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ATAÍS BACCHI

RESIN CEMENTS MODIFIED WITH THIOURETHANE POLYMER ADDITIVES: CEMENT LAYER AND BONDING INTERFACE PROPERTIES

CIMENTOS RESINOSOS MODIFICADOS COM ADITIVOS POLIMÉRICOS TIOURETANOS: PROPRIEDADES DA CAMADA DE CIMENTO E DA INTERFACE ADESIVA

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2014

Universidade Estadual de Campinas
Faculdade de Odontologia de Piracicaba

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Thesis presented to Piracicaba Dental School of the State University of Campinas in partial fulfillment requirements for Degree of Doctor in Dental Clinic - Prosthodontics area.

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Este exemplar corresponde à versão final da Tese
defendida pelo aluno Ataís Bacchi e orientada
pelo Prof. Dr. Rafael Leonardo Xediek Consani

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RESUMO

O objetivo neste estudo foi formular cimentos resinosos a partir de oligômeros tiouretanos, com o propósito de melhorar as propriedades mecânicas do material e minimizar a contração e a tensão de polimerização. Materiais fotopolimerizados e de ativação dupla foram avaliados. Dois oligômeros foram sintetizados ao combinar 1,6-hexanodiol-diisocianato (HDDI) (alifático) com pentaeritritol tetra-3-mercaptopropionato (PETMP) ou 1,3-bis(isocianato-1-metiletil) benzeno (BDI) (aromático) com trimetilol-tris-3-mercaptoproprianato (TMP), na proporção de 1:2 de isocianato e tiol, mantendo grupos tiol pendentes. Inicialmente, 10-30% em peso de ambos os tiouretanos foram adicionados à matriz orgânica formada por BisGMA-UDMA-TEGDMA (nas proporções 50-30-20%, em peso) para o cimento experimental fotopolimerizado. A este, 25% em peso de partículas inorgânicas foram adicionadas. Para o cimento de cura dual, composto pela mesma matriz orgânica e partículas de carga, e para dois materiais comerciais – RelyX Veneer e RelyX Ultimate (3M Espe) - apenas a versão aromática em 10 e 20% em peso foi avaliada. Para todos os materiais, as propriedades mecânicas foram avaliadas através do teste de flexão por três pontos (ISO 4049) para a resistência à flexão (RF), módulo de elasticidade (E) e tenacidade (T). A tenacidade à fratura (K_{Ic}) foi avaliada em amostras entalhadas (ASTM Standard E399-90). A tensão de polimerização (TP) foi avaliada usando o aparelho *Bioman*. Os materiais fotopolimerizados foram avaliados quanto à contração de polimerização (CP) pelo método do disco aderido e a cinética de polimerização (grau de conversão (GC), taxa máxima de polimerização (Rp_{max}) e vitrificação) avaliadas por infravermelho. A união de uma cerâmica vítrea e um compósito restaurador indireto à dentina foi avaliada com o cimento comercial dual com 0, 10 e 20 % de tiouretano. Os resultados foram submetidos à Análise de Variância e teste de Tukey (α=5%). Quanto ao GC, ocorreu aumento pela utilização da versão alifática nos cimentos experimentais fotoativados; entretanto, a versão aromática não promoveu alteração relevante no GC final dos materiais. Rp_{max} foi menor nos grupos tiouretanos sendo também significantemente menor para os alifáticos quando comparados aos aromáticos. Apesar de os tiouretanos influenciarem a vitrificação (p=0,035) no cimento experimental, os resultados não foram conclusivos pela análise de Tukey. No cimento comercial foi observado aumento da vitrificação pelo uso do oligômero. Nos cimentos experimentais, RF aumentou com o oligômero aromático e 20% em peso do alifático nos cimentos fotopolimerizados; para E, a versão aromática no cimento com ativação dupla e 10% em peso no material fotopolimerizado causou aumento nos valores. Os materiais comerciais tiveram redução de E com 20% em peso de oligômero, decorrente da redução da proporção de carga inorgânica da matriz. Aumento significante em tenacidade ocorreu nos grupos alifáticos no material fotopolimerizado e para 20% em peso de aromático no cimento dual. K_{1c} aumentou significativamente em ambos os materiais experimentais contendo tiouretano em ambas as concentrações, sendo mais pronunciada em alifáticos na versão fotopolimerizada. Ainda, K_{Ic} aumentou com 20% em peso do oligômero em materiais comerciais. A CP reduziu significantemente nos grupos tiouretanos, especialmente para o oligômero alifático no cimento experimental fotopolimerizado. A TP reduziu com os oligômeros de maneira mais acentuada para alifáticos no cimento experimental fotopolimerizado. O uso dos aromáticos em cimentos de ativação dupla também causou redução na TP, e quando com 20% em peso nos materiais comerciais. A modificação do cimento comercial de ativação dupla com 20% em peso do oligômero aromático aumentou a adesão do compósito indireto e da cerâmica vítrea à dentina coronária. Em geral, oligômeros tiouretanos melhoraram as propriedades dos cimentos resinosos avaliados.

Palavras-chave: Odontologia, Prostodontia.

ABSTRACT

The aim of this study was to formulate resin cements with thio-urethane oligomers to improve mechanical properties and minimize shortcomings related to the volumetric shrinkage and polymerization stress. Light- and dual-cured materials were evaluated. Oligomers were synthesized by combining 1,6-Hexanediol-diissocyante (aliphatic) with pentaerythritol tetra-3-mercaptopropionate (PETMP) or 1,3-bis(1-isocyanato-1-methylethyl)benzene (aromatic) with trimethylol-tris-3-mercaptopropionate (TMP), at 1:2 isocyanate:thiol, leaving pendant thiols. Oligomers were added at 10-30wt% to BisGMA-UDMA-TEGDMA (5:3:2). 25wt% silanated inorganic fillers were added. The dual-cured cement, composed by the same organic matrix and filler particles, and for two commercial cements (RelyX Veneer e RelyX Ultimate; 3M Espe) were only evaluated with the addition of the aromatic version in 10 and 20 wt%. For all materials, the mechanical properties were evaluated by the three-point bending test (ISO 4049) for the flexural strength (FS) elastic modulus (E) and toughness (T). The fracture toughness was evaluated with notched specimens (ASTM Standard E399-90). The polymerization stress (PS) was evaluated in the Bioman. For the light-cured materials, the volumetric shrinkage (VS) was evaluated by the bonded-disc method and the polymerization kinetics – degree of conversion (DC), maximum rate of polymerization (Rp_{max}) and vitrification – evaluated by near-infrared (NIR). The bonding of a glass ceramic and an indirect composite to dentin were evaluated with the dual-cured commercial cement with 0, 10 and 20 wt% of thio-urethane. Data were analyzed with ANOVA and Tukey's test (α=5%). Regarding the DC, an increase was observed in the light-cured materials containing the aliphatic version. The aromatic oligomer did not promote relevant influence the materials. Rp_{max} was lower for thio-urethane groups being also significantly lower for the aliphatic group when compared to the aromatic. ANOVA has shown the thio-urethane influencing the vitrification (p=0.035) in the experimental cement, but the results were not conclusive by the Tukey's test. For the commercial cement, an increase in the vitrification was observed in the thio-urethane-modified group. For experimental cements, FS increased with the use of 10-30 wt% aromatic oligomer and with 20 wt% of aliphatic for light-cured cements. E was only higher for the aromatic version at 10 wt%. The commercial cements presented a reduction in E with 20 wt% of oligomer caused by the reduction in the filler proportion. A significant increase in T occurred in the aliphatic groups for the light-cured group and for 20 wt% of aromatic in the dual-cured cement. K_{Ic} significantly increased in both experimental materials formulated with thio-urethane for both concentrations, being more evident for the aliphatic group in the light-cured version. K_{Ic} also increased with the aromatic oligomer in commercial materials. The VS was significantly reduced in the thio-urethane groups, mainly for the aliphatic version in the light-cured cement. The PS decreased in the groups formulated with oligomers in the light-cured experimental materials, being also significant for aliphatics. The use of aromatic oligomer also reduced the PS when added to a 20 wt% proportion of organic matrix. The modification of a dual-cured commercial cement with 20wt% of aromatic oligomer led to an increase in the bond strength of an indirect composite and a glass ceramic to the coronal dentin. Thus, it can be concluded that thio-urethane oligomers improved the properties of resin cements.

Key-words: Dentistry, Prosthodontics.

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INTRODUÇÃO

Restaurações indiretas constituem uma grande parcela dos tratamentos de reabilitação bucal contemporânea (Peumans *et al*., 2000). Desta forma, a utilização de cimentos resinosos tem se tornado cada vez mais comum devido à capacidade de união à estrutura dentária e aos materiais restauradores (Manso *et al*., 2011). Exemplos de tratamentos indiretos nos quais os cimentos resinosos são empregados englobam cimentação de facetas laminadas, restaurações parciais posteriores (*onlay, inlay e overlay*), coroas dentárias, próteses parciais fixas e pinos intracanais. Ainda, a cimentação resinosa adesiva tem sido apontada não só como importante para a resistência da união à estrutura dental e ao material restaurador, mas também importante para aumentar a resistência à fratura do material restautrador, em especial as cerâmicas odontológicas (Scherrer *et al*., 1994; Mormann *et al*., 1998; Blind *et al*., 2006). Devido ao formato expulsivo dos preparos dentais onde as restaurações indiretas são aderidas, uma resistente união entre as estruturas e elevadas propriedades mecânicas do material de cimentação são consideradas pré-requisitos para a longevidade do tratamento, uma vez que constantes forças de tração, compressão e oblíquas são transmistidas ao material de união. Ainda, resistência à dissolução, fácil manipulação e compatibilidade biológica com o substrato tem sido apontadas como condições inerentes aos cimentos (Meyer *et al*., 1998; Rosenstiel *et al*., 1998; Manso *et al*., 2011).

Os cimentos resinosos convencionais atualmente disponíves são formulados baseados em monômeros de metacrilato, os quais sofrem vitrificação em estágios iniciais do processo de polimerização, característica que causa tensão de polimerização no material. Além dessa característica da rede polimérica, outro fator que contribui para aumentar a tensão de polimerização é a contração volumétrica. Uma avaliação de cimentos resinosos de ativação dupla demonstrou contração entre 1,77 a 5,28% quando os materiais foram somente polimerizados quimicamente e valores entre 4,1% e 5,29% quando polimerizados por ativação dupla (Spinell *et al*., 2009). Esta condição promove formação de fenda na interface dente-restauração, podendo aumentar a solubilidade do material e causar microinfiltração e pigmentação, compromentendo a longevidade do tratamento.

Técnicas para atenuação da contração de polimerização têm sido aplicadas em compósitos restauradores, como por exemplo, ativação com menor pulso de irradiação inicial e técnicas restauradoras incrementais que consideram a relação da quantidade de paredes unidas pelo material e as virtuais (fator-C). Entretanto, não há técnicas eficazes para reduzir a contração e a tensão de polimerização durante a cimentação devido às condições de confinamento onde os cimentos são aplicados. Sendo assim, é importante o desenvolvimento de materiais com pequena contração (Braga *et al*., 2005).

A aplicação de tiol-enos em compósitos dentais tem sido proposta e tem apresentado resultados satisfatórios em relação à redução na tensão de polimerização. O mecanismo de polimerização por etapas, característico de tiol-enes e tiol-metacrilatos, ocorre por reação de transferência de cadeia dos tiols ao eno e ao vinil, proporcionando formação de redes poliméricas mais homogêneas e com maior nivel de conversão final em comparação aos metacrilatos puros (Lu *et al*., 2005; Cramer *et al*., 2010a; Cramer *et al*., 2010b; Boulden *et al*., 2011; Hoyle & Bowman 2010). Além disso, esse mecanismo de polimerização proporcionaria melhora em propriedades como resistência à flexão, profundidade de polimerização e solubilidade (Lu *et al*., 2005; Cramer *et al*., 2010a; Cramer *et al*., 2010b; Boulden *et al*., 2011). Entretanto, a redução das propriedades mecânicas e da estabilidade do material (vida-útil) tem retardado a aplicação comercial de materiais à base de tiol-eno (Lu *et al*., 2005; Beigi *et al*., 2013). Outra desvantagem de materiais formulados com base em tiol-enos diz respeito ao odor desagradável alegado aos compostos tiol de baixo peso molecular.

A utilização de materiais baseados em tiouretanos tem sido propostosta para melhorar as propriedades mecânicas em geral, mais precisamente à tenacidade (Senyurt & Hoyle 2007; Li *et al.*, 2009). Esta característica tem sido creditada ao fato de que tiouretanos promovem a formação de uma rede polimérica mais homogênea em relação aos uretanos convencionais (Senyurt & Hoyle 2007; Li *et al.*, 2009). Recentemente, oligômeros baseados em tiuretanos foram sintetizados e propostos como aditivos de matrizes de metacrilato para fornecer suas vantagens à polimerização de materiais odontológicos. Quando oligômeros são sintetizados com tióis pendentes na estrutura, a reação de transferência de cadeia à matriz secundária de metacrilato resultaria no retardo da vitrificação, o que causaria redução da tensão de polimerização (Pfeifer *et al.*, 2012). Além disso, a característica de pré-polimerizado dos tiouretanos e o alto peso molecular proporcionariam menor contração de polimerização (Patel *et al.*, 1987). Outro fator importante seria o aumento no grau de conversão final promovido pelos tiouretanos, fato devido a maior homogeneidade da rede polimérica resultante das reações de transferência de cadeia entre os grupos tiol pendentes e o metacrilato da matriz secundária (Berchtold *et al.*, 2002).

Assim, o objetivo neste trabalho foi formular cimentos resinosos contendo oligômeros tiouretano e avaliar a influência nas propriedades mecânicas e aquelas associadas ao processo de polimerização. A aplicação de um oligômero em materiais comerciais e a influência de materiais contendo tiouretanos na adesão de dois materiais restauradores (uma resina composta indireta e uma cerâmica odontológica) à dentina coronária dental também foram objetivos neste estudo.

CAPÍTULO 1

Thio-urethane oligomers improving the properties of light-cured resin cements

ABSTRACT

Thio-urethanes were synthesized by combining 1,6-Hexanediol-diissocyante (aliphatic) with pentaerythritol tetra-3-mercaptopropionate or 1,3-bis(1-isocyanato-1-methylethyl)benzene (aromatic) with trimethylol-tris-3-mercaptopropionate at 1:2 isocyanate:thiol, leaving pendant thiols. Oligomers were added at 10-30wt% to BisGMA-UDMA-TEGDMA (5:3:2). 25wt% silanated inorganic fillers were added. Commercial cement (Relyx Veneer, 3M Espe) was also evaluated with 10-20wt% of aromatic oligomer. Near-IR was used to follow methacrylate conversion (DC) and rate of polymerization (Rp_{max}). Mechanical properties were evaluated in three-point bending (ISO 4049) for flexural strength/modulus (FS/FM, and toughness), and notched specimens (ATM Standard E399- 90) for fracture toughness (K_{IC}). Polymerization stress (PS) was measured on the Bioman. Volumetric shrinkage (VS, %) was measured with the bonded disk technique. Results were analyzed with ANOVA/Tukey's test (α=5%). For experimental cement, DC and toughness increased with aliphatic oligomer. FS increased for all aromatic groups and in 20wt% of aliphatic. FM increased with 10wt% aromatic thio-urethanes. Aromatic oligomers led to superior FS/FM than aliphatic. Rp_{max} decreased for both materials with statistical reduction to aliphatic from aromatic. Statistical influence of thio-urethanes on vitrification was observed, although the experimental groups did not differ from the control. K_{IC} increased and PS reduced with both oligomers, with aliphatic superior to aromatic. VS reduced for both thio-urethanes. For commercial cement, 20 wt% of oligomer increased DC, vitrification, reduced Rp_{max} and also significantly increased K_{IC}, and reduced PS and FM. Thio-urethane oligomers were shown to favorably modify conventional dimethacrylate networks. Increase of toughness and FT and reduction of PS and VS are the more improved properties.

