UNIVERSIDADE DE SÃO PAULO
FACULDADE DE ODONTOLOGIA DE BAURU

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Influence of differente MDP concentrations on the bond strength of a resin cement to zirconia

Influência de adesivos contendo diferentes concentrações de MDP na resistência de união de um cimento resinoso à zircônia

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Orientador: Prof. Dr. Adilson Yoshio Furuse

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DEDICATÓRIA

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“A maior recompensa para o trabalho do homem
não é o que ele ganha com isso, mas o que ele se torna com isso”

John Ruskin

ABSTRACT

Influence of differente MDP concentrations on the bond strength of a resin cement to zirconia

The composition of dental adhesives may influence their performance when used for adhesion to dental structures or ceramics. The purpose of the present study was to evaluate influence of different MDP concentrations on the shear bond strength of a resin cement to zirconia. Six experimental adhesives were prepared with the following composition: 0.50 % CQ by wt, 1.0 % DABE by wt, 0.20% BHT by wt, 0.45% DPHIF by wt, 10% HEMA by wt, 15% TEGDMA by wt, 25% BIS-EMA by wt, 10% ethanol by wt, 25% UDMA by wt, and 12.85% BIS-GMA by wt . The MDP monomer was added at 0% by wt, 3% by wt, 6% by wt, 9% by wt, 12% by wt, or 15% by wt. As a control, four commercially available adhesives were evaluated: Single Bond Universal, Single Bond 2, Ambar and Signum Zirconia Bond. The shear bond strength to zirconia was evaluated in a universal testing machine. Failure modes were analyzed with a stereoscopic loupe. Statistical analyses were performed with one-way Anova and Tukey's HSD test ($\alpha = 0.05$). There were significant differences between groups ($p < 0.00001$). The highest shear bond strength values were obtained with Signum Zirconia Bond and Single Bond Universal. Singlebond 2 showed the lowest values. There were no differences between experimental adhesives. All groups showed adhesive failures. MDP-containing adhesives are important for bonding resin cements to zirconia, however, the concentration of MDP is not the only factor to be considered.

Keywords: Ceramics. Dental Cements. Shear Strength.

RESUMO

Influência de adesivos contendo diferentes concentrações de MDP na resistência de união de um cimento resinoso à zircônia

A composição de adesivos dentários pode influenciar o seu desempenho quando utilizado para união às estruturas dentárias ou cerâmica. O objetivo do presente foi avaliar a influência de diferentes concentrações de MDP na resistência ao cisalhamento de um cimento resinoso à zircônia. Seis adesivos experimentais foram preparados com a seguinte composição: 0,50% em peso de CQ, 1,0% em peso de DABE, 0,20% em peso de BHT, 0,45% em peso de DPHIF, 10% em peso de HEMA, 15% em peso de TEGDMA, 25% em peso de Bis-EMA, 10% em peso de etanol, 25% em peso de UDMA, e 12,85% em peso de BIS-GMA. O monômero MDP foi adicionado em seis porcentagens em peso: 0%, 3%, 6%, 9%, 12%, ou 15%. Como grupo controle, quatro adesivos disponíveis comercialmente foram avaliados: Single Bond Universal, Single Bond 2, Ambar e Signum Zirconia Bond. A resistência de união à zircônia foi avaliada em uma máquina de universal de ensaios através de teste de cisalhamento. Os modos de falha foram analisados com lupa estereoscópica. A análise estatística foi realizada com Anova a um critério e Tukey (α = 0,05). Foram encontradas diferenças significativas entre os grupos (p < 0,00001). Os valores de resistência ao cisalhamento mais elevados foram obtidas com o Signum Zirconia Bond e o Single Bond Universal. O adesivo sem MDP Single Bond 2 apresentou os valores mais baixos. Não houve diferenças entre os adesivos experimentais. Todos os grupos mostraram falhas adesivas. Concluiu-se adesivos que contenham MDP são importantes para a união à zircônia, entretanto, a concentração de MDP não é o único fator a ser considerado.

Palavras-chave: Cerâmica. Cimentos Dentários. Resistência ao Cisalhamento.

SUMMARY

1 INTRODUCTION

1 INTRODUCTION

Currently, the ceramics have a prominent place in cosmetic dentistry. They have been used to make crowns, fixed prostheses, inlays, onlays, overlays, veneers, pins and cores, and implant-supported prostheses. This is mainly because of the incomparable characteristics of this material such as chemical stability, high compressive strength, excellent and long-lasting aesthetics, biocompatibility and mimetic to tooth structures. (KELLY et al. 1996, PEUTZFELDT, 2001). However, to obtain success and longevity in treatments employing dental ceramics, is necessary that the prosthetic pieces are properly adhered to both dental structure and resin cement. (DELLA BONA et al., 2007).

Among the ceramic systems, the most widely used until the '90s, was the porcelain-fused-to-metal in 1962. Its use and dissemination was of such a magnitude, that is considered the most important development in the twentieth century in the field of dental ceramics (ROSENBLUM, 1997). At the end of the twentieth century, seeking to improve the material, many innovative systems were introduced to the market in order to provide the manufacture of metal-free ceramic restorations (GOMES et al. 2008). Therefore, there were new ceramic systems that suffered structural changes in order to make them tougher and more aesthetically pleasing, allowing a wider range of indications (MCLEAN, 2001, ANUSAVICE, 2005). For the purpose of improving the mechanical properties such as strength, thermal expansion and contraction behavior, manufacturers have added filler particles such as alumina, leucite, lithium disilicate and zirconia in the basic composition (KELLY et al., 2008). Nowadays, highly aesthetic dental ceramics are predominantly vitreous, and ceramic materials for infrastructure present greater resistance and are generally crystalline (KELLY et al., 2011 e 2008). Due to the differences in the ceramics composition and microstructure, cementation protocol changes and the treatment of the inner surface varies greatly. It is necessary to obtain a good adhesion of the restoration to the dental structures and, therefore, it is important to understand the mechanisms of formation of the adhesive interface, which include the method of surface treatment of the ceramic substrate and the type of cement used (COSTA, 2006).

Polycrystalline ceramics are more resistant and stronger than the glass-ceramics. This is because they do not contain glass within the composition (KELLY et al., 2011). Yttria-stabilized tetragonal zirconia polycrystal, commonly referred as zirconia or Y-TZP, is polycrystalline ceramics that is widely recognized for its excellent mechanical, physical and thermal properties, having a high mechanical strength, excellent biocompatibility, high fracture toughness, hardness and wear resistance (CAVALCANTI et al, 2009). Besides these excellent properties, a current issue of Y-TZP is related to the effectiveness of adhesive cementation procedures. as would be the application of hydrofluoric acid and silanization, this is due to the absence of silica and a glass phase in its composition (DERAND et al., 2005; OZCAN et al, 2008).

Looking for solutions to improve the bonding between resin cements and Y-TZP, different procedures of inner surface treatment have been suggested, such as surface preparation with erbium-doped and yttrium-aluminum-garnet (Er: YAG) laser (CAVALCANTI et al, 2009), grinding with diamond rotary instruments (QEBLAWI et al., 2010), selective infiltration etching (DE MUNCK et al., 2012), surface roughening by aluminum oxide blasting of different particle sizes, applied before or after sintering (ABI-RACHED et al., 2015, DEMIR et al., 2012), surface roughening by alumina-silica particles before silanization (JEVNIKAR et al., 2010 OZCAN et al., 2008), liner application (BALDISSARA et al., 2013), and application of low-fusing ceramics (DERAND et al., 2005).

