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DIEGO MARTINS DE PAULA

INFLUÊNCIA E CARACTERIZAÇÃO DOS EFEITOS DO 10-MDP NA ADESÂO ZIRCÔNIA E CÁLCIO

FORTALEZA
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Dissertação de Mestrado apresentada ao Programa de Pós-Graduação em Odontologia da Faculdade de Farmácia, Odontologia e Enfermagem da Universidade Federal do Ceará, como requisito parcial para a obtenção do Título de Mestre em Odontologia.

Área de Concentração: Clínica Odontológica.

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RESUMO

A substituição da infraestrutura metálica pela cerâmica odontológica traz boa estética e maior biocompatibilidade às próteses fixas. Suas excelentes propriedades mecânicas têm levado a zircônia (ZrO_2) ser o material de escolha. Técnicas convencionais de cimentação não se mostram efetivas para esse tipo de infraestrutura, devendo-se lançar mão do 10-MDP (10-metacriloiloxi-decil-di-hidrogenofosfato) como constituinte do agente de união. O presente estudo tem o objetivo de caracterizar união do 10-MDP com a zircônia e com o cálcio utilizando a espectroscopia micro-Raman. Para isso, foi utilizado a (1) espectroscopia micro-Raman para encontrar o pico vibracional das ligações do ZrO_2 com o 10-MDP e cálcio, ainda não demonstrado na literatura. (2) A resistência de união ao micro-cisalhamento do cimento resinoso dual à zircônia com a presença do 10-MDP na composição do primer cerâmico e do cimento resinoso autoadesivo. (3) Se a presença do 10-MDP no primer cerâmico altera o grau de conversão do cimento resinoso dual convencional sobre a zircônia. Nesse estudo foi descoberto os picos 1545cm^{-1} e 1562cm^{-1} referentes a ligação da zircônia com o 10-MDP e os picos 3391cm^{-1} e 3442cm^{-1} referentes a ligação do 10-MDP ao cálcio. A presença do 10-MDP tanto no primer cerâmico como no cimento resinoso autoadesivo melhoraram a resistência de união ao micro-cisalhamento do cimento resinoso. A concentração de 40% do 10-MDP não foi tamponada pelo ZrO_2 e reduziu o grau de conversão do cimento resinoso com os primers experimentais, mas não com o comercial contendo menor concentração de 10-MDP. Podemos concluir que método não destrutivo da espectroscopia micro-Raman foi capaz de caracterizar a união química do 10-MDP com a zircônia, e que tal monômero deve ser usado em baixa concentração em primers para zircônia para evitar reduzir a polimerização do cimento resinoso.

Palavras-chave: Espectroscopia Raman, Materiais Dentários, Zirconium.

ABSTRACT

The replacement of metallic infrastructure by dental ceramics brings good aesthetics and greater biocompatibility of fixed prostheses. The material of choice is zirconia (ZrO_2) because of its excellent mechanicals properties. Conventional cementing techniques are not effective for this type of infrastructure, and 10-methacryloyloxy-decyl-dihydrogenphosphate (10-MDP) should be used as a bonding agent. The present study aims to characterize 10-MDP with zirconia using micro-Raman spectroscopy. For this, (1) micro-Raman spectroscopy was used to find the vibrational peak of ZrO_2 binding with 10-MDP and calcium, not yet demonstrated in the literature. (2) The micro-shear bond strength of the dual resin zirconia cement with the presence of 10-MDP in the composition of the primer and the self-adhesive resin cement. (3) If the presence of 10-MDP without ceramic primer changes the degree of conversion of the conventional dual resin cement to a zirconia. In this study the 1545cm^{-1} and 1562cm^{-1} peaks were found to refer to zirconia binding with 10-MDP and the 3391cm^{-1} and 3442cm^{-1} peaks relative to the 10-MDP calcium binding. The presence of 10-MDP in both the ceramic primer and the self-adhesive resin cement improved a micro-shear bond strength of the resin cement. The high concentration of 10-MDP was not buffered by ZrO_2 and reduced the degree of conversion of the resin cement to the experimental primers, but not with the low concentration of 10-MDP. We can conclude that the non-destructive method of micro-Raman spectroscopy was able to characterize a chemical union of 10-MDP with a zirconia, and that such monomer should be used in low concentrations in primers for zirconia to avoid reducing the polymerization of the cement residue.

Keywords: Raman Spectroscopy, dental materials, zirconia

SUMÁRIO

Introdução Geral

1 INTRODUÇÃO GERAL

A exigência por um resultado estético tem tornado popular a utilização de restaurações protéticas *metal-free*. A substituição do metal pela cerâmica odontológica traz de benefício, além da estética, biocompatibilidade, baixa condutividade térmica, estabilidade química e inatividade sob efeitos galvânicos (DELLA BONA, 2009; HALLMANN et al, 2015). Há uma riqueza de informações na literatura científica sobre o uso da zircônia (ZrO_2) em aplicações dentárias (DENRY; KELLY, 2008; GAUTAM et al, 2016).

A zircônia pode ser utilizada como biomaterial. O óxido de zircônio, ou zircônia, é um óxido de metal que foi primeiramente identificado pelo químico alemão Martin Heinrich Klaproth em 1789. A zircônia é de natureza polimórfica, pois possui um equilíbrio diferente na sua estrutura cristalina em diferentes temperaturas sem alterações na sua química. Ela possui três formas cristalinas: 1) monoclínicas: em baixas temperaturas; 2) tetragonais: temperaturas acima de 1170 °C; e 3) cúbica: temperaturas acima de 2370 °C. Uma característica desse material é que sofre uma alteração na estrutura cristalina durante o seu resfriamento, resultando em um aumento de volume 3-5%. Alguns óxidos metálicos como óxido de césio (CeO_2), magnésio (MgO) e ítria (Y_2O_3) têm sido utilizados para estabilizar a zircônia na fase cúbica ou monoclínica à temperatura ambiente (THOMPSON et al, 2011). Isso interfere nas propriedades de tenacidade à fratura da zircônia. Por exemplo, se uma zircônia estabilizada por ítria (Y-TZP) estiver na fase monoclínica pode se transformar na fase tetragonal perto da ponta da fenda. A expansão do volume resultante causada pela transformação cria tensões compressivas na ponta da rachadura. Isso dificulta ativamente a propagação, porque mais energia é agora necessária para a fenda continuar a propagando (DELLA BONA, 2009).

A prótese fixa *metal-free* combinada de uma infraestrutura de cerâmica à base de ZrO_2 com cerâmica de revestimento com cerâmica vítrea torna possível a capacidade de mimetizar com sucesso um dente natural. A infraestrutura à base de ZrO_2 possui propriedades (resistência à fratura, resistência e dureza) comparáveis à de uma infraestrutura metálica. Assim, sendo possível a fabricação de coroas totais unitárias e pontes fixas sobre dentes e implantes (GAUTAM et al, 2016).

As técnicas convencionais de cimentação que utilizam ácido hidrofluorídrico e silano usadas para coroas protéticas à base de cristais de ZrO_2 não proporcionam resistência de união duradoura suficiente para sua aplicação (FERRACANE; STANSBURY; BURKE, 2011). Técnicas de cimentação devem ser diferenciadas para os sistemas à base zircônia, pois ácido fluorídrico é incapaz de criar rugosidade adequada e imbricamento micromecânico (HALLMANN et al, 2015). Isso pode interferir na obtenção de alta retenção, prevenção de microinfiltração e aumento da resistência à fratura/fadiga (THOMPSON et al, 2011). A combinação de pré-tratamentos mecânicos de superfície de zircônia e união química contribui para uma durabilidade da ligação de cimentos resinosos à zircônia (INOKOSHI, et al, 2014).

