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PROGRAMA DE PÓS-GRADUAÇÃO
MESTRADO EM ODONTOLOGIA
ÁREA DE CONCENTRAÇÃO CLÍNICA ODONTOLÓGICA –
MATERIAIS DENTÁRIOS

Influência da incorporação de um sal de ônio nas propriedades de cimentos
resinosos autoadesivos

Carolina Rocha Augusto

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Dissertação apresentada como requisito obrigatório para obtenção de título de **Mestre em Odontologia** na área de concentração em Clínica Odontológica.

Prof. Dr. Fabrício Mezzomo Collares

Orientador

Porto Alegre, 2013

"Sabemos como é a vida: num dia dá tudo certo e no outro as coisas já não são tão perfeitas assim. Altos e baixos fazem parte da construção do nosso caráter. Afinal, cada momento, cada situação, que enfrentamos em nossas trajetórias é um desafio, uma oportunidade única de aprender, de se tornar uma pessoa melhor. Só depende de nós, das nossas escolhas...

Não sei se estou perto ou longe demais, se peguei o rumo certo ou errado. Sei apenas que sigo em frente, vivendo dias iguais de forma diferente. Já não caminho mais sozinho, levo comigo cada recordação, cada vivência, cada lição. E, mesmo que tudo não ande da forma que eu gostaria, saber que já não sou a mesma de ontem me faz perceber que valeu a pena. Procure ser uma pessoa de valor, em vez de procurar ser uma pessoa de sucesso. O sucesso é só consequência."

Autor desconhecido

DEDICATÓRIA

Dedico a realização desse sonho aos meus **pais Ademar e Cristina**, exemplos de determinação e força. Agradeço pelo amor e carinho em todos os momentos, estando perto ou longe, além do incentivo e apoio na conclusão de mais essa jornada da minha vida. Vocês me ensinaram os primeiros passos e sempre encorajam os próximos.

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RESUMO

O objetivo deste estudo foi avaliar propriedades de cimentos resinosos autoadesivos de ativação dual com incorporação de hexafluorofosfato de difeniliodônio (DPIHFP). Para isso, DPIHFP foi adicionado aos cimentos resinosos RelyX U100 e BisCem nas concentrações: $G_{0,5\%}$: 0,5% mol de DPIHFP; $G_{1\%}$: 1% mol; e $G_{2\%}$: 2% mol, além do grupo-controle sem adição do fotoiniciador. Após a incorporação do sal, os cimentos foram submetidos aos seguintes ensaios: resistência de união push-out; resistência à flexão (ISO 4049/2009); grau de conversão (FTIR); profundidade de polimerização; coeficiente de inchamento; e degradação em solvente. Todas as concentrações de DPIHFP adicionadas resultaram em um maior grau de conversão do RelyX U100 após 24h e 1 semana ($p < 0,05$), entretanto para o BisCem não houve diferença entre os grupos ($p > 0,05$). A adição de 0,5% mol de DPIHFP aumentou a resistência de união e a dureza inicial do RelyX U100, além de promover menor degradação após imersão em solvente. O grupo controle do cimento BisCem não apresentou diferença estatisticamente significativa entre os grupos na resistência de união e somente o grupo controle e 0,5% não apresentaram degradação em solvente. Para o coeficiente de inchamento e resistência à flexão, não houve diferença entre os grupos do BisCem ($p < 0,05$) e o grupo 2% do RelyX U100 apresentou menores valores ($p > 0,05$). Não houve diferença na profundidade de polimerização entre os grupos em ambos os cimentos ($p > 0,05$). A adição de 0,5% mol de DPIHFP melhorou as propriedades físicas do cimento resinoso autoadesivo de ativação dual RelyX U100.

Palavras-chave: Fotoiniciador; canforoquinona; hexafluorofosfato de difeniliodônio; amina terciária; cimento resinoso, resistência de união.

ABSTRACT

The aim of the current study was to evaluate the properties of dual-cure self-adhesive resin cements with the addition of an onium salt (DPIHFP). The experimental groups were set according to the molar concentration of DPIHFP (0.5, 1 and 2 mol%). The resin cements were assessed using: push-out bond strength test; flexural strength (ISO 4049/2009); degree of conversion (FTIR); depth of cure; swelling coefficient and degradation in solvent. All groups of RelyX U100 with onium salt showed highest degrees of conversion after 24 hours and 7 days ($p < 0.05$), however for BisCem there was no statistical difference between the groups ($p > 0.05$). The addition of 0.5 mol% of DPIHFP increased the push-out bond strength and microhardness of RelyX U100, and promoted less degradation after immersion in solvent. The control group of BisCem did not present statistical difference among the groups in the bond strength and the control group and 0.5 mol% showed no degradation in solvent. For swelling coefficient and flexural strength, there was no difference between BisCem groups ($p > 0.05$) and for RelyX U100 cement, the 2 mol% showed the lowest value ($p < 0.05$). Depth of cure was not statistical different in the experimental groups of both resin cements ($p > 0.05$). The addition of 0.5 mol% of diphenyliodonium hexafluorphosphate improved the properties of dual-cure self-adhesive resin cement RelyX U100.

Keywords: Photoinitiator; camphorquinone; diphenyliodonium hexafluorphosphate; onium salt; tertiary amine; resin cement; bond strength.

SUMÁRIO

INTRODUÇÃO

A restauração de dentes tratados endodonticamente ainda apresenta um desafio clínico (Zorba, *et al.*, 2011) muitas vezes exigindo a utilização de pinos intra-radiculares (Leitune, *et al.*, 2010), os quais apresentam um alto risco de fratura devido a força direcionada ao dente tratado ser diretamente relacionada com a resistência do remanescente dentário (Milot, Stein, 1992). Com o desenvolvimento de coroas totalmente cerâmicas (Ho, *et al.*, 2011), o uso de núcleos metálicos tem apresentado limitações estéticas, apesar de apresentarem boas propriedades mecânicas (Asmussen, *et al.*, 1999). Com isso, a popularidade do uso de materiais não metálicos tem aumentado (Qualtrough, Mannocci, 2003), tornando-se uma alternativa viável associada ao aperfeiçoamento das propriedades dos agentes de cimentação (Fokkinga, *et al.*, 2004). Além da aparência estética, os pinos pré-fabricados não metálicos exibem uma elevada resistência à fadiga e tração, além de módulo de elasticidade semelhante com o da dentina (Fokkinga, *et al.*, 2004).

Os pinos pré-fabricados, de fibra de carbono ou de vidro, constituem-se de uma alta fração volumétrica de fibras unidirecionais embebidas em uma matriz polimérica epóxica (Seefeld, *et al.*, 2007) e são indicados em casos de pouca perda coronária e presença do efeito férula (Goracci, Ferrari, 2011). Por apresentarem flexibilidade, reduzindo a concentração de estresse e prevenindo fraturas, a cimentação desses tipos de pinos com cimentos resinosos tem se mostrado mais efetiva, associada ou não ao uso de sistemas adesivos (Boschian Pest, *et al.*, 2002).

Cimentos resinosos tiveram sua utilização aumentada na odontologia, desde que exibiram avanços em suas propriedades mecânicas, físicas e adesivas, comparados aos agentes de cimentação convencionais (Attar, *et al.*, 2003).

Entretanto, esses materiais apresentam alta sensibilidade técnica devido a dificuldade de controle adequado da umidade (Van Meerbeek, *et al.*, 2005), necessidade de condicionamento da dentina, aplicação de sistema adesivo e polimerização, podendo comprometer o sucesso do procedimento clínico (Mak, *et al.*, 2002).