Y-TZP materials exhibit a stress-induced transformation toughening mechanism, which means that when the material is under stress, microstructural changes occurs. Thus, Y-TZP has a defense system against cracks propagation, changing from a tetragonal phase to a monoclinic phase at the beginning of the crack, which is also accompanied with a volume increase (PICONI., 1999). Due to the possibility of phase transformation, one must administer care when using the abrasion methods with different particles since they have shown different percentages of martensitic transformation in the treated surface (SRIAMPORN et al., 2014;. ABI-RACHED et al, 2015). Therefore, phosphate monomers, such as 10-metacriloxidecil dihydrogen phosphate (MDP) were incorporated in adhesives, and are used to obtain a bonding between acid resistant Y-TZP ceramic materials and resin cements. MDP can interact with metal oxides, enabling chemical bonding of ceramic oxides with or without an additional coupling agent (YOSHIDA et al., 2006). This monomer may also chemically interact with the presence of residual hydroxyapatite. This double binding mechanism (micro-mechanical and chemical bond) is believed to be advantageous in terms of durability of the restorations. (DABSIE et al., 2012). However, the influence of different MDP concentrations on the bond strength of a resin cement to zirconia still needs to be addressed. The purpose of the present study was to evaluate the influence of different MDP concentrations in six experimental adhesives as compared to four commercially available adhesives on the shear bond strength of a resin cement to Y-TZP.

2 ARTICLE

2 ARTICLE

Bonding polycrystalline zirconia with 10-MDP-containing adhesives

Running title: Bonding Y-TZP with 10-MDP-containing adhesives

Clinical Relevance: 10-MDP-containing adhesives are important for bonding resin cements to zirconia. However, the 10-MDP concentration is not the only factor responsible for improving the bonding to Y-TZP.

SUMMARY

Objective. To evaluate the influence of adhesives with different 10-MDP concentrations on the shear bond strength of a resin cement to zirconia.

Methods and Materials: Six experimental adhesives were prepared with the following composition: CQ, DABE, BHT, diphenyliodonium hexafluorophosphate, HEMA, TEGDMA, BIS-EMA, UDMA, BIS-GMA, and ethanol. The 10-MDP monomer was added at 0wt%, 3wt%, 6wt%, 9wt%, 12wt%, or 15wt%. Three commercially available adhesives were evaluated: Single Bond Universal, Single Bond 2 and Signum Zirconia Bond. Resin cement cylinders made with RelyX Ultimate were bond to Y-TZP with one of the evaluated adhesives and were subjected to the shear bond strength evaluation. Failure modes were analyzed with a stereoscopic loupe. Statistical analyses were performed with one-way Anova and the Tukey's HSD test (α=0.05). Pearson's was used to correlate % of 10-MDP in the experimental adhesives and shear bond strength.

Results: There were significant differences between adhesives (p<0.00001). The highest shear bond strength values were obtained with the Signum Zirconia Bond and Single Bond Universal. Single Bond 2 showed the lowest values. There were no differences between experimental adhesives. All groups showed adhesives failures. A non-linear correlation was found between bond strength and % of 10-MDP in experimental adhesives (r=0.872).

Conclusions: The commercially available adhesives indicated for bonding to zirconia showed the highest bonding values.

INTRODUCTION

The clinical success of all-ceramic yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) indirect restorations not only depends on the correct knowledge and handling of the material itself but also the use of an adhesive system associated with resin-based cement to provide satisfactory bonding of the prosthetic work to the dental structures.[1] Y-TZP is widely recognized for its excellent mechanical, physical and thermal properties, biocompatibility, high fracture toughness, hardness and wear resistance.[2] Although Y-TZP ceramics presents all these excellent properties, the effectiveness of adhesive cementation procedures is still a problem, since Y-TZP ceramics cannot be conditioned by the application of hydrofluoric acid and conventional silane coupling agents due to the absence of silica and glass phase.

In search of solutions, different procedures to improve the bond of the resin cement to the inner surface of zirconia have been tested, such as surface preparation with erbium-doped and yttrium-aluminum-garnet laser (Er: YAG), grinding with diamond rotary instruments, selective infiltration etching, surface roughening by aluminum oxide blasting of different particle sizes before or after sintering, surface roughening by alumina-silica particles before silanization, and application of a liner.[2-10] All these methods seek to improve the mechanical and micromechanical interlocking through the increase in the roughness of the surface. However, some of these treatments have proved to be ineffective and, in several cases, they may cause a possible surface damage.[11]

A different approach to improve the bond strength to zirconia is to develop a chemical interaction between the surface and the applied resin cement. [12] For this task, researches have been focusing in the use of primers that contain phosphate monomers that have an affinity for metal oxides. The 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP) is one of the most frequently monomers used for this purpose.[13, 14] However, although important for bonding to both dental substrates and zirconia, the maximum concentration of 10-MDP monomers that should be added to dental adhesives still needs to be evaluated, as it has been suggested that the polymerization of CQ/amine-based adhesives may be negatively affected by the interaction between functional monomers such as 10-MDP and tertiary amines.[15] Therefore, it is important to evaluate how the incorporation of different concentrations of 10-MDP may improve or jeopardize the bonding of adhesive systems to zirconia.

It is well known that light-cured resin-based materials such as adhesives commonly contain camphorquinone (CQ) and tertiary amines to allowing visible-light-initiated free-radical polymerization. On the other hand, it has been suggested that the inclusion of a third component to the CQ/amine photoinitiating system such as iodonium salts could improve the photo-activation induced by visible light sources.[16]

These monomers are required to obtain bonding with acid resistant policrystalline ceramic materials such as zirconia. It has been suggested that 10-MDP can interact with metal oxides, enabling chemical bonding of ceramic oxides with or without an additional coupling agent.[17] Thus, the purpose of the present study is to evaluate the influence of different 10-MDP concentrations on the shear bond strength of a resin cement to zirconia. For this purpose, 10-MDP was added to six experimental adhesives and compared to three commercially available materials. The null hypotheses evaluated were: 1) the concentration of 10-MDP monomers in the experimental adhesives would not influence the shear bond strength; 2) there would be no differences between the experimental and commercially available adhesives.

METHODS AND MATERIALS

Experimental adhesives consisted of a mixture of 2-hydroxyethyl methacrylate - HEMA; triethylene glycol dimethacrylate - TEGDMA; ethoxylated bisphenol A glycol dimethacrylate - Bis-EMA; urethane dimethacrylate - UDMA; and bisphenol A diglycidyl methacrylate - Bis-GMA. Ethanol (10wt%); camphorquinone - CQ (0.50wt%); 1,2-diaminobenzene - DABE (1.00wt%); and iodonium salt diphenyliodonium hexafluorophosphate - DPIHP (0.45wt%), butylhydroxytoluene - BHT (0.20wt%) were added. Five concentrations of 10-MDP were added to this basic adhesive: 3wt%, 6wt%, 9wt%, 12wt%, or 15wt%. Materials were used without further purification. As control, three commercially available adhesive systems were evaluated: Single Bond 2 (not indicated for bonding to zirconia), Single Bond Universal (indicated for bonding to zirconia), and Signum Zirconia Bond (not indicated for bonding to zirconia). Table 1 describes the composition, manufacturers and instructions for the use of these adhesives.

Table 1 - Materials and composition.

Adhesive (Manufacturer)	Composition	Instructions for use
Adper Single Bond 2 (3M ESPE, Sumaré, SP, Brazil)	BisGMA, HEMA, dimethacrylates, silica nanofiller, ethanol, water, photoinitiator system and methacrylate functional copolymer of polyacrylic and polyitaconic acids	a) apply 2-3 consecutive coats of adhesive to the ceramic surface for 15 s with gentle agitation using a fully saturated applicator; b) gently air thin for 5 s to evaporate solvents; c) light cure for 10 s.
Single Bond Universal (3M ESPE, Seefeld, Germany)	MDP phospate monomer, dimethacrylate resins, HEMA, Vitrebond copolymer, filler, ethanol, water, initiators, silane	a) clean the surface with alcohol and dry it with compressed air; b) apply with a micro brush to the surface for 20 s; c) Apply compressed free oil air for 5 s; d) light cure for 10 s.
Signum Zirconia Bond (Heraeus Kulzer, Hanau, Germany)	Signum zirconia bond I*: Acetone, 10-MDP, acetic acid. Signum zirconia bond II*: methyl methacrylate, diphenyl(2,4,6- trimethy lbenzoyl) phosphine oxide. MMA, initiators.	a) clean the surface with alcohol and dry it with compressed air;; b) Signum Zirconia bond I is dispensed and applied with a suitable brush to the entire surface and air-dried for 5 s; c) Signum Zirconia bond II is applied and light cured for 40 s.