Algumas metodologias já comprovaram a união química do 10-MDP tanto com a zircônia, quanto com o cálcio da hidroxiapatita. A união química com zircônia foi bastante melhorada após a inclusão do 10-MDP (10-metacriloiloxi-decil-diidrogeno fosfato) no primer cerâmico e no cimento resinoso por causa de sua característica de capacidade de aderência bifuncional entre óxido metálico e a matriz resinosa adesiva (XIE et al, 2015). O condicionamento químico com 10-MDP visa criar uma superfície "reativa" na zircônia que facilita a ligação química entre os grupos fosfato do 10-MDP com os óxidos da superfície da zircônia (XIE et al, 2015). Outra vantagem da utilização do 10-MDP é sua capacidade de sua união química com o cálcio da hidroxiapatita (VAN MEEBEEK et al, 2011). A acidez dos monômeros ácidos dentro dos adesivos resinosos dificulta a sua polimerização quando o sistema de fotoiniciadores canforoquinona e amina terciária é utilizado (YOKOTA et al, 2015), o que interfere na longevidade da união.

A espectroscopia micro-Raman é um método já utilizado para comprovação de união química na odontologia. Esse método utiliza a dispersão inelástica da luz, a partir de um laser no visível ou perto do infravermelho e ultravioleta, para fornecer informações vibracionais das uniões químicas. Tem a vantagem de não ser destrutivo e pode avaliar substâncias líquidas e em poucas quantidades, além de não necessitar de um tratamento prévio como nas microscopias de transmissão (MARSHALL et al, 2010).

O entendimento e caracterização do mecanismo exato da reação química entre 10-MDP com o ZrO_2 e 10-MDP com o cálcio é extremamente benéfica para projetar produtos mais eficazes. Na literatura atual não há informações sobre a interferência da acidez do monômero funcional ácido na polimerização dos cimentos resinosos sobre a zircônia. Bem como não há informações da caracterização da união química com o cálcio e a zircônia pela espectroscopia micro-Raman.

Proposição

2 PROPOSIÇÃO

O presente trabalho tem como objetivos:

2.1 Objetivo Geral

Caracterizar união do 10-MDP com a zircônia e com o cálcio utilizando a espectroscopia micro-Raman.

2.2 Objetivos Específicos

- Encontrar o pico vibracional das ligações do 10-MDP com o ZrO_2 utilizando a espectroscopia micro-Raman;

- Encontrar o pico vibracional das ligações do 10-MDP com o cálcio utilizando a espectroscopia micro-Raman;

- Avaliar a resistência de união ao microcisalhamento do cimento resinoso dual à zircônia com a presença do 10-MDP na composição do primer cerâmico e do cimento resinoso autoadesivo;

- Avaliar se a presença do 10-MDP no primer cerâmico comercial e experimental altera o grau de conversão do cimento resinoso dual convencional sobre a zircônia.

- Avaliar se a influência do 10-MDP contido no primer cerâmico sobre o grau de conversão do cimento resinoso é influenciada pelo de tipo de iniciador.

Capítulos

3 CAPÍTULOS

Esta dissertação está baseada no Artigo 46 do Regimento Interno do Programa de Pós-Graduação em Odontologia da Universidade Federal do Ceará que regulamenta o formato alternativo para dissertações de Mestrado e teses de Doutorado, e permite a inserção de artigos científicos de autoria ou coautoria do candidato. Assim sendo, esta dissertação é composta de dois capítulos contendo artigos científicos que serão submetidos para publicação em revistas científicas, conforme descrito abaixo:

- Capítulo 1

“Lack of 10-MDP primers neutralization by zirconia may affect the degree of conversion of resin cement” de-Paula DM, Loguercio AD, Reis A, Yoshihara K, Feitosa VP. ***Journal of Applied Oral Science.***

- Capítulo 2

Micro-Raman vibrational identification of 10-MDP bond to calcium and zirconia with correlative shear bond strength analysis de-Paula DM, Loguercio AD, Reis A, Feitosa VP. ***Dental Materials***

3.1Capítulo 1

“Lack of 10-MDP primers neutralization by zirconia may affect the degree of conversion of resin cement” de-Paula DM, Loguercio AD, Reis A, Yoshihara K, Feitosa VP. ***Journal of Applied Oral Science.***

ABSTRACT

Introduction. Conventional luting techniques are not effective for zirconia all-ceramics fixed prostheses, and 10-methacryloyloxy-decyl-dihydrogenphosphate (10-MDP) is highly indicated in ceramic primers.

Objective. The aim of this investigation was to assess different concentrations of 10-MDP included in experimental and commercial ceramic primers and the effect on the degree of conversion (DC) of a conventional dual-cure resin cement.

Material and Methods. Experimental ceramic primers were formulated, 10-MDP was employed as acidic functional monomer and camphoroquinone/amine or 1-phenyl-1,2-propanedione (PPD) as photoinitiator systems. Clearfil Ceramic Primer (Kuraray) was used as commercial control primer. The pH of primers was assayed. Micro-Raman spectroscopy analysis was used to assess the DC of ratios between the heights of 1639cm^{-1} and 1609cm^{-1} peaks of uncured and light-cured resin cements applied after primers ceramics onto zirconia surfaces. Statistical analysis was performed by one-way ANOVA and Tukey's test ($p<0.05$).

Results. The high concentration of 10-MDP in experimental primers was not buffered by ZrO_2 and reduced the DC of the resin cement, what did not occur with low-concentration 10-MDP in commercial primer.

Conclusion. 10-MDP monomer should be used in low concentrations in zirconia primers to avoid reduction on polymerization of the resin cement.

Key words: methacrylate, degree of conversion, Raman spectroscopy, zirconia

1. INTRODUCTION

Seeking for aesthetic dental rehabilitations has increased the demand for metal-free prosthetic restorations. By replacing the metal framework for reinforced dental ceramics, several benefits are acquired beyond aesthetics, such as higher biocompatibility, lower thermal conductivity, higher hardness and chemical stability[7,23]. Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) ceramics may be applied as an alternative for traditional metal frameworks[9]. Nevertheless, due to its high chemical stability nature, conventional hydrofluoric acid conditioning is less effective than on glass ceramics, thereby reducing the bonding ability when used along with dual-cure resin cements[20].

Different chemical and mechanical surface pre-treatments were, thus, recommended in order to improve the bonding of resin cements to zirconia ceramics[9,17]. The usage of chemical agents for resin cement luting Y-TZP structures has shown to ameliorate fracture strength and fatigue resistance of crowns[19]. Therefore, techniques promoting less damage to Y-TZP ceramics[3] along with producing functionalized surfaces are desirable. Among these techniques, tribochemical silica coating and subsequent silanization already demonstrated efficacy in enhancing long-term durability of resin-zirconia bonds[11], although such procedure demands further laboratory steps and special equipment. More recently, there were increasing investigations and clinical application of zirconia primers and self-adhesive resin cements based on acidic functional monomers[17], which improved the shear bond strength to Y-TZP ceramics[9].

The presence of acidic monomers in self-adhesive resin cements warrants simultaneous demineralization and infiltration of dentin and enamel[13] as well as chemical interaction with dental substrates[21] and Y-TZP[4,22]. However, the presence of such monomers may interfere on the polymerization of dental adhesives based on type II photoinitiator systems like camphoroquinone with tertiary amine (CQ/amine), which might jeopardize the degree of conversion[8].