Com o objetivo de simplificar os procedimentos de cimentação, diminuindo a sensibilidade da técnica com condicionamento dentinário, um novo grupo de cimentos resinosos, os cimentos autoadesivos foi introduzido (Gerth, *et al.*, 2006). Além das partículas de carga, o agente de união e os componentes do sistema ativador-iniciador, esses novos agentes de cimentação apresentam em sua composição monômeros ácidos e hidrófilos, os quais simultaneamente desmineralizam e infiltram na dentina, resultando em um embricamento micromecânico (Moraes, *et al.*, 2011), dispensando as etapas de aplicação de sistemas adesivos. Em uma revisão de literatura Ferracane e colaboradores em 2011 avaliaram a composição química, propriedades físicas, biológicas e performance dos cimentos resinosos autoadesivos, demonstrando que esses cimentos exibem bom desempenho nas propriedades de resistência a flexão, resistência ao desgaste, dureza e resistência de união a diversos substratos, que combinados com a facilidade de manuseio indicam sua crescente utilização.

Atualmente estão disponíveis no mercado os cimentos resinosos fotoativados, autoativados e de ativação dual (Caughman, *et al.*, 2001). Enquanto os cimentos fotoativados possuem em sua pasta catalisadora um fotoiniciador, geralmente canforoquinona, os quimicamente ativados possuem o peróxido de benzoíla como iniciador (Asmussen, 1981). Apesar de ativações distintas, o mecanismo de polimerização desses materiais é o mesmo: os radicais livres gerados pela reação

química entre o agente iniciador e a amina terciária, iniciam a polimerização (Silva, *et al.*, 2010).

Quando comparados, os cimentos fotoativados oferecem a vantagem clínica de ter o tempo de trabalho maior, controle de presa e estabilidade da cor (Braga, *et al.* 2002). Entretanto, o uso somente da polimerização ativada por luz é limitada em situações onde a mesma não consegue penetrar no material, como no terço médio e apical de condutos radiculares que receberão retentores intra-radiculares (Leloup, *et al.*, 2002). Nesses casos, o cimento indicado é o de ativação dual, pois a intensidade de luz podendo não ser suficiente para ativar o processo de polimerização, conta com uma ativação química, necessária para atingir o máximo de conversão possível em locais onde a luz não penetra (Breeding, *et al.*, 1991). Os cimentos de ativação dual foram desenvolvidos com o objetivo de conciliar as características favoráveis do cimento de ativação química com a fotoativada, proporcionando um cimento com um tempo de trabalho estendido, capaz de apresentar um grau de conversão adequado, na ausência ou presença de luz (Braga, *et al.*, 2002).

Enquanto alguns materiais autoadesivos são de ativação exclusivamente química, a maioria combina a ativação química e física, apresentando-se como cimentos duais (Ferracane, *et al.*, 2011). Alguns estudos indicam um aumento do grau de conversão dos monômeros nos cimentos de ativação dual, quando comparados aos de ativação exclusivamente química (Kumbuloglu, *et al.*, 2004; Vrochari, *et al.*, 2009; Yan, *et al.*, 2010). Mesmo tendo um grau de conversão superior aos demais materiais (Silva, *et al.*, 2010), esses cimentos ainda possuem uma limitação quanto ao grau de conversão em profundidade (Leloup, *et al.*, 2002).

O grau de polimerização dos cimentos de ativação física ou dual é diretamente proporcional a quantidade de luz a que são expostos (Leloup, *et al.*, 2002). Alguns

estudos têm demonstrado o significativo efeito da atenuação da luz no interior do conduto radicular (Roberts, *et al.*, 2004; Giachetti, *et al.*, 2009). Sendo assim, eles polimerizam até certa profundidade que varia de acordo com a penetração do feixe de luz no material (Asmussen, 1982). Esse alcance pode ser afetado devido a distância entre a superfície dentária, onde a ponta ativa do aparelho fotoativador está posicionada e o material no interior do conduto radicular (Vandewalle, *et al.*, 2005). Tem sido relatado que um baixo grau de conversão dos monômeros pode comprometer o compósito em termos de dureza final, resistência a fratura e ao desgaste, módulo de elasticidade, solubilidade, degradação hidrolítica (Tezvergil-Mutluay, *et al.*, 2007) e biocompatibilidade (Issa, *et al.*, 2004).

Uma das alternativas propostas para minimizar esse efeito é a utilização de pinos translúcidos (Roberts, *et al.*, 2004), os quais tem a proposta de transmitir a luz para dentro do canal radicular, entretanto alguns estudos têm demonstrado que não há aumento do grau de conversão dos cimentos resinosos fotoativados associados a esses pinos (Ho, *et al.*, 2011). Por outro lado, outra possibilidade seria aumentar a reatividade do material fotoativado utilizando sistemas iniciadores mais efetivos (Ye, *et al.*, 2009). O fotoiniciador mais comumente utilizado em compósitos resinosos odontológicos é a canforoquinona, a qual é capaz de absorver luz na região de espectro visível, com comprimento de onda entre 400 e 500nm (Neumann, *et al.*, 2006).

A incorporação de sistemas iniciadores mais reativos, como cloreto de trimetilamônio (QTX) (Hayakawa, *et al.*, 2005), óxido de trimetilbenzoíla-difenilfosfina (TPO) (Miletic, Santini, 2012) e α-dimetoxi-α-fenilacetofenona (Irgacure®) (Dai, *et al.*, 2011), tem sido proposta na tentativa de obter um grau de conversão maior. A aplicação do sal de difeniliodônio em sistemas adesivos de matriz polimérica de

metacrilato tem mostrado resultados favoráveis (Ogliari, *et al.*, 2007; Guo, *et al.*, 2008). O sal de difeniliodônio, na presença de luz, se decompõe em um radical cátion ariliodo, um radical aril reativo e um ânion, atuando na geração de radicais livres, agindo como fotoiniciador para reações de polimerização catiônica (Crivello, Lam, 1977).

Na odontologia, o uso do sal de difeniliodônio apresenta as vantagens de ser solúvel em água, onde seu caráter iônico pode promover a polimerização de monômeros hidrofílicos (Wang, *et al.*, 2006), ser compatível com compósitos de resina epóxica (Millich, *et al.*, 1998), apresentar significativo aumento da taxa de polimerização radicalar (Gómez, *et al.*, 2003), além da habilidade de aumentar a reatividade dos radicais livres (Timpe, *et al.*, 1993).

Diferentemente da canforoquinona, o pico de absorção do sal de difeniliodônio é na região ultravioleta, portanto a geração de radicais livres a partir desse composto não é eficiente quando se utiliza lâmpada halógena ou diodo emissor de luz (LED). Como a luz ultravioleta é contra indicada no campo biológico, é necessária a utilização de corantes que absorvam espectro de luz visível, pois eles reagem com o sal de ônio, promovendo a decomposição dos radicais livres necessários para o processo de polimerização (Timpe, *et al.*, 1993). Segundo Hua, *et al.*, em 2002 a reação de polimerização envolve a presença de um corante, a canforoquinona, que ao absorver luz, forma espécies excitadas, reduzindo o sal de difeniliodônio, o qual se decompõe, gerando radicais livres. Esses radicais são efetivos na iniciação da reação de polimerização de metacrilatos, além de aumentarem a reatividade do sistema obtido. Portanto, cimentos resinosos autoadesivos de ativação dual que possuam em sua composição o sal de difeniliodônio, podem ter o grau de conversão

dos monômeros aumentado, proporcionando um polímero com propriedades melhoradas.

OBJETIVO

Avaliar propriedades de cimentos resinosos autoadesivos de ativação dual com incorporação de hexafluorofosfato de difeniliodônio, por meio da resistência de união *push-out*, grau de conversão, profundidade de polimerização, degradação em solvente, resistência à flexão e coeficiente de inchamento.