*Obtained from the manufacturer’s safety data sheet

Polycrystalline ceramic blocks (IPS e.max ZirCAD, Ivoclar Vivadent, Schaan, Liechtentein) were cut into 2 mm thick slices with a cutting machine (Isomet 1000 Low Speed, Buehler, LakeBluff, IL, USA) and a diamond disc (15LC diamond nº 11-4254, Buehler, LakeBluff, IL, USA) at a speed of 275 rpm under constant water refrigeration. Four ceramic slices were used in each group. The slices were polished with sequential sandpaper discs (grain sizes, #800, #1000, and # 1200, K2000 Polishing Paper, Exact, Nordestedt, Schleswing-Holstein, Germany) using a metallographic polishing machine (Exact, Nordestedt, Schleswing-Holstein, Germany) to standardize the ceramic surfaces. Forty slices were prepared.

After surface standardization, the ceramics slices were sintered (INFIRE Oven HTC Speed, Sirona Dental Systems, Long Island City, NY, USA) according to the recommendations of the ceramics manufacturer. The slices were then randomly divided into nine groups and embedded in acrylic resin. The surfaces were then polished with sequential sandpaper discs (grain sizes # 800 up to # 1200, K2000 Polishing Paper, Exact) to remove any acrylic resin that might have covered the samples. Samples were abundantly washed with deionized water and dried. Experimental adhesives were applied as follows: all the ceramic surfaces were cleaned and dried; adhesives were applied with a microbrush and remained untouched for 20 s; compressed oil-free air was applied at 90˚ from a distance of 15 cm for 5 s; adhesives were light cured for 10 s with an LED device (VALO Cordless, Ultradent Products, South Jordan, UT, USA) operating at an irradiance of 1100 mW/cm^2. Commercially available adhesives were applied as per manufacturers' instructions and were light cured with the same device.

Surgical catheters with an internal diameter of 1.40 mm and a height of 1 mm were used for the resin cement cylinders (RelyX Ultimate, 3M ESPE, St. Paul, MN, USA). Four cylinders per ceramic surface were prepared, counting 16 of them for each group. The cement was mixed according to the manufacturer's recommendations, inserted into the catheters and light cured for 20 s with the VALO curing device with irradiance of 1100 mW/cm^2. After light curing, the surgical catheters were kept untouched for 10 min before being removed with #11 scalpel blades (Embramed, Jurubatuba, SP, Brazil) to expose the resin cement cylinders. Samples lost during removal of the catheters were counted and considered as 0 MPa in the statistical analysis.

The samples were stored in deionized water for 24 h at 37ºC. After storage, the samples were subjected to the shear bond strength evaluation using a 0.2 mm wire-loop positioned as close as possible of the adhesive interface and adapted to a universal testing machine (Instron 3342, Illinois Tool Works, Norwood, MA, USA), using a load cell with a 500 N load cell, operating at a crosshead speed of 0.5 mm/min.

Data were analyzed with one-way Anova and the Tukey HSD test. A global significance level of 5% was adopted. Pearson correlation analysis was used to determine if there was a correlation between the percentages of 10-MDP in the experimental adhesives and shear bond strength. The failure modes were evaluated with a stereoscopic loupe.

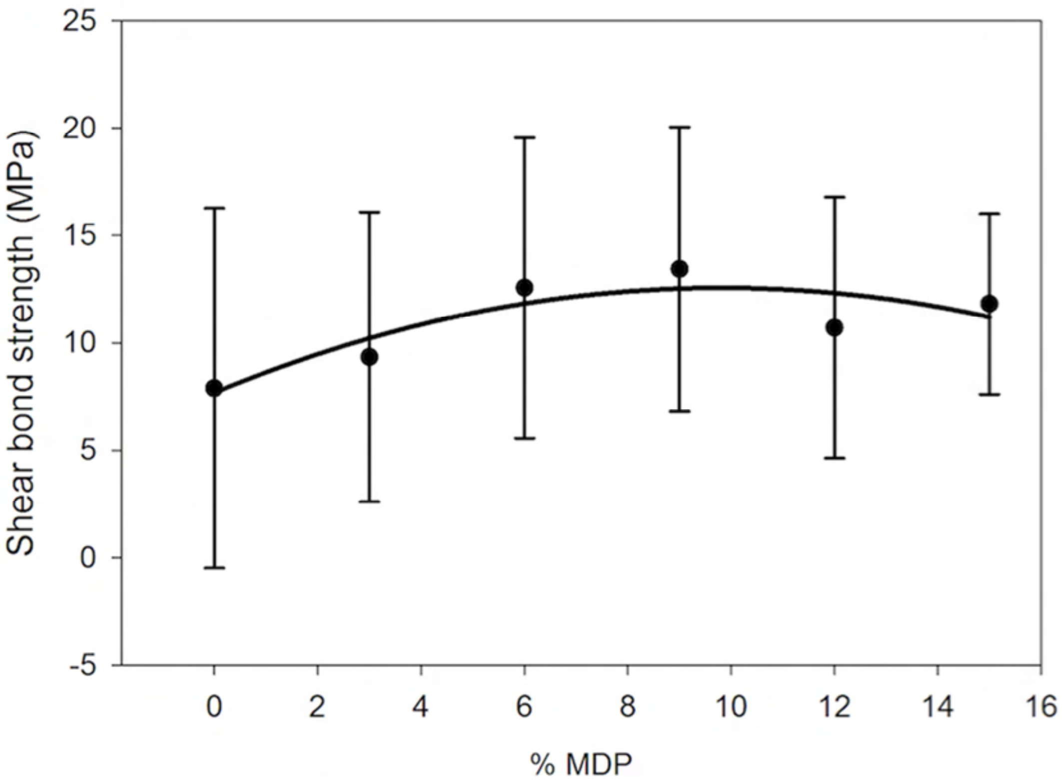
RESULTS

Mean values, number of lost samples for each group and standard deviations for the shear bond strength are shown on Table 2.

Table 2 - Mean values (in MPa) and standard deviations for the shear bond strength. Different superscript letters represent statistically significant differences ($p < 0.05$)

Adhesive	Shear bond strength	Sample losses (% out of 16 samples)
Single Bond 2	6.06 ± 5.78^{a}	4 (25%)
Single Bond Universal	14.02 ± 6.5^{bc}	2 (12.5%)
Signum Zirconia Bond	20.86 ± 6.11^{c}	0 (0%)
0% 10-MDP	7.89 ± 8.38^{ab}	6 (37.5%)
3% 10-MDP	9.34 ± 6.75^{ab}	2 (12.5%)
6% 10-MDP	12.56 ± 7^{ab}	1 (6.25%)
9% 10-MDP	13.43 ± 6.62^{ab}	3 (18.75%)
12% 10-MDP	10.7 ± 6.08^{ab}	2 (12.5%)
15% 10-MDP	11.81 ± 4.2^{ab}	0 (0%)

There were significant differences between groups (F=6.5741; p<0.00001). The highest shear bond strength values were obtained with the Signum Zirconia Bond and Single Bond Universal. There were no differences between the experimental adhesives. Single Bond 2 showed the lowest values. The failure mode was adhesive for all specimens. A non-linear correlation was found between bond strength and % of 10-MDP in the experimental adhesives (r = 0.872) (Figure 1).