Key-words: resin cements; thio-urethane oligomers; polymerization stress; mechanical resistance.

1. Introduction

Bonded indirect restorations play one of the major roles in contemporary dentistry [1]. Resin cements have become popular clinically because of their ability to bond both to the tooth structure and to the restoration [2]. Examples of their clinical applications include adhesion of ceramic fragments, crowns, bridges, and intracanal posts. Due to the necessary (and sometimes excessive) taper on tooth preparations, and to constant incidence of tensile, compressive and oblique loads, resin cements must have resistance to dissolution, strong bond to structures and high mechanical properties [2-4].

Conventional resin cements are based on methacrylate monomers which undergo vitrification at early stages of polymerization, increasing the strain/stress at the bonded interface and in the bulk of the material structure. This condition increases the risk of gap formation at the interface of cementation, which may lead to an increase of the material solubility, microleakage and staining, ultimately compromising the longevity of treatment. Based on the confined geometry in which the cement is applied, current operatory techniques available are not efficient in avoiding the development of strain/stress during the indirect restoration placement and, therefore, the solution to minimize stress generation needs to be based on improvements made directly to the material [5].

The use of thiol-enes has been proposed in dental composites, with successful results as stress reducing agents. The step growth nature of the thiol-ene and thiol-methacrylate polymerizations, given by chain-transfer reactions of the thiol to the ene/vinyl, lead to more homogeneous network formation and ultimately increased conversion in comparison to the pure methacrylate counterparts [6-10] and for selected compositions, improvements in flexural strength, depth of cure and water solubility have also been reported [6-9]. However, concerns over the somewhat compromised mechanical properties and the stability (shelf-life) of the fully formulated composite materials have delayed the commercial translation of thiol-ene-based materials [6,11]. Another concern that applies to small molecule thiols is the foul odor associated with the material.

As an alternative to conventional thiol-enes or thiol-methacrylates, others have proposed the use of thio-urethane networks in applications where mechanical properties in general, but more specifically toughness and resistance to impact, are desirable [12,13]. Some studies have demonstrated the more homogeneous nature of thio-urethane networks compared to the simple urethane counterparts, as well as the increased toughness values [12,13]. In those studies, thiols are combined with isocyanates *in situ*, in a reaction catalyzed by a base. Currently, these are two-part systems (at least until compounds such as photo-base generators are readily accessible), not suitable for dental composite applications. However, previous study has demonstrated it to be possible to synthesize high molecular weight pre-polymerized thio-urethane oligomers to be later added to a secondary monomer matrix, polymerizable through a radical mechanism [14]. When the oligomer is designed to have pendant thiols from the backbone, chain-transfer reactions to the surrounding methacrylate matrix result in delayed gelation and vitrification and, as consequence, reduction in polymerization stress [14]. Due to the high molecular weight, reductions in the volumetric shrinkage are also expected, as well as the elimination of the odor concerns. Importantly, thiol-terminated thio-urethanes are capable of forming a more homogeneous network with the methacrylate, and also increase final conversion [15].

Therefore, the objectives of this study were to synthesize thiol-terminated thio-urethane oligomers with different backbone structures and to assess the properties of methacrylate-based resin cements modified with the oligomers. The hypotheses of this study were that the thio-urethanes would (I) increase the degree of conversion, (II) improve the material mechanical properties and (III) reduce the volumetric shrinkage/polymerization stress.

2. Materials and Methods

2.1 Experimental materials composition

The experimental resin cement formulated for the study (BUT) was composed of Bis-phenol A diglycidyl dimethacrylate (Bis-GMA; Esstech, Essington, PA, USA), urethane dimethacrylate (UDMA; Esstech) and tri-ethylene glycol dimethacrylate (TEGDMA; Esstech) in a 50:30:20 mass ratio. Photoinitiators were added to the matrix as follows: 0.6 wt% of a tertiary amine (EDMAB - ethyl 4-dimethylaminobenzoate; Avocado, Heysham, England), 0.2 wt% of dl-camphoroquinone (Polysciences Inc., Warrington, PA, USA), and 0.5 wt% inhibitor (BHT - 2,6-di-tert-butyl-4-methylphenol; SigmaAldrich, St. Louis, MO, USA).

Oligomers were synthesized in solution (methylene chloride) by combining 1,6-Hexanediol-diissocyante (HDDI) (aliphatic) with pentaerythritol tetra-3-mercaptopropionate (PETMP) or 1,3-bis(1-isocyanato-1-methylethyl)benzene (BDI) (aromatic) with trimethylol-tris-

3-mercaptopropionate (TMP), at 1:2 isocyanate:thiol molar ratio, leaving pendant thiols. Triethylamine was used as a base in catalytic amounts. Oligomers were purified by precipitation in hexanes and rotaevaporation, and then characterized by ^{1}H-NMR and mid-IR spectroscopy. Thio-urethane oligomers were added to organic matrix in proportions of 0 (control), 10, 20 and 30 wt%.

Filler was introduced at 25 wt% (15% OX-50 - 0.04 µm; 85% Barium glass 0.7µm, density 3.0 g/ml, refractive index 1.553 - V117 4107, Esstech), with the aid of a mechanical mixer (DAC 150 Speed mixer, Flacktek, Landrum, SC, USA) for 5 min at 2400 rpm. All procedures were carried out under safe yellow light.

One commercial light-cured cement (RelyX Veneer, 3M Espe, St. Paul, USA – lot N521803; Ref 7614A1, A1/light yellow shade) composed by BisGMA/TEGDMA and 66wt% zirconia/silica filler was modified by addition of 10 and 20 wt% of aromatic oligomer to organic matrix. The non-modified material served as control.

2.2 Photopolymerization reaction kinetics and degree of conversion

The degree of conversion (DC) was obtained using near–infrared (NIR) spectroscopy in specimens of 10 mm in diameter and 0.8 mm thick laminated between two glass slides, based on the methacrylate =CH_2 absorption at 6165 cm^{-1} [16] before and after 60s of irradiation at 700 mW/cm^2 (Bluephase, Ivoclar vivadent, Lichtenstein) with the light source in direct contact with the glass slide mold. Real-time monitoring of the polymerization kinetics was carried out in specimens of the same size at 2 scans per spectrum with 4 cm^{-1} resolution, which provides a greater than 2 Hz data acquisition rate. Kinetic data was collected continuously for 5 min. Samples (*n*=3) were irradiated with a LED lamp for 60 s at an incident irradiance of 550 mW/cm^2. The light attenuation in this case was due to a distance of 2 cm separating the tip of the light guide and the surface of the specimen.

2.3 Flexural strength, elastic modulus and toughness

Flexural strength of the samples was measured according to the 3-point bending method carried out with a universal test machine (Q-test, MTS, Eden Prairie, WI) at a cross-head speed of 0.5 mm min^{-1}. The bar specimens were prepared in dimensions of 2 mm × 2 mm × 25 mm according to ISO 4049 [17]. The specimens (n=10) were fabricated between glass slides and photopolymerized with three overlapping 60 s exposures at 700 mW/cm^2. Specimens were stored for one week in dark containers at room temperature. The flexural strength (FS) in MPa was then calculated as:

$$\mathrm{FS}\ (\sigma) = \frac{3Fl}{2bh^2}$$

where F stands for load at fracture (N), l is the span length (20 mm), and b and h are the width and thickness of the specimens in mm, respectively.

The elastic modulus was determined from the slope of the initial linear part of stress–strain curve.

$$\mathrm{E} = \frac{Fl^3}{4bh^3d}$$

F= the load at some point on the linear region of the stress-strain curve

d = the slack compensated deflection at load F *l*, *b*, and *h* are as defined above

Toughness was calculated in MPa from the integration of the stress x strain curve using software (Origin 9.1, OriginLab Corporation, Northampton, MA, USA).

2.4 Volumetric Shrinkage

The bonded disk method was used to evaluate volumetric shrinkage. Resin cements were placed into a brass ring of approximately 16 mm in diameter and 1.5 mm in height bonded to a glass slide. The cement (*n*=5) was placed so that it did not come in contact with the brass ring, and then the assembly was covered with a microscope cover slip (approximately 0.1 mm thick). A linear variable differential transducer (LVDT) probe was placed in contact with the center of the cover slip. The cement was photoactivated at an incidence of 650mW/cm^2 for 60 s. As the cement cures and shrinks, it pulls the cover slip down and its deflection is monitored by the LVDT probe. Displacement data was obtained from the signal output of the transducer (in mV). The volumetric shrinkage (%VS) value was calculated as follows:

$$\%VS = \frac{(V_f - V_i) \times 2}{h} \times 100$$

Where: V_f, is the final displacement value given after polymerization and, V_i, is the initial value given by the LVDT probe, in mV and *h*, is the cement specimen thickness after the polymerization, in µm.

2.5 Polymerization stress

Polymerization stress development was followed in real-time using the Bioman, described previously [18]. This system consists of a cantilever load cell whose extremity is fitted to a rigid integral clamp on its free end. The clamp holds a 10 mm diameter and 22 mm tall steel rod vertically and perpendicular to the load cell axis. A 5-mm diameter, 0.5-mm tall steel rod was fixed at the center of the lower face of the standard rod with a cyanoacrylate adhesive to produce a rod substrate with a reduced surface area to be consistent with a C-factor of 4. The surface of the rod was treated with a thin layer of Metal primer (Z-prime plus, Bisco, Schaumburg, IL). The opposite surface was a rigid fused silica glass plate of 3 mm thickness, treated with a thin layer of silane ceramic primer (3M ESPE, St. Paul, MN, USA). The cement was then inserted into the 0.5-mm gap between the upper rod and the lower glass slide and shaped into a cylinder. The specimens (*n*=5) were photoactivated through the glass during 60 s at an incident irradiance of 670 mW/cm^2 (Bluephase) and the stress followed for 500 s. The load signal from the cantilever cell was amplified and acquired by a computer.

2.6 Fracture toughness

The fracture toughness of all materials was determined from the stress intensity factor (*K*) during crack propagation. To determine the fracture toughness (FT), single-edge notch beam (SENB) specimens (*n*=5) were fabricated according to ASTM Standard E399- 90 [19] in a 5 mm × 2 mm × 25 mm split steel mold with a razor blade providing a 2.5 mm notch in the center of the specimens. The cement was photoactivated at an incidence of 700mW/cm^2 for 60 s. The bending fracture test was performed at a cross-head speed of 0.5 mm min^{-1} using a universal test machine (Q-test) and the fracture toughness (critical stress intensity factor, K_{IC}) was calculated according the following equation:

$$K_{IC} = \frac{3PL}{2BW^{3/2}} \left\{ 1.93\left(\frac{a}{W}\right)^{1/2} - 3.07\left(\frac{a}{W}\right)^{3/2} + 14.53\left(\frac{a}{W}\right)^{5/2} \right.$$
$$\left. -25.11\left(\frac{a}{W}\right)^{7/2} + 25.8\left(\frac{a}{W}\right)^{9/2} \right\}$$

where P is load at fracture (N), L, W, B, and a are length, width, thickness, and notch length (in mm), respectively. The span length and load cell capacity were 20 mm and 60 N, respectively. The subscript IC denotes mode I crack opening under a normal tensile stress perpendicular to the crack [11,20].

2.7 Statistical analysis

For the experimental cement, statistical analysis was carried out by two-way ANOVA (thio-urethane concentration and thio-urethane type). One-way ANOVA was performed for the commercial cements, once they used only aromatic oligomers. Multiple comparisons were done using Tukey's test (α=0.05%).

3. Results

3.1 Photopolymerization reaction kinetics and degree of conversion

3.1.1 Experimental cement

The degree of conversion (Table 1) in the groups modified with the aliphatic version of thio-urethanes increased significantly from 64.87±0.44% (control) to up to 73.5±0.3% (30 wt% thio-urethane) (p=0.000). In the groups modified with aromatic thio-urethanes, a slight reduction was observed in DC for the 20 wt% group compared to the control (from 64.87±0.44% to 63.6±0.4%), which was statistically significant. Aliphatic thio-urethanes were statistically significant to aromatics for all groups within the same concentration ($p=0.000$). The two factors (thio-urethane type and concentration) presented significant interaction ($p=0.000$).

A statistical reduction in the rate of polymerization (Rp_{max}) values was observed for all experimental groups in comparison to the control ($p=0.000$). For groups modified with the aliphatic thio-urethanes, there was no statistical difference amongst all concentrations. For the aromatic thio-urethanes, Rp_{max} was statistically higher for the 10 wt% compared to 30 wt%. The 20 wt% group was statistically similar to 10 and 30 wt%. Rp_{max} was also influenced by the thio-urethane type, with aromatic thio-urethane groups presenting higher Rp_{max} within the same concentration ($p=0.004$). No interaction between the two factors was observed for Rp_{max} ($p=0.188$). All values are presented in Table 1.

The conversion at Rp_{max} was used as a measure of network vitrification (Odian, 2004), as shown in Table 1. Even though there were statistical differences between some groups ($p=0.035$), all experimental groups presented results statistically similar to the control. Therefore, the presence of thio-urethane significantly influenced the vitrification results, while the thio-urethane type showed to be not statistically significant ($p=0.693$). There was interaction between the factors ($p=0.028$).

Figure 1 presents the kinetic profiles of all groups formulated with BisGMA/UDMA/TEGDMA. For some examples (20 and 30 wt% aliphatic – 20 AL and 30 AL, respectively, and 30 wt% aromatic – 30 AR), not only is the maximum rate of polymerization (Rp_{max}) lower than the control, but the rate of deceleration is lower also, as evidenced by the plateau in the Rp_{max} x DC curves shown in Figure 1.

3.1.2 Commercial cement

All results for the commercial cements are represented in Table 2. The use of 20 wt% of aromatic thio-urethane oligomer led to an increase in DC (p=0.030) in comparison with the control, which in turn was statistically similar to the 10 wt% group. Thio-urethane caused a statistically significant reduction of the Rp_{max} for both concentrations (p=0.000), which did not differ from each other. A higher conversion at vitrification for the thio-urethane-modified groups in relation to the control was observed (p=0.048).

3.2 Flexural strength, elastic modulus and toughness

3.2.1 Experimental cement

All aromatic groups caused an increase in the flexural strength (FS) (Table 3) in regards to the control, which was only observed for 20 wt% in aliphatic (p=0.000). The aromatic thio-urethane presented statistically higher values of FS compared to the aliphatic version (p=0.004). There was no statistical interaction between the factors thio-urethane concentration and type (p=0.265).

The groups presented flexural modulus similar to the control, with two exceptions. The use of 10 wt% of aromatic thio-urethane caused a statistically significant increase in the flexural modulus, whereas the use of 30 wt% aliphatic thio-urethane led to a statistically significant decrease in modulus (p=0.000) (Table 3). The thio-urethane type showed to be statistically significant, with aromatic group being superior to aliphatic (p=0.000). The interaction between the factors was significant (p=0.020). After these evaluations, the analyses with 30 wt% of oligomer were discontinued.