MANUSCRITO

Laboratory Research

Influence of an iodonium salt on the properties of dual-cure self-adhesive resin cements

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Abstract

The aim of the current study was to evaluate the properties of dual-cure self-adhesive resin cements with the addition of an onium salt (DPIHFP). The experimental groups were set according to the molar concentration of DPIHFP (0.5, 1 and 2 mol%). The resin cements were assessed using: push-out bond strength test; flexural strength (ISO 4049/2009); degree of conversion (FTIR); depth of cure; swelling coefficient and degradation in solvent. All groups of RelyX U100 with onium salt showed highest degrees of conversion after 24 hours and 7 days ($p < 0.05$), however for BisCem there was no statistical difference between the groups ($p > 0.05$). The addition of 0.5 mol% of DPIHFP increased the push-out bond strength and microhardness of RelyX U100, and promoted less degradation after immersion in solvent. The control group of BisCem did not present statistical difference among the groups in the bond strength and the control group and 0.5 mol% showed no degradation in solvent. For swelling coefficient and flexural strength, there was no difference between BisCem groups ($p > 0.05$) and for RelyX U100 cement, the 2 mol% showed the lowest value ($p < 0.05$). Depth of cure was not statistical different in the experimental groups of both resin cements ($p > 0.05$). The addition of 0.5 mol% of diphenyliodonium hexafluorphosphate improved the properties of dual-cure self-adhesive resin cement RelyX U100.

Keywords: Photoinitiator; camphorquinone; diphenyliodonium hexafluorphosphate; onium salt; tertiary amine; resin cement; bond strength.

Introduction

Self-adhesive resin cements are cements based on filled polymers designed to adhere to tooth structure without pretreatment of adhesive or etchant.[1] Almost all commercial materials presents a polymerization system composed of photo and chemical activation.[2] In cases of intra canal post cementation the light-curing is insufficient to polymerize the material along the root canal. Therefore, the use of dual-cure resin cements is necessary[3] to achieve increased mechanical properties at middle and apical thirds of the canal.

Mechanical properties of resin based composites are related to high degree of conversion.[4] The binary system of camphorquinone (CQ) and tertiary amine are traditionally used, however, when compared to ternary systems lower polymerization efficiency is observed.[5] Photo-initiators are increasingly being evaluated to provide a high degree of conversion and consequently improved mechanical properties.[6]

Diaryliodonium salts are efficient photoinitiators for cationically mediated polymerization.[7] This photo-initiator is active when irradiated in a light range below 300nm, but the use of ultra-violet light is not indicate in the biological field.[8] However, the use of dyes that absorb the visible light would allow the reaction with onium salts, promoting it decomposition.[9] Onium salt can promote the polymerization of hydrophilic monomers,[10] are compatible with epoxy-based resins[11] and significant increase the rate of polymerization.[12]

Previous studies showed that diphenyliodonium hexafluorphosphate improved the polymerization rate[13] and maintained increased bond strength to dentin of model self-etching adhesive systems after one year of aging.[14] However, the influence of this ternary photo-initiator was not evaluated in dual-cure self-adhesive resin

cements. The aim of this study is to evaluate the properties of dual-cure self-adhesive resin cements with the addition of an onium salt.

Materials and methods

Materials

The dual-cure self-adhesive resin cements used in this study were RelyX U100 (3M ESPE, St Paul, MN, USA) and BisCem (Bisco Inc., Schaumburg, IL, USA). The compositions of the materials are shown in Table 1. Diphenyliodonium hexafluorphosphate (DPIHFP) were purchased from Aldrich Chemical Co (Milwaukee, WI, USA) and used without further processing. To perform the monomer light activation a light-emitting diode unit (Radii Cal, SDI Ltd., Bayswater, Victoria, Australia) was used, which had an output intensity of 1200 mW/cm^2. The power of the light curing unit was gauged with a radiometer (Model 100, Demetron Research Group, Danbury, CT, USA). The experimental groups were set according to the molar concentration of diphenyliodonium hexafluorphosphate (0.5, 1 and 2 mol%).

Push-out test

Ninety-six (n=12) bovine teeth with similar lengths and diameters were used in this study. Freshly extracted teeth were immediately stored fully immersed in distilled water at 4°C for no more than 6 months.[15,16] To be included in this study, the following criteria had to be met: straight roots and a root length of at least 15 mm. External debris were removed with a periodontal curette. The crown surfaces of each

tooth were sectioned below the cementum-enamel junction, perpendicular to their long axis, using a low speed diamond disc under water coolant.

The post space of each specimen was enlarged with a no. 2 drill from the Exacto post system (Angelus, Londrina, PR, Brazil) 14 mm. The fiber post was 20 mm in length, 1.4 mm in cervical diameter, and 0.9 mm in apical diameter. To standardize the method, the same operator performed all of the procedures. Following post space preparations, the roots were randomly divided.

The resin cements were applied according to the manufacturers' instructions. The fiber posts were cleaned with 96% ethanol, and silane was applied with disposable microbrush tips. The cements were inserted into the root canal with Accudose (Centrix Inc, Shelton, CT, USA) needle tubes and a Centrix syringe (Centrix Inc, Shelton, CT, USA). The fiber post was then inserted and excess cement was removed. The roots were wrapped in a polyvinyl siloxane matrix and light activation was performed through the coronary portion of the root for 30 seconds at the buccal and lingual surfaces for a total of 60 seconds of light exposure, with 5 mm of distance between the source and the root.

The roots were stored in 37°C distilled water for 7 days and then serially sectioned into nine 0.7 mm thick sections in a precision cutting machine (Low Speed Saw, Buehler, Lake Bluff, IL) under constant water cooling. The slices of all roots were stored in 37°C distilled water for 24 hours before the push-out tests. One slice of each post space region (cervical, middle and apical) was randomly chosen and measured. The cervical and apical diameters of the canal and the thickness of all of the slices were measured with a digital caliper. Each section was marked on its apical side and positioned on a base with a central hole in a universal testing machine (DL2000, EMIC, São José dos Pinhais, PR, Brazil). The push-out test was

performed by applying a compressive load to the apical side of each slice by using a 0.7 mm-diameter cylindrical plunger attached to the upper portion of the testing machine. A crosshead speed of 0.5 mm/min was applied until bond failure occurred. To express the bond strength in megapascals (MPa), the load upon failure was recorded in newtons (N) and divided by the bond area (mm^2).[17]

After bond strength testing, failure type was determined by analyzing each sample under a stereomicroscopic (Wild Heerbrugg, Switzerland) at 40X magnification. Type of failure was classified into 4 categories as follows: (1) adhesive failure between post and luting material; (2) adhesive failure between dentin and luting material; (3) cohesive failure of the post system; (4) mixed failure (a combination of 2 of the above).

Depth of cure

The depth of cure of the materials was assessed by Micro-Raman spectroscopic analysis (Senterra, Bruker Optics, Ettlingen, Germany), using backscattering geometry. Twenty-four roots (n=3) selected, prepared and cemented like the description of the push-out test were stored in 37°C distilled water for 24 hours and then sectioned parallel to their long axis, using a low speed diamond disc under water coolant. Spectra were acquired from one half-tooth of each root. On each section, in the region of the cement, 14 mm in length were evaluated, cervical to apical region, each 500µm, totalizing twenty-eight measurements of degree of conversion.

Raman spectra were collected in the range of 451-1811 cm^{-1} using the 785 nm laser excitation line and automatic fluorescence rejection (AFR). OPUS® software

(version 6.5, Bruker Optics GmHb 2009, Billerica, MA) was used for data acquisition. The degree of conversion was calculated as described in a previous study,[18] considering the intensity of carbon-carbon double bond stretching vibration (peak height) at 1635 cm^{-1}, and using the peak at 1610 cm^{-1} from the monomer and polymer samples, as an internal standard.