DISCUSSION

The present study evaluated the shear bond strength of a resin cement to zirconia after the application of 10-MDP-containing experimental and commercially available adhesives. Although a non-linear correlation was found between bond strength and percentage of 10-MDP added to the experimental adhesives (Figure 1), in this study, the first null hypothesis was accepted since no statistically significant difference was found between experimental adhesives. The second null hypothesis was rejected, since there were differences between experimental and commercially available adhesives.

In order to solve the adhesion problem, several treatments have been suggested and studied in the literature, and sandblasting with aluminum oxide (alumina) is the reference pretreatment methods.[10, 18] Although the advantages of sandblasting, such as increased surface roughness, modified wettability and surface energy of the ceramics and improved the micromechanical retention,[18] Y-TZP ceramics may suffer a phase transformation from tetragonal to monoclinic, which may be detrimental for the durability and mechanical properties of this ceramic.[10] Besides showing the described limitations, as the present study was designed to address the bond strength of different adhesive systems without the interference of surface-related characteristics such as roughness, no sandblasting or any other mechanical surface treatment were conducted. Additionally, after been embedded in acrylic resin Y-TZP discs were polished with #1200 sandpapers, so the influence of the different adhesives evaluated could be more directly understood.

Another point to be addressed is the fact that in the present study the light activation of the resin-cement was conducted directly, without the influence of a ceramic material between the light source and the resin-cement. However, the light attenuation caused by the ceramics may play a role on the properties of resin cement.[19-21] It has been suggested that the thickness of the interposing ceramic material influences the light transmittance and as ceramic thickness increases longer irradiation periods are required.[21]

Regarding the shear bond strength method, some points should also be discussed. As described in the literature, two experimental designs, shear and tensile tests both in micro or macro scale, are commonly used in this type of study.[22] In general the shear bond strength test is used because it is simpler than tensile tests. On the other hand, shear tests have a nonhomogeneous stress distribution at the adhesive interface.[23] For this reason, absolute numerical results obtained from one research cannot be directly compared to another one. It should be noted that, despite the described limitations regarding the bond strength evaluations, different materials are similarly ranked, as correlations between different methods have been found.[24, 25]

In the present study, the shear bond strength evaluation was conducted on 24-hour-water-stored samples. It was shown that the concentration of 10-MDP monomers on the experimental adhesives did not influence the bond strength of the evaluated resin cement, while the two commercially available adhesives indicated for bonding to zirconia that also contain 10-MDP showed a better performance. These results are in agreement with others studies.[17, 26, 27] It is, however, important to note that, while no long-term storage or aging was conducted in the present study, the differences between materials containing different 10-MDP concentrations could be demonstrated if a long-term evaluation of the bond strength was conducted. Other studies confirm that active parts of 10-MDP react with the zirconia surface, but this is vulnerable to instability after aging.[1, 28]

For a better interpretation of this study, it is important to understand how does 10- MDP monomer work. Chemically, this monomer bonds to oxide metals and tooth substrates. Structurally, it has an amphiphilic build with the vinyl group, such as the hydrophobic half, and the phosphate group such as the hydrophilic half.[29] The 10-MDP monomer is an effective strong bonder between the resin cement, zirconia and other oxide metals materials.[30] Authors such as Yoshida et al.,[17] evaluated the interaction of hydroxyl groups of the phosphate half with the hydroxyl groups on the zirconia surface through Van der Waals forces or hydrogen bonds. Thanks to these studied properties, many commercial products such as adhesives, primers and resin cements have incorporated 10-MDP in their composition, seeking to improve the bonding properties to Y-TZP ceramic materials.[31]

Signum Zirconia Bond is a 10-MDP-containing material especially designed for the purpose of bonding resin cements to Y-TZP ceramics. This bonding material presents two different bottles. MDP monomers, acetic acid and acetone are present in the bottle number 1, while bottle number 2 contains diphenyl phosphinoxide and methyl methacrylate. In the present study, this material has shown increased shear bond strength. Other studies have also shown similar results.[18, 32] According to Ural et al.,[33] the key factor of this material could be the methyl methacrylate, which establishes primary bonds with the methacrylate present in the resin cement, and improves in that way the bond strength. Thus, a further study with more focus on MDP and methyl methacrylate interaction is suggested. Although important for bonding resin cements to zirconia, the 10-MDP concentration alone is not the only factor to be considered.

CONCLUSIONS

According to the results of the present study, it may be concluded that the commercially available adhesives indicated for bonding to Y-TZP showed the highest bonding values and the concentration of 10-MDP on experimental adhesives was not significant.

REFERENCES

1. Dias de Souza GM, Thompson VP & Braga RR (2011) Effect of metal primers on microtensile bond strength between zirconia and resin cements *Journal of Prosthetic Dentistry* **105(5)** 296-303.

2. Cavalcanti AN, Foxton RM, Watson TF, Oliveira MT, Giannini M & Marchi GM (2009) Y-TZP ceramics: key concepts for clinical application *Operative Dentistry* **34(3)** 344-351.

3. Abi-Rached FO, Martins SB, Almeida-Junior AA, Adabo GL, Goes MS & Fonseca RG (2015) Air abrasion before and/or after zirconia sintering: surface characterization, flexural strength, and resin cement bond strength *Operative Dentistry* **40(2)** E66-75.

4. Baldissara P, Querze M, Monaco C, Scotti R & Fonseca RG (2013) Efficacy of surface treatments on the bond strength of resin cements to two brands of zirconia ceramic *Journal of Adhesive Dentistry* **15(3)** 259-267.

5. Demir N, Subasi MG & Ozturk AN (2012) Surface roughness and morphologic changes of zirconia following different surface treatments *Photomedicine and Laser Surgery* **30(6)** 339-345.

6. Jevnikar P, Krnel K, Kocjan A, Funduk N & Kosmac T (2010) The effect of nano-structured alumina coating on resin-bond strength to zirconia ceramics *Dental Materials* **26(7)** 688-696.

7. Melo RM, Souza R, Dursun E, Monteiro E, Valandro LF & Bottino MA (2015) Surface treatments of zirconia to enhance bonding durability *Operative Dentistry* **40(6)** 636-643.

8. Ozcan M & Bernasconi M (2015) Adhesion to zirconia used for dental restorations: a systematic review and meta-analysis *Journal of Adhesive Dentistry* **17(1)** 7-26.

9. Qeblawi DM, Munoz CA, Brewer JD & Monaco EA, Jr. (2010) The effect of zirconia surface treatment on flexural strength and shear bond strength to a resin cement *Journal of Prosthetic Dentistry* **103(4)** 210-220.

10. Tzanakakis EGC, Tzoutzas IG & Koidis PT (2016) Is there a potential for durable adhesion to zirconia restorations? A systematic review *Journal of Prosthetic Dentistry* **115(1)** 9-19.

11. Hallmann L, Ulmer P, Wille S, Polonskyi O, Kobel S, Trottenberg T, Bornholdt S, Haase F, Kersten H & Kern M (2016) Effect of surface treatments on the properties and morphological change of dental zirconia *Journal of Prosthetic Dentistry* **115(3)** 341-349.

12. de Souza G, Hennig D, Aggarwal A & Tam LE (2014) The use of MDP-based materials for bonding to zirconia *Journal of Prosthetic Dentistry* **112(4)** 895-902.

13. Koizumi H, Nakayama D, Komine F, Blatz MB & Matsumura H (2012) Bonding of resin-based luting cements to zirconia with and without the use of ceramic priming agents *Journal of Adhesive Dentistry* **14(4)** 385-392.