As far as toughness (Table 3), aliphatic thio-urethane groups caused a statistically significant increase in the results (p=0.000), independent of the concentration. Aromatic oligomers did not affect toughness. The aliphatic oligomer was statistically superior to the aromatic for both concentrations (p=0.000). The interaction between the two factors was also significant (p=0.023).

3.2.2 Commercial cement

The addition of 20 wt% of aromatic thio-urethane led to a statistically significant reduction in the flexural modulus (p=0.000) of the commercial cement, whereas the 10 wt% group was similar to the unmodified control. For flexural strength (p=0.062) and toughness (p=0.104), no statistical difference was observed among the groups. All values are presented in Table 2.

3.3 Polymerization Volumetric Shrinkage

For the BisGMA/UDMA/TEGDMA experimental cement, all groups containing thio-urethane oligomers provided a statistically significant reduction in the volumetric shrinkage values in relation to the control (p=0.000), which was not dependent of the thio-urethane concentration (Figure 2A). The thio-urethane type also influenced the volumetric shrinkage, with the aliphatic one leading to lower values for both concentrations (p=0.000). Significant interaction between the two factors was observed (p=0.001). The groups with 10 wt% and 20 wt% of aromatic thio-urethane led to a reduction of 15.5% and 19.5% of the volumetric shrinkage, respectively, in relation to control. For the aliphatic oligomers, the addition of 10 and 20 wt% led to shrinkage reductions of 39.8% and 52,4%, respectively. The same tendency in reduction was observed in the commercial material for thio-urethane groups, although not statistically significant (p=0.106) (Figure 2B). The groups with 10 wt% and 20 wt% of thio-urethane concentration led to a reduction of 5.6% and 21.2% in relation to the control group, respectively.

3.4 Polymerization stress

The polymerization stress was statistically reduced in the thio-urethane groups (p=0.000) for the experimental material, with 20 wt% of aliphatic material showing the lowest values (Figure 3A). The thio-urethane type (p=0.120) and the interaction between the factors (0.311) were not statistically significant. The concentration of 10 wt% and 20 wt% led to a reduction of polymerization stress of 47.6% and 61.5%, respectively, in the aromatic material and 55.1% and 86% in the aliphatic material. A statistically significant reduction in the polymerization stress was observed for the commercial cement, with 20 wt% of aromatic oligomer (p=0.033), 36.7% lower than control, which in turn was similar to the material with 10 wt% thio-urethane (Figure 3B).

3.5 Fracture toughness

Fracture toughness results for both thio-urethane-modified groups were statistically higher than the control, with 20 wt% aliphatic showing the highest values among them (p=0.000). The aliphatic oligomer in 20 wt% of concentration was statistically superior to the aromatic in the same concentration (p=0.011). Interaction between the two factors was significant (p=0.034). The addition of aromatic thio-urethanes led to increases of 88.8% and 108.5% in fracture toughness and the addition of aliphatic versions led to an increase of 105.9%

and 176% in fracture toughness, for the 10 and 20 wt% concentrations, respectively (Figure 4A). For the commercial material, the addition of 20 wt% of aromatic thio-urethane led to a significant increase in fracture toughness (p=0.020) 25.5% higher than control, which was also similar to the 10 wt% group (Figure 4B).

4. Discussion

This study evaluated the potential for mechanical properties improvement and stress reduction with the use of light-cured resin cements modified by the addition of thio-urethane oligomers. The kinetics of polymerization was used as a way to assess network formation and final degree of conversion. The maximum rate of polymerization marks the end of autoacceleration, or the point in conversion at which network mobility restrictions impair chain propagation, with further contributions to conversion occurring in the vitrified state [21]. For pure methacrylates, deceleration almost immediately follows Rp_{max} (Figure 1), which typically occurs at lower conversion, around 15-20 % [22]. The addition of molecules with potential for chain-transfer, such as the thiol-terminated oligomers, tended to delay the end of auto acceleration to achieve higher conversion [14,23], with the modified groups showing nearly constant rates of polymerizations through a much wider interval in conversion before deceleration is observed (Figure 1). Delayed vitrification then can be attributed to chain-transfer reactions of the pendant thiols to the methacrylate, which delay network formation and the build-up of diffusional limitations to propagation [15]. In general, the use of thio-urethane-modified materials not only increased the degree of conversion in relation to the control, but was also able to reduce the rate of polymerization and delay vitrification for selected compositions. Chain-transfer reactions also likely contributed to the formation of more homogeneous networks, with decreased internal stresses [10,12]. Assuming that the thiol concentration and the molecular weight of the oligomer were similar in all groups, it can be inferred that the effect on conversion and network formation was dependent on the thio-urethane structure, as well as on the secondary matrix to which they were added. For the experimental cements, comprised of BisGMA/UDMA/TEGDMA, the addition of the aliphatic version of the thio-urethane was better able to increase conversion while reducing $Rp_{max.}$ This fact can be explained by the flexibility of the structure given not only by the thio-urethane bonds but also by the absence of aromatic rings or other rigid substitutions. So, the first hypothesis that the oligomers would increase the degree of conversion was partially accepted. Indeed, a similar effect was only observed for aromatic thio-urethanes at higher concentrations (Figure 1). The increased flexibility may have facilitated the chain-transfer reactions within the methacrylate matrix, even though the effect on the conversion at Rp_{max} (vitrification) was not as marked in relation to the control. Statistical differences (p=0.035) were still observed amongst thio-urethane-modified groups. It is noteworthy that the degree of conversion calculated from the kinetic runs was based on an irradiance of 550 mW/cm^2, and resulting radiant exposure of 33 J/cm2, due to test geometry limitations. The degree of conversion obtained from specimens directly irradiated (700 mW/cm^2 with radiant exposure of 42 J/cm2) were, as expected, significantly higher. At that higher irradiance, the ranking of conversions presented by cements modified by the aliphatic x aromatic versions of the thio-urethanes is the same as presented from the kinetics run (Table 1). The influence of irradiance on network formation was beyond the scope of this study, but will be the subject of future work. For the commercial cement (Table 2), even the aromatic version of the thio-urethane was able to increase conversion by 4.4 % and delay vitrification to a conversion 46.6 % higher. In this case, the exact composition of the methacrylate matrix is not known, but it can be speculated that the flexibility of the thio-urethane bond (in spite of the presence of a more rigid core structure) may have been enough to facilitate the formation of a more homogeneous network, as can be inferred from the reduction of Rp_{max} and extended deceleration profile shown in Figure 1.

The addition of aromatic thio-urethanes to materials formulated with BisGMA/UDMA/TEGDMA led to an increase of flexural strength of up to 35% (20 wt%). For the aliphatic versions, the increase in flexural strength was not as marked, reaching about 19% for the 20 wt% concentration. The same trend was observed in terms of flexural modulus, except that for the aliphatic version at 30 wt% concentration, in which a reduction was actually observed (Table 3). This can be explained based on the rigidity of the aromatic rings present in the aromatic versions of the thio-urethane, while for the aliphatic version the combination of the flexible thio-urethane bonds with the flexible backbone of both the thiol and the isocyanate precursors were not as efficient at improving flexural strength and modulus of the secondary matrix . This was true in spite of the potentially higher ability to form crosslinks by the aliphatic thio-urethane, once the thiol precursor used in the synthesis is tetra-functional, as opposed to the tri-functional thiol used to make the aromatic thio-urethane. On the other hand, it is evident that the aliphatic version of the thio-urethanes was much more efficient at increasing toughness than the aromatic version, which can also be credited to the greater flexibility of the structure of the former. The toughness value achieved with 20 wt% aliphatic thio-urethane (8.21 MPa) represented a 3.5 fold increase in comparison with the control (2.37 MPa). Similar trends have been previously reported in studies where the reaction between isocyanate and thiol took place in situ to form thio-urethane networks in the presence of a base [10,12]. In the case previous study, thio-urethanes were shown to form much more homogeneous networks compared to simple urethanes, though with a slight decrease in glass transition temperature in some cases [15]. Dynamic mechanical analysis will be performed as part of future studies to evaluate the influence of thio-urethane structure on the glass transition temperature of networks.

The values of flexural strength and toughness were not affected by the addition of thio-urethane for the commercial material, while the flexural modulus decreased for the 20 wt% concentration in relation to the control (Table 2). In this case, the correlation between mechanical properties and thio-urethane concentration is complicated by the fact that the oligomers were added to the fully formulated material, and therefore, the filler content for the modified materials was progressively lower than for the un-modified control. Since the commercial material contains 66 wt% filler according to the manufacturer literature, adding 10 and 20 wt% thio-urethane brings the filler content to 63.6% and 60.8 wt%, respectively. This fact may explain the lack of statistical significance for flexural strength and toughness and the decrease in flexural modulus observed in this study, considering that these properties are heavily dependent on the inorganic content [24]. In fact, a previous study has shown that the elastic modulus drops from 5.9 to 4.3 GPa when the filler content was reduced from 60 to 55 vol.% [24], which represents roughly a 30 % reduction in modulus. In the current study, the reduction in filler content led to a drop in modulus of about 20%, lower than expected based on these previous results [24]. It is also interesting to note that, in spite of higher filler content in the commercial materials, the toughness results obtained with the addition of thio-urethanes to BisGMA/UDMA/TEGDMA are not much lower than the ones obtained with the modified commercial materials, which demonstrates the potential for toughening of methacrylate networks with the thio-urethanes.

One of the mechanical properties that have been shown to correlate with clinical results is fracture toughness [25]. The groups modified with the aromatic version of the thiourethanes presented an increase of 88.8% and 108.5% and the groups modified by aliphatic showed an increase of 105.9% and 176% in the K_{1c} for 10 wt% and 20 wt% concentrations, respectively, for the material formulated with BisGMA/UDMA/TEGDMA. The more than 2-fold increase for the 20 wt% concentration can be explained both by a more homogenous network, as already explained, but mainly by the combined contributions of the thio-urethane and the thiol-methacrylate bonds. Moreover, the most flexible structure of PETMP combined with the aliphatic diisocyanate, HDDI, showed to lead to significant higher values than the aromatic version. In the same way, the modification of commercial cement also significantly increased the K_{1c} in 25%, with 20 wt% of oligomer. This is important for resin cements because their clinical application consists in a thin layer of material placed in tapered preparation constantly subjected to tensile, compressive and oblique loads, with relatively common micro-defects into its structure. In addition, not only this modification is important for resin cements, it also provides another factors for increase in mechanical properties in heavily filled composites, as will be explored in a different study. Generally, the second hypothesis, that thio-urethanes would improve the mechanical properties of resin cements, was accepted.

The volumetric shrinkage (VS) showed significant reductions of 15.5% and 19.5% for aromatic and 39.8% and 52.4% for aliphatic thio-urethane oligomers when added to the non-commercial cement at 10 and 20 wt% concentrations, respectively. This was expected based on the decrease in concentration of methacrylate double-bonds per unit volume of the material. Indeed the percent reductions in shrinkage, at least for the aromatic versions, are in agreement with the amount of thio-urethane added [10,26]. It is important to note that the reduction in shrinkage was not accompanied by a reduction in conversion, as previously discussed. Conversely, conversion values either stayed constant or increased, as was the case for the aliphatic version. Interestingly, the aliphatic thio-urethane showed shrinkage reductions of 39.7 and 52.3 % with the addition of 10 and 20 wt% oligomer in comparison to the control, much higher than the prediction based on the molar shrinkage coefficient and the increased conversion [27]. One hypothesis that may explain this finding is the free volume entrapment within the pre-polymerized network, as is the case of more flexible structures such as the aliphatic thio-urethane [28]. Free volume analysis using positron annihilation will be conducted in future studies. The correlation between the percent reduction in shrinkage (5.6% and 21.2% for the 10 and 20 wt% of aromatic concentrations, respectively) for the commercial material is complicated by the dilution of the filler content for the modified materials compared to the un-modified control, as well as the higher filler content on the commercial materials, as already discussed for the mechanical properties. This may help explain why there was no statistically significant difference among the commercial materials groups in terms of shrinkage.

The volumetric shrinkage reduction helps explain the significant lower polymerization stress obtained with thio-urethane-based materials. The addition of 10 and 20 wt% of thio-urethanes led to reductions in stress values of 44.2% and 61.6%, respectively for the aromatic version, and 55.1% and 86%, respectively, for the aliphatic version in relation to the control for the non-commercial materials. It is important to note that the elastic modulus and the conversion were similar or greater for all modified formulations in relation to the control. However, even though there was a reduction in shrinkage, it was not large enough to justify the level of reduction in stress observed in this study. Hence, it can be inferred that chain-transfer reactions from the pendant thiols on the thio-urethane backbone to the surrounding methacrylate matrix indeed delayed gelation/vitrification [14], as further demonstrated by the kinetic profiles for these materials (Figure 1). Even though the conversion at vitrification did not seem to be significantly affected by the addition of thio-urethane, the rate of deceleration was significantly lower, which was possible by avoiding extended early-stage diffusion limitations to polymerization [23], reducing the stress development, which increases as soon as diffusion limitation occurs [6]. For the commercial cement, only the aromatic thio-urethane was tested for stress. The addition of 10 and 20 wt% oligomer led to stress reductions of 11.1% and 36.7%, respectively, although only the 20 wt% group was statistically lower than the control. Again, for the 20 wt% group, the stress reduction was higher than predicted based on the shrinkage reduction alone, especially when the increase in conversion is considered. On the other hand, in the case of the commercial material, the stress reduction is partially explained by the reduction in modulus, which in turn stemmed from the dilution of filler content, as already discussed. Therefore, because the composition was not completely controllable for the commercial material, and given the complex nature of the factors leading to polymerization stress, the effect of thio-urethanes in stress reduction in commercial materials was not conclusive. Taking in consideration the experimental material formulated front controlled proportions, it can be established that the third hypothesis, that oligomers would cause a reduction in the volumetric shrinkage and polymerization stress, can be accepted.

5. Conclusion

When the cement composition was completely known (BisGMA/UDMA/TEGDMA experimental cements, 25 wt% filler) the thio-urethane oligomers, specially the aliphatic versions, were able to improve conversion and mechanical properties, with more than 2 fold increases in toughness and fracture toughness. At the same time, conversion and properties improved, and polymerization shrinkage and stress are significantly reduced.

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References

1. Peumans M, Van Meerbeek B, Lambrechts P, Vanherle G. Porcelain veneers: a review of the literature. J Dent 2000; 28(3):163–177.
2. Manso AP, Silva NRFA, Bonfante EA, Pegoraro TA, Dias RA, Carvalho RM. Cements and Adhesives for all-ceramic restorations. Dent Clin North Am 2011; 55(2):311-332.
3. Meyer JM, Cattani-Lorente MA, Dupuis V. Compomers: between glass–ionomer cements and composites. Biomaterials 1998;19(6):529–539.
4. Rosenstiel SF, Land MF, Crispin BJ. Dental luting agents: a review of the current literature. J Prosthet Dent 1998; 80(3):280–301.
5. Braga RR, Ferracane JL, Condon JR. Polymerization contraction stress in dual-cure cements and its effect on interfacial integrity of bonded inlays. J Dent 2002; 30(7-8):333-340.
6. Lu H, Carioscia JA, Stansbury JW, Bowman N. Investigatios of step-growth thiol-ene polymerizations for novel dental restoratives. Dent Mater 2005; 21(12):1129-1136.
7. Cramer NB, Couch CL, Schreck KM, Carioscia JA, Boulden JE, Stansbury JW, Bowman CN. Investigation of thiol-ene and thiol-ene-methacrylate based resins as dental restorative materials. Dent Mater 2010; 26(1):21-28.
8. Cramer NB, Couch CL, Schreck KM, Boulden JE, Wydra R, Stansbury JW, Bowman CN. Properties of methacrylate-thiol-ene formulations as dental restorative materials. Dent Mater 2010; 26(8):799-806.
9. Boulden JE, Cramer NB, Schreck KM, Couch CL, Bracho-Troconis C, Stansbury JW, Bowman CN. Thiol-ene-methacrylate composites as dental restorative materials. Dent Mater 2011; 27(3):267-272.

