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**ALTERNATIVAS PARA A REDUÇÃO DO STRESS DE POLIMERIZAÇÃO EM
RESTAURAÇÕES DE INCREMENTO ÚNICO**

PORTO ALEGRE

2018

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RESTAURAÇÕES DE INCREMENTO ÚNICO**

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Orientador: Prof. Dr. Jonas de Almeida Rodrigues

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RESUMO

O objetivo desta tese foi avaliar alternativas para a redução do stress de polimerização em restaurações de incremento único, através da adição de tiouretanos em resinas compostas e do uso de resinas compostas aquecidas. Para tanto, este trabalho foi dividido em três diferentes artigos com objetivos específicos, sendo eles: (1) testar o efeito da silanização de cargas inorgânicas com um novo silano contendo tiouretano em diferentes concentrações; (2) comparar o efeito da adição de tiouretano na matriz orgânica, carga silanizada ou associado à carga e matriz de resinas compostas experimentais; (3) testar o efeito de diferentes técnicas de incremento único utilizando resina composta pré-aquecida e uma resina experimental com adição de tiouretano no stress de polimerização, temperatura intrapulpar e grau de conversão. No primeiro artigo, dois diferentes tiouretanos foram sintetizados e uma carga inorgânica de vidro foi silanizada com diferentes concentrações destes tiouretanos. O uso destas cargas em resinas compostas experimentais causou um aumento no grau de conversão e na tenacidade à fratura associado com uma redução no stress de polimerização. No segundo artigo um tiouretano foi sintetizado e adicionado em resinas compostas experimentais: 1) somente na matriz orgânica; 2) através de uma carga silanizada; ou 3) na matriz e na carga. Além disto, diferentes matrizes orgânicas foram testadas. A adição de tiouretano aumentou significativamente a tenacidade à fratura e reduziu o stress de polimerização das resinas experimentais. A associação de tiouretano na matriz e na carga potencializou a redução do stress de polimerização observado. No terceiro artigo cavidades classe I com 4mm de profundidade foram restauradas em incremento único com uma resina composta em temperatura ambiente ou aquecida, ou com uma resina experimental modificada através da adição de tiouretano na matriz e na carga, ou uma resina composta tipo "bulk-fill" de consistência regular. O pré-aquecimento não resultou em uma redução do stress de polimerização. Por outro lado, o material experimental contendo tiouretano apresentou uma redução significativa do stress de polimerização juntamente com um aumento do grau de conversão. A incorporação de tiouretanos em novos materiais de incremento único é capaz de gerar materiais com melhores propriedades e reduzido stress de polimerização. Entretanto, o pré-aquecimento de resinas compostas não

parece uma alternativa clinicamente viável para redução do stress de polimerização ou aumento do grau de conversão.

Palavras-chave: Análise do estresse dentário. Estresse mecânico. Resinas compostas. Aquecimento.

ABSTRACT

The aim of this thesis was to evaluate alternatives for reducing the polymerization stress in single increment restorations, such as the addition of thio-urethanes in composite resins and the use of heated composite resins. For this, this work was divided in three different articles with specific objectives: (1) to approach a novel filler functionalization for dental composites with the synthesis and silanization of two different thio-urethanes to a glass filler, including different concentrations for the silanization process; (2) to evaluate the effect of adding a thio-urethane to experimental composites through filler silanization, resin matrix addition, or both strategies together; (3) to test the effect of different bulk-fill techniques using a pre-heated resin composite and a thio-urethane modified version of this material to the polymerization stress, intrapulpal temperature change and degree of conversion. In the first article, two different thio-urethanes were synthesized and an inorganic glass filler was silanized with different concentrations of these additives. The use of these fillers in experimental resin composites caused an increase in the degree of conversion and fracture toughness associated with a reduction in the polymerization stress. In the second article a thio-urethane was synthesized and added in experimental resin composites only in the organic matrix, only through a silanized filler or in the matrix as well as in the filler. In addition, different resin matrix compositions were tested. The addition of thio-urethane significantly increased the fracture toughness and reduced the stress of polymerization of experimental composites. The association of thio-urethane in the matrix and glass filler enhanced the polymerization stress reduction. In the third article, 4mm depth class I cavities were restored in a single increment with a conventional resin composite (pre-heated or at room temperature), an experimental resin with thio-urethane in the resin matrix and filler, and a commercial bulk-fill resin. Pre-heating did not result in polymerization stress reduction. On the other hand, the experimental material containing thio-urethane showed a significant reduction of the polymerization stress along with an increase in the degree of conversion. The incorporation of thio-urethanes into new bulk-fill composites is capable of generating materials with improved properties and reduced polymerization stress. However,

preheating of composite resins does not appear to be a clinically viable alternative for reducing polymerization stress or increasing the degree of conversion.

Keywords: Dental stress analysis. Mechanical stress. Composite resins. Heating.

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1 INTRODUÇÃO

As resinas compostas utilizadas para restaurações dentais passaram por grandes evoluções tecnológicas nas suas formulações, e conseqüentemente na sua performance, desde a sua primeira concepção por Bowen em 1963 (1). Uma grande parte desta evolução esteve focada na melhoria das propriedades mecânicas do material, através do desenvolvimento de novos monômeros e de partículas de carga de tamanhos, formas e até aglomerações diferentes (2). Atualmente, acompanhamentos clínicos de restaurações diretas em resina já demonstram uma excelente longevidade destes materiais mesmo em comparação com restaurações metálicas (3-5).

Tendo em vista os grandes avanços na performance dos materiais, as pesquisas voltadas para o desenvolvimento de novos materiais resinosos estão bastante direcionadas, nos últimos anos, para a facilitação dos procedimentos restauradores. Quando comparadas com as restaurações em amálgama, as restaurações diretas em resina composta apresentam a desvantagem de ser um procedimento mais sensível à técnica e com um número maior de passos. Isto ocorre, pois, as resinas compostas apresentam profundidade de cura limitada, devido à necessidade de luz para a iniciação do processo de polimerização (6), e pelo aumento no stress de polimerização, que é causado pela contração de polimerização (7). Portanto, mudanças nestes fatores específicos estão sendo alvo de pesquisas para que o material restaurador se torne mais fácil de ser usado e com resultados similares entre diferentes operadores (2).

Atualmente já estão disponíveis no mercado diversas opções de resinas compostas tipo bulk-fill para restaurações diretas. Estas possuem a proposta de facilitar o procedimento através da diminuição do número de incrementos devido ao aumento na profundidade de cura do material, juntamente com baixo stress de polimerização. Este apelo está fortemente ligado a redução do tempo do procedimento clínico, sendo assim uma vantagem tanto ao paciente quanto ao profissional pela otimização do seu tempo clínico. Porém, nem todos os materiais utilizam a mesma tecnologia para alcançar o mesmo objetivo (8-10). Entre os sistemas presentes no mercado hoje em dia, grande parte destes utiliza materiais mais fluídos, que geralmente apresentam menor quantidade de carga

(11) orgânica maior translucidez (12). As alternativas encontradas pelos fabricantes para tornar possível o uso dos seus materiais em incrementos maiores inclui resinas com maior capacidade de transmissão de luz, monômeros modificados e iniciadores diferentes. A capacidade de transmissão de luz de uma resina composta pode ser aumentada pela diminuição da sua carga inorgânica, porém, esta alteração leva a uma diminuição das propriedades mecânicas e da viscosidade do material. Devido a isto, alguns fabricantes utilizam partículas de carga de tamanho e forma diferentes, que apresentem índice de refração semelhantes à matriz resinosa. Desta forma, o material obtido permite uma maior passagem de luz e conseqüente maior profundidade de cura (13, 14). Por outro lado, alguns sistemas utilizam iniciadores mais eficientes que a canforoquinona, como o patenteado "Ivocerin". A resina Tetric EvoCeram Bulk Fill aposta neste iniciador que tem o seu pico de absorção em um comprimento de onda entre 400 e 450 nm e possui uma absorção superior à canforoquinona, facilitando a reação de polimerização (15). Outra resina conhecida no mercado é a Surefil SDR Flow, que utiliza uma modificação no centro das cadeias dos monômeros chamada de modulador de polimerização. Estes monômeros modificados permitem um relaxamento das tensões de contração dentro do material durante a polimerização e uma reação mais lenta (16).

A formulação de uma resina composta deve levar em consideração diversos fatores para se chegar a um material desejado. Sabe-se que a quantidade de matriz orgânica e carga, além do tamanho e forma da carga, pode influenciar desde a consistência do material até as suas propriedades mecânicas (2, 17, 18). Portanto, cada fabricante utiliza algum recurso dentro da sua formulação para tentar fazer com que o seu material polimerize em maiores profundidades e/ou tenha uma contração de polimerização menor. Desta forma, estes materiais acabam se tornando mais fáceis de serem utilizados em incrementos maiores ou até únicos. Porém, muitas vezes esta melhoria em uma propriedade acaba levando a deterioração de outra, principalmente em relação às características mecânicas. Em função disto, foi observada uma redução nas propriedades mecânicas de materiais de incremento único em comparação aos sistemas convencionais (9). Foi observado ainda que as resinas de incremento único de baixa viscosidade apresentam propriedades mecânicas inferiores

quando comparadas as mesmas de alta viscosidade (10). Este padrão de diminuição nas propriedades mecânicas dos materiais pode ser preocupante clinicamente em relação à longevidade das restaurações (5).

As resinas de bulk-fill presentes no mercado apresentam duas consistências e indicações diferentes de uso. Os materiais menos viscosos, de consistência “flow”, apresentam características mecânicas inferiores às resinas compostas convencionais. Estas são indicadas somente como material de base, devendo ser recobertas por uma camada final, de aproximadamente 2 mm, de resina composta convencional. Um exemplo destes materiais é a resina Surefil SDR Flow, que já foi observada por acompanhamento clínico de 6 anos, apresentando uma taxa anual de falha similar à de uma resina composta convencional (19). Porém, parte do desempenho deste material está ligado à performance da resina composta de cobertura, visto que esta resina é de baixa viscosidade e necessita de recobrimento. Existem ainda as resinas de bulk-fill de consistência regular, que apresentam alta viscosidade. Estas dispensam a necessidade de recobrimento, podendo ser utilizadas para preenchimento de toda a cavidade, devido à sua maior resistência mecânica.

Na busca por tecnologias capazes de reduzir o stress de contração de resinas compostas surgiu o uso de tiouretanos (20). Tiouretanos são oligômeros, capazes de polimerizar juntamente com uma matriz orgânica à base de metacrilato, que possuem tióis pendentes de sua cadeia. Tióis são conhecidos por possibilitarem reações de transferência de cadeia, na qual uma cadeia polimérica crescente é terminada e dá início ou continuidade a outra cadeia. Estas reações modificam a cinética da reação de polimerização de resinas compostas reduzindo a taxa de polimerização e atrasando o ponto de geleificação (21). Por sua vez, o aumento da fase pré-gel permite ao composto um relaxamento do stress de polimerização com o deslizamento e acomodação das moléculas (7). Após isto, com a chegada do ponto de geleificação a viscosidade do material atinge um ponto em que a mobilidade das cadeias e monômeros fica comprometida, levando ao início da fase de terminação da polimerização.

O uso de tiouretanos parece especialmente promissor devido à uma melhora nas propriedades mecânicas do material obtida junto com a redução do stress. Estudos prévios demonstram melhora na tenacidade à fratura, resistência flexural e grau de conversão de materiais com estes aditivos, quando adicionados dentro da matriz orgânica (20, 22-25). Outra possível forma de incorporação de tiouretano em resinas compostas seria através da funcionalização de cargas inorgânicas. Entretanto, esta alternativa ainda não foi reportada.

Foi descrito na literatura que o pré-aquecimento de resinas compostas resulta em uma elevação do grau de conversão (26) e reduz a viscosidade do material (27). Sabe-se que a resina composta fica mais sensível à fotoativação quando aquecida e que mesmo tempos menores de irradiação conseguem levar a um grau de conversão adequado ou até superior (26). Associado a este aumento na conversão da resina ocorre um grande aumento na profundidade de cura em relação ao material em temperatura ambiente (28). Sabe-se que o grau de conversão está diretamente relacionado com as propriedades mecânicas da resina.

Apesar de o aumento da conversão ser positivo para as propriedades mecânicas da resina composta, o aumento da contração de polimerização associado ao grau de conversão (29). Em um estudo laboratorial, a contração de polimerização de uma resina composta foi de 2,0% em temperatura ambiente e alcançou 4,5% quando aquecida a 68° C, aproximadamente (30). Por outro lado, acredita-se que mesmo com a maior contração de polimerização linear, a resina aquecida pode ter um menor stress de contração quando polimerizada aderida a uma superfície. Este comportamento é possivelmente explicado por um maior relaxamento das tensões nas cadeias dentro do material quando ele está aquecido e apresentando menor viscosidade (31). Foi relatado que quando uma resina composta é fotopolimerizada por 5 segundos a 60° C ela apresenta um grau de conversão de 53% e um stress final de contração de 2,7 MPa, enquanto a temperatura ambiente (22° C) sendo ativada por 20 segundos ela chega a 45% de conversão e 5,1 MPa de stress (32).