Degree of conversion

Fourier transform infrared (FTIR) spectroscopy was used to evaluate the degree of conversion. The FTIR measurements were performed in the Vertex 70 FTIR spectrophotometer (Bruker Optics, Ettlingen, Germany). The materials were dispensed over a diamond crystal of Attenuate Total Reflectance (ATR) accessory. A support was coupled to the spectrometer to fix the light-curing unit and standardize the distance between the unit and sample at 5 mm. The OPUS® software in monitoring scan mode was used, with Blackman-Harris 3-Term appodization in a range of 1750 to 1550 cm^{-1}, resolution of 8 cm^{-1}, and mirror speed of 2.8 mm/s. Analysis was performed at a controlled room temperature of 23°C ±1°C and 60% ±1% relative humidity. The sample was directly dispensed onto the diamond crystal using a polyvinyl siloxane matrix (3 mm diameter and 1 mm thickness) and light activated for 40s (n=6). The measurements were performed immediately after the light activation, 24 hours and 7 days after. The degree of conversion was calculated as described in depth of cure.

Degradation in solvent

To determinate the softening in ethanol, the specimens were subjected to a microhardness test. To determine the Knoop microhardness (KHN), the specimens produced for degree of conversion evaluation were used. Six specimens for each material were embedded in acrylic resin and polished in a polisher (Model 3v, Arotec, Cotia, SP, Brazil) with a felt disc embedded in aluminium suspension (Alumina 1.0 µm, Arotec, Cotia, SP, Brazil). The specimens were dried and stored at 37°C for 24 h. The specimens were subjected to a microhardness test in which 3 indentations (25 g/15 s), 100 µm apart, were assessed using a digital microhardness tester (HMV 2, Shimadzu, Tokyo, Japan). The calculation of the initial hardness value (KHN_1) was performed.[19]

The specimens were immersed in ethanol for 4 hours. After this period, microhardness test was performed again (KHN_2). The difference between the initial and final values of hardness was performed in percentage using the follow equation:

$\Delta KHN\% = (100 \times (KHN_1 - KHN_2)) / KHN_1$

Swelling coefficient

Swelling coefficient measurements were performed gravimetrically. Cement samples (n=3) of each material were produced in a polyvinyl siloxane matrix (2 x 2 x 12 mm). The specimens were stored in a desiccator at 37°C until complete evaporation of water. They were immersed in distilled water and weighed daily after the removal of water excess with absorbent paper until swelling equilibrium was reached. Then, samples were removed, the excess solution that had deposited on the film surface was quickly removed with blotting paper, and the samples were weighed.

The values of the swelling coefficients (α) of all materials were calculated using the following equation:

$$\alpha = ((M_{eq} - M_0) / M_0) \times 1/d_s$$

where M_{eq} is the mass of the sample (polymer+solvent) after equilibrium, M_0 the mass of the polymer, and d_s is the density of the solvent.[20]

Flexural Strength

The resin cements specimens were fabricated using customized stainless steel molds according to ISO 4049/2009 specifications,[21] except for the dimensions (12 mm in length, 2 mm in width and 2 mm in height).[22] The materials were placed into the mold, which was positioned on the top of an acetate strip. The top and bottom surfaces of the specimens were light-polymerized with two irradiations of 20 s on each side. After polymerization, specimens were removed from the matrix and stored in distilled water at 37 ± 1°C for 24 h. Forty specimens were produced (n=5) and the flexural strength tests were performed using a universal testing machine (EMIC, São José dos Pinhais, PR, Brazil) at a crosshead speed of 1.0 mm/min. The flexural strength of each specimen was calculated in megapascal (MPa).[18]

Statistical analysis

Statistical analysis was performed using SigmaStat (version 4, Ashburn, Georgia, USA). The normality of the results was tested using the Kolmogorov-Smirnov test. Statistical analysis was performed using one-way ANOVA (onium salt

concentration) and Tukey´s post hoc test for flexural strength and push-out bond strength. Degree of conversion were analyzed by two-way repeated measures ANOVA (onium salt concentration and time) and Tukey´s post hoc test and depth of cure was analyzed by two-way ANOVA (onium salt concentration and root region). Kruskal-Wallis and Dunn multiple comparison tests were performed for swelling coefficient. For the analysis of degradation in solvent, a paired Student t-test (KHN1 and KHN2) and a one-way ANOVA (onium salt concentration) for KHN1 and ΔKHN% were used. A significance level of 0.05 was performed for all tests.

Results

The results of push-out bond strength are presented in Fig. 1 and 2. For RelyX U100 the group with 0.5 mol% presented the highest value of bond strength, 8.5 (±3.5) MPa ($p<0.05$), and the control group did not showed statistical difference among 1 and 2 mol% ($p>0.05$). The adhesive cement/dentin failure was the mostly observed mode in all groups, but adhesive cement/post was also detected. For BisCem the 0.5 mol% group showed higher bond strength (7.4 ±3.2 MPa) than 1 mol% group (5.5 ±1.7 MPa), and did not presented statistical difference between control and 2 mol% group. The 0.5 mol% group presented the adhesive cement/post failure as the most frequent and in the others groups the adhesive cement/dentin was the mostly observed.

All groups of RelyX U100 with onium salt showed degrees of conversion after 24 hours that were higher than 31.2% and presented an increasing of values after 7 days. The 0.5 and 2 mol% groups of BisCem presented an increase of degree of conversion after 7 days, but did not presented a statistical difference between the

control and 1 mol% groups. The values of degree of conversion are shown in Fig. 3 and 4. The addition of onium salt influenced the degree of conversion in RelyX U100.

The depth of cure vary from 67% to 83.3% of degree of conversion for RelyX U100 groups and 87.3% to 94.5% for BisCem groups and did not presented statistical difference between them. The results of depth of cure are shown in Fig. 5 and 6.

The Knoop microhardness values before and after solvent immersion are shown in Table 2. For RelyX U100 the addition of 0.5 mol% of onium salt increased microhardness values before solvent immersion. After the immersion in solvent, all groups with onium salt showed the lowest decreased values of microhardness. For BisCem the control, 1 and 2 mol% showed the highest microhardness values before immersion, however, the control and 0.5 mol% groups did not presented polymer degradation after immersion in ethanol.

The swelling coefficient of the RelyX U100 groups decreased with the addition of onium salt but the control group showed no statistical difference between 0.5 and 1 mol% groups. For BisCem there were no significant difference between the experimental and the control groups. The means and standard deviations are shown in Table 3.

The flexural strength values of both resin cements are presented in Table 4. For RelyX U100 the control group showed no difference between the 0.5 and 1 mol% groups ($p > 0.05$) and 2 mol% group presented the lowest value of flexural strength (93.4 Mpa). There were no significant differences between the BisCem groups.

Discussion

The incorporation of diphenyliodonium hexafluorphosphate in dual-cure self-adhesive resin cements improved degree of conversion, immediately push-out bond strength and polymer degradation in solvent of the RelyX U100 resin cement and showed no influence in the flexural strength and the swelling coefficient. The increased reactivity of these cements with the addition of DPIHFP is related to the very low bond energy of the carbon-iodine bond (26-27 kcal/mol) which facilitates the decomposition of the excited iodonium compound to an anion, an aryl radical and a radical-cation.[7] Dental methacrylate monomers containing camphorquinone (CQ) are commonly photoactivated and absorbs light in the range between 450 and 500 nm[23] which induce the decomposition of DPIHFP, allowing the generation of free radicals that can start the polymerization process.[24] Previous studies[14,25] demonstrated that the incorporation of DPIHFP increased degree of conversion of adhesive systems improving its mechanical properties; therefore it is important to evaluate the influence of the addition of an onium salt in the properties of dual-cure self-adhesive resin cements. The results of this study were influenced by the resin cement tested and the concentration of DPIHFP.

