Er:YAG (erbium-doped yttrium aluminium garnet), but only limited studies on all ceramics materials laser treatments are available (Gökçe *et al.*, 2007; Cavalcanti *et al.*, 2009; Cavalcanti *et al.*, 2009; Ersu *et al.*, 2009) (Table 4). Er:YAG with appropriate parameters can create an irregular surface that enhances the micromechanical retention to ceramic materials (Cavalcanti *et al.*, 2009). Still, high laser intensity can damage surface properties, resulting in crack formation and consequent low bond strength values (Akın *et al.*, 2011).

The surfaces of the zirconia specimens can be treated with Nd:YAG or Er:YAG laser. After treating surfaces with laser a silane can be applied and proceed with the adhesive technique. It was reported that the adhesive strength of the laser-treated zirconia is superior when compared with the one that follows sandblasting (Spohr *et al.*, 2008). However, the measured forces vary considerably depending on the type of laser used (Akyil *et al.*, 2010).

Table 4. Resume table of relevant articles using zirconia surface conditioning with laser treatment.

Authors	Title	Year	Material and Methods		Conclusion
			Zirconia surface treatments	Testing methods	
Demir *et al.* (Demir et al., 2012)	Surface roughness and morphologic changes of zirconia following different surface treatments	2012	- Er:YAG with 200,300 and 400 mJ - APA with 110 µm Al_2O_3	- Surface roughness evaluation using a surface texture measuring instrument - Microscope analysis	- 400 mJ Er: YAG or APA obtain micromechanical retentions - APA is more effective
Akın et al.(Akın et al., 2011)	Shear bond strength of resin cement to zirconia ceramic after aluminum oxide sandblasting and various laser treatments	2011	- No treatment - APA - Er:YAG - Nd:YAG - CO_2 laser	- SBS test on the zirconia/ dentin adhesion	Er:YAG and Nd:YAG increased zirconia/dentin bond strength when compared to APA and CO_2 laser treatment
Subasi *et al.* (Subasi et al., 2012)	Influence of surface treatments and resin cement selection on bonding to zirconia	2012	- No treatment - Er:YAG (400mJ, 10 Hz, 1 mm) - Tribochemical silica coating (30 µm Al_2O_3. SiO_x) - APA with 110 µm Al_2O_3	- Surface roughness evaluation - AFM and SEM analysis	-All the treatments can be used for roughening zirconia prior to cementation. - APA is the more effective to obtain micromechanical retention.
Foxton *et al.*(Foxton et al., 2011)	Durability of resin cement bond to aluminium oxide and zirconia ceramics after air abrasion and laser treatment	2011	- No treatment - APA with Al_2O_3 - Er:YAG (200 mJ)	- µSBS test on the zirconia/ dentin adhesion -aging of the samples by water storage	Er:YAG did not result in a durable dentin/zirconia bond.
Akın *et al.*	Effect of Er:YAG laser application on the shear bond strength and microleakage between resin cements and Y-	2012	- No treatment - Er:YAG (150 mJ, 10 Hz)	- SBS test - Microleakage evaluation	Conditioning Y-TZP ceramic with Er:YAG increased the ceramic/dentin SBS strength and reduced microleakage scores.

	TZP ceramics				
Akyil et al.(Akyil et al., 2010)	Bond strentgh of resin cement to yttrium-stabilized tetragonal zirconia ceramic treated with air abrasion, silica coating and laser irradiation.	2010	- No treatment - APA - Silica coating - Er:YAG - Nd:YAG - CO_2 laser - several combinations of the above mentioned methods	- SBS test	- APA and silica coating were the most effective treatments to obtain high bond strength. - CO_2 laser; Er:YAG and the combination APA+Nd:YAG may be used as an alternative method to increase resin/zirconia bond strength.
Cavalcanti *et al* .(Cavalcanti et al., 2009a)	Evaluation of the surface roughness and morphologic features of Y-TZP ceramics after different surface treatments	2009a	- No treatment - APA with 53µm Al_2O_3 - Er:YAG (200, 400 and 600 mJ, 10 Hz)	- Surface roughness evaluation	Higher laser power settings (400 and 600 mJ) cause excessive material deterioration.
Cavalcanti *et al* .(Cavalcanti et al., 2009b)	Bond strength of resin cements to a zirconia ceramic with different surface treatments	2009b	- No treatment - APA with 53µm Al_2O_3 - Er:YAG (200 mJ, 10 Hz)	- µSBS test - SEM evaluation	APA with Al_2O_3 particles and selected metal primers increased resin/zirconia bond strength.
Paranhos *et al*.(Paranhos et al., 2011)	Effect of Nd:YAG laser and CO_2 laser treatment on the resin bond strength to zirconia ceramic	2011	- No treatment - APA with 50µm Al_2O_3 - Silica coating (30 µm $Al_2O_3.SiO_x$) - Nd:YAG (100 mJ, 20 Hz) - CO_2 laser (5 J, 1 Hz) - several combinations of the above mentioned methods	- SBS test - Surface roughness evaluation	-Nd:YAG created consistent roughness on the zirconia surface and significantly increased the SBS. - Silica coating could potentially increase the SBS of lased and non lased zirconia. - Significant microcracks were found on specimens treated with CO_2 laser.

I.4.6 Other surface conditioning methods

I.4.6.1 Zirconia coating with nano-structured alumina

This method makes the hydrolysis of aluminum nitride to form boehmite (γ-AlOOH) on the zirconia surface. It is done set of heat treatments, and the boehmite undergoes a series of phase transformations to be converted into α-alumina. A discontinuous nano-structured alumina layer surface is formed onto the zirconia surface (Jevnikar *et al.,* 2010). This coating technique followed by silanization was reported effective to improve the zirconia/resin adhesion (Kitayama *et al.*, 2010).

I.4.6.2 Vapor phase deposition

Exposing the zirconia, in a vacuum chamber, to a vapor mixture of tetrachlorosilane and water, achieves a silica coating layer with thickness controlled by the deposition time. Zirconia coated with a SiO_x film, followed by silanization and resin cement bonding, showed increased bond strength values when compared to sandblasting and tribochemical silica coating (Piascik *et al.,* 2009).

The fluorination of the zirconia surface, in a plasma reactor, with a continuous flow of sulfur hexafluoride gas forms an oxyfluoride layer on the surface of the zirconia (Piascik *et al.,* 2011). The application of silane on both zirconia coated surfaces obtained promising resin/zirconia adhesion values (Piascik *et al.*, 2009; Piascik *et al.*, 2011). The process uses molecular vapor deposition (MVD), an enhancement on conventional vapor deposition, to deposit ultra thin, uniform coating on substrates using an *in situ* plasma treatment. Nevertheless, these techniques require the handling of dangerous substances and, on the other hand, further studies are needed to evaluate the long term durability of the adhesion accomplished (Lung *et al.*, 2012).

I.5 *In vitro* testing methodology

I.5.1 Interfacial degradation by artificial aging

The most common *in vitro* interfacial fatigue (fastened aging) techniques are water storage and thermocycling. This aging methods, widely used and based on International Standardization Organization (ISO) standards for dental materials (ISO TR11450 standard, 1994) and can be used separately or combined.

There are many bonding procedures able to obtain a strong bond with Y-TZP initially. However, this bond must be adequate over years under the relatively aggressive circumstances of the oral environment: humidity, temperature shocks, pH fluctuation and mastication forces. Several studies, using water storage and/or thermocycling, observed that fatigue can take to a reduction of the zirconia-resin bond strength, which can deteriorate with time, causing loss of retention and increasing microleakage (Wegner *et al.*, 2000; Amaral *et al.*, 2006) (Table 5).

I.5.1.1 Chemical degradation

The most usually used artificial aging technique is long term water storage (de Munck *et al.*, 2005). It was suggested that the decrease in bonding effectiveness reported was caused by degradation of the interface component by hydrolysis (de Munck *et al.*, 2005). Hydrolytic degradation of the bonding interface is related to the diffusion of liquids. This diffusion is dependent on time – it takes time to water penetrate the bonding interface and cause chemical breakdown (Ferracane *et al.*, 1995). Water can infiltrate and decrease the mechanical properties of the polymer matrix, by swelling and reducing the frictional forces between the polymer chains, a process known as “plasticization” (Ferracane *et al.*, 1998; Santerre *et al.*, 2001). Some interface components, such as uncured monomers and break-down products of previous reactions, can elute and weaken the bond (Hashimoto *et al.*, 2002). To simulate more accurately the clinical situation, artificial saliva solutions can also be used, but bond strength reductions related were very similar to those obtained with pure water degradation (Kitasako *et al.*, 2000).

I.5.1.2 Thermal degradation

Another commonly used aging technique is thermocycling. The ISO TR 11450 standard (1994) determines that a thermocycling regimen comprised of 500 cycles in water between 5-55ºC is an appropriate artificial aging method (de Munck *et al.*, 2005). A literature review (Gale *et al.*, 1999) concluded that 10000 cycles correspond approximately to one year of *in vivo* functioning, standing the proposition of 500 cycles as being minimal for simulating long term bonding effectiveness.

Two main mechanisms of deterioration of the established bond strength have been proposed: a) hydrolytic degradation (as well as in long-term water storage) and b) mechanical fatigue. The last results from stresses affecting the bond, for example, thermal expansion and contraction.

Different linear coefficient values of thermal expansion (LCTE) of resin and ceramic may have an effect on the failure mechanism at the bonding interface. Ceramic materials LCTEs are typically lower than resin luting cements LCTEs. This difference causes thermal stresses at the bonding interface, generating unequal changes in dimensions, and eventually, the bond failure (Tezvergil *et al.*, 2003; Meric *et al.*, 2008). These stresses may lead to cracks that propagate along bonded interfaces, once the gap is formed, changing the gap dimensions can cause an in- and outflow of fluids, known as “percolation” (Gale *et al.*, 1999). Percolation takes us again to hydrolytic degradation.

Thermocycling results in combined contraction/expansion stress and accelerated chemical degradation. The contribution of each is highly dependent on the specific test setup. In the light of the first aging effect (hydrolysis), thermocycling should be applied to very small specimens, and any further preparation after aging is to be avoided (de Munck *et al.*, 2005).

I.5.1.3 Mechanical degradation

Mechanical loading may also affect adhesion. To mimic the *in vivo* stress, is possible to "age" interfaces in a chewing simulator and measure the bonding effectiveness afterward (Nikaido *et al.*, 2002; Frankenberger *et al.*, 2003).

The dynamic loading long term influence is not known or completely understood and thus further investigations are needed to understand the complex interactions and their effects on the performance of zirconia-resin bond strength.

Table 5. Resume table of relevant articles about zirconia adhesion using different interfacial degradation by artificial aging.

Authors and Year	Title	Materials and Methods			Conclusion
		Materials	Aging process	Bond strength assessment	
(Kern *et al.*, 1998)	Bonding to zirconia ceramic: adhesion methods and their durability	- zirconia discs - different luting systems -different surface conditioning methods	- water storage for 3 d at 37ºC - water storage for 150 d with 37500 TC[1] (5-55ºC)	- TBS test	A durable bond to Y-PSZ was achieved only by using a 10-MDP containing cement, all the other methods investigated did not resulted in a long term durable bond.
(Özcan *et al.*, 2003)	Effect of surface conditioning methods on the bond strength of luting cement to ceramic.	- different ceramics - different surface conditioning methods - one luting cement	- 6,000 TC (5-55ºC)	- SBS test	- Bond strength varied in accordance with ceramic types. - SBS was significantly affected by TC
(Blatz *et al.*, 2004)	*In vitro* evaluation of shear bond strengths of resin to densely-sintered high-purity zirconium-oxide ceramic after long-term storage and thermal cycling.	- different cements - different adhesives - zirconia plates square shaped - composite cylinders - APA with 50µm Al_2O_3	- water storage for 3 d at 37ºC - water storage for 180 d with 12000 TC (5-60ºC)	- SBS test	- TC and long-term water storage had significant effects on resin bond. - An adhesive coupling agent containing 10-MDP, combined with both cements used, had significant highest bond strength after artificial aging
(Lüthy *et al.*, 2006)	Effect of thermocycling on bond strength of luting cements to zirconia ceramic	- zirconia discs - different luting systems - APA with 110µm Al_2O_3	-water storage for 48 h at 37ºC - 10000 TC (5-55ºC) for 333h	- SBS test	- After TC, bond strengths for non adhesive cements was low. -With 10-MDP containing adhesive cements, after TC, a no significant increase in SBS was observed.
(Palacios *et al.*, 2006)	Retention of zirconium oxide ceramic crowns with three types of cement	- zirconia copings - APA with 50µm Al_2O_3 - different luting systems	- water storage for 24h at 34ºC - 5000 TC (5-55ºC)	- copings submitted to forces along the apico-occlusal axis until fracture	All the cements are capable of retaining zirconia successfully with no additional internal surface treatment other than APA followed by appropriate cleaning of the crown prior to cementation.
(Yoshida *et al.*, 2006)	Bonding of dual-cured resin cement to zirconia ceramic using phosphate acid ester monomer and zirconate coupler	- zirconia discs - different primers - one luting system	- water storage for 24h at 37ºC - water storage for 24h at 37ºC followed by	- SBS test	- Statistically significant differences is SBS before and after TC were observed. - -the primer mixture of an acid MDP monomer and a zirconate coupling agent is

[1] TC – Thermal Cycles

			10000TC (4º-60ºC)		effective for strong bonding between resin and zirconia.
(Blatz *et al.*, 2007)	Influence of surface treatment and simulated aging on bond strengths of luting agents to zirconia	- zirconia plates square shaped - different surface conditioning methods - composite cylinders - different luting systems	- water storage for 3 d at 37ºC - water storage for 180 d with 12000 TC (5-60ºC)	- SBS test	- Surface treatment, luting agent and storage conditions significantly influenced bond strengths. - APA combined with a 10-MDP containing cement or tribochemical silica coating combined with any resin cement tested provided superior bond strengths to zirconia.
(Wolfart *et al.*, 2007)	Durability of the resin bond strength to zirconia ceramic after using different surface conditioning methods.	- zirconia discs - different surface conditioning methods - different luting systems - composite cylinders	- water storage for 3 d at 37ºC - water storage for 150 d with 37500 TC (5-55ºC)	- TBS test	- After TC, only samples luted with a 10-MDP containing cement showed high bond strengths, whereas most other specimens debonded spontaneously or showed very low bond strengths. - APA can be recommended as a promising surface conditioning method.
(Amaral *et al.*, 2008)	Effect of conditioning methods on the microtensile bond strength of phosphate monomer-base cement on zirconia ceramic in dry and aged conditions.	- zirconia blocks - different surface conditioning methods - one luting system	- dry conditions - water storage for 150 d with 6000 TC (5-55ºC)	- µTBS test	- Silica coating followed by silanization showed durable bond strength. After aging APA with 110µm Al_2O_3 and silanization showed the largest decrease.
(Kern *et al.*, 2009)	Surface conditioning influences zirconia ceramic bonding	- zirconia discs - different surface conditioning methods - different adhesive systems - one luting system	- water storage for 3 d at 37ºC - water storage for 150 d with 37500 TC (5-55ºC)	- TSB test	- The combination of APA and priming improved long-term resin bonding to zirconia ceramic significantly. - With low-pressure APA, surface roughness was reduced without affecting long-term bond strength, provided that adequate adhesive primers were applied.

(Oyagüe *et al.*, 2009)	Effect of water aging on microtensile bond strength of dual-cured resin cements to pre-treated sintered zirconium-oxide ceramics	- zirconia discs - different surface conditioning methods - different luting systems - composite cylinders	- water storage for 24 h at 37ºC - water storage for 6 months at 37ºC	- µTBS test	- Resin/zirconia interfacial longevity depended on cement selection rather than on surface conditioning. - Water storage played an important role in the durability of the interface chemical bonds.
(Phark *et al.*, 2009)	An in vitro evaluation of the long-term resin bond to a new densely sintered high-purity zirconium-oxide ceramic surface	- zirconia discs with modified or machined surface - different surface conditioning methods - different luting systems - composite cylinders	- water storage for 3 d at 37ºC - water storage for 90 d with 20000 TC (5-55ºC)	-SBS test	- Long-term SBS to modified zirconia surface without APA is significantly higher. APA had a deleterious effect on SBS to modified zirconia. - APA of the machined zirconia increased long-term SBS significantly (regardless the particle size) - Water storage and TC reduced SBS of all the cements tested.
(de Souza *et al.*, 2010)	Bond strength to high-crystalline content zirconia after different surface treatments	- zirconia discs - different adhesive systems - one luting system	- water storage for 72 h at 37ºC - water storage for 60 d at 37ºC with 5000 TC (5-55ºC)	- µTBS test	- Luting zirconia with an MDP-based luting system did not increase bond strength and aged samples presented lower bond strength. - A MDP-containing primer may increase bond strength between the luting system and flat and smooth zirconia substrate.
(May *et al.*, 2010)	Effect of silica coating combined to a MDP based primer on the resin bond to Y-TZP ceramic.	- zirconia blocks - different surface conditioning methods - different adhesive systems - one luting system	- water storage for 24 h at 37ºC - water storage for 90 d at 37ºC with 12000 TC (5-55ºC)	- SBS test	- After TC a combination of silica coating with a MDP-containing primer promoted the highest SBS. - Silica coating presented a relevant influence upon the bond strength and durability.
(Qeblawi *et al.*, 2010)	The effect of zirconia surface treatment on flexural strength and shear bond strength to a resin cement	- zirconia bars - different surface conditioning methods - different adhesive systems - dentin specimens - one luting system	- dry conditions - water storage for 90 d at 37ºC with 6000 TC (5-55ºC)	- SBS test	- Artificial aging resulted in significantly lower SBS for the silicoated/silanated and the zirconia primer groups. - The resin bond to Y-TZP was improved by surface conditioning. - A combination of mechanical and chemical conditioning was essential to develop a durable resin bond to zirconia.

(Shahin *et al.*, 2010)	Effect of air abrasion on the retention of zirconia ceramic crowns luted with different cements before and after artificial aging	- human premolars prepared for all ceramic crowns - zirconia crowns - different surface conditioning methods - different luting systems	- water storage for 3 d at 37ºC - water storage for 150 d with 37500 TC (5-55ºC) and 300000 DL [2]	- copings submitted to forces along the apico-occlusal axis until fracture	-Artificial aging decreased significantly retention. - APA increased crown retention - The use of a MDP-containing resin cement on air abraded zirconia can be recommended as most retentive luting method.
(Yang *et al.*, 2010)	Influence of air-abrasion on zirconia ceramic bonding using an adhesive composite resin	- zirconia discs - composite discs - different surface conditioning methods - different adhesive systems - one luting system	- water storage for 3 d at 37ºC - water storage for 150 d with 37500 TC (5-55ºC)	- TBS test	- Without priming, the cement showed durable bond strength to APA abraded ceramic. - 10-MDP primer in combination with APA resulted in durable TBS to zirconia even at reduced abrasion pressure.
(Attia *et al.*, 2011)	Long-term resin bonding to zirconia ceramic with a new universal primer	- zirconia discs - composite discs - different surface conditioning methods - different cleaning methods - different adhesive systems - one luting system	- water storage for 3 d at 37ºC - water storage for 150 d with 37500 TC (5-55ºC)	- TBS test	- A new universal primer provided significantly better long-term resin bonding to zirconia than a conventional silane. - Cleaning methods had little effect on long-term resin/zirconia bonding.
(Smith *et al.*, 2011)	Long-term microtensile bond strength of surface modified zirconia	-- zirconia blocks - different surface conditioning methods - different adhesive systems - one luting system	- water storage at 37ºC for 0, 1, 3, and 6 months	- µTBS test	- The deposition of silica layer on zirconia resulted in similar or superior long-term resin bond strength when compared to traditional silanation and bonding techniques for zirconia but lower than that for silane treated porcelain..
(Inokoshi *et al.*, 2013)	Durable bonding to mechanically and/or chemically pre-treated dental zirconia	-- zirconia blocks - different surface conditioning methods - different adhesive systems - different luting systems	- water storage for 7 d at 37ºC - water storage for 10 d with 10000 TC (5-55ºC) - water storage at 37ºC for 6 months	- µTBS test	- As a standard procedure to durable bond to zirconia both mechanical (tribochemical silica coating) and chemical (silane/ MDP combined ceramic primers) is clinically highly recommended.

[2] DL – Dinamic Loading Cycles

I.5.2 Adhesive strength mechanical assay and microestrutural evaluation

The bonding performance of the adhesive materials can be evaluated using various methods. In general, tensile bond test (TBS) and shear bond test (SBS) have been applied. The main purpose of bond strength tests is to do a comparative evaluation of the the materials bonding fulfillment (Tagami *et al.*, 2010). It is important to refer that a bond strength value cannot be considered as a material property (van Noort *et al.*, 1989), and the results depend on experimental factors and the test methodology (Sudsangiam *et al.*, 1999). For this reason, only relative study outcomes, in the comparative sense (for example: A is better than B) are a valid basis for the results interpretation. Bond strength values can reveal valuable clinical information when gathered in a well controlled design (de Munck *et al.*, 2005). According to Kelly (1994): *"Strength values (whether from testing a monolithic specimen or a bonded specimen) simply provide insight into the stress a particular material support given the flaw size distribution"* (Kelly 1994).

Bond strength testing has been predominantly accomplished by creating specimens that are loaded to failure in either shear (SBS) or tensile (TBS) manner. Nowadays, a new approach is to load multiple test specimens from each sample in either micro-tensile (μTBS) or micro-shear (μSBS) system. Sano *et al.* introduced microtensile testing in dentistry (Sano *et al.*, 1994). The advantages and limitations of micro testing are summarized in Table 6. These test methods are based on the application of a load in order to generate stress at the adhesive joints until fracture occurs (Valandro *et al.*, 2008). Therefore, for the test to measure accurately the bond strength value between an adherent and a substrate, it is crucial that the bonding interface should be the most stressed region, regardless the method used (De Hoff *et al.*, 1995; Della Bona *et al.*, 1995). For example, the measured bond strength and the failure mode on the debonded pathway produced are dependent of flaws existing within or between materials, specimen size and geometry, material properties of each component of the bonded assembly and method of local application (Armstrong *et al.*, 2009). Smaller test specimens have lower probability of having a critical sized defect present.

Table 6. Micro-testing advantages and drawbacks (based in(Armstrong *et al.*, 2009)

	Advantages	**Drawbacks**
µTBS	More adhesive failures Less cohesive failures Measurement of higher interfacial bond strengths Means and variance can be evaluated for a single sample Permits testing irregular surfaces Permits testing of very small areas Facilitates SEM examinations for the failed bonds	Labor intensity Technical demand Dehydration potential of the smaller samples
µSBS	The specimen is only pre-stressed prior testing only by mold removal Permits testing of very small areas Means and variance can be evaluated for a single sample Facilitates SEM examinations for the failed bonds	The SBS disadvantages hold true to µSBS: Tensile stresses produced by the bending moment at load application are responsible for fracture initiation Highly non-uniform stress distribution concentrated in the substrate Measured bond strength underestimates the true stress the specimen resisted at fracture

Shear bond strength tests have been criticized for the development of a non-homogeneous stress distribution in the bonding interphases, inducing either an underestimation or a misinterpretation of the results since the failure often starts in one of the substrates and not at the adhesive zone (Valandro *et al.*, 2008). The general finding based upon Finite Element Analysis (FEA) and failure mode analysis for SBS testing remain true to μSBS methods (Table 6). Nevertheless, μSBS continues to be an especially useful test for substrates particularly susceptible to the specimen preparation effects and testing conditions of μTBS (Armstrong *et al.*, 2009). With all its' advantages, μTBS allow a better alignment of the specimens and a more homogeneous distribution of stress, in addition to a more sensitive bond strength comparison or evaluation (Betamar *et al.*, 2007). Both micro bond strength tests were used in this study to accomplish the objectives (Fig. 3).

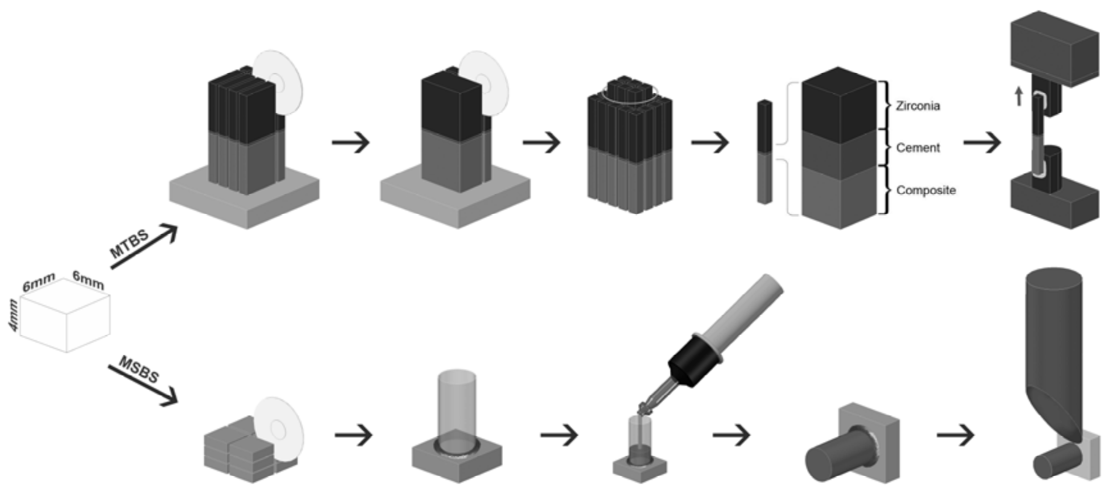

Fig. 3. Schematic representation of both micro bond strength evaluation methods used in this study.

Within the scientific community, there is no agreement concerning the appropriate usage and interpretation of these tests, and the attempts standardization have been difficult. Bond strength test remains useful and necessary for the screening of new products and study of experimental variable (Armstrong *et al.,* 2009).

II. OBJECTIVES AND JUSTIFICATION

As Y-TZP is a relatively new and innovative material there is a lot of controversy, from the scientific point of view, about the best method for optimizing and promote an effective bonding to substrates used in dentistry. A clinical problem with the use of zirconia based components is the difficulty in achieving suitable adhesion with intended synthetic substrates or natural tissues. There are special circumstances where a durable and reliable resin bond to zirconia is necessary. In these cases adhesion is difficult to achieve, and there are not clear guidelines to the clinicians to follow. It is therefore, necessary to find an adhesion protocol that is available to all clinicians to get a resin-zirconia bond with high efficiency.

The specific aims of this study were:

1. To review the literature on Y-TZP ceramics, addressing the state of the art of its recent use as implant abutment.
2. To evaluate the sandblasting particle size effect on the bond strength in the zirconia/resin interface.
3. To investigate the effect of the zirconia surface treatment with tribochemical silica coating and/or Er:YAG irradiation on the zirconia/resin interface bond strength.
4. To assess if the resin cement composition influences its bond strength to zirconia and determine the better type of cement and surface conditioning combination to provide a reliable resin/zirconia bonding.

5. To evaluate the thermocycling impact on several self-adhesive resin cements bond strength to pretreated zirconia.

Objetivos y Justificación

La circona es un material protético prometedor aunque sigue existiendo controversia científica y clínica acerca del mejor método para optimizar y promover su adhesión fiable y duradera al sustrato dentario. Dado que los mejores cementos en odontología son los cementos de resina, sería deseable conocer el mejor protocolo de adhesión entre la resina y el óxido de circonio, ya que hasta la fecha no hay unas directrices claras para el clínico rehabilitador. Esta carencia de directrices de adhesión se pone de manifiesto cuando entre los clínicos sigue existiendo una concepción muy extendida de que el circonio se puede adherir con cualquier cemento y con o sin tratamiento de superficies.

Por lo tanto los objetivos principales de este trabajo de investigación *in vitro* fueron:

1. Revisar la literatura sobre la circona, con especial enfoque al estado del arte de su reciente uso como pilar del implante.
2. Evaluar el efecto del tamaño de partícula de arenado en la fuerza de adhesión en la interfase de circona/resina.
3. Investigar el efecto del tratamiento de superficie de la circona con recubrimiento triboquímico de sílice y/o con irradiación de Er: YAG en la fuerza de adhesión de la interfaz circona/resina.
4. Determinar si la composición de cemento de resina influye en su fuerza de adhesión al óxido de circonio y cuál es la mejor combinación de tipo de cemento y de acondicionamiento de superficie para proporcionar una adhesión fiable circona/resina.

5. Valorar el impacto del termociclado en la fuerza de adhesión de varios cementos de resina auto-adhesivos a circona pretratada.

III. ORIGINAL PUBLICATIONS

III.1 Gomes AL, Montero J. Zirconia implant abutments: A review. Med Oral Patol Oral Cir Bucal. 2011 Jan 1;16 (1):e50-5

Journal section: Oral Surgery
Publication Types: Review

doi:10.4317/medoral.16.e50
http://dx.doi.org/doi:10.4317/medoral.16.e50

Zirconia implant abutments: A review

Ana-Luísa Gomes [1], Javier Montero [2]

[1] Postgraduate in Dentistry. Department of Surgery. University of Salamanca. Spain
[2] Tenured Lecture Professor in Prosthodontics. Department of Surgery. University of Salamanca. Spain

Correspondence:
Department of Surgery.
University of Salamanca.
C/ Alfonso X el Sabio. S/N.
Campus Unamuno.
37007. Salamanca. Spain.
javimont@usal.es

Received: 21-12-2009
Accepted: 23-04-2010

Gomes AL, Montero J. Zirconia implant abutments: A review. Med Oral Patol Oral Cir Bucal. 2011 Jan 1;16 (1):e50-5.
http://www.medicinaoral.com/medoralfree01/v16i1/medoralv16i1p50.pdf

Article Number: 16951 http://www.medicinaoral.com/

eMail: medicina@medicinaoral.com
Indexed in:
Science Citation Index Expanded
Journal Citation Reports
Index Medicus, MEDLINE, PubMed
Scopus, Embase and Emcare
Indice Médico Español

Abstract
Objectives: An increasing aesthetic demand within developed populations conducted to the fabrication of metal-free restorations and to a wide use of ceramic materials, due to its excellent characteristics of biocompatibility and aesthetics. With the incessant increase of commercial labels involved in this technological advance, a review is imposed on ceramic abutments, specifically on zirconia. We made a search of articles of peer-reviewed Journals in PubMed/ Medline, crossing the terms "Dental Abutments", "Dental Porcelain" and "Zirconia". The review was divided by subtopics: zirconia physical and mechanical properties, precision fit in the implant-abutment interface, zirconia abutments strength and, finally, bacterial adherence and tissues response. Several studies demonstrate that zirconia abutments offer good results at all the levels but relevant issues need further studies and evaluation. One of the most important is the clinical long term success of zirconia abutments on implants, given that in the literature there are no sufficient in vivo studies that prove it.