Levando em consideração estes conhecimentos prévios, existe a possibilidade de que a resina composta aquecida possa ser usada com uma técnica de incremento único no lugar das atuais resinas designadas para este fim. O uso de uma resina composta convencional leva a vantagem da utilização de materiais já conhecidos e testados, com melhores propriedades mecânicas e com um menor custo em relação a esta nova geração de materiais. Para isto, testes laboratoriais devem ser feitos para observar a influência do tempo de irradiação, profundidade de cura e os efeitos da contração de resinas compostas aquecidas em restaurações diretas. Além disto, mais pesquisas de desenvolvimento de materiais com a utilização de tiouretanos em resinas compostas ainda podem auxiliar no entendimento e na implementação desta tecnologia. A incorporação de tiouretanos em resinas compostas de bulk-fill parece especialmente promissor devido à redução do stress de polimerização e aumento do grau de conversão obtidos em estudos utilizando estes aditivos.

2 OBJETIVOS

Objetivo geral:

O objetivo desta tese foi avaliar alternativas para a redução do stress de polimerização em restaurações de incremento único, através da adição de tiouretanos em resinas compostas experimentais ou do uso de resinas compostas aquecidas.

Objetivos específicos:

- Testar o efeito da silanização de cargas inorgânicas com um novo silano contendo tiouretano, incluindo diferentes concentrações no processo de silanização, nas propriedades de resinas compostas experimentais;

- Comparar o efeito da adição de tiouretano na matriz orgânica, carga silanizada ou associado na carga e matriz de resinas compostas experimentais;

- Testar o efeito de diferentes técnicas de incremento único utilizando resina composta pré-aquecida e uma resina experimental com adição de tiouretano no stress de polimerização, temperatura intrapulpar e grau de conversão.

3 METODOLOGIA

Esta tese se dividiu em três artigos redigidos de acordo com as normas básicas para submissão de cada uma das revistas consideradas para publicação. Os artigos 1 e 2 foram formatados para submissão ao periódico “Journal of Dental Research”. O artigo 3 foi redigido e formatado para submissão ao periódico “Dental Materials”.

3.1 Artigo 1

Thio-urethane filler functionalization for dental resin composites

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Abstract

The aim of this study was to approach a novel filler functionalization for dental composites with the synthesis and silanization of two different thio-urethane oligomers to a glass filler. Also, various thio-urethane silane concentrations were tested during the silanization process to check its effect on silane coupling and on an experimental composite conversion, polymerization stress and fracture toughness. Two different thio-urethane silanes were synthesized by combining 1,6-hexanediol-diisocyanate (HDDI), pentaerythritol tetra-3-mercaptopropionate and 3-(Triethoxysilyl)propyl isocyanate or 1,3-bis(1-isocyanato-1-methylethyl) benzene (BDI), pentaerythritol tetra-3-mercaptopropionate and 3-(Triethoxysilyl)propyl isocyanate at 1:2,5:1 molar ratio. Glass fillers were silanized in ethanol/distilled water solutions with 1 wt%, 2 wt% or 4 wt% of each thio-urethane silane. The mass of silane coupled to the fillers was measured by thermogravimetric analysis. Resin composites were prepared with 50% Bis-GMA/UDMA/TEGDMA and camphorquinone/amine matrix and 50% glass filler. Polymerization kinetics and degree of conversion were tested using Near-IR. Bioman was used to test polymerization stress. Higher concentrations of thiourethane in the silanizing solution resulted in higher

masses of silane coupled to the filler. Thio-urethane containing groups exhibited significantly higher degree of conversion compared to control groups, except for BDI 4%. HDDI 4%, BDI 2% and BDI 4% showed significantly lower polymerization stress than control groups. HDDI 4% exhibited significantly higher fracture toughness. Novel filler functionalization with thio-urethane silanes may be a promising alternative for improving dental composites properties by significantly increasing the degree of conversion, fracture toughness and reducing the polymerization stress. Thio-urethane concentration and type during filler silanization affected silane coupling and final material properties.

Key-Words: Composite resins. Mechanical strength. Polymerization stress. Glass filler. Filler functionalization.

Introduction

Resin composites have constantly evolved since their introduction and are widely used in Restorative Dentistry. Direct restorations using resin composites have been reported with good annual failure rates in long term follow-up (Da Rosa Rodolpho et al., 2011). Despite that, the most common failure reported is restoration fracture (Da Rosa Rodolpho et al., 2011; Opdam et al., 2010). Therefore, material properties still play an important role on the restoration survival.

Thio-urethanes are oligomer molecules that comprises thiol pendant groups that are able to polymerize together with a methacrylate matrix (Bacchi et al., 2014). Thiols are chain transfer agents that changes the polymerization kinetics leading to delayed vitrification and stress reduction while improving final conversion (Boulden et al., 2011; Pfeifer et al., 2011). The addition of thio-urethanes in the matrix of dental resin composites has shown promising results with higher conversion, lower polymerization stress and mechanical properties improvement (Bacchi et al., 2014; Bacchi et al., 2015).

Inorganic filler is responsible for modifying resin composite properties. Filler's shape and loading affects mechanical properties like flexural strength, moduli, hardness and fracture toughness (Habib et al., 2017; Kim et al., 2002). Whereas, light transmission, depth of cure, surface roughness and maximum loading is affected by filler size (Habib et al., 2017; Kim et al., 2002; Marghalani, 2010). Also, filler functionalization has been proposed for different applications in dental composites such as antibacterial activity, as well as fluoride or calcium phosphate ion release (Tezvergil-Mutluay et al., 2017; Wille et al., 2016).

The addition of thio-urethanes in the resin matrix improves important material properties for dental composites. Although, the benefits of thio-urethanes may be availed with the presence of the oligomer in the inorganic filler. Therefore, the aim of the present study was to approach a novel filler functionalization for dental composites with the synthesis and silanization of two different thio-urethanes to a glass filler. Also, various thio-urethane silane concentrations were tested during the silanization process to check its effect on silane coupling and on the final composite conversion, polymerization stress and

fracture toughness. The null hypothesis was that different thio-urethane silane concentrations does not imply in different material properties.

Materials and methods

Two different thio-urethane silanes were synthesized for this study. The reaction was done at room temperature in 60 ml of methylene chloride by combining 1,6-hexanediol-diisocyanate (HDDI), pentaerythritol tetra-3-mercaptopropionate and 3-(Triethoxysilyl)propyl isocyanate or 1,3-bis(1-isocyanato-1-methylethyl) benzene (BDI), pentaerythritol tetra-3-mercaptopropionate and 3-(Triethoxysilyl)propyl isocyanate (Sigma–Aldrich, St. Louis, MO, USA) at 1:2,5:1 molar ratio, resulting in pendant thiols from the oligomer structure. Triethylamine was used to catalyze the reaction and oligomers were purified by precipitation in hexane. Solvent evaporation was done in a rotary evaporator and under vacuum. Formation of thio-urethane bonds and initial products absence was verified by H-NMR and mid-IR spectroscopy (Bacchi et al., 2015). After this, one aromatic (BDI) and one aliphatic (HDDI) thio-urethane silanes were obtained to use for filler silanization.

The silanization process was performed in 65 ml solutions of 80 vol% ethanol and 20 vol% distilled water. Each solution pH was adjusted to 4.5 with the addition of glacial acetic acid. After this, 1 wt%, 2 wt% and 4 wt% of HDDI and BDI oligomers were added to each silanizing solution together with 5 grams of 1.5 μm unsilanized glass filler. The solution was kept under mechanical agitation for 24 hours, filtered and dried for 4 days in an oven at 37°C.

Resin matrix consisted of a mixture of 50 wt% bis-phenol A diglycidyl dimethacrylate, 30 wt% urethane dimethacrylate and 20 wt% triethylene glycol dimethacrylate (Esstech, Essington, PA, USA). The photo-initiator system was added to this resin matrix by total matrix weight. It consisted of 0.2 wt% dI-camphoroquinone, 0.8 wt% ethyl 4-dimethylaminobenzoate, and 0.2 wt% 2,6-di-tert-butyl-4-methylphenol (Sigma-Aldrich, St. Louis, MO, USA). Mixing was realized in a room with yellow light with a mechanical mixer (DAC 150 Speed mixer, Flacktek, Landrum, SC, USA). Experimental composites were obtained by adding 50 wt% of each different thio-urethane silanized filler to a separate amount

of Araldite matrix control positive and control negative groups were produced with a regular methacrylate silanized and an unsilanized glass filler with the same particle size.

A small sample (approx. 10 mg) of each filler was taken to Thermogravimetric analysis (TGA) to verify the mass of silane coupling to the filler. Baseline temperature was 25°C and was taken up to 850°C at 10°C/min. Temperature was held at 850°C for 2 minutes and then cooled. The test was performed in a nitrogen atmosphere. Two batches of each filler that came from separate thio-urethane synthesis and silanization processes were analyzed in TGA (n=2).

For polymerization kinetics and degree of conversion, composite discs (0.8 mm thick and 10 mm diameter) were tested between two glass slides (n=3) using near-infrared spectroscopy (NIR). Each sample was light cured with a mercury arc lamp (EXFO Acticure 4000 UV Cure; Mississauga, Ontario, Canada) filtered at 320-500 nm for 300 seconds. Incident irradiance was 20 mW/cm² considering the distance from the sample to the light guide tip. A very low light irradiance was used for polymerization kinetics in this study as an attempt to study different kinetics on the polymerization reaction. Polymerization kinetics was assessed recording the methacrylate absorption peak at 6165 cm⁻¹ during light curing.

Fracture toughness was determined according to the American Society for Testing Materials standard (E399-90). Five single-edge notch beam specimens (n=5) were fabricated in a split steel mold (5 x 2 x 25 mm) with a razor blade insert of 2.5 mm and light cured for 240 seconds. tested in 3-point bend at a cross-head speed 0.5 mm/minute on a universal testing machine. Fracture toughness was calculated from the critical stress intensity factor (K_{IC}) as described before (Ferracane and Berge, 1995).

To assess the polymerization stress, the Bioman method was used as previously described (Watts and Satterthwaite, 2008). A standard amount of composite (n=5) with 0.5 mm thickness was polymerized between a silanized silica slab and a roughened steel piston. The piston was also covered with a metal primer to improve adhesion to the metal. The test settings corresponded to a C-factor of 4. Composites were light cured through the silica slab for 300 seconds

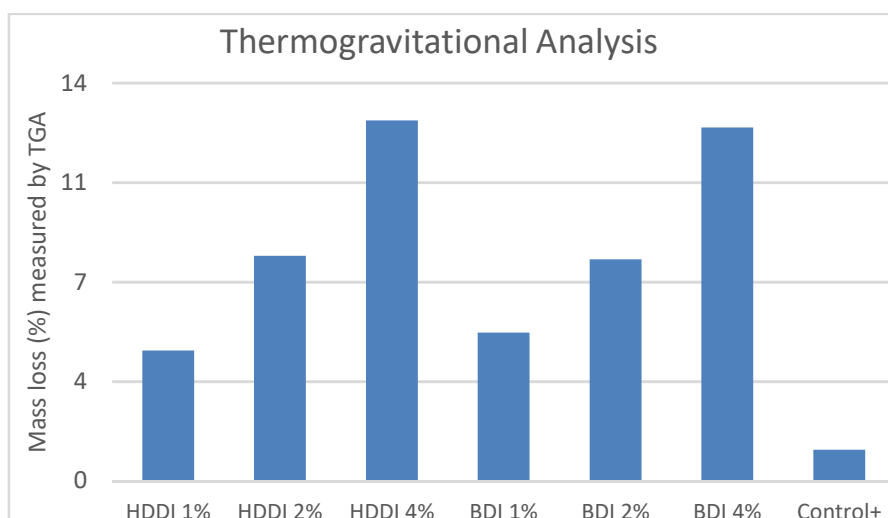
with the mercury arc lamp. The incident irradiance reaching the samples through the slabs was the same as for polymerization kinetics and degree of conversion.

Data were analyzed using the statistical software SPSS (IBM Corp, Armonk, NY, USA). Two-way ANOVA, one-way ANOVA, and Tukey post-hoc tests were used at a significance level of 0.05. Two-way ANOVA factors were: (1) thio-urethane type (HDDI and BDI) and (2) thio-urethane concentration (1%, 2% and 4%).

Results

The mass of silane coupled to the filler is reported in the Figure 1. TGA shows that all the higher concentrations of thiourethane in the silanizing solution presented higher masses of silane on the filler. Control groups with conventional methacrylate silane presented the lowest masses of coupled silane measured by TGA.