10. Hoyle CE, Bowman CN. Thiol–ene click chemistry. Angew Chem 2010;49:1540–73.

11. Beigi S, Yeganeh H, Atai M. Evaluation of fracture toughness and mechanical properties of ternary thiol-ene-methacrylate systems as resin matrix for dental restorative composites. Dent Mater 2013; 29(7):777-787.

12. Senyurt AF, Hoyle CE. Thermal and mechanical properties of cross-linked photopolymers based on multifunctional thiol-urethane ene monomers. Macromolecules 2007; 40(9): 3174-3182.

13. Li Q, Wicks DA, Hoyle CE. Thiouretane-Based Thiol-Ene High T_g Networks: Preparation, Thermal, Mechanical, and Physical Properties. J Polymer Sci Part A: Polymer chemistry 2007; 45(22): 5103-5111.

14. Pfeifer C, Lewis S, Stansbury J. Thio-urethane oligomers as low-stress, tough additives in methacrylate polymerizations. IADR 2012.

15. Berchtold KA, Lovestead TM, Bowman CN. Coupling chain length dependent and reaction diffusion controlled termination in the free radical polymerization of multivinyl (meth)acrylates. Macromolecules 2002; 35(21):7968-7975.

16. Stansbury JW, Dickens SH. Determination of double bond conversion in dental resins by near infrared spectroscopy. Dent Mater 2001;17:71–9.

17. Standard I. ISO 4049 polymer based filling, restorative and luting materials. International Organization for Standardization; 2000. p. 1–27.

18. Watts DC, Satterthwaite JD. Axial shrinkage-stress dependens upon both C-factor and composite mass. Dent Mater 2008; 24(1):1-8.

19. Designation A. E399-90. Standard test method for plane-strain fracture toughness of metallic materials. Philadelphia, PA: American Society for Testing Materials; 1997. p. t990.

20. Sakai M, Bradt R. Fracture toughness testing of brittle materials. International Materials Reviews 1993;38: 53–78.

21. Odian G. Principles of polymerization. New York: Wiley-Interscience; 2004.

22. Pfeifer CS, Wilson ND, Shelton ZR, Stansbury JW. Delayed gelation through chain-transfer reactions: mechanism for stress reduction in methacrylate. Polymer 2011; 52(15):3295-3303.

23. Lecamp L, Houllier F, Youssef B, Bunel C. Photoinitiated cross-linking of a thiol methacrylate system. Polymer 2001; 42(7):2727-2736.

24. Gonçalves F, Kawano Y, Braga RR. Contraction stress related to composite inorganic content. Dent Mater 2010; 26(7):704-9.

25. Ferracane JL. Resin-based composite performance: are there some things we can't predict? Dent Mater 2013; 29(1):51-58.

26. Lee TY, Carioscia J, Smith Z, Bowman CN. Thiol-allyl ether-methacrylate ternary systems. Evolution mechanism of polymerization-induced shrinkage stress and mechanical properties. Macromolecules 2007; 40(5):1473-1479.

27. Patel MP, Braden M, Davy KW. Polymerization shrinkage of methacrylate esters. Biomaterials 1987; 8(1):53-56.

28. Pfeifer CS, Shelton ZR, Braga RR, Windmoller D, Machado JC, Stansbury JW. Characterization of dimethacrylate polymeric networks: a study of the crosslinked structure formed by monomers used in dental composites. Eur Polym J, 2011;47(2):162-170.

Table 1. Degree of conversion, maximum rate of polymerization (Rp_{max}) and conversion at vitrification for experimental cements. Values followed by the same letter within the same test are statistically similar (α=5%).

	Degree of conversion (%)*		Rp_{max} (%.s^{-1})**		Vitrification (%)**	
	aromatic	**aliphatic**	**aromatic**	**aliphatic**	**aromatic**	**aliphatic**
control	64.87(0.44)^{d}		4.5(0.6)^{a}		15.7(1.1)^{ab}	
10wt%	64.8(0.3)^{d}	66.2(0.3)^{c}	2.2(0.3)^{b}	1.7(0.1)^{b,c}	13(1.8)^{ab}	11.6(1.6)^{b}
20wt%	63.6(0.4)^{e}	69.4(0.3)^{b}	2.1(0.1)^{b,c}	1.2(0.0)^{c}	11.8(1.5)^{b}	17.7(3.8)^{a}
30wt%	64.9(0.4)^{d}	73.5(0.3)^{a}	1.6(0.1)^{c}	1.2(0.2)^{c}	18.2(2.2)^{a}	15.2(4.1)^{ab}

*obtained from photoactivation accomplished with the light guide in direct contact with the specimen

**obtained from specimens photoactivated in the IR chamber.

Table 2. Mean and standard deviation for degree of conversion, maximum rate of polymerization (Rp_{max}), conversion at vitrification, flexural strength, flexural modulus and toughness for RelyX Veneer cement modified with aromatic thio-urethane oligomers. Values followed by the same letter within the same test are statistically similar (α=5%).

	Degree of conversion (%)	Rp_{max} (%.s^{-1})	Vitrification (%)	Flexural strength (MPa)	Flexural modulus (GPa)	Toughness (MPa)
Control	65.35(0.16)^{b}	4.69(0.13)^{a}	10.93(0.50)^{a}	234(24.86)^{a}	8.06(0.79)^{a}	4.76(0.55)^{a}
10wt%	66.77(1.23)^{ab}	1.35(0.34)^{b}	15.36(1.17)^{b}	226.42(27.89)^{a}	7.09(0.94)^{ab}	5.48(0.49)^{a}
20wt%	68.25(1.15)^{a}	0.75(0.03)^{b}	16.03(3.39)^{b}	205.03(28.03)^{a}	6.42(0.74)^{b}	5.5(0.8)^{a}

Table 3. Mean and standard deviation for flexural strength, flexural modulus and toughness for the BisGMA/UDMA/TEGDMA cements modified with aromatic or aliphatic thio-urethane oligomers. Values followed by the same letter within the same test are statistically similar (α=5%).

	Flexural strength (MPa)		Flexural modulus (GPa)		Toughness (MPa)	
	aromatic	**aliphatic**	**aromatic**	**aliphatic**	**aromatic**	**aliphatic**
control	90.61(18.91)^{c}		2.02(0.17)^{b}		2.37(0.62)^{b}	
10wt%	108.56(20.68)^{ab}	100.96(15.84)^{bc}	2.23(0.26)^{a}	2.04(0.13)^{ab}	3.83(0.78)^{b}	7.32(1.96)^{a}
20wt%	122.52(12.78)^{a}	108.13(9.84)^{ab}	2.15(0.11)^{ab}	2.08(0.19)^{ab}	3.48(1.36)^{b}	8.21(3.69)^{a}
30wt%	112.5(8.62)^{ab}	95.28(6.28)^{bc}	2.03(0.08)^{b}	1.72(0.13)^{c}	-	-

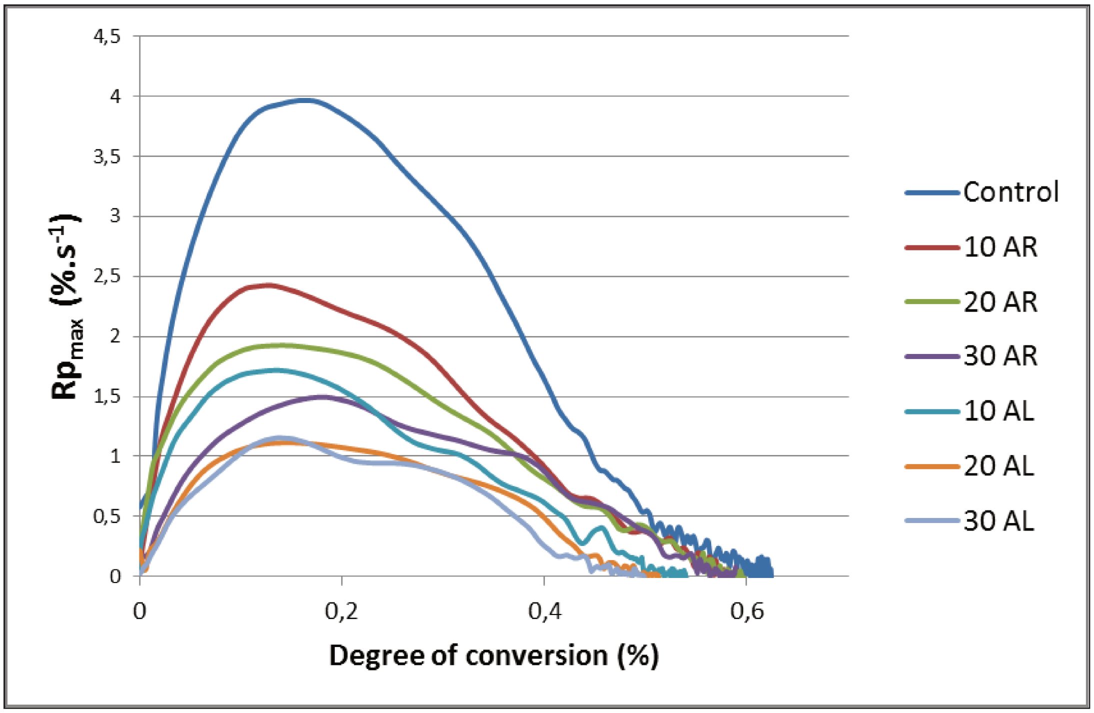

Figure 1: Degree of conversion as a function of the rate of polymerization for the control and experimental groups. The organic matrix is composed of BisGMA/UDMA/TEGDMA and aromatic (AR) or aliphatic (AL) thio-urethanes at increasing concentrations (10-30 wt%).

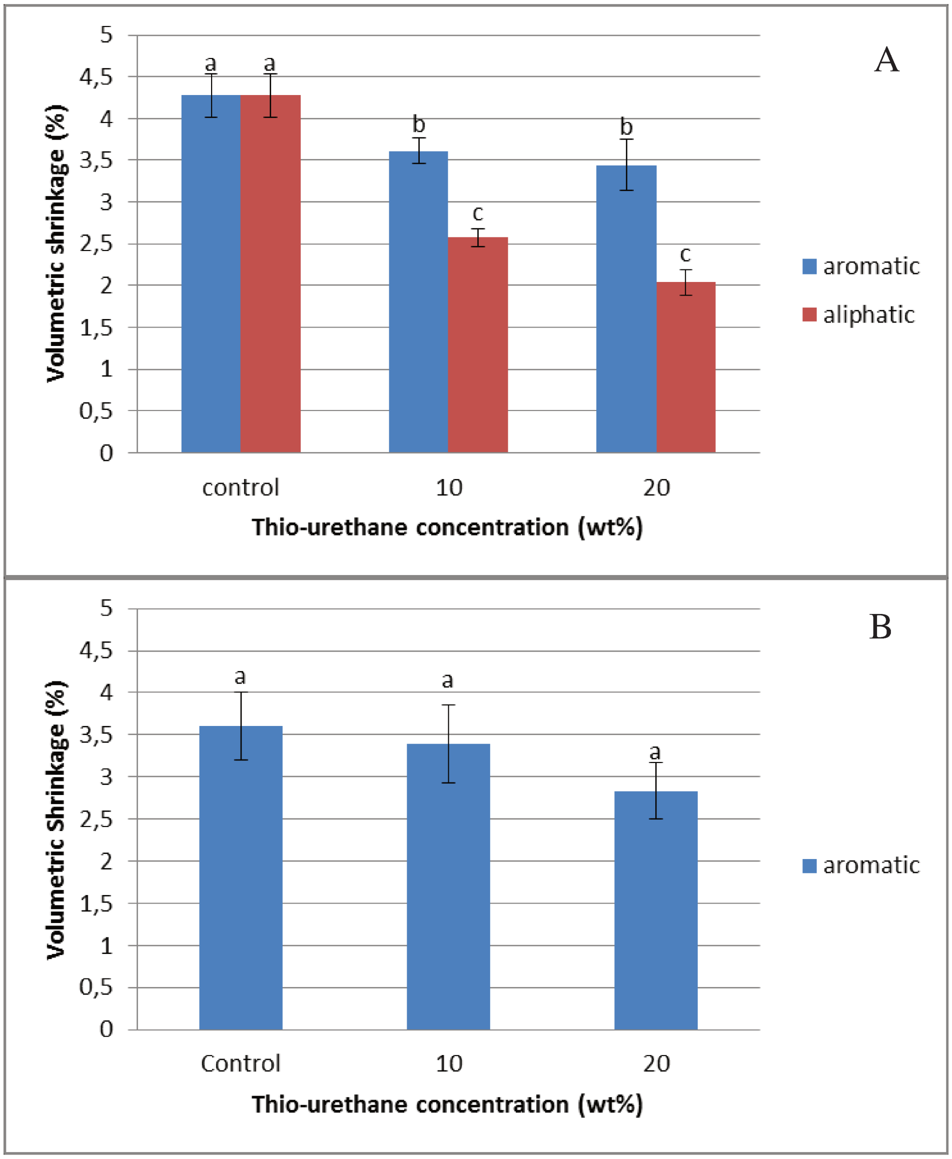

Figure 2: Volumetric shrinkage for (A) BisGMA/UDMA/TEGDMA cement and (B) commercial cement (RelyX Veneer).