Key words: *Zirconia, dental ceramics, implant abutment.*

Introduction
The anterior sector rehabilitation with dental implants is a clinical challenge. One of the most challenging scenarios for the dental practitioner is to give answer to the patient expectations with a good result of the implant integration and excellent esthetical crown incorporation in the dental arch.
The use of osteo-integrated dental implants, with an history of confirmed success and long term following of the patient, propelled dentistry to a new era that involve more and more clinicians and investigators interested all over the world. A high esthetical demand lead to the fabrication of metal free restorations that allow better results in aesthetically compromised areas. Ceramic materials are being highly used in Odontology due to its ideal properties of biocompatibility and aesthetics.
Since there is a never-ending increase in the number of enterprises that develop zirconia abutments, but the scientific studies valuing its clinical success are rare, this review is relevant to access the state-of-art.

Material and Methods
A bibliographic review was made in peer-reviewed journals in PubMed /Medline. Initially a simple search was made with the keywords "zirconia implant abutment", which was lengthened with the sequence:

"Dental abutments" [Mesh] AND "Dental Porcelain" [Mesh] AND zirconia. The publication period was the last twenty years and only articles in English were considered. A review of related articles was also made, selecting the articles considered of interest within the previously chosen manuscripts. Within the search results, the articles were divided by subtopics: zirconia physical and mechanical properties, precision fit in the implant/abutment interface and finally, bacterial adherence and tissue response to zirconia abutments.

Results

In the first search the results were insufficient, only 8 articles in peer-reviewed journals in PubMed, so we made a new search crossing Mesh terms and reviewing some related articles. The results of this search were 20 articles that included bibliographic reviews, in vitro and in vivo studies and case reports. The most relevant contributions of these studies are presented in Tables 1 and 2.

Discussion

Historically implant abutments were manufactured in metal. To fulfil the esthetical demand of dentists and patients, pre-fabricated or custom abutments of different metals were designed. The use of titanium abutments prevents the occurrence of galvanic and corrosive reactions in the implant/abutment interface, which enhances the peri-implant soft tissues health due also to its high biocompatibility. However, excessive oxidation of titanium at ceramic melting temperatures and the low adhesion of the oxides to the surface of this material may be a problem in the titanium/porcelain systems. Metal abutments only solve partially the esthetical, functional and hygienic questions fundamental to the restorations over implants success (1).

The soft tissue discoloration in the cervical third of the implant anterior portion of the restorations can result in the visibility, by transparency, of the abutment material over the implant. The presence of a greyish gum can be due to a thin gingival tissue around the abutment which cannot block the reflected light from the metallic abut-

Table 1. Summary of the most relevant studies reviewed.

AUTHORS AND YEAR	TYPE OF STUDY	CONCLUSIONS
Piconi and Maccauro, 1999 (10)	Review	Review about zirconia biophysical and biomechanical properties, giving relevance to its biocompatibility.
Manicone *et al*, 2007 (11)	Review	Different uses of zirconia as a material used in Odontology due to its properties.
Andersson *et al*, 1999 (5)	PS[1] and CS[2] in vivo	There was a good cumulative survival rate of the zirconia abutments. Bone loss was higher in the titanium abutments than when using the Zirconia ones.
Andersson *et al*, 2003 (6)	PS and CS in vivo	Good results, stable aesthetical and functionally using abutments CerAdapt, can be obtained in the support of small bridges.
Glauser *et al*, 2004 (14)	PS in vivo	During 4 years there were no fracture of the experimental zirconia abutments used in the study.
Vigolo *et al*, 2006 (13)	CS in vitro	All the tested groups had satisfactory results concerning the adaptation in the interface implant/abutment. The best values were obtained in the titanium and zirconia groups.
Yildirim *et al*, 2003(7)	CS in vivo	Zirconia ceramic abutments withstood fracture loads more than twice as higher as those recorded for Alumina ones.
Att *et al*, 2006 (3)	CS in vitro	With a similar method of the study above mentioned from Yildirim et al (7) the results were very different, probably due to the artificial aging of the specimens.
Gehrke *et al*, 2006(18)	CS in vitro	Loosening torque registered only slightly decrease after the 80000 loading cycles in the zirconia abutments tested.
Scarano *et al*, 2004*(20)*	In vivo and in vitro studies	Zirconia accumulates less quantity of bacterial plaque than titanium; this colonization is also less pathogenical in the zirconia disc.
Rimondini *et al*, 2002*(19)*		

1 Prospective Study
2 Comparative Study

Table 2. Summary of recent relevant in vitro studies.

ARTICLE AND YEAR	IMPLANT ABUTMENTS STUDIED	METHODS	RESULTS/ DISCUSSION	CONCLUSION
Yldirim et al, 2003 (7)	CerAdapt[1] (Alumina) Wohlwend Innovative[2] (Zirconia)	Static Load of 5 N at a cross-head speed of 0.1 mm/s over ceramic crows luted to the abutment until rupture	Higher fracture loads to Zirconia group. Fracture analysis revealed that the fatal crack emanated primarily from the cervical part of the abutments near the platform of the dental implant. Zirconia abutments showed an inhomogeneous fracture pattern.	Zirconia ceramic abutments withstood fracture loads more than twice as higher as those recorded for Alumina ones. Both groups withstood an appropriated fracture load for use on anterior dental implants.
Butz et al, 2005 (16)	ZiReal[3] (external hex of Ti) CerAdapt (Alumina) GingiHue[4] (titanium)	1,2 million cycles of thermo mechanical fatigue in a computer-controlled dual axis chewing simulator.	Fracture strength after static loading of the artificially aged specimens was significantly higher for ZiReal than CerAdapt abutments. ZiReal performed similar to titanium abutments.	Titanium-reinforced zirconia abutments can be recommended as an esthetic alternative for the restoration of single implants in the anterior region.
Att et al, 2006 (3)	Esthetic Abutment (Titanium) Esthetic Alumina Abutment Esthetic Zirconia Abutment All from Nobel Biocare AB	1,2 million cycles of thermo mechanical fatigue in a computer-controlled dual axis chewing simulator. Compressive loading at an angle of 130º to the horizontal axis	All the specimens survived to the chewing simulator The highest median fracture value occurred in the titanium group, followed by zirconia and finally alumina groups. The abutments failed in proximity to the implant interface	All the 3 abutments have the potential to withstand physiologic occlusal forces applied in the anterior region
Gehrke et al, 2006 (18)	Straight Cercon zirconium implant abutment [5]	5 million loading cycles at 15 Hz with loads between 100-450 N, compressive load 30º off the axis of the implant	The abutments showed fracture strength superior for the maximum reported in anterior bite force. Removal torque slightly occurred after cyclic loading and screw loosening did not occur.	Cercon abutments can safely be used in the incisor region of the maxilla and mandible, while caution is recommended in the molar regions.
Sundh and Sjögren, 2008 (17)	Denzir M (Mg-PSZ) Denzir (Y-TZP)[6] Titanium abutment	Static load (compressive) perpendicular at the long axis (until the force was 1% below the highest level recorded during the test)	Fractures were observed in close proximity to the implant/abutment interface. Bending resistance of the ceramic specimens was equal or superior to the titanium control.	The combination of ceramic abutments and copies exceeded the reported value for the maximal incisal bite force (300N).
Aramouni et al, 2008 (2)	ZiReal synOcta Ceramic Blanks[7] UCLA (titanium)	Static load at an angulation of 45º to the longitudinal axis of the crown until fracture	The ZiReal abutment load fracture resistance was comparable to the UCLA abutment	The mean load-to-fracture of all the groups was well above the reported normal maximal incisal load range.
Adatia et tal, 2009 (15)	Zirconia Abutments Astra Tech[8]	Vertical load until fracture (abutments inclined 30º to the vertical)	Preparation of the abutments without fracture. During the testing procedures all screws became loose. All the abutments fractured at the abutment/analog interface.	The preparation of the abutments did not adversely affect the fracture strength of the abutments. The weakest point of the abutment seemed to be the abutment/analog interface.

1 CerAdapt; Nobel Biocare, Gotemborg, Sweden
2 Wohlwend Innovative; Zurich, Switzerland
3 ZiReal; 3i/Implant Innovations, Palm Beach Gardens, FL, USA
4 Gingi Hue; 3i/Implant Innovations, Palm Beach Gardens, FL, USA
5 Dentsply/ Friadent; GmbH
6 Denzir and Denzir M, 3i/Biomet, Palm Beach Gardens, FL, USA
7 synOcta ® Ceramic Blanks abutments; 3i/Implant Innovations, Palm Beach Gardens, FL, USA
8 Astra Tech, Inc., Waltham, MA

ment (2-4). The fabrication of ceramic abutments was developed to overcome this limitation of conventional abutments.
Due to the zirconia mechanical properties it was suggested its use as implant abutments. The first ceramic abutments were the CerAdapt™ (Nobel Biocare, Goteborg, Sweden) made of alumina and designed to fit the extern hexagon of Brånemark implant type (5).
Andersson et al in 1999 (5) evaluated the short and long term clinical function of CerAdapt™ abutments. They inserted 105 implants in 32 patients of 3 clinics. After two years, the cumulative survival rate was of 97.1% for the implants, and 97.2% for the restorations over the implants (94.7 % for ceramic abutments and 100% for titanium abutments). In all the cases the peri-implant mucosa was stable; nevertheless there was a higher loss of marginal bone around the titanium abutments (0.4 mm) than around the ceramic ones (0.2 mm). The authors found that the results were encouraging for the use of ceramic abutments.
In 2003, the results of the long term study showed that in 5 years, the cumulative rate of success was of 97.2% (94.7% for ceramic abutments and 100% for the titanium abutments) (6). The authors concluded that the ceramic abutments CerAdapt™ had liable results aesthetical and functionally to support short span fixed prostheses.
A recent in vitro investigation (7) studied the fracture strength of alumina and zirconia abutments restored with ceramic crowns (IPS Empress). Although both resist the values established in the literature as maximum load in the incisal bite (90-370 N), the zirconia abutments results were more than twice than the alumina abutments strength (7). The use of zirconia abutments is well documented in the literature with several case reports of its clinical success (8, 9). Zirconia mechanical properties are the best ever reported for dental ceramics. This can allow the production of posterior fixed partial dentures (FPD) and a decrease of the thickness of the crown core.

- Physical and Mechanical properties of zirconia

Zirconia is a polymorphic crystal that can be found in 3 crystallographic forms: monoclinic (M), cubic (C) and tetragonal (T). The zirconia is monoclinic at room temperature, being stable till 1170º C, above this temperature it becomes tetragonal and, over 2370º C, passes to the cubic phase, this is stable until the melting point at 2380º C is reached (10). During cooling, a tetragonal-monoclinic (T-M) transformation takes place in a temperature range of about 100º C below 1070º C. This transformation phase is associated to a volume expansion of about 3-4 %. The stress generated in the expansion originates fractures that after sinterization (between 1500-1700º C) are able of break in peaces the zirconia at room temperature (10, 11).
The addiction of stabilizing doping agents like CaO, MgO, CeO and Y2O3 to the pure zirconia allows the production of multiphase materials known as Partially Stabilized Zirconia (PSZ) which microstructure consists generally, at room temperature, in a cubic zirconia matrix with tetragonal and monoclinic zirconia precipitates in a minor phase (10).
Garvie et al in 1975, reviewed by Manicone (11), demonstrated how to obtain the better phase transformation in PSZ, improving zirconia mechanical strength and toughness. They observed that tetragonal metastable precipitates finely dispersed within the cubic matrix were able to be transformed into the monoclinic phase, when the constraint exerted on them by the matrix was relieved, that is by a crack advancing in the material. In that case, the stress field associated with expansion due to the phase transformation acts in opposition to the stress fields that promotes the propagation of the crack. An enhancement in toughness is obtained, because the energy associated with crack propagation is dissipated, both in the tetragonal—monoclinic transformation and in overcoming the compression stresses due to the volume expansion. The authors stabilized zirconia with 8% mol of MgO. In this model, where the zirconia properties were rationalized, the authors mention this material as "ceramic steel".
PSZ can be obtained with the system ZrO2-Y2O3 or with ZrO2- CeO2, in this system is possible to do ceramics, at room temperature, with only tetragonal phase called TZP (tetragonal zirconia polycrystals). Both systems are abbreviated to Y-TZP and Ce-TZP respectively (11).
This material with 2-3% mol Y2O3 (3Y-TZP), is composed by tetragonal grains sized in nanometres. Above a critical grain size, the 3Y-TZP is less stable and more favourable to the spontaneous transformation T-M, so to a smaller grain size (< 1 μm) is associated a smaller rate of transformation. The tetragonal phase, at room temperature, depends in grain size, yttrium content and the compression of the matrix around the grains, conditioning, in this way the mechanical properties of the TZP (10).

- Precision fit in the interface Implant/ Abutment

The adjustment between implants and the implant-supported prosthesis has been described as a relevant factor in stress transference, biological answer of peri-implant tissues and in complications of the prosthetic restoration. The adjustment between the external hexagon of implant and the internal hexagon of the abutment will have to allow less than 5º of rotational movement to maintain the screw union stable, this value was established by Binon in 1996 and reviewed by Garine et al in 2007 (12).
The vertical or horizontal misalignment applies extra loads to the different restoration components, to the implant and to the bone causing: loosening of the prosthe-

sis retention, abutment fractures, bone microfractures, lost of crestal bone and osteointegration lost.

Vigolo et al in 2006 (13) studied the rotational freedom of Procera abutments made in different materials: titanium, alumina and zirconia. The values registered for the three types of abutments were consistently demonstrated as inferior to 3º. Nevertheless, the groups of titanium and zirconia did not have significant differences, being their values significantly inferior to those of the group of the alumina abutments (13).

In 2007, Garine et al (12) analyzed the rotational misalignment between abutments and implants. All the groups obtained values inferior to 5º and significantly different average values among them. The groups of totally ceramic abutments had a superior rotational misalignment when compared with the ceramic abutments with a metallic ring (12).

Finally, there are also authors who consider that the zirconia abutments can be the cause of wearing down and abrasion of the connection metallic part, thus, as a result of positioning/removal of the zirconia abutments during their individualization, we can originate smoothing of the corners of the external hexagon, for example (6).

- *Zirconia abutments strength*

In order to consider them as a viable alternative, the ceramic abutments must display mechanical and biological qualities identical or superior to those of universally used titanium abutments. The strength values of the abutments will have to be superior to the registered maximum values for the anterior sector that can fluctuate between 90-370 N. In a prospective study of 4 years, with experimental zirconia abutments placed directly on an implant of external hexagon, abutments fractures were not registered (14).

In 2003, Yildirim et al. (7) studied the fracture resistance of different materials abutments covered by Empress Crowns, when subjected to static loads. They registered that zirconia abutments obtained values more than twice higher than the alumina ones. Both materials revealed a resistance able to bear incisal forces documented in the literature.

Att et al (3), in a similar study, achieved disrupting results with the study of Yildirim et al (7). They found a similar strength between zirconia and alumina abutments. Authors justify their results with the fact that, in this study, the abutments were subjected to artificial aging. Both studies previously mentioned, consider the cervical part of the abutment as the higher stress concentration area after the torque generated by the screwing (3, 7).

In a recent study, Adatia et al. (15) proceeded with an in vitro study to assess the effect of different degrees of zirconia abutments clinical reduction, and their resistance to fracture, submitted to clinical similar conditions. When original zirconia abutments (without clinical reduction) were tested, they fractured in the cervical region, such as stated in other studies (3, 7), in the adjacent region to the gold screw and the platform of the implant, for all this the design of the interface implant/pillar seems to have a main paper in the fracture mode (7, 15). The zirconia abutments registered values of strength at least 15% higher than the anterior bite force, and it was checked that the abutments preparation did not affect adversely their resistance to the fracture (15).

In Butz et al work (16), was compared the fracture strength, rate of survival and way of failure of the ceramic abutments. The authors concluded that after being under the mastication simulator and static loads, the strength of the zirconia abutments was comparable to those of titanium (281N versus 305N) (2, 16), being the rate of fracture also similar to the titanium abutments one. Thus, the authors recommend zirconia abutments as an alternative for restoration of unitary implant rehabilitations in the anterior region.

Sundh and Sjögren in 2008 (17) studied the flexion strength of the zirconia abutments when is used a cantilever structure. The results demonstrate that the flexion strength of the zirconia abutments is greater or similar to the titanium abutments that were the control group (17).

According to Gehrke et al (18) the zirconia abutments under static load exhibited maximum fracture values of 672 N, being manifestly smaller (269 N) after 80000 cycles, supporting loads that exceed the established maximum values of force at incisal level. In addition loosening torque was evaluated, that decreased very slightly at the end of the cycles and the total loosening was not observed (18).

In conclusion, the majority of the studies consider that the ceramic abutments failure is more frequent in the cervical region, very close to the interface implant/abutment (2, 3, 15-17).

- *Bacterial adherence and response of the tissues*

Dental implants require a biological sealing to inhibit the epithelial recession and the bacterial invasion of the sub-epithelial conjunctive tissue and of implant interfaces. It was emphasized the need of promoting the formation of an adhered gingival tissue to create a biological barrier to the bacterium migration and toxins to the biological space (19).

Zirconia is a biocompatible material that has optimal aesthetic and mechanical properties (10). The properties related to the biocompatibility of the zirconia are even better than those of titanium.

The bacterial adhesion, which is important in the maintaining of zirconia restorations without periodontal problems, was proven satisfactorily low (19, 20).

Scarano et al (20) registered a degree of bacterial coating of 12.1% in the zirconia, compared to 19.3% in the titanium. Rimondini et al (19) confirmed these results with an in vivo study in which crystals of Y-TZP accumulated fewer bacteria than titanium, in terms of total number of bacteria, but also considering their potential pathogenicity.

The protective barrier of adhered gum around the transmucosal abutments requires a nontoxic material and that enhances the adhesion and the growth of surrounding tissues. Different ideas like changing the zirconia surface topography or emergence profile had outcome in the scientific community, needing to be deeply stu-died.

Conclusions

Although zirconia abutments presented values of fracture strength not as good as conventional titanium abutments they are indicated in aesthetically compromised areas. On the other hand these abutments revealed a good adjustment in the interface with dental implants, excellent biocompatibility and good aesthetical appearance, especially in patients with unitary rehabilitations over implants with a thin gingival biotype.

Thereby several aspects remain to be studied and assessed, on top of all the long term clinical success of ceramic restorations on implants with zirconia abutments, once in the literature there are not enough in vivo studies that prove it.

References

References with links to Crossref - DOI

1. Prestipino V, Ingber A. All-ceramic implant abutments: esthetic indications. J Esthet Dent. 1996;8:255-62.
2. Aramouni P, Zebouni E, Tashkandi E, Dib S, Salameh Z, Almas K. Fracture resistance and failure location of zirconium and metallic implant abutments. J Contemp Dent Pract. 2008;9:41-8.
3. Att W, Kurun S, Gerds T, Strub JR. Fracture resistance of single-tooth implant-supported all-ceramic restorations: an in vitro study. J Prosthet Dent. 2006;95:111-6.
4. Yildirim M, Edelhoff D, Hanisch O, Spiekermann H. Ceramic abutments--a new era in achieving optimal esthetics in implant dentistry. Int J Periodontics Restorative Dent. 2000;20:81-91.
5. Andersson B, Schärer P, Simion M, Bergström C. Ceramic implant abutments used for short-span fixed partial dentures: a prospective 2-year multicenter study. Int J Prosthodont. 1999;12:318-24.
6. Andersson B, Glauser R, Maglione M, Taylor A. Ceramic implant abutments for short-span FPDs: a prospective 5-year multicenter study. Int J Prosthodont. 2003;16:640-6.
7. Yildirim M, Fischer H, Marx R, Edelhoff D. In vivo fracture resistance of implant-supported all-ceramic restorations. J Prosthet Dent. 2003;90:325-31.
8. Román-Rodríguez JL, Roig-Vanaclocha A, Fons-Font A, Granell-Ruiz M, Solá-Ruiz MF, Bruguera-Alvarez A. Full maxillary rehabilitation with an all-ceramic system. Med Oral Patol Oral Cir Bucal. 2010;15:e523-5.
9. Kollar A, Huber S, Mericske E, Mericske-Stern R. Zirconia for teeth and implants: a case series. Int J Periodontics Restorative Dent. 2008;28:479-87.
10. Piconi C, Maccauro G. Zirconia as a ceramic biomaterial. Biomaterials. 1999;20:1-25.
11. Manicone PF, Rossi Iommetti P, Raffaelli L. An overview of zirconia ceramics: basic properties and clinical applications. J Dent. 2007;35:819-26.
12. Garine WN, Funkenbusch PD, Ercoli C, Wodenscheck J, Murphy WC. Measurement of the rotational misfit and implant-abutment gap of all-ceramic abutments. Int J Oral Maxillofac Implants. 2007;22:928-38.
13. Vigolo P, Fonzi F, Majzoub Z, Cordioli G. An in vitro evaluation of titanium, zirconia, and alumina procera abutments with hexagonal connection. Int J Oral Maxillofac Implants. 2006;21:575-80.
14. Glauser R, Sailer I, Wohlwend A, Studer S, Schibli M, Schärer P. Experimental zirconia abutments for implant-supported single-tooth restorations in esthetically demanding regions: 4-year results of a prospective clinical study. Int J Prosthodont. 2004;17:285-90.
15. Adatia ND, Bayne SC, Cooper LF, Thompson JY. Fracture resistance of yttria-stabilized zirconia dental implant abutments. J Prosthodont. 2009;18:17-22.
16. Butz F, Heydecke G, Okutan M, Strub JR. Survival rate, fracture strength and failure mode of ceramic implant abutments after chewing simulation. J Oral Rehabil. 2005;32:838-43.
17. Sundh A, Sjögren G. A study of the bending resistance of implant-supported reinforced alumina and machined zirconia abutments and copies. Dent Mater. 2008;24:611-7.
18. Gehrke P, Dhom G, Brunner J, Wolf D, Degidi M, Piattelli A. Zirconium implant abutments: fracture strength and influence of cyclic loading on retaining-screw loosening. Quintessence Int. 2006;37:19-26.
19. Rimondini L, Cerroni L, Carrassi A, Torricelli P. Bacterial colonization of zirconia ceramic surfaces: an in vitro and in vivo study. Int J Oral Maxillofac Implants. 2002;17:793-8.
20. Scarano A, Piattelli M, Caputi S, Favero GA, Piattelli A. Bacterial adhesion on commercially pure titanium and zirconium oxide disks: an in vivo human study. J Periodontol. 2004;75:292-6.

III.2 Gomes AL, Oyagüe RC, Lynch CD, Montero J, Albaladejo A. Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. J Dent. 2012; 41:31-41

journal of dentistry xxx (2012) xxx–xxx

Available online at www.sciencedirect.com
SciVerse ScienceDirect
ELSEVIER
journal homepage: www.intl.elsevierhealth.com/journals/jden

Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks

Ana Luísa Gomes [a], *Raquel Castillo-Oyagüe* [b,*], *Christopher D. Lynch* [c], *Javier Montero* [a], *Alberto Albaladejo* [a]

[a] *Department of Surgery, Faculty of Medicine, University of Salamanca (USAL), C/Alfonso X el Sabio, s/n, Campus de Unamuno, 37007 Salamanca, Spain*
[b] *Department of Buccofacial Prostheses, Faculty of Dentistry, Complutense University of Madrid (UCM), Pza. Ramón y Cajal, n° 3, 28040 Madrid, Spain*
[c] *Tissue Engineering and Reparative Dentistry, School of Dentistry, Cardiff University, Cardiff, UK*

A R T I C L E I N F O

Article history:
Received 19 July 2012
Received in revised form
18 September 2012
Accepted 21 September 2012

Keywords:
Zirconia
Ceramic surface treatment
Airborne particle abrasion
Dual-cure resin cements
10-MDP
Self-adhesive resin cements

A B S T R A C T

Objectives: To evaluate the effect of the particle size of sandblasting and the composition of the resin cement on the microtensile bond strength (MTBS) to zirconia.

Methods: Forty zirconia blocks (Cercon, Dentsply) were polished and randomly treated as follows: Group 1 (NT): no treatment; Group 2 (APA-I): airborne particle abrasion (Cobra, Renfert) using 25-μm aluminium-oxide (Al_2O_3)-particles; Group 3 (APA-II): APA with 50-μm Al_2O_3-particles; and Group 4 (APA-III): APA using 110-μm Al_2O_3-particles. Ceramic blocks were duplicated in composite resin. Samples of each pretreatment group were randomly divided into two subgroups depending on the resin cement used for bonding the composite disks to the treated zirconia surfaces. Subgroup 1 (PAN), which was a 10-MDP-containing luting system, used Clearfil Ceramic Primer plus Panavia F 2.0 (Kuraray) and Subgroup 2 (BIF) used Bifix SE (VOCO) self-adhesive cement. After 24 h, bonded specimens were cut into 1 ± 0.1 mm^2 sticks. MTBS values were obtained using a universal testing machine (cross-head speed = 0.5 mm/min). Failure modes were recorded and the interfacial morphology of the debonded microbars was SEM-assessed. Two-way ANOVA, Student–Newman–Keuls tests, and the step-wise linear regression analysis were performed with the MTBS being the dependent variable ($p < 0.05$).

Results: Despite the sandblasting granulometry, PAN bonded to air-abraded surfaces attained the highest MTBS and frequently showed mixed fractures. BIF recorded no significant differences in MTBS depending on the conditioning method, and registered the highest rates of premature and adhesive failures.

Conclusions: The 10-MDP-containing luting system seems to be the most suitable to bond zirconium-oxide ceramic, mainly after sandblasting.

* *Corresponding author*. Tel.: +34 607367903; fax: +34 913942029.
E-mail address: raquel.castillo@odon.ucm.es (R. Castillo-Oyagüe).
0300-5712/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jdent.2012.09.013

1. Introduction

Sintered zirconia CAD/CAM ceramic has become a suitable alternative to dental alloys as framework material for all-ceramic fixed rehabilitations because of its non-metallic colour and exceptional fracture resistance (higher than 1000 MPa). It has demonstrated long-term success in all positions of the dental arch in a wide variety of clinical situations, such as monolithic prostheses without overlying porcelain, or more aesthetic cases with veneering ceramic layered onto the zirconia substrate.[1,2]

However, luting zirconia still presents a challenge, and a standardized adhesive cementation protocol for zirconia-based restorations is not yet available.[3] Zirconia (ZrO_2) is a silica-free, polycrystalline ceramic that does not contain amorphous silica (SiO_2), which makes it resistant to traditional glass-etching treatments, such as hydrofluoric acid (HF_l) followed by silane.[4,5]

Concerning the conditioning systems, several innovative ceramic surface treatments have been suggested to overcome this issue, including: (1) sandblasting or airborne particle abrasion (APA)[6,7]; (2) silica[8] and multi-phase glaze[9]; and (3) CO_2, Er:YAG- and Nd:YAG-laser irradiation.[10,11] All of these methods enhance the micromechanical retention between CAD/CAM ceramics and luting agents, as rough surfaces have wider contact areas and microporosities.[11–13] Despite the excellent results achieved with the Nd:YAG laser,[12] recent research has shown air-abrasion to be more effective than the Er:YAG laser for obtaining microretentive zirconia surfaces. In contrast to other mechanical methods, like grinding, which may cause substantial strength degradation, sandblasting has proven to strengthen zirconia ceramics[14] and improve bonding.[7] Nowadays, APA, which may be applied chair-side, has become the most popular conditioning method for treating the zirconia surfaces.

The cross-section of the aluminium-oxide microspheres employed for sandblasting in previous experiments usually ranges between 50 μm and 125 μm,[7,10,11,13,15–18] with the 50-μm and 110-μm particles being the most commonly used.[7,10,11,13,15,16] However, such granulometries are not based on scientific evidence, but on empirical data, as no study has been found that compared the effect of different sizes of air-abrasion alumina particles on the microtensile bond strength between resin cements and zirconia dental ceramic.

However, achieving a chemical adhesion at the cement/ceramic interface may be essential for successful bonds. Recent investigations have reported that cement selection is the most important factor for luting zirconia.[17,18] Although conventional cements may be used for full-coverage zirconia-based restorations, there are special circumstances where a long-term bond to zirconia is required, such as compromised retention (*i.e.*, short abutment teeth), veneers, and bonded fixed partial dentures (FPDs).[19] In such cases, dual-cure resin cements may be the best choice, although the adhesive capability of luting materials lies behind their chemical composition and content of functional phosphate monomers, priming conditions, silanization, setting reaction, and other physical and biological properties.[17–22] This may help predict their clinical performance and determine their indications and limitations in contemporary prosthodontics.

Therefore, the aim of this study is to evaluate the effect of the sandblasting granulometry and the composition of dual-cure resin cements on the microtensile bond strength to zirconia surfaces.

The null hypothesis affirms that neither the particle size of sandblasting nor the presence of functional phosphate monomers in the resin cement composition influences the bond strength at the cement/zirconia interface.

2. Materials and methods

2.1. *Sample preparation: ceramic surface treatment and luting procedure*

Forty cylinder-shaped (Ø 19.5 mm × 10.25 mm high) zirconia sintered CAD/CAM blocks (Cercon Zirconia, Dentsply, Konstanz, Germany) were selected for the study.

Composite cylinders (Ø 19.5 mm × 4 mm high) were obtained by duplicating the ceramic blanks using a mould constructed with silicon-impression material (Express, 3M/ESPE, Seefeld, USA). One composite disk was obtained for each ceramic block.

Each composite sample was made inside the mould by layering 2 mm-thick increments of a microhybrid composite resin (Tetric EvoCeram, Ivoclar-Vivadent, Schaän, Liechtenstein). Composite layers were condensed with a clean plastic filling instrument to avoid contamination, and light cured for 40 s (QTH, XL 3000, 3M/ESPE, St. Paul, MN, USA; light intensity: 500 mW/cm^2, distance 0 mm) until the build was completed. The last increment was compressed with a glass microscope slide to obtain a flat surface. After removing each composite disk from the mould, an additional 40 s polymerisation was performed on the areas that were previously in contact with the impression material.[17,18]

The bonding surfaces of the zirconia blocks were polished with 600-grit silicon carbide paper on a rotating device under water-cooling. The ceramic cylinders were numbered from 1 to 40 and randomly assigned to four groups ($n = 10$ each) by using specific software (Random Allocation Software 2.0, Microsoft Corporation, WA, USA). The program was ran by setting the sample size ($n = 40$), the number of groups ($n = 4$) and the name of each group according to the tested ceramic pre-treatments. The "simple method" was chosen and a randomized list of numeric unique identifiers (UI) was produced by the software,[23] thus obtaining the following study groups: Group 1 (NT): no treatment; Group 2 (APA-I): airborne particle abrasion (Cobra, Renfert GmbH, Hilzingen, Germany) using 25 μm aluminium-oxide (Al_2O_3)-particles; Group 3 (APA-II): APA with 50 μm Al_2O_3-particles and Group 4 (APA-III): APA using 110 μm Al_2O_3-particles. In groups 2–4, air-abrasion was applied for 20 s at 0.25 MPa and 10 mm of distance, following the manufacturers' instructions. A master dental sandblaster machine having a regulator that can be adjusted on the inside and a filter for compressed air to ensure ideal blasting was utilized (Basic Master, Renfert GmbH, Hilzingen, Germany).

After surface conditioning, all of the ceramic and composite specimens were cleaned ultrasonically in 96% ethanol at room temperature (23.0 ± 1.0 °C) for 2 min and gently air-dried

Please cite this article in press as: Gomes AL, et al. Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. Journal of Dentistry (2012), http://dx.doi.org/10.1016/j.jdent.2012.09.013

Table 1 – Chemical composition and application mode of the materials tested.