Figure 1. Thermogravital analysis of different manufactured fillers



Results of polymerization kinetics and degree of conversion are presented in Table 1. Thio-urethane containing groups exhibited significantly higher degree of conversion compared to control groups, except for BDI 4%. Control negative

and BDI 4% presented similar conversion, higher than the Control positive. Rmax was significantly lower for BDI 4%.

Both factors, thio-urethane type and thio-urethane concentration, significantly affected fracture toughness ($p=0.001$). There was no interaction between factors for fracture toughness. HDDI 4% exhibited significantly higher fracture toughness than all other groups (Figure 2).

Thio-urethane type and thio-urethane concentration also significantly affected polymerization stress ($p<0.001$). There was a significant interaction between factors ($p=0.005$). HDDI 4%, BDI 2% and BDI 4% showed significantly lower polymerization stress than control groups (Figure 3). BDI 4% reduced over than 50% the stress caused by control groups.

Table 1. Degree of conversion and polymerization kinetics

	DC	Rmax	DC at Rmax
Control +	46.6 (0.18) ^a	1.06 (0.06) ^{a,b}	9.89 (0.92) ^a
Control -	48.2 (0.29) ^b	1.10 (0.05) ^{a,b}	12.49 (1.44) ^a
HDDI 1%	50.9 (0.44) ^{c,d}	1.06 (0.06) ^{a,b}	10.55 (0.84) ^a
HDDI 2%	51.2 (0.42) ^d	1.16 (0.02) ^a	10.25 (1.00) ^a
HDDI 4%	50.3 (0.24) ^c	1.03 (0.07) ^{a,b}	9.09 (0.54) ^a
BDI 1%	50.7 (0.23) ^{c,d}	1.09 (0.03) ^{a,b}	10.61 (2.46) ^a
BDI 2%	50.4 (0.38) ^{c,d}	0.97 (0.06) ^b	10.59 (2.83) ^a
BDI 4%	48.0 (0.16) ^b	0.71 (0.03) ^c	13.83 (4.89) ^a

Figure 2. Fracture toughness from experimental composites

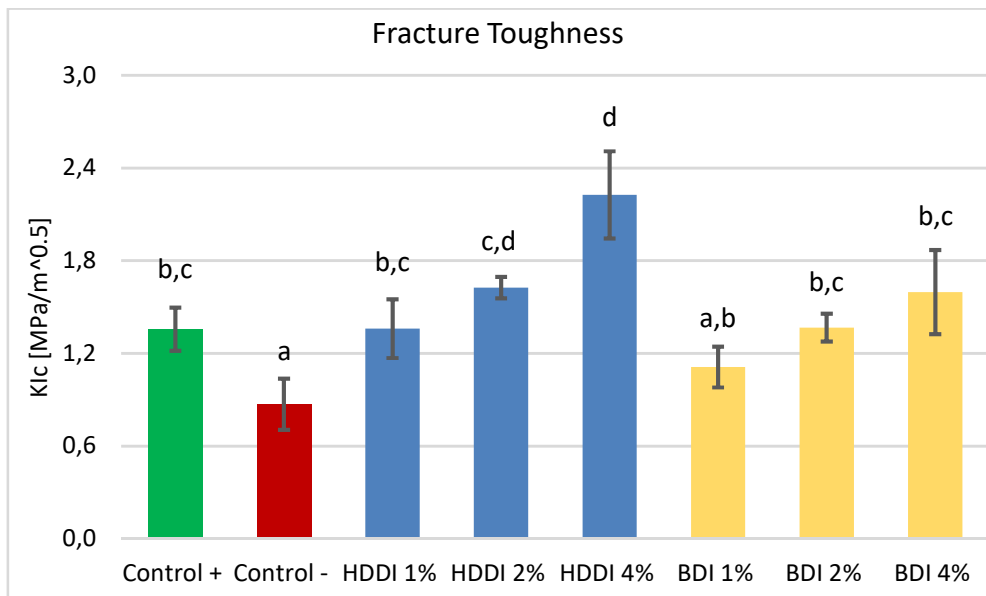
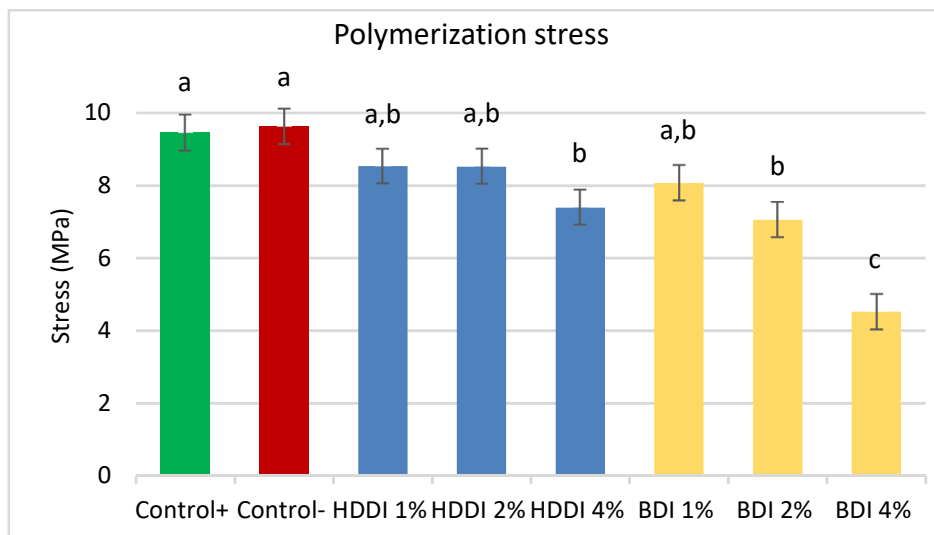


Figure 3. Polymerization stress from experimental composites



Discussion

Different concentrations of thio-urethane silane during silanization process implicated in higher masses of silane coupled to the filler and different polymerization kinetics, degree of conversion, fracture toughness and polymerization stress. Therefore, the null hypothesis of this study was rejected. Higher fracture toughness and lower polymerization stress was obtained with

increasing concentrations of thio-urethane. For concentrations used in this study, higher masses of thio-urethane silane on the filler presented higher thio-urethane effects on the experimental resin composites.

Silane coupling agents are indispensable to chemically bond a resin matrix and an inorganic filler in dental composites. This interaction is responsible for an improve in mechanical properties and chemical resistance (Soderholm, 1981; Zanchi et al., 2015). Silane reactions to glass filler particles are not simple and may be affected by catalyst, pH, solvent and concentration of the solution (Chen and Brauer, 1982; Karmaker et al., 2007). In this study higher concentrations of up to 4% of silane in the silanization solution promoted higher masses of silane bonding to the filler as verified by TGA. Another study has already shown an increase in γ -MPS silane bonding, though concentrations higher than 5% do not seem to increase silane bonding more drastically (Sideridou and Karabela, 2009). Filler particle surface area may limit silane bonding to the available silanol groups. Also, higher concentrations of silane may change the molecular orientation of silane at the filler surface and create multi-layered depositions instead of monolayers (Sideridou and Karabela, 2009). The amount of silane coupled to the filler has been studied for years and some studies have reported different optimal concentrations of silane. This happens because non silanized fillers or fillers with less silane coupled are more hydrophilic. Thus, higher water sorption and hydrolytic degradation can be expected as previously reported (Karmaker et al., 2007; Zanchi et al., 2015). On the other hand, high concentrations of silane may lead to interphase degradation caused by hydrolysis of the oxane bonds between different silane molecules (Zanchi et al., 2015). The effect of degradation was not tested in this study, as only immediate properties were tested. Long-term degradation and properties were not the aim of the present study.

TGA results showed over twice times higher masses of silane coupled to the filler with 2% thio-urethane silane concentration in the silanization solution in relation to the control methacrylate silane. As TGA does not measure filler particle coverage by silane, this result may not represent more silane coupling. Higher masses of silane for thio-urethane silanes can be attributed to the higher molecular weight of thio-urethane molecules in comparison to conventional methacrylate silanes. This can also explain different interaction of the silanized

filler particles with the resin matrix which can cause different viscosity in the unpolymerized composite. Viscosity was not measured in this study, but during composite preparation fillers with higher thio-urethane silane concentration were apparently harder to mix.

Novel functionalized fillers with thio-urethane silanes were able to increase the degree of conversion of resin composites in this study. This conversion increase was already reported in other dental composites modified with thio-urethanes, when added to the resin matrix as monomers (Bacchi et al., 2014; Bacchi et al., 2016). This shows that thiols present in thio-urethane silanes coupled to the surface of filler particles were able to act as chain transfer agents the same way as they do when present in the resin matrix. The degree of conversion increase happens because chain transfer reactions delays the time where diffusion limitations start to terminate the polymerization. Thus, by the time the polymerization reaction reaches its maximum rate and starts to slow down, the degree of conversion is already higher (Berchtold et al., 2002; Pfeifer et al., 2011). Moreover, our results show that unsilanized fillers may lead to higher conversions in comparison to silanized fillers. This is evidenced by a significantly difference in the degree of conversion between the positive and negative control groups and corroborates with previous findings where lower amounts of silane treated fillers resulted in higher conversions (Ferracane et al., 1998).

The delayed vitrification caused by chain transfer reactions not only affects conversion, but also reduces polymerization stress. This stress reduction is related to stress relief by chain rearrangement and flow as growing chains stop and initiates other chains. Both thio-urethane silanes tested in this study presented significant stress reduction. However, the aromatic (BDI) thio-urethane stress reduction was significantly higher compared to the aliphatic (HDDI) oligomer, confirming another study findings (Bacchi et al., 2018). BDI 4% group presented the lowest polymerization stress for all tested materials. The same group also presented lower conversion than other thio-urethane groups and this could be related to the lower polymerization stress. Although, the degree of conversion of this group was still significantly higher than the control positive. Thus, this polymerization stress reduction can be attributed to the effect of thio-urethane addition in the composite.

Mechanical properties like fracture toughness are affected by filler silanization and degree of conversion of the composite. Our results show that silanized fillers promoted higher fracture toughness than unsilanized fillers. Other studies reported this behavior that can be explained by harder crack propagation inside the material with inorganic fillers bonded to the resin matrix through an organofunctional silane (Ferracane et al., 1998). The effects of thio-urethanes addition to the composite was also noted on fracture toughness. Similar to other studies, thio-urethane additives resulted in composites with higher fracture toughness (Bacchi and Pfeifer, 2016; Bacchi et al., 2018). Although only HDDI 4% presented statistically higher fracture toughness to the control positive group, a tendency of increasing toughness with increasing thio-urethane concentrations was noted.

Different thio-urethane oligomers have already been synthesized and tested before. The present study results suggest that the aliphatic thio-urethane (HDDI) is more prone to improve fracture toughness than the aromatic oligomer (BDI). This result is in agreement with another study where a pentafunctional thiol (TMP) was also used and the aliphatic structure resulted in higher fracture toughness than the aromatic (Bacchi et al., 2018). This could be explained by the increased flexibility of the aliphatic structure against the more rigid aromatic conformation.

The evident benefit of using thio-urethane additives was already reported before on the literature. However, different approaches for adding these oligomers to dental composites are still possible. This study showed promising results for improving important material properties through filler functionalization. Thio-urethane silanization of glass fillers may be an alternative for achieving improved dental composites. This approach resulted in improved properties similar to the addition of thio-urethanes in the resin matrix.

Conclusion

Novel filler functionalization with thio-urethane silanes may be a promising alternative for improving dental composites properties by significantly increasing the degree of conversion, fracture toughness and reducing the polymerization

stress. Thio-urethane concentration during filler silanization affected silane coupling and final material properties.

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3.2 Artigo 2

Effect of different strategies for using thio composites

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Abstract

The aim of this study was to evaluate the effect of adding a thio-urethane to experimental composites through filler silanization, resin matrix addition, or both strategies together. The thio-urethane was synthesized by reacting 4,4-methylenebis (cyclohexyl isocyanate), trimethylol-tris-3-mercaptopropionate and 3-(Triethoxysilyl) propyl isocyanate. An unsilanized barium-aluminium-borosilicate-glass filler was silanized with the synthesized thio-urethane in an ethanol/distilled water solution under mechanical agitation. A commercial methacrylate silanized filler was also used. Three different photopolymerizable basic resin matrixes were prepared with Bis-GMA/UDMA/TEGDMA, BisGMA/UDMA/Bis-EMA, and Bis-GMA/TEGDMA mixtures. Methacrylate or thio-urethane silanized glass fillers were added by 50 wt%. Thermogravimetric analysis was used to assess the mass of silane coupled to the filler. Polymerization kinetics and degree of conversion were tested using Near-IR spectroscopy. Fracture toughness, polymerization stress, and viscosity were also tested. The addition of thio-urethane significantly improved fracture toughness and polymerization stress from experimental composites. Viscosity was affected

by resin matrix composition and thio-urethane addition. Degree of conversion, maximum rate of polymerization and degree of conversion at maximum rate of polymerization were significantly affected by thio-urethane addition and basic resin matrix composition. An interaction between factors was also exhibited. The addition of thio-urethanes in dental composites is a good alternative to achieve materials with lower polymerization stress combined with higher mechanical properties. The use of this additive inside the resin matrix together with a thio-urethane silanized glass filler is able to enhance composites properties even further.

