

Marcela Gonçalves Borges Faria

**Avaliação da composição química, do desafio bacteriano, do acabamento/polimento e de protocolos de cimentação de diferentes materiais restauradores**

*Evaluation of chemical composition, bacterial challenge, finishing/polishing and luting protocols of different restorative materials*

Tese apresentada à Faculdade de Odontologia da Universidade Federal de Uberlândia, para obtenção do Título de Doutora em Odontologia na Área de Concentração em Clínica Odontológica Integrada.

Uberlândia, 2020

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Orientador: Prof. Dr. Murilo de Sousa Menezes

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Uberlândia, 2020


**UNIVERSIDADE FEDERAL DE UBERLÂNDIA**

Coordenação do Programa de Pós-Graduação em Odontologia  
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Reuniu-se no Anfiteatro/Sala 31 Bloco 4L - Anexo A, Campus Umuarama, da Universidade Federal de Uberlândia, a Banca Examinadora, designada pelo Colegiado do Programa de Pós-graduação em Odontologia, assim composta: Professores Doutores: [Alfredo Júlio Fernandes Neto \(UFU\)](#); [Carlos José Soares \(UFU\)](#); [Hugo Lemes Carlo \(UFJF\)](#); [Luís Roberto Marcondes Martins \(UNICAMP\)](#); [Murilo de Sousa Menezes \(UFU\)](#) orientador(a) do(a) candidato(a). O Prof. Dr. Hugo Lemes Carlo, participou da defesa de tese por meio de vídeo-conferência desde a cidade de Governador Valadares; e o Prof. Dr. Luís Roberto Marcondes Martins, participou da defesa de tese por meio de vídeo-conferência desde a cidade de Piracicaba; e os demais membros da Banca participaram *in loco*.

Iniciando os trabalhos o(a) presidente da mesa, Dr(a). Murilo de Sousa Menezes, apresentou a Comissão Examinadora e o candidato(a), agradeceu a presença do público, e concedeu ao Discente a palavra para a exposição do seu trabalho. A duração da apresentação do Discente e o tempo de arguição e resposta foram conforme as normas do Programa.

A seguir o senhor(a) presidente concedeu a palavra, pela ordem sucessivamente, aos(às) examinadores(as), que passaram a arguir o(a) candidato(a). Ultimada a arguição, que se desenvolveu dentro dos termos regimentais, a Banca, em sessão secreta, atribuiu o resultado final, considerando o(a) candidato(a):

**Aprovado(a).**

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O competente diploma será expedido após cumprimento dos demais requisitos, conforme as normas do Programa, a legislação pertinente e a regulamentação interna da UFU.

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## DEDICATÓRIA

Dedico esse trabalho a Deus e à minha família.

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“A vida é construída nos sonhos e  
concretizada no amor.”

**Chico Xavier**



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# R esumo

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Avaliação da composição química, do desafio bacteriano, do acabamento/polimento e de protocolos de cimentação de diferentes materiais restauradores – MARCELA GONÇALVES BORGES FARIA – Tese de Doutorado – Programa de Pós-Graduação em Odontologia – Faculdade de Odontologia – Universidade Federal de Uberlândia.

## RESUMO

O objetivo geral desse estudo foi investigar a composição química, o desafio bacteriano, o acabamento/polimento e os protocolos de cimentação de diferentes materiais restauradores. Este estudo foi dividido em 4 capítulos, de acordo com cada objetivo específico: **capítulo 1)** avaliar como a adição de tiouretano influencia a composição do método de síntese sol-gel e a estrutura da rede polimérica de metacrilatos; **capítulo 2)** avaliar o efeito do desafio bacteriano na resistência de união de resinas compostas reparadas com silano modificado com tiouretano; **capítulo 3)** avaliar os efeitos da inibição de oxigênio e dos procedimentos de acabamento/polimento nas propriedades de resinas compostas convencionais e de incremento único; **capítulo 4)** avaliar os protocolos de cimentação e o momento para a realização do preparo protético na resistência de união e padrões de falha de pinos de fibra de vidro à dentina do canal radicular de incisivos bovinos. Os métodos experimentais utilizados foram grau de conversão, sorção e solubilidade, análise dinâmico-mecânica e de extração, ensaio mecânico de microcissalhamento, alteração de cor, opacidade, ensaio mecânico de micro *push-out* e microscopia óptica. Após a análise estatística dos dados, concluiu-se que a adição de tiouretano nos metacrilatos afetou a composição no método de síntese sol-gel nas redes de ligações cruzadas, as quais apresentaram ser mais homogêneas, com menor quantidade de lixiviados potencialmente tóxicos; após o desafio bacteriano, o silano modificado com tiouretano foi capaz de manter a resistência de união das interfaces entre a resina composta original e reparada; o acabamento e polimento resultou em menor grau de conversão das resinas compostas se comparado ao uso de um agente inibidor de oxigênio (glicerina), porém apresentou resultados similares para o manchamento com café; o protocolo de cimentação dos pinos de fibra de vidro e o momento para a realização do preparo protético não influenciaram a resistência da união do pino à dentina radicular, mas a interação entre estes fatores foi significativa; nenhuma falha coesiva foi observada e duas falhas adesivas na interface de união entre pino e dentina radicular foram detectadas.