Dissolution of hydroxyapatite from enamel/dentin reduces this phenomenon due to the buffering of acidic media and binding of functional monomer with calcium[5] thereby avoiding the decrease on degree of conversion during polymerization[8]. Such buffering has been demonstrated with self-etch adhesives[8] as well as with self-adhesive resin cements[12]. Nevertheless, no reports are available concerning the role of reaction between acidic functional monomer and Y-TZP ceramic on the buffering of acidic pH from ceramic primers, which could potentially interfere on the resin cement polymerization in cases with minimal dental substrate such as luting on cast post and core reconstructions.

The aim of this investigation was to assess the influence of 10-MDP (10-methacryloyloxy-decyl-dihydrogen-phosphate) in different concentrations included in experimental and commercial ceramic primers on degree of conversion of a conventional dual-cure resin cement on Y-TZP ceramic. The null hypotheses tested are 1) the presence of acidic functional monomer does not interfere on the degree of conversion of resin cement; 2) there is no difference on the cement’s degree of conversion between the two photoinitiators included in experimental ceramic primers.

2. MATERIALS AND METHODS

2.1. - Reagents

The monomer 10-MDP (10-methacryloyloxy-decyl-dihydrogen-phosphate) was gently donated by FGM Company (Joinville, Brazil) and used without further purification. Camphoroquinone (CQ, photoinitiator) and ethyl 4-(dimethylamino)benzoate (EDAB, coinitiator) were donated by Esstech Inc. (Essington, USA) whilst type 1 photoinitiator PPD (1-phenyl-1,2-propanedione, photoinitiator) was purchased from Sigma Aldrich Chemicals (St. Louis, USA).

2.2. Experimental Primers

To formulate experimental ceramic primers, 10-MDP was employed as acidic functional monomer and included in 38wt%, diluted first in ethanol (30wt%) and distilled water (30wt%). In order to evaluate the influence functional monomer acidity on photoinitiators, the primers were made light-curable by means of the inclusion of CQ/EDAB (0.5/1.5 wt%) or PPD (2 wt%). Clearfil Ceramic Primer (Kuraray Medical, Tokyo, Japan) was used as commercial control primer. The pH of primers was assayed using a digital pHmeter (Tecnal Tec-3MP, Piracicaba, Brazil).

2.3. Specimen Preparation

A Primers were applied according to the experimental design presented in Table 1, and no application of ceramic primer was the Control group. Y-TZP ceramic (Zirconcad, Angelus, Londrina, Brazil) slabs were prepared in 14X12X2mm dimensions and polished with wet 2000-grit SiC papers for 60s to obtain standardized flat surfaces, they were then randomly assigned in one of the four groups (n=3). Primers were applied actively for 20s using a micro-brush and gently air-dried for 3s with air-spray. Thereafter, the conventional dual-cure resin cement RelyX ARC (3M ESPE, St. Paul, USA) was manipulated according to manufacturers' instructions; a thin layer (1±0.2mm thick) was applied onto each zirconia slab and then directly light-cured for 40s using a LED unit DB 685 (1100 mW/cm^2; Dabi Atlante, Ribeirao Preto, Brazil).

2.4. Degree of Conversion

Micro-Raman spectroscopy analysis was used to assess the degree of conversion of resin cement 10 minutes after light-curing. The micro-Raman spectrophotometer (Xplora, Horiba JobinYvon, Paris, France) was firstly calibrated using a silicon standard sample supplied by the manufacturer. HeNe laser with 3.2mW power and 532nm wavelength was employed with 1.5 µm spatial resolution, 2,5cm^{-1} spectral resolution associated with 10X magnification lens (Olympus, London, UK) to attain approximately 60x70 µm field area. The degree of conversion was calculated based in a previous investigation[14] by means of the formula:

$$\mathrm{DC} = \left(1 - \frac{\mathrm{Rcured}}{\mathrm{Runcured}}\right) \mathrm{x}\ 100$$

Where R is the ratio between the heights of 1639cm^{-1} and 1609cm^{-1} peaks of uncured and light-cured material. Three readings were undertaken on the top surface of each specimen[14].

2.5. Statistical Analysis

The results of degree of conversion were statistically analyzed by Shapiro-Wilk normality test ($p>0.05$) and after proving normal data ($p= 0.41$), the data were analyzed by one-way ANOVA and Tukey’s test ($p<0.05$).

3. RESULTS

The degree of conversion (DC) outcomes are depicted in Figure 1. Clearfil Ceramic Primer (89.0% mean DC) and Control (89.0% mean DC) treatments induced statistically similar conversion (p=0.95). The zirconia treatments using PRIM-CQ (70.1% mean DC) and PRIM-PPD (44.7% mean DC) presented significantly lower conversion than Clearfil and Control. However, PRIM-CQ achieved higher conversion than PRIMER-PPD (p=0.038). The pH of all experimental primers (PRIM-PPD and PRIM-CQ) was 1.5 and that from Clearfil Ceramic primer was 4.0.

4. DISCUSSION

The efficiency and durability of adhesion between resin cement and zirconia ceramics depends upon several factors such as wettability, micro-retentions and chemical interaction of functional monomers. Indeed, the interaction of acidic monomer with Y-TZP surface is a great challenge nowadays[4]. Besides, an optimal polymerization of resin cement is crucial to obtain high mechanical strength and stability of ceramic-cement-dentin interface. In the present investigation, the degree of conversion of a commercial dual-cure resin cement applied onto Y-TZP surface was investigated after usage of three different ceramic primers containing 10-MDP functional monomer and different photoinitiators. Both null hypotheses tested need to be rejected, as the presence of acidic monomer and both photoinitiators altered the degree of conversion.

The conditioning of feldspatic, leucite-reinforced and lithium dissilicate ceramics by hydrofluoric acid (HFA) and subsequent silanization is a well-established method for luting glass ceramic prosthesis with resin cements[9]. Silane increases surface energy of these ceramics, thereby providing chemical bonding between siloxane functionality of the molecule and silica-rich inorganic phases[19].

As Y-TZP is a monolithic ceramic without the presence of glass or silica in composition, conventional conditioning with HFA does not increase surface roughness as well as silane does not ameliorate the bond strength[3]. In this regard, several methods have been proposed to improve the bond strength of resin cements to zirconia ceramics[17]. Some strategies enhance the micro-mechanical interlocking by increasing the surface roughness such as alumina air-abrasion[17]. Other investigations are based on physicochemical activation of zirconia surface by means of silica-coated alumina with sequential silanization[9]. A recent review from Ozcan and Bernasconi[17] concluded that among all these strategies, the optimal durability of resin cement-zirconia bonds is attained by using 10-MDP containing primers and cements, even after thermocycling.

Degree of conversion of adhesives and further dental materials containing camphoroquinone/amine photoinitiator system may be affected by the presence of acidic functional monomers[15]. Excited camphoroquinone after light exposure turns into a singlet state that reacts with hydrogen donators, such as tertiary amines, thereby transferring electrons and protons, generating free radicals and starting polymerization[18]. However, tertiary amines in dental resins may also react as Lewis bases being neutralized by acidic functional monomers and impairing polymerization[15]. Hanabusa et al[8] demonstrated this reaction with 10-MDP and 4-META functional monomers, and depicted the negative effects on methacrylate-based polymerization initiated by CQ/amine photoinitiator system. Nevertheless, in presence of hydroxyapatite (from enamel/dentin), its dissolution before light-curing buffers acidic monomers and reduces the inhibitory influence on polymerization[8].