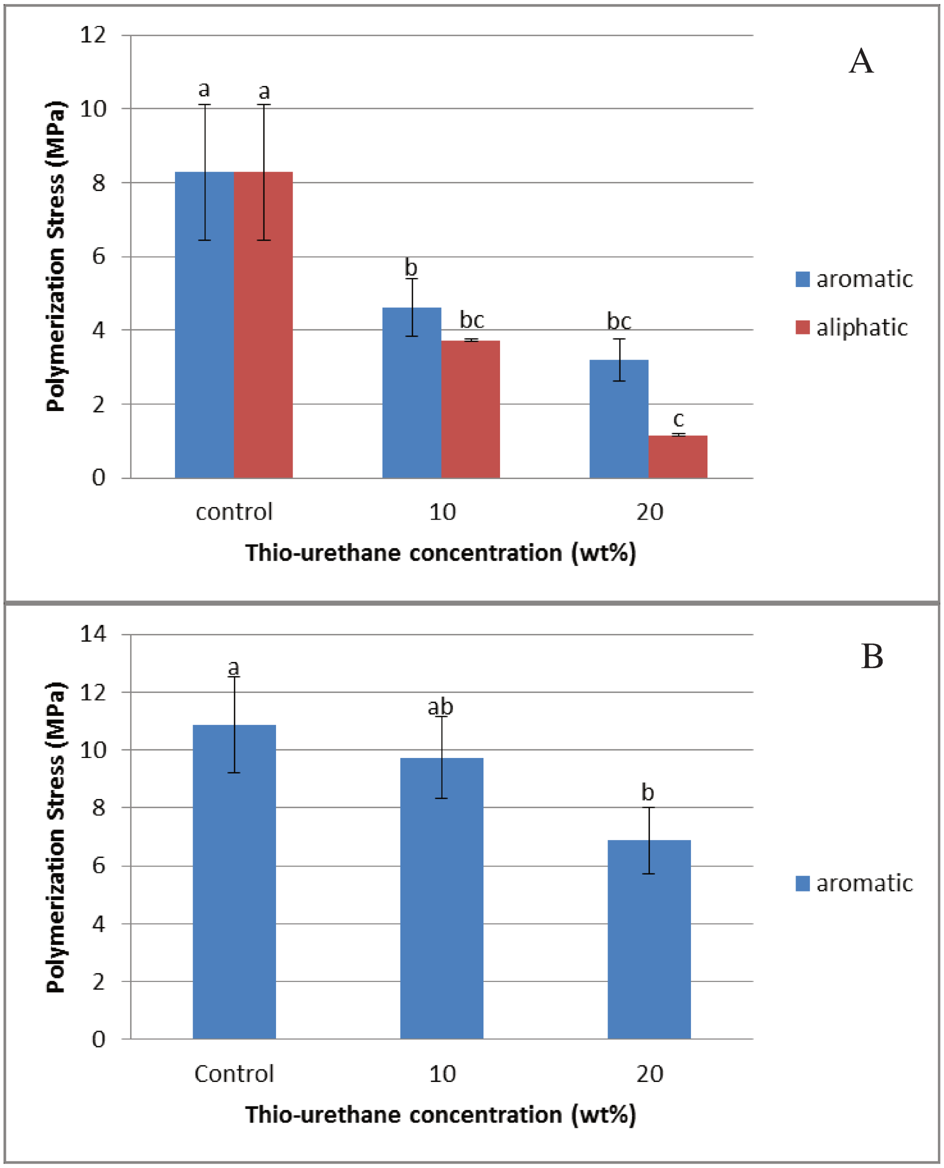

Figure 3: Polymerization stress values for (A) BisGMA/UDMA/TEGDMA cement and (B) commercial cement (RelyX Veneer).

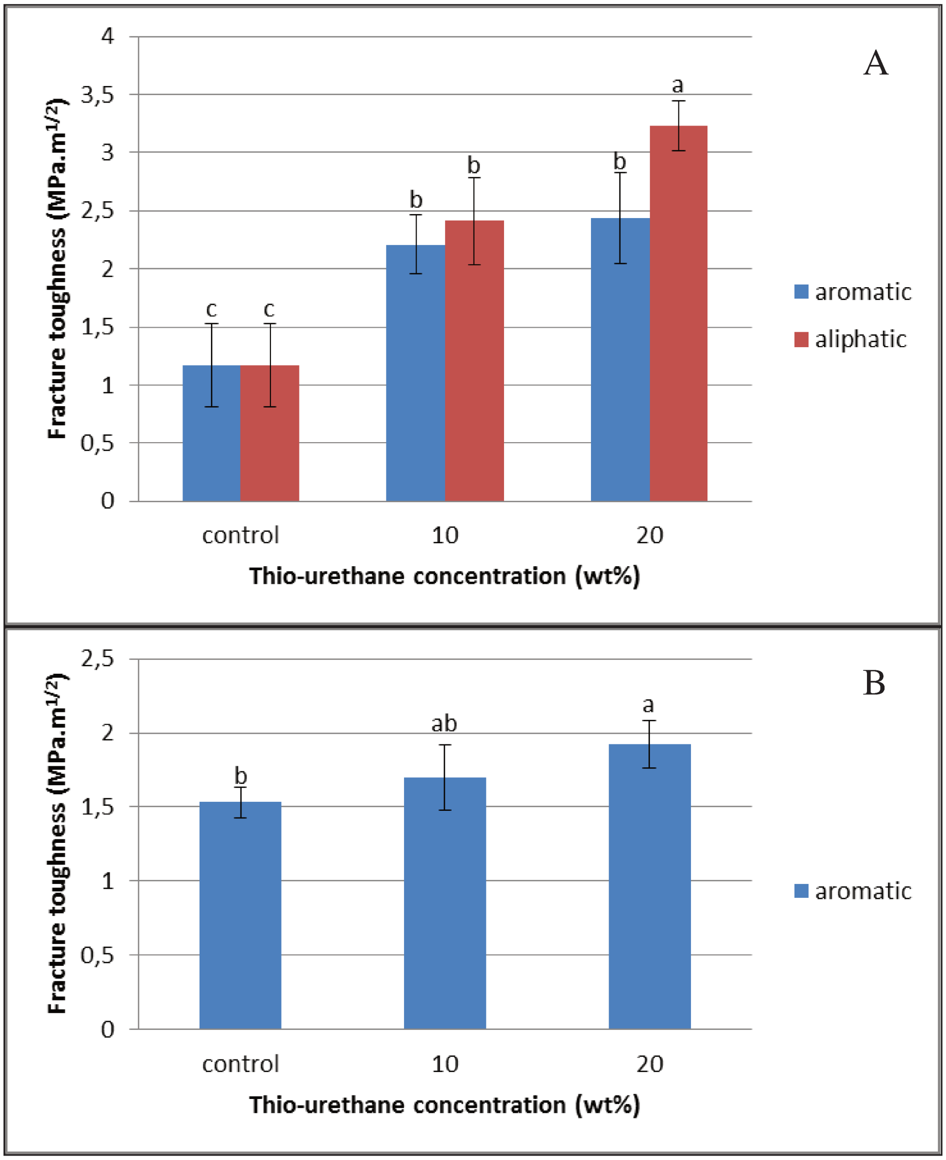

Figure 4: Fracture toughness values for (A) BisGMA/UDMA/TEGDMA cement and (B) commercial cement (RelyX Veneer).

CAPÍTULO 2

Thio-urethanes improving properties of dual-cured resin cements

ABSTRACT

This study aims at modifying dual-cure resin cements by adding thio-urethane oligomers to improve mechanical properties, especially fracture toughness, and reduce polymerization stress. Thiol-functionalized oligomers were synthesized by combining 1,3-bis(1-isocyanato-1-methylethyl)benzene with trimethylol-tris-3-mercaptopropionate, at 1:2 isocyanate:thiol. Oligomer was added at 0, 10 or 20 wt% to BisGMA-UDMA-TEGDMA (BUT, 5:3:2, with 25wt% silanated inorganic fillers) or to one commercial resin cement (Relyx Ultimate, 3M Espe). Near-IR was used to measure methacrylate conversion after photoactivation (700 mW/cm^2 x 60s) and after 72 h. Flexural strength/modulus (FS/FM) and toughness and fracture toughness (K_{IC}) were evaluated in three-point bending . Polymerization stress was measured with the Bioman. The microtensile bond strength (µTBS) of an indirect composite and a glass ceramic to dentin was also evaluated. Results were analyzed with ANOVA/Tukey's test (α=0.05). For BUT cements, conversion values were not affected by the addition of thio-urethanes. FS/FM increased significantly for both oligomer concentrations, with a 3-fold increase in toughness at 20wt%. Fracture toughness increased over 2-fold for the thio-urethane modified groups. Contraction stress was reduced by 40-50% with the addition of thio-urethanes. The addition of thiourethanes to the commercial cement, led to similar FS, toughness and conversion at 72h compared to the control. FM decreased for the 20 wt% group, due to the dilution of the overall filler volume, which also led to decreased stress. However, K_{IC} increased by up to 50%. The μTBS was increased for the experimental resin cement with 20 wt% thio-urethane bonding for both an indirect composite and a glass ceramic. Novel dual-cured resin cements containing thio-urethanes showed increased toughness, fracture toughness and bond strength to dentin while demonstrating reduced contraction stress. All of these benefits are derived without compromising the methacrylate conversion of the resin component. The modification does not require changes on the operatory technique.

Key-words: resin cements; thio-urethane oligomers; polymerization stress; mechanical resistance; bond-strength.

INTRODUCTION

Dual-cured resin cements are extensively used in Restorative Dentistry. Examples of their clinical applications include the bonding of ceramic fragments, crowns, bridges and intra-canal posts. Due to the tapered configuration of the tooth preparation for indirect restorations, characteristics such as resistance to dissolution, strong bond to tooth and prosthetic structures and excellent mechanical properties are requisites for resin cements (Meyer *et al.*, 1998; Rosenstiel *et al.*, 1998; Manso *et al.*, 2011). Current commercial methacrylate-based materials present some drawbacks, such as polymerization shrinkage values between 1.77% and 5.28% (Spinell *et al.*, 2009), which increases the risk of stress concentration and gap formation at the cement margin and ultimately may lead to adhesion failure (D'Arcangelo *et al.*, 2009).

At least for more heavily filled composites, reduction in polymerization shrinkage and stress can be accomplished through the substitution of monomers with pre-polymerized resin particles (Moraes *et al.*, 2011). Polymerization stress reduction can also be achieved through delayed vitrification, achieved by adding thiol-modified molecules, such as thiol-ene oligomers. Chain-transfer reactions of the thiol to the ene/vinyl lead to more homogeneous network formation, while delaying vitrification to higher conversion levels, thus reducing stress with the added benefit of increased final conversion (Lu *et al*., 2005; Cramer *et al*., 2010; Boulden *et al*., 2011), but unfortunately with some loss in mechanical properties (Lu *et al*., 2005).

Thio-urethane oligomers present an attractive alternative to common non-functionalized pre-polymers and even thiol-ene oligomers, due to the high toughness imparted by the flexible thio-urethane bonds to the polymer matrix and an overall more homogeneous network formation (Senyurt *et al*., 2007). Materials involving thiol/isocyanate reactions have been used to produce two-part systems for applications requiring high fracture toughness and impact resistance (Senyurt *et al*., 2007).

This study describes a novel approach, not previously attempted for dental applications, through the use of thiol-terminated thio-urethane oligomers as additives in methacrylate matrices for dental resin cements with enhanced toughness, reduced stress and improved bond strength. The rationale behind these materials is to verage the delayed gelation resulting from the pendant thiol functionalities in order to reduce stress, increase conversion and improve network homogeneity (Pfeifer *et al*., 2012), reduce shrinkage through the addition of pre-polymerized particles (Moraes *et al*., 2011), and increase toughness/fracture toughness and bond strength through the flexible thio-urethane bonds (Senyurt *et al*., 2007). Finally, by improving fracture toughness, improved bond strength of indirect restorations cemented with the thio-urethane modified cements can be expected.

Therefore, the aim of this study was to synthesize pre-polymerized oligomers based on thio-urethane chemistry, containing pendant thiol functionalities for improving the properties of dual-cured resin cements. The hypotheses of this study were that the thio-urethanes would (I) increase the degree of conversion, (II) improve mechanical properties, (III) reduce the polymerization stress of a secondary crosslinked methacrylate network and (IV) improve the bond strength of indirect resin composites and ceramics cemented to dentin.

MATERIALS & METHODS

Oligomers were synthesized by combining 1,3-bis(1-isocyanato-1-methylethyl)benzene with trimethylol-tris-3-mercaptopropionate in solution, at 1:2 isocyanate:thiol, resulting in pendant thiols from the aromatic (AR) oligomer structure. The reaction was carried out in solution at room temperature using triethylamine in catalytic amounts. The oligomers were purified by precipitation in hexanes and the solvent was removed under vacuum. The resulting product is a viscous liquid.

Experimental dual-cured resin cements were produced by combining Bis-phenol A diglycidyl dimethacrylate (Bis-GMA), urethane dimethacrylate (UDMA) and tri-ethylene glycol dimethacrylate (TEGDMA), all from Esstech (Essington, PA, USA) in a 50:30:20 mass ratio (BUT materials). To this resin 0.2 wt% of dl-camphoroquinone, 0.6 wt% of a tertiary amine (EDMAB - ethyl 4-dimethylaminobenzoate), and 0.8 wt% inhibitor (BHT - 2,6-di-tert-butyl-4-methylphenol; SigmaAldrich, St. Louis, MO, USA) were added. Thio-urethane oligomers were added at 0 (control), 10 and 20 wt% to produce component A. A second component, B, was made by the addition of 0.5 wt% of benzoyl-peroxide (SigmaAldrich) to paste A .

To each component (A and B) was added a total of 25 wt% filler composed of 15% of 0.04μm average silane-treated silica, (OX-50) and 85% of 0.7μm silane-treated silica(Esstech), with the aid of a mechanical mixer (DAC 150 Speed mixer, Flacktek, Landrum, SC, USA) operated for 5 min at 2400 rpm.

A BisGMA/TEGDMA-based commercial dual-cured cement (RelyX Ultimate, 3M Espe, St. Paul, USA – lot 498131, translucent) was also used in the as received form as well as modified by the addition of 10 and 20 wt% of oligomer, resulting cements with filler contents of 66, 63.6 and 60.8 wt%, respectively (based on manufacturer data).

Materials were mixed immediately before use. Composite discs (0.8 mm thick, 10 mm in diameter, n=3) were formed between two glass slides. Degree of conversion (DC) was obtained using near–infrared (NIR) spectroscopy (2 scans/spectrum, 4 cm^{-1} resolution, >2 Hz data acquisition rate) based on the area of the methacrylate vinyl overtone at 6165 cm^{-1} (Stansbury & Dickens, 2001) before and after 60s of direct irradiation with a LED light source (Bluephase, Ivoclar Vivadent, Lichtenstein) at an incident irradiance of 700 mW/cm^2. Specimens were stored dry in dark containers for 72 h and tested again.

Bar specimens (*n*=10, 2x2x25 mm) were fabricated using silicone molds between glass slides and photopolymerized as described above, then stored dry for one week in dark containers at room temperature. Flexural strength of the samples was measured according to ISO 4049 (Standard I, 2009) in 3-point bending using a universal test machine (Q-test, MTS, Eden Prairie, WI) at a cross-head speed of 0.5 mm/min. Elastic modulus (GPa) was determined by the software from the slope of the initial linear portion of the stress–strain curve. Toughness (MPa) was calculated from the integration of the stress x stain curve (Origin 9.1, OriginLab Corporation, Northampton, MA, USA).

To determine the fracture toughness (FT), single-edge notch beam (SENB) specimens (*n*=5) were fabricated according to ASTM Standard E399- 90 (Designation A, 1997) in a 5x2x25 mm split steel mold with a razor blade insert providing a 2.5 mm notch at the center of the specimens. The test was performed in three-point bending at a cross-head speed of 0.5 mm min^{-1} on the universal test machine (Q-test) and the fracture toughness (critical stress intensity factor, K_{IC}) was calculated as previously described (Ferracane & Berge, 1995).

Polymerization stress development was followed in real-time for 30 min using the Bioman, as described previously (Watts & Satterthwaite, 2008). Briefly, the resin cement (*n*=5) was applied between a silica slab and a roughened steel piston producing a cement of 0.5-mm thickness, corresponding to a C-factor of 4, then photoactivated through the glass during 60 s with an incident irradiance of 670 mW/cm^2 (Bluephase; Ivoclar-Vivadent).