Keywords: Composite resins. Mechanical strength. Polymerization stress. Glass filler. Filler functionalization.

Introduction

Dental composites are the most commonly used materials in modern restorative dentistry. It has already been proved that direct restorations using resin composites exhibit good survival rates in long-term follow-ups. (Da Rosa Rodolpho et al., 2011) Nonetheless, restoration fracture is still one of the most important reasons for restoration failure. (Moraschini et al., 2015) Polymerization shrinkage is also a major concern during resin composite restorative procedures. The polymerization stress caused by shrinkage is related to cuspal deflection, lower bond strength, lower fracture resistance, crack formation, gap formation, and marginal staining. (Bicalho et al., 2014; Rosatto et al., 2015) Therefore, resin composite development research has been focused on reducing polymerization stress and improving mechanical properties even further.

Thio-urethanes have already been used as additives in dental composites showing significant material properties improvement. Several studies have reported increased degree of conversion, lower polymerization stress and better mechanical properties with the addition of thio-urethanes to dental composites. (Bacchi et al., 2014; Bacchi et al., 2015; Bacchi et al., 2016; Bacchi and Pfeifer, 2016; Faria and Pfeifer, 2017) Briefly, thiols are efficient chain transfer agents that are able to reduce the rate of polymerization and polymer chain length during methacrylate polymerization. (Hacioglu et al., 2002) Shorter polymer chain length caused by chain transfer delays gelation providing enhanced mobility during conversion. (Pfeifer et al., 2011) As a result higher conversion is achieved when the reaction reaches the diffusion limitation and stress relief is possible by viscous flow before the network gets too rigid.

Thio-urethane additives were first tested inside the composite resin matrix. (Bacchi et al., 2014) After that, a filler silanization alternative was proposed with similar benefits to the resin matrix modification (unpublished data). Although previous studies have already tested the addition of thio-urethanes to dental composites as an oligomer inside the resin matrix and as a modified silane for glass fillers, the combination of these two strategies has never been reported yet.

Therefore, the aim of this study was to evaluate the effect of adding a thio-urethane to experimental composites through filler silanization, resin matrix

addition, both the strategies at the different approaches for adding thio-urethanes to experimental dental composites present similar properties improvement. Also, different basic resin matrix compositions present similar benefits from the addition of thio-urethane.

Materials and Methods

A single thio-urethane was synthesized for this study by reacting 4,4-methylenebis (cyclohexyl isocyanate), trimethylol-tris-3-mercaptopropionate and 3-(Triethoxysilyl) propyl isocyanate in 60 ml of methylene chloride at room temperature. The reaction was catalyzed by triethylamine and oligomers were purified by precipitation in hexane. A rotary evaporator and vacuum were used for solvent evaporation. Formation of thio-urethane bonds and initial products absence was verified by H-NMR and mid-IR spectroscopy as described before. (Bacchi et al., 2015)

A scale-up process was performed for filler silanization based on the filler silanization technique used in a previous study (unpublished data). The silanization process was performed in an ethanol/distilled water solution (80%/20%). Glacial acetic acid was added to adjust the pH to 4.5. After this, 2 wt% of the oligomer was added to the silanizing solution together with 0.7 μm unsilanized barium-aluminium-borosilicate-glass filler. (GM27884 – Schott AG, Landshut - Germany) The solution was kept under mechanical agitation for 24 hours, filtered and dried for 4 days in an oven at 37°C. The amount of silane mass coupled to the filler was verified by taking one small sample of this filler to Thermogravimetric analysis (TGA). Baseline temperature was 25°C and was taken up to 850°C at 10°C/min. The temperature was held at 850°C for 2 minutes and then cooled. The test was performed in a nitrogen atmosphere. An extra sample of a regular methacrylate silanized filler bought from the manufacturer was also analyzed to serve as a control comparison.

A total of 12 experimental composites were manufactured for this study. Groups were distributed according to 3 different resin matrix compositions and presence of thio-urethane. Thio-urethane was added by 20 wt% to the resin

matrix, as a filler silane or both at the resin matrix and as a filler silane. Control groups did not contain any thio-urethane. The resin matrixes used were a mixture of 50 wt% bis-phenol A diglycidyl dimethacrylate, 30 wt% urethane dimethacrylate and 20 wt% triethylene glycol dimethacrylate (BUT), 50 wt% bis-phenol A diglycidyl dimethacrylate, 30 wt% urethane dimethacrylate and 20 wt% ethoxylated bis-phenol A diglycidyl dimethacrylate (BUE) or 70 wt% bis-phenol A diglycidyl dimethacrylate and 30 wt% triethylene glycol dimethacrylate (BT). All monomers were bought from the manufacturer (Esstech, Essington, PA, USA). The photo-initiator system was added to this resin matrix by total matrix weight. It consisted of 0.2 wt% dl-camphoroquinone, 0.8 wt% ethyl 4-dimethylaminobenzoate, and 0.2 wt% 2,6-di-tert-butyl-4-methylphenol (Sigma-Aldrich, St. Louis, MO, USA). Resin composites were manufactured by the addition of 50 wt% of filler. Groups that presented thio-urethane only in the resin matrix and control groups received conventionally manufacturer silanized 0.7 barium-aluminium-borosilicate-glass filler.

A rheometer (HR-1; TA Instruments, New Castle, DE, USA) was used to test the viscosity. Three samples of approximately 1 g of each composite were tested between 20-mm diameter plates in a gap of 0.3 mm. The test was performed with materials at room temperature. A mean value of each sample was obtained until the point at the test where no shear thinning occurred.

Near-infrared spectroscopy (NIR) was used to test polymerization kinetics and degree of conversion. Composite discs (0.8 mm thick and 10 mm diameter) were tested between two glass slides ($n=3$). Disc samples were light cured with a mercury arc lamp (EXFO Acticure 4000 UV Cure; Mississauga, Ontario, Canada) filtered at 320-500 nm for 300 seconds. Incident irradiance was 20 mW/cm² considering the distance from the sample to the light guide tip. A low light irradiance was used for polymerization kinetics in this study as an attempt to study different kinetics on the polymerization reaction. Polymerization kinetics was assessed recording the methacrylate absorption peak at 6165 cm⁻¹ during light curing.

Fracture toughness was tested according to the American Society for Testing Materials standard (E399-90). Single-edge notch beam specimens ($n=6$)

were manufactured in a split steel mold (5 x 2 x 25 mm) with a razor blade insert of 2.5 mm and light cured for 240 seconds. Specimens were tested in 3-point bend at a cross-head speed of 0.5 mm/minute on a universal testing machine. Fracture toughness was calculated from the critical stress intensity factor as previously described. (Ferracane and Berge, 1995)

Bioman method was used to assess the polymerization stress (Watts and Satterthwaite, 2008). A standard amount of composite (n=5) with 0.5 mm thickness was polymerized between a silanized silica slab and a roughened steel piston. The piston was also covered with a metal primer to improve adhesion to the metal. The test settings corresponded to a C-factor of 4. Composites were light-cured through the silica slab for 300 seconds with the same mercury arc lamp. Light irradiance reaching the samples through the slabs was the same as used for polymerization kinetics and degree of conversion. Maximum value during the test was considered the polymerization stress for each sample.

Data were analyzed using the statistical software SPSS (IBM Corp, Armonk, NY, USA). Two-way ANOVA, one-way ANOVA, and Tukey post-hoc tests were used at a significance level of 0.05. Two-way ANOVA factors were: (1) basic resin matrix composition (BUT, BUE and BT) and (2) thio-urethane addition (no thio-urethane, thio-urethane filler, thio-urethane matrix and thiourethane filler + matrix).

Results

TGA results are reported in Figure 1. The mass of silane coupled to the filler corresponded to 7.8% of the filler total mass. Higher silane mass was found for the experimental silanized filler compared to the conventional methacrylate control.

Degree of conversion (DC), maximum rate of polymerization (Rmax) and degree of conversion at maximum rate of polymerization (DC at Rmax) results are presented at Table 1. DC, Rmax, and DC at Rmax were significantly affected by the two factors, basic resin composition ($p < 0.001$) and thio-urethane addition ($p < 0.001$). A significant effect of the interaction between factors was also

detected ($p < 0.001$). BUE composites presented lower DC and Rmax than other basic matrix compositions.

Figure 1. Thermogravital analysis for thio-urethane and methacrylate silanized fillers

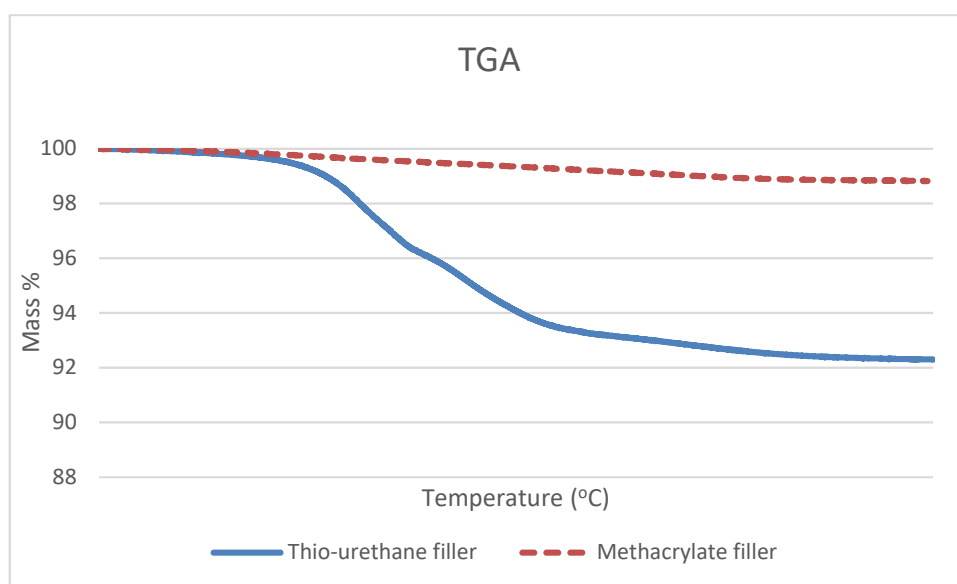


Table 1. Degree of conversion and polymerization kinetics

	DC (%)	Rmax (%/s)	DC at Rmax (%)
Control BUT	50.3 (0.92) a	1.36 (0.38) a	10.2 (0.45) a,b,c
TU filler BUT	51.6 (0,17) a	0.97 (0.01) b	14.1 (1.32) c,d
TU matrix BUT	36.7 (0.43) c	0.32 (0.04) h	16.6 (2.58) d
TU filler + matrix BUT	50.0 (0.87) a	0.59 (0.03) d,e,f	10.8 (0.79) a,b,c
Control BUE	45.3 (0.24) a,b	0.68 (0.01) d	8.5 (0.39) a,b
TU filler BUE	45.4 (1,00) a,b	0.58 (0.03) e,f	13.2 (2.87) c,d
TU matrix BUE	40.6 (0.43) b,c	0.41 (0.02) g	11.2 (0.80) a,b,c
TU filler + matrix BUE	39.8 (0.64) b,c	0.42 (0.02) g	13.6 (2.75) c,d
Control BT	51.7 (0.43) a	1.09 (0.04) a	8.2 (0.67) a
TU filler BT	50.9 (0.31) a	0.86 (0.03) c	11.2 (0.48) a,b,c
TU matrix BT	50.1 (0.26) a	0.64 (0.05) d,e	13.0 (1.23) b,c,d
TU filler + matrix BT	51.2 (0.72) a	0.54 (0.02) f	10.6 (1.18) a,b,c

Viscosity results are reported in Figure 2. Two-way ANOVA showed a significant effect for the addition of thio-urethane and basic resin matrix composition over viscosity ($p < 0.001$). The interaction between factors was also significant ($p < 0.001$). All BUE groups showed higher viscosity compared to other resin matrixes. The addition of thio-urethane to the matrix of BUE and BT groups significantly increased material viscosity.

Figure 3 shows fracture toughness results. Two-way ANOVA detected an effect of thio-urethane addition to fracture toughness ($p < 0.001$). No effect of the basic resin matrix was detected for this test. Thio-urethane addition to the resin matrix and filler presented the highest fracture toughness values.

Polymerization stress results are presented in Figure 4. Thio-urethane addition and basic matrix composition had a significant effect over polymerization stress according to two-way ANOVA (both $p < 0.001$). The interaction between factors was also significant ($p < 0.001$). Lowest polymerization stress values were observed for all groups with the addition of thio-urethane to the resin matrix and filler together.