Material type	System	Manufacturer	Main components (according to manufacturers)	Manipulation sequence (at room temperature of $23 \pm 1\,^{\circ}C$)
CAD/CAM ceramic	Cercon Zirconia *Batch No. 51247*	Dentsply, Germany	Zirconium-oxide (92%), yttrium-oxide (5%), hafnium-oxide (<2%), aluminium-oxide + silicon-oxide (<1%)	Sinter the ceramic cylinders in a special oven (Cercon Heat, Dentsply) keeping the temperature at 1350 °C for 6 h
Airborne particle abrasion	Cobra *Batch No. 1594-115 (25 μm); 1594-1205 (50 μm); and 1583-1005 (110 μm)*	Renfert GmbH, Hilzingen, Germany	Precious corundum (Al_2O_3) of different particle sizes: 25 μm, 50 μm, and 110 μm	Sandblasting for 20 s at 0.25 MPa and 10 mm of distance
Dual-cure resin cements	Bifix SE *Batch No. 1023271*	VOCO GmbH, Cuxhafen, Germany	*BiFix SE base*: Bis-GMA, UDMA, acidic phosphate monomers, glycerindimethacrylate, benzoyl peroxide, aerosol silica, hydroxypropylmethacrylate, catalysts, initiators, stabilizers, glass fillers *(70 wt%)* *Bifix SE catalyst*: UDMA, glycerindimethacrylate, catalysts, initiators	Dispense the cement from a dual-barreled automix syringe and a spiral mixing tip. Apply the cement on the ceramic surface. Remove excess after luting the composite disk under pressure. Self-cure for 5 min and light-cure each axial surface for 40 s
	Panavia F 2.0 *Batch No. 41244*	Kuraray Ltd., Osaka, Japan	*Clearfil Ceramic Primer*: 3-MPS, 10-MDP, ethanol *Panavia F 2.0 Cement Paste AU*: 10-MDP, hydrophobic and hydrophilic aliphatic dimethacrylate, silanated silica, silanated barium, silanated colloidal silica, dl-camphorquinone, benzoil peroxide, poliethoxy dimethacrylate, *catalysts, initiators *Panavia F 2.0 Cement Paste BU*: hydrophobic and hydrophilic aromatic dimethacrylate, silanated barium silanated titanium oxide, sodium fluoride, bisphenol A, poliethoxy dimethacrylate, colloidal silica, diethanol-p-toluidine, sodium 2,4,6-triisopropyl benzene sulfinate, *catalysts, accelerators, pigments **Catalysts: Bis-GMA, TEGDMA; fillers: 76.9 ± 0.23 wt%)*	Apply the Clearfil Ceramic Primer on the zirconia bonding surface for 40 s. Gently air dry. Mix equal lengths of Paste A and B for 10 s until a uniform colour is achieved and apply the mixture on the ceramic surface. Remove excess after luting the composite disk under pressure. Self-cure for 5 min and light-cure each axial surface for 40 s
Composite resin	Tetric Evo Ceram *Batch No. H34328*	Ivoclar-Vivadent, Liechtenstein	Matrix: dimethacrylates *(17–18 wt%)*. Fillers: barium glass, ytterbium trifluoride, mixed oxide and prepolymer *(82–83 wt%)*, additives, catalysts, stabilizers and pigments *(<1 wt%)*	Condense 2 mm-thick layers. Light-cure each increment for 20 s

Abbreviations: Bis-GMA: bisphenol A glycidyl methacrylate; UDMA: urethane dimethacrylate; 3-MPS: 3-methacryloxypropyl trimethoxysilane; 10-MDP: 10-methacryloxydecyl dihydrogen phosphate; TEGDMA: triethylene glycol-dimethacrylate.

prior to cement application.[21] No side effects of sandblasting, such as like starting crack propagation, was identified in any sample.

The zirconia cylinders from each surface treatment group were renumbered from 1 to 10 and randomly divided into two subgroups ($n = 5$ each). The ''simple method'' of randomization was applied using the abovementioned system software (Random Allocation Software 2.0).[23] The sample size of each treatment group ($n = 10$), the number of subgroups ($n = 2$) and the name of each subgroup depending of the luting system were programmed. As a result, four randomized lists of numeric UI allowed configuring the next subgroups: Subgroup 1 (PAN), which was a 10-MDP (10-methacryloloxydecyl dihydrogen phosphate)-containing

Please cite this article in press as: Gomes AL, et al. Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. Journal of Dentistry (2012), http://dx.doi.org/10.1016/j.jdent.2012.09.013

luting system, used Clearfil Ceramic Primer (Kuraray Medical Ltd., Osaka, Japan) plus Panavia F 2.0 dual-cure resin cement (Kuraray Medical Ltd.); and Subgroup 2 (BIF) used non 10-MDP-containing self-adhesive Bifix SE dual-cure resin cement (VOCO GmbH, Cuxhafen, Germany). All of the materials were handled following the manufacturers' instructions, at room temperature (RT: 23.0 ± 1.0 °C) and relative humidity (50 ± 5%).[17] The chemical composition and operation mode of the investigated materials are detailed in Table 1.

Ceramic-to-composite luting procedures were carried out by means of a customized metallic tool that produced a constant axial load of 1 kg (1249 MPa) to counteract the thixotropic behaviour of cements under a standardized pressure.[12] The compressive force was applied for the first 5 min, leaving the material to set in the self-curing modality. Any excess cement was removed. Finally, an additional 40 s of light irradiation (QTH, XL 3000, 3 M/ESPE; light intensity: 500 mW/cm^2) from each side of the specimens was performed to ensure an optimal polymerization. The bonded specimens were removed from the press and stored in distilled water for 24 h at 37 °C prior to microtensile testing.

2.2. Microtensile bond strength (MTBS) test

The composite portion of each bonded block was fixed with thermoplastic glue to an acrylic support that was coupled to an adapted cutting machine (Secotom 10, Struers A/S, Ballerup, Denmark). Next, each zirconia-composite set was sectioned vertically into 1 mm-thick slabs using a slow-speed diamond saw under water-cooling. The first cut was disregarded because the results could be influenced by an excess or absence of resin cement at the interface. The support was rotated 90° and perpendicular cuts of ±1 mm thick were performed. The samples obtained from the first perpendicular slab were also disregarded for the above-mentioned reason.[22] The sticks selected for the study had the following characteristics: untrimmed, nearly symmetric squared with a cross-sectional area of 1.0 ± 0.1 mm^2, and 10 mm long.[22] Only the internal microbars were used for microtensile testing (Fig. 1). Twenty beams were obtained per experimental subgroup.

The extremities of each stick were bonded with cyanoacrylate glue (Zapit, Dental Ventures of America, Corona, CA, USA) parallel to the long axis of an adapted assembly to minimize the bending forces in the adhesive zone during the microtensile test.[24] This set (device with specimen) was attached to a universal testing machine (AGS-X, Shimadzu High Precision Testing Machine, Kyoto, Japan) and loaded in tension until failure at a cross-head speed of 0.5 mm/min.[11] The area of the debonded ceramic surfaces was measured using a pair of digital callipers. The microtensile bond strength was calculated in MPa according to the formula $MTBS = L/A$, where L is the load in the moment of rupture (Kgf) and A is the bonding area of the sample (mm^2).[24]

2.3. Scanning electron microscopy (SEM) evaluation

Five representative fractured sticks from each experimental subgroup were rinsed with 96% ethanol, mounted on metallic stubs, and sputter-coated with 10 nm particles of platinum in a SEM coating unit (Polaron E5100, Quorum Technology, Hertfordshire, England, UK). The micromorphology of the debonded surfaces was subsequently evaluated under a scanning electron microscopy (DSM-940, Karl-Zeiss, Oberkochen, Germany) at different magnifications (from 50× to 500×) and an accelerating voltage of 20 kV.[11,12] The surface topography of differently pre-treated zirconia surfaces was also studied under SEM at 400× magnification.

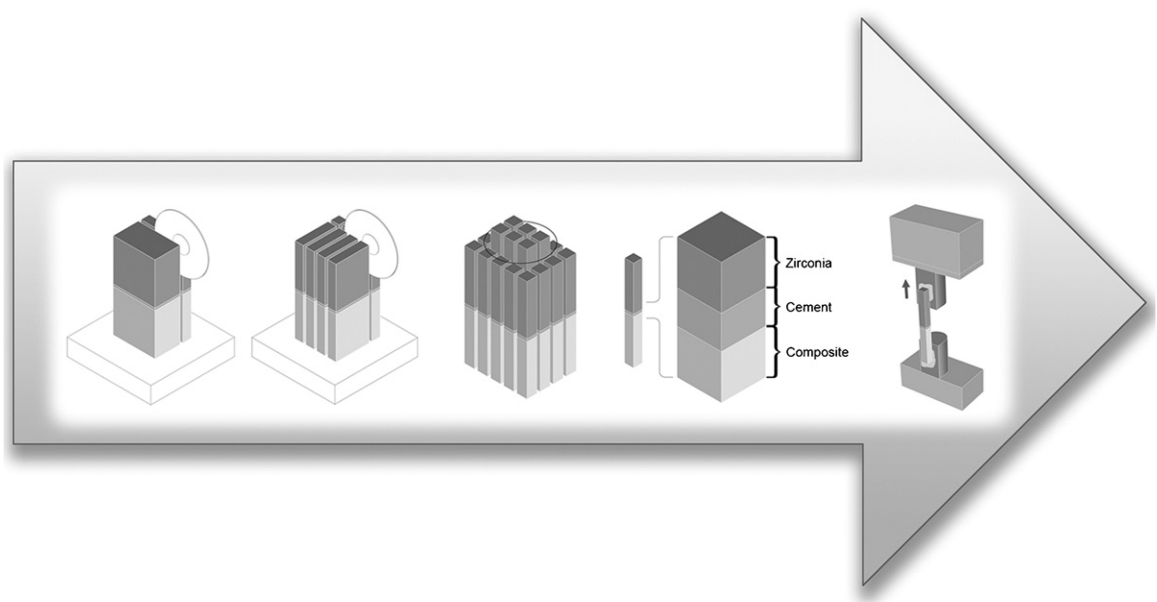

Fig. 1 – Schematic images of the cutting procedure and the microtensile test: (1) Slice cut from the cemented block. (2) Perpendicular cuts performed after rotating the basis 90°. (3) Internal sticks obtained and used in this study. The outer specimens were disregarded. (4) Microbar composition. (5) Sample fixed to the universal testing machine for microtensile testing.

Please cite this article in press as: Gomes AL, et al. Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. Journal of Dentistry (2012), http://dx.doi.org/10.1016/j.jdent.2012.09.013

Table 2 – Mean (SD: standard deviation) values of microtensile bond strength (MPa) recorded in the experimental groups.

Ceramic surface treatment	Dual-cure resin cement type	
	Panavia F 2.0	Bifix SE
	Mean MTBS (SD)*	
NT (no treatment)	9.17 (7.97)^{A,b}	0.86 (3.28)^{B,b}
APA-I (25-μm Al_2O_3-particles)	17.57 (5.27)^{A,a}	1.56 (3.74)^{B,b}
APA-II (50-μm Al_2O_3-particles)	20.18 (4.42)^{A,a}	2.27 (4.46)^{B,b}
APA-III (110-μm Al_2O_3-particles)	20.26 (5.96)^{A,a}	0.79 (2.98)^{B,b}

* Identical capital letters reveal no significant differences within the same row and different lowercase letters show significant differences within the same column ($p < 0.05$).

Failure modes of all sticks were assessed by the same trained operator under a stereomicroscope (SMZ800, Nikon Corporation, Tokyo, Japan) at 40× magnification and classified as adhesive (between ceramic and cement or at the cement/composite level), cohesive (within the cement or ceramic), or mixed (containing both adhesive and cohesive phases).[17,18]

2.4. Statistical analysis

A two-way ANOVA was applied to analyze the contributions of ceramic surface treatment and resin cement type to microtensile bond strength. Multiple comparisons were performed by the Student–Newman–Keuls test.[17] Premature failures of the beams, which occurred during handling prior to microtensile testing, were counted as ''zero bonds'' (MPa = 0).[12] A step-wise linear regression model was also estimated considering the MTBS as the dependent variable and both the surface treatment and the cement type as predictor variables.[25] All the statistical analyses were made using the Statistical Package for the Social Sciences (SPSS/PC+ v.17.0, Inc., Chicago, IL, USA), taking the cut-off level for statistical significance at $\alpha = 0.05$.[18]

The proportions of fracture patterns observed (adhesive or cohesive *versus* mixed failures, and premature *versus* functional failures) were compared by using the Chi-square test and the Odds Ratio (OR), which were expressed with a confidence interval of 95% (CI-95%).[26]

3. Results

3.1. Microtensile bond strength (MTBS) test

Means and standard deviations (SD) of MTBS are outlined in Table 2. Both the zirconia surface treatment ($p < 0.01$) and the luting agent ($p < 0.001$) influenced bond strength. Interactions were significant ($p < 0.05$).

PAN achieved significantly higher MTBS than BIF notwithstanding the ceramic surface treatment ($p < 0.001$). When using PAN, NT ceramic samples recorded lower MTBS than did zirconia sticks conditioned with APA-I, APA-II, and APA-III, which showed no significant differences to each other. Using BIF, no significant differences in MTBS were found depending on the surface conditioning method (Table 2).

BIF registered the highest rates of premature failures in the study (Table 3). The total OR = 34.6 states that premature failures occurred 34.6 times more when using BIF than when PAN was applied. Independent of the particle size, the combination of PAN and APA significantly reduces the risk of spontaneous debonding prior to microtensile testing (Chi = 40.748; $p < 0.001$) (Table 3).

The failure mode distribution is outlined in Table 4. Within the PAN subgroups, the untreated samples mainly failed adhesively, showing significant differences with respect to the sandblasted sticks, which mostly exhibited a mixed fracture

Table 3 – Comparison of the distribution of premature failures among the groups tested.

Ceramic surface treatment	Cement type				Comparison between surface treatment groups	Odds ratio premature/functional failures (CI-95%)
	Panavia F 2.0		Bifix SE			
	Premature failures (%)					
	Yes	No	Yes	No		
NT (no treatment)	38.3	61.7	91.7	8.3	Chi = 37.509 $p < 0.001$	17.7 (6.2–50.7)
APA-I (25-μm Al_2O_3-particles)	0.0	100.0	83.3	16.7	Chi = 56.250 $p < 0.001$	No sense
APA-II (50-μm Al_2O_3-particles)	0.0	100.0	76.7	23.3	Chi = 47.045 $p < 0.001$	No sense
APA-III (110-μm Al_2O_3-particles)	0.0	100.0	93.3	6.7	Chi = 74.118 $p < 0.001$	No sense
Total	15.3	84.7	86.3	13.7	Chi = 191.847 $p < 0.001$	34.6 (19.5–61.6)
	Chi = 40.748 $p < 0.001$		Chi = 9.100 $p = 0.028$			

Please cite this article in press as: Gomes AL, et al. Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. Journal of Dentistry (2012), http://dx.doi.org/10.1016/j.jdent.2012.09.013

Table 4 – Comparison of the failure mode distribution among the groups tested.

Ceramic surface treatment	Cement type				Comparison between surface treatment groups	Odds ratio adhesive/mixed failures (CI-95%)
	Panavia F 2.0		Bifix SE			
	Failure mode (%)					
	Adhesive	Mixed	Adhesive	Mixed		
NT (no treatment)	53.3	46.7	98.3	1.7	Chi = 33.149 $p < 0.001$	51.6 (6.7–397.2)
APA-I (25 μm Al_2O_3-particles)	16.7	83.3	98.3	1.7	Chi = 64.931 $p < 0.001$	295.0 (32.8–2655.4)
APA-II (50 μm Al_2O_3-particles)	23.3	66.7	93.3	6.7	Chi = 46.667 $p < 0.001$	46.0 (12.3–172.4)
APA-III (110 μm Al_2O_3-particles)	20.0	80.0	100.0	0.0	Chi = 65.455 $p < 0.001$	No sense
Total	33.3	67.7	97.5	2.5	Chi = 192.027 $p < 0.001$	78.0 (32.4–187.8)
	Chi = 18.300 $p < 0.001$		Chi = 6.154 $p = 0.104$			

pattern (Chi = 33.149; $p < 0.001$) (Table 4). No significant differences were observed among BIF samples concerning the failure mode (Chi = 6.154; $p = 0.104$). Regardless of the APA granulometry, BIF shows higher risk of adhesive failure than PAN (Table 4). This gains more expression when APA-I is performed (OR = 295.0).

The lineal regression model revealed a significant increase of 13.1–15.4 MPa in MTBS when PAN is used instead of BIF regardless of the surface treatment ($p < 0.001$). Also, for each augmented micron in the size of the Al_2O_3 particles of APA, the MTBS of PAN increases within a range of 0.024–0.052 MPa (CI-95%).

The determination coefficient ($R^2 = 0.60$) of this model implies a high predictor capacity such that 60% of the results could be envisaged by knowing the sandblasting granulometry and the luting material.

3.2. *SEM analysis*

Representative SEM micrographs of fractured beams are displayed in Fig. 2. The Fig. 2b (untreated surface), Fig. 2d (treated with APA-II), and Fig. 2f (treated with APA-III) contain mixed failures with PAN cement remnants layering on the zirconia surfaces. A large cohesive phase of PAN is visible in all cases.

The Fig. 2a (untreated surface) and Fig. 2e (treated with APA-III) show an adhesive fracture pattern with a complete detachment of the BIF luting agent from the ceramic substrate. The Fig. 2c sample (treated with APA-II), exhibits a mixed failure of BIF with remaining cement on the porcelain surface.

Results of the microscope analyses revealed changes in the surface morphology after surface conditioning (Fig. 3). In untreated microbars (Fig. 3a), marked scratches in different directions are observed as a consequence of the polishing procedure with silicon carbide paper. Fig. 3b and c shows edge-shaped microretentions and microgrooves on the ceramic surface, owing to the APA treatment. However, the final architecture of the sandblasted zirconia surfaces demonstrates no noteworthy differences using 50-μm (Fig. 3b) or 110-μm (Fig. 3c) Al_2O_3 particles.

4. Discussion

Along with an adequate fracture resistance and marginal fit, achieving durable bonds at the tooth/cement, cement/zirconia, and zirconia/veneering ceramic interfaces are essential factors for the long-term success of all-ceramic zirconia-based restorations. The current investigation is focused on the bond strength of dual-cure resin cements to zirconia, and analyzes the influence of the sandblasting granulometry and the cement type. Thus, in this experiment, the zirconia cylinders were luted to composite disks rather to dental tissues to avoid tooth microstructural variations that could misread the findings.[17,18]

The microtensile test was chosen because it offers versatility that cannot be obtained by conventional methods. It is more labour-intensive than tensile and shear testing, but holds greater potential for providing insight into the strength of adhesion of luting materials to clinically relevant substrates[27] such as zirconia frameworks for all-ceramic prostheses. It is still debatable whether pre-test failures should be excluded from the statistical calculations, included as zeros,[27] or rather as greater-than-zero values through the assumption that it must have taken some stress to produce failure during sectioning.[28,29] As in related research,[12] in this experiment the decision was made to include the values as zero bonds, although the authors are aware that this may have biased the test towards a slight infraestimation of the bonding potential.

The findings of this study require the rejection of the null hypothesis, since differences among the experimental groups were found.PAN attained higher MTBS than BIF regardless of the ceramic surface treatment (Table 2). Both cements have a typical glass filler content in the range of 60–75 wt%, as well as other types of methacrylate monomers that are present in most resin-based materials (*i.e.*, Bis-GMA, UDMA and TEGDMA).[18] However, the 10-MDP acidic functional monomer, which has been rated as relatively hydrolysis stable due to its long carbonyl chain,[17] is only present in the PAN luting system. Prior to PAN application, the ceramic microgaps resulting from air-abrasion were infiltrated by the silane, which was spread on the treated ceramic surfaces according to

Please cite this article in press as: Gomes AL, et al. Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. Journal of Dentistry (2012), http://dx.doi.org/10.1016/j.jdent.2012.09.013

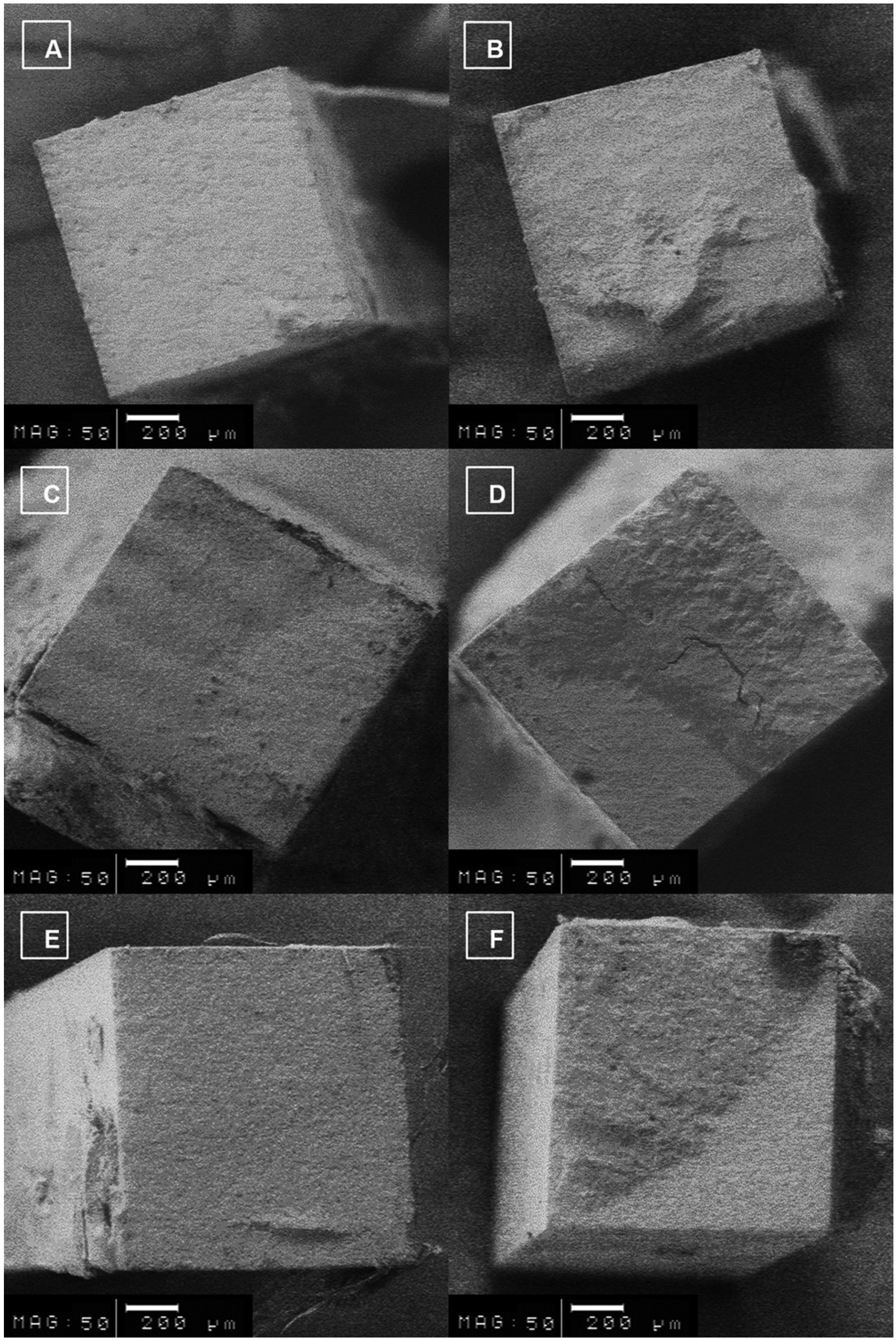

Fig. 2 – Representative SEM images of zirconia debonded surfaces (50×, 20 kV, bar 200 μm). (a, e) Adhesive failures of BIF luted to an untreated surface, and to a stick sandblasted with 110-μm alumina particles, respectively. A complete detachment of the luting agent from the porcelain substrate is observed in both cases. (c) Mixed fracture of BIF from a ceramic microbar sandblasted with 50-μm aluminium-oxide particles. A cohesive phase with cements remnants showing porosities is detectable on the left side of the image. (b, d, f) Mixed failures of PAN luted to an untreated surface and to beams sandblasted using 50-μm, and 110-μm alumina particles, respectively. The fractured cement layer covers more than half of the debonded zirconia surfaces. Pores in remaining cement residuals are noticeable.

Please cite this article in press as: Gomes AL, et al. Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. Journal of Dentistry (2012), http://dx.doi.org/10.1016/j.jdent.2012.09.013

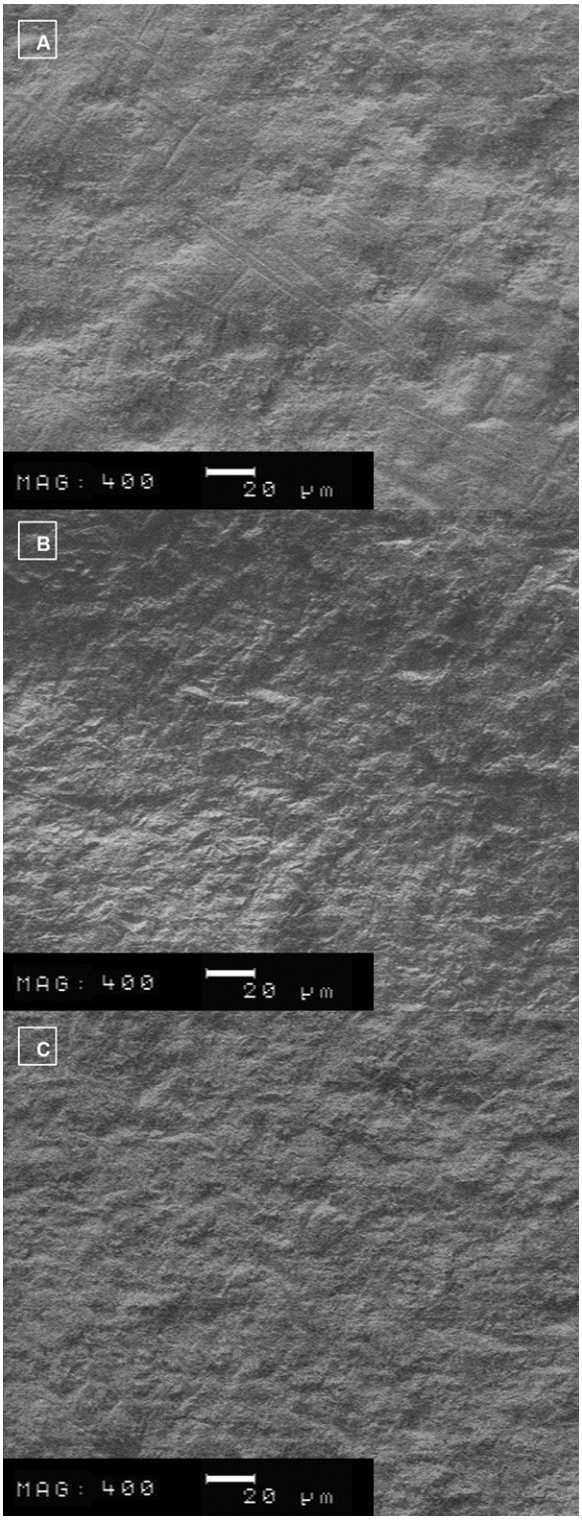

Fig. 3 – SEM micrographs of zirconia ceramic surfaces after conditioning treatments (400×, 20 kV, bar 20 μm). (a) No treatment: an inherent microroughness with scratches resulting from the polishing procedure may be observed. (b) Sandblasting with APA-I (25-μm Al_2O_3 particles): the high-speed impaction of the aluminium-oxide particles produced edge-shaped microretentions on the porcelain substrate. (c) Sandblasting with APA-III (110-μm Al_2O_3 particles): a similar surface texture to that of the previous image is detectable regardless of the different granulometry used for air-abrasion.

the manufacturer's instructions. Besides such micromechanical retention, the 3-MPS (3-methacryloxypropyl trimethoxysilane) and the 10-MDP monomers mixed in this silane-coupling solution (Clearfil Ceramic Primer) (Table 1) create an acid environment that may support the chemical bonding reaction, enhancing the ceramic surface wettability and protecting against moisture. As a result, the 10-MDP monomers of the silane form cross-linkages: (a) with the –OH radicals of the zirconium-oxide ceramic surfaces and (b) with the 10-MDP groups dispersed in the PAN resin matrix.[30–32]

Furthermore, PAN recorded the best overall bond strength values when applied to air-abraded zirconia surfaces (Table 2), yielding comparable results to those of a related investigation that combined a 10-MDP-containing luting system with sandblasting of 125-μm particles (Clearfil, Kuraray: 18.63 ± 6.4 MPa).[17] Air-abrasion produced microretentions where the ceramic primer might have easily penetrated (Fig. 3b and c). This could somewhat explain why no premature failures were obtained when the silane was used (Table 3). Thus, the use of PAN on sandblasted zirconia surfaces seems to reduce the risk of spontaneous debonding regardless of the particle size of air-abrasion. Moreover, in line with the findings of the abovementioned study,[17] most air-abraded microbars luted with PAN exhibited a mixed fracture pattern with remaining cement layers above the porcelain substrate (Table 4 and Fig. 2d,f). Although the combination of air-abrasion and 10-MDP-containing luting systems that use primers has already shown significant enhancement of the durability of bonds to zirconia,[7,21,31–33] the novelty of the current research is that the sandblasting granulometry caused no significant effect in the MTBS and fracture pattern of zirconia surfaces when different dual-cure resin cements were used (Table 2).

On the contrary, more than one-third of the untreated sticks bonded with PAN failed prematurely (Table 3). A flat surface was discovered in untreated ceramic surfaces (Fig. 3a). This may also explain that most untreated zirconia samples luted with PAN showed adhesive fractures (Table 4). Accordingly, in a previous study, omitting air-abrasion resulted in debonding during artificial ageing independent of using primers.[21] Mixed failures are considered clinically preferable over adhesive ones, since the latter are usually associated with low bond strength values,[18] which is consistent with the data shown in Table 2.

As has been previously stated, BIF recorded significantly lower MTBS than PAN despite the ceramic surface treatment (Table 2). In addition to the micromechanical interlocking between the resin cement and the rough sandblasted ceramic surfaces, the chemo-mechanical adhesion of BIF at the cement/zirconia interface may be compared to that of glass-ionomer cements.[34] The glass silicate particles dissolved in the cement matrix may react with the acidic phosphoric esters forming a silicate gel in which particles of unreacted glass are embedded.[35] The resin matrix of BIF contains multifunctional-phosphoric adhesive dimethacrylate monomers with at least two unsaturated C=C double bonds. Those monomers react

Please cite this article in press as: Gomes AL, et al. Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. Journal of Dentistry (2012), http://dx.doi.org/10.1016/j.jdent.2012.09.013

with the inorganic fillers dissolved in the resin matrix, thus forming chemical cross-linkages.[12] Other self-adhesive luting agents reported higher MTBS values in former studies,[11,17] which may be attributed not only to slight differences in the cement composition, but also to disparities in the study protocols.