14. Lorenzoni FC, Leme VP, Santos LA, de Oliveira PC, Martins LM & Bonfante G (2012) Evaluation of chemical treatment on zirconia surface with two primer agents and an alkaline solution on bond strength *Operative Dentistry* **37(6)** 625-633.

15. Hanabusa M, Yoshihara K, Yoshida Y, Okihara T, Yamamoto T, Momoi Y & Van Meerbeek B (2016) Interference of functional monomers with polymerization efficiency of adhesives *European Journal Oral Science* **124(2)** 204-209.

16. Cook WD & Chen F (2011) Enhanced photopolymerization of dimethacrylates with ketones, amines, and iodonium salts: The CQ system *Journal of Polymer Science Part A: Polymer Chemistry* **49(23)** 5030-5041.

17. Yoshida K, Tsuo Y & Atsuta M (2006) 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* **77(1)** 28-33.

18. Pereira Lde L, Campos F, Dal Piva AM, Gondim LD, Souza RO & Ozcan M (2015) Can application of universal primers alone be a substitute for airborne-particle abrasion to improve adhesion of resin cement to zirconia? *Journal of Adhesive Dentistry* **17(2)** 169-174.

19. Calgaro PA, Furuse AY, Correr GM, Ornaghi BP & Gonzaga CC (2013) Influence of the interposition of ceramic spacers on the degree of conversion and the hardness of resin cements *Brazilian Oral Reserch* **27(5)** 403-409.

20. Inokoshi M, Pongprueksa P, De Munck J, Zhang F, Vanmeensel K, Minakuchi S, Vleugels J, Naert I & Van Meerbeek B (2016) Influence of light irradiation through zirconia on the degree of conversion of composite cements *Journal of Adhesive Dentistry* **18(2)** 161-171.

21. Watanabe H, Kazama R, Asai T, Kanaya F, Ishizaki H, Fukushima M & Okiji T (2015) Efficiency of dual-cured resin cement polymerization induced by high-intensity LED curing units through ceramic material *Operative Dentistry* **40(2)** 153-162.

22. Kim JH, Chae S, Lee Y, Han GJ & Cho BH (2014) Comparison of shear test methods for evaluating the bond strength of resin cement to zirconia ceramic *Acta Odontologica Scandinavica* **72(8)** 745-752.

23. Inokoshi M, De Munck J, Minakuchi S & Van Meerbeek B (2014) Meta-analysis of bonding effectiveness to zirconia ceramics *Journal Dental Research* **93(4)** 329-334.

24. Cardoso PE, Braga RR & Carrilho MR (1998) Evaluation of micro-tensile, shear and tensile tests determining the bond strength of three adhesive systems *Dental Materials* **14(6)** 394-398.

25. Hu M, Weiger R & Fischer J (2016) Comparison of two test designs for evaluating the shear bond strength of resin composite cements *Dental Materials* **32(2)** 223-232.

26. Oba Y, Koizumi H, Nakayama D, Ishii T, Akazawa N & Matsumura H (2014) Effect of silane and phosphate primers on the adhesive performance of a tri-n-butylborane initiated luting agent bonded to zirconia *Dental Materials Journal* **33(2)** 226-232.

27. Yoshida Y, Nagakane K, Fukuda R, Nakayama Y, Okazaki M, Shintani H, Inoue S, Tagawa Y, Suzuki K, De Munck J & Van Meerbeek B (2004) Comparative study on adhesive performance of functional monomers *Journal of Dental Research* **83(6)** 454-458.

28. Ozcan M, Nijhuis H & Valandro LF (2008) Effect of various surface conditioning methods on the adhesion of dual-cure resin cement with MDP functional monomer to zirconia after thermal aging *Dental Materials Journal* **27(1)** 99-104.

29. Kim JH, Chae SY, Lee Y, Han GJ & Cho BH (2015) Effects of multipurpose, universal adhesives on resin bonding to zirconia ceramic *Operative Dentistry* **40(1)** 55-62.

30. Magne P, Paranhos MP & Burnett LH, Jr. (2010) New zirconia primer improves bond strength of resin-based cements *Dental Materials* **26(4)** 345-352.

31. Lehmann F & Kern M (2009) Durability of resin bonding to zirconia ceramic using different primers *Journal of Adhesive Dentistry* **11(6)** 479-483.

32. Maeda FA, Bello-Silva MS, de Paula Eduardo C, Miranda Junior WG & Cesar PF (2014) Association of different primers and resin cements for adhesive bonding to zirconia ceramics *Journal of Adhesive Dentistry* **16(3)** 261-265.

33. Ural C, Kulunk T, Kulunk S, Kurt M & Baba S (2011) Determination of resin bond strength to zirconia ceramic surface using different primers *Acta Odontologica Scandinavica* **69(1)** 48-53.

3 Discussion

3 DISCUSSION

In the present study, the first null hypothesis was accepted since the use of MDP monomers in experimental and commercial adhesives were significantly different from the adhesives without MDP. The second null hypothesis was accepted, since there were differences between the experimental and commercially available adhesives.

In the present study, no sandblasting was conducted before the bonding procedures. As known, with all the different benefits of zirconia, it can be assumed that it has a wide range of possible clinical applications. (MAEDA et al., 2014). On the other hand, despite all the great benefits, zirconia has presented an important disadvantage, reflected on its weak potential for adhesion to resin cements. This problem is due to the lack of a glassy phase in its high crystalline composition (DERAND et al., 2005). In order to solve the adhesion problem, several treatments have been suggested and studied in the literature, and sandblasting with aluminum oxide (alumina) is the "gold standard" treatment (LUCENA PEREIRA et al., 2015). Although the advantages of sandblasting, such as increased surface roughness, modified the wettability and surface energy of the ceramics and improved the micromechanical retention (LUCENA PEREIRA et al., 2015), Y-TZP ceramics may suffer a phase transformation from tetragonal to monoclinic, which may be detrimental for the durability and mechanical properties of this ceramic. This phase transformation, known as a toughening mechanism called "transformation toughening" (t→m), where the crack propagation is contained thanks to the phase change from tetragonal to monoclinic through an increase in volume (4.5%) inducing compressive stress over the crack tip (KERN & WEGNER., 1998, SATO et al., 2008, SOUZA ROA et al., 2013, MORADABADI et al., 2014, MAEDA et al., 2014). In the use of sandblasting, this phase transformation is related to the grain size (25 to 250μm), distance (5 to 20 mm) from the nozzle to the specimen, propulsion pressure (0.05 to 0.45 MPa) and time of application (5 to 30 seconds) (TZANAKAKIS et al., 2016). Besides showing the described limitations, the present study was designed to address the bond strength of different adhesive systems without the interference of surface-related characteristics such as roughness, no sandblasting or any other mechanical surface treatment. In the present study, after sinterization, Y-TZP discs were embedded in acrylic resin and polished with #800 up to #1200 sandpapers (Polishing Paper K2000, Exact, Nordestedt, Schleswing-Holstein, Germany).

However, this polishing is not what is commonly conducted when Y-TZP frameworks are processed by CAD-CAM devices and could negatively influence the bond strength since polished surfaces are less favorable for bonding procedures. Thus, with this method design, the influence of the different adhesives evaluated could be more directly understood.

Regarding the method, some points should also be discussed. In accordance with other authors and researches (Piascik et al., 2009, Aboushelib et al., 2007), in the present study, a shear bond strength test was employed to evaluate the bond strength of the resin cement to zirconia. As described in the literature, two experimental designs, shear and tensile tests both in micro or macro scale, are commonly used in this type of study (Jae Hoon et al., 2014). The most often used test is the shear bond strength test because it involves a simpler experimental mechanism than tensile tests (Watanabe & Nakabayashi., 1994). On the other hand, shear tests are also put in trial due to the nonhomogeneous distribution of stress at the adhesive interface, probably leading to an overestimation or misinterpretation of the results (INOKOSHI et al., 2014). Moreover, absolute numerical results obtained from one research cannot be directly compared to another one. It should be noted that, despite the described limitations regarding the bond strength evaluations, different materials are similarly ranked as correlations between different methods. (Hu et al. 2016; Cardoso et al. 1998).