The degree of conversion presented values in accordance with the literature,[17,26] even with the addition of DPIHFP. In the control group of RelyX U100, the degree of conversion was lower than the groups with the incorporation of DPIHFP after 24h and 7 days. When the CQ is used alone associated with an electron/proton donor substance, a tertiary amine (EDAB), a limited excited state is expected[27] considering its very short half-life. Therefore, polymers formed using CQ + EDAB have a low degree of conversion when compared to ternary photo-initiator

systems.[6,25] In BisCem groups, no statistical difference in degree of conversion after 24 hours was observed. The different functional monomers contained in the dual-cure self-adhesive resin cements used in this study could explain the similar results[28] between the BisCem groups, independent of DPIHFP incorporation. All groups of the resin cements with diphenyliodonium hexafluorphosphate, after 24 hours, presented an increase of degree of conversion, indicating that the chemically polymerization occurred in the presence of the ternary system and allowed higher values of degree of conversion.

In order to improve the bond durability, several studies[6,24,29] evaluated the polymerization and the potential interference of the photo-initiator system and other composites compounds. However, the depth of cure of dual-cure self-adhesive resin cement into root canal has not been evaluated. In this study, all groups from both resins cements presented degree of conversion throughout the root canal with no statistical difference, presenting values in accordance with the literature.[30] The depth of cure of photoactivated composites depends on the material filler composition,[31] the intensity of light source[32] and the distance from de curing tip.[33] Methods like microhardness[34] or optical microscopy[35] can be employed, however, the micro-Raman technique is suggested to be more convenient and also more accurate than others techniques[36] for calculating the local degree of conversion. There was no difference in degree of conversion between the cervical, middle and apical regions in all groups. These results may be due to the effective self-curing process of tested cements.

Since the degree of conversion is of paramount importance to the mechanical properties of the polymer formed,[28] it is expected that a higher conversion of double bonds improve bond strength.[37] The RelyX group with 0,5 mol% of DPIHFP showed

higher push-out bond strength than the control group indicating the enhance methacrylate polymerization with ternary photo-initiator system. Previous studies demonstrated that this association of CQ, EDAB and DPIHFP were more reactive than CQ alone or a binary photo-initiator system.[14] The diphenyliodonium hexafluorphosphate does not absorb the visible light wavelength,[24] which would difficult the cleavage of the carbon-iodine bond when the light-emitting diode unit is used. Therefore it is necessary to associate a photoinitiador sensitive to blue light.[13,38] There are two mechanisms described for the function of DPIHFP as a catalyst to the polymerization reaction. Gómez et al.[12] relates that DPIHFP reacts with CQ in its triplex stage, the amino radical generated by CQ cleavage the carbon-iodine bond generating two phenyl radicals, which can react with the residual amines forming other radicals starting the polymerization process. Other mechanism is related to the tertiary amine that promotes the regeneration of iodonium salts. The regenerated DPIHFP could produce new excited states by the reaction with non-reacted CQ molecules.[39]

An increased degree of conversion, promoted by the addition of DPIHFP produces a polymer with enhanced cross-linking and mechanical properties, increasing the push-out bond strength to root dentin.[24] Despite there was no statistical difference in the depth of cure among the RelyX U100 groups, the groups with addition of DPIHFP presented a higher degree of conversion, as shown in Fig. 5. Furthermore DPIHFP improved the microhardness in RelyX U100. The 0,5 mol% group presented the highest value of microhardness, differing statically from the others groups. All groups of RelyX U100 presented a reduction of microhardness after 4 hours of immersion in solvent, however, the control group showed the highest reduction (-24.9%) indicating that the addition of DPIHFP can produce a polymer with

improved properties. On the other hand, the BisCem groups with incorporation of 1 and 2 mol% of DPIHFP presents reduction in the microhardness values after the solvent immersion while the control and 0.5 mol% groups did not presented any degradation. Important structural factors include the porosity of the network and the cross-linking density[40] that influences the behavior of the material after immersion in solvent. The higher polymerization rates induces more extensive cross-linking of the polymer, making the diffusion of solvents inside the network more difficult.[22]

The diffusion of solvent through the polymers chains affects the surface properties such as hardness and longevity of the restorative treatment[40] which was showed based on the microhardness of RelyX U100 group with addition of 0.5 mol% of DPIHFP. However, the incorporation of DPIHFP showed no influence on the flexural strength values in comparison with the control groups, except for the group with addition of 2 mol% of DPIHFP in RelyX U100. The swelling coefficient is directly related to the quality of the network formed during polymerization.[41] A higher degree of cross-linking confers better mechanical properties of the polymer and prevents solvent absorption and swelling.[22] Beyond monomer conversion, the degree of swelling of a polymer depends on the pore size of the polymer network and the interaction between the polymer and the solvent.[42] In this study, there was no statistical difference in the swelling coefficient between all groups of BisCem and control, 0.5 and 1 mol% groups with DPIHFP of RelyX U100.

In RelyX U100 the addition of 2 mol% of DPIHFP did not improved the swelling coefficient, microhardness and flexural strength. The push-out bond strength was not influenced by the incorporation of 2 mol% of the salt. During the manipulation of the resin cements, it was not possible to obtain a homogenous bulk after the incorporation of the DPIHFP in 1 and 2 mol% which could be noted on the optic

microscope. This difficulty could have influenced the results due the incompletely dissolution of the salt. However, the addition of 0.5 mol% produced a homogenous material. Furthermore, all properties evaluated in the present study presented different results among the two resin cements tested, which is related to the difference of functional monomers contained in RelyX U100 and BisCem, above the differences in concentration of CQ and EDAB. Several studies compared physicals and mechanical properties of this two dual-cure self-adhesive resin cement which describe different results of degree of conversion, hardness and flexural strength between the two materials,[2,17,43] accordingly to the results showed in this study.

The results present in this study indicate that the addition of diphenyliodonium hexafluorphosphate affects the dual-cure self-resin cements. A reduced level of degradation of resin cement, demonstrated by the groups with 0.5 mol% of DPIHFP, could lead to a more stable and durable restorative treatment.[44] The increased degree of conversion promoted by the addition of this salt produced a polymer with enhanced cross-linking and mechanical properties. Self-adhesive resin cements that present decreased degradation are required, since leachable components could be a biological concern and lead to restorative procedures more prone to failure.

Conclusion

The addition of 0.5 mol% of diphenyliodonium hexafluorphosphate improved the properties of RelyX U100 dual-cure self-adhesive resin cement, increasing degree of conversion, push-out bond strength and microhardness.

The incorporation of diphenyliodonium hexafluorphosphate did not improve BisCem resin cement properties.

Acknowledgements

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Table 1: Chemical compositions of materials

Material		Composition	Lot
RelyX U100	Base	Glass powder, methacrylated phosphoric acid esters, triethylene glycol dimethacrylates, sialane treated silica, sodium persulfate.	366321
	Catalyst	Glass powder, substituted dimethacrylate, sialane treated silica, sodium p-toluenesulfinate, calcium hydroxide.	
BisCem	Base	Bis-GMA, uncured dimethacrylate monomer, glass filler.	1100008370
	Catalyst	Phosphate acidic monomer, glass filler.	
Exacto Post		Fiberglass, epoxy resin	22162

Data reported by manufacturers

Table 2: Means and standard deviations of Knoop microhardness before (KHN1) and after (KHN2) immersion in ethanol and percentage of reduction (ΔKHN%).