Figure 2. Viscosity for experimental composites

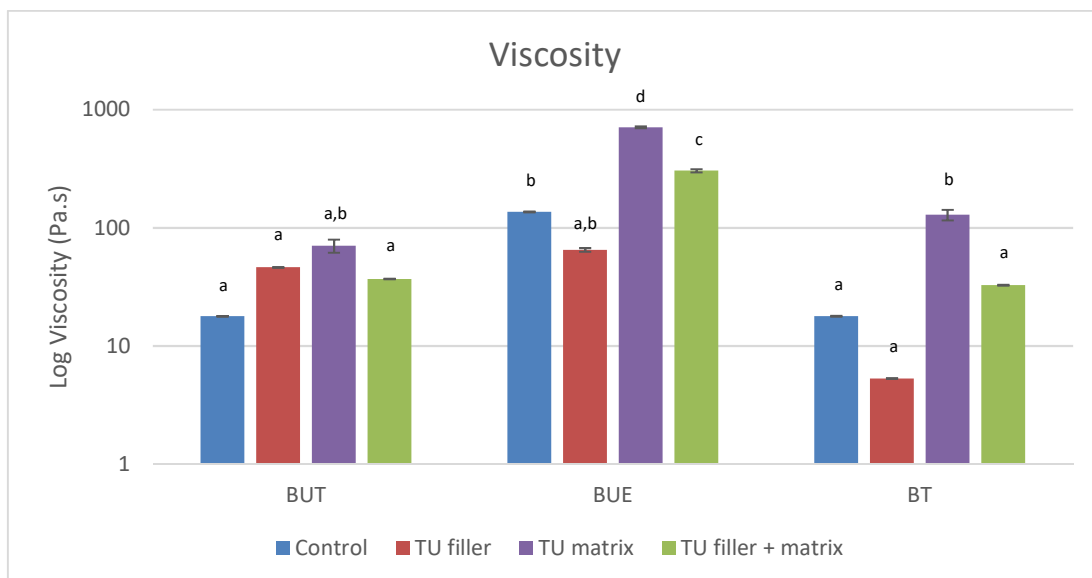


Figure 3. Fracture toughness for experimental composites

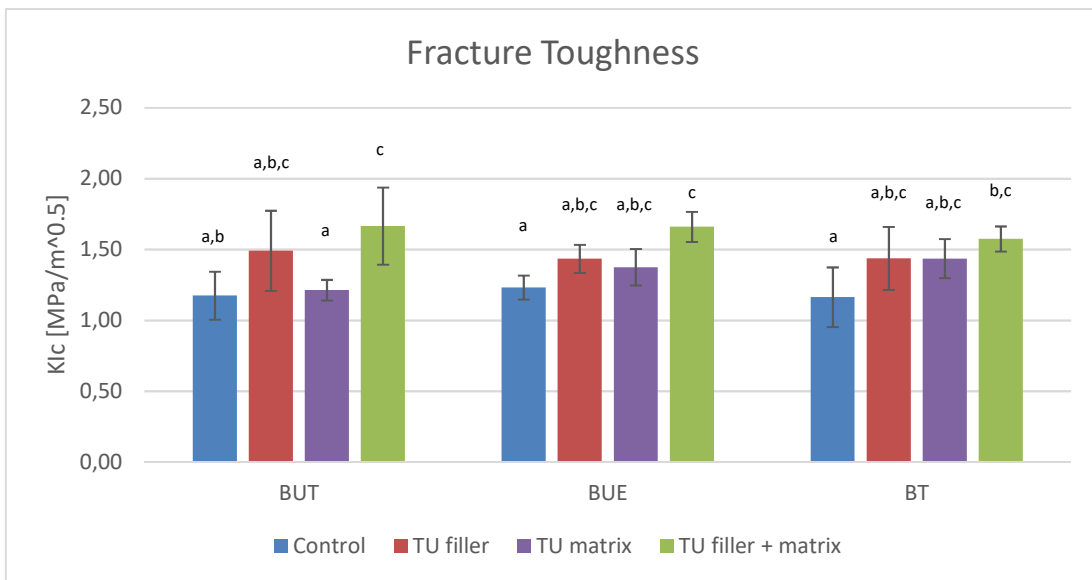
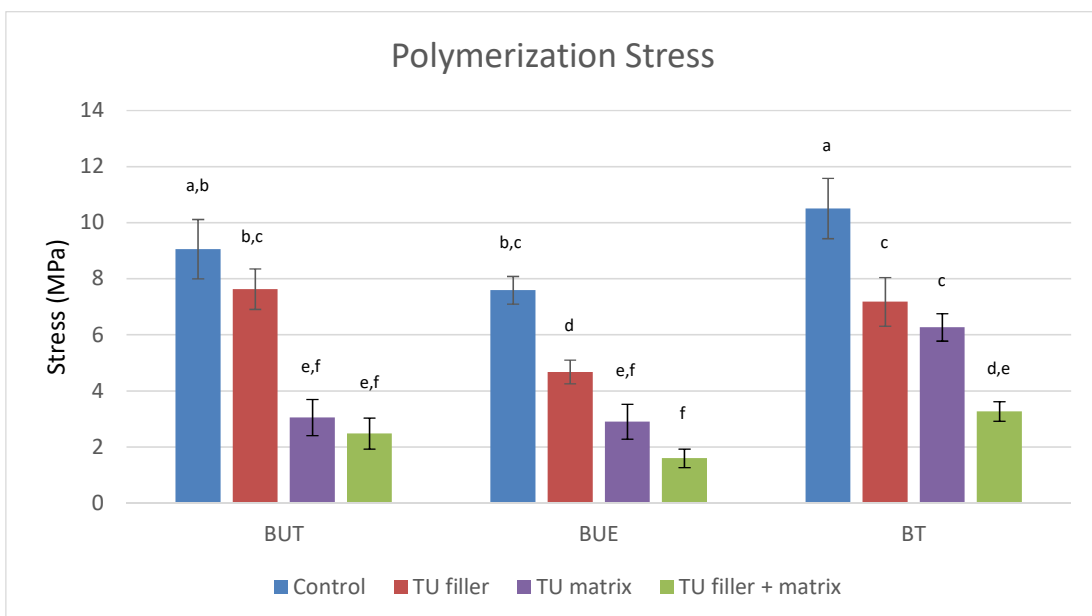


Figure 4. Polymerization stress for experimental composites



Discussion

According to our results, the addition of thio-urethanes to experimental resin composites through different approaches resulted in significantly different material properties. Also, the basic resin matrix composition affected all the

properties evaluated in this study. Therefore, the null hypothesis was rejected. The addition of thio-urethanes to the resin matrix together with a silanized glass filler presented improved benefits for experimental dental resin composites.

TGA showed higher mass of silane coupled to the filler for the experimental silanized filler compared to a commercial methacrylate silanized filler. Results from TGA express only the mass of silane present on the filler before high-temperature increase. A quantitative analysis of particle coverage cannot be performed by TGA. Other studies have already characterized the adsorption of silane on the filler using FTIR. (Karmaker et al., 2007; Soderholm and Shang, 1993) In the present study, the experimental thio-urethane silanized filler exhibited higher silane mass than the methacrylate control. This could be expected as the thio-urethane silane has a higher molecular weight.

Viscosity of dental resin composites is affected by filler loading, filler size, monomer composition and temperature. (Al-Ahdal et al., 2014; Lee et al., 2006) Changes in viscosity of experimental composites were already reported for silanized and unsilanized fillers. (Karmaker et al., 2007) BUE and BT groups that received thio-urethane silanized fillers presented higher viscosity than control groups. On the other hand, opposite results were observed for BUT. This could be explained by the different interaction of the silanized filler with various resin matrixes. The interaction between the two factors detected by two-way ANOVA evidenced this behavior. Groups with different basic matrix compositions presented significantly different viscosities as expected. Also, highest viscosities were observed for groups where thiourethane was added to the resin matrix because the thio-urethane oligomer used in this study is much more viscous than the other diluent monomers used. Increased viscosity for materials containing thio-urethanes was already reported before. (Bacchi and Pfeifer, 2016)

Polymerization kinetics can be affected by material viscosity. Homopolymers from monomers with higher viscosity present lower degree of conversion because increased viscosity reduces mobility, impairing the polymerization reaction. (Gajewski et al., 2012) The effect of basic resin matrix viscosity in final conversion was observed in our results. Significantly lower degree of conversion was observed for BUE followed by BUT with both groups

presenting higher viscosity. The effect was detected by two-way ANOVA. Likewise, R_{max} can also be influenced by resin viscosity. (Dickens et al., 2003)

Thiols present on thio-urethane oligomers are able to modify polymerization kinetics. Chain transfer reactions caused by thiols during conversion reduce the polymerization rate. This reduction was already reported on other studies and corroborates with our results. (Bacchi et al., 2018; Pfeifer et al., 2011) Slower polymerization rates may also lead to changes on the final conversion of the system. When lower polymerization rates are associated with delayed deceleration, higher degree of conversion may occur. (Berchtold et al., 2002) Higher conversion was reported for experimental composites containing thio-urethane, inside the resin matrix, with 25 to 40 wt% filler. (Bacchi et al., 2016) On the other hand, thio-urethane containing composites with filler loading of 70 wt% did not present higher degree of conversion than control groups. (Bacchi et al., 2018) This may be explained by a lower overall concentration of thio-urethane on the total mass of composite. BUT group with thio-urethane added to the matrix presented higher viscosity and lower degree of conversion between BUT groups. However, when thio-urethane was added to the resin matrix and filler, a lower viscosity material associated with higher conversion was obtained. Thus, the increased viscosity caused by thio-urethane addition to the resin matrix and basic resin matrix composition could explain the lower degree of conversion achieved by some groups.

The addition of thio-urethane to experimental composites resulted in higher fracture toughness. Thio-urethane addition effect was noticed by the factorial analysis. Despite that, the significantly lower degree of conversion observed in some groups associated with high fracture toughness highlights the benefit of thio-urethanes for this property. Similarly to other studies, using thio-urethanes as additives for dental composites increases fracture toughness. (Bacchi et al., 2016; Bacchi et al., 2018) Although, this is the first study that directly compares the use of this additives in the resin matrix or on a silanized filler. Also, the combination of this strategies has never been tested in previous studies.

Polymerization stress is an important material property for dental composites that affects the tooth and restoration integrity. Polymerization stress is also related to the composite ease of use for the professional. This is the reason why bulk-fill materials have been gaining so much popularity over the last years. Materials that are able to generate less stress can significantly reduce resin insertion time by facilitating incremental technique. (Vianna-de-Pinho et al., 2017) Thio-urethane additives significantly reduce polymerization stress. (Bacchi et al., 2014; Bacchi et al., 2015; Bacchi et al., 2016) Moreover, the approach of adding thio-urethanes to both resin matrix and filler silane resulted in higher stress reduction.

Manufacturers use different alternatives for developing bulk-fill materials. A fundamental characteristic of this type of materials is low polymerization stress. New monomers have been developed to achieve this feature. (Ilie et al., 2007; Ilie and Hickel, 2011) Modern bulk-fill composites are able to cure properly in higher depths and present reduced polymerization stress. (Goracci et al., 2014; Jang et al., 2015) However, current bulk-fill composites generally present limitations on their mechanical properties. (Leprince et al., 2014) New resin composites using thio-urethanes may result in excellent bulk-fill materials with enhanced mechanical properties. Further studies comparing commercial bulk-fill composites to thio-urethane containing materials could demonstrate the advantages of using this technology over current low-stress options.

Conclusion

The addition of thio-urethanes in dental composites is a good alternative to achieve materials with lower polymerization stress combined with higher mechanical properties. Adding thio-urethanes to the resin matrix or to a silanized filler are beneficial for material properties. However, the use of both strategies together may enhance composites properties even further.

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3.3 Artigo 3

Effect of pre-heating on resin composites and thio-urethane addition to bulk-filled restorations

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Highlights

Pre-heating does not reduce polymerization stress of resin composite restorations

Thio-urethane addition increases resin composite degree of conversion

Thio-urethane addition reduces resin composite polymerization stress

Summary

Objectives: The aim of this *in vitro* study was to test the effect of different bulk-fill techniques using a pre-heated resin composite and a thio-urethane modified version of this material to the polymerization stress, intrapulpal temperature change and degree of conversion.

Methods: Forty-eight extracted third molars were divided in 6 groups. A conventional resin composite (Z250XT/3M) was used at two temperatures, room

temperature and pre-heated at 68°C, and with two light-curing times, 20 and 40 seconds. For the experimental composite a thio-urethane was synthesized and added to the resin matrix and silanized in a glass filler. A commercial bulk-fill resin composite was used as a comparison (Filtek BulkFill/3M). Class I cavities (4mm depth x 5mm diameter) were filled with a single increment. Acoustic emission test was used as a real-time polymerization stress assessment. The intrapulpal temperature change was recorded with a thermocouple and bottom/top degree of conversion measured by Raman spectroscopy.