Oguri et al.[15] also tested the polymerization of CQ/amine- and borate- (type I photoinitiator) resins in presence of MAC-10 (11-methacryloxy-1,1-undecane dicarboxylic acid) acidic functional monomer. The degree of conversion in CQ/amine system was significantly dropped whilst borate was not affected by acidic monomer. In the present investigation, higher concentrations of acidic functional monomer in experimental primer containing CQ/amine induced lower degree of conversion of resin cement, but lower concentration in commercial primer had no influence. Indeed, zirconia primers using acidic monomers may be applied, even without buffering effect from ceramic substrate, but in low (<10%) concentrations.

Further factor decreasing significantly the degree of conversion of dual-cure resin cements when used to lute zirconia ceramics is the high opacity of zirconia. This reduces the light transmission and proper irradiance that reachs the cement, thereby diminishing the polymerization, mechanical properties and durability of resin cement[10]. In this study, light-curing was performed directly over resin cement without zirconia between cement and light-unit tip, disregarding the interference of ceramic opacity. Therefore, the polymerization tested was predominantly light-initiated. Indeed, chemical cure of dual-cure resin cements could compensate the negative effect of acidic functional monomers from zirconia primers.

Camphoroquinone is the photoinitiator more used in dental materials. Although its long clinical success, there are still some concerns regarding the yellowing in anterior restorations and prosthesis. Phenyl-propanedione (PPD) is suggested as alternative photoinitiator to reduce the yellow colour in presence of CQ[2]. PPD is classified as type I photoinitiator due to its photolysis and C-C cleavage between carbonyl groups of PPD molecule, providing free radical formation and photo-initiation[1]. However, unlike CQ, absorption peak of PPD is near UV region (approximately 410nm wavelength) slightly extending to blue spectrum[16]. Indeed, a feasible explanation for the lower degree of conversion (mean 44.7%) in PRIM-PPD group is that the second generation LED curing unit possesses only blue-light emission with wavelengths very close to 468nm (excitation of CQ). Therefore, such curing unit was not able to excite and properly initiate the polymerization in presence of PPD.

Reduction of polymerization conversion was concentration dependent in 10-MDP containing primers (Fig. 1). Regarding Clearfil Ceramic Primer, the low concentration of 10-MDP, induces higher pH, and may leave free-amine to react with CQ during light-curing. Conversely, with experimental primers, the high concentrations of 10-MDP (40wt%) decreased the pH to 1.5 and possibly most functional monomers chemically bonded to zirconia, but a significant amount was free to react with amine, thereby reducing resin cement's degree of conversion. In a clinical view, the viability of using self-etch or universal adhesives with higher concentrations of 10-MDP than ceramic primers should be reconsidered and checked in terms of potential negative effects for dual-cure resin cement polymerization. Further alternative could be the use of other acidic monomers in ceramic primers and universal adhesives. Chen et al.[3] studied PENTA (dipentaerythritol penta-acrylate phosphate) to replace 10-MDP in ceramic primers. They concluded that bond strength of resin cement to Y-TZP may be improved by using this alternative monomer and the increase in monomer concentration only augments bond affinity, but not necessarily the efficacy. Therefore, PENTA might be applied in very low concentration, reducing potential inhibitory effects on resin cement's polymerization.

5. CONCLUSION

According to the findings and within the limitations of the presente investigation, zirconia ceramic does not possess the buffering capacity for very acidic ceramic primers generated by functional monomer in high concentration. Future studies should be undertaken to verify the ideal concentration and functional monomer to be used in ceramic primers.

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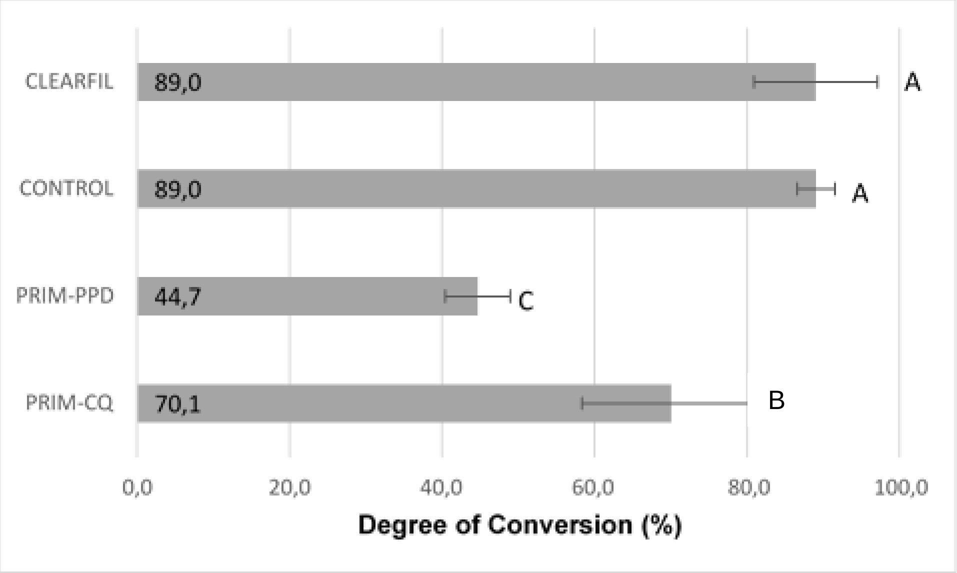
APPENDICES

Table and figure

Table 1

Groups	Composition
(PRIMER-CQ)	38% 10-MDP, 0,5% CQ, 1.5% EDAB
(PRIMER-PPD)	38% 10-MDP, 2% PPD
Clearfil Ceramic Primer (CLEARFIL)	1-5% 10-MDP, 3-TMSPMA, ethanol
CONTROL	No primer

Figure 1



Captions to tables and figures

Table 1 – Spreading of groups and main compositions of primers.

Figure 1 – Results of degree of conversion (%) of resin cement (RelyX ARC) light-cured onto Y-TZP ceramic treated with different primers. CQ: canforoquinone; EDAB: ethyl 4-(dimethylamino)benzoate; PPD: 1-Phenyl 1,2-propanedione; 3-TMSPMA: 3-(trimethoxysilyl)propyl methacrylate). Different letters indicate statistical difference between groups.

3.2 Capítulo 2

Micro-Raman vibrational identification of 10-MDP bond to calcium and zirconia with correlative shear bond strength analysis de-Paula DM, Loguercio AD, Reis A, Feitosa VP. ***Dental Materials***

ABSTRACT

Objectives: To identify the Raman peaks related to the bonds of 10-MDP with zirconia, and 10-MDP with calcium.

Methods: Micro-Raman spectroscopy was used to assess the vibrational peak of 10-MDP binding with zirconia or calcium. Micro-shear bond strength of the dual resin cement to zirconia with the presence of 10-MDP in the composition of the experimental primer and self-adhesive resin cement was also surveyed. Statistical analysis was performed by one-way ANOVA and Tukey's test ($p<0.05$).

Results: Peaks at 1545cm^{-1} and 1562cm^{-1} were found referring to zirconia binding with 10-MDP whereas 3391cm^{-1} peak was observed relative to the 10-MDP bond to calcium. The presence of 10-MDP in both ceramic primer and self-adhesive resin cement improved a micro-shear bond strength to zirconia ceramic.

Conclusion: It can be concluded that the non-destructive method of micro-Raman spectroscopy was able to characterize chemical bonds of 10-MDP with a zirconia and calcium, which improves the bond strengths of resin cement.