Cement	Group	KHN1	KHN2	ΔKHN(%)	Cement	Group	KHN1	KHN2	ΔKHN(%)
RelyX U100	$G_{0\%}$	51.9 (±2.3) [B,a]	39.0 (±2.5) [b]	-24.9 (±4.6) [A]	BisCem	$G_{0\%}$	48.9 (±2.5) [A,a]	50.0 (±1.5) [a]	2.4 (±5.2) [B]
	$G_{0.5\%}$	61.2 (±2.5) [A,a]	55.9 (±1.7) [b]	-8.6 (±2.1) [B]		$G_{0.5\%}$	40.0 (±1.7) [B,a]	41.0 (±3.2) [a]	2.6 (±9.2) [B]
	$G_{1\%}$	47.8 (±2.2) [C,a]	43.0 (±2.3) [b]	-10.0 (±3.3) [B]		$G_{1\%}$	45.7 (±1.9) [A,a]	40.9 (±3.5) [b]	-10.3 (±6.6) [A]
	$G_{2\%}$	41.7 (±2.0) [D,a]	37.6 (±2.4) [b]	-9.8 (±5.8) [B]		$G_{2\%}$	47.1 (±2.2) [A,a]	42.3 (±3.0) [b]	-10.3 (±3.5) [A]

Capital letters indicate significant difference in columns, small letters indicate significance difference in rows ($p<0.05$).

Table 3: Means and standard deviations of swelling coefficient (α) of the resin cements with different onium salt concentrations

Cement	Group	α (mLg)
RelyX U100	$G_{0\%}$	0.0196 (±0.0038) A
	$G_{0.5\%}$	0.0161 (±0.0002) A.B
	$G_{1\%}$	0.0150 (±0.0002) A.B
	$G_{2\%}$	0.0148 (±0.0003) B

Cement	Group	α (mLg)
BisCem	$G_{0\%}$	0.0415 (±0.0015) A
	$G_{0.5\%}$	0.0383 (±0.0024) A
	$G_{1\%}$	0.0356 (±0.0026) A
	$G_{2\%}$	0.0358 (±0.0033) A

Different letters indicate significant difference among means ($p < 0.05$).

Table 4: Means and standard deviations of flexural strength (δ) of the resin cements with different onium salt concentrations

Cement	Group	δ (Mpa)
	$G_{0\%}$	145.0 (±23.6) ^{A}
RelyX	$G_{0.5\%}$	119.7 (±17.9) ^{A,B}
U100	$G_{1\%}$	109.4 (±34.9) ^{A,B}
	$G_{2\%}$	93.4 (±22.9) ^{B}

Cement	Group	δ (Mpa)
	$G_{0\%}$	96.5 (±11.3) ^{A}
	$G_{0.5\%}$	86.7 (±28.8) ^{A}
BisCem	$G_{1\%}$	87.6 (±5.8) ^{A}
	$G_{2\%}$	70.2 (±16.9) ^{A}

Different letters indicate significant difference among means (p<0.05).