Microtensile bond strength was tested with thirty-six caries-free human molars extracted for periodontal reasons. Deep dentin was exposed by cutting the occlusal crown 2.0 mm above the CEJ. The commercial cement (control and modified groups with 10 and 20 wt% of oligomer) was used with an etch-and-rinse adhesive (Adper Singlebond 2; 3M ESPE) for bonding an indirect composite (Z250, 3M ESPE, built in a silicone mold cured in a TRIAD oven, Dentsply) or a glass ceramic (IPS Empress, Ivoclar Vivadent). Samples (*n*=6) were stored for one week in distilled water (37°C) before being sectioned in ~1 mm^2 match-sticks. The sticks were glued to a testing fixture (obtained from Bisco, Inc., Schaumburg, IL) and then pulled in tension in an universal testing machine at 0.5mm/min. The failure pattern was evaluated by stereomicroscopy/SEM.

Results within each cement material group were analyzed by one-way ANOVA and Tukey's test for making multiple comparisons (α=0.05).

RESULTS

There was a trend for the degree of conversion to be increased by the addition of thio-urethanes to the experimental (BUT) cement when measured immediately after photoactivation (p=0.145) or after 72 h (p=0.053), but the difference was not significant (Table 1). For the commercial material, the thio-urethane modified groups showed a significant reduction in DC when evaluated immediately (p=0.002), but where similar to the control after 72 h storage (p=0.930). .

Flexural strength and modulus significantly increased at both concentrations for the thio-urethane-modified BUT materials in relation to the control (p=0.000) (Table 2). The toughness increased by 3-fold for the 20 wt% oligomer concentration (p=0.000). The addition of thio-urethanes to the commercial material did not significantly affect FS (p=0.345) or toughness (p=0.202), but led to a reduction in the FM (p=0.018) for the 20 wt% oligomer concentration. The groups with 10 and 20 wt% oligomer showed 40.9% and 53.4%, reduced stress, respectively, vs. the control (p=0.003) for experimental cement (Figure 1A). A significant 65.7% reduction was observed when 20 wt% of thio-urethane was added to the commercial cement (p=0.000).

The addition of 10 and 20% thio-urethane produced significant increases of 54.5% and 136.3%, respectively, in the fracture toughness of the experimental cement (p=0.000) (Figure 1B). For the commercial cement, a significant increase in fracture toughness was produced at 20 wt% of oligomer (p=0.002), being 50% higher than the control.

The addition of 20 wt% oligomer led to a significant increase in μTBS values for both bonding substrates - indirect composite (p=0.039) or glass ceramic (p=0.005) (Table 2). Groups with 10 wt% of oligomer presented results intermediary between the control and the 20 wt% group. The failure patterns were predominantly mixed adhesive/cohesive for all groups. Control groups presented smoother fracture surfaces in comparison to the modified groups (Figures 2 and 3).

DISCUSSION

The addition of thiol-ene and thio-urethane oligomers to secondary methacrylate light-cured resins improves the formation of homogeneous polymer networks with higher degree of conversion (Lu *et al.*, 2005; Cramer *et al.*, 2010; Pfeifer *et al.*, 2012). Chain-transfer reactions between the thiol and the vinyl group are chain-breaking, which means the polymerization progresses through a radically-assisted step-growth mechanism (Cramer, 2001; Reddy, 2006), delaying the point at which diffusion limitations start to hamper polymerization to a much higher conversion, resulting in a higher conversion overall (Berchtold *et al.*, 2002). In the present study, the cements were polymerized through a dual-cure mechanism, making it difficult to follow the reaction kinetics in real-time. Therefore, conversion was only measured at two time points, immediately after polymerization and after 72 hours. For the experimental cements, immediate DC was around 70% for all groups, increasing to around 83% at 72 hours. At both evaluation times, the addition of thiol-functionalized thio-urethanes did not interfere with conversion, likely due to the fact that the materials have a redox component to the polymerization, which in itself contributes to delayed vitrification (Odian, 2004), masking the influence of the additives on conversion. For the commercial cement, the immediate conversion values decreased with the addition of thio-urethanes , and it is speculated that the slower progression of the reaction was due to delayed network formation. The values at 72 hours were all statistically similar at around 70%, and increased more markedly for the thio-urethane-modified materials. The difference in DC and curing rate between the experimental and commercial cements is attributed to differences in resin and catalyst formultion. It is also important to note that the overall conversion of the commercial materials was lower than the experimental counterparts, and other components in the formulation, outside of the control of the operator, likely played a role in kinetics for the former. In general, the addition of thiol-functionalized thio-urethanes did not affect conversion at 72 h for all dual-cured materials. Therefore, the first hyphothesis must be rejected.

In spite of the similar conversion values, a significant increase in the flexural strength, modulus and toughness was achieved via thio-urethane addition to the experimental cement. This was expected based on the more homogeneous network formed, as well as on the rigidity of the aromatic rings present in this particular thio-urethane oligomer. For the commercial cement, the values of flexural strength and toughness were not affected by the addition of thio-urethane, while the flexural modulus decreased, but only when 20 wt% thio-urethane was added (Table 2). Because the oligomers were added to the fully formulated commercial cement, there was an unavoidable reduction in the overall filler content for the modified materials which accounts for the 20% reduction in flexure modulus. According to the manufacturer, the commercial material contains 66 wt% filler, which means that adding 10 and 20 wt% thio-urethane brings the filler content to 63.6% and 60.8 wt%, respectively. A previous study demonstrated a larger 30% reduction in elastic modulus when the filler content of a composite was reduced by a mere 5 vol% (Gonçalves *et al.*, 2010), so the reduction in the present study was . actually lower than expected. However, the inability to control filler content may explain why the significant toughening effect seen for the experimental cement with 20% thio-urethane was not replicated for the commercial cement with 20%.

The most encouraging results, however, were presented by the fracture toughness tests. For the experimental cements (BUT), the addition of 10 and 20 wt% oligomer led to fracture toughness values 54.5% and 136.3% higher than the control, respectively, representing more than a two-fold increase. In the commercial cement, the addition of 20 wt% thio-urethane led to an increase of 50% in fracture toughness, in spite of the decrease in modulus described above due to the reduction in filler content. This points to the relevant contribution of the flexible thio-urethane bonds to the resistance to crack propagation and, ultimately, to the integrity of the network. Therefore, the second hypothesis is accepted.

The polymerization stress of the experimental cement was approximately 40% and 53% lower than the control for the groups with 10 and 20 wt% of thio-urethane oligomer, respectively. For both concentrations, this was accomplished without compromising the conversion and modulus – the latter actually increased by 27%. One explanation for the reduction in stress is the decrease in the concentration of methacrylate double-bonds per unit-volume of material given by the addition of pre-polymerized oligomers, leading to reduction of the volumetric shrinkage (Patel *et al.*, 1987). Second, the chain-transfer reactions from the pendant thiols on the thio-urethane structure to the surrounding methacrylate matrix has been demonstrated to delay gelation/vitrification, leading to lower stress development at the later stages of polymerization (Pfeifer *et al.*, 2011; Pfeifer *et al.*, 2012). For the commercial material, stress for the 20 wt% oligomer also presented a significant reduction of 65.7%. However, in this case, on top of the expected reduction in shrinkage and delayed vitrification, the reduction in stress is also explained by the reduction in flexural modulus observed for this group (Pfeifer *et al.*, 2008) due to the dilution of the filler content with the addition of the thio-urethanes. Therefore, the third hypothesis is partially accepted.

This study also evaluated the potential of thio-urethane modified matrix to increase the micro-tensile bond strength (µTBS) of an indirect composite and a glass ceramic to dentin. The improvement in fracture toughness was expected to enhance the bond strength for the thio-urethane-modified commercial cement (Fritz *et al.*, 1996). For this analysis only the commercial material was utilized to cement blocks of indirect resin composite and Empress ceramic to mid-coronal dentin. For both restorative materials, the use of 20 wt% of thio-urethane significantly increased µTBS values, being 23% higher for the composite substrate and 40% higher for ceramic compared to the control. The demonstrated increase in toughness and fracture toughness presented by this cement when modified with 20 wt% of oligomer is likely the main factor explaining the higher bond strength. Moreover, the reduced polymerization stress also likely decreased the residual stresses concentrated at the interfaces and in the bulk of the cement. When analyzing the fractured surfaces, the majority of the failure patterns were mixed, both for the control and for the modified groups. However, for the ceramic material, control groups presented smoother fracture surfaces in comparison to the modified groups, as demonstrated by SEM images. The increased roughness on the fracture surfaces of the modified materials indicates a greater energy required for fracture of the toughened materials (Quinn, 2007), consistent with the higher results obtained in the three-point bending test. As for the indirect composite groups, a greater incidence of exposed dentin tubules was observed for the groups modified by thio-urethane oligomers. It can be inferred that the toughening of the cement in those groups forced the crack to propagate at the dentin/adhesive interface, exposing the tubules on the surface. Therefore, the fourth hypothesis must be accepted, as the increase in fracture toughness and decrease in polymerization stress contributed to ultimately higher bond strengths of dentin with indirect restorative substrates. This was accomplished without reducing conversion and general mechanical properties and without disrupting current operatory techniques, which greatly facilitates the translation of this novel technology from bench-top to chair-side.

CONCLUSION

The addition of thio-urethanes to experimental and commercial dental resin cements significantly reduced the polymerization stress and increased the fracture toughness, as well as improved the bond strength of an indirect composite and a glass ceramic to dentin.

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CONFLICT OF INTEREST

The authors have no conflict of interest to disclose.

REFERENCES

Berchtold KA, Lovestead TM, Bowman CN (2002). Coupling chain length dependent and reaction diffusion controlled termination in the free radical polymerization of multivinyl (meth)acrylates. *Macromolecules* 35:7968-7975.

Boulden JE, Cramer NB, Schreck KM, Couch CL, Bracho-Troconis C, Stansbury JW, Bowman CN (2011). Thiol-ene-methacrylate composites as dental restorative materials. *Dent Mater* 27:267-272.

Cramer NB, Bowman CN (2001). Kinetics of thiol-ene and thiol-acrylate photopolymerization with real-time Fourier transform infrared. *J Polym Sci Part A: Polym Chem* 39:3311-3319.

Cramer NB, Couch CL, Schreck KM, Carioscia JA, Boulden JE, Stansbury JW, Bowman CN (2010). Investigation of thiol-ene and thiol-ene-methacrylate based resins as dental restorative materials. *Dent Mater* 26:21-28.

D'Arcangelo C, de Angelis F, D'Amario M, Zazzeroni S, Ciampoli C, Caputi S (2009). The influence of luting systems on the microtensile bond strength of dentin to indirect resin-based composite and ceramic restorations. *Oper Dent* 34:328-336.

Designation A (1997). E399-90. Standard test method for plane-strain fracture toughness of metallic materials. Philadelphia, PA: *American Society for Testing Materials*; p. t990.

Ferracane JL, Berge HX (1995). Fracture toughness of experimental dental composites aged in ethanol. *J Dent Res* 74:1418-23.

Fritz UB, Finger WJ, Uno S (1996). Resin-modified glass ionomer cements: bonding to enamel and dentin. *Dent Mater* 12:161-166.

Gonçalves F, Kawano Y, Braga RR (2010). Contraction stress related to composite inorganic content. *Dent Mater* 26:704-9.

Lu H, Carioscia JA, Stansbury JW, Bowman N (2005). Investigatios of step-growth thiol-ene polymerizations for novel dental restoratives. *Dent Mater* 21:1129-1136.

Manso AP, Silva NRFA, Bonfante EA, Pegoraro TA, Dias RA, Carvalho RM (2011). Cements and Adhesives for all-ceramic restorations. *Dent Clin North Am* 55:311-332.

Meyer JM, Cattani-Lorente MA, Dupuis V (1998). Compomers: between glass–ionomer cements and composites. *Biomaterials* 19:529–539.

Moraes RR, Garcia JW, Barros MD, Lewis SH, Pfeifer CS, Liu J, Stansbury JW (2011). Control of polymerization shrinkage and stress in nanogel-modified monomer and composite material. *Dent Mater* 27:509-519.

Odian G (2004). Principles of polymerization. New York: Wiley-Interscience.

Patel MP, Braden M, Davy KW (1987). Polymerization shrinkage of methacrylate esters. *Biomaterials* 8:53-56.

Pfeifer CS, Ferracane JL, Sakaguchi RL, Braga RR (2008). Factors affecting photopolymerization stress in dental composites. *J Dent Res* 8:1043-1047.

Pfeifer CS, Wilson ND, Shelton ZR, Stansbury JW (2011). Delayed gelation through chain-transfer reactions: mechanism for stress reduction in methacrylate. *Polymer* 52:3295-3303.

Pfeifer C, Lewis S, Stansbury J (2012). Thio-urethane oligomers as low-stress, tough additives in methacrylate polymerizations. *IADR General Section and Exhibition*.

Quinn GB (2007). Fractography of ceramics and glasses. NIST recommended practice guide. Special publication 960-916. Washington, DC: National Institute of Standards and technology.

Reddy SK, Cramer NB, Bowman CN (2006). Thiol-vinyl mechanisms, 1. Termination and propagation kinetics in thiol-ene photopolymerizations. *Macromolecules* 39:3673-3680.

Rosenstiel SF, Land MF, Crispin BJ (1998). Dental luting agents: a review of the current literature. *J Prosthet Dent* 80:280–301.

Senyurt AF, Hoyle CE (2007). Thermal and mechanical properties of cross-linked photopolymers based on multifunctional thiol-urethane ene monomers. *Macromolecules* 40:3174-3182.

Spinell T, Schedle A, Watts DC (2009). Polymerization shrinkage kinetics of dimethacrylate resin-cements. *Dent Mater* 25:1058–66.

Standard I (2000). ISO 4049 polymer based filling, restorative and luting materials. *International Organization for Standardization*; p. 1–27.

Stansbury JW, Dickens SH (2001). Determination of double bond conversion in dental resins by near infrared spectroscopy. *Dent Mater* 17:71–9.

Watts DC, Satterthwaite JD (2008). Axial shrinkage-stress dependens upon both C-factor and composite mass. *Dent Mater* 24:1-8.

Table 1: Mean and standard deviation for degree of conversion (%) for experimental and commercial cements immediately after light irradiation and after 72 h. Values followed by the same superscript within the same test are statistically similar (p=0.05).

Degree of conversion (%)

	Experimental		Commercial	
	immediate	After 72 h	immediate	After 72 h
Control	70.6(2.3)a	80.7(2.4)a	65.8(0.8)a	69.5(1.7)a
10wt%	72.4(1.0)a	83.5(1.5)a	59.7(3.2)b	69.5(1.4)a
20wt%	73.7(1.1)a	85.1(0.8)a	54(1.7)b	69.9(0.9)a

Table 2. Mean and standard deviations for flexural strength, flexural modulus and toughness for experimental (BUT) and commercial (CM) cements. Also shown in the table are the microtensile bond strength (µTBS) of an indirect composite and glass ceramic to dentin for the commercial (CM) cement modified with thio-urethanes. Values followed by the same superscript within the same test are statistically similar (α=5%).