Key word: 10-MDP compound; dental bonding, resin cement, zirconia

1. INTRODUCTION

Highly crystalline ceramics based on zirconium oxide have been applied for over a decade in Restorative Dentistry, providing successful rehabilitations. Its principal characteristics are the great mechanical properties such as high flexural strength (900-1200 MPa), fracture toughness (9-10 MPa.m$^{1/2}$), compression strength (~2000 MPa) and Young's modulus (100-210 GPa) as well as adequate aesthetics and biocompatibility. Overall, these features make zirconia the ideal material for core and frameworks of prosthesis in anterior and posterior region [1,2,3].

The large content of polycrystals (up to 99.9%) affords chemical stability of zirconia, thereby reducing the reactivity with acids (even hydrofluoric acid). Indeed, one of the major shortcomings of zirconia's usage is the difficulty to bond it with resin-based cements and the luting on dental substrate [4]. In a recent systematic review, Inokoshi et al. [5] concluded that most effective and durable protocol for adhesion to zirconia ceramics involves the pre-treatment with silica air-abrasion followed by application of primers containing silane/10-MDP (10-methacryloyloxydecyldihydrogenphosphate) before luting using dual-cure hydrophobic resin cements.

Acidic functional monomer 10-MDP is currently considered as gold-standard in terms of chemical bonding and clinical longevity [6,7] thanks to the unique chemical structure with long and hydrophobic spacer carbon chain [8,9]. The rationale for employing a 10-MDP primer on zirconia surface is to create a "reactive" surface, favouring the binding of 10-MDP phosphate functionalities with zirconium oxide [10]. Furthermore, 10-MDP possesses a well-established [11,12] chemical interaction with calcium and hydroxyapatite. This was demonstrated by several methods in literature [11] and has positive correlation with dentin bond strength and durability [8,13]. However, to date there are no reports in literature regarding the identification of Micro-Raman vibrational peak of the chemical bond between 10-MDP with calcium or zirconia as well as the likely improvements afforded by such bonding on the bond strengths of resin cements to zirconia substrate.

Therefore, the objective of this study was to assess the Raman peak related to the bond of 10-MDP with zircônia, and between 10-MDP and calcium from hydroxyapatite. Further aim was to survey the bond strengths to zirconia when 10-MDP is used in a ceramic primer or in self-adhesive resin cement. Study hypothesis is that the presence of 10-MDP does ameliorate the bond strength of resin cements to zirconia.

2. MATERIALS AND METHODS

2.1 Formulation of Materials

The monomers 2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane (Bis-GMA) and triethylene glycoldimethacrylate (TEGDMA) were donated by Esstech Inc. (Essington, PA, USA) and used as received. Acidic monomer 10-MDP (10-methacryloyloxy-decyl-dihydrogen-phosphate) was donated by FGM (Joinville, SC, Brasil). Photoinitiator system was composed by camphorquinone (CQ, Esstech), chemical initiator benzoyl peroxide (Sigma Aldrich, St. Louis, USA) and coinitiator ethyl 4-(dimethylamino)benzoate (EDAB, Sigma Aldrich). Silanated barium borosilicate glass particles (0.4 µm average size, Esstech) were used as filler particles.

To formulate the experimental primer, 20wt% 10-MDP was mixed with 40wt% distilled water and 40wt% absolute ethanol. Experimental resin cement was prepared in two pastes in order to avoid chemically initiated polymerization and pre-ionization of acidic monomers. The composition of each paste was:

Paste A: BisGMA (20wt%), TEGDMA (20wt%), fillers (50wt%), 10-MDP (10wt%), CQ (1wt%), benzoyl peroxide (1wt%).

Paste B: BisGMA (20wt%), TEGDMA (20wt%), fillers (50wt%), 10-MDP (10wt%), 2% EDAB (2wt%).

Commercial materials used in the present study are listed in Table 1.

2.2 Specimen preparation

Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) ceramic blocks (Zirconcad, Angelus, Londrina, Brazil) with 13.2 x 13.2 x 3.2 mm dimensions were obtained and sintered according to manufacturers' instructions. They were embedded and fixed in PVC pipes by means of acrylic resin (Jet, Artigos Odontologicos Classico Ltda., Campo Limpo Paulista, Brazil). The exposed flat zirconia surfaces were polished for 30s with 600-, 800- and 1200-grit SiC papers under water irrigation and then ultrasonicated for 10 minutes.

Micro-shear bond strength (µ-SBS) specimens were bonded to the zirconia surfaces using cylindrical translucent moulds (Tygon tubing, TYG-030; Saint-Gobain Performance Plastic, Clearwater, FL) as previously reported [14]. Six cylinders (0.75mm diameter X 3mm height) were randomly bonded for each group (n=6) using the conventional dual-cure resin cement RelyX ARC (3M-ESPE, St. Paul, USA). Previously to cement application, 10-MDP containing ceramic primers were applied onto Y-TZP surfaces. Either experimental primer (EP) or the commercial primer (CP) Clearfil Ceramic Primer (Kuraray Medical Inc., Tokyo, Japan) were actively applied for 20s followed by a gentle air-blast. In negative control group, no primer was used before resin cement bonding.

Further Y-TZP blocks (n=6) were prepared as previously described and bonded with the experimental self-adhesive resin cement (EC) or with the commercial cement (CC) RelyX U200 (3M-ESPE). The control resin cement (CRC) group for this part was undertaken by using the experimental resin cement without the addition of 10-MDP or other acidic functional monomer. Resin cements were mixed according to the manufacturer's instructions using same volume of each paste and mixing for 30s until obtaining homogeneous mixture. The experimental cements also followed this protocol, and then cements were carefully inserted in the Tygon tubes to avoid blisters. Light-curing was performed with LED light-curing unit DB-685 (1100 mW/cm^2; Dabi Atlante, Ribeirao Preto, Brazil) for 40s and the specimens were protected from light during 30 minutes for final cut of Tygon tubes with scalpel blades. Cylinders were analyzed and those with defects were discarded and replaced. Before bond strength survey, all specimens were stored immersed in distilled water at 37ºC for 48h in darkness to warrant high polymerization of the cements.

Bonded specimens were mounted in a device for µ-SBS test (Odeme Dental Research, Joaçaba, Brazil) adapted in a universal testing machine (EMIC DL 2000, Sao Jose dos Pinhais, Brazil). An orthodontic wire (0.4 mm diameter) was positioned surrounding and in contact with half of the cylinder and connected to the load cell (500N) of the machine to exert shear force in upward direction. Each cylinder was tested individually with 1mm/min crosshead speed up to fracture. Maximum µ-SBS was recorded in N and transformed to MPa with the analysis of each cylinder diameter to obtain the bonded area (mm^2).

After debonding, all zirconia surfaces were examined with a stereomicroscope (SMZ800, Nikon, Tokyo, Japan) to determine the mode of failure, that were classified in three types: A – adhesive fracture between ceramic and cement without signs of residual cement of zirconia surface; C – cohesive failure of the cement with full area presenting cement remnants; and M – mixed fracture with areas depicting adhesive debonding and some residual cement indicating partical cohesive failure. µ-SBS outcomes were statistically analyzed with one-way ANOVA and Tukey's test ($p<0.05$).

2.3 Synthesis of 10-MDP-calcium salts

The salts of 10-MDP-Ca were synthesized using 5mL ethanol solution containing 3mmol of 10-MDP dissolved. Further 5mL of water:ethanol (1:1) solution containing 6mmol of $CaCl_2$ was mixed drop by drop with 10-MDP solution to allow the ionic interaction of functional monomer and calcium. After 12h stirring, the final solution was centrifuged and supernatant was discarded. Thereafter, the powder was washed twice with absolute ethanol to remove all unreacted 10-MDP and $CaCl_2$. The MDP-Ca salt was dried at 20ºC for Micro-Raman spectroscopic analysis by a protocol similar to that of Yokota and Nishiyama [15].