**PALAVRAS-CHAVE:** tiouretano, inibição de oxigênio, técnica para retentor intrarradicular.

# Abstract

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Avaliação da composição química, do desafio bacteriano, do acabamento/polimento e de protocolos de cimentação de diferentes materiais restauradores – MARCELA GONÇALVES BORGES FARIA – Tese de Doutorado – Programa de Pós-Graduação em Odontologia – Faculdade de Odontologia – Universidade Federal de Uberlândia.

## **ABSTRACT**

The general objective of this study was to investigate the chemical composition, finishing and polishing and luting protocols of different restorative materials. This study was divided into 4 chapters, according to the specific objectives: chapter 1) to evaluate how the addition of thiourethane influences the composition of the sol-gel composition and network structure of methacrylate-based materials; chapter 2) to evaluate the effect of bacterial challenge on the bond strength of composite resins repaired with silane modified with thiourethane; chapter 3) to evaluate the effects of oxygen inhibition and finishing/polishing procedures on the surface of conventional and bulk-fill composite resins; chapter 4) to evaluate luting protocols and the time to prosthetic preparation, in the bond strength and failure modes of fiber post to the root dentin of bovine incisors. The experimental methods used were degree of conversion, water sorption and solubility, dynamic mechanical analysis, extraction methods, micro-shear bond strength, color stability, opacity, micro push-out bond strength and optical microscopy. After statistical analysis of the data, it was concluded that the addition of thiouretane in methacrylates affected the composition in the sol-gel synthesis method in cross-link networks, which presented to be more homogeneous, with a lower amount of leached potentially toxic; after bacterial challenge, the use of TU silanes was able to maintain the bond strength of repaired interfaces of composites; post-polymerization polishing procedures resulted in lower conversion than using an oxygen inhibitor agent (Gly condition), but similar staining caused by coffee; both time to prosthetic preparation and luting protocol influenced the bond strength of the fiber post to the root dentin with combined effect; no cohesive failures were observed, and two adhesive failures in the interface between the post and root dentin were found.

**KEYWORDS:** thiourethane, oxygen inhibition, post and core technique.

# **I**NTRODUÇÃO **E** REFERENCIAL TEÓRICO

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Avaliação da composição química, do desafio bacteriano, do acabamento/polimento e de protocolos de cimentação de diferentes materiais restauradores – MARCELA GONÇALVES BORGES FARIA – Tese de Doutorado – Programa de Pós-Graduação em Odontologia – Faculdade de Odontologia – Universidade Federal de Uberlândia.

## 1. INTRODUÇÃO E REFERENCIAL TEÓRICO

A odontologia restauradora abrange o uso de materiais restauradores e técnicas operatórias para a realização de procedimentos adesivos em dentes anteriores e posteriores.

Ao longo do tempo, restaurações com resinas compostas tornam-se menos estáveis devido à exposição prolongada a solventes orgânicos e cargas mecânicas na cavidade bucal (Finer Y *et al.*, 2004; Sarrett DC *et al.*, 2000), o que pode promover degradação hidrolítica. Dentre os materiais odontológicos existentes no mercado (cimentos resinosos, adesivos e resinas compostas), o monômero mais comumente utilizado é o bisfenol dimetacrilato diglicidil (BisGMA), combinado com monômeros diluentes de menor viscosidade para melhorar o grau de conversão, o conteúdo inorgânico e também reduzir componentes capazes de sofrer lixiviação (Pfeifer CS *et al.*, 2017). A inclusão de monômeros adicionais ou oligômeros na composição química destes materiais pode alterar a sua reação de polimerização. Os aditivos à base de oligômeros de tiouretanos têm sido propostos como modificadores nos materiais dentários, por apresentarem vantagens como o aumento significativo da resistência à fratura e a redução da tensão de polimerização (Bacchi A *et al.*, 2014). Este fato é explicado pela influência dos thiois pendentes (presentes na estrutura química dos tiouretanos) na formação da rede polimérica dos metacrilatos, os quais podem ser capazes de realizar transferência de cadeia para as redes polimerizadas, atrasando as etapas de gelificação/vitrificação. Assim, a tensão de polimerização é reduzida e, ao mesmo tempo, a conversão final do material aumenta (Bacchi A *et al.*, 2014).