In the present study, the shear bond strength evaluation was conducted on 24-hour-water-stored samples. It was shown that the concentration of MDP monomers on the experimental adhesives did not influence the bond strength of the evaluated resin cements. Only two commercially available materials that also contain MDP showed a better performance. These results are in agreement with others studies (Yoshida et al., 2004 and 2006, Oba et al., 2014). It should be noted that the differences between materials containing different MDP concentrations could be demonstrated if a long-term evaluation of the bond strength was conducted. Other studies confirm that active parts of MDP react with the zirconia surface, but this is vulnerable to instability after aging (Ozcan et al., 2008, De Souza et al., 2011).

For a better interpretation of the present study, it is important to understand how 10-methacryloxydecyl dihydrogen phosphate (MDP) monomers work. Chemically, this monomer bonds to oxide metals and tooth substrates. Structurally, it has an amphiphilic build with the vinyl group, such as the hydrophobic half, and the phosphate group such as the hydrophilic half (Kim et al., 2015). The MDP monomer is an effective strong bonder between the resin cement, zirconia and other oxide metals materials. (Magne et al., 2010). Authors such as Yoshida et al. (2006) evaluated the possible interaction of hydroxyl groups of the phosphate half with the hydroxyl groups on the zirconia surface through Van der Waals forces or hydrogen bonds. Thanks to these studied properties, many commercial products such as adhesives, primers and resin cements have incorporated MDP in their composition, seeking to improve the bonding properties to Y-TZP ceramic materials (Lehmann et al., 2009).

Signum Zirconia Bond is an MDP-containing material especially designed for the purpose of bonding resin cements to Y-TZP ceramics. This bonding material presents two different bottles. MDP monomers, acetic acid and acetone are present in bottle number 1, while bottle number 2 contains diphenyl phosphinoxide and methyl methacrylate. In the present study, this material has shown increased shear bond strength. Other studies have also shown similar results (Maeda et al., 2014, Lucena Pereira et al., 2015). According to Ural et al., (2011), the key factor of this material could be the methyl methacrylate, which establishes primary bonds with the methacrylate present in the resin cement which improves the bond strength. Thus, a further study with more focus on MDP and methyl methacrylate interaction is suggested. Although important for bonding resin cements to zirconia, the MDP concentration alone is not the only factor to be considered.

REFERENCES

REFERENCES

ABI-RACHED, F.O. et al. Air abrasion before and/or after zirconia sintering: surface characterization, flexural strength, and resin cement bond strength. **Oper Dent**, Seattle, v.40, n.2, p.66-75. Mar 2015.

ANUSAVICE, K.J. Cerâmicas Odontológicas. In: Anusavice KJ, editor. Phillips, **Materiais Dentários**. São Paulo: Elsevier, p. 619-77. 2005.

BALDISSARA, P. et al. Efficacy of surface treatments on the bond strength of resin cements to two brands of zirconia ceramic. **J Adhes Dent**, New Malden, v15, p.259-67. Sep 2013.

CARDOSO, P.E, BRAGA, R.R, CARRILHO, M.R. Evaluation of micro-tensile, shear and tensile tests determining the bond strength of three adhesive systems. **Dent Mater**, Oxford, v.14, p.394-8. Nov 1998.

CAVALCANTI, A.N. et al. Y-TZP ceramics: key concepts for clinical application**. Oper Dent**, Seattle, v. 34, n. 3, p. 344-51. Jun 2009.

COSTA, J.L.V. et al. O estágio atual das cerâmicas Odontológicas. **PCL**, v.8, p.193-198. 2006.

DABSIE, F, GRÉGOIRE, G, SHARROCK, P. Critical Surface Energy of Composite Cement Containing MDP (10-Methacryloyloxydecyl Dihydrogen Phosphate) and Chemical Bonding to Hydroxyapatite. J Biomater Sci Polym Ed, **Utrecht,** v.23, p.543-554, Oct 2012.

DE MUNCK, J. et al. Meta-analytical review of parameters involved in dentin bonding. **J Dent Res**, Washington, v.91, n.4, p.351-7. Apr 2012.

DE SOUZA, G.M, THOMPSON, V, BRAGA, R. Effect of metal primers on micro-tensile bond strength between zirconia and resin cements. **J Prosthet Dent**, St. Louis, v. 105, p. 296-303. May 2011.

DELLA BONA, A. et al. Characterization and surface treatment effects on topography of a glass-infiltrated alumina/zirconia-reinforced ceramic. **Dent Mater**, Oxford, v. 23, n. 6, p. 769-75, Jun 2007.

DEMIR, N, SUBAS, M.G, OZTURK, A.N. Surface roughness and morphologic changes of zirconia following different surface treatments. Photomed Laser Surg, **Larchmont**, n.30, p.339-45. Jan 2012.

DERAND, T, MOLIN, M, KVAM, K. Bond strength of composite luting cement to zirconia ceramic surfaces. **Dent Mater**, Oxford, v.21, n.12, p.1158-62.Dec 2005.

GOMES E.A, ASSUNÇÃO W.G, ROCHA E,P. Cerâmicas Odontológicas: o estado atual. v. 54, p. 319-325. 2008.

HU, M, WEIGER, R, FISCHER, J. Comparison of two test designs for evaluating the shear bond strength of resin composite cements. **Dent Mater**, Oxford, v. 32, p. 223-232, Feb 2016.

INOKOSHI, M, et al. Meta-analysis of bonding effectiveness to zirconia ceramics. **J Dent Res**, Washington, v. 93, p. 329-34. Apr 2014.

JEVNIKAR, P. et al. The effect of nano-structured alumina coating on resin-bond strength to zirconia ceramics. **Dent Mater**, Oxford, v.26, n.7, p.688-96. Jul 2010.

KELLY, J.R.; NISHIMURA, I.; CAMPBELL, S.D. Ceramic in dentistry: historical roots and current perspectives. **J Prosthet Dent**, St. Louis, v. 75, n. 1, p. 18-32, Jan. 1996.

KELLY, J.R, BENETTI, P. Ceramic materials in dentistry: historical evolution and current practice. **Aust Dent J**, Sydney, v.56, n.1Suppl, p.84-96, Oct.2011.

KELLY, J.R. Dental Ceramics: What Is This Stuff Anyway? **J Amer Dent Assoc**, Chicago, v.139, n.139, p.4S-7S, Sep.2008.

KERN M, WEGNER SM. Bonding to zirconia ceramic: adhesion methods and their dura- bility. **Dent Mater**, Oxford, v. 14, p. 64-71. Jan 1998.

KIM, J. et al. Comparison of shear test methods for evaluating the bond strength of resin cement to zirconia ceramic. **Acta Odont Scand**, Stockholm, v. 10, p. 1-8. Nov 2014.

KIM, J. et al. Effects of Multipurpose, Universal Adhesives on Resin Bonding to Zirconia Ceramic. **Oper Dent**, Seattle, v. 40, p. 55-62. Jan 2015.

LEHMANN, F, KERN, M. Durability of resin bonding to zirconia ceramic using different primers. **J Adhes Dent**, New Malden, v. 11, p. 479–83. Dec 2009.

MAEDA, F.A. et al. Association of Different Primers and Resin Cements for Adhesive Bonding to Zirconia Ceramics. **J Adhes Dent,** New Malden, v. 16, p. 261-265. Dec 2014.