2.4 Micro-Raman spectroscopy

To obtain the vibrational analysis of the bonds between 10-MDP and zirconia, and between 10-MDP and calcium, the Micro-Raman spectrophotometer (Xplora, Horiba JobinYvon, Paris, France) was calibrated internally in zero using the silicon standard sample provided by the manufacturer. The configurations of the equipment were HeNe laser with 3.2mW power, 633nm laser wavelength, 10s acquisition time, 3 accumulations, 1.5µm spatial resolution, 2.5cm^{-1} spectral resolution, 10X magnification lens (Olympus, London, UK) and 60x70 µm field area.

For observation of Raman peak referring to the bond of calcium with phosphate functionality of 10-MDP, readings were undertaken on pure 10-MDP and later on synthesized 10-MDP-Ca salt powder. Initially, the spectral range was between 100 and 4000cm^{-1}, and after first observation, the range was narrowed to 3400-3500cm^{-1} which was the variation presenting difference between spectra.

To obtain the peak referred to the bond between 10-MDP and zirconia three blocks were used. From each block, three initial readings (Y-TZP) were performed. Afterwards, the 10-MDP primers were applied as aforementioned for 20s. After 10 minutes, the primed blocks were thoroughly rinsed with distilled water and dried with air-blast to remove unbound monomer, and then further three readings per group (n=3) were conducted in experimental primer treated samples (Y-TZP + EXP.PRIM) and those treated with commercial primer (Y-TZP + COM.PRIM). Initially, the spectral range was set from 100 to 4000cm^{-1}. Following first observation, the range was narrowed to 1500-2000cm^{-1}, region that depicted differences between spectra. The chemical shift and intensity of each peak were processed for baseline correction and determined for a series of sorts of 10-MDP-Ca salts.

3. RESULTS

The presence of 10-MDP in ceramic primer applied previously to the dual-cure resin cement increased the µ-SBS to Y-TZP both for experimental primer (mean 12.9 MPa) and commercial one (mean 13.9 MPa), groups that did not depict statistical difference between these groups. Negative control group showed very low bond strength (Figure 1). When 10-MDP was tested as a component of self-adhesive resin cement, experimental cement achieved mean 4.07 MPa µ-SBS whilst commercial cement attained mean 3.08 MPa and control (MDP-free) resin cement obtained mean 2.00 MPa bond strengths. All three groups demonstrated significant difference between each other (EC>CC>CRC, $p<0.05$) as presented in Figure 2. The failure pattern analysis showed predominantly mixed failure pattern for experimental and commercial primers whilst adhesive fractures were most frequent in negative control. All specimens of self-adhesive resin cements depicted adhesive failures.

Micro-Raman spectra are presented in Fig. 3. Peaks 1636 cm^{-1} and 1803 cm^{-1} are referring to Zr-O bonds of Y-TZP. In figures 3D, 3E and 3F, it was possible to verify only peaks at 1630 cm^{-1} and 1710 cm^{-1} from C=C e C=O vibrations of 10-MDP respectively. Figures 3B and 3C were obtained from Y-TZP after ceramic primers application and showed less evidence (lower height) of 1636 cm^{-1} and 1803 cm^{-1} peaks (Zr-O) and presence of 1630 cm^{-1} and 1710 cm^{-1} peaks from 10-MDP. However, a wide peak was observed between 1545 cm^{-1} and 1562 cm^{-1}, which was not detected in pure 10-MDP and Y-TZP alone. Therefore, it is suggested that the wide peak is referring of coordinate bond between 10-MDP phosphate functionality and zirconia ceramic.

Image 4 shows micro-Raman 2600 cm^{-1} to 3600 cm^{-1} spectral range of 10-MDP and synthesized MDP-Ca salt. Peak at 3391 cm^{-1} was detected only in MDP-Ca salt spectrum, thereby suggesting the new ionic bond formed between calcium and phosphate group of the acidic functional monomer.

4. DISCUSSION

In the present investigation, 10-MDP was employed as chemical method to improve the bonding of resin cement to Y-TZP, what actually occurred either when included in ceramic primers and in self-adhesive resin cement, increasing statistically the bond strength to zirconia ceramic. Therefore, the study hypothesis needs to be accepted.

Currently, zirconia frameworks for dental prosthesis are well-established [16,17] due to its optimal mechanical and biological properties [18,19]. With atmospheric pressure, pure zirconia presents three crystallographic conformations, depending upon the temperature. Below 1170ºC, crystal structure is monoclinic (m), between 1170ºC and 2370ºC tetragonal (t) conformation is presented, and above 2370ºC up to melting point the structure is cubic. For dental purposes, zirconia structure may be stabilized in tetragonal conformation in ambient temperature by yttrium oxide (Y_2O_3), the so-called Y-TZP. This augments fracture toughness, once there is phase transformation (t → m) when a crack or micro-crack appears. Such transformation is followed by volume increase (3-5%) sufficient to reduce crack propagation [2,20,21].

In metal-free indirect restorations, feldspathic ceramic is applied in high temperatures as covering to zirconia frameworks [22]. Residual thermal stresses might be formed in zirconia-porcelain interface during cooling, which increases the likelihood of crack formation/propagation under chewing [23]. Zhang and Kim [24] developed a graded zirconia (glass/zirconia/glass) by infiltration of silica-rich ceramic. Indeed, such structure improves the aesthetics (external glass) as well as luting (silanization of internal glass ceramic) [25,26,27].

However, conventional zirconia, required a different process of luting, once traditional hydrofluoric acid-etching and silanization are only successful for silica-containing ceramics. Surface grinding is an alternative to enhance the roughness and micro-mechanical interlocking of resin cement [28]. This procedure may be achieved with abrasive papers (SiC ou Al_2O_3), alumina air-abrasion and diamond burs in high-speed handpieces [29]. Thermal treatment (1200°C/2h) is also a choice after adjustment in absence of monoclinic phase [2]. Tribochemical silica coating of internal zirconia and alumina ceramic crowns is a common procedure favouring increase of roughness along with deposition of silica to subsequent silanization [10]. 10-MDP incorporation in ceramic primers or self-adhesive resin cements improves effectively bonding to zirconia [28,30] by the chemical bonding (ionic and hydrogen bonds) of phosphate functionalities of 10-MDP and zirconium dioxide [10]. The acidic functional monomer is a feasible, simple and cost-effective strategy for zirconia bonds that may be applied alone or associated with silane (for instance in Clearfil Ceramic Primer) to be used for all types of dental ceramics [5,29,31].

Functional monomer 10-MDP is nowadays one of the most efficient in terms of chemical interaction to calcium [6] providing clinical longevity [7]. Several companies have started to add 10-MDP to their products after its patent was expired [30]. Its long and hydrophobic carbon chain promotes stability for MDP-Ca salts formed with low solubility [11]. This is particularly correlated also for metallic oxides such as zirconia [10]. Methacrylate group accomplishes the co-polymerization with further monomers in adhesives and resin cements whereas its hydrophobic feature warrant low hydrolytic degradation as previous demonstrated [6,8,13].