Despite the conditioning method, BIF has confirmed a higher risk of suffering a spontaneous detachment from the ceramic substrate than PAN (Table 3) and predominantly failed adhesively, leaving no cement residuals on the ceramic surface (Table 4 and Fig. 2a,e), which is in accordance with the literature for other self-adhesive cements.[4,17] This study did not reveal significant differences in MTBS between the four subgroups of BIF specimens luted either to untreated or air-abraded zirconia surfaces using different particle sizes (Table 2). This can strengthen the concept that the mechanical adhesion by itself does not provide the resin bond strength required for CAD/CAM dental ceramics, so a reliable chemical adhesion is also recommended. In this regard, it has recently been proven that the combination of a self-adhesive resin cement with a 10-MDP-containing primer results in durable bond strength to sand-blasted zirconia ceramic.[36] However, with this formula, self-adhesive resin cements lose their announced advantages of being applied in one clinical step and might be as technique-sensitive as other dual-cure resin cements.

Nonetheless, as the MTBS values of BIF were quite low under the tested experimental conditions, PAN in combination with air-abrasion seems to be the best alternative to bond zirconia. Hence, when the cement is changed from BIF to PAN in the current study, the bond strength is significantly enhanced in a range between 13.1 and 15.4 MPa, independently of the conditioning method. Despite the methodological differences, these findings are in agreement with those of a former study, which found significantly higher MTBS to zirconia for 10-MDP-containing Clearfil Esthetic Cement than for the self-adhesive resin RelyX Unicem, regardless of the surface treatment.[17]

No differences were identified in the architecture of zirconia surfaces sandblasted with different-sized Al_2O_3, particles, that showed comparable microretentive grooves at the micrometre scale (Fig. 3b and c). However, a trend towards a positive correlation between the particle size of APA and the MTBS at the cement/zirconia interface was observed when PAN was used. In this experiment, for each increased micron in the size of the Al_2O_3 particles the bond strength of PAN would augment between 0.024 and 0.052 MPa (CI-95%). Although no study has been found on the effect of the sandblasting particle size on the bond strength to zirconia, an investigation on the optimal surface treatments for carbon/epoxy composite adhesive joints concluded that the surface roughness, eroded length and eroded depth increased as the particle size of sandblasting augmented,[37] which concurs with the results of this paper, as rough surfaces increase the area of the adhesive joint and the effect of interlocking[38] mainly after priming.[32] Nonetheless, the surface energy parameters of luting cements should be assessed using a profilometer and contact angle measurements to evaluate their adhesive properties to zirconia ceramic.[39]

Bonding 10-MDP-based resin cement to untreated zirconia and luting a self-adhesive resin agent without priming the ceramic surfaces yielded low bond strength values in this investigation (Table 2). Thus, based in the current results, the use of flat ceramic surfaces and the direct application of the luting cement without silanization may be inhibiting factors in gaining bond strength at the cement/zirconia interface. Furthermore, acid compounds in dentinal fluids, oral bacteria, proteolytic residues and salivary enzymes may interfere with the stability of adhesive interfaces and have recently been considered has potential sources of chemical bond degradation.[40–42]

To date, there are still no explicit, ideal criteria in selecting bonding materials for zirconia-based all-ceramic prostheses and little information is available in the literature about the longevity of such bonds.[18,43] Considering the study findings and the presence of hydrophobic 10-MDP monomers[44] both in the CEC primer and in the PAN resin cement matrix (Table 1), air-abraded zirconia surfaces in combination with a ceramic primer and a 10-MDP-based resin cement may be supposed to keep high bond strength values in the long-term. However, this *in vitro* experiment provides only a recommendation protocol for bonding zirconia and further research is required to refine these conclusions. Different ageing methods, such as water storage or thermocycling,[18,22,45,46] as well as controlled clinical trials[18,43] should be performed to assess the possible contribution of the sandblasting granulometry to the stability of cement-to-zirconia bonds depending on the luting system. Moreover, a strict following of the instructions given by the manufacturers avoiding saliva contamination during the luting procedure may be essential for clinical success.[42] Resin-based materials are so technique-sensitive that receiving an appropriate training on how to use them is necessary.[47–49]

5. Conclusions

Within the limitations of this study, the 10-MDP-containing luting system seems to be more suitable to bond zirconia than the self-adhesive resin cement, mainly in combination with sandblasted ceramic surfaces. Bifix requires no surface treatment before luting, but has quite low bond strength to zirconia and a higher risk of spontaneous debonding and adhesive failure.

Thus, applying a dual-cure resin cement system that contains 10-MDP functional monomers both in the silane coupling agent and in the resin cement matrix onto a sandblasted ceramic substrate may be the key to successful bonds to zirconia structures for all-ceramic restorations regardless of the sandblasting granulometry. However, the stability of such chemical bonds should be further evaluated, taking into account the possible influence of different particle sizes of air-abrasion in the long-term.

Acknowledgements

The authors would like to thank Dentsply (Germany), VOCO (Germany), Kuraray (Japan) and Ivoclar Vivadent (Liechtenstein) for providing some of the materials used in this study. We also thank the Dental Lab *Aragoneses* (Madrid, Spain) for their technical support in this research.

Please cite this article in press as: Gomes AL, et al. Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. Journal of Dentistry (2012), http://dx.doi.org/10.1016/j.jdent.2012.09.013

REFERENCES

1. Beuer F, Stimmelmayr M, Gernet W, Edelhoff D, Güh JF, Naumann M. Prospective study of zirconia-based restorations: 3-year clinical results. *Quintessence International* 2010;**41**:631–7.
2. Guess PC, Zavanelli RA, Silva NR, Bonfante EA, Coelho PG, Thompson VP. Monolithic CAD/CAM lithium disilicate versus veneered Y-TZP crowns: comparison of failure modes and reliability after fatigue. *International Journal of Prosthodontics* 2010;**23**:434–42.
3. Denry I, Kelly JR. State of the art of zirconia for dental applications. *Dental Materials* 2008;**24**:299–307.
4. Blatz MB, Sadan A, Kern M. Resin-ceramic bonding: a review of the literature. *Journal of Prosthetic Dentistry* 2003;**89**:268–74.
5. Dérand P, Dérand T. Bond strength of luting cements to zirconium oxide ceramics. *International Journal of Prosthodontics* 2000;**13**:131–5.
6. Aboushelib M, Kleverlaan CJ, Feilzer AJ. Selective infiltration-etching technique for a strong and durable bond of resin cements to zirconia-based materials. *Journal of Prosthetic Dentistry* 2007;**98**:379–88.
7. Blatz MB, Chiche G, Holst S, Sadan A. Influence of surface treatment and simulated aging on bond strengths of luting agents to zirconia. *Quintessence International* 2007;**38**:745–53.
8. Aboushelib MN, Mirmohamadi H, Matinlinna JP, Kukk E, Ounsi HF, Salameh Z. Innovations in bonding to zirconia-based materials. Part II: focusing on chemical interactions. *Dental Materials* 2009;**25**:989–93.
9. Ntala P, Chen X, Niggli J, Cattell M. Development and testing of multi-phase glazes for adhesive bonding to zirconia substrates. *Journal of Dentistry* 2010;**38**:773–81.
10. Paranhos MP, Burnett Jr LH, Magne P. Effect of Nd:YAG laser and CO_2 laser treatment on the resin bond strength to zirconia ceramic. *Quintessence International* 2011;**42**:79–89.
11. Oyagüe RC, Osorio R, da Silveira BL, Toledano M. Comparison of bond stability between dual-cure resin cements and pretreated glass-infiltrated alumina ceramics. *Photomedicine and Laser Surgery* 2011;**29**:465–75.
12. Oyagüe RC, Osorio E, Toledano M, Osorio R. Influence of surface nano-roughness of dental alumina ceramic on bond strength to dual-cure resin cements. *Journal of Adhesion Science and Technology* 2011;**25**:2909–22.
13. Borges GA, Sophr AM, de Goes MF, Sobrinho LC, Chan DC. Effect of etching and airborne particle abrasion on the microstructure of different dental ceramics. *Journal of Prosthetic Dentistry* 2003;**89**:479–88.
14. Kosmac T, Oblak C, Jevnikar P, Funduk N, Marion L. The effect of surface grinding and sandblasting on flexural strength and reliability of Y-TZP zirconia ceramic. *Dental Materials* 1999;**15**:426–33.
15. Demir N, Subaşı MG, Ozturk AN. Surface roughness and morphologic changes of zirconia following different surface treatments. *Photomedicine and Laser Surgery* 2012;**30**:339–45.
16. Ural Ç., Külünk T, Külünk S, Kurt M. The effect of laser treatment on bonding between zirconia ceramic surface and resin cement. *Acta Odontologica Scandinavica* 2010;**68**:354–9.
17. de Oyagüe RC, Monticelli F, Toledano M, Osorio E, Ferrari M, Osorio R. Influence of surface treatments and resin cement selection on bonding to densely-sintered zirconium-oxide ceramic. *Dental Materials* 2009;**25**:172–9.
18. Oyagüe RC, Monticelli F, Toledano M, Osorio E, Ferrari M, Osorio R. Effect of water aging on microtensile bond strength of dual-cured resin cements to pre-treated sintered zirconium-oxide ceramics. *Dental Materials* 2009;**25**:392–9.
19. Sasse M, Eschbach S, Kern M. Randomized clinical trial on single retainer all-ceramic resin-bonded fixed partial dentures: influence of the bonding system after up to 55 months. *Journal of Dentistry* 2012;**40**:783–6.
20. Ferracane JL, Stansbury JW, Burke FJ. Self-adhesive resin cements – chemistry, properties and clinical considerations. *Journal of Oral Rehabilitation* 2011;**38**:295–314.
21. Kern M, Barloi A, Yang B. Surface conditioning influences zirconia ceramic bonding. *Journal of Dental Research* 2009;**88**:817–22.
22. Attia A. Bond strength of three luting agents to zirconia ceramic – influence of surface treatment and thermocycling. *Journal of Applied Oral Science* 2011;**19**:388–95.
23. Saghaei M. Random allocation software for parallel group randomized trials. *BMC Medical Research Methodology* 2004;**4**:26.
24. Valandro LF, Mallmann A, Della Bona A, Bottino MA. Bonding to densely sintered alumina- and glass infiltrated aluminum/zirconium-based ceramics. *Journal of Applied Oral Science* 2005;**13**:47–52.
25. Della Bona A, Anusavice KJ, Mecholsky Jr JJ. Apparent interfacial fracture toughness of resin/ceramic systems. *Journal of Dental Research* 2006;**85**:1037–41.
26. Egilmez F, Ergun G, Cekic-Nagas I, Vallittu PK, Lassila LV. Influence of cement thickness on the bond strength of tooth-colored posts to root dentin after thermal cycling. *Acta Odontologica Scandinavica* 2012, in press.
27. Pashley DH, Carvalho RM, Sano H, Nakajima M, Yoshijama M, Shono Y, *et al*. The microtensile bond strength: a review. *Journal of Adhesive Dentistry* 1999;**1**:299–309.
28. Nikolaenko SA, Lohbauer U, Roggendorf M, Petschelt A, Dasch W, Frankenberger R. Influence of *c*-factor and layering technique on microtensile bond strength to dentin. *Journal of Adhesive Dentistry* 2004;**20**:579–85.
29. Goracci C, Cury AH, Cantoro A, Papacchini F, Tay FR, Ferrari M. Microtensile bond strength and interfacial properties of self-etching and self-adhesive resin cements used to lute composite on lays under different seating forces. *Journal of Adhesive Dentistry* 2006;**8**:327–35.
30. Kern M, Wegner SM. Bonding to zirconia ceramic: adhesion methods and their durability. *Dental Materials* 1998;**14**:64–71.
31. Wolfart M, Lehmann F, Wolfart S, Kern M. Durability of the resin bond strength to zirconia ceramic after using different surface conditioning methods. *Dental Materials* 2007;**23**:45–50.
32. Yoshida K, Tsuo Y, Atsuta M. Bonding of dual-cured resin cement to zirconia ceramic using phosphate acid ester monomer and zirconate coupler. *Journal of Biomedical Materials Research Part B Applied Biomaterials* 2006;**77**:28–33.
33. May LG, Passos SP, Capelli DB, Ozcan M, Bottino MA, Valandro LF. Effect of silica coating combined to a MDP-based primer on the resin bond to Y-TZP ceramic. *Journal of Biomedical Materials Research Part B Applied Biomaterials* 2010;**95**:69–74.
34. Yap AU, Tan AC, Goh AT, Goh DC, Chin KC. Effect of surface treatment and cement maturation on the bond strength of resin-modified glass ionomers to dentin. *Operative Dentistry* 2003;**28**:728–33.
35. Nicholson JW. Chemistry of glass-ionomer cements: a review. *Biomaterials* 1998;**19**:485–94.
36. Yang B, Barloi A, Kern M. Influence of air-abrasion on zirconia ceramic bonding using an adhesive composite resin. *Dental Materials* 2010;**26**:44–50.
37. Kim JK, Kim HS, Lee DG. Investigation of optimal surface treatments for carbon/epoxy composite adhesive joints. *Journal of Adhesion Science and Technology* 2003;**17**:329–52.

Please cite this article in press as: Gomes AL, et al. Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. Journal of Dentistry (2012), http://dx.doi.org/10.1016/j.jdent.2012.09.013

38. Kinloch AJ. Adhesion adhesives. London: Chapman & Hall; 1987.
39. Kim MJ, Kim YK, Kim KH, Kwon TY. Shear bond strengths of various luting cements to zirconia ceramic: surface chemical aspects. *Journal of Dentistry* 2011;**39**:795–803.
40. De Munck J, Braem M, Wevers M, Yoshida Y, Inoue S, Suzuki K, *et al*. Micro-rotatory fatigue of tooth-biomaterial interfaces. *Biomaterials* 2005;**26**:1145–53.
41. Monticelli F, Osorio R, Pisani-Proença J, Toledano M. Resistance to degradation of resin–dentin bonds using a one-step HEMA-free adhesive. *Journal of Dentistry* 2007;**35**:181–6.
42. Yang B, Lange-Jansen HC, Scharnberg M, Wolfart S, Ludwig K, Adelung R, *et al*. Influence of saliva contamination on zirconia ceramic bonding. *Dental Materials* 2008;**24**: 508–13.
43. Osorio R, Castillo-de Oyagüe R, Monticelli F, Osorio E, Toledano M. Resistance to bond degradation between dual-cure resin cements and pre-treated sintered CAD-CAM dental ceramics. *Medicina Oral Patología Oral y Cirugía Bucal* 2012;**17**:e669–77.
44. Van Landuyt KL, Snauwaert J, De Munck J, Peumans M, Yoshida Y, Poitevin A, *et al*. Systematic review of the chemical composition of contemporary dental adhesives. *Biomaterials* 2007;**28**:3757–85.
45. Bagheri R, Mese A, Burrow MF, Tyas MJ. Comparison of the effect of storage media on shear punch strength of resin luting cements. *Journal of Dentistry* 2010;**38**:820–7.
46. Guarda G, Correr A, Gonçalves L, Costa A, Borges G, Sinhoreti M, et al. Effects of surface treatments, thermocycling, and cyclic loading on the bond strength of a resin cement bonded to a lithium disilicate glass ceramic. *Operative Dentistry* 2012, in press.
47. Lynch CD, McConnell RJ, Wilson NH. Teaching the placement of posterior resin-based composite restorations in U.S. dental schools. *Journal of the American Dental Association* 2006;**137**:619–25.
48. Lynch CD, McConnell RJ, Wilson NH. Challenges to teaching posterior composites in the United Kingdom and Ireland. *British Dental Journal* 2006;**201**:747–50.
49. Castillo-de Oyagüe R, Lynch C, McConnell R, Wilson N. Teaching the placement of posterior resin-based composite restorations in Spanish dental schools. *Medicina Oral Patología Oral y Cirugía Bucal* 2012;**17**:e661–8.

Please cite this article in press as: Gomes AL, et al. Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. Journal of Dentistry (2012), http://dx.doi.org/10.1016/j.jdent.2012.09.013

III.3 Gomes AL, Ramos JC, Santos-del Riego SE, Montero J, Albaladejo A. Thermocycling effect on microshear bond strength to zirconia ceramic using Er:YAG and tribochemical silica coating as surface conditioning. 2013. Lasers Med Sci (sent for second review)

ABSTRACT

The purpose of this study is to evaluate the thermocycling effect on the micro-shear bond strength (µSBS) of different self-adhesive resin cements to zirconia using tribochemical silica coating Rocatec™ and Er:YAG as surface conditioners. Two hundred and forty square like zirconia samples were polished and randomly assigned in four groups according surface treatment applied as follows: 1) no treatment (NT); 2) silica coating with Rocatec™ (ROC); 3) Er:YAG laser irradiation (LAS: 2.940 nm, 200 mJ, 10 Hz) and; 4) laser followed by Rocatec™ (LAROC). Each group was divided into two subgroups according the resin tested: A) BiFix SE (BIF) and B) Clearfil SA (CLE). After 24h, half of the specimens from each subgroup were tested. The other half was stored and thermocycled (5º-55ºC/5000 cycles). A µSBS test was performed using a universal testing machine (cross head speed = 0,5 mm/min). Failure modes were recorded and observed by scanning electronic microscopy. Data was analyzed with ANOVA, Student T, chi square tests and linear regression were performed ($p < 0.05$). Before thermocycling, both cements showed higher µSBS results with ROC and LAROC. After aging, 1) all BIF specimens evidenced severely decreased adhesion with mostly adhesive failures and 2) CLE maintained the initial results in ROC and LAROC groups, performing better with ROC. Thermocycling did not negatively influence the resin-zirconia µSBS results in the self adhesive resin cement containing 10-MDP when used on zirconia surface coated with silica, independently of previous Er:YAG surface treatment.

Keywords: Er:YAG, zirconia, adhesion, silica coating, thermal aging, µSBS

A. L. Gomes[1], J. C. Ramos[2], S. E. Santos-del Riego[3], J. Montero[4], A. Albaladejo[4]

1 - Dental School (Faculty of Medicine), University of Salamanca. Paseo Universidad de Coimbra s/n, 37007, Salamanca, Spain.

2 - Tenured Lecturer, Department of Dentistry (University School of Medicine), University of Coimbra, Hospitais da Universidade de Coimbra, Av. Bissaya Barreto - Blocos de Celas, 3000, Coimbra, Portugal.

3 - Tenured Lecturer. Department of Medicine, University of A Coruña. Edificio Universitario de la Facultad de Ciencias de la Salud, Oza S/N. 15005. A Coruña, Spain.

4 - Tenured Lecturer, Dental School (Faculty of Medicine), University of Salamanca. Paseo Universidad de Coimbra s/n, 37007, Salamanca, Spain.

Corresponding author:

Alberto Albaladejo

Clínica Odontológica. Universidad de Salamanca (USAL).

Prolongación del paseo de la Universidad de Coimbra S/N; C.P.: 37007. Salamanca, Spain.

Phone: +34-923294400.

E-mail: albertoalbaladejo@hotmail.com

INTRODUCTION

The use of zirconia ceramics as a dental restorative material is now the focus of extensive clinical, research and industrial activity. Due to its mechanical properties, combined with its biocompatibility and optical benefits, yttrium stabilized tetragonal zirconia (Y-TZP) has become widely used in esthetic dentistry [1,2].

The long-term performance and adhesive effectiveness of ceramic prostheses depend strongly on the cementation procedure [3]. Among the resin cement luting systems currently available, self-adhesive resin cements are a relatively new category of resin luting agents claimed to provide good bond strengths to tooth structures and restorative materials without any pre-treatment or bonding agents [4]. They are widely used because of their properties and the cementation technique's simplicity [5].

There is no consensus regarding the best surface conditioning method for achieving optimal bond strength between composite resins and zirconia. Several adhesive strategies have been suggested to overcame this issue, by changing the ceramic surface, including 1) new surface roughening procedures [6,7], 2) chemical bonding [8-11], and 3) laser treatments [12,13].

With the purpose of cleaning the surfaces, creating a highly retentive surface, and most of all, enhancing their silanizability, there are several methods to silicatize, *i.e.*, silica coat, prosthodontic material surfaces. Tribochemical silica coating can be used chairside in the form of sandblasting, with a specifically surface modified alumina (Al_3O_2) with silica (SiO_2) coating the particles' surfaces. This technique yields the zirconia with a reactive silica outer layer favorable to silanization and the following resin cementing procedures [3,14].

Another alternative method for ceramic surface conditioning is laser irradiation [15]. Lasers were proposed to modify the surfaces of materials in a relatively safe and easy way [16-19], but only limited studies on all ceramics materials laser treatments are available [16-18,20]. One of the most often used lasers in research, as well as in clinical practice, is the Er:YAG (erbium-doped yttrium aluminum garnet). This laser operates at the wavelength of 2940 nm and one of its distinctive features is to operate in a pulse mode. Er:YAG with appropriate parameters can create an irregular surface that enhances the micromechanical retention to ceramic materials [20]. Still, high laser intensity can damage surface properties, resulting in crack formation and consequent low bond strength values [21].

First, there are several procedures capable of achieving a strong bond with Y-TZP. However, this bond strength should remain adequate over years in the surrounding oral environment: temperature shocks, pH variation, humidity, and mastication forces. Bond strength can decay with time, causing retention loss and microleakage increases. One of the main mechanisms of the zirconia/resin interface degradation can be thermal fatigue that can result in stress affecting the bond interface, *e.g.*, thermal expansion and contraction [22] and could lead to unequal changes in dimensions and eventually to bond failure [23].

Many factors like ceramic wettability, surface roughness or bonding agents composition can influence the quality and stability of the resin cement-zirconia adhesion [24]. If, on one hand, little data is available concerning the roughening capacity of the Er:YAG laser for enhanced microretention of the Y-TZP for optimized adhesive luting procedures [20], on the other hand there is still controversy about the best luting system for Y-TZP ceramics [25]. It is important to study if laser irradiation is a valuable alternative method for high-strength ceramics' surface conditioning, capable of providing a resin-zirconia bond with high efficiency and, foremost, durability.

The aim of this study is to evaluate the thermocycling effect on the micro shear bond strength (μSBS) of different self-adhesive resin cements to zirconia when using a tribochemical silica coating and Er:YAG as surface conditioners. The null hypothesis was that neither the different surface conditioning methods, the thermocycling effect, nor the resin cement composition modifies the μSBS to zirconia ceramics.

MATERIALS AND METHODS

Specimen preparation

The study used 240 square-like specimens (measuring 3 x 3 x 1 mm) of densely sintered Y-TZP (Cercon®, DeguDent, Hanau, Germany). The specimens' surfaces were wet-polished with 600-grit silicon carbide paper. Zirconia samples were randomly assigned to four experimental surface treatments (n = 60) (Table 1).

1) No surface treatment was applied (*NT*).

2) Tribochemical silica coating using Rocatec system (*ROC*) (Rocatec™ Soft, 3M Espe, Seefeld, Germany): The surfaces were treated by means of tribochemical silica coating (30 μm alumina coated with silica particles) that was applied perpendicularly for 20 sec, at a working distance of 10 mm and a pressure of 2.8 bar; silanization was performed before bonding with Rely X™ ceramic primer (3M Espe, Seefeld, Germany) following the manufacturer's instructions.

3) Er:YAG laser irradiation (*LAS*): The surfaces were coated with graphite prior to laser irradiation to increase energy of absorption, and the laser equipment used was an Er:YAG laser (Key laser 3^+, Kavo, Biberach/Riß, Germany) emitting a 2940 nm

wavelength. A no-contact probe was used perpendicular to the surface with a working distance of 5 mm. The surfaces were irradiated until the whole ceramic area was scanned using a fine water spray. The pulse repetition was set at 10 Hz and energy intensity was set at 200 mJ [20].

4) Er:YAG laser followed by Tribochemical silica coating (*LAROC*): Both procedures were developed as previously described.

Luting procedure

Each group was divided into two subgroups depending on the luting system applied. Two self adhesive resin cements were used: A) BiFix® SE (*BIF*) (BiFix® SE, VOCO, Cuxhafen, Germany) and B) Clearfil™ SA Cement (*CLE*) (Clearfil™ SA Cement, Kuraray, Osaka, Japan) (Table 1). Adhesion procedures were performed at room temperature according to manufacturers recommendations.

After preparing the zirconia specimens, plastic molds (Tygon, Norton Performance Plastic Co, Cleveland, USA) with an inner diameter of 1 mm and height of 2 mm, were positioned in the centre of the specimens. The cement was carefully packed into the tube against the substrate and stubs were light-polymerized for 40 sec (XL 3000, 3M/ESPE; light intensity 500 mW cm^{-2}, distance 0) from the top of the stub and from two lateral directions at the contact area. The mold was gently removed and the cement cylinder was light cured for extra 40 sec. Thereby, a small cylinder of resin cement with 1 mm in diameter and 2 mm in height was bonded to the ceramic surface. Thirty specimens were created in each subgroup. Specimens were stored for 24h in distilled water at 37ºC. After 24h, half of the specimens from each subgroup (n = 15) were tested immediately for microshear bond strength. The other half was subjected to thermo-cycling (TC) in distilled water for 5000 cycles between 5ºC and 55ºC. The dwelling time at each temperature was 30 sec and the transfer time was 2 sec.

Microshear bond strength (μSBS) test

Each ceramic plate with its cement cylinder was fixed with cyanoacrylate adhesive (Zapit, Dental Ventures of America, Corona, USA) to a microshear device adapted to a universal testing machine (AGS-X Autograph, Shimadzu Corporation, Kyoto, Japan). A shear load, cross-head speed of 0.5 mm/min, was applied until fracture. Bond strength values were calculated by dividing the maximum load recorded on failure by the circular bonding area in square millimeters and expressed in MPa.

After fracturing, the ceramic surfaces were evaluated with a stereoscopic zoom microscope (SMZ800, Nikon Corporation, Tokyo, Japan) at 40× magnifications to assess the failure mode and classify it as adhesive (at the cement/ceramic interface, including pretesting failure) or mixed (with both adhesive and cohesive phases).

Statistical Analysis

Descriptive statistics used the mean of SBS (MPa) and its standard deviation (SD). A two-way analysis of variance (ANOVA) and Bonferroni's Post Hoc correction were used to determine the statistical significance of any inter-group differences in mean SBSs. Student T tests were performed for comparing the SBS between cement groups. Chi Square Tests and Odds Ratio were used in two-by-two tables for quantify the risk of adhesive failure versus mixed failure among subgroups. A linear regression analysis was implemented using a step-wise selection method for introducing all potential predictors of SBSs (*i.e.*, surface, cement, and aging). Significance for all statistical tests was predetermined at $p < 0.05$. All the statistical analyses were performed using SPSS 18.0 for Windows (SPSS, Chicago, IL).

SEM examination

Representative samples from each sub-group were prepared for SEM analysis. Samples were dehydrated for 48h in a desiccator (Sample Dry Keeper Simulate Corp., Tokyo, Japan) and sputter coated with a 10 nm platinum layer in a Polaron E5100 SEM coating unit (Polaron Equipment Ltd., Hertfordshire, England, UK). The morphology of the debonded zirconia surfaces was then examined with a variable-pressure SEM (Zeiss EVO MA 25; Carl-Zeiss, Jena, Germany).

Specific surface areas were explored, focusing with different magnifications (from x70 to x1000) to identify possible differences in the surface topography and morphology of the debonded interfaces among the experimental groups.

RESULTS

Microshear bond strength (μSBS) test

Mean and standard deviations (SD) of the μSBS are summarized in Table 3. According to these results the cement type, the surface treatment and the artificial aging significantly influenced the shear bond strength to the zirconia (Table 3).

When using BIF, without thermocycling, ROC and LAROC showed similar μSBS and were significantly higher than NT and LAS (which were not significantly different). After TC, all BIF groups had identical bond strength results, showing adhesion effectiveness had decreased to values near to zero (Table 3), when compared with the previous cited groups. In the specimens cemented with CLE, ROC exhibited the bond strengths that were statistically the highest, regardless the thermocycling process. The LAROC group achieved higher μSBS values than NT and LAS, and had similar results pre- or post-artificial aging.

Without thermocycling BIF registered similar values to CLE, except with LAROC treatment. When the surface was conditioned with LAROC the highest μSBS results were observed in the BIF samples. After TC, CLE had higher μSBS values than BIF when ROC or LAROC was used, and the other groups presented identical values to BIF. A single T Test comparison of the μSBS between BIF (n = 120; mean 6.6 ± 8.0 Mpa) versus CLE (n = 120; mean 8.4 ± 6.5 Mpa) confirmed the CLE's global higher performance, with an almost significant *p*-value of 0.06 (result not shown).

The failure mode distributions in the experimental groups are outlined in Table 4. Within the BIF group, the samples mainly failed adhesively. Only the samples where Rocatec was used, with or without the laser, and that were tested after 24h, presented mixed failures. After TC, 100% of the BIF samples failed adhesively. Using CLE, in general, NT and LAS groups failed adhesively without considering the artificial aging process. In combination with ROC, with or without the laser, when the samples were tested 24h later, mostly mixed failures were observed. Thermocycling influenced only the LAROC group failure mode that registered a majority of mixed pattern in 24h that became adhesive after the aging process; ROC maintained a higher percentage of mixed failures (Table 4).

Given the similarities between NT and LAS and between ROC and LAROC results, the surface treatment groups were assembled into two groups: 1) no surface treatment or laser and 2) Rocatec with or without laser. A two-by-two analysis of the type of failures distribution (adhesive *versus* mixed) was made according to the surface treatment between both BIF and CLE subgroups, is evident in Table 5.

Within the BIF subgroup, the risk of get an adhesive failure is 12.4 times more when NT or LAS were applied (OR adhesive/mixed = 12.4), and the percentage values of adhesive failures for BIF subgroup were significantly higher (Chi: 15.36, $p < 0.001$) (Table 5). Otherwise, using CLE in combination with ROC or LAROC, the percentage of mixed failures was significantly higher (Chi: 45.69; $p < 0.001$) and the risk of an adhesive failure was 23.7 (OR adhesive/mixed = 23.7) when NT or LAS was used.

A significant linear regression model (F = 104.558; $p < 0.001$) confirmed that SBS could be predicted (corrected $R^2 = 0.57$) when surface treatment, artificial aging, and cement are known. The strongest predictor is the surface treatment (codified as ROC or LAROC versus NT or LAS) that increases the baseline μSBS (expected to range from 5.2 to 7.6 MPa) in 6.7 to 9.2 MPa (T = 12.58; $p < 0.001$). The following predictor is the artificial aging (T = -11.95; $p < 0.001$), which reduces the baseline μSBS in 6.2-8.7 MPa. The weakest, although significant predictor of the μSBS is the type of cement, which implies that μSBS could be increased from 0.6 to 3.0 MPa if we use CLE instead of BIF (T = 2.85; $p = 0.005$).

SEM analysis

Failure mode analysis

Representative SEM images of debonded zirconia surfaces after μSBS are presented in Fig 1. A zirconia sample with different magnifications is shown in each picture. First, in the upper right, a lower magnification (approximately ×70) used to assess the type of failure. Details of the debonded area obtained are highlighted with a magnified view (about ×700). Images A, B, and E present adhesive failure patterns with no luting residuals remaining. Images C, D, F, G, and H demonstrate mixed failures with cement remnants layering on the zirconia surface, namely in C, D, G, and H, that correspond to ROC and LAROC groups, where a large cohesive phase is visible.