Figure 1: Results of push-out bond strength (means and standard deviations) comparing different groups of RelyX U100. The different capital letter demonstrates that were statically significant differences among the means (p<0.05).
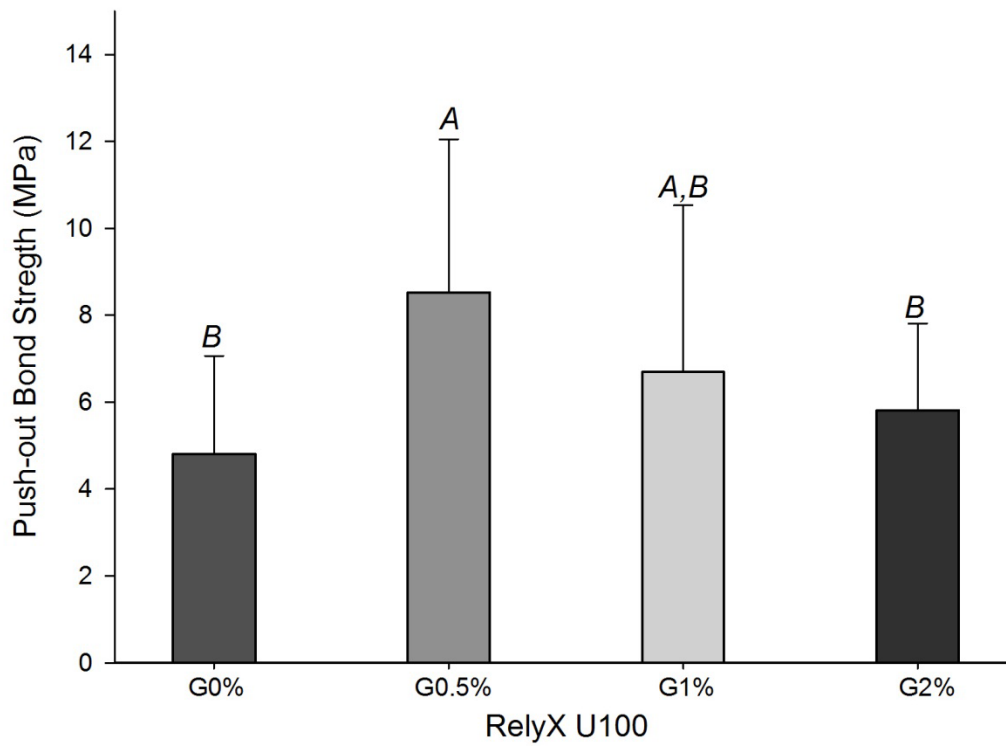
Figure 2: Results of push-out bond strength (means and standard deviations) comparing different groups of BisCem. The different capital letter demonstrates that were statically significant differences among the means (p<0.05).
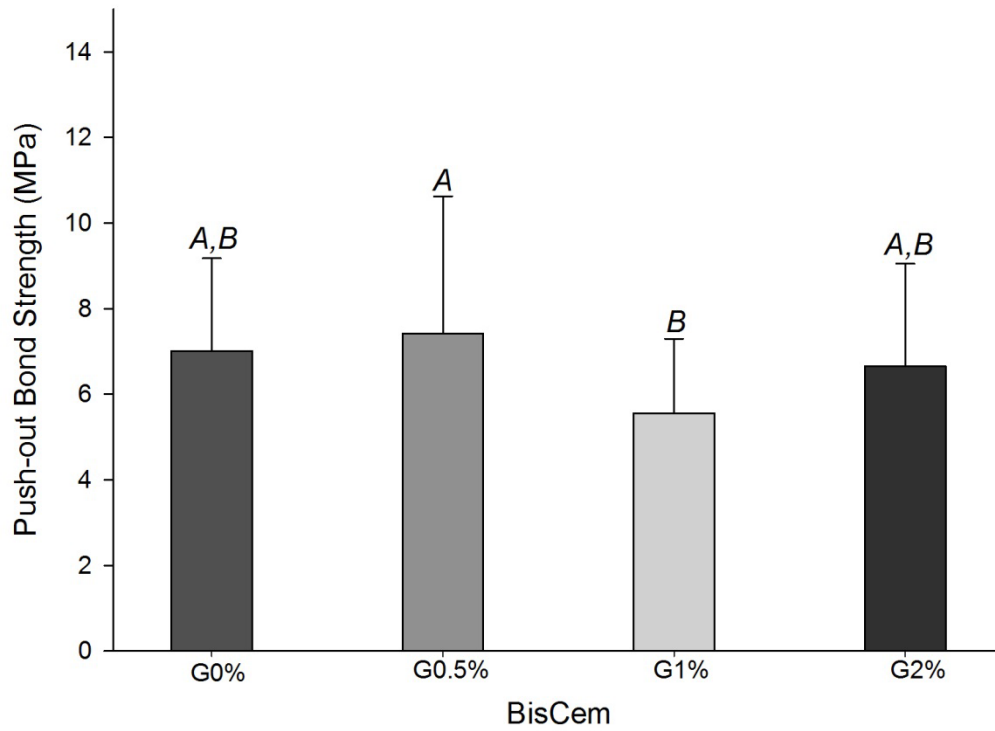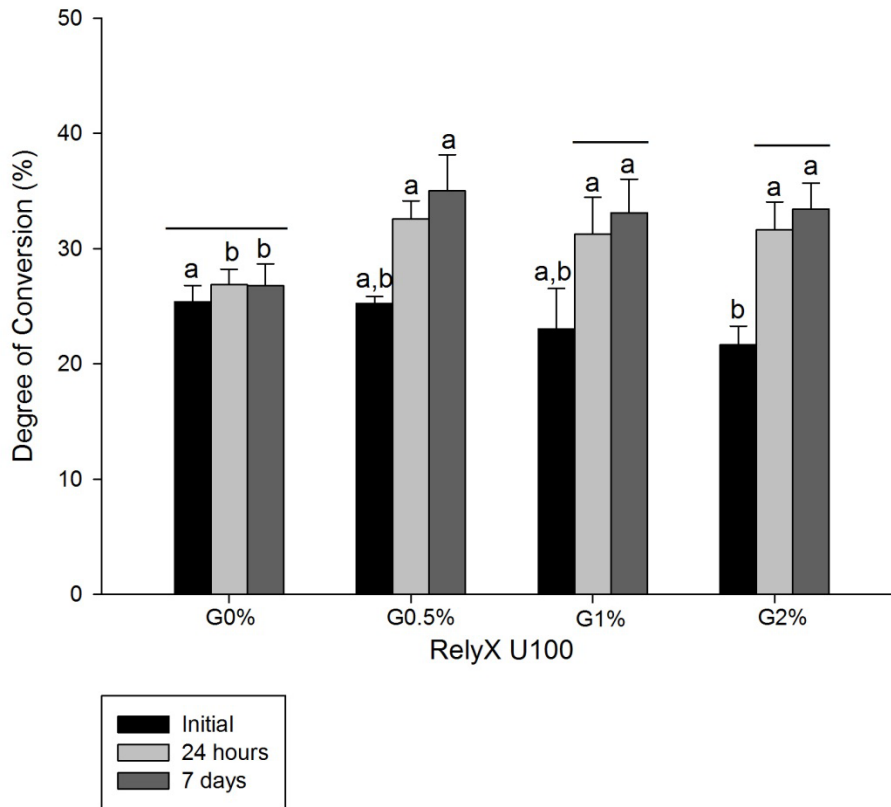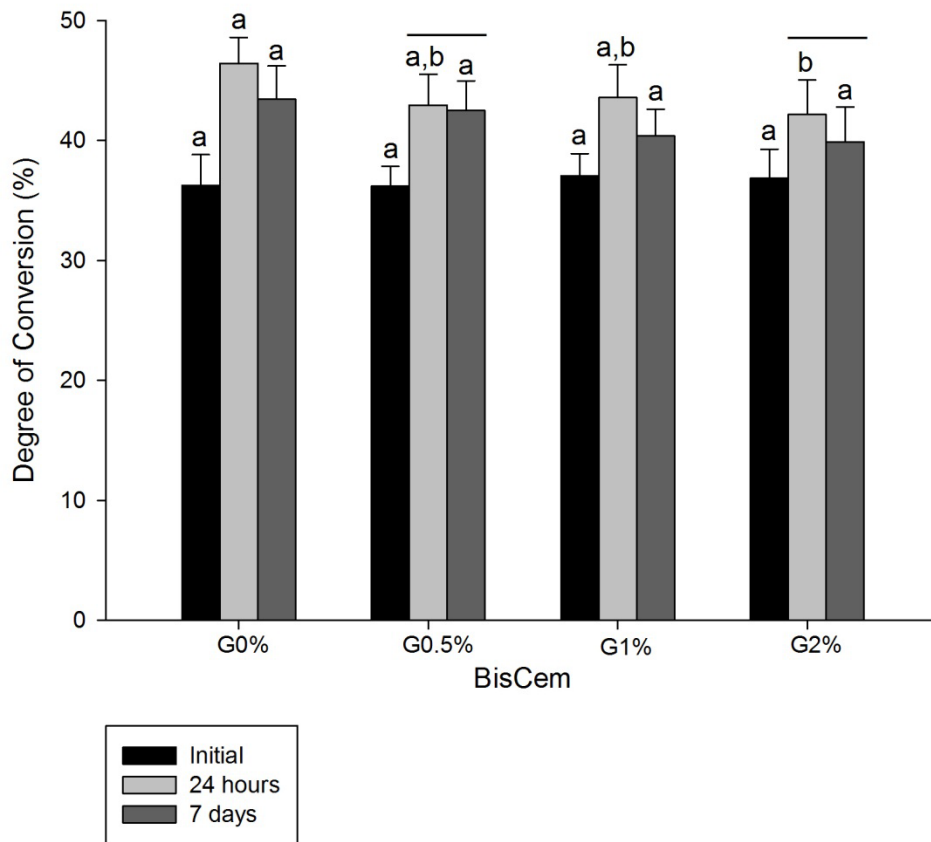
Figure 3: Results of degree of conversion (means and standard deviations) comparing different groups of RelyX U100.

Different letters represents statistically significant difference among groups in the same evaluation period (p<0.05). Evaluation period in which the degree of conversion was not significantly different are connected by a horizontal line (p>0.05).

Figure 4: Results of degree of conversion (means and standard deviations) comparing different groups of BisCem.

Different letters represents statistically significant difference among groups in the same evaluation period ($p < 0.05$). Evaluation period in which the degree of conversion was not significantly different are connected by a horizontal line ($p > 0.05$).