The “reactive” surface of Y-TZP generated by 10-MDP occurs due to the bifunctional characteristic of the monomer that bond zirconia and resin matrix. In the present investigation, this was depicted by the increase of μ-SBS when in presence of 10-MDP either in ceramic primer or in self-adhesive resin cement. It also was showed that the presence of 10-MDP in the primer is the most important, because its bond strength was much higher than in the self-adhesive resin cement. (Figs. 1 and 2). Herein, no method to increase the surface roughness of zirconia was employed, what is not usual in literature [5], that suggests the combination of chemical agents (10-MDP containing primers) with alumina air-abrasion as gold standard strategy [28]. The evidence of such chemical bond is highly relevant towards the design of new (and better) acidic functional monomers. Some analytical methods proved this bonding mechanism (10-MDP/zirconia), such as photo-electric X-ray spectroscopy (XPS) [32], Fourier-transform infrared spectroscopy (FTIR) [33] and mass spectroscopy [34], but no reports were found regarding Micro-Raman spectroscopy, although it is an established method for chemical characterization in Dentistry [35].

Micro-Raman has some advantages like non-destructive sample preparation, analysis of liquids, powders and no need for previous preparations. It utilizes the inelastic dispersion of light from a visible laser near to infrared or ultra-violet range in order to yield vibrational information of chemical bonds [35]. In this study, Rama peaks of Y-TZP (1636cm^{-1} and 1803cm^{-1}) decreased and a wide shoulder appeared with peaks at 1545cm^{-1} and 1562cm^{-1}. These peaks were not found in commercial primer, neat 10-MDP and experimental primer. It is suggested that these new peaks are related to –P–O–Zr bonds, likely representing simple and double coordinate bonds showed by Xie et al [10].

The chemical bond of 10-MDP to calcium and hydroxyapatite has been investigated for more than a decade [11]. The improvements of bond strength by using 10-MDP in dentin adhesive is well-established in literature [11] explaining the absence of bond strength data in the present study. Several methods demonstrated such (MDP-Ca) chemical bonding [11,15], but, again, no reports about Micro-Raman identification is sparse. Herein, after preparing 10-MDP-Ca salts, peak at 3391cm^{-1} arose in the Raman spectra of salt, but was not found in pure

10-MDP (Fig. 4). Indeed, such peaks might represent the simple and double bonds between 10-MDP and calcium. Therefore, this could be used to track 10-MDP-Ca bonds in resin-dentin interfaces in Raman mapping and line analyses. Future works should focus on the in situ identification of these bonds.

5. CONCLUSION

Within the limitations of this investigation, Micro-Raman identification of bonds formed between 10-MDP and Y-TZP attained the formation of peaks 1545cm^{-1} and 1562cm^{-1} whilst with calcium peak 3391cm^{-1} appeared. The presence of 10-MDP in the primer and the self-adhesive resin cement increased the μ-SBS to Y-TZP ceramic.

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TABLES AND FIGURES

Table 1 – Characteristics of materials used in the present study.

Materials	**Composition**	**Fabricant**
Zirconcad	99.0% $ZrO_2 + Y_2O_3$ 0.5%Y_2O_3	Angelus, Londrina, Brazil
RelyX ARC	Paste A: BisGMA, TEGDMA, silane treated silica, functionalized dimethacrylate polymer, 2-benzotriazolyl-4-methylphenol, 4-(Dimethylamino)-Benzeneethanol. Paste B: Silane treated ceramic, TEGDMA, BisGMA, silane treated silica, functionalized dimethacrylate polymer, 2-benzotriazolyl-4-methylphenol, benzoyl peroxide (72/wt).	3M ESPE, St. Paul, MN, USA
RelyX U200	Base: Methacrylate monomers containing phosphoric acid groups, methacrylate monomers, initiators, stabilizers, rheological additives. Catalyst: Methacrylate monomers, alkaline fillers, silanated fillers, initiador components, stabilizers, pigments, rheological additives. Zirconia/silica fillers	3M ESPE, St. Paul, MN, USA
Clearfil Ceramic Primer	10-Methacryloyloxydecyl dihydrogen phosphate, 3-(Trimethoxysilyl)propyl methacrylate, ethanol	Kuraray Medical Inc, Tokyo, Japan

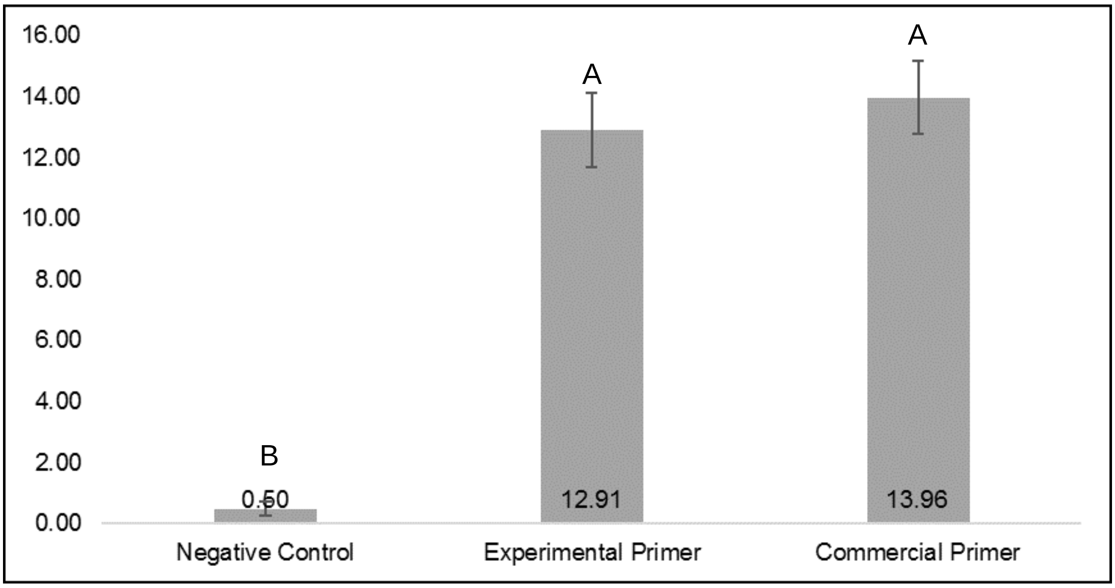

Figure 1 – Outcomes of µ-SBS test of ceramic primers used on Y-TZP ceramics. Different capital letters indicate statistical difference (p<0.05).

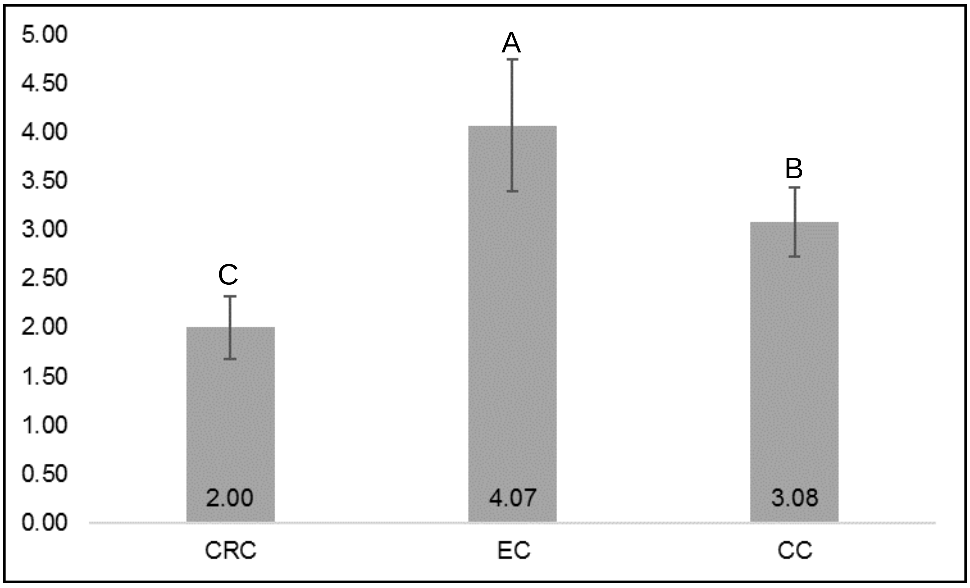

Figure 2 – Results of µ-SBS test of self-adhesive resin cements bonded to Y-TZP ceramics. EC represents the experimental self-adhesive resin cement, CC the commercial cement RelyX U200 (3M-ESPE), CC the control resin cement. Different capital letters indicate significant difference (p<0.05).