MAGNE, P, PARANHOS, M, BURNETT, L. New zirconia primer improves bond strength of resin-based cements. **Dent Mater**, Oxford, v. 26, p. 345-52. Apr 2010.

McLEAN, J.W. Evolution of dental ceramics in the twentieth century. **J Prosthet Dent**, St. Louis, v.85, n.1, p.61-66, Jan. 2001.

MIRMOHAMMADI, H. et al. Innovations in bonding to zirconia ceramics: Part III Phosphate monomer resin cements. **Dent Mater**, Oxford, v. 26, p. 786-92. Aug 2010.

MORADABADI, A. et al. Effects of surface treatment on bond strength between dental resin agent and zirconia ceramic. **Mater Sci Eng C Biomim Supramol Syst**, Amsterdam, v. 34, p. 311-317. Jan 2014.

OBA, Y. et al. Effect of silane and phosphate primers on the adhesive performance of a tri-n- butylborane initiated luting agent bonded to zirconia. **Dent Mater**, Oxford, v. 33, p. 226-32. Mar 2014.

OZCAN, M, KERKDIJK, S, VALANDRO, L.F. Comparison of resin cement adhesion to Y-TZP ceramic following manufacturers' instructions of the cements only. **Clin Oral Investig**, Berlin, v.12, n.3, p.279-82. Sep 2008.

OZCAN, M, NIJHUIS, H, VALANDRO, L. Effect of various conditioning methods on the adhesion of dual cure resin cement with MDP functional monomer to zirconia after thermal aging. **Dent Mater**, Oxford, v. 27, p. 99-104. Jan 2008.

PEREIRA, L. et al. Can Application of Universal Primers Alone Be a Substitute for Airborne-Particle Abrasion to Improve Adhesion of Resin Cement to Zirconia?. **J Adhes Dent**, New Malden, v. 17, p. 169-174. Apr 2015.

PEUTZFELDT A. Indirect resin and ceramic systems. **Oper Dent**, Seattle, v.6, p.153-176, Fev 2001.

PIASCIK, J.R. et al. Surface modification for enhanced silanation of zirconia ceramics. **Dent Mater**, Oxford, v. 25, p. 16-21. Sep 2009.

PICONI, C.; MACCAURO, G. Zirconia as a ceramic biomaterial. **Int J Biomaterials**, New York, v. 20, n. 1, p. 1-25, Jan 1999.

QEBLAWI, D. M. et al. The effect of zirconia surface treatment on flexural strength and shear bond strength to a resin cement. **J Prosthet Dent**, St. Louis, v.103, n.4, p. 210-20, Apr 2010.

ROSENBLUM, M. A.; SCHULMAN, A. A review of all-ceramic restorations. **J Amer Dent Assoc**, Chicago, v.128, n.3, p.297-307, Mar. 1997.

SATO, H. et al. Mechanical properties of dental zirconia ceramics changed with sandblasting and heat treatment. **Dent Mater**, Oxford, v. 27, p. 408-414. Sep 2008.

SOUZA, R.O.A. et al. Air-particle abrasion on zirconia ceramic using different protocols: Effects on biaxial flexural strength after cyclic loading, phase transformation and surface topography. **J Mech Behav Biomed Mater**, Amsterdam, v. 26, p. 155-163. Oct 2013.

SRIAMPORN, T. et al. Dental zirconia can be etched by hydrofluoric acid. **Dent Mater**, Oxford, v.33, n.79, Jun 2014.

TZANAKAKIS E.G, TZOUTZAS I.G, KOIDIS P.T. Is There a potential for durable adhesion to zirconia restorations? A systematic review. **J Prosthet Dent**, St. Louis, v. 115, p. 9-19. Jan 2016.

URAL, Ç.et al. Determination of Resin Bond Strength to Zirconia Ceramic Surface Using Different Primers. **Acta Odont Scand**, Stockholm, v. 69, p. 48-53. Jan 2011.

WATANABE, I, NAKABAYASHI, N. Measurement methods for adhesion to dentine. **J Dent**, Bristol, v. 22, p. 67-72. Apr 1994.

YOSHIDA, Y. et al. Comparative study on adhesive performance of functional monomers. **J Dent Res**, Washington, v. 83, p.454-458. Jun 2004.

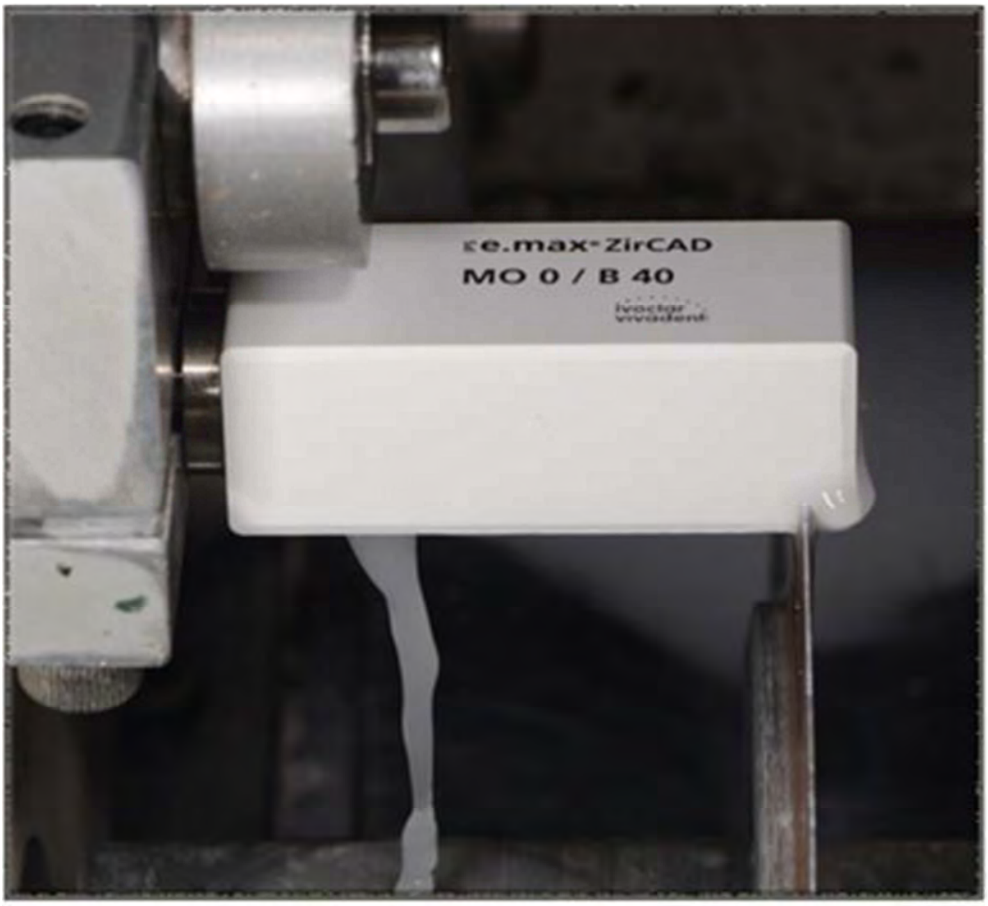
YOSHIDA, K, TSUO, Y, ATSUTA, M. Bonding of dual-cured resin cement to zirconia ceramic using phosphate acid ester monomer and zirconate coupler. **J Biomed Mater Res B**, Hoboken, Appl Biomater, v.77, n.1, p.28-33. Apr 2006.