Results: Two-way ANOVA detected a significant effect of light curing time over temperature increase ($p < 0.001$). Pre-heating the resin composite did not influence the intrapulpal temperature change ($p = 0.077$). The experimental composite containing thio-urethane exhibited significantly less acoustic events (AE). Groups with pre-heated composites did not result in significantly different AE. Filtek BulkFill and the thio-urethane experimental composite presented significantly higher degree of conversion.

Significance: Resin composite pre-heating may not be able to reduce polymerization stress in direct restorations. However, thio-urethane addition to a resin composite could reduce the polymerization stress while improving the degree of conversion.

Key-words: Dental restoration. Polymerization stress. Heating. Composite resins. Thio-urethane additives.

1. Introduction

Dental resin composites are widely used for adhesive restorative procedures. Their physical and mechanical properties have significantly evolved since their introduction in the market. The approximation of monomers during the polymerization reaction causes material shrinkage. In this way, volumetric shrinkage induces stress to the surface where the resin composite is being adapted [1]. Although volumetric shrinkage is related to polymerization stress, other factors including elastic modulus, gelation point and novel monomers can also help determine polymerization stress [2-4]. The effect of the polymerization stress generated during placement of direct restorations can lead to microleakage, cuspal deflection, cuspal fractures, and marginal defects [5-9]. Therefore, reducing polymerization stress through incremental techniques or new material development is a constant research aim.

Resin composite pre-heating is able to modify some of the material properties. At higher temperatures resin viscosity is reduced and higher conversion can be achieved [10, 11]. Conversion reaction is favored at higher temperatures because in this situation monomer mobility is increased and a higher polymerization rate also occurs [12]. As a result of higher conversion, an unfavorable increase in polymerization stress can be expected [13]. Despite this, significant stress relaxation was observed when a resin composite is heated to 60°C [14]. Stress relaxation during conversion is possible due to viscous flow or chain relaxation [15]. Moreover, as conversion increases, better mechanical properties are also expected [16]. Therefore, there is a possibility that pre-heated resin composites could be used in a bulk-fill incremental technique with reduced polymerization stress.

Thio-urethane additives have been developed in the search for materials with reduced polymerization stress. Thio-urethanes are oligomers that have pending thiols from the backbone and are able to copolymerize in a methacrylate matrix [17]. Thiols are chain transfer agents able to delay the gelation and reduce the polymerization rate leaving opportunity for increased final conversion and viscous flow [18]. Studies testing experimental and commercial composites modified with thio-urethanes have reported significant stress reduction combined

with increased degree of conversion and mechanical properties [17, 19-21]. Although several studies reported important properties improvement with these new additives, no studies have tested them as bulk fill materials against commercially available materials. If thio-urethane modified composites present same or higher stress reduction than commercial bulk-fill composites, a new class of low-stress materials with even higher mechanical properties could be achieved. Testing a thio-urethane modified composite against a commercial bulk-fill composite in high C-factor cavities should help clarify if this mechanism of stress reduction works better than the ones available on the market.

Therefore, the aim of this *in vitro* study was to test the effect of different bulk-fill techniques using a pre-heated resin composite and a thio-urethane modified version of this material to the polymerization stress, intrapulpal temperature change and degree of conversion. A conventional resin composite was used at room temperature and pre-heated at 68°C and compared to a high viscosity bulk-fill resin composite. The tested hypothesis was that pre-heating would reduce the polymerization stress and increase the degree of conversion. Also, a thio-urethane modified resin composite would present similar stress reduction to a bulk-fill resin composite.

2. Methods and materials

2.1. Thio-urethane synthesis and filler silanization

A thio-urethane was synthesized for this study by reacting 4,4-methylenebis (cyclohexyl isocyanate), trimethylol-tris-3-mercaptopropionate and 3-(Triethoxysilyl) propyl isocyanate in 60 ml of methylene chloride at room temperature. Triethylamine was used to catalyze the reaction and oligomers were purified by precipitation in hexane. A rotary evaporator and vacuum were used for solvent evaporation. Formation of thio-urethane bonds and initial products absence was verified by H-NMR and mid-IR spectroscopy as previously described [19].

A glass filler was silanized with the synthesized thio-urethane. Silanization process was performed in an ethanol/distilled water solution (80%/20%). Glacial

acetic acid was added to adjust the pH to 4.5. After this, 2 wt% of the oligomer was added to the silanizing solution together with 0.7 μm unsilanized barium-aluminium-borosilicate-glass filler. (GM27884 – Schott AG, Landshut - Germany) The solution was kept under mechanical agitation for 24 hours, filtered and dried for 4 days in an oven at 37°C. A thio-urethane silanized filler was obtained for the experimental resin composite.

2.2. Experimental thio-urethane composite

An experimental composite was prepared using a commercial resin composite (Z250XT, 3M ESPE, St Paul, MN, USA). Previous studies have reported good properties improvement with the addition of 20 wt% of thio-urethane in relation to the resin matrix weight [17]. Therefore, 20 wt% of the synthesized thio-urethane was added to the commercial composite, considering that this composite has 18 wt% resin matrix. To add the thio-urethane to the resin composite filler and keep the initial filler loading, the thio-urethane silanized filler was added until filler loading reached 82 wt% again.

2.3. Specimen preparation

Forty-eight freshly extracted human third molars were used in this study. Teeth were stored refrigerated in 0.5% chloramine-T solution before use. All teeth were extracted due to therapeutic reasons and the protocols used were approved by the local ethics committee review board (n. 1.173.555).

Roots were removed using a low-speed diamond saw by performing a cut 3 mm below the cement-enamel junction. Pulpal tissue was gently removed with a dentin excavator to clear the pulpal chamber. After this, a small hole was done with a round diamond bur next to the cement-enamel junction to create a lateral access to the pulpal chamber. Occlusal 4 mm deep class I cavities were performed with a large round end taper diamond bur (#3131 – KG Sorensen, Cotia, SP, Brazil). A 5mm diameter round template was placed over the center of the occlusal surfaces to establish the conformation of the cavity preparation. Cavities were manually done with a highspeed handpiece using water spray refrigeration and the dimensions were checked with a probe during the preparation. Teeth were randomly assigned to one of the 6 experimental groups.

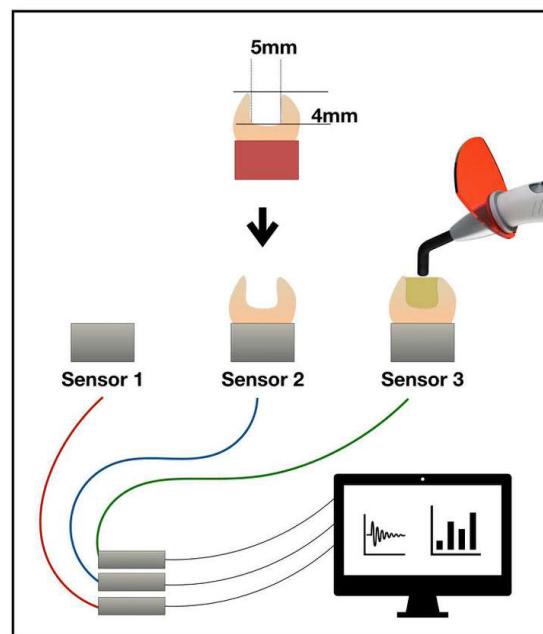
2.4. Acoustic emission

Before the restoration procedure samples were attached to a WDI differential acoustic emission sensor from Physical Acoustics Corporation (PAC), see figure 1. Root surfaces were attached to the sensor with cyanoacrylate adhesive. Three channels from a PAC Disp 16C acoustic emission system were used to record acoustic events generated by polymerization stress. Each channel was connected to a different acoustic sensor of the same model and pre-amplified with a 60dB gain. The first channel received the signal from the sensor where the testing tooth was attached. Second and third channels were used as guard sensors to detect false calls. Second channel received the signal from a sensor with a non-testing tooth and third channel from a sensor with a free surface. After the test, signals recorded from second and third sensors were used to compare and remove false signals from the environment. A threshold of 32dB was used for all the channels. The number of acoustics events and their respective amplitudes were recorded from the start of light curing until 20 minutes after. The resulting signals were filtered and reported as total AE and AE higher than 60 dB.

2.5. Intrapulpal temperature

The remaining dentin thickness at the pulpal floor was measured with a caliper at 3 different spots. A mean remaining dentin thickness was calculated for each teeth and group to avoid different test conditions. The pulpal chambers were filled with thermal conducting paste. A type K thermocouple was inserted inside the pulpal chamber through the lateral hole near the cement-enamel junction. Tests were done in a controlled temperature room with constant baseline temperatures. Temperature changes (Δt) were recorded between the start of light curing and the maximum temperature reached. Temperature changes during adhesive activation were also recorded. One-way ANOVA and Tukey post-hoc tests were used for statistical analysis ($\alpha=0.05$).

Figure 1. Schematic diagram of the Acoustic Emission test set-up with two guard and one test sensors.



2.6. Restorative procedures

After attached to the AE sensor, teeth were restored according to the different experimental groups. A universal adhesive (SingleBond Universal, 3M ESPE, St Paul, MN, USA) was used as self-etch in dentin and selective enamel etch was performed for 30 seconds. Enamel was washed with water spray for 30 seconds and cavities were dried with cotton pellets. The adhesive was applied for 20 seconds with active application. Solvent evaporation was performed with 10 seconds of gentle air. A LED curing light was used for 10 seconds. Light irradiance was checked with a radiometer throughout the study. Constant light irradiance ($1,300 \text{ mW/cm}^2$) was observed during all the experiment. Two materials (Filtek Z250XT and Filtek BulkFill, 3M ESPE, St Paul, MN, USA) were divided into 6 experimental groups. Cavities were restored with a single increment according to the following groups:

1. Filtek Z250XT – Activated for 20 seconds
2. Filtek Z250XT – Activated for 40 seconds
3. Filtek Z250XT at 68°C – Activated for 20 seconds
4. Filtek Z250XT at 68°C – Activated for 40 seconds

5. Filtek BulkFill – Activated for 20 seconds (according to manufacturer instructions)
6. Filtek Z250XT w/ thio-urethane – Activated for 40 seconds

For groups with pre-heated material, compules were loaded with resin composite and placed inside a digital heating device set to 68°C for at least 5 minutes. A Centrix syringe was used to deliver the resin composite inside the cavity in a single increment. Time was controlled so that each restoration had to start the light activation at 1 minute after removing the compule from the heating device.

2.7. Degree of conversion

After restored, teeth were sectioned in 1 mm slices with a low-speed diamond saw under water irrigation. Slices were taken to micro-Raman spectroscopy (SENTERRA, Bruker Optics, Ettlingen, Germany). An initial spectrum was collected for each resin composite before polymerization to identify and compare the reaction peaks. Five samples from each group were analyzed for calculating the degree of conversion. Only central slices from restorations were used to standardize for light exposure. One reading 50 μm from the top surface and one from the bottom surface of the restoration were recorded. The phenyl peak, observed at 1,610 cm^{-1} , was used as the reference peak and the vinyl peak, observed at 1,640 cm^{-1} , as the reaction peak. The degree of conversion was calculated using the ratio between the reaction and internal reference peak areas as the ratio of polymerized to unpolymerized resin composite. One-way ANOVA and Tukey post-hoc test was used for statistical analysis ($\alpha=0.05$).

3. Results

3.1. Intrapulpal temperature

Table 1 shows remaining dentin thickness on the pulpal floor and intrapulpal temperature change during the restorative procedures. Pulpal dentin thickness was similar for all groups ($p=0.834$). Two-way ANOVA detected a

significant effect of light curing time over temperature increase ($p < 0.001$). Pre-heating the resin composite did not influence the intrapulpal temperature change ($p = 0.077$). Z250XT 68°C 40s presented significantly higher temperature change, similar to the other two groups activated for 40s. For pre-heated groups, temperature change during light-curing (after resin composite insertion) was also significantly higher when extended light-curing was performed. Adhesive polymerization induced similar temperature changes to the restorations light-cured for 20 seconds.

Table 1. Remaining pulpal dentin thickness and intrapulpal temperature variations during restorative procedures.

	Pulpal dentin thickness	Δt °C (total)	Δt °C (during light-curing)
Adhesive*		1.9 (0.6) A	
Z250XT 20s	1.7 (0.6) A	1.7 (0.5) A	
Z250XT 40s	1.7 (0.6) A	2.4 (1.2) A,B	
Z250XT 68° 20s	1.9 (0.7) A	1.7 (0.3) A	1.1 (0.2) A
Z250XT 68° 40s	1.7 (0.6) A	3.2 (0.7) B	2.1 (0.5) B
Filtek BulkFill 20s	1.8 (0.7) A	1.4 (0.1) A	
Z250XT TU 40s	2.0 (0.7) A	2.5 (0.9) A,B	

*Samples from all groups during adhesive polymerization, prior to resin composite insertion.

Groups with different letters in the same column represent statistically significant differences.