Surface treatment analysis

The SEM micrographs in Fig. 2 show the zirconia surface morphology after the different surface conditioning methods were applied. Image A represents the NT group with marked scratches in different directions as result of the polishing procedure with silicon carbide paper. In the ROC group, image B, due to the high-speed particles' impact, the porcelain substrate suffered surface modification and edge-shaped microretentions are present. Signs of fusion and solidification may be observed in Image C (LAS group), but no superficial cracks are observed and the scratches, resulting from the polishing are still visible after the laser treatment. Finally, in image D, an irregular and rough appearance, similar to image B, is evident. Although the laser alters the zirconia surface, the Rocatec® overcomes that and LAROC (image D) produces an identical surface conditioning to ROC group (image B).

DISCUSSION

This study assessed the effects of surface conditioning and resin cements in the adhesion shear bond strength to zirconia under aging. Our findings make us reject the null hypothesis proposed, because significant differences among the experimental groups were found as detailed next.

A µSBS significant predictor was the type of cement, which implies that its value could be increased from 0.6 to 3.0 MPa if CLE was used instead of BIF. Both cements are self-adhesive resin cements and were used in a single step on the zirconia surface (following the manufacturers' instructions). However, given their common composition, present in most resin-based materials (Table 2), we should highlight the 10-MDP existence in CLE luting system. This acidic functional monomer was reported as able of chemically adhering to zirconium oxide by interacting with the –OH radical in the ceramic surface [11,14,26] and rated as relatively hydrolysis stable, due to its long carbonyl chain [27].

The surface conditioning procedure, the strongest predictor factor in the regression model used, seems to be a more relevant factor in bonding to zirconia surface, contrary to other studies that advocate the cement choice as fundamental to attain reliable adhesion to zirconia [15,28]. Both cements had higher μSBS values after silica coating the ROC and LAROC groups. SEM observations revealed considerable qualitative differences in the ceramic surface architecture after the different conditioning methods (Fig. 2). These findings can be directly related to bond strength results, once the treated surface is rough with a uniform presence of shaped microretentions and shallow pits, but no microcracks (Fig. 2B and D). The resultant improvement in resin bond strength can be explained not only by the attained roughness, but also because the silica coating process allows chemical coupling through the silane [9,12]. Prior cement application, the ceramic surface irregularities, resulting from Rocatec™ particles' impact, were infiltrated by Rely X™ Ceramic Primer, a pre-hydrolyzed 3-MPS (3-methacryloxypropyltrimethoxysilane) ready for direct use as supplied by the manufacturer. Silane coupling agents have silicon linked to reactive organic radicals, which become chemically bonded to resin molecules and form siloxane linkages with the silica coated surface. Their use enhances the ceramic wettability (producing better contact and infiltration of the resin in the ceramic irregularities), protects against moisture, and creates an acid environment that may support the bonding reaction [29].

Both cements recorded similar μSBS when irradiated with Er:YAG and without surface treatment, regardless thermocycling process. Although laser treatment creates a rougher surface (Fig. 2C) it does not improve bond strength. The surface irregularities created by Er:YAG (probably due to local increases of the substrate temperature that generates an erosive effect) have insufficient micro depth without micromechanical retention. This results in limited penetration of the cement. Er:YAG laser had minimal impact on zirconia since it is a water free material that present a white and opaque coloration. The Rocatec™ employment after the laser in the LAROC treatment easily overcame and covered the LAS surface modification and a similar surface to ROC group was observed (Fig. 2B and D). These results are in line with a recent study findings [28].

Bond strength results demonstrate that laser irradiation was less effective in improving bond strength than tribochemical silica coating, for both resin cements. A recent study also registered low bond strength of all luting systems tested to Er:YAG irradiated zirconia. The authors suggested that during laser irradiation the micro-explosions could form debris which might adhere to the melted ceramic surfaces. Such a layer would be able to bond strongly to the resin cement but would be poorly attached to the infra-layer surface, resulting in low bond strengths [28]. However, this hypothesis was not confirmed and further research is needed. While Subaşı *et al.* [28,30] and Akyil *et al.* [31] reported similar results to our study, others suggested that Er:YAG laser significantly increased the SBS of ceramic to dentin [20,32,33].

Thermocycling affected negatively all the specimens' bond strength, except when CLE was used in ROC and LAROC groups. A slight decrease in bond strength was observed after TC, which was not statistically significant. The aging effect induced by thermocycling can occur by repetitive contraction/expansion stresses generated by different thermal coefficient of the restorative materials or by hydrolysis of the interfacial components (water can infiltrate and decrease the mechanical properties of the polymer matrix, by swelling and reducing the frictional forces between the polymer chains) [23]. When silica coating was performed, CLE was able to adhere to the silica present on the ceramic surface through the interaction between 10-MDP monomer and 3-MPS, producing more durable bonding values, as demonstrated in previous studies [34,35].

Failure modes were assessed and supported the bond strength results. Both cements in NT and LAS groups had a tendency to fail adhesively at the resin-zirconia interface, presenting the substrate surface free of cement residues (Fig. 1A, B and E), which is in accordance with the literature for other self-adhesive cements [3,27]. Mixed failures were observed mostly in ROC and LAROC groups (Table 3). These are clinically preferred to adhesive failures because there are usually associated with high bond strength values [22], which is consistent with the data in Table 3. The high prevalence of mixed and adhesive failures indicates that the different results among experimental groups were caused by the differences of adhesive interface between the cements and the ceramic that was treated with distinct procedures [32].

In the present study, a lower power setting (200mJ) was selected. Microcracks were not observed in SEM micrographs (Fig.2C) and the absence of cohesive ceramic fractures (Table 4) suggests that the laser treatment did not induced internal weakening in the ceramic. The principle effect of laser energy is the conversion of light energy into heat and the most important interaction between laser and substrate is the absorption of energy by the substrate [16]. The mechanical properties of Y-TZP ceramics can be negatively affected by changes in temperature, which can induce phase transformation [20]. Higher laser power settings (400 and 600 mJ) can cause excessive material deterioration, making them unsuitable as surface treatments for zirconia [16].

CONCLUSION

Results suggest that thermocycling does not affect μSBS obtained in the resin-zirconia interface when applying a self-adhesive resin cement with 10-MDP in its composition over a zirconia surface pretreated with silica coating with or without Er:YAG. Nevertheless, the adhesive effectiveness is higher if the surface is only conditioned with silica coating (not applying the laser) despite the artificial aging process. The Er:YAG laser has been reported as creating thermo-mechanical effects on substrate; however, this study demonstrated that zirconia Er:YAG etching is not effective in increasing its bond strength to resin.

Acknowledgments

The authors would like to thank Dentsply (Germany), VOCO (Germany), Kuraray (Japan) and 3M (Germany) for providing some of the materials used in this study. We also thank the Dental Lab Aragoneses (Madrid, Spain), Judith Gomez for their technical support and, Spanish Pulsed Laser Center (CLPU) for instrument (SEM) use in this research.

REFERENCES

1. Denry I, Kelly JR (2008) State of the art of zirconia for dental applications. Dent Mater 24 (3):299-307

2. Manicone PF, Iommetti PR, Raffaelli L (2007) An overview of zirconia ceramics: basic properties and clinical applications. J Dent 35 (11):819-826

3. Blatz MB, Sadan A, Kern M (2003) Resin-ceramic bonding: a review of the literature. J Prosthet Dent 89 (3):268-274

4. Blatz M, Phark J-H, Ozer F, Mante F, Saleh N, Bergler M, Sadan A (2010) In vitro comparative bond strength of contemporary self-adhesive resin cements to zirconium oxide ceramic with and without air-particle abrasion. Clin Oral Investig 14 (2):187-192

5. Ferracane JL, Stansburry JW, Burke FJT (2011) Self-adhesive resin cements – chemistry, properties and clinical considerations. J of Oral Rehabil 38 (4):295-314

6. Aboushelib M, Kleverlaan C, Feilzer A (2007) Selective infiltration-etching technique for a strong and durable bond of resin cements to zirconia-based materials. J Prosthet Dent 98 (5):379-388

7. Phark JH, Duarte SJr, Blatz M, Sadan A (2009) An in vitro evaluation of the long-term resin bond to a new densely sintered high-purity zirconium-oxide ceramic surface. J Prosthet Dent 101 (1):29-38.

8. Aboushelib MN, Mirmohamadi H, Matinlinna JP, Kukk E, Ounsi HF, Salameh Z (2009) Innovations in bonding to zirconia-based materials. Part II: Focusing on chemical interactions. Dent Mater 25 (8):989-993

9. Atsu SS, Kilicarslan MA, Kucukesmen HC, Aka PS (2006) Effect of zirconium-oxide ceramic surface treatments on the bond strength to adhesive resin. J Prosthet Dent 95 (6):430-436

10. Blatz MB, Sadan A, Martin J, Lang B (2004) In vitro evaluation of shear bond strengths of resin to densely-sintered high-purity zirconium-oxide ceramic after long-term storage and thermal cycling. J Prosthet Dent 91 (4):356-362

11. Wolfart M, Lehmann F, Wolfart S, Kern M (2007) Durability of the resin bond strength to zirconia ceramic after using different surface conditioning methods. Dent Mater 23 (1):45-50

12. Paranhos MP, Burnett LHJr, Magne P (2011) Effect of Nd:YAG laser and CO2 laser treatment on the resin bond strength to zirconia ceramic. Quintessence Int 42 (1):79-89

13. Ural Ç, Külünk T, Külünk Ş, Kurt M (2010) The effect of laser treatment on bonding between ceramic surface and resin cement. Acta Odontol Scand 68 (6):354-359

14. Kern M, Wegner SM (1998) Bonding to zirconia ceramic: adhesion methods and their durability. Dent Mater 14 (1):64-71

15. Oyagüe RC, Osorio R, da Silveira BL, Toledano M (2011) Comparision of bond stability between dual-cure resin cements and pretreated glass-infiltrated alumina ceramics. Photomed Laser Surg 29 (7):465-475

16. Cavalcanti AN, Pilecki P, Foxton RM, Watson TF, Oliveira MT, Giannini M, Marchi GM (2009) Evaluation of the surface roughness and morphologic features of Y-TZP ceramics after different surface treatments. Photomed Laser Surg 27 (3):473-479

17. Ersu B, Yuzugullu B, Ruya YA, Canay S (2009) Surface roughness and bond strength of glass-infiltrated alumina-ceramics prepared using various surface treatments. J Dent 37 (11):848-856

18. Gökçe B, Özpınar B, Dündar M, Çömlekoglu E, Sen BH, Güngör MA (2007) Bond stregths of all ceramics: acid vs laser etching. Oper Dent 32 (2):168-173

19. Spohr AM, Borges GA, Júnior LH, Mota EG, Oshima HM (2008) Surface modification of In-Ceram Zirconia ceramic by Nd:YAG laser, Rocatec system, or aluminum oxide sandblasting and its bond stregth to a resin cement. Photomed Laser Surg 26 (3):203-208

20. 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

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

22. Toledano M, Osorio R, Osorio E, Aguilera FS, Yamauti M, Pashley DH, Tay F (2007) Durability of resin-dentin bonds: effect of direct/indirect exposure and storage media. Dent Mater 23 (7):885-892

23. De Munck J, Van Landuyt K, Peumans M, Poitevin A, Lambrechts P, Braem M, Van Meerbeek B (2005) A critical review of the durability od adhesion to tooth tissue: methods and results. J Dent Res 84 (2):118-132

24. Yang B, Lange-Jansen HC, Scharnberg M, Wolfart S, Ludwig K, Adelung R, Kern M (2008) Influence of saliva contamination on zirconia ceramic bonding. Dent Mater 24 (4):508-513

25. Gomes AL, Oyagüe RC, Lynch CD, Montero J, Albaladejo A (2012) Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. J Dent. doi:10.1016/j.jdent.2012.09.013.

26. Yoshida K, Tsuo Y, Astuta M (2006) Bonding of dual-cured resin cement to zirconia ceramic using phosphate acid ester monomer and zirconate coupler. J Biomed Mater Res B Appl Biomater 77 (1):28-33

27. de Oyagüe RC, Monticelli F, Toledano M, Osorio E, Ferrari M, Osorio R (2009) Influence of surface treatments and resin cement selection on bonding to densely-sintered zirconium-oxide ceramic. Dent Mater 25 (2):172-179

28. Subaşi MG, Inan O (2011) Evaluation of the topographical surface changes and the roughness of zirconia after different surface treatments. Lasers Med Sci 27 (4):735-742

29. Matinlinna JP, Vallitu PK (2007) Bonding of resin composites to etchable ceramic surfaces-an insight overview of the chemical aspects on surface conditioning. J Oral Rehabil 34 (8):622-630

30. Subaşi MG, Inan O (2012) Influence of surface treatments and resin cement selection on bonding to zirconia. Lasers Med Sci [Epub ahead of print]

31. Akyil MS, Uzun IH, Bayindir F (2010) Bond strentgh of resin cement to yttrium-stabilized tetragonal zirconia ceramic treated with air abrasion, silica coating and laser irradiation. Photomed Laser Surg 28 (6):801-808

32. Usumez A, Hamdemirci N, Kotoglu BY, Parlar O, Sari T (2013) Bond strength of resin cement to zirconia ceramic with different surface treatments. Lasers Med Sci 28 (1):259-266

33. Akin H, Tugut F, Akin GE, Mutaf B (2012) 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

34. Akgungor G, Sen D, Aydin M (2008) Influence of different surface treatments on the short-term bond strength and durability between a zirconia post and a composite resin core material. J Prosthet Dent 99 (5):388-399

35. May LG, Passos SP, Capelli DB, Ozcan M, Bottino MA, Valandro LF (2010) Effect of silica coating combined to a MDP based primer on the resin bond to Y-TZP ceramic. J Biomed Mater Res B Appl Biomater 95 (1):69–74

FIGURES:

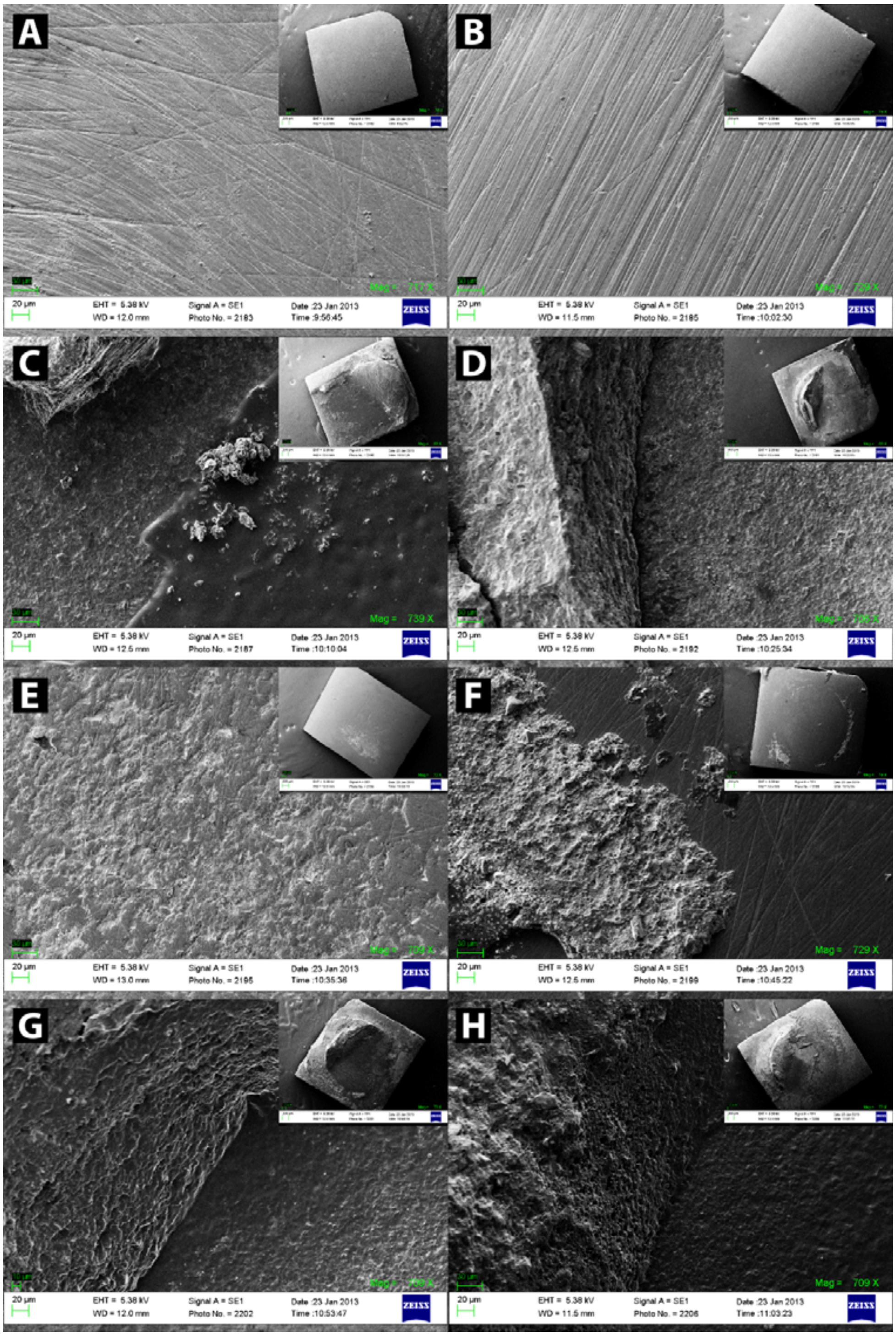

Fig. 1 SEM (×70 and ×700 magnification) images of zirconia surfaces to assess the failure type of each subgroup: A) BIF NT; B) CLE NT; C) BIF ROC; D) CLE ROC; E) BIF LAS; F) CLE LAS; G) BIF LAROC and H) CLE LAROC. Images A, B and E

show adhesive failure and a complete detachment of the luting agent from the porcelain substrate and, C, D, F, G and H show mixed failure with presence of cement residues on the zirconia surface.

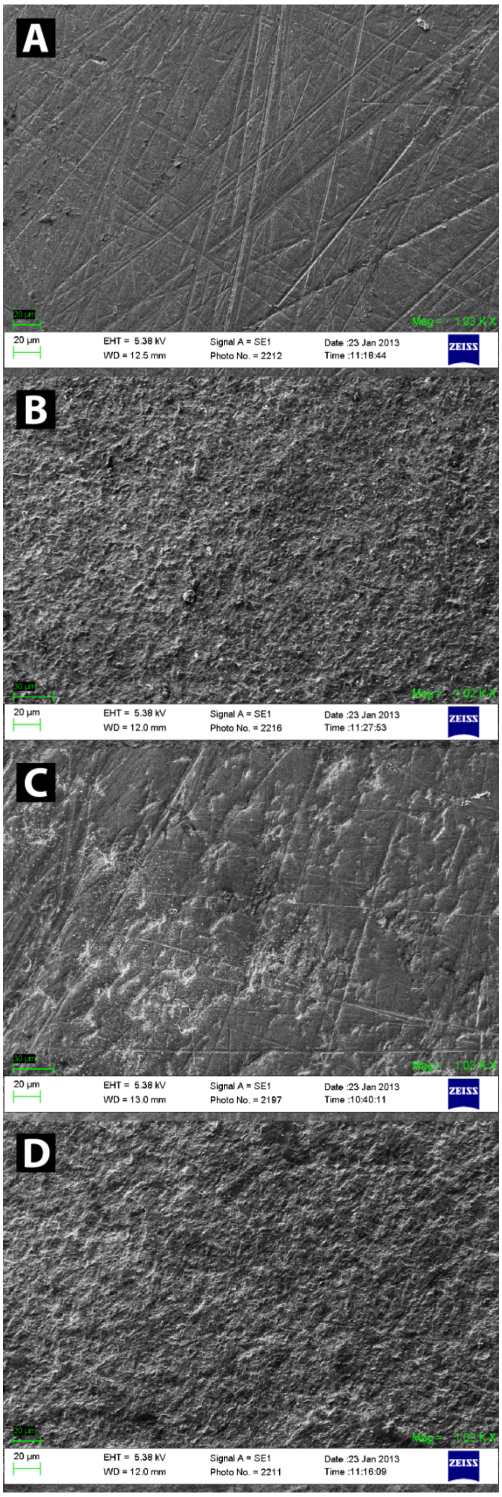

Fig. 2 SEM (×1000 magnifications) images of zirconia after the different surface treatments used: A) NT (No treatment); B) ROC (Rocatec™ Soft); C) LAS (Er:YAG laser with 200 mJ) and D) LAROC (Laser followed by silica coating).

TABLES

Table 1. Study design with the distribution of the samples among the different groups.

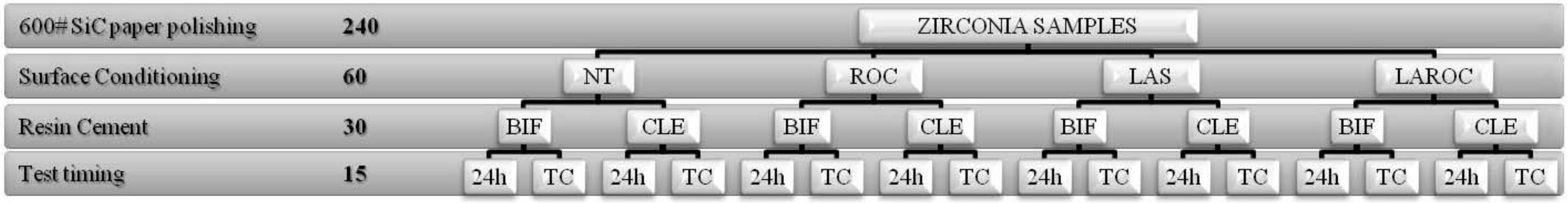

Table 2. Materials brands, composition and manipulation sequence used in the study.

Material	*Manufacturer*	*Batch nr*	*Composition*	*Manipulation Sequence*
Cercon®	DeguDent GmbH, Germany	Lot: 20023 3692	Zirconium Oxide (92%), Yttrium Oxide (5 %), Hafnium Oxide (<2%), Aluminium Oxide + Silicon Oxide (< 1%)	Sinter the ceramic cylinders in a special oven (Cercon Heat, Dentsply) keeping the temperature at 1,350ºC for 6h.
BiFix® SE	VOCO, Cuxhafen, Germany	Lot:12 21264 Ref 1794	Bis-GMA, UDMA, Gly-DMA, phosphate monomers, initiators, stabilizers, glass fillers, aerosol silica (filler = 70 wt%)	Dispense the cement from a dual-barreled automix syringe and a spiral mixing tip. Apply the cement on the ceramic surface. Self-cure for 5 min and light-cure each axial surface for 40 sec.
Clearfil™ SA Cement	Kuraray, Osaka, Japan	Lot:00 56AA Ref #2800 EU	10-MDP, hydrophobic aromatic dimethacrylate, hydrophobic	Dispense the cement from a dual-barreled automix syringe and a spiral mixing tip. Apply the cement on the ceramic surface. Self-cure for 5 min

			aliphatic dimethacrylate, colloidal silica, barium glass (filler 66 wt%)	and light-cure each axial surface for 40 sec.
Rocatec™ Soft	3M Espe, Seefeld, Germany	Lot: 410254	30 µm silica-modified alumina oxide	Sandblasting for 20 sec at 28 Bar and 10 mm of distance.
Rely X™ Ceramic primer	3M Espe, Seefeld, Germany	Lot:N 375992 Ref 2721	Ethyl alcohol, water, Methacryloxypropyl trimethoxysilane	Using a brush apply on the zirconia bonding surface for 40 sec. Gently air dry.

Table 3. Microshear bond strength mean (MPa ± Standard deviation) and ANOVA results.

	BiFix SE (BIF)		Clearfil SA (CLE)	
	24h	Thermocycled (TC)	24h	Thermocycled (TC)
No treatment (NT)	7.5 ± 5.6 $^{B, a}$	0.0 ± 0.0 $^{A, b}$	6.8 ± 3.4 $^{C, a}$	1.5 ± 2.6 $^{C, b}$
Rocatec (ROC)	17.3 ± 6.6 $^{A, a}$	1.9 ± 1.5 $^{A, b}$	15.8 ± 4.8 $^{A, a}$	15.3 ± 5.8 $^{A, a}$
Er:YAG (LAS)	5.7 ± 2.3 $^{B, a}$	1.8 ± 3.8 $^{A, b}$	6.9 ± 2.0 $^{C, a}$	0.0 ± 0.0 $^{C, b}$
Er:YAG + Rocatec (LAROC)	18.9 ± 4.6 $^{A, a}$	0.9 ± 2.2 $^{A, c}$	11.1 ± 3.8 $^{B, b}$	9.9 ± 3.5 $^{B, b}$

Different lower case letters in rows and upper case letters in columns indicate significant differences ($p < 0.05$).

Table 4. Failure mode distribution (%) in the experimental groups.

	BIF				CLE			
	24h		TC		24h		TC	
	A	M	A	M	A	M	A	M
NT	86.6	13.3	100	-	93.3	6.6	100	-
ROC	46.6	53.3	100	-	20	80	6.6	93.3
LAS	100	-	100	-	73.3	26.6	100	-
LAROC	33.3	66.6	100	-	40	60	66.6	33.3

(A) Adhesive failure; (M) Mixed failure

Table 5. Type of failures (adhesive *versus* mixed) percentages distribution according to the surface treatment among both BIF and CLE subgroups.

	BIF		CLE	
	NT +LAS	ROC +LAROC	NT +LAS	ROC +LAROC
ADHESIVE FAILURE (%)	97	70	92	32
MIXED FAILURE (%)	3	30	8	68
	Chi: 15.36; $p < 0.001$		Chi: 45.69; $p < 0.001$	
	OR (Adhesive/ Mixed) = 12.4		OR (Adhesive/ Mixed) = 23.7	
	CI 95%: 2.7-56.5		CI 95%: 8.2-68.9	

OD - Odds Ratio

CI - Confidence Interval

Gmail by Google

Ana Caseiro <acaseiro@gmail.com>

Decision on your manuscript #LIMS-1703

Lasers in Medical Science <erica.fajardo@springer.com> 22 de Maio de 2013 às 15:42
Para Ana Luísa Gomes <acaseiro@gmail.com>

Dear Ana:

We are pleased to inform you that your manuscript, "Thermocycling effect on microshear bond strength to zirconia ceramic using Er:YAG and tribochemical silica coating as surface conditioning" will be accepted for publication in Lasers in Medical Science pending some minor changes recommended by the reviewers. These comments are located at the bottom of the page.

When preparing your revised manuscript, you are asked to submit a list of responses to the comments. Your list of responses should be uploaded as a file in addition to your revised manuscript.

In order to submit your revised manuscript electronically, please access the following web site:

http://lims.edmgr.com/

Your login is: acaseiro
Your password is: [redacted]

Click "Author Login" to submit your revision.

We look forward to receiving your revised manuscript.

Best regards,

Keyvan Nouri
Lasers in Medical Science

Reviewer #2: Well done, well writen!

Needs a better abstract, with more information about the groups.

May be useful to create another table with groups. Its hard to understanding in the first moment.

IV. DISCUSSION

Our literature review on the zirconia use as implant abutments reported cases of clinical success as well as *in vitro* studies indicating their applicability. The topics of precision fit, abutment strength, bacterial adherence and soft tissues response were addressed. Although zirconia implant abutments did not present fracture strength values as good as conventional titanium abutments, they are indicated to use in esthetically compromised areas. These abutments revealed a good adjustment, excellent biocompatibility and optimal esthetic appearance. All these benefits are particularly relevant in patients with single-tooth implant rehabilitations with a thin gingival biotype.

Along with an adequate fracture resistance and marginal fit, achieving durable bond at the tooth/cement, zirconia/cement, and zirconia/veneering ceramic interfaces is essential for the long-term success of all-ceramic zirconia-based restorations. There is a wide range of materials and surface conditioning methods suggested for cementing Y-TZP without adequate information on their action mode or function. Achieving a successful long-term zirconia bonding requires a well-documented knowledge on adhesive dental materials as well as control over pre-treatment techniques. Nowadays, total ceramic restorations are considered the best option to be used when minimal invasive procedure is followed. The restoration retention may be insufficient due to the resultant tooth preparation. Therefore, a proper adhesive bonding can not be neglected.

Scientific literature may be difficult to interpret as there still controversy on the zirconia bonding thematic. The experimental work done was designed to determine some guidelines for improving the zirconia/resin interface. The individual practitioner working with these contemporary dental biomaterials needs clarified information and cementation protocols to reach the patient expectations and fulfill a successful prosthetic treatment.

Firstly, the microtensile bond strength test was chosen to evaluate the bond strength of dual-cure resin cements to zirconia, and analyze the sandblasting granulometry and the cement composition influence in the zirconia/resin interface bond strength (Chapter III.2). This is a more labour-intensive test than tensile and shear testing, but holds greater potential for providing insight into the strength of adhesion of luting materials to clinically relevant substrates (Pashley *et al.,* 1999) such as zirconia frameworks for all-ceramic prostheses. It is still debate whether pre-test failures should be excluded from the statistical calculations, included as zeros (Pashley *et al.,* 1999), or rather as greater-than-zero values through the assumption that it must have taken some stress to produce failure during sectioning (Nikolaenko *et al.,* 2004; Gorraci *et al.,* 2006). As in related research (Oyagüe *et al.,* 2011), in our experiment the decision was made to include the values as zero bonds, although we are aware that this may have biased the test toward a slight infra-estimation of the bonding potential. Because of this drawback, micro shear bond strength test was used, in order to assess the effect of surface conditioning and self-adhesive resin cement in the adhesion to zirconia under aging, in the second essay performed (Chapter III.3). The SBS test is one of the most frequently used bond strength test. Shear forces are considered the major stress in *in vivo* bonding failures of restorative materials (Ersu *et al.,* 2009).

In both tests, for the resin-zirconia interface bond strength analysis, the luting cement was directly applied on the zirconia surface instead of using tooth structures due to the homogeneous resin structure. Thus, the zirconia was luted right to resin rather to dental tissues to avoid tooth microstructural variations that could misread the results (de Oyagüe *et al.,* 2009; Oyagüe *et al.,* 2009).

The findings of the first experiment (Chapter III.2) determined that both factors evaluated, sandblasting granulometry and the composition of resin cements influenced zirconia/resin interface bond strength, since differences among the experimental groups were found. The 10-MDP containing cement attained higher MTBS than the non 10-MDP containing cement regardless of the ceramic surface treatment. Both cements have a typical glass filler content in the range of 60-75 wt%, as well as other types of methacrylate monomers that are present in most resin-based materials (i.e., Bis-GMA, UDMA and TEGDMA) (Oyagüe *et al.,* 2009). However, the 10-MDP acidic functional monomer, which has been rated as relatively hydrolysis stable due to its long carbonyl chain (de Oyagüe *et al.,* 2009), is only present in *Panavia 2.0 F* (Kuraray Medical Ltd, Osaka, Japan). According to the manufacturer's instructions, prior to *Panavia* application, a silane was spread over the ceramic surface. The 3-MPS (3-methacryloxypropyl trimethoxysilane) and the 10-MDP monomers mixed in this silane-coupling solution (*Clearfil Ceramic Primer*) enhance the ceramic surface wettability, protect against moisture, and create an acid environment that may support the bonding reaction. As a result, the 10-MDP monomers of the silane form cross-linkages with the 10-MDP groups dispersed in the cement resin matrix and with the -OH radicals of the zirconium-oxide surfaces (Kern *et al.,* 1998; Yoshida *et al.,* 2006; Wolfart *et al.,* 2007).