APPENDIX

APPENDIX A

Materials and Methods Fotographs and descriptions

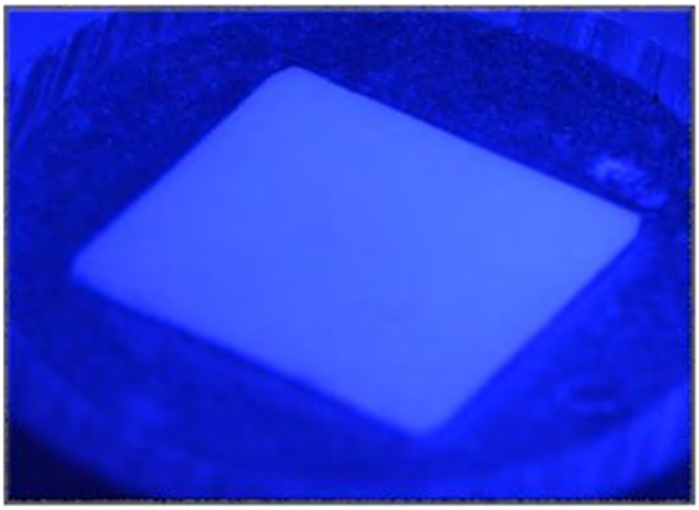
a) Experimental Adhesives



b) Y-TZP ceramic block cutted.

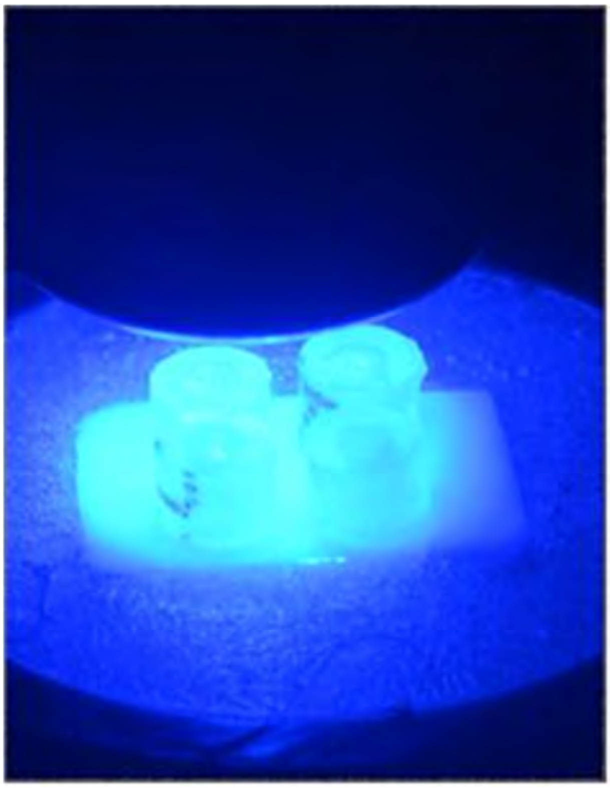
c) Y-TZP embedded in acrylic resin.

d) Experimental Adhesives were applied with a micro brush for 20 seconds.

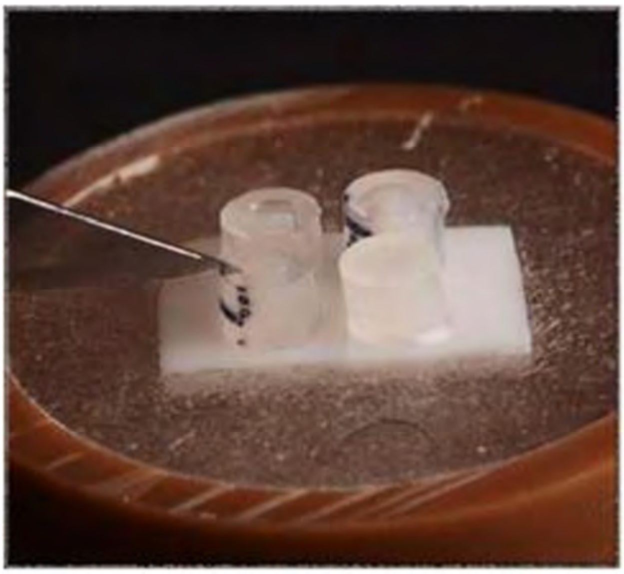


e) Experimental Adhesives were light cured for 20 seconds with a LED lamp device.

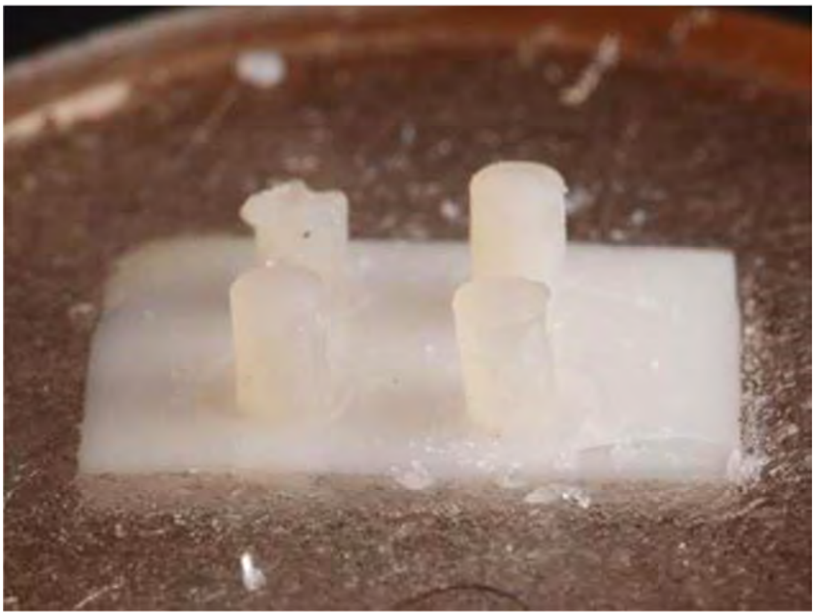
f) Surgical catheters with an internal diameter of 1.40 mm and a height of 1 mm were used for the resin cement cylinders.



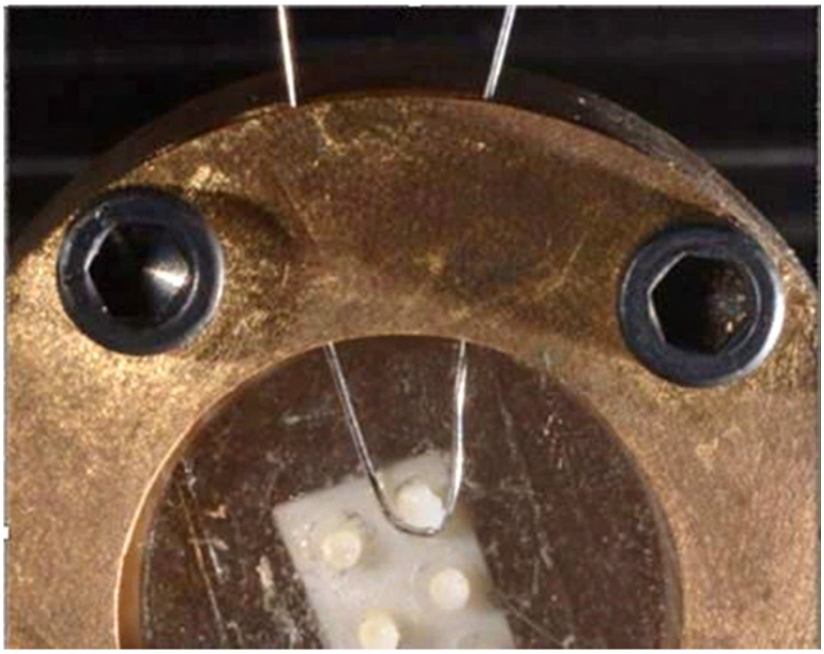
g) Four cylinders per ceramic surface were prepared



h) The surgical catheters were removed with #11 scalpel blades to expose the resin cement cylinders.



i) Resin cement cylinders



j) The samples were subjected to the shear bond strength evaluation with a universal testing machine