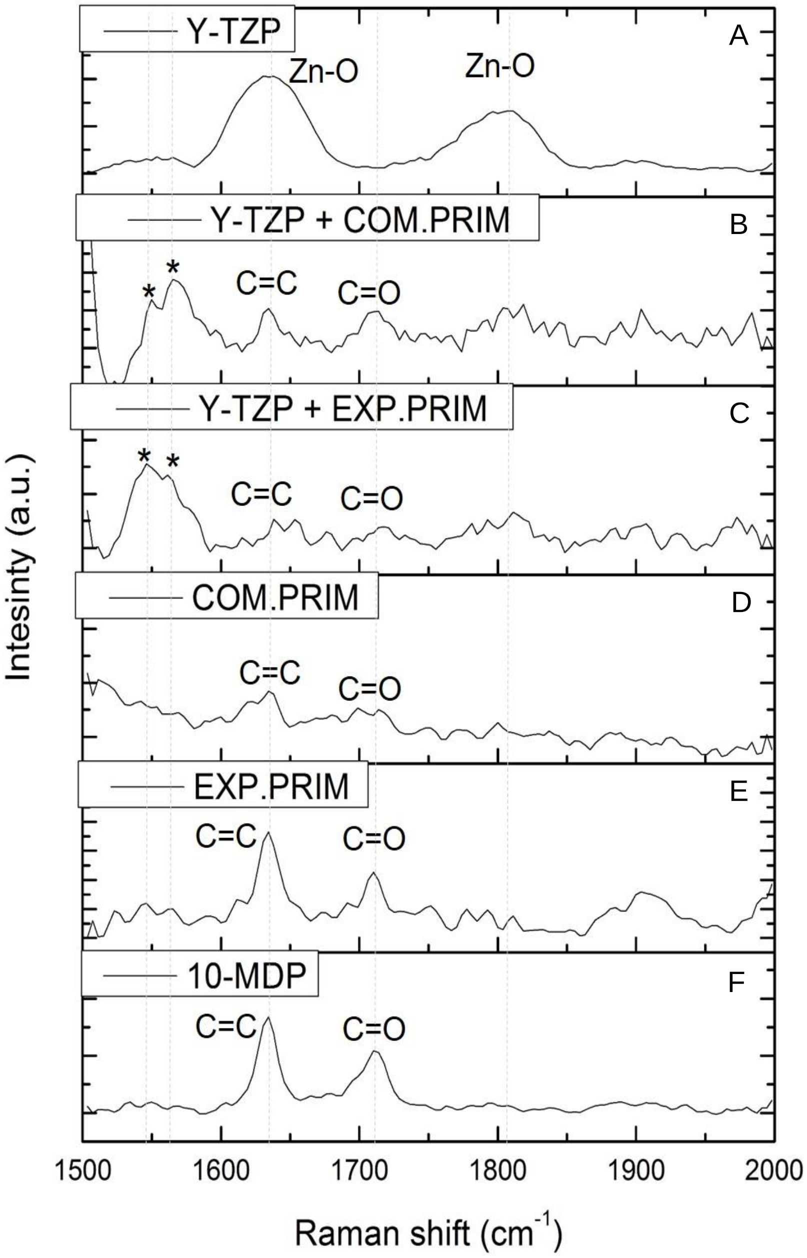

Figure 3 – Micro-Raman spectra of Y-TZP ceramic (A), primers-treated ceramics (B and C), comercial primer (D), experimental primer (E) and neat 10-MDP (F). Peaks at 1636cm^{-1} and 1803cm^{-1} are referred to Zr-O bonds, peak at 1630cm^{-1} is relative to C=C bonds and 1710cm^{-1} to C=O bonds of 10-MDP. Asterisks (*) are indicating 1545cm^{-1} and 1562cm^{-1} peaks which only appeared after application of 10-MDP containing primers on Y-TZP ceramics.

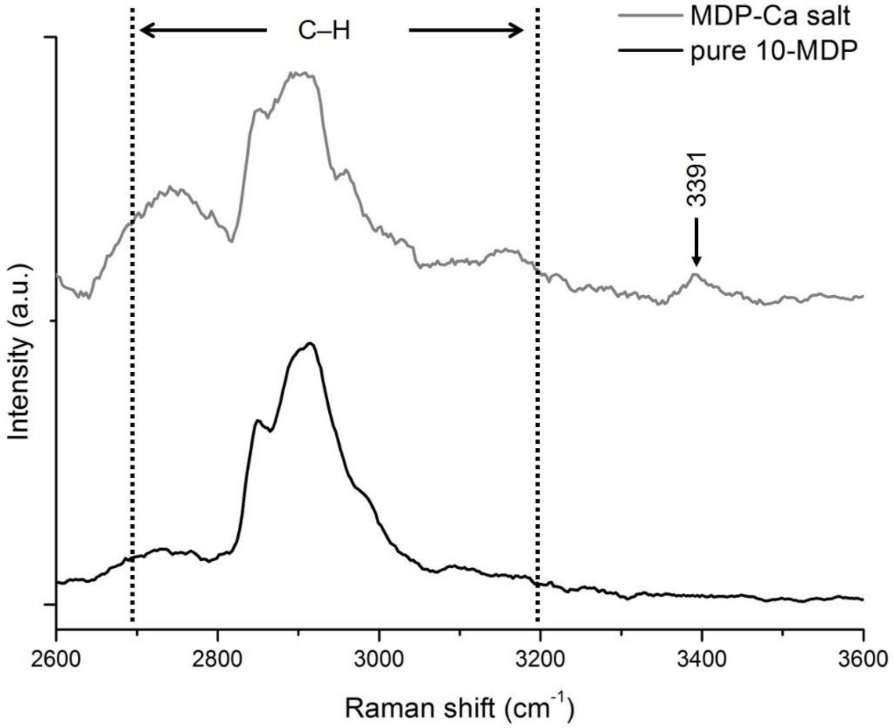

Figure 4 – Raman spectra of pure 10-MDP and MDP-Ca salt. The peaks among dotted lines (3000±200 cm^{-1}) are ascribed to C-H bonds of functional monomer. Arrow indicate bond that appeared only in MDP-Ca salt, likely indicating the ionic bond between phosphate functionality and calcium.

Conclusão Geral

4 CONCLUSÃO GERAL

A espectroscopia micro-Raman foi capaz de identificar a ligação formada do 10-MDP com a Y-TZP (1545cm^{-1} e 1562cm^{-1}) e com o cálcio (3391cm^{-1}). A resistência de união ao microcisalhamento foi superior com a presença do 10-MDP no primer cerâmico e no cimento resinoso autoadesivo. A acidez do 10-MDP em altas concentrações reduziu o grau de conversão do cimento resinoso dual convencional sobre a zircônia.

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