Furthermore, 10-MDP containing cement recorded the best overall bond strength values when applied to air-abraded zirconia surfaces, yielding comparable results to those of a related investigation that combined a 10-MDP containing luting system with sandblasting of 125-μm particles (*Clearfil*, Kuraray: 18.63 ± 6.4 MPa) (de Oyagüe *et al.,* 2009). Air-abrasion produced microretentions where the ceramic primer might have been able to penetrate and interlock (Figs. III.2.3 b,c). This could probably explain why no premature failures were obtained in these groups. Thus, the use of 10-MDP containing cement on sandblasted zirconia surfaces seems to reduce the risk of spontaneous debonding regardless of the particle size of air-abrasion. Moreover, in line with the findings of the abovementioned study (de Oyagüe *et al.,* 2009), most air-abraded microbars luted with 10-MDP containing cement exhibited a mixed fracture pattern with remaining cement layers above the porcelain substrate (Figs. III.2.2 d,f). Although the combination of APA and 10-MDP containing luting systems that use primers has already shown significant enhancement of the durability of bonds to zirconia (Yoshida *et al.,* 2006; Blatz *et al.,* 2007; Wolfart *et al.,* 2007; Kern *et al.,* 2009), the novelty of our research was that the sandblasting granulometry caused no significant effect in the μTBS and fracture pattern of zirconia surfaces when different dual-cure resin cements were used.

On the contrary, more than one-third of the untreated sticks bonded with 10-MDP containing cement failed prematurely. A flat surface was discovered in untreated ceramic surfaces (Fig. III.2.3 a). This may also explain that most untreated zirconia samples luted with 10-MDP containing cement showed adhesive fractures. Accordingly, in a previous study, omitting air-abrasion resulted in debonding during artificial aging independent of using primers (Kern *et al.,* 2009). Mixed failures are considered clinically preferable than adhesive ones since the latest are usually associated with low bond strength values (Toledano *et al.,* 2007).

As has been previously stated, the non 10-MDP containing cement (*BiFix SE,*VOCO, Cuxhafen, Germany) recorded significantly lower µTBS than 10-MDP containing one despite the ceramic surface treatment. The resin matrix of non 10-MDP containing cement used contains multifunctional-phosphoric adhesive dimethacrylate monomers with at least two unsaturated C=C double bonds. Those monomers react with the inorganic fillers dissolved in the resin matrix, thus forming chemical cross-linkages (Oyagüe *et al.,* 2011). The mechanical interlocking of non 10-MDP containing cement at the cement/ceramic interface may be compared to that of glass-ionomer cements (Yap *et al.,* 2003). In such cases, the glass silicate particles dissolved in the cement matrix may react with the acidic phosphoric esters forming a silicate gel in which particles of unreacted glass are embedded (Nicholson 1998). Other self-adhesive luting agents reported higher µTBS values in former studies (de Oyagüe *et al.,* 2009; Oyagüe *et al.,* 2011), which may be attributed not only to slight differences in the cement composition, but also to disparities in the studies protocols.

Despite the conditioning method, *BiFix SE* has demonstrated a higher risk of suffering a spontaneous detachment from the ceramic substrate than the 10-MDP containing cement and predominantly failed adhesively, leaving no cement residuals on the ceramic surface (Figs. III.2.2 a,e), which is in accordance with the literature for other self-adhesive cements (Blatz *et al.,* 2003; de Oyagüe *et al.,* 2009). This study did not reveal significant differences in µTBS between the four subgroups of non 10-MDP containing cement specimens luted either to untreated or air-abraded zirconia surfaces using different particle sizes. This can strengthen the concept that the mechanical adhesion by itself does not provide the resin bond strength required for CAD/CAM dental ceramics, so a reliable chemical adhesion is also recommended. In this regard, it has recently been proven that the combination of a self-adhesive resin cement with a 10-MDP containing primer results in durable bond strength to sandblasted zirconia ceramic (Yang *et al.,* 2010). However, with this formula, self-adhesive resin cements lose their announced advantages of being applied in one clinical step and might be as technique-sensitive as other dual-cure resin cements.

Nonetheless, as the µTBS values of the non 10-MDP containing cement were quite low under the tested experimental conditions, the 10-MDP containing cement in combination with air-abrasion seems to be the best alternative to bond zirconia. When the cement is changed from *BiFix SE* to *Panavia 2.0 F* in the current study, the bond strength was significantly enhanced in a range between 13.1 and 15.4 MPa, independently of the conditioning method. Despite the methodological differences, these findings are in agreement with those of a former study, which found significantly higher µTBS to zirconia for 10-MDP containing *Clearfil Esthetic Cement* than for the self-adhesive resin *Rely X Unicem*, regardless of the surface treatment (de Oyagüe *et al.,* 2009).

No differences were identified in the architecture of zirconia surfaces sandblasted with different-sized Al_2O_3 particles that showed comparable micro-retentive grooves at the micrometer scale (Figs. III.2.3 b,c). However, a trend toward a positive correlation between the particle size of APA and the µTBS at the cement/zirconia interface was observed when 10-MDP containing cement was used. In this experiment, for each increased micron in the size of the Al_2O_3 particles the bond strength of 10-MDP containing cement would augment between 0.024–0.052 MPa (CI 95%). Although no study has been found on the effect of the sandblasting particle size on the bond strength to zirconia, an investigation on the optimal surface treatments for carbon/epoxy composite adhesive joints concluded that the surface roughness, eroded length and eroded depth increased as the particle size of sandblasting increased (Kim *et al.,* 2003), which concurs with the results of this paper, considering that roughened surfaces increase the bond area of the adhesive joint and the effect of interlocking (Kinloch 1987), mainly after priming (Yoshida *et al.,* 2006). Nonetheless, the surface energy parameters of luting cements should be assessed using a profilometer and contact angle measurements to evaluate their adhesive properties to zirconia ceramic (Kim *et al.,* 2011).

The results of the second experiment (Chapter III.3) determined that the factors studied, composition of resin cements, surface conditioning with silica coating and/or Er:YAG, and thermocycling, influenced zirconia/resin interface bond strength because significant differences among the experimental groups were found, as detailed next.

A μSBS significant predictor was the type of cement, which implies that its value could be increased from 0.6 to 3.0 MPa if *Clearfil™ SA Cement* (Clearfil™ SA Cement, Kuraray, Osaka, Japan) was used instead of *BiFix® SE* (BiFix® SE, VOCO, Cuxhafen, Germany). Both cements belong to the self-adhesive resin cements category and were used in a single step on the zirconia surface (following the manufacturers' instructions). Nevertheless, given their common composition, present in most resin-based materials, we should highlight the 10-MDP existences in the first. This acidic functional monomer was reported as able of chemically adhering to zirconium oxide by interacting with the –OH radical in the ceramic surface (Kern *et al.,* 1998; Yoshida *et al.,* 2006; Wolfart *et al.,*

2007) and rated as relatively hydrolysis stable, due to its long carbonyl chain (de Oyagüe *et al.,* 2009).

The surface conditioning procedure, the strongest predictor factor in the regression model used, seems to be a more relevant factor in bonding to zirconia surface, contrary to other studies that advocate the cement choice as fundamental to attain reliable adhesion to zirconia (Oyagüe *et al.,* 2011; Subaşi *et al.,* 2011). Both cements had higher μSBS values after tribochemical silica coating. SEM observations revealed considerable qualitative differences in the ceramic surface architecture after the different conditioning methods (Fig. III.3.2). These findings can be directly related to bond strength results, as the treated surface is rough with uniform presence of shaped microretentions and shallow pits, but no microcracks (Fig. III.3.2B and D). The resultant improvement in resin bond strength can be explained, not only by the attained roughness, but also because the silica coating process allows chemical coupling through the silane (Atsu *et al.,* 2006; Paranhos *et al.,* 2011). Prior cement application, the ceramic surface irregularities, resulting from *Rocatec*™ particles' impact, were infiltrated by *Rely X*™ *Ceramic Primer*, a pre-hydrolyzed 3-MPS (3-methacryloxypropyltrimethoxysilane) ready for direct use as supplied by the manufacturer. Silane coupling agents have silicon linked to reactive organic radicals, which become chemically bonded to resin molecules and form siloxane linkages with the silica-coated surface. Their application enhances the ceramic wettability (causing better contact and infiltration of the resin in the ceramic irregularities), protects against moisture, and creates an acidic environment that may support the bonding reaction (Matinlinna *et al.,* 2007).

Both cements recorded similar μSBS when samples were only irradiated with Er:YAG, regardless thermocycling process. Although the laser treatment creates a rougher surface (Fig. III.3.2C), it did not improve bond strength. The surface irregularities created, probably as a result of local increases of the substrate temperature generating an erosive effect, have insufficient micro depth without micromechanical retention resulting in limited penetration of the luting cement. Er:YAG laser had minimal impact on zirconia thanks to the fact it is a water-free material that presents a white and opaque coloration. The *Rocatec*™ employment after the laser easily overcame and covered the laser effect on surface modification and a similar surface to the group that used only tribochemical silica coating was observed (Fig. 2B and D). These results are in line with the other recent study findings (Subaşi *et al.,* 2011).

Bond strength results indicate that laser irradiation was less effective in improving bond strength than tribochemical silica coating, for both resin cements. A recent study also registered low bond strength of all luting systems tested to Er:YAG irradiated zirconia. The authors suggested that during laser irradiation, the micro-explosions could form debris that might adhere to the melted ceramic surfaces. Such a layer would be able to bond strongly to the resin cement but would be poorly attached to the infra-layer surface, resulting in low bond strengths (Subaşi *et al.,* 2011). However, this hypothesis has not been confirmed, and this fact would need further investigation. While Subaşı *et al.* (Subaşi *et al.,* 2011; Subaşi *et al.,* 2012) and Akyil *et al.*(Akyil *et al.,* 2010) reported similar results to our study, others suggested that Er:YAG laser significantly increased the SBS of ceramic to dentin (Cavalcanti *et al.,* 2009; Akın *et al.,* 2012; Usumez *et al.,* 2013).

Thermocycling affected negatively all the specimens' bond strength, except when the 10-MDP containing cement was used in combination with *Rocatec*™ with or without laser groups. A slight decrease in bond strength was observed after TC, which was not statistically significant. The aging effect induced by thermocycling can occur by repetitive contraction/expansion stresses generated by different thermal coefficient of the materials or by hydrolysis of the interfacial components (water can infiltrate and decrease the mechanical properties of the polymer matrix, by swelling and reducing the frictional forces between the polymer chains) (De Munck *et al.,* 2005). When silica coating was performed, *Clearfil*™ *SA Cement* was able to adhere to the silica present on the ceramic surface through the interaction between 10-MDP monomer and 3-MPS, producing more durable bonding values as demonstrated in previous studies (Akgungor *et al.,* 2008; May *et al.,* 2010).

Failure modes patterns were assessed and supported the bond strength results. Both cements in control and laser treated groups had a tendency to fail adhesively at the resin-zirconia interface, presenting the substrate surface free of cement residues (Fig. III.3.1A, B and E), which is in accordance with the literature for other self-adhesive cements (Blatz *et al.,* 2003; de Oyagüe *et al.,* 2009). Mixed failures were observed mostly when tribochemical silica coating was performed followed or not by laser treatment. These are clinically preferred to adhesive failures because there are usually associated with high bond strength values (Toledano et al., 2007), which is consistent with our results. The high prevalence of mixed and adhesive failures indicates that the different results among experimental groups were caused by the differences of adhesive interface between the cements and the ceramic that was treated with distinct procedures (Usumez *et al.,* 2013).

With the selected lower power setting of the laser (200mJ) used, microcracks were not observed in SEM micrographs (Fig. III.3.2C). The absence of cohesive ceramic fractures suggested that laser treatment did not induce internal weakening in the ceramic. The principal effect of laser energy is the conversion of light energy into heat and the most important interaction between laser and substrate is the absorption of energy by the substrate (Cavalcanti *et al.,* 2009). The mechanical properties of Y-TZP ceramics can be negatively affected by changes in temperature, which can induce phase transformation (Cavalcanti *et al.,* 2009). Higher laser power setting (400 and 600 mJ) can cause excessive material deterioration, making them unsuitable as surface treatments for zirconia (Cavalcanti *et al.,* 2009).

Bonding self-adhesive resin cements, 10-MDP-based or not, to untreated or laser irradiated zirconia and without priming the surface yielded low bond strength values. Based in the current results, the use of flat ceramic and the luting agent direct application may be considered adverse factors to gain bond strength at the resin-zirconia interface. On the other hand, silica coating combined with the use of a 10-MDP containing self-adhesive resin cement seems to be promising.

In the interest of obtaining the highest bond strength, it can be summarized that the clinician should choose a cementation protocol that provides micromechanical retention in the ceramic surface, a reliable silicatizing method and both primer and adhesive resin containing 10-MDP monomer to yield chemical adhesion.

Another important point to consider is the possible contamination of the ceramic restoration during handling and fit checking. The best option consists in an immediate chairside surface conditioning method, without relying only on the laboratory pretreatment. All the steps in surface treatment, priming and cementing must be carried out carefully to achieve the best of what techniques and materials can offer, optimizing results.

The crystalline ceramic surface inertness against chemical treatment has been reported to be the most difficult obstacle to the bonding procedure. On the other hand, the particle abrasion effects have been reported variously as an increase or decrease in the material flexural strength depending on the structure damage induced by the abrasion method used (Kosmac *et al.,* 1999; Guazzato *et al.,* 2005). Consequently the search for gentle and careful zirconia surface roughening procedures is worth having regard to.

Choosing techniques and materials meticulously an acceptable long-term bond can be achieved, although a premium chemical bonding is yet to come. The search for a chemical agent that forms stable bonds to crystalline ceramics, particularly zirconia, continues. Besides testing the bonding strength, it will also be interesting to know how it affects the longevity, structural stability and microleakage of the ceramic FPDs. The research of any of these subjects will benefit the use of these materials and help the progress of prosthodontics.

V. CONCLUSIONS

1. Zirconia implant abutments use is well documented in literature with several *in vitro* studies and case reports of their success. They present identical properties to the universally used titanium abutments considering the precision fit and superior characteristics on the topic of bacterial adherence and biocompatibility. Although zirconia abutments have fracture strength values not as good as conventional titanium ones, they are indicated in the anterior sector prosthetic rehabilitation, providing a favorable esthetic and functional addition to implant dentistry.
2. The sandblasting implementation before cementation is determinant to assure a good bond strength results in the zirconia/resin interface, regardless of the particles size. However, there is a trend toward a positive correlation between the sandblasting particle granulometry increase and the bond strength at the zirconia/resin interface if a 10-MDP containing cement is used.
3. The adhesive effectiveness is higher if the surface is only conditioned with silica coating (not applying the laser). Zirconia Er:YAG etching is not effective in increasing its bond strength to resin.
4. The presence of 10-MDP monomer on the cement composition positively influences the bonding because it enhances chemical adhesion to a zirconia substrate. The application of a cement system that contain 10-MDP, both in the coupling agent and the resin matrix on a sandblasted or silica coated substrate may be the key to a successful zirconia/resin bonding.

5. The thermocycling impact on the bond strength depends on the materials used. A specific self-adhesive resin cement with 10-MDP in its composition over a zirconia surface pretreated with silica coating (with or without Er:YAG associated) is not influenced by thermocycling.

Conclusiones

1. El uso de pilares circona sobre implantes está bien documentado en la literatura con varios estudios *in vitro* y algunos trabajos clínicos que avalan su indicación. Estos pilares de circona tienen un ajuste marginal similar a los pilares de titanio, utilizados universalmente, y ostentan una baja adherencia bacteriana y una alta biocompatibilidad. Aunque los pilares de circona tienen valores de resistencia a la fractura inferiores a los de titanio, se indican en la rehabilitación protésica del sector de anterior, proporcionando un resultado estético y funcional superior.

2. La aplicación de arenado antes de la cementación es determinante para asegurar una buena adhesión en la interfase de circona/resina, independientemente del tamaño de las partículas de alumina. Sin embargo, hay una tendencia evidente entre el aumento de la granulometría de la partícula del arenado y la resistencia de la unión en la interfase circona/resina si se utiliza un cemento que contiene 10-MDP.

3. La eficacia de adhesivo es mayor si la superficie sólo está condicionado con revestimiento de sílice (sin aplicar el láser). El grabado de circona con laser de Er: YAG no es eficaz en el aumento de su resistencia de la adhesión a la resina.

4. La presencia de monómero de 10-MDP en la composición de cemento influye positivamente en la adhesión una vez que es capaz de mejorar la adhesión química a un sustrato de circona. La aplicación de un sistema de cemento que contiene 10-MDP, tanto en el *primer* como en la matriz de resina sobre un sustrato recubierto de sílice o arenado puede ser la clave para el éxito de la adhesión circona/resina.

5. El impacto termociclado en la resistencia de la unión depende de los materiales utilizados. Un cemento auto-adhesivo, específico de resina con 10-MDP en su

composición sobre una superficie de circona pretratada con revestimiento de sílice (con o sin Er: YAG asociada) no se afecta por el termociclado.

VI. REFERENCES

Aboushelib MN, Feilzer AJ and Kleverlaan CJ. Bonding to Zirconia Using a New Surface Treatment. J Prosthodont 2010; 19: 340-46.

Aboushelib MN, Kleverlaan CJ and Feilzer AJ. Selective infiltration-etching technique for a strong and durable bond of resin cements to zirconia-based materials. J Prosthet Dent. 2007; 98: 379-88.

Aboushelib MN and Matinlinna JP. Combined novel bonding method of resin to zirconia ceramic in dentistry: a pilot study. J Adhesive Sci Technol. 2011; 25: 1049-60.

Aboushelib MN, Matinlinna JP, Salameh Z and Ounsi H. Innovations in bonding to zirconia-based materials: Part I. Dent Mater. 2008; 24: 1268-72.

Aboushelib MN, Mirmohamadi H, Matinlinna JP, Kukk E, Ounsi HF and Salameh Z. Innovations in bonding to zirconia-based materials. Part II: Focusing on chemical interactions. Dent Mater. 2009; 25: 989-93.

Adatia ND, Bayne SC, Cooper LF and Thompsom JY. Fracture resistance of yttria-stabilized zirconia dental implant abutments. J Prosthodont. 2009; 18: 17-22.

Akgungor G, Sen D and Aydin M. Influence of different surface treatments on the short-term bond strength and durability between a zirconia post and a composite resin core material. J Prosthet Dent. 2008; 99: 388-99.

Akın H, Ozkurt Z, Kımalı O, Kazazoglu E and Ozdemir AK. Shear bond strength of resin cement to zirconia ceramic after aluminum oxide sandblasting and various laser treatments. Photomed Laser Surg. 2011; 29: 797-802.

Akın H, Tugut F, Akin GE and Mutaf B. Effect of Er:YAG laser application on the shear bond strength and microleakage between resin cements and Y-TZP ceramics. Lasers Med Sci. 2012; 27: 333-38.

Akyil MS, Uzun IH and Bayindir F. Bond strength of resin cement to yttrium-stabilized tetrgonal zirconia ceramic treated with air abrasion, silica coating and laser irradiation. Photomed Laser Surg. 2010; 28: 801-08.

Álvarez-Fernandez MA, Peña-Lopez JM, González-González IR and Olay-Garcia MA. Características generales y propiedades de las cerámicas sin metal. RCOE. 2003; 8: 525-46.

Amaral R, Özcan M, Valandro LF, Balducci I and Bottino MA. Effect of conditioning methods on the microtensile bond strength of phosphate monomer-base cement on zirconia ceramic in dry and aged conditions. J Biomed Mater Res B Appl Biomater. 2008; 85: 1-9.

Amaral R, Özcan M, Valandro LF and Bottino MA. Microtensile bond strength of a resin cement to glass infiltrated zirconia-reinforced ceramic: the effect of surface conditioning. Dent Mater. 2006; 22: 283- 90.

Andersson B, Glauser R, Maglione M and Taylor A. Ceramic implant abutments used for short-span FPDs: a prospective 5-year multicenter study. Int J Prosthodont. 2003; 16: 640-6.

Andersson B, Schärer P, Simion M and Bergström C. Ceramic implant abutments used for short-span fixed partial dentures: a prospective 2-year multicenter study. Int J Prosthodont. 1999; 12: 318-24.

Anthonson SA and Anusavice KJ. Contrast ratio of veneering and core ceramics as a function of thickness. Int J Prosthodont. 2001; 14: 316-20.

Anusavice KJ. Dental Ceramics. in Phillips' Science of Dental Materials. Ed. K. J. Anusavice. Missouri, USA: Saunders 2003. p. 655-719.

Aramouni P, Zebouni E, Tashkandi E, Dib S, Salameh Z and Almas K. Fracture resistance and failure location of zirconium and metallic implant abutments. J Contemp Dent Pract. 2008; 9: 41-48.

Armstrong S, Geraldeli S, Maia R, Raposo LHA, Soares CJ and Yamagawa J. Adhesion to tooth structure: a critical review of "micro" bond stength test methods. Dent Mater. 2009; 26: e50-e62.

Atsu SS, Kilicarslan MA, Kucukesmen HC and Aka PS. Effect of zirconium-oxide ceramic surface treatments on the bond strength to adhesive resin. J Prosthet Dent. 2006; 95: 430-36.

Att W, Kurun S, Gerds T and Strub JR. Fracture resistance of single-tooth implant-supported all-ceramic restorations: an in vitro study. J Prosthet Dent. 2006; 95: 111-6.

Attia A. Bond strength of three luting agents to zirconia ceramic-influence of the surfae treatment and thermocycling. J Appl Oral Sci. 2011; 19: 388-95.

Attia A and Kern M. Long-term resin bonding to zirconia ceramic with a new universal primer. J Prosthet Dent. 2011; 106: 319-27.

Bagheri R, Mese A, Burrow MF and Tyas MJ. Comparision of the effect of storage media on shear punch strength of resin luting cements. J Dent. 2010; 38: 820-27.

Ban S. Reliability and properties of core materials for all-ceramic dental restorations. Jpn Dent Sci Rev. 2008; 44: 3-21.

Bertrand M and Rocca J. Er:YAG laser and conservative dentistry. EMC-Stomatologie. 2005; 1: 104-115.

Betamar N, Cardew G and Van Noort R. Influence of specimen designs on the microtensile bond strength to dentin. J Adhes Dent. 2007; 9: 159-68.

Beuer F, Stimmelmayr M, Gernet W, Edelhoff D, Güh JF and Naumann M. Prospective study of zirconia-based restorations: 3-year clinical results. Quintessence Int. 2010; 41: 631-7.

Blatz M, Phark J-H, Ozer F, Mante F, Saleh N, Bergler M *et al*. In vitro comparative bond strength of contemporary self-adhesive resin cements to zirconium oxide ceramic with and without air-particle abrasion. Clin Oral Investig. 2010; 14: 187-92.

Blatz M, Sadan A, Martin J and Lang B. In vitro evaluation of shear bond strengths of resin to densely-sintered high-purity zirconium-oxide ceramic after long-term storage and thermal cycling. J Prosthet Dent. 2004; 91: 356-62.

Blatz MB, Chiche G, Holst S and Sadan A. Influence of surface treatment and simulated aging on bond strengths of luting agents to zirconia. Quintessence Int. 2007; 38: 745-53.

Blatz MB, Sadan A and Kern M. Resin-ceramic bonding: a review of the literature. J Prosthet Dent. 2003; 89: 268-74.

Blatz MB, Sadan A, Martin J and Lang B. In vitro evaluation of shear bond strengths of resin to densely-sintered high-purity zirconium-oxide ceramic after long-term storage and thermal cycling. J Prosthet Dent. 2004; 91: 356-62.

Borges GA, Sophr AM, Goes MF, Sobrinho LC and Chan DCN. Effect of etching and airborne particle abrasion on the microstructure of different dental ceramics. J Prosthet Dent. 2003; 89: 479-88.

Burke FJT. Trends in indirect dentistry: 3. Dent Update. 2005; 32: 251-54.

Burkes EJ, Hoke J, Gomes E and Wolbarsht M. Wet versus dry enamel ablation by Er:YAG laser. J Prosthet Dent. 1992; 67: 847-51.

Butz F, Heydecke G, Okutan M and Strub J. Survival rate, fracture strength and failure mode of ceramic implant abutments after chewing stimulation. J Oral Rehabil. 2005; 32: 838-43.

Cardoso MV, Coutinho E, Ermis RB, Poitevin A, Van Landuyt K, de Munck J *et al*. Influence of Er, Cr:YSGG laser treatment on the microtensile bond strength of adhesives to dentin. J Adhes Dent. 2008; 10: 25-33.

Castillo de Oyagüe R, Lynch C, McConnell R and Wilson N. Teaching the placement of posterior rein-based composite restorations in Spanish schools. Med Oral Patol Oral Cir Bucal. 2012; 17: e661-68.

Casucci A, Osorio E, Osorio R, Monticelli F, Toledano M, Mazzitelli C *et al*. Influence of different surface treatments on surface zirconia frameworks. J Dent. 2009; 37: 891-97.

Cavalcanti AN, Foxton RM, Watson TF, Oliveira MT, Giannini M and Marchi GM. Bond strength of resin cements to a zirconia ceramic with different surface treatments. Oper Dent. 2009a; 34: 280-87.

Cavalcanti AN, Pilecki P, Foxton RM, Watson TF, Oliveira MT, Giannini M *et al*. Evaluation of the surface roughness and morphologic features of Y-TZP ceramics after different surface treatments. Photomed Laser Surg. 2009b; 27: 473-79.

Chevalier J. What future for zirconia as a biomaterial? Biomaterials. 2006; 27: 535-43.

Craig RG and Powers JM (2002). Restorative Dental Materials. St. Louis.

Darvell BW, Samman N, Luk WK, Clark RK and Tidemen H. Contamination of titanium casting by aluminium oxide blasting. J Dent. 1995; 23: 319-22.

De Hoff PH, Anusavice KJ and Wang Z. Three-dimensional finite analysis of the shear bond test. Dent Mater. 1995; 11: 123-31.

De Munck J, Braem M, Wevers M, Yoshida Y, Inoue S, Suzuki K *et al*. Micro-rotatory fatigue of tooth-biomaterial interfaces. Biomaterials. 2005; 26: 1145-53.

De Munck J, Van Landuyt K, Peumans M, Poitevin A, Lambrechts P, Braem M *et al*. A critical review of the durability od adhesion to tooth tissue: methods and results. J Dent Res. 2005; 84: 118-32.

de Oyagüe RC, Monticelli F, Toledano M, Osorio E, Ferrari M and Osorio R. Influence of surface treatments and resin cement selection on bonding to densely-sintered zirconium-oxide ceramic. Dent Mater. 2009; 25: 172-9.

de Souza GM, Silva NR, Paulillo LA, Goes MF, Rekow ED and Thompson VP. Bond strength to high-crystalline content zirconia after different surface treatments. J Biomed Mater Res B Appl Biomater. 2010; 93: 318-23.

Della Bona A, Anusavice KJ and Mecholsky JJr. Apparent Interfacial Fracture Toughness of Resin/Ceramic Systems. J Dent Res. 2006; 85: 1037-41.

Della Bona A and Van Noort R. Shear *vs* tensile bond strength of the resin composite bonded to ceramic. J Dent Res. 1995; 74: 1591-96.

Demir N, Subaşi MG and Ozturk AN. Surface roughness and morphologic changes of zirconia following different surface treatments. Photomed Laser Surg. 2012; 30: 339-45.

Denry I and Holloway JA. Ceramics for Dental Applications: A Review. Materials. 2010; 3: 351-68.

Denry I and Kelly JR. State of the art of zirconia for dental applications. Dent Mater. 2008; 24: 299-307.

Dérand P and Dérand T. Bond strength of luting cements to zirconium oxide ceramics. Int J of Prosthodont. 2000; 13: 131-35.

Díaz-Romeral Bautista P, López Soto E, Malumbres Viscarret F and Gil Villagrá LJ. Porcelanas dentales de alta resistencia para restauraciones de recubrimiento total: Una revisión bibliográfica. Parte I. Revista Internacional de Prótesis Estomatológica. 2008; 10: 19-31.

Egilmez F, Ergun G, Cekic-Nagas I, Vallitu PK and Lassila LV. Influence of cemente thickness on the bond strength of tooth-colored posts to root dental after thermal cycling. Acta Odontol Scand. 2012 (in press).

Erhardt MC, Osorio R, Viseras C and Toledano M. Adjunctive use of an anti-oxidant agent to improve resistance of hybrid layers of degradation. J Dent. 2011; 39: 80-7.

Ersu B, Yuzugullu B, Ruya Y and Canay S. Surface roughness and bond strength of glass-infiltrated alumina-ceramics prepared using various surface treatments. J Dent. 2009; 37: 848-56.

Ferracane JL, Berge HX and Condon JR. In vitro aging of dental composites in water- effect of degree of conversion, filler volume, and filler/matrix coupling. J Biomed Mater Res. 1998; 42: 465-72.

Ferracane JL, Hopkin JK and Condon JR. Properties of heat-treated composites after aging in water. Dent Mater. 1995; 11: 354-58.

Ferracane JL, Stansburry JW and Burke FJT. Self-adhesive resin cements – chemistry, properties and clinical considerations. J of Oral Rehabil. 2011; 38: 295-314.

Fischer TE. Tribochemestry. Annu Rev Mater Sci. 1988; 18: 303-23.

Fons-Font A, Solá-Ruiz M and Martinez-González A. Clasificación actual de las cerámicas dentales. RCOE. 2001; 6: 645-56.

Foxton RM, Cavalcanti AN, Nakajima M, Pilecki P, Sherriff M, Melo L *et al*. Durability of resin cement bond to aluminium oxide and zirconia ceramics after air abrasion and laser treatment. J Prosthodont. 2011; 20: 84-92.

Frankenberger R, Strobel WO, Krämer N, Lohbauer U, Winterscheidt J, Winterscheidt B *et al*. Evaluation of the fatigue behavior of the resin-dentin bond with the use of different methods. J Biomed Mater Res B Appl Biomater. 2003; 67: 712-21.

Gale MS and Darvell BW. Thermal cycling procedures for laboratory testing of dental restorations. J Dent. 1999; 27: 89-99.

Garine WN, Funkenbusch PD, Ercoli C, Wodenscheck J and Murphy WC. Measurement of the rotational misfit and implant-abutment gap of all-ceramics abutments. Int J Oral Maxillofac Implants. 2007; 22: 928-38.

Garvie RC, Haninnk RH and Pascoe RT. Ceramic steel? Nature. 1975; 258: 703-4.