	Flexural strength (MPa)		**Flexural modulus (GPa)**		**Toughness (MPa)**		**µTBS composite (MPa)**	**µTBS ceramic (MPa)**
	BUT	CM	BUT	CM	BUT	CM	CM	CM
Control	94.5(16.5)b	134(15.3)a	2.2(0.25)b	5.5(0.44)a	3.37(1.48)b	1.95(0.57)a	23.1(4.47)b	15.3(2.89)b
10 wt%	119.8(15.5)a	129.1(20.5)a	2.8(0.16)a	4.9(0.67)ab	3.89(1.54)b	1.81(0.49)a	26.95(1.66)ab	16.7(3.25)ab
20 wt%	131.6(6.6)a	121.5(16.3)a	2.8(0.24)a	4.3(0.11)b	10.22(2.61)a	2.36(0.84)a	28.41(2.05)a	21.4(2.17)a

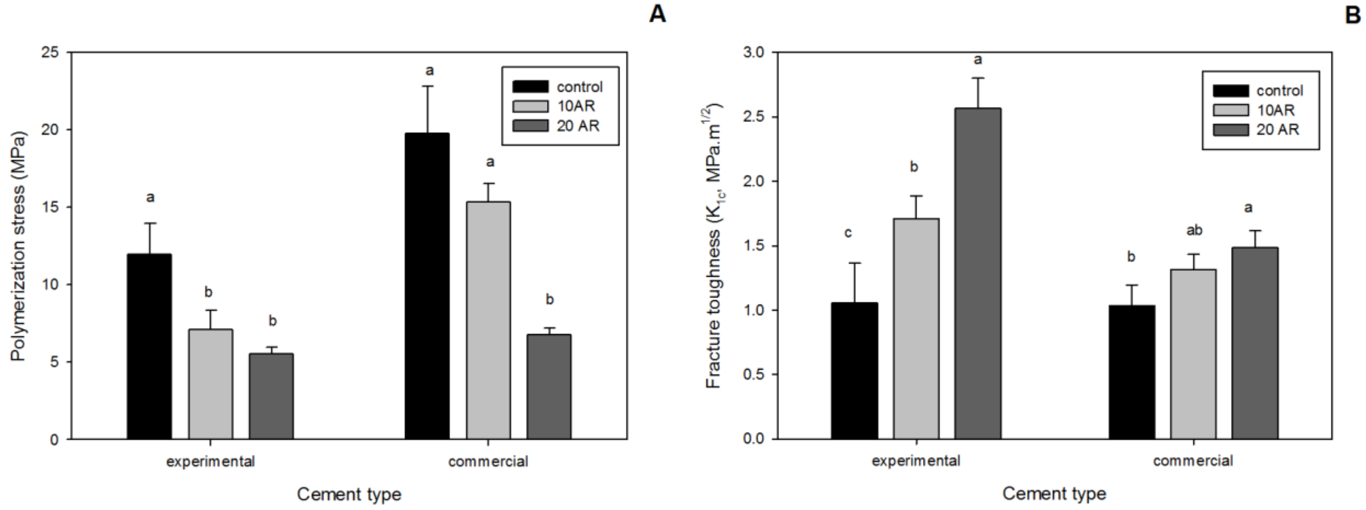


Figure 1. (A) Polymerization stress and (B) Fracture toughness values for the BisGMA/UDMA/TEGDMA cement and for the commercial cement (RelyX Ultimate) with 0 (control), 10 and 20 wt% of thio-urethane oligomer added.

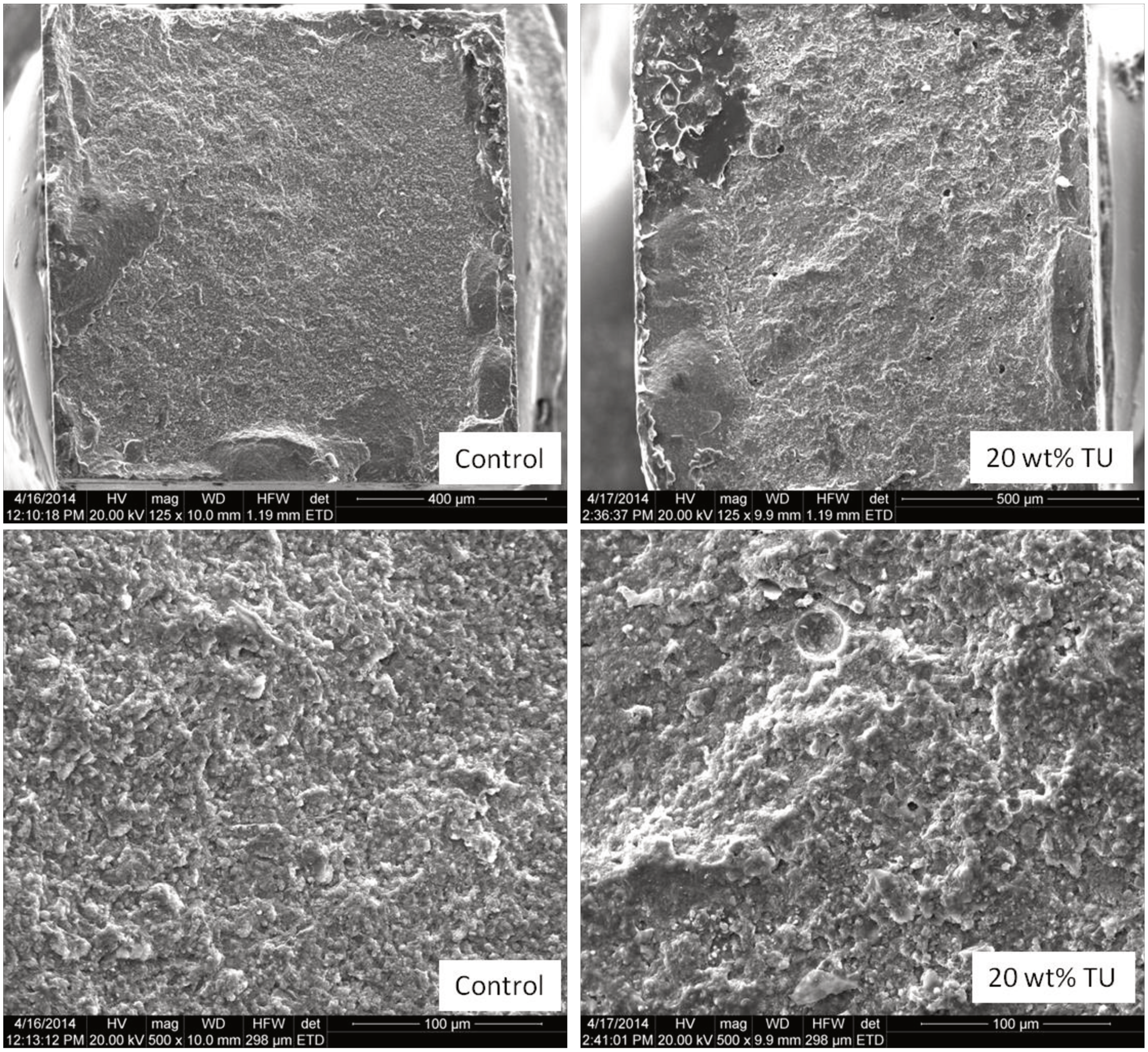


Figure 2. Scanning electron microscope images of fractured surfaces of microtensile bond strength **ceramic** specimens. In general, the modified groups presented rougher surfaces compared to the control materials. However, the majority of failures were mixed adhesive/cohesive regardless of the treatment.

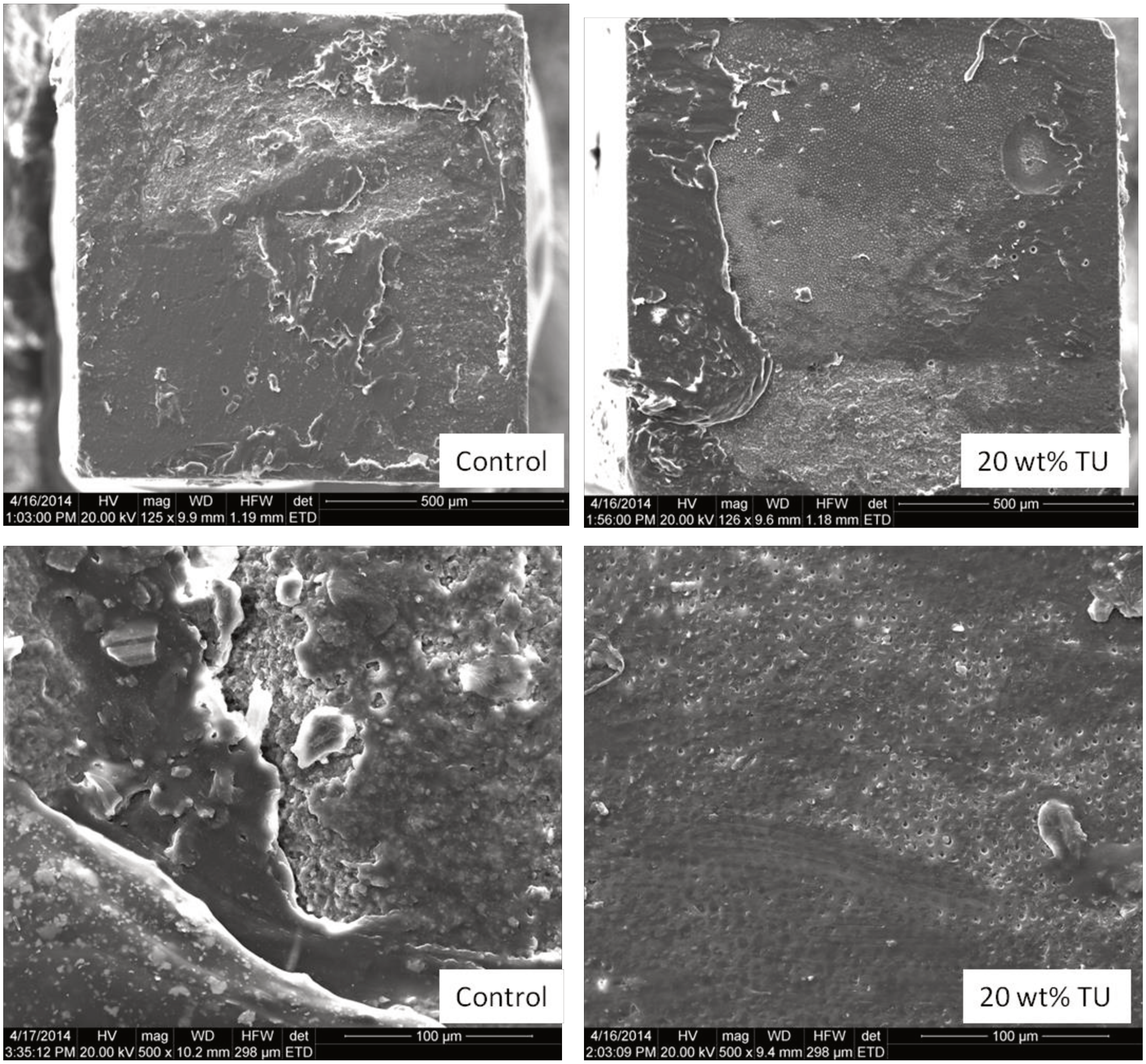


Figure 3. Scanning electron microscope images of fractured surfaces of microtensile bond strength **composite** specimens. Both specimens showed a mixed adhesive/cohesive failure pattern. However, exposed dentin tubules can be seen only for the modified groups, indicating that the increased toughness on the cement led the crack to propagate through the interface and not through the bulk of the material.

DISCUSSÃO

Este trabalho analisou cimentos resinosos formulados por oligômeros tiouretanos, com o propósito de obter melhora das propriedades mecânicas e minimizar problemas relacionados à contração de polimerização. Materiais fotopolimerizados e de ativação dupla foram avaliados. Os cimentos fotoativados têm sido apontados como vantajosos em função de proporcionar maior tempo de trabalho e maior estabilidade de cor (Buchalla *et al.*, 2002; Koishi *et al.*, 2002). Entretanto, quando em situações de restaurações espessas (cavidades profundas), materiais restauradores opacos e condutos radiculares a foto polimerização é pouco efetiva, resultando em menor grau de conversão (Faria e Silva *et al.*, 2007; Kim *et al.*, 2009). Assim, nessas ocasiões os cimentos resinosos de ativação dupla são necessários, considerando que a polimerização química irá ocorrer em regiões do cimento onde a luz não é capaz de atingir (Jongsma *et al.*, 2012).

Em relação ao processo de polimerização dos materiais avaliados, o uso de oligômeros alifáticos em cimentos experimentais fotoativados demonstrou potencial para aumentar o grau de conversão, o qual também foi influenciado pelo percentual de oligômero. Maior homogeneidade da rede polimérica tem sido relatada como resultante da aplicação dos tiouretanos e consequente aumento do grau de conversão (Hoyle & Bowman 2010; Senyurt & Hoyle 2007). Entretanto, a aplicação de oligômeros aromáticos, quando realizada em cimentos resinosos de ativação dupla ou fotoativados, mostrou tendência de grau de conversão final compatível com os grupos controle. Os valores da taxa máxima de polimerização (Rp_{max}) mostrou redução compatível com o aumento da concentração do oligômero nos cimentos foto ativados. O índice Rp_{max} representa o fim da autoaceleração, ou seja, o ponto de conversão em que a restrição da mobilidade das cadeias poliméricas diminui a propagação e terminação da reação química (Odian 2004). Nos grupos controle, a desaceleração ocorre imediatamente após atingir a taxa máxima, enquanto nos grupos tiouretano a desaceleração é retardada até atingir o maior grau de conversão, com intervalo constante na taxa de polimerização antes da desaceleração. Esta característica dá-se pela transferência da cadeia das terminações de tiol pendentes aos metacrilatos, importante para reduzir a tensão de polimerização. Quanto à vitrificação (grau de conversão na taxa máxima de polimerização), a influência dos oligômeros tiouretanos não foi conclusiva durante a avaliação dos materiais experimentais, quando apesar da diferença significativa (p=0.035), os grupos com tiouretanos não diferiram do controle pelo teste de Tukey (5%). Entretanto, na avaliação do cimento comercial fotopolimerizável foi observado aumento significativo na vitrificação de 40,53% e 46,66% para as concentrações de 10 e 20 % em peso de tiouretano aromático, respectivamente.

Propriedades mecânicas (resistência à flexão, módulo de elasticidade e tenacidade) dos cimentos foram avaliadas de acordo com a recomendação da ISO 4049 (Standard I, 2000). Para os cimentos experimentais fotoativados e de ativação dupla, formulados a partir da matriz de BISGMA/UDMA/TEGDMA, os grupos contendo tiouretanos promoveram aumento na resistência à flexão e no módulo de elasticidade, mais especificamente para a versão aromática do oligômero. Além da maior homogeneidade da matriz polimérica promovida pelos tiouretanos, esta condição também deve ser atribuída à rigidez dos anéis aromáticos do oligômero. Quando as mesmas propriedades foram avaliadas em materiais comercias (RelyX Veneer e RelyX Ultimate, 3M ESPE), a adição de tiouretanos não influenciou a resistência à flexão e promoveu redução no módulo de elasticidade para concentrações maiores do que 10% em peso. De certa forma um comportamento seria esperado, considerando que os oligômeros passaram a fazer parte da matriz orgânica de um material que já constava da formulação final. Assim, com a adição dos tiouretanos houve também redução na relação da proporção da carga inorgânica presente no cimento, componente importante para as propriedades mecânicas. Assim, a adição de 10 e 20 % em peso dos oligômeros reduziu para 63.6% e 60.8% o percentual de carga inorgânica, respectivamente, a qual era originalmente de 66% em peso. No estudo de Gonçalves *et al.*, (2010) foi demostrado que reduzindo a matriz inorgânica de 60% para 55% em volume, ocorria redução de aproximadamente 27% no módulo de elasticidade.