3.2. Acoustic emission

Acoustic emission results are presented at Table 2. The experimental composite containing thio-urethane exhibited significantly less total AE and $AE > 60$ dB. Filtek BulkFill presented different results when only higher than 60 dB were considered. For total AE, Filtek BulkFill presented significantly more events than all groups. Groups with pre-heated composites did not result in significantly different AE. Groups with 20 and 40 seconds of light-curing presented similar AE. The effects of light curing time and composite pre-heating were not significant in Two-way ANOVA. Figure 2 shows the cumulative number of AE over time for all

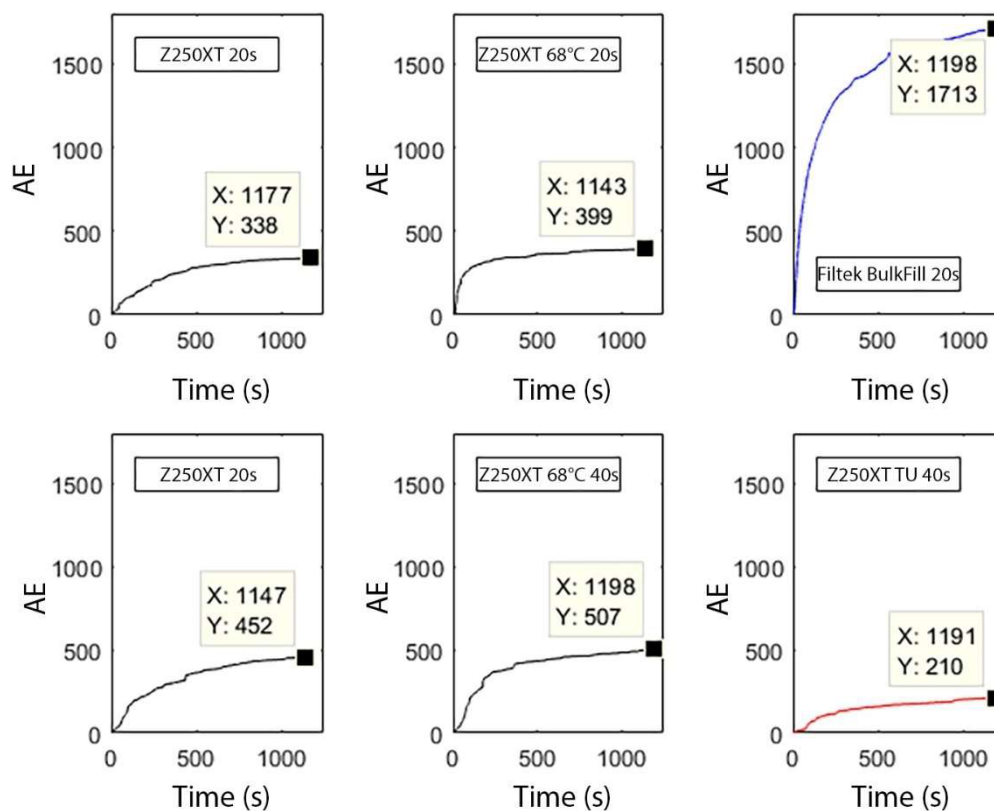
samples of each group. An acceleration on the cumulative number of AE was observed for pre-heated groups.

Table 2. Mean number of Acoustic Events (AE) from light curing start until 20 minutes after.

		AE total		AE>60 dB	
		Light curing time		Light curing time	
		20 s	40 s	20 s	40 s
Z250XT	At room temperature	42.4 (19.3) A,a	56.5 (16.4) A,a	4.6 (4.2) A,a	5.4 (2.1) A,a
	Pre-heated at 68 °C	49.9 (27.1) A,a	63.5 (32.9) A,a	4.1 (3.9) A,a	5.9 (3.6) A,a
Filtek BulkFill		214.1 (127.2) b	-	3.5 (3.2) a	-
Z250XT TU		-	26.3 (15.4) b	-	1.4 (1.4) b

Groups with different upper case letters in the same line represent statistically significant differences. Groups with different lower case letters in the same column represent statistically significant differences.

Figure 2. Cumulative number of total Acoustic Events (AE) for all specimens



3.3. Degree of conversion

Table 3 shows degree of conversion results. Filtek BulkFill and the thio-urethane experimental composite presented significantly higher conversion than other groups, at top and bottom. Except for Filtek BulkFill, all groups presented lower degree of conversion at the bottom. Bottom to top ratios are listed in Table 3 and are all above 0.80. Pre-heating and light curing time did not affect the degree of conversion at the top or bottom surfaces from the restorations.

Table 3. Degree of conversion measured by Raman spectroscopy and bottom to top ratio.

	Degree of conversion		Bottom/top ratio
	Top	Bottom	
Z250XT 20s	67.3 (2.7) A	57.2 (2.5) A	0.85
Z250XT 40s	68.5 (1.0) A	61.5 (2.3) A	0.89
Z250XT 68° 20s	67.2 (2.7) A	62.2 (8.8) A	0.92
Z250XT 68° 40s	69.8 (2.6) A	61.3 (6.3) A	0.88
Filtek BulkFill 20s	76.3 (2.9) B	79.0 (2.4) B	1.0
Z250XT TU 40s	78.0 (3.3) B	73.6 (1.2) B	0.93

Groups with different letters in the same column represent statistically significant differences.

4. Discussion

Different bulk-fill techniques were tested with pre-heated resin composites and a thio-urethane modified material in this *in vitro* study. Resin composite pre-heating did not affect the intrapulpal temperature change. Also, pre-heating did not affect the polymerization stress and degree of conversion of the high C-factor bulk-filled restorations. Therefore, the first hypothesis was rejected as resin composite pre-heating did not reduced the polymerization stress or increased the restoration degree of conversion. On the other hand, a thio-urethane modified resin composite presented significant stress reduction according to the acoustic emission test. Thus, the second hypothesis was accepted.

Despite having good results in laboratory tests, obtaining the benefits of pre-heating resin composites in clinical situations may be a challenge. Higher degree of conversion and improved mechanical properties have been shown in some laboratorial studies testing the effect of pre-heating on dental composites [11, 12, 16]. However, this improvement may not be achieved when a resin composite is used for a restoration in a patient. Under clinical conditions handling time is a crucial problem that causes the material to lose temperature before light-curing. It has been shown that after removing the pre-heated resin composite inside a compule from the heating device the material temperature drops 50% within 2 minutes [22]. Moreover, the temperature drop before the start of light-curing may be even higher when the material is adapted and sculpted inside a cavity. After removed from the heated compule the heat dissipation to the tooth and the ambient temperature should increase temperature drop even further. Therefore, at the time light-curing starts the resin composite may be in a temperature where pre-heating benefits are not observed.

In this study the intrapulpal temperature change for pre-heated resin composites was similar to the exhibited by room temperature materials when light-cured with the same time. Temperature change was only significantly higher when longer light-curing times were used. This result corroborates with another study where 40 seconds of light exposure induced significantly higher intrapulpal temperatures than 20 seconds [23]. Also, according to Daronch *et al*, the temperature of the resin composite is not expected to affect the intrapulpal temperature before or after light-curing [24]. Several studies have shown that light exposure is responsible for considerable intrapulpal temperature change and some of the factors associated increased temperatures changes are light energy, time of exposure and light source [25-28].

Intrapulpal temperature change with extended light-curing time (40 seconds) ranged between 2.4 and 3.2°C in this study. Although temperature increase was statistically higher for this light-curing time, this temperature change may not be significant. The most known temperature threshold responsible for pulpal injury is 5.5°C, in which 15% of pulps evolved to necrosis. This threshold comes from a study performed in monkeys [29]. In this study temperature changes were induced too drastically with a soldering iron of 275° and may not

translate to the temperature changes occurring in dental procedures. However, another study performed in humans with different methods has reported no symptomatic or histological pulp injury with temperature increases ranging from 8.9 to 14.7°C [30]. Thus, all temperature changes caused in this study were minor and could be considered safe to the pulpal tissue.

Acoustic emission has been used for estimating *in vitro* real time polymerization stress caused by resin composites in direct restorations. Previous studies show a correlation between polymerization stress and the number of AE [31-33]. AE are usually explained by other authors as the occurrence of interfacial debonding. Interestingly, in our study two completely different results for AE can be observed. When total AE were considered, the bulk-fill resin composite exhibited almost 4 times more AE than the conventional material. This result was obviously not expected as Filtek BulkFill should not have higher polymerization stress than Z250XT [34]. Furthermore, the same materials presented similar number of AE in a recent acoustic emission study [35]. One important fact that must be noticed regarding these results is the difference between the total number of AE captured by different studies. The same previous study reports mean AE ranging from 6.0 to 12.6 for different bulk-fill and conventional resin composites [35]. Some of the other previous studies present even less mean AE [31, 36]. The difference between our results and the others found in the literature is explained by the difference in the detection levels from each study.

Acoustic emission is a widely used non-destructive test that is capable of detecting structural defects such as crack formation and propagation, deformation, sliding, and fracture [37]. Although acoustic emission is a very sensitive test that is even able to locate the AE source, comparison of results from different test set-ups may not be possible. Different acoustic emission sensors present specific response curves with higher or lower response to varying wave frequencies. Thus, an AE may be recorded with different amplitudes (dB) or even not recorded when different sensors are used. Moreover, pre-amplification and amplification gain is also responsible for different signal acquisition. In our study a higher detection level setting was used in comparison to the previous studies. The differential wideband sensor and gain used captured more AE than the others previously used. This explains why our number of AE

was higher. When filtering only AE higher than 60 dB the number of AE observed was similar to the results reported by other studies.

Results from AE>60 dB showed slightly fewer AE for Filtek BulkFill in comparison to Z250XT pre-heated or at room temperature, although not statistically different. This result could be expected and corroborates with the results from a previous study [35]. Light curing-time and pre-heating did not significantly affect total AE and AE>60 db. On the other hand, the thio-urethane modified resin composite exhibited statistically significant lower total AE and AE>60 dB. Experimental thio-urethane composites have been reported with considering low polymerization stress [20, 21, 38] and according to our results this technology seem to be a more effective low-stress additive compared to a commercial bulk-fill resin composite.

Few acoustic emission studies observing the effect of resin composite polymerization stress are present in the literature. Further studies with high detection levels should observe the reason for much higher number of AE in specific materials. An AE may not be explained merely by resin composite debonding, other factors including stress relaxation inside the material could be responsible for generating an AE. A free shrinking resin composite placed over an acoustic emission sensor was already reported with no detectable AE, however this is the only report in the literature from a single material [32]. Also, number of acoustic events alone may not be enough to understand the effects of polymerization stress on resin-tooth interfaces. For example, one AE with longer duration or higher amplitude may represent a more important structural defect than a number of AE with shorter durations and lower amplitudes. Attention must be taken for these parameters when analyzing acoustic emission results in further studies to avoid wrong results interpretation for some materials.

Resin composite pre-heating increases the degree of conversion by favoring radical mobility and increasing the polymerization rate [39]. In a previous study, restorations performed with pre-heated resin composites did not enhance the degree of conversion [40]. Similarly, an increase in the degree of conversion was not observed in our results. However, cumulative AE graph shows that the stress evolved more rapidly for the pre-heated materials. This could be caused

by a higher resin composite temperature at the time of light-curing slightly altering the polymerization kinetics. Other factor that can contribute to quicker stress evolution is a larger temperature loss after conversion of pre-heated materials causing higher volumetric shrinkage.

The light-curing device used in this study was a high-intensity LED. Light irradiance was monitored in a radiometer ($\sim 1,300 \text{ mW/cm}^2$) and kept stable over the experiments. Although conventional resin composite increments of 4 mm depth are not indicated, the conventional resin composite used presented adequate degree of conversion in the bottom of the restoration. Bottom/top ratios were high for all experimental groups and similar to the most used parameter for degree of conversion (0.9) [41]. Interestingly, the bulk-fill resin composite presented a bottom/top ratio higher than 1.0. This result show that a high-intensity curing-light may be able to cure deep resin increments. However, light attenuation is an important issue that must be considered and resin composites with different shades or opacities can present lower light transmission [42].

Experimental resin composites with the addition of thio-urethanes have been reported with higher degree of conversion, lower polymerization stress and improved mechanical properties [20, 21, 38]. Despite that, this is the first study to test a thio-urethane experimental resin composite against a commercial bulk-fill material. Our results suggest that this new technology present a more effective stress reduction effect. The experimental resin composite modified with a thio-urethane presented significant higher degree of conversion compared to the unmodified material irrespective of light-curing time or pre-heating. Also, the lowest number of AE (total and $>60 \text{ dB}$) was observed with the thio-urethane composite. The benefits of incorporating thio-urethanes to dental composites seems to be a promising advance especially for bulk-fill resin composites.

5. Conclusion

Resin composite pre-heating may not be able to reduce polymerization stress in clinical situations. However, thio-urethane addition to a resin composite could reduce the polymerization stress while improving the degree of conversion.