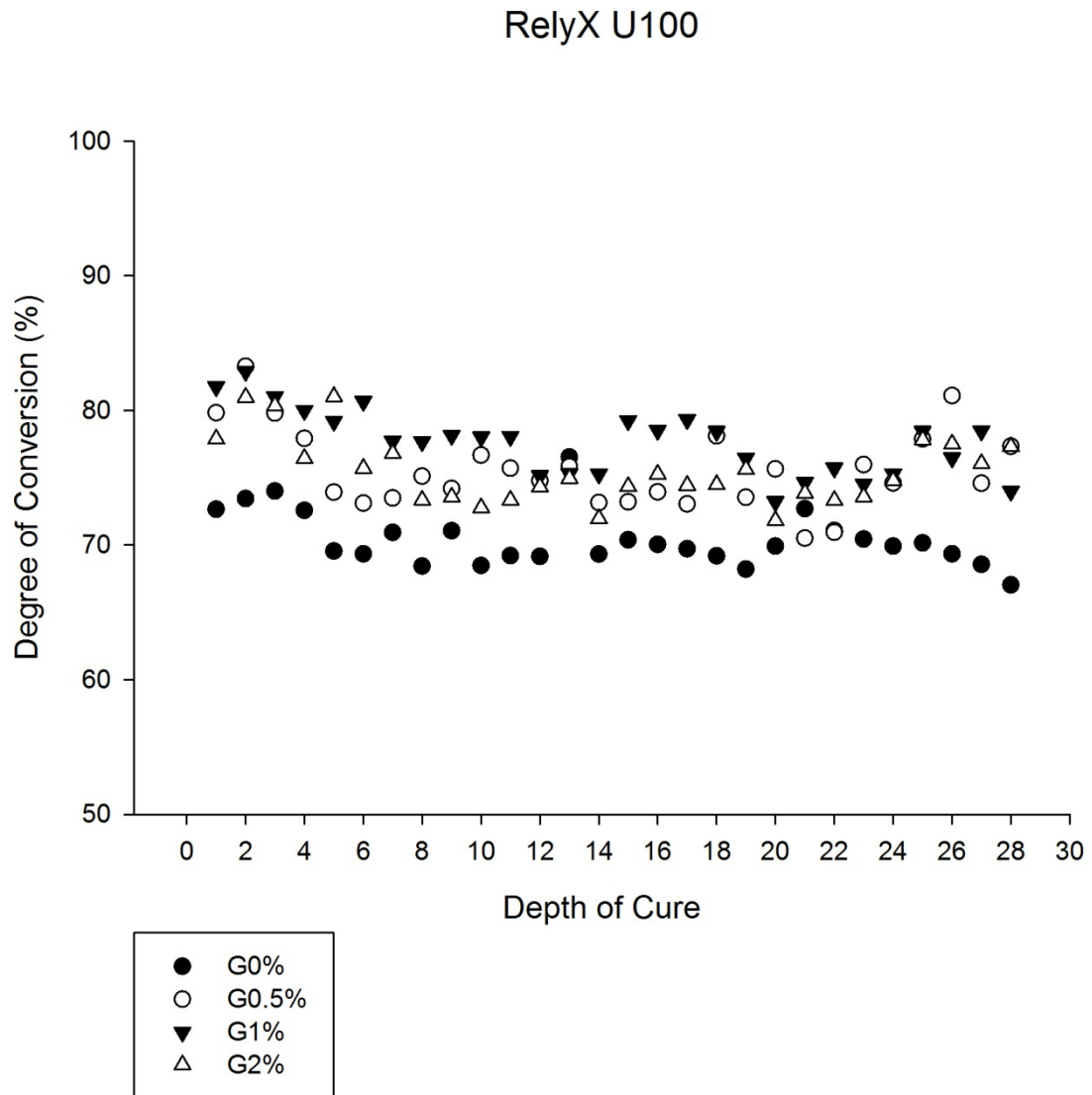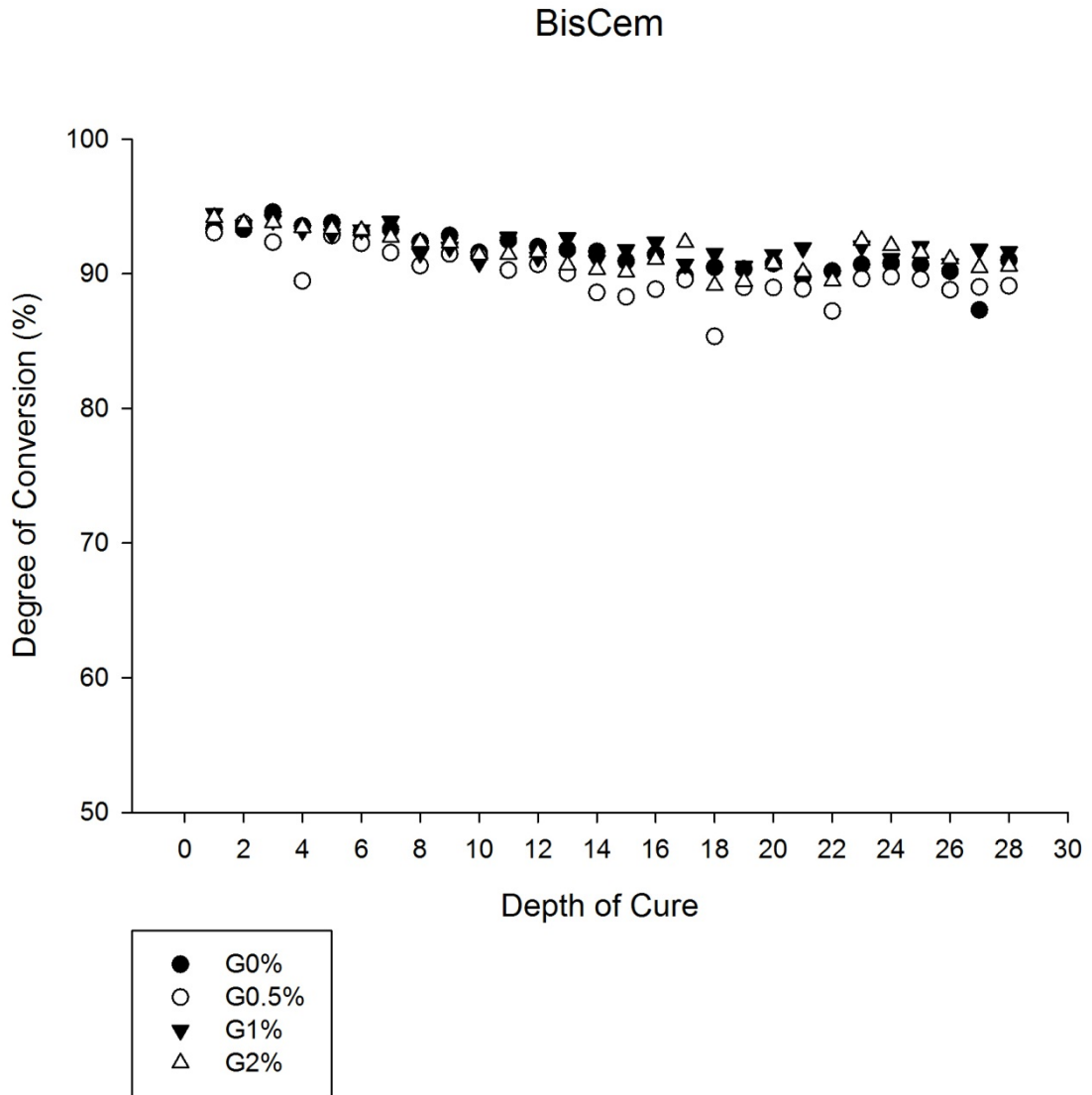Figure 5: Results of depth of cure (means) comparing different groups of RelyX U100.

RelyX U100

Figure 6: Results of degree of conversion (means) comparing different groups of BisCem.

BisCem

CONSIDERAÇÕES FINAIS

Os achados deste estudo sugerem que polímeros que contenham o sistema fotoiniciador ternário composto por canforoquinona, amina terciária e hexafluorofosfato de difeniliodônio apresentam melhores propriedades mecânicas. Analisando-se os resultados, verifica-se que os dois cimentos resinosos testados apresentaram comportamentos diferentes frente a incorporação do sal de ônio, entretanto os grupos com adição de 0,5% mol de DPIHFP apresentaram propriedades como grau de conversão, dureza e resistência de união push-out melhoradas, entretanto a concentração de 2% mol gerou um polímero com propriedades inferiores.

Atualmente o sistema fotoiniciador binário é o mais utilizado nos compósitos resinosos, tendo os cimentos resinosos que utilizam esse sistema associado a uma ativação química, altas taxas de sucesso nos tratamentos restauradores. Entretanto a falha na cimentação é uma das principais causas de fracasso em tratamentos restauradores de dentes com retentores intra-radiculares (Monticelli, Grandini et al. 2003), sendo a degradação da interface cimento/dentina uma das causas. Baseado nos achados desse estudo conclui-se que a adição do DPIHFP a esse sistema, em baixas concentrações, pode ser uma alternativa promissora para aumentar a reatividade do material e obter um polímero com propriedades melhoradas.

O aumento do grau de conversão promovido pela adição deste sal, na concentração de 0,5%, produziu um polímero com maior número de ligações cruzadas, o que gerou uma menor degradação polimérica após imersão em álcool, sugerindo que tratamentos restauradores realizados com este material possam ter uma maior longevidade.

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