Em relação à tenacidade, na avaliação dos cimentos experimentais (BISGMA/UDMA/TEGDMA) fotopolimerizados foi observado significante aumento das propriedades nos grupos contendo tiouretanos alifáticos em relação aos grupos controle e aromáticos. Contrário à rigidez dos anéis aromáticos, as ligações alifáticas são caracterizadas por uma combinação de ligações flexíveis formadas pelas cadeias do tiol e isocianatos precursores. Além disso, deve-se apontar a maior capacidade da versão alifática em formar cadeias poliméricas cruzadas, considerando que o tiol precursor possui característica tetra-funcional enquanto o tiol precursor da versão aromática é tri-funcional. Para os cimentos com ativação dupla, a adição do tiouretano aromático aumentou significantemente a tenacidade. Quanto aos materiais comerciais, alterações significantes não foram observadas com a presença de oligômeros aromáticos, apesar da tendência de aumentar os valores conforme aumentava o percentual de material. Conforme já mencionado, as alterações na proporção da carga inorgânica nos grupos experimentais mascararam as propriedades do oligômero.

A tenacidade à fratura é outra propriedade mecânica que mantém correlação com a longevidade clínica dos compósitos (Ferracane, 2013). Esta propriedade caracteriza-se pela capacidade do material em resistir à propagação de trincas (Callister, 2007). Em relação aos cimentos, esta propriedade é particularmente importante porque esses materiais estão sujeitos a constantes incidências de carga (Azar *et al.*, 2012). A formulação de cimentos baseados na matriz de BisGMA/UDMA/TEGDMA e em oligômeros tiouretanos demonstrou significante aumento da tenacidade à fratura para ambas as concentrações de oligômero (10 e 20 % em peso), tanto em materiais fotopolimerizados quanto nos de ativação dupla. Como mencionado, este fato foi atribuído à maior homogeneidade da rede polimérica e também pela formação das ligações tiouretano e tiol-metacrilato. No material fotopolimerizado, a associação do mais flexível tiol (PETMP) com o isocianato alifático (HDDI) promoveu maior aumento da tenacidade à fratura quando comparado à versão aromática. Ainda, para ambos os materiais comerciais (RelyX Veneer e RelyX Ultimate, 3M ESPE), a adição de 20% em peso da versão aromática à matriz orgânica causou aumento significante da tenacidade à fratura.

A contração de polimerização foi avaliada apenas nos cimentos fotoativados por razões metodológicas. Nos cimentos formulados a partir do BisGMA/UDMA/TEGDMA houve redução na contração de polimerização em todos os grupos experimentais em relação ao controle, não diferindo quanto à concentração de tiouretano. Ainda, a versão alifática dos oligômeros causou redução significativa quando comparada aos aromáticos. Isso ocorreu pela redução na concentração de ligações duplas de metacrilato por unidade de volume quando da adição de partículas pré-polimerizadas, sendo mais eficaz em estruturas mais flexíveis como os oligômeros alifáticos (Pfeifer *et al.*, 2011). A adição da versão aromática dos tiouretanos ao cimento comercial causou tendência para reduzir a contração de polimerização, mostrando valores médios de 5,6% e 21,2% menores que o controle para as concentrações de 10 e 20% em peso de oligômero, respectivamente; entretanto, esses valores não foram estatisticamente significantes. O aumento da quantidade da matriz orgânica nos grupos experimentais devido à adição dos oligômeros, promovendo aumento da contração volumétrica, pode ter minimizado a função dos tiouretanos no material não promovendo diferenças em relação ao grupo controle.

A redução da contração de polimerização observada pela presença de tiouretanos nos cimentos experimentais pode esclarecer o motivo da redução na tensão de polimerização dos cimentos compostos pelos oligômeros. Tanto para os materiais fotopolimerizados quanto para os de ativação dupla em compostos a partir de BisGMA/UDMA/TEGDMA foi observada redução da tensão em ambos os grupos experimentais, qualquer que fosse o tipo de oligômero e concentração. Além de relacionada à contração de polimerização, a tensão de polimerização é diretamente proporcional ao grau de conversão e ao módulo de elasticidade do material. Como já mencionado, os oligômeros reduziram a tensão mantendo ou aumentando do grau de conversão e o módulo de elasticidade nos materiais experimentais. A redução da contração não é suficiente para explicar a significante redução na tensão; entretanto, tem sido especulado que a reação de transferência de cadeia dos tióis pendentes ao metacrilato prolongaria a fase gel e a pré-vitrificação, como demonstrado pela cinética do material fotopolimerizado. Apesar de o grau de conversão na taxa máxima de polimerização não ter sido afetado, a taxa de desaceleração foi menos acentuada e ocorreu em estágios finais do processo de polimerização nos grupos tiouretanos, fato que poderia ter causado redução relevante nas tensões desenvolvidas (Lecamp *et al.*, 2001; Lu *et al.*, 2005). A adição do oligômero aromático em 20 % em peso da matriz orgânica dos cimentos comerciais também causou redução da tensão de polimerização desses materiais. Apesar da influência das propriedades do tiouretano na redução da contração, como já mencionada, no caso dos materiais comerciais a real influência do oligômero na tensão não foi conclusiva em virtude da redução do módulo de elasticidade do material, causado redução da carga inorgânica após a adição do tiouretano.

A resistência da união de uma cerâmica vítrea e de um compósito restaurador indireto à dentina coronária foi avaliada com um cimento de ativação dupla modificado com oligômeros tiouretanos aromáticos nas concentrações 0 (controle), 10 e 20% em peso. Para ambos os materiais restauradores, o uso de 20% do oligômero promoveu significante aumento da resistência da união (aproximadamente 23% para o compósito indireto e 40 % para a cerâmica). Os principais fatores relacionados a esse aumento podem ser o aumento da tenacidade à fratura e da tenacidade do material. Além disso, a redução da tensão de polimerização também diminuiu a tensão entre as estruturas aderidas e as tensões internas na camada de cimento, o que pode explicar o aumento na resistência de união.

CONCLUSÃO

De acordo com os resultados obtidos e discutidos neste estudo pode ser concluído que:

- Tiouretanos promoveram aumento das propriedades mecânicas, em especial tenacidade e tenacidade à fratura;
- O uso dos oligômeros causou redução da contração e da tensão de polimerização dos materiais;
- Aumento nas propriedades de adesão de materiais restauradores indiretos (compósito e cerâmica vítrea) à dentina foi obtido com a adição desses oligômeros aos cimentos de cura dual.

REFERÊNCIAS*

Azar MR, Bagheri R, Burrow MF. Effect of storage media and time on the fracture toughness of resin-based luting cements. Aust Dent J 2012; 57(3):349-354.

Beigi S, Yeganeh H, Atai M. Evaluation of fracture toughness and mechanical properties of ternary thiol-ene-methacrylate systems as resin matrix for dental restorative composites. Dent Mater 2013; 29(7):777-787.

Berchtold KA, Lovestead TM, Bowman CN. Coupling chain length dependent and reaction diffusion controlled termination in the free radical polymerization of multivinyl (meth)acrylates. Macromolecules 2002; 35(21):7968-7975.

Bindl A, Lüthy H, Mörmann WH. Strength and fracture pattern of monolithic CAD/CAM-generated posterior crowns. Dent Mater 2006; 22(1):29–36.

Braga RR, Ferracane JL, Condon JR. Polymerization contraction stress in dual-cure cements and its effect on interfacial integrity of bonded inlays. J Dent 2002; 30(7-8):333-340.

Boulden JE, Cramer NB, Schreck KM, Couch CL, Bracho-Troconis C, Stansbury JW, Bowman CN. Thiol-ene-methacrylate composites as dental restorative materials. Dent Mater 2011; 27(3):267-272.

Buchalla W, Attin T, Hilgers RD, Hellwig E. The effect of water storage and light exposure on the color and translucency of a hybrid and a microfilled composite. J Prosthet Dent 2002;87(3):264–70.

Callister WD. Materials Science and Engineering: An introduction. John Wiley & Sons: New York, 2008; 8th.

Cramer NB, Couch CL, Schreck KM, Carioscia JA, Boulden JE, Stansbury JW, Bowman CN. Investigation of thiol-ene and thiol-ene-methacrylate based resins as dental restorative materials. Dent Mater 2010a; 26(1):21-28.

Cramer NB, Couch CL, Schreck KM, Boulden JE, Wydra R, Stansbury JW, Bowman CN. Properties of methacrylate-thiol-ene formulations as dental restorative materials. Dent Mater 2010b; 26(8):799-806.

*De acordo com a norma da FOP/UNICAMP baseada na norma do International Committee of Medical Journal Editors – Grupo de Vancouver. Abreviatura dos periódicos em conformidade com Medline.

Faria e Silva AL, Arias VG, Soares LE, Martin AA, Martins LR. Influence of fiber-post translucency on the degree of conversion of a dual-cured resin cement. J Endod 2007; 33(3):303–5.

Ferracane JL. Resin-based composite performance: are there some things we can't predict? Dent Mater 2013; 29(1):51-58.

Gonçalves F, Kawano Y, Braga RR. Contraction stress related to composite inorganic content. Dent Mater 2010; 26(7):704-9.

Hoyle CE, Bowman CN. Thiol–ene click chemistry. Angew Chem 2010; 49(9):1540–73.

Jongsma LA, de Jager N, Kleverlaan CJ, Pallav P, Feizer AJ. Shear bond strength of three dual-cured resin cements to dentin analyzed by finite element analysis. Dent Mater 2012; 28(10):1080-1088.

Lecamp L, Houllier F, Youssef B, Bunel C. Photoinitiated cross-linking of a thiol methacrylate system. Polymer 2001; 42(7):2727-2736.

Lu H, Carioscia JA, Stansbury JW, Bowman N. Investigatios of step-growth thiol-ene polymerizations for novel dental restoratives. Dent Mater 2005; 21(12):1129-1136.

Li Q, Wicks DA, Hoyle CE. Thiouretane-Based Thiol-Ene High T_g Networks: Preparation, Thermal, Mechanical, and Physical Properties. J Polymer Sci Part A: Polymer chemistry 2007; 45(22): 5103-5111.

Kim YK, Kim SK, Kim KH, Kwon TY. Degree of conversion of dual-cured resin cement light-cured through three fibre posts within human root canals: an ex vivo study. Int Endod J 2009; 42(8):667–74.

Koishi Y, Tanoue N, Atsuta M, Matsumura H. Influence of visible-light exposure on color stability of current dual-curable luting composites. J Oral Rehabil 2002; 29(4):387–93.

Manso AP, Silva NRFA, Bonfante EA, Pegoraro TA, Dias RA, Carvalho RM. Cements and Adhesives for all-ceramic restorations. Dent Clin North Am 2011; 55(2):311-332.

Meyer JM, Cattani-Lorente MA, Dupuis V. Compomers: between glass–ionomer cements and composites. Biomaterials 1998;19(6):529–539.

Mormann WH, Bindl A, Luthy H, Rathke A. Effects of preparation and luting system on all-ceramic generated crowns. Int J Prosthodont 1998; 11(4):333–9.

Odian G. Principles of polymerization. New York: Wiley-Interscience; 2004.

Patel MP, Braden M, Davy KW. Polymerization shrinkage of methacrylate esters. Biomaterials 1987; 8(1):53-56.

Peumans M, Van Meerbeek B, Lambrechts P, Vanherle G. Porcelain veneers: a review of the literature. J Dent 2000; 28(3):163–177.

Pfeifer CS, Shelton ZR, Braga RR, Windmoller D, Machado JC, Stansbury JW. Characterization of dimethacrylate polymeric networks: a study of the crosslinked structure formed by monomers used in dental composites. Eur Polym J, 2011;47(2):162-170.

Pfeifer C, Lewis S, Stansbury J. Thio-urethane oligomers as low-stress, tough additives in methacrylate polymerizations. IADR 2012.

Rosenstiel SF, Land MF, Crispin BJ. Dental luting agents: a review of the current literature. J Prosthet Dent 1998; 80(3):280–301.

Scherrer SS, Rijk WG, Belser UC, Meyer J. Effect of cement film thickness on the fracture resistance of a machinable glass-ceramic. Dent Mater 1994; 10(3):172–7.

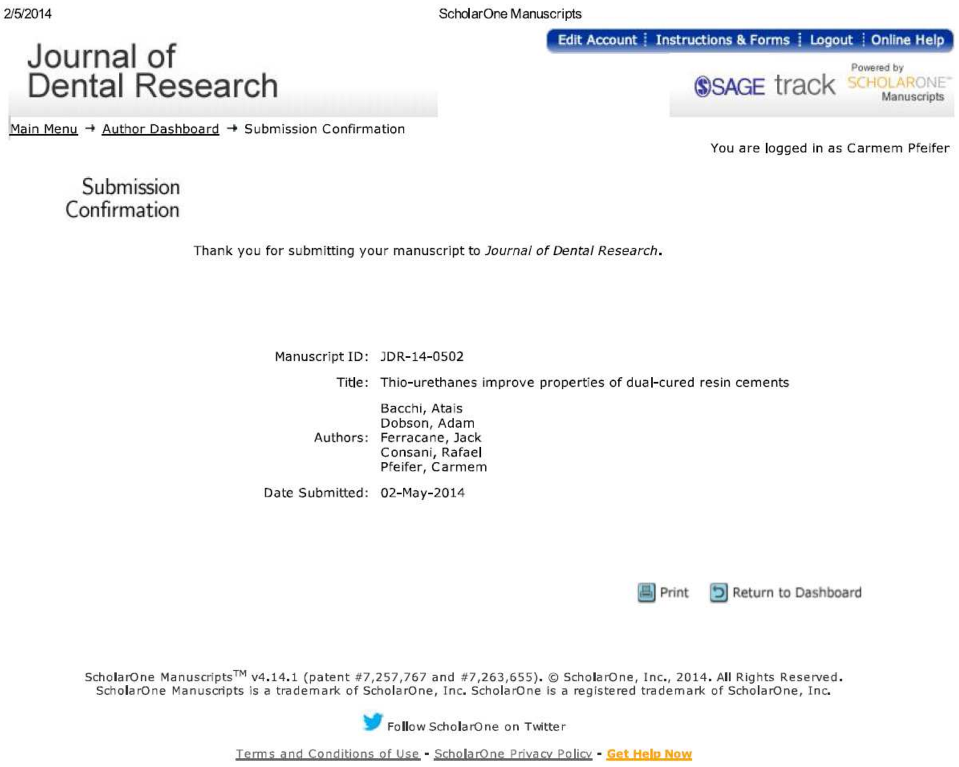
Senyurt AF, Hoyle CE. Thermal and mechanical properties of cross-linked photopolymers based on multifunctional thiol-urethane ene monomers. Macromolecules 2007; 40(9): 3174-3182.

Spinell T, Schedle A, Watts DC. Polymerization shrinkage kinetics of dimethacrylate resin-cements. Dent Mater 2009; 25(8):1058–66.

Standard I. ISO 4049 polymer based filling, restorative and luting materials. International Organization for Standardization; 2000. p. 1–27.

ANEXOS

Anexo 1. Carta de submissão do Capítulo 2



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Title:	Thio-urethanes improve properties of dual-cured resin cements
Authors:	Bacchi, Atais Dobson, Adam Ferracane, Jack Consani, Rafael Pfeifer, Carmem
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