Gehrke P, Dhom G, Brunner J, Wolf D, Degidi M and Piattelli A. Zirconium implant abutments: fracture strength and influence of cyclic loading on retaining-screw loosening. Quintessence Int. 2006; 37: 19-26.

Glauser R, Sailer I, Wohlwend A, Studer S, Schibli M and Schärer P. Experimental zirconia abutments for implant-supported single tooth restorations in esthetically demanding regions: 4-year results of a prospective clinical study. Int J Prosthodont. 2004; 17: 285-90.

Gökçe B, Özpınar B, Dündar M, Çömlekoglu E, Sen BH and Güngör MA. Bond stregths of all ceramics: acid vs laser etching. Oper Dent. 2007; 32: 168-73.

Gomes AL, Oyagüe RC, Lynch CD, Montero J and Albaladejo A. Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. J Dent. 2012; 41: 31-41.

Gorraci C, Cury AH, Cantoro A, Papacchini F, Tay FR and Ferrari M. Microtensile bond strength and interfacial properties of self-etching and self adhesive resin cements used to lute composite onlays under different seatong forces. J Adhes Dent. 2006; 8: 327-35.

Griggs JA. Recent Advances in Materials for All- Ceramics Restorations. Dent Clin North Am. 2007; 51: 713-27.

Guarda G, Correr A, Gonçalves L, Costa A, Borges G, Sinhoreti M *et al*. Effects of Surface Treatments, Thermocycling, and Cyclic Loading on the Bond Strength of a Resin Cement Bonded to a Lithium Disilicate Glass Ceramic. Oper Dent. 2012; (In Press).

Guazzato M, Quach L, Albakry M and Swain MV. Influence of surface and heat treatments on the flexural strength of Y-TZP dental ceramic. J Dent. 2005; 33: 9-18.

Guess PC, Zavanelli RA, Silva NR, Bonfante EA, Coelho PG and Thompson VP. Monolithic CAD/CAM lithium dissilicate versus veneered Y-TZP crowns: comparision of failure modes and reliability after fatigue. Int J of Prosthodont. 2010; 23: 434-42.

Hashimoto M, Ohno H, Sano H, Tay FR, Kaga M, Kodou Y *et al*. Micromorphological changes in resin-dentin bonds after 1 year of water storage. J Biomed Mater Res. 2002; 63: 306-11.

Hummel SK, Pace LL and Marker VA. A comparision of two silicoating techniques. J Prosthodont. 1994; 3: 108-13.

Inokoshi M, Kameyama A, de Munck J, Minakuchi S and Van Meerbeek B. Durable bonding to mechanically and/or chemically pre-treated dental zirconia. J Dent. 2013; 41: 170-79.

International Standardization Organization. ISO TR 11405 dental materials guidance on testing of adhesion tooth structure. Geneva Switzerland: WHOO. 1993

Isgro G, Pallav P, van der Zel JM and Feilzer AJ. The influence of the veneering porcelain and different surface treatments on the biaxial flexural strength of a heat-pressed ceramic. J Prosthet Dent. 2003; 90: 465-73.

Janda R, Roulet JF, Wulf M and Tiller HJ. A new adhesive technology for all-ceramics. Dent Mater. 2003; 19: 567-73.

Jevnikar P, Krnel K, Kocjan A, Funduk N and Kosmac T. The effect of nao-structured alumina coating on resin-bond strength to zirconia ceramics. Dent Mater. 2010; 26: 688-96.

Kelly J and Denry I. Stabilized zirconia as a structural ceramic: An overview. Dent Mater. 2008; 24: 289-98.

Kelly JR. Extrapolation from bond strength: *Caveat Emptor*. ADM Trans. 1994; 7: 16-22.

Kelly JR. Ceramics in restorative and prosthetic dentistry. Annu Rev Mater Sci. 1997; 27: 443-68.

Kelly JR, Nishimura I and Campbell SD. Ceramics in dentistry: Historical roots and current perspectives. J Prosthet Dent. 1996; 75: 18-32.

Kern M, Barloi A and Yang B. Surface conditioning influences zirconia ceramic bonding. J Dent Res. 2009; 88: 817-22.

Kern M and Wegner SM. Bonding to zirconia ceramic: adhesion methods and their durability. Dent Mater. 1998; 14: 64-71.

Kim JK, Kim HS and Lee DG. Investigation of optimal surface treatments for carbon/epoxy composite adhesive joints. J Adhes Sci Technol. 2003; 17: 329-52.

Kim MJ, Kim JK, Kim KH and Kwon TY. Shear bond strengths of various luting cements to zirconia ceramic: surface chemical aspects. J Dent. 2011; 39: 795-803.

Kinloch AJ (1987). Adhesion and Adhesives. London, Chapman & Hall.

Kitasako Y, Burrow MF, Nikaido T and Tagami J. The influence of storage solution on dentin bond durability of resin cement. Dent Mater. 2000; 16: 1-6.

Kitayama S, Nikaido T and Ikeda M. Internal coating of zirconia restorarion with silica based ceramic improves bonding resin cement to dental zirconia ceramic. Bio-Med Mater Eng. 2010; 20: 77-87.

Kohal RJ and Klaus G. A zirconia implant-crown system: a case report. Int J Periodontics Restorative Dent. 2004; 24: 147-53.

Kollar A, Huber S, Mericske E and Mericske-Stern R. Zirconia for teeth and implants: a case series. Int J Periodontics Restorative Dent. 2008; 28: 479-87.

Kolodney H, Puckett AD and Brown K. Shear strentgh of laboratory-processed composite resins bonded to a silica-coated nickel-chromium-beryllium. J Prosthet Dent. 1992; 67: 419-22.

Kosmac T, Oblak C, Jevnikar P, Funduk N and Marion L. The effect of surface grinding and sandblasting on flexural strength and reliability of Y-TZP zirconia ceramic. Dent Mater. 1999; 15: 426-33.

Koutayas S, Vagkopoulou T, Pelekanos S, Koidis P and Strub JR. Zirconia in Dentistry: Part 2. Evidence-based clinical breakthrough. Eur J Esthet Dent. 2009; 4: 348-80.

Kutsch VK. Lasers in dentistry: comparing wavelengths. JADA. 1993; 124: 49-54.

Lange FF. Transformation toughening, Part 3 - Experimental observations in the ZrO_2-Y_2O_3 system. J Mater Sci. 1982; 17: 240-46.

Lee BS, Lin PY, Chen MH, Hsieh TT, Lin CP, Lay JY *et al*. Tensile bond strength of Er,Cr:YSGG laser-irradiated human dentin and analysis of dentin-resin interface. Dent Mater. 2007; 23: 570-78.

Lung CYK and Matinlinna JP. Resin bonding to silicatized zirconia with two isocyanatosilanes and a cross-linking silane. Part I. Experimental. Silicon. 2010; 2: 153-61.

Lung CYK and Matinlinna JP. Aspects of silane coupling agents and surface conditioning in dentistry: An overview. Dent Mater. 2012; 28: 467-77.

Luthardt RG, Sandkuhl O and Reitz B. Zirconia- TZP and alumina- advanced technologies for the manufacturing of single crowns. Eur J Prosthodont Restor Dent. 1999; 7: 113-19.

Luthardt RG, Holzhüter M, Sandkuhl O, Herold V, Schnapp JD, Kuhlisch E *et al*. Reliability and Properties of Ground Y-TZP-Zirconia Ceramics. J Dent Res. 2002; 81: 487-91.

Luthardt RG, Holzhüter MS, Rudolph H, Herold V and Walter MH. CAD/CAM-machining effects on Y-TZP zirconia. Dent Mater. 2004; 20: 655-62.

Lüthy H, Loeffel O and Hammerle CHF. Effect of thermocycling on bond strength of luting cements to zirconia ceramic. Dent Mater. 2006; 22: 195-200.

Lynch CD, McConnell RJ and Wilson NH. Challenges to teaching posterior composites in the United Kingdom and Ireland. Br Dent J. 2006; 201: 747-50.

Lynch CD, McConnell RJ and Wilson NH. Teaching the placement of posterior resin-based composite restorations in U.S. dental schools. J Am Dent Assoc. 2006; 137: 619-25.

Manicone PF, Iommetti PR and Raffaelli L. An overview of zirconia ceramics: basic properties and clinical applications. J Dent. 2007; 35: 819-26.

Martinéz-Rus F, Pradiés-Ramiro G, Suárez García MJ and Rivera Gómez B. Cerámicas dentales: clasificacion y criterios de selección. RCOE. 2007; 12: 253-63.

Matinlinna JP and Vallitu PK. Bonding of resin composites to etchable ceramic surfaces-an insight overview of the chemical aspects on surface conditioning. J Oral Rehabil. 2007; 34: 622-30.

May LG, Passos SP, Capelli DB, Ozcan M, Bottino MA and Valandro LF. Effect of silica coating combined to a MDP based primer on the resin bond to Y-TZP ceramic. J Biomed Mater Res B Appl Biomater. 2010; 95: 69–74.

McLean JW. The alumina reinforced porcelain jacket crown. J Am Dent Assoc. 1967; 75: 621-28.

McLean JW and Hughes TH. The reinforcement of dental porcelain with ceramic oxides. Br Dent J. 1965; 119: 251-67.

Meric G and Ruyter IE. Influence of thermal cycling on flexural properties of composites reinforced with unidirectional silica-glass fibers. Dent Mater. 2008; 24: 1050-57.

Monticelli F, Osorio R, Pisani-Proença J and Toledano M. Resistance to degradation of resin-dentin bonds using a one-step HEMA-free adhesive. J Dent. 2007; 35: 181-86.

Nicholson JW. Chemestry of glass-ionomer cements: a review. Biomaterials. 1998; 19: 485-94.

Nikaido T, Kunzelman KH, Chen H, Ogata M, Harada N, Yamaguchi S *et al*. Evaluation of thermal cycling and mechanical loading on bond strength of a self-etching primer system to dentin. Dent Mater. 2002; 18: 269-75.

Nikolaenko SA, Lohbauer U, Roggendorf M, Petschelt A, Dasch W and Frankenberger R. Influence of c-factor and layering technique on microtensile bond strength to dentin. J Adhes Dent. 2004; 20: 579-85.

Ntala P, Chen X, Niggli J and Cattell M. Development and testing of multi-phase glazes for adhesive bonding to zirconia substrates. J Dent. 2010; 38: 773-81.

Osorio R, Castillo-de Oyagüe R, Monticelli F, Osorio E and Toledano M. Resistance to bond degradation between dual-cure resin cements and pre-treated sintered CAD-CAM dental ceramics. Med Oral Patol Oral Cir Bucal. 2012; 17: e669-77.

Oyagüe RC, Monticelli F, Toledano M, Osorio E, Ferrari M and Osorio R. Effect of water aging on microtensile bond strength of dual-cured resin cements to pre-treated sintered zirconium-oxide ceramics. Dent Mater. 2009; 25: 392-99.

Oyagüe RC, Osorio E, Toledano M and Osorio R. Influence of Surface Nano-roughness of Dental Alumina Ceramic on Bond Strength to Dual-Cure Resin Cements. J Adhes Sci Technol. 2011a; 25: 2909-22.

Oyagüe RC, Osorio R, da Silveira BL and Toledano M. Comparision of bond stability between dual-cure resin cements and pretreated glass-infiltrated alumina ceramics. Photomed Laser Surg. 2011b; 29: 465-75.

Özcan M and Vallittu PK. Effect of surface conditioning methods on the bond strength of luting cement to ceramic. Dent Mater. 2003; 19: 725-31.

Paghdiwala AF, Vaidyanathan TK and Paghdiwala MF. Evaluation of erbium:YAG radiation of hard dental tissues: analysis of temperature changes, depth of cuts and structural effects. Scanning Microsc. 1993; 7: 989-97.

Palacios RP, Johnson GH, Philips KM and Raigrodski AJ. Retention of zirconium oxide ceramic crowns with three types of cement. J Prosthet Dent. 2006; 96: 104-14.

Paranhos MP, Burnett LHJr and Magne P. Effect of Nd:YAG laser and CO2 laser treatment on the resin bond strength to zirconia ceramic. Quintessence Int. 2011; 42: 79-89.

Pashley DH, Carvalho RM, Sano H, Nakajima M, Yoshijama M, Shono Y *et al*. The microtensile bond test: a review. J Adhes Dent. 1999; 1: 299-309.

Peutzfeldt A and Asmussen E. Silicoating. Evaluatiion of a new method of bonding composite resin to metal. Scand J Dent Res. 1988; 96: 171-6.

Phark JH, Duarte SJr, Blatz M and Sadan A. An in vitro evaluation of the long-term resin bond to a new densely sintered high-purity zirconium-oxide ceramic surface. J Prosthet Dent. 2009; 101: 29-38.

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

Piascik JR, Wolter SD and Stoner BR. Enhanced bonding between YSZ surfaces using a gas-phase fluorination pretreatment. J Biomed Mater Res B Appl Biomater. 2011; 98B: 114–19.

Piconi C and Maccauro G. Zirconia as a ceramic biomaterial. Biomaterials. 1999; 20(1): 1-25.

Piwowarczyk A, Lauer H and Sorensen J. The shear bond strength between luting cements and zirconia ceramics after two pre-treatments. Oper Dent. 2005; 30: 382-8.

Poujade JM and Zerbib C. Céramiques dentaires. EMC- Dentisterie. 2004; 1: 101-17.

Prestipino V and Ingber A. All-ceramic implant abutments: esthetic indications. J Esthet Dent. 1996; 8: 255-62.

Probster L and Diel J. Slip casting alumina ceramics for crown and bridge restorations. Quintessence Int. 1992; 23: 25-31.

Proença JP (2010). Estudio in vitro de la eficacia de unión de cementos autoadhesivos a sustratos biológicos en Odontologia: Efecto de pretratamientos de superficie. Dpto. de Estomatologia. Granada, Universidad de Granada**:** 1-164.

Qeblawi DM, Muñoz CA, Brewer JD and Monaco EA. The effect of zirconia surface treatment on flexural strength and shear bond strength to a resin cement. J Prosthet Dent. 2010; 103: 210-20.

Raigrodski AJ. Contemporary materials and technologies for all-ceramic fixed partial dentures: a review of the literature. J Prosthet Dent. 2004; 92: 557-62.

Rimondini L, Cerroni L, Carrassi A and Torricelli P. Bacterial colonization of zirconia ceramic surfaces an *in vitro* and *in vivo* study. Int J Oral Maxillofac Implants. 2002; 17: 793-8.

Román-Rodríguez J, Roig-Vanaclocha A, Fons-Font A, Granell-Ruiz M, Solá-Ruiz M and Bruguera-Álvarez A. Full maxillary rehabilitation with an all-ceramic system. Med Oral Patol Oral Cir Bucal 2009 Dec 29 [Epub ahead of print].

Ruff O, Ebert F and Stephen E. Contributions to the ceramics of highly refractory materials: II. System zirconia-lime. Z Anorg Allg Chem. 1929; 180: 215-24.

Rüttermann S, Fries L, Raab WH and Janda R. The effect of different bonding techniques on ceramic/ resin shear bond strength. J Adhes Dent. 2008; 10: 197-203.

Saghaei M. Random allocation software for parallel group randomized trials. BMC Med Res Methodol. 2004; 4: 26.

Sano H, Ciucchi B, Matthews WG and Pashley DH. Tensile properties of mineralized and demineralized human and bovine dentin. J Dent Res. 1994; 73: 1205-11.

Santerre JP, Shajii L and Leung BW. Relation of dental composite formulations to their degradation and the release of hydrolyzed polymeric-resin-derived products. Crit Rev Oral Biol Med. 2001; 12: 136-51.

Sasse M, Eschbach S and Kern M. Rabdomized clinical trial on single retainer all-ceramic resin-bonded fixed dental prostheses: Influence of the bonding system after up to 55 months. J Dent. 2012; 40: 783-86.

Scarano A, Piattelli M, Caputi S, Favero GA and Piattelli A. Bacterial adhesion on commercially pure titanium and zirconium oxide disks: an *in vivo* human study. J Periodontol. 2004; 75: 292-6.

Shahin R and Kern M. Effect of air abrasion on the retention of zirconia ceramic crowns luted with different cements before and after artificial aging. Dent Mater. 2010; 26: 922-28.

Shenoy A and Shenoy N. Dental Ceramics: An update. J Conserv Dent. 2010; 13: 195-203.

Smith RL, Villanueva C, Rothrock JK, Garci-Godoy CE, Stoner BR, Piascik JR *et al*. Long-term microtensile bond strength of surface modified zirconia. Dent Mater. 2011; 27: 779-85.

Söderholm KJ and Shang SW. Molecular orientation of silane at the surface of colloidal silica. J Dent Res. 1993; 72: 1050-54.

Sorensen JA, Engleman MJ, Torres TJ and Avera SP. Shear bond strength of composite resin to porcelain. Int J Prosthodont. 1991; 4: 17-23.

Spohr AM, Borges GA, Júnior LH, Mota EG and Oshima HM. Surface modification of In-Ceram Zirconia ceramic by Nd:YAG laser, Rocatec system, or aluminum oxide sandblasting and its bond stregth to a resin cement. Photomed Laser Surg. 2008; 26: 203-08.

Subasi MG and Inan O. Influence of surface treatments and resin cement selection on bonding to zirconia. Lasers Med Sci. 2012; [Epub ahead of print].

Subaşi MG and Inan O. Evaluation of the topographical surface changes and the roughness of zirconia after different surface treatments. Lasers Med Sci. 2011; 27: 735-42.

Sudsangiam S and Van Noort R. Do dentin bond strength tests serve a useful purpose? J Adhes Dent. 1999; 1: 57-67.

Sukumaran VG and Bharadwaj N. Ceramics in Dental Aplications. Trends Biomater Artif Organs. 2006; 20: 7-11.

Sundh A, Molin M and Sjögren G. Fracture resistance of yttrium oxide partially-stabilized zirconia all-ceramic bridges after veneering and mechenical fatigue testing. Dent Mater. 2005; 21: 476-82.

Sundh A and Sjögren G. A study of the bending resistance of implant-supported reinforced alumina and machined zirconia abutments and copies. Dent Mater. 2008; 24: 611-7.

Swab JJ. Low temperatura degradation of Y-TZP materials. J Mater Sci. 1991; 26: 6706-14.

Tachibana A, Marques MM, Soler JM and Matos AB. Erbium, chromium:yttrium scandium gallium garnet laser for caries removal: influence on bonding of a self-etching adhesive system. Lasers Med Sci. 2008; 23: 435-41.

Tagami J, Nikaido T, Nakajima M and Shimada Y. Relationship between bond strength tests and other in vitro phenomena. Dent Mater. 2010; 26: e94-e99.

Tezvergil A, Lassila LVJ and Vallittu PK. The effect of fiber orientation on the thermal expansion coefficients of fiber-reinforced composites. Dent Mater. 2003; 19: 471-77.

Thompsom JY, Stoner BR, Piascik JR and Smith R. Adhesion/cementation to zirconia and other non-silicate ceramics: Where are we now? Dent Mater. 2011; 27: 71-82.

Tinschert J, Zwez D, Marx R and Anusavice KJ. Structural reliability of alumina-, feldspar-, leucite-, mica- and zirconia-based ceramics. J Dent. 2000; 28: 529-35.

Toledano M, Osorio R, Osorio E, Aguilera FS, Yamauti M, Pashley DH *et al*. Durability of resin-dental bonds: effects of direct/indirect exposure and storage media. Dent Mater. 2007; 23: 885-892.

Ural Ç, Külünk T, Külünk S and Kurt M. The effect of laser treatment on bonding between zirconia ceramic surface and resin cement. Acta Odontol Scand. 2010; 68: 354-59.

Usumez A, Hamdemirci N, Kotoglu BY, Parlar O and Sari T. Bond strength of resin cement to zirconia ceramic with different surface treatments. Lasers Med Sci. 2013; 28: 259-66.

Vagkopoulou T, Koutayas S, Koidis P and Strub JR. Zirconia in Dentistry: Part 1. Discovering the nature of an upcoming bioceramic. Eur J Esthet Dent. 2009; 4: 130-51.

Valandro LF, Mallmann A, Della Bona A and Bottino MA. Bonding to densely sintered alumina and glass infiltrated aluminium/zirconium- based ceramics. J Appl Oral Sci. 2005; 13: 47-52.

Valandro LF, Özcan M, Amaral R, Vanderlei A and Bottino MA. Effect of testing methods on the bond strength of resin to zirconia-alumina ceramic: microtensile *versus* shear test. Dent Mater J. 2008; 27: 849-55.

van As G. Erbium lasers in dentistry. Dent Clin North Am. 2004; 48: 1017-59.

Van Landuyt KL, Snauwaert J, De Munck J, Peumans M, Yoshida Y, Poitevin A *et al*. Systematic review of the chemical composition of contemporary dental adhesives. Biomaterials. 2007; 28: 3757-85.

van Noort R (2002). Introduction to dental materials. London.

van Noort R, Noroozi S, Howard IC and Cardew G. A critique of bond strength measurements. J Dent. 1989; 17: 61-67.

Vigolo P, Fonzi F, Majzoub Z and Cordioli G. An in vitro evaluation of titanium, zirconia and alumina procera abutments with hexagonal connection. Int J Oral Maxillofac Implants. 2006; 21: 575-80.

Visuri SR, Walsh JT and Wigdor HA. Shear strength of composite bonded to Er:YAG laser-prepared dentin. J Dent Res. 1996; 55: 599-605.

Walsh LJ. The current status of laser aplication in dentistry. Austral Dent J. 2003; 48: 146-55.

Wegner SM and Kern M. Long-term resin bond strength to zirconia ceramic. J Adhes Dent. 2000; 2: 139-47.

Weinstein M, Katz S and Weinstein AB (1962). Fused Porcelain to metal teeth. U. S. Patent. US. 3052983.

Weinstein M and Weinstein AB (1962). Porcelain-covered metal-reinforced teeth. U. S. patent. US. 3052983.

Wigdor H, Abt E, Ashrafi S and Walsh JTJ. Theeffect of lasers on dental hard tissues. JADA. 1993; 124: 65-70.

Wolfart M, Lehmann F, Wolfart S and Kern M. Durability of the resin bond strength to zirconia ceramic after using different surface conditioning methods. Dent Mater. 2007; 23: 45-50.

Yang B, Barloi A and Kern M. Influence of air-abrasion on zirconia ceramic bonding using an adhesive composite resin. Dent Mater. 2010; 26: 44-50.

Yang B, Lange-Jansen HC, Scharnberg M, Wolfart S, Ludwig K, Adelung R *et al*. Influence of saliva contamination on zirconia ceramic bonding. Dent Mater. 2008; 24: 508-13.

Yap AU, Tan AC, Goh DC and Chin KC. Effect of surface treatment and cement maturation on the bond stregth of resin-modified glass ionomers to dentin. Oper Dent. 2003; 28: 728-33.

Yildirim M, Edelhoff D, Hanisch O and Spiekermann H. Ceramic abutment--a new era in achieving optimal esthetics in implant dentistry. Int J Periodontics Restorative Dent. 2000; 20: 81-91.

Yildirim M, Fischer H, Marx R and Edelhoff D. In vivo fracture resistance of implant-supported all-ceramic restorations. J Prosthet Dent. 2003; 90: 325-31.

Yoshida K, Tsuo Y and Astuta M. Bonding of dual-cured resin cement to zirconia ceramic using phosphate acid ester monomer and zirconate coupler. J Biomed Mater Res B Appl Biomater. 2006; 77: 28-33.

VII. APPENDICES

Appendix I. Original articles quality ratings (JCR 2012)

- **Gomes AL, Montero J. Zirconia implant abutments: A review. Med Oral Patol Oral Cir Bucal. 2011 Jan 1;16 (1):e50-55**

  ISSN: 1698-6946

  Impact Factor: 1.017 JCR Science Edition: 2012.

  Category: Dentistry, Oral Surgery & Medicine.

  Position in the category: 53 de 82 (T2/Q3).

- **Gomes AL, Oyagüe RC, Lynch CD, Montero J, Albaladejo A. Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. J Dent. 2012; 41:31-41**

  ISSN: 0300-5712

  Impact Factor: 3.200 - JCR Science Edition: 2012

  Category: Dentistry, Oral Surgery & Medicine

  Position in the category:7 de 82 (T1/Q1).

- **Gomes AL, Ramos JC, Santos-del Riego SE, Montero J, Albaladejo A. Thermocycling effect on microshear bond strength to zirconia ceramic using Er:YAG and tribochemical silica coating as surface conditioning. 2013. Lasers Med Sci (sent for second review).**

ISSN: 0268-8921.

Impact Factor: 2.402. - JCR Science Edition: 2012

Category: Surgery.

Position in the category: 45 de 198 (T1/Q1).

Appendix II. Tesis resumida en Castellano

INTRODUCCIÓN

Diferentes materiales utilizados en prótesis y su comportamiento cuando se unen componentes con distinta naturaleza (concepto interfacial)

La investigación en materiales dentales está dirigida cada vez más hacia las restauraciones sin metal para mejorar la estética de las prótesis. Su objetivo es la restauración biocerámica que mimetice el resultado óptico del diente natural. Un aspecto natural de los tejidos blandos se puede lograr teniendo en cuenta el espesor gingival y el material de restauración. Hoy en día, junto con los acrílicos, los metales y las resinas, las cerámicas dentales son un tipo de materiales con una proyección creciente en el campo de la restauración odontológica.

En la búsqueda del material de restauración de excelencia, los sistemas de cerámica sin metal se consideran como la mejor opción (Kelly 1997). Las cerámicas son materiales con comportamiento mecánico único: tienen muy elevada resistencia a la compresión, aunque también son frágiles o quebradizas a la flexión, ya que pueden fracturarse al no sufrir deformación elástica debido a su baja resistencia a la flexión (Kelly *et al.,* 1996). Cuando se compromete la estética un concepto subjetivo, influenciado por las tendencias socio-culturales las cerámicas dentales se utilizan comúnmente. Actualmente, la odontología restauradora estética está íntimamente asociada al uso de restauraciones cerámicas sin metal, porque éstas permiten preservar el color natural de los tejidos blandos sin generar pigmentación gingival por corrosión, y además consigue imitar las propiedades ópticas de la dentición natural (Denry *et al.,* 2008).

Para cumplir estos objetivos estéticos es necesaria la conexión de materiales orgánicos e inorgánicos. Sin embargo, la distinta naturaleza de estos componentes que deben unirse estructuralmente mediante una conexión interfacial está comprometida ya que no hay ninguna interacción química entre sus superficies (Casucci *et al.,* 2009). La modificación de las superficies de contacto, así como la búsqueda de agentes de adhesión que eleven la compatibilidad interfacial de ambas superficies, permiten aminorar este problema.

En prostodoncia, el concepto de adhesión no era realmente importante hasta la aparición de las restauraciones libres de metal y la odontología mínimamente invasiva, ya que la mayoría de las restauraciones fijas basaban su conexión en una retención geométrica que implicaba preparaciones invasivas en los dientes pilares con el objetivo de ofrecer unos parámetros geométricos (altura, anchura, conicidad...) que garantizaran la retención pasiva entre estructuras protésicas y diente natural. La longevidad de las prótesis dentales fijas puede verse afectada por varios factores, pero para evitar complicaciones biológicas y mecánicas es esencial un buen ajuste prótesis-diente y una cementación fiable que garanticen una adecuada retención, un sellado marginal duradero y una integración óptica adecuada.

Desde finales de la década de 1990, la introducción de la cerámica a base de óxido de circonio como un material de restauración estético y altamente resistente, generó un gran interés en la comunidad científica y clínica. Esta biocerámica presenta una amplia gama de aplicaciones dada su alta biocompatibilidad y sus aventajadas propiedades mecánicas y ópticas (Koutayas *et al.,* 2009).

OBJETIVOS Y JUSTIFICACIÓN

La circona es un material protético prometedor aunque sigue existiendo controversia científica y clínica acerca del mejor método para optimizar y promover su adhesión fiable y duradera al sustrato dentario. Dado que los mejores cementos en odontología son los cementos de resina, sería deseable conocer el mejor protocolo de adhesión entre la resina y el óxido de circonio, ya que hasta la fecha no hay unas directrices claras para el clínico rehabilitador. Esta carencia de directrices de adhesión se pone de manifiesto cuando entre los clínicos sigue existiendo una concepción muy extendida de que el circonio se puede adherir con cualquier cemento y con o sin tratamiento de superficies.

Por lo tanto los objetivos principales de este trabajo de investigación *in vitro* fueron:

1. Revisar la literatura sobre la circona, con especial enfoque al estado del arte de su reciente uso como pilar del implante.
2. Evaluar el efecto del tamaño de partícula de arenado en la fuerza de adhesión en la interfase de circona/resina.
3. Investigar el efecto del tratamiento de superficie de la circona con recubrimiento triboquímico de sílice y/o con irradiación de Er: YAG en la fuerza de adhesión de la interfaz circona/resina.
4. Determinar si la composición de cemento de resina influye en su fuerza de adhesión al óxido de circonio y cuál es la mejor combinación de tipo de cemento y de acondicionamiento de superficie para proporcionar una adhesión fiable circona/resina.

5. Valorar el impacto del termociclado en la fuerza de adhesión de varios cementos de resina auto-adhesivos a circona pre-tratada.

ARTICULOS ORIGINALES

Gomes AL, Montero J. Zirconia implant abutments: A review. Med Oral Patol Oral Cir Bucal. 2011 Jan 1;16 (1):e50-5

RESUMEN

Objetivos: El aumento de la demanda estética dentro de las sociedades desarrolladas conduce la industria y la odontología hasta la fabricación de restauraciones libres de metal y para un amplio uso de materiales cerámicos, debido a sus excelentes características de biocompatibilidad y estética. Con el aumento incesante de las marcas comerciales que participan en este avance tecnológico, la revisión sobre pilares cerámicos, específicamente fabricados en circona, resulta insoslayable. Hicimos una búsqueda de artículos de revistas revisadas por pares en PubMed/Medline cruzando los términos "Pilares Dentales", "Porcelana Dental" y "Circona". La revisión se dividió por subtemas: propiedades físicas y mecánicas de la circona, ajuste de precisión en la interfase implante-pilar, resistencia de los pilares de circona y, por último, adhesión bacteriana y la respuesta de los tejidos. Varios estudios demuestran que los pilares de circona ofrecen buenos resultados en todos los niveles, pero hay temas relevantes que necesitan reevaluarse. Uno de los más importantes es el éxito clínico a largo plazo de los pilares de circona sobre implantes, dado que en la literatura no hay suficientes estudios *in vivo* que lo avalen.