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4 CONSIDERAÇÕES FINAIS

Este estudo se propôs a avaliar alternativas para a redução do stress de polimerização em restaurações de incremento único, através da adição de tiouretanos em resinas compostas e do uso de resinas compostas aquecidas. A estratégia de funcionalização de cargas inorgânicas adotada através da silanização com tiouretanos foi eficaz na obtenção dos benefícios da utilização destes aditivos. O processo de silanização de cargas realizado neste estudo gerou crescentes massas de silano ligados à carga (conforme a concentração de silano na solução utilizada no processo), sendo que cargas com maiores quantidades de tiouretano apresentaram maior efeito na redução do stress de polimerização e maior tenacidade à fratura.

A presença de tiouretanos na carga de um compósito odontológico parece levar a uma redução de stress de polimerização semelhante ao obtido com a incorporação destes na matriz orgânica do material, como visto na segunda parte deste trabalho. No entanto, quando combinados, o uso de tiouretano tanto na matriz como na carga resultou em um efeito potencializado principalmente na redução do stress de polimerização. Durante a confecção das resinas compostas experimentais foi notada a diferença de viscosidade e consequente maior dificuldade de mistura e incorporação de carga nos materiais contendo tiouretano em comparação aos controles. Esta diferença foi posteriormente notada no teste de viscosidade dos materiais finais. A alta viscosidade destes aditivos deverá ser levada em conta no momento do desenvolvimento de materiais para o uso clínico, para que dessa forma um balanço entre os componentes e proporções da matriz orgânica possibilite um material com alta incorporação de carga e boa manipulação.

Diferente dos trabalhos anteriores (20, 22, 23), os dois primeiros estudos desta tese utilizaram fontes de luz com irradiância bastante reduzidas. O motivo disto foi testar os efeitos da adição de tiouretanos na cinética de polimerização em uma reação de polimerização mais lenta. Apesar dos efeitos destes aditivos terem sido observados no stress de polimerização, tenacidade à fratura e até mesmo no grau de conversão, o efeito sobre a cinética de polimerização parece ter sido minimizado em relação aos estudos anteriores. Atualmente, o uso de

fontes de luz com irradiâncias superiores a 1.000 mW/cm² é comumente empregado (33). Portanto, a utilização de irradiâncias muito baixas não permite uma simulação da situação clínica de uso dos materiais resinosos. Novos trabalhos devem utilizar fontes de luz semelhantes à clínica, principalmente para materiais que apresentem diferentes resultados causados em parte pela sua cinética de polimerização.

Quanto ao uso de resinas compostas pré-aquecidas para a redução do stress de polimerização, a terceira parte deste trabalho mostrou que este efeito pode não ser obtido em restaurações diretas. O uso de resina composta pré-aquecida para o aumento no grau de conversão ou possível relaxamento de stress de polimerização necessita que o material ainda esteja em temperatura aumentada durante o momento da fotoativação. Porém, clinicamente este pré-requisito é dificultado devido à rápida perda de temperatura do material em condições de temperatura não isotérmicas (34). O tempo gasto depois da remoção do material da fonte de aquecimento até a inserção, acomodação e subsequente fotoativação do material pode ser responsável por uma queda na temperatura até níveis próximos a temperatura ambiente. Neste estudo os procedimentos foram padronizados para que o tempo após a remoção do material da fonte de aquecimento até a fotoativação fosse de no máximo 1 minuto. Em procedimentos laboratoriais este tempo é facilmente realizado visto que todas as condições são controladas, diferentemente de situações clínicas. Porém, mesmo desta forma o aquecimento não influenciou no aumento do grau de conversão ou stress de polimerização. Portanto, acredita-se que no momento da fotoativação o material já estava em temperatura próxima ao material não aquecido. Finalmente, o uso de resinas compostas pré-aquecidas não parece uma alternativa viável para a obtenção de restaurações diretas com maior grau de conversão e menor stress de polimerização.

O teste de emissão acústica ainda é uma metodologia recente em pesquisas na área da Odontologia. A emissão acústica vem sendo utilizada para a observação em tempo real dos efeitos do stress de polimerização. Trabalhos prévios mostraram uma boa correlação entre resinas compostas com maior ou menor stress de polimerização e o número de eventos acústicos captados (35-37). Até hoje o número de eventos acústicos gerados após o início da

fotoativação do material tem sido descrito como a ocorrência de descolamento na interface adesiva causado pela contração do material resinoso. Porém, diferentes condições de teste, incluindo o tipo de sensor acústico e amplificação do sinal, podem levar a uma maior detecção de eventos acústicos.

Este trabalho mostrou alguns resultados diferentes da literatura, visto que uma resina de bulk-fill que apresenta stress de polimerização próximo ao da resina convencional utilizada apresentou um número muito mais elevado de eventos acústicos (38). Além disto, o número médio de eventos acústicos deste trabalho foi bastante elevado em comparação aos reportados anteriormente (35-37, 39). Portanto, o nível de detecção de ondas acústicas deste estudo parece ter sido maior. Quando filtrados somente os eventos acústicos que apresentaram amplitude maior que 60 dB, os resultados deste trabalho ficaram semelhantes aos previamente encontrados na literatura. Esta mudança deixa clara a diferença dos níveis de detecção dos trabalhos, sendo que o presente estudo foi então capaz de captar ondas sonoras de amplitude mais baixa.

O acontecimento responsável pela geração de um evento acústico deverá ser devidamente investigado e compreendido. A interpretação dos resultados de emissão acústica poderá ser diferente conforme o entendimento do motivo causador de um evento acústico e da sua importância para a estrutura do dente e da restauração. O material de bulk-fill utilizado neste estudo, que apresentou um número total de eventos acústicos 4 vezes mais alto que a resina convencional, pode ter apresentado descolamentos ou defeitos na interface em uma quantidade mais alta, mas de magnitude mais baixa. Por exemplo, um material pode apresentar uma trinca ou descolamento grande, representado por um evento acústico de duração ou amplitude alta, enquanto outro material apresenta uma trinca ou descolamento progredindo em pequenos passos, representado por uma sequência de eventos acústicos de menor duração e/ou amplitude. Portanto, acredita-se que mais estudos deverão abordar melhor a utilização desta metodologia em si para que não existam problemas de interpretação dos resultados de trabalhos futuros.

Finalmente, o uso de tiouretanos como aditivos para materiais resinosos odontológicos parece uma boa alternativa para melhoria de propriedades mecânicas juntamente com uma importante redução do stress de polimerização.

Diferentes estratégias para a incorporação desta tecnologia poderão ser utilizadas no momento do desenvolvimento de novos materiais, conforme observado neste trabalho. Por outro lado, o uso de resina composta aquecida, apesar de segura, não parece ser uma alternativa clinicamente viável para o aumento do grau de conversão ou redução do stress de polimerização em restaurações diretas.

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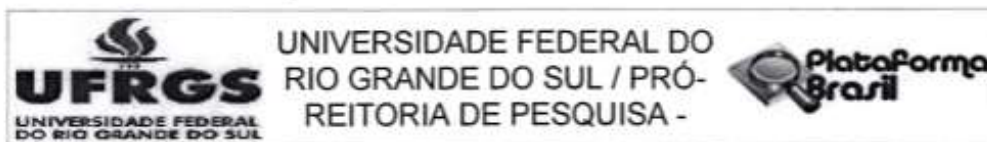
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ANEXO A – Parecer do Comitê de Ética em Pesquisa



PARECER CONSUBSTANCIADO DO CEP

DADOS DO PROJETO DE PESQUISA

Título da Pesquisa: Avaliação do uso de resina composta aquecida como material restaurador direto pela técnica de incremento único

Pesquisador: Maria Carolina Guilherme Erhardt

Área Temática:

Versão: 2

CAAE: 46562215.6.0000.5347

Instituição Proponente: UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL

Patrocinador Principal: Financiamento Próprio

DADOS DO PARECER

Número do Parecer: 1.173.555

Data da Relatoria: 06/08/2015

Apresentação do Projeto:

Retorno de diligência

Projeto de doutorado

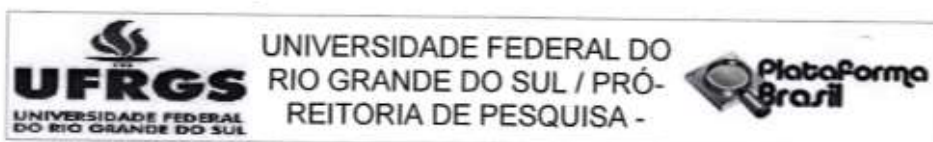
Entre os materiais utilizados para os tratamentos restauradores de cavidades dentárias, as resinas compostas têm evoluído tanto em relação às propriedades mecânicas quanto à praticidade de utilização na clínica (ex.: diminuição do tempo de atendimento). Vários materiais/procedimentos têm sido utilizados para este objetivo, como resinas de incremento único e utilização de técnicas de aquecimento da resina; entretanto, poucos são os trabalhos clínicos demonstrando a performance destes materiais.

O objetivo deste projeto é determinar a possibilidade de uso da resina composta aquecida como um material restaurador de incremento único. Para tanto, serão utilizados dentes humanos que serão submetidos in vitro a tratamento restaurador com diferentes protocolos e serão analisadas as propriedades mecânicas da restauração (total de 20 condições experimentais).

De acordo com cálculo amostral, serão utilizados 108 pré-molares e 64 terceiros molares hígidos humanos.

Os dentes, indicados para terapêutica (molares) ou razões ortodônticas (pré-molares), serão

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Bairro: Farroupilha **CEP:** 90.040-060
UF: RS **Município:** PORTO ALEGRE
Telefone: (51)3308-3738 **Fax:** (51)3308-4085 **E-mail:** etica@propesq.ufrgs.br



Continuação do Parecer: 1.173.555

coletados logo após a extração, limpos e armazenados para os ensaios experimentais (emissão acústica, deflexão de cúspides, microdureza, espectroscopia Raman, temperatura intrapulpar, microtração e formação de gaps).

Os locais de coleta do material serão de consultórios particulares. Usualmente, o cirurgião dentista responsável pelo paciente costuma perguntar ao paciente se o mesmo deseja levar consigo o dente extraído ou se deseja que o cirurgião despreze este. Caso o paciente não desejar levar o dente consigo o profissional irá perguntar ao paciente se ele deseja que este material participe do presente estudo. Para isto, será explicado ao paciente os objetivos do estudo e o destino dado ao dente doado. Os pacientes doadores preencherão e assinarão dois termos de doação idênticos, dos quais uma cópia ficará de posse do paciente e outra do pesquisador. Além disto, cada dente doado (inclusive no caso de mais de um dente para um mesmo paciente) terá um termo de doação individual preenchido pelo doador. Estes dentes serão coletados, em recipientes específicos e individuais com um sistema de identificação com códigos disponível apenas ao pesquisador.

Objetivo da Pesquisa:

O objetivo deste projeto é determinar a possibilidade de uso da resina composta aquecida como um material restaurador de incremento único. Para tanto, serão utilizados dentes humanos que serão submetidos in vitro a tratamento restaurador com diferentes protocolos e serão analisadas as propriedades mecânicas da restauração (total de 20 condições experimentais).

Avaliação dos Riscos e Benefícios:

Os riscos previstos do projeto estão relacionados ao procedimento de coleta (cirurgia dos dentes - indicação ortodôntica/terapêutica) e à manipulação das amostras. Estes riscos foram minimizados através do treinamento dos dentistas convidados para coletar a amostra e a criação de um biorrepositório pelos pesquisadores. Adicionalmente, os pesquisadores adicionaram no projeto o modo de descarte da amostra.

Os benefícios são indiretos e envolvem o desenvolvimento de novos protocolos de restauração dentária.

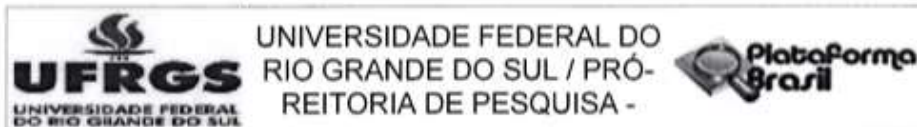
Comentários e Considerações sobre a Pesquisa:

Projeto bem delineado e com mérito científico

Considerações sobre os Termos de apresentação obrigatória:

Os pesquisadores atenderam de maneira satisfatória as alterações no termo de doação de

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Continuação do Parecer: 1.173.555

material.

Recomendações:

Conclusões ou Pendências e Lista de Inadequações:

Os pesquisadores atenderam de maneira satisfatória todas as colocações previamente colocadas.

Situação do Parecer:

Aprovado

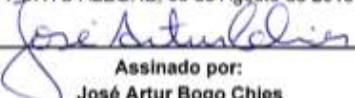
Necessita Apreciação da CONEP:

Não

Considerações Finais a critério do CEP:

Aprovado.

PORTO ALEGRE, 06 de Agosto de 2015


 Assinado por:
 José Artur Bogo Chies
 (Coordenador)

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