Palabras clave: Circona, cerámicas dentales, pilares de implantes

Gomes AL, Oyagüe RC, Lynch CD, Montero J, Albaladejo A. Influence of sandblasting granulometry and resin cement composition on microtensile bond strength to zirconia ceramic for dental prosthetic frameworks. J Dent. 2012; 41:31-41

RESUMEN

Objetivos**:** Evaluar el efecto del tamaño de partícula de arenado y de la composición del cemento de resina en la fuerza de adhesión de microtensión (MTBS) a circona. Métodos**:** Cuarenta bloques de circona (Cercon, Dentsply) fueron pulidos y tratados aleatoriamente de la siguiente manera: Grupo 1 (NT): sin tratamiento; Grupo 2 (APA-I): Arenado (APA) con partículas de óxido de aluminio (Al_2O_3) con 25 micras (Cobra, Renfert); Grupo 3 (APA-II): APA con partículas de Al_2O_3 con 50 micras, y Grupo 4 (APA-III): APA utilizando partículas de Al_2O_3 con 110 micras. Los bloques cerámicos se duplicaron en resina compuesta. Las muestras de cada grupo de tratamiento previo fueron divididas aleatoriamente en dos subgrupos, en función del cemento de resina utilizado para la adhesión de los elementos de composite a las superficies de circona tratados. Subgrupo 1 (PAN), que era un sistema de cementación que contiene 10-MDP, utilizando *Clearfil Ceramic Primer* además de *Panavia F 2.0* (Kuraray), y Subgrupo 2 (BIF) utilizado *Bifix SE* (VOCO) un cemento auto-adhesivo. Después de 24 h, las muestras fueron cortadas en mini barras con $1 \pm 0.1mm^2$ de sección. Los valores del test de microtension se obtuvieron usando una máquina de ensayo universal (velocidad de cruceta= 0.5mm/min). Los modos de fallo se registraron y se evaluó con microscopia electronica (SEM) la morfología interfacial de las micro-barras desunidas. Como análisis estadístico se realizaron ANOVA, Tests de Student-

Newman-Keuls, y regresión lineal múltiple por pasos, siendo los valores de MTBS la variable dependiente ($p < 0,05$). Resultados**:** Independientemente de la granulometría de arenado, PAN adherido a superficies tratadas con APA alcanza los valores más altos de MTBS y con frecuencia mostró fracturas mixtas. BIF registró diferencias significativas en MTBS dependiendo del método de acondicionamiento, y registró los mayores índices de fallos prematuros y adhesivos. Conclusiones**:** El sistema de cementación que contiene 10-MDP parece ser el más adecuado a la cerámica de circona, principalmente después de tratar la superficie con arenado.

Importancia clínica**:** La aplicación de un sistema de cemento de resina de curado dual que contiene monómeros funcionales de 10-MDP, tanto en el silano como en la matriz de cemento de resina, a la cerámica cristalina pre-tratada con arenado puede ser la clave para el éxito de la adhesión a las estructuras circona para restauraciones de cerámica sin metal, independientemente de la granulometría de arenado.

Palabras clave: Circona, tratamiento de superficie, arenado, cementos de resina de fraguado dual, 10-MDP, cementos de resina autoadhesivos.

Gomes AL, Ramos JC, Santos-del Riego SE, Montero J, Albaladejo A. Thermocycling effect on microshear bond strength to zirconia ceramic using Er:YAG and tribochemical silica coating as surface conditioning. 2013. Lasers Med Sci (enviado para segunda revisión de los *referees*)

RESUMEN

El propósito de este estudio fue evaluar el efecto de termociclado en la fuerza de adhesión de micro-cizalla (μSBS) de diferentes cementos de resina auto-adhesivos a circona pre-tratada con recubrimiento triboquímico de sílice *Rocatec*™ e irradiación con laser de Er: YAG como acondicionadores de superficie. Doscientos cuarenta muestras de circona cuadradas fueron pulidas y asignadas al azar en cuatro grupos de acuerdo con el tratamiento de superficie aplicado de la siguiente manera: 1) sin tratamiento (NT); 2) revestimiento de sílice con *Rocatec*™ (ROC); 3) irradiación con láser Er:YAG (LAS: 2.940 nm, 200 mJ, 10 Hz) y, 4) láser seguido por *Rocatec*™ (LAROC). Cada grupo se dividió en dos subgrupos según la resina a probar: A) *Bifix SE* (BIF) y B) *Clearfil SA* (CLE). Después de 24 horas, la mitad de las muestras de cada subgrupo se pusieron a prueba. La otra mitad se almacenó y fue termociclada (5º-55ºC/5000 ciclos). El test de μSBS se realizó utilizando una máquina de ensayo universal (velocidad de cruceta = 0,5 mm/min). Los modos de fallo se registraron y observaron por microscopía electrónica de barrido. Los datos se analizaron con ANOVA, Test de Student, pruebas de chi cuadrado y regresión lineal (p <0,05). Antes de termociclado, ambos cementos mostraron mayores resultados de μSBS con ROC y LAROC. Después del envejecimiento, 1) todas las muestras BIF evidencian disminución severa de la adhesión con fallos principalmente de tipo adhesivo y 2) CLE

mantiene los resultados iniciales de los grupos ROC y LAROC aunque mostró mejores resultados con ROC. El termociclado no influyó negativamente en los resultados de μSBS cuando se utiliza, en la superficie de circona recubierta con sílice, el cemento de resina autoadhesivo que contiene 10-MDP, independientemente del tratamiento superficial mediante irradiación con laser de Er: YAG.

DISCUSIÓN

Nuestra revisión de la literatura sobre el uso circona en pilares de implantes encontró trabajos clínicos, así como estudios *in vitro* que avalarían su exitosa aplicabilidad. Se abordaron los temas del ajuste de precisión, la resistencia del pilar, la adhesión bacteriana y la respuesta de los tejidos blandos. Aunque los pilares de implantes de circona no tienen valores de resistencia a la fractura tan buenos como pilares convencionales de titanio, su uso estaría especialmente indicado en áreas de alta exigencia estética. Estos pilares mostraron un buen ajuste, una excelente biocompatiblidad y una apariencia estética óptima. Todos estos beneficios son especialmente importantes en los pacientes con rehabilitaciones unitarias sobre implantes en presencia de un biotipo gingival fino.

Junto con la adecuada resistencia a la fractura y el buen ajuste marginal, la creación de una adhesión duradera en las interfases diente/cemento, circona/cemento y circona/recubrimiento de cerámica, es un factor esencial para el éxito a largo plazo de las restauraciones de óxido de circonio. Hay una amplia gama de materiales y métodos de acondicionamiento de superficies sugeridas para la cementación de la circona, pero se requiere un análisis científico fundamentado acerca del rendimiento de cada combinación. Para alcanzar un éxito a largo plazo de una rehabilitación con circona, se requiere un conocimiento extenso de los materiales dentales adhesivos, así como un manejo adecuado de las técnicas de pre-tratamiento. Hoy en día, las restauraciones totalmente cerámicas se consideran la mejor opción para ser utilizadas cuando se sigue un procedimiento mínimamente invasivo. La retención geométrica de la restauración suele ser insuficiente debido a la escasa preparación del diente receptor, por lo que será la unión adhesiva la que garantizará la integración ultraestructural de ambos materiales.

La literatura científica puede ser difícil de interpretar dada la controversia sobre la adhesión a la circona. Los estudios *in vitro* de esta tesis fueron diseñados para ensayar algunas pautas para mejorar la interfase de circona/resina. El clínico que trabaja con estos biomateriales dentales contemporáneos necesita conocer los factores esenciales en los protocolos de cementación para realizar un tratamiento protésico con éxito.

En primer lugar, se eligió la prueba de fuerza de adhesión de microtension (µTBS) para evaluar la resistencia de la adhesión de cementos de resina de fraguado dual al óxido de circonio, y analizar si la granulometría del arenado y la composición del cemento influían en la resistencia de adhesión en la interfase circona/resina (Capítulo III.2). Este es un test de resistencia a la tensión más trabajoso que el test de resistencia a la cizalla, pero tiene un mayor potencial para proporcionar una idea de la fuerza adhesiva de materiales de cementación a sustratos clínicamente relevantes (Pashley *et al.,* 1999) como sería la cofia de circona de una prótesis de total cerámica. Todavía es discutible si los fallos antes de la prueba deben ser excluidos de los cálculos estadísticos, incluidos como ceros (Pashley *et al.,* 1999) o más bien como valores superiores a cero, basándose en la premisa de que deben haber sufrido algo de estrés durante el corte (Nikolaenko *et al.,* 2004; Gorraci *et al.,* 2006). Al igual que en un estudio relacionado (Oyagüe *et al.,* 2011) en nuestro experimento se tomó la decisión de incluir los valores de los fallos prematuros como zero, aunque los autores son conscientes de que puede haber predispuesto hacia una ligera infra-estimación del potencial de adhesión. Debido a este inconveniente, en el segundo ensayo realizado, se utilizó la prueba de micro cizalla de la fuerza de adhesión (µSBS), con el fin de evaluar el efecto de acondicionamiento de la superficie y cemento de resina auto-adhesivo en la adhesión de óxido de circonio bajo envejecimiento artificial (Capítulo III.3). El test de cizalla es uno de los test de fuerza de adhesión más frecuentemente utilizado. Las fuerzas de cizalla se consideran los determinantes de los fallos adhesivos de los materiales de restauración en su rendimiento *in vivo* (Ersu *et al.,* 2009).

En ambas pruebas, para la análisis de fuerza de adhesión del interfase de resina/circona, el cemento de resina se aplico directamente sobre la superficie de la circona en lugar de utilizar las estructuras dentales debido a la estructura homogénea de la resina. Por lo tanto, la circona se cementó directamente a la resina en lugar de los tejidos dentales para evitar que las variaciones micro estructurales de los dientes pudieran alterar los resultados (de Oyagüe *et al.,* 2009; Oyagüe *et al.,* 2009).

Los resultados del primer ensayo (Capítulo III.2) determinaron que los factores estudiados, granulometría del arenado y la composición de los cementos de resina, influenciaron la fuerza de adhesión de la interfase circona/resina, ya que se encontraron diferencias significativas entre los grupos experimentales. El cemento que contiene 10-methacriloloxydecyl de dihidrogenofosfato (10-MDP) alcanza valores de µTBS más altos que el cemento que no contiene 10-MDP independientemente del tratamiento de la superficie de cerámica. Ambos cementos tienen una carga similar de vidrio que oscila entre el 60-75% del peso, así como otros tipos de monómeros de metacrilato que están presentes en la mayoría de los cementos de base de resina (es decir, Bis-GMA, UDMA y TEGDMA) (Oyagüe *et al.,* 2009). Sin embargo, el monómero funcional ácido 10-MDP, que ha sido calificado como relativamente estable a la hidrólisis debido a su larga cadena de carbonilo (de Oyagüe *et al.,* 2009), solo está presente en *Panavia 2.0 F* (Kuraray Medical Ltd, Osaka, Japan). De acuerdo con las instrucciones del fabricante, antes de la aplicación *Panavia*, un silano se extendió sobre la superficie cerámica. El 3-MPS (3-metacriloxipropil trimetoxisilano) y los monómeros de 10-MDP se mezclan en esta solución de silano (*Clearfil Ceramic Primer*) que mejora la humectabilidad de la superficie de cerámica, protege contra la humedad, y crea un ambiente ácido para favorecer la adhesión. Como resultado, los monómeros de 10-MDP del silano forman uniones cruzadas con los grupos 10-MDP dispersados en la matriz de resina de cemento y con el radical -OH presente en la superficie de la circona (Kern *et al.,* 1998; Yoshida *et al.,* 2006; Wolfart *et al.,* 2007).

Además, el cemento que contiene 10-MDP registró los mejores valores globales de fuerza de adhesión cuando se aplica a superficies de óxido de circonio arenado, obteniéndose resultados comparables a los de una investigación relacionada que combina un sistema de cementación que contiene 10-MDP con el arenado de partículas de 125 micras (*Clearfil* , Kuraray: 18,63 ± 6,4 MPa) (de Oyagüe *et al.,* 2009). El arenado produce micro-retenciones donde el adhesivo cerámico podría haber penetrado (Figs. III.2.3, b, c). Esto podría explicar por qué no se obtuvieron fallos prematuros en estos grupos. Por lo tanto, el uso de un cemento que contiene 10-MDP en las superficies de óxido de circonio arenadas parece reducir el riesgo de pérdida de adherencia espontánea independientemente del tamaño de las partículas del tratamiento de superficie. Por otra parte, de acuerdo con los hallazgos del mencionado estudio (de Oyagüe *et al.,* 2009), la mayoría de las micro-barras arenadas y cementadas con cemento que contiene 10-MDP exhibieron un patrón de fractura mixto, que implica la presencia de restos de cemento en el sustrato de cerámica (Figs. III.2.2 d, f). Aunque la combinación de APA y los sistemas de cementación que utilizan *primers* y contienen 10-MDP ya habían demostrado un aumento significativo de la durabilidad de la adhesión óxido de circonio (Yoshida *et al.,* 2006; Blatz *et al.,* 2007; Wolfart *et al.,* 2007; Kern *et al.,* 2009), la novedad de nuestra investigación fue que la granulometría del arenado no causó ningún efecto significativo en los valores de μTBS o en el patrón de fallos en las superficies de circona cuando se utilizaron diferentes cementos de resina de fraguado dual.

Por el contrario, más de un tercio de las micro-barras cementadas con cemento que contiene 10-MDP pero sin tratar la superficie de circona fallaron prematuramente. Una superficie plana fue descubierta en superficies de cerámica sin tratar (Fig. III.2.3 a). Esto también puede explicar que las mayor parte de las muestras de circona no tratadas y cementadas con cemento que contiene 10-MDP mostraron fracturas adhesivas. Así, en un estudio anterior, la omisión de arenado dio lugar a pérdida de adhesión durante el envejecimiento artificial independiente de la utilización de adhesivos (Kern *et al.,* 2009). Fallos mixtos se consideran clínicamente preferibles a los adhesivos, ya que los últimos se asocian generalmente con valores de resistencia de adhesión mas bajos (Toledano *et al.,* 2007).

Como se ha indicado anteriormente, el cemento sin 10-MDP (*Bifix SE*, VOCO, Cuxhafen, Alemania) registró valores de μTBS significativamente más bajos que el cemento que contiene 10-MDP independientemente del tratamiento de la superficie de cerámica. La matriz de resina del cemento utilizado sin 10-MDP, contiene monómeros adhesivos de dimetacrilato multifuncional-fosfórico con al menos dos enlaces dobles no saturados C=C. Estos monómeros reaccionan con los materiales de carga inorgánicos disueltos en la matriz de resina, formando de este modo uniones cruzadas químicas (Oyagüe *et al.,* 2011). La interconexión mecánica del cemento que no contiene 10-MDP en la interfase circona/resina se puede comparar a la observada con los cementos de ionómero de vidrio (Yap et al., 2003). En tales casos, las partículas de silicato de vidrio disueltos en la matriz de cemento pueden reaccionar con los ésteres de ácido fosfórico formando un gel de silicato en la que están incorporadas partículas de vidrio sin reaccionar (Nicholson 1998). Otros cementos de resina autoadhesivos obtuvieron valores de µTBS elevados en estudios anteriores (de Oyagüe *et al.,* 2009; Oyagüe *et al.,* 2011), lo que puede atribuirse no sólo a pequeñas diferencias en la composición de cemento, sino también a las diferencias metodológicas de los protocolos de estudio.

A pesar del método de acondicionamiento, *Bifix SE* ha demostrado un mayor riesgo de sufrir un separación espontánea del sustrato de cerámica que el cemento que contiene 10-MDP, presentando además predominantemente fallos adhesivos, es decir, sin dejar residuos de cemento en la superficie de cerámica (Figs. III.2.2 a, e), lo que está de acuerdo con la literatura para otros cementos auto-adhesivas (Blatz *et al.,* 2003; de Oyagüe *et al.,* 2009). Este estudio no reveló diferencias significativas en los valores de µTBS entre los cuatro subgrupos del cemento sin 10–MDP cementadas tanto a las superficies de circona no tratadas como a las arenadas utilizando diferentes tamaños de partículas. Esto puede reforzar la idea de que la adhesión mecánica por sí misma no proporciona la fuerza de unión de resina necesaria para cerámica dental CAD/CAM, por lo que también se recomienda una adhesión química fiable. En este sentido, recientemente se ha demostrado que la combinación de un cemento auto-adhesivo de resina que contiene un *primer* con 10-MDP genera una adhesión duradera a cerámica de circona arenada con partículas de alumina (Yang *et al.,* 2010). Sin embargo, con esta fórmula, los cementos autoadhesivos de resina pierden una de sus principales ventajas que motivaron su aparición en el mercado, como es su capacidad para conseguir adhesión tras ser aplicado en un solo paso clínico, siendo por tanto merecedores de una técnica previa de acondicionamiento químico, como requieren los cementos duales o autopolimerizables de resina.

Por otro lado, como los valores de µTBS del cemento sin 10-MDP eran bastante bajos en las condiciones experimentales probadas, el cemento que contiene 10-MDP en combinación con el arenado parece ser la mejor alternativa para conseguir adhesión a la circona. Según nuestros resultados, cuando se cambia el cemento de *Bifix SE* a *Panavia a 2.0 F* la resistencia de la adhesion se mejora significativamente en un rango entre 13,1 y 15,4 MPa, independientemente del método de acondicionamiento. A pesar de las diferencias metodológicas, estos resultados están de acuerdo con los de un estudio anterior que encontró valores de µTBS significativamente superiores a circona para *Clearfil Esthetic Cement* (que contiene 10-MDP) que para la resina autoadhesivo *Rely X Unicem*, independientemente del tratamiento de la superficie (de Oyagüe *et al.,* 2009).

No se identificaron diferencias en la arquitectura de las superficies de circona arenado con diferentes tamaños partículas de Al_2O_3, que mostraron ranuras micro-retentivas en escala micrométrica (Figs. III.2.3, b, c). Sin embargo, se observó una tendencia hacia una correlación positiva entre el tamaño de partícula de APA y los valores de µTBS en la interface cemento/circona cuando se utilizó el cemento que contiene 10-MDP. En este experimento, por cada micra que aumente el tamaño de las partículas de Al_2O_3, la resistencia de la adhesión de *Panavia* aumentaría entre 0,024 hasta 0,052 MPa (IC del 95%). Aunque no hemos encontrado ningún estudio que evalúe el efecto del tamaño de partícula de chorro de arena en la resistencia de la adhesión a circona, una investigación sobre los tratamientos de superficie para uniones adhesivas de material compuesto de carbono/epoxi concluyó que la rugosidad de la superficie, la longitud erosionada y profundidad de erosión aumenta a medida que lo hace el tamaño de la partícula del chorreado (Kim *et al.,* 2003). Nuestros resultados están en consonancia con los resultados de este trabajo, y podrían fundamentarse en que las superficies asperizadas aumentan el área de unión adhesiva y el efecto de entrelazado (Kinloch 1987), principalmente después de utilizar *primer* (Yoshida *et al.,* 2006). No obstante, los parámetros de la energía superficial deben ser evaluados usando un perfilómetro y mediciones del ángulo de contacto para evaluar su impacto en la adhesión a la cerámica de circona (Kim et al., 2011).

Los resultados del segundo experimento (Capítulo III.3) determinaron que los factores estudiados: la composición de cementos de resina, el acondicionamiento de la superficie con revestimiento de sílice y/o irradiación con laser de Er: YAG, así como el termociclado, influenciaron la resistencia de la adhesión en la interfase circona/resina, ya que se encontraron diferencias significativas entre los grupos experimentales, como se detalla a continuación.

Un factor importante para predecir los valores de μSBS fue el tipo de cemento, lo que implica que su valor podría aumentar entre 0,6-3,0 MPa si se utiliza *Clearfil ™ SA Cement* (Clearfil ™ SA Cemento, Kuraray, Osaka, Japón) en lugar de *Bifix ® SE* (Bifix ® SE, VOCO, Cuxhafen, Alemania). Ambos cementos pertenecen a la categoría de cementos de resina auto-adhesivos y se utilizaron en un solo paso sobre la superficie de la circona (siguiendo las instrucciones del fabricante). No obstante, dada similitud de composición, que es coincidente además con la presente en la mayoría de los cementos de resina, hay que destacar la existencia del monómero 10-MDP en el primero. Este monómero funcional ácido parece capaz de adherirse químicamente al óxido de circonio mediante la interacción con el radical-OH en la superficie de cerámica (Kern *et al.,* 1998; Yoshida *et al.,* 2006; Wolfart *et al.,* 2007) y ha sido clasificado como relativamente estable a la hidrólisis, debido a su larga cadena de carbonilo (de Oyagüe *et al.,* 2009).

El tipo de acondicionamiento de la superficie, según nuestro modelo de regresión, resultó ser el factor predictor más fuerte en la unión a la superficie de circona, contrariamente a lo estimado por otros estudios que consideran la elección de cemento el factor fundamental para alcanzar la adhesión fiable a circona (Oyagüe *et al.,* 2011; Subaşi *et al.,* 2011). Ambos cementos tuvieron valores más altos μSBS después del revestimiento triboquímico con sílice. Las observaciones a microscopio electrónico de barrido mostraron diferencias cualitativas considerables en la arquitectura de la superficie cerámica después de los diferentes métodos de acondicionamiento (Fig. III.3.2). Estos resultados pueden estar directamente relacionados con los resultados de resistencia de adhesión, una vez que en la superficie tratada se observa la presencia uniforme de microrretenciones y hendiduras poco profundas, pero no micro-fisuras (Fig. III.3.2b y D). La mejora resultante en la resistencia de la unión de resina puede explicarse no sólo por la rugosidad alcanzada, sino también porque el proceso de recubrimiento de sílice que permite el acoplamiento químico a través del silano (Atsu *et al.,* 2006; Paranhos *et al.,* 2011). Antes de la aplicación del cemento, las irregularidades de la superficie de cerámica, generadas tras el impacto de las partículas de *Rocatec*™, fueron infiltradas por *Rely X* ™ *Ceramic Primer*, un pre-hidrolizado de 3 MPS (3 metacriloxipropiltrimetoxisilano) listo para su uso directo, según el fabricante. Los silanos contienen silicio ligado a radicales orgánicos reactivos, que se unen químicamente a moléculas de resina y forman enlaces de siloxano con la superficie recubierta de sílice. Su aplicación mejora la humectabilidad de la cerámica, produciendo un mejor contacto e infiltración de la resina en las irregularidades de cerámica, protegiéndola de la humedad, y creando un ambiente ácido que puede favorecer la reacción de adhesion (Matinlinna *et al.,* 2007).

Ambos cementos registraron valores µSBS similares cuando las muestras sólo se irradiaron con Er: YAG, sin proceso de termociclado. Aunque el tratamiento con láser crea una superficie más rugosa (Fig. III.3.2C), no mejoró la fuerza de adhesión. Las irregularidades creadas en la superficie, probablemente como resultado erosivo de los aumentos locales de la temperatura del sustrato, no generan microretenciones de suficiente profundidad para permitir que la penetración del cemento de composite genere una unión ultraestructural. El laser de Er:YAG tuvo un impacto mínimo en el sustrato de óxido de circonio gracias al hecho de que éste es un material libre de agua. El empleo de *Rocatec*™ después del tratamiento con láser cubrió las ligeras modificaciones producidas por el láser generando una arquitectura superficial similar a la que produce cuando sólo se utiliza revestimiento triboquímico de sílice (Fig. III.2B y D). Estos resultados están en línea con el resto de resultados de los estudios recientes (Subaşi *et al.,* 2011).

Los resultados de resistencia de adhesión indican que la irradiación láser fue menos eficaz en la mejora de fuerza de adhesión que el recubrimiento triboquímico de sílice, para ambos cementos de resina. Un estudio reciente (Subaşi *et al.,* 2011) también registró fuerza de adhesión baja de todos los sistemas de cementación probados en circona irradiada por laser de Er: YAG. Los autores sugirieron que durante la irradiación láser las micro-explosiones podrían formar *detritus* que quedarían fundidos sobre la superficie cerámica. Esta capa de *detritus* sería capaz de unirse fuertemente al cemento de resina pero estaría poco adherida a la infraestructura cerámica, lo que produciría baja resistencia adhesiva (Subaşi *et al.,* 2011). Sin embargo, esta hipótesis no ha sido confirmada, y este hecho necesita más investigación. Mientras Subasi *et al.* (Subaşi *et al.,* 2011; Subaşi *et al.,* 2012) y Akyil *et al.* (Akyil *et al.,* 2010) ofrecieron resultados similares a los nuestros, otros autores han sugerido que el láser de Er: YAG aumenta significativamente los valores de SBS entre cerámica y dentina (Cavalcanti *et al.,* 2009; Akın *et al.,* 2012; Usumez *et al.,* 2013).

El termociclado afecta negativamente a las fuerza de adhesión de todas las muestras, excepto en los grupos en los que se utilizó el cemento que contenía 10-MDP en combinación con *Rocatec*™ , con o sin de láser. Se observó una ligera disminución en la fuerza de adhesión después del termociclado, pero ésta no fue estadísticamente significativa. El efecto de envejecimiento artificial inducido por termociclado se puede producir por la contracción/expansión repetitiva y tensiones generadas por los diferentes coeficientes térmicos de los materiales, y también por hidrólisis de los componentes interfaciales (el agua puede infiltrarse y disminuir las propiedades mecánicas de la matriz de polímero, por el hinchamiento y la reducción de las fuerzas de fricción entre las cadenas de polímero) (De Munck *et al.,* 2005). Cuando se realizó el revestimiento de sílice, *Clearfil* ™ *SA* fue capaz de adherirse a la sílice presente en la superficie de la cerámica a través de la interacción entre la monómero 10-MDP y 3-MPS, produciendo valores de adhesión más duraderos, como se ha demostrado en estudios anteriores (Akgungor *et al.,* 2008; May *et al.,* 2010).

Los modos de fallo de la adhesión fueron evaluados y apoyaron los resultados del test a la resistencia de adhesión. Ambos cementos en los grupos de control (NT) y los grupos tratados con láser (LAS) demostraron una tendencia a fallar adhesivamente en la interfase resina/óxido de circonio que implica la presencia de una superficie de circona libre de residuos de cemento (Fig. III.3.1A, B y E), tal y como se evidencia en la literatura para otros cementos autoadhesivos (Blatz *et al.,* 2003; de Oyagüe *et al.,* 2009). Se observaron sobre todo fallos mixtos cuando se realizó el revestimiento triboquímico de sílice precedido o no de tratamiento con láser. Estos son clínicamente preferibles a los fallos adhesivos ya que por lo general se asocian con valores superiores de fuerza de adhesión (Toledano et al., 2007), lo que está de acuerdo con nuestros resultados. La alta prevalencia de fallos mixtos y el adhesivo indica que los resultados entre los diferentes grupos experimentales fueron causados por las diferencias en la interfase adhesiva entre los cementos y la cerámica que fue tratada con procedimientos distintos (Usumez *et al.,* 2013).

Utilizado un ajuste de energía baja en el láser (200mJ), no se observaron microfisuras en las micrografías SEM (Fig. III.3.2C). La ausencia de fracturas cohesivas de cerámica sugiere que el tratamiento con láser no indujo debilitación interna en la cerámica. El principal efecto de la energía láser es la conversión de energía de la luz en calor y la interacción más importante entre el láser y el sustrato es la absorción de energía por el sustrato (Cavalcanti *et al.,* 2009). Las propiedades mecánicas de la cerámica de Y-TZP pueden resultar afectadas negativamente por cambios en la temperatura, que induzcan la transformación de fase (Cavalcanti *et al.,* 2009). Una potencia superior del láser (400 y 600 mJ) puede causar el deterioro excesivo de material, invalidándolo como tratamiento de superficie para la circona (Cavalcanti *et al.,* 2009).

La utilización de cementos de resina autoadhesivos sin *primer*, basados o no en 10-MDP, sobre una circona sin tratamiento o irradiada con láser produjo valores de resistencia de adhesión bajos. En base nuestros resultados, el uso de cerámica sin tratamiento y la aplicación directa de agente de cementación se puede considerar un protocolo inadecuado que no optimiza las fuerzas de adhesión en la interfase resina/circona. Por otro lado, el revestimiento de sílice combinado con el uso de un cemento de resina autoadhesivo que contenga 10-MDP tiene un comportamiento prometedor.

Para la obtención de mayor fuerza de adhesión, el clínico debería elegir un protocolo de cementación que proporcione la mayor retención micro-mecánica en la superficie de la cerámica, un método fiable de revestimiento del sustrato de circona mediante sílice, que además sea acondicionado mediante *primer* y un adhesivo que contenga monómero 10-MDP que promoverá la adhesión química .

Otro punto importante a considerar, es la posible contaminación de la restauración cerámica durante su manipulación para comprobar su adaptación en el modelo y dentro de la boca. La mejor opción es disponer de un método de acondicionamiento de superficies inmediato (en la clínica) y no fiarse sólo del tratamiento previo de laboratorio. Todos los pasos clínicos adhesivos (tratamiento de la superficie, la aplicación del *primer* y la cementación) deben llevarse a cabo con meticulosidad para optimizar los resultados clínicos.

El principal obstáculo para conseguir una adhesión a la superficie cristalina es el difícil acondicionamiento químico de ésta. Además, los efectos del arenado parecen generar un aumento o disminución en la resistencia a la flexión de material en función de la topografía del daño ocasionado por el método de abrasión utilizado (Kosmac *et al.,* 1999; Guazzato *et al.,* 2005). En consecuencia, la búsqueda de procedimientos que permitan obtener una rugosidad superficial suave pero extensa mantendrá abierta la línea de investigación del presente trabajo.

Aunque con la adecuada elección de técnicas y materiales se consigue lograr una unión aceptable a medio-largo plazo según la literatura científica, hasta la fecha no existe un agente químico que por conseguir enlaces estables a las cerámicas cristalinas se considere el *gold-standard*. Además de la resistencia de la adhesión, será interesante conocer cómo afecta a la longevidad, estabilidad estructural y la micro-filtración de las prótesis cerámicas en estudios clínicos. La investigación de cualquiera de estos temas será esencial en el progreso de la prostodoncia.

CONCLUSIONES

1. El uso de pilares circona sobre implantes está bien documentado en la literatura con varios estudios *in vitro* y algunos trabajos clínicos que avalan su indicación. Estos pilares de circona tienen un ajuste marginal similar a los pilares de titanio, utilizados universalmente, y ostentan una baja adherencia bacteriana y una alta biocompatibilidad. Aunque los pilares de circona tienen valores de resistencia a la fractura inferiores a los de titanio, se indican en la rehabilitación protésica del sector de anterior, proporcionando un resultado estético y funcional superior.

2. La aplicación de arenado antes de la cementación es determinante para asegurar una buena adhesión en la interfase de circona/resina, independientemente del tamaño de las partículas de alumina. Sin embargo, hay una tendencia evidente entre el aumento de la granulometría de la partícula del arenado y la resistencia de la unión en la interfase circona/resina si se utiliza un cemento que contiene 10-MDP.

3. La eficacia de adhesivo es mayor si la superficie sólo está condicionado con revestimiento de sílice (sin aplicar el láser). El grabado de circona con laser de Er: YAG no es eficaz en el aumento de su resistencia de la adhesión a la resina.

4. La presencia de monómero de 10-MDP en la composición de cemento influye positivamente en la adhesión una vez que es capaz de mejorar la adhesión química a un sustrato de circona. La aplicación de un sistema de cemento que contiene 10-MDP, tanto en el *primer* como en la matriz de resina sobre un sustrato recubierto de sílice o arenado puede ser la clave para el éxito de la adhesión circona/resina.

5. El impacto termociclado en la resistencia de la unión depende de los materiales utilizados. Un cemento auto-adhesivo, específico de resina con 10-MDP en su

composición sobre una superficie de circona pre-tratada con revestimiento de sílice (con o sin Er: YAG asociada) no se afecta por el termociclado.