Outros fatores inerentes às resinas compostas no meio bucal são a ação de enzimas salivares, variações no pH, presença de dieta cariogênica, acúmulo de biofilme, desgaste por pastas dentárias abrasivas e pela escovação dentária, além da fadiga oclusal (Bagheri R *et al.*, 2005; Topcu FT *et al.*, 2009). Combinados, estes fatores contribuem principalmente para o desenvolvimento de hipersensibilidade dentinária, infiltração marginal, cárie secundária e fraturas, levando, em última instância, à necessidade de substituição das restaurações (Musanje L *et al.*, 2003; Demarco FF *et al.*, 2017). A realização de reparos destas restaurações é indicada em muitos casos clínicos por possuir vantagens como

economia de tempo (Hickel R *et al.*, 2013), custo-benefício, conservação da estrutura dentária, além da ausência da necessidade de anestesia local (Demarco FF *et al.*, 2017). Sendo assim, tal procedimento representa a odontologia minimamente invasiva com abordagem conservadora (Blum IR *et al.*, 2014; Bacchi A *et al.*, 2013). No entanto, a resistência de união imediata e a longo prazo do reparo depende da composição química dos materiais utilizados, das condições de envelhecimento da superfície original e/ou reparada, bem como da maneira que a técnica do reparo é realizada (Alqarni D *et al.*, 2019; Loomans BA *et al.*, 2011). O desenvolvimento de silanos à base de tiouretanos pode ser uma alternativa no tratamento de superfície para o reparo imediato e/ou tardio de restaurações com resinas compostas (Faria-e-Silva AL *et al.*, 2019; Faria-e-Silva AL *et al.*, 2018).

Em relação à etapa de fotopolimerização das resinas compostas, o contato do oxigênio produz uma camada superficial de resina não polimerizada (Yamaji A *et al.*, 2014), o que pode inibir a sua reação de polimerização, resultando na formação de uma cadeia polimérica mais propensa a pigmentar e desgastar (Shawkat ES *et al.*, 2009). A espessura da camada inibida pelo oxigênio depende do tipo de morfologia das partículas do material (Imazato S *et al.*, 2009; Gauthier MA *et al.*, 2005), das concentrações de radicais livres (Andrzejewska E, 2001) e da taxa de consumo de oxigênio (Lee TY *et al.*, 2004). Como métodos de inibição de oxigênio na técnica restauradora, existem a aplicação do gel de glicerina e do gel solúvel em água no último incremento de resina composta. Sendo assim, a literatura é escassa em relação aos efeitos do veículo inibidor de oxigênio na superfície das resinas compostas e maneiras para a realização de procedimentos de acabamento/polimento, os quais podem influenciar na absorção de pigmentos, especialmente nas áreas de difícil acesso, como a superfície proximal ou oclusal de dentes posteriores.

Por outro lado, materiais dentários adesivos também são utilizados para cimentação de dentes tratados endodonticamente, confecção do núcleo de preenchimento com resina composta e da coroa definitiva, em situações clínicas de extensa destruição coronária. O deslocamento do pino no canal radicular e a fratura do núcleo de preenchimento são causas frequentes de falhas clínicas (Cagidiaco MC *et al.*, 2008), possivelmente devido à complexidade de obtenção de adesão satisfatória, sensibilidade da técnica operatória e habilidade do



profissional (Faria-e-Silva AL *et al.*, 2012). Além disto, as diferenças na dentina intrarradicular ao longo da profundidade da raiz (Ferrari M *et al.*, 2000) e a quantidade de desgaste que se faz para a realização do alívio do canal radicular e inserção do retentor (Bouillaguet S *et al.*, 2003) também são desafios para os procedimentos de fixação realizados em um canal radicular. Quanto à preparação protética do núcleo de preenchimento para recebimento da coroa definitiva, muitos profissionais optam por realizá-lo imediatamente à cimentação do pino de fibra de vidro e à confecção do núcleo, durante a mesma sessão clínica. No entanto, o uso de pontas diamantadas pode gerar vibração do pino e induzir tensão nas interfaces de união entre pino, substratos dentários e materiais restauradores.

# Capítulos

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Avaliação da composição química, do desafio bacteriano, do acabamento/polimento e de protocolos de cimentação de diferentes materiais restauradores – MARCELA GONÇALVES BORGES FARIA – Tese de Doutorado – Programa de Pós-Graduação em Odontologia – Faculdade de Odontologia – Universidade Federal de Uberlândia.

## **2. CAPÍTULOS**

Essa tese foi subdividida em quatro capítulos:

### **2.1 Capítulo 1) Artigo publicado no periódico *Dental Materials*: “EFFECT OF THE ADDITION OF THIOURETHANE OLIGOMERS ON THE SOL-GEL COMPOSITION OF BISGMA/TEGDMA POLYMER NETWORKS”**

O objetivo deste estudo foi avaliar como a adição de um oligômero de tiouretano influencia a composição do método de síntese sol-gel e a estrutura da rede polimérica de materiais à base de metacrilato, por meio das análises do grau de conversão, sorção e solubilidade, dinâmico-mecânica e de extração.

### **2.2 Capítulo 2) Artigo submetido ao periódico *Operative Dentistry*: “EFFECT OF BACTERIAL CHALLENGE ON THE MICRO-SHEAR BOND STRENGTH OF DENTAL COMPOSITES REPAIRED USING A THIOURETHANE-BASED SILANES”**

O objetivo deste estudo foi avaliar o efeito do desafio bacteriano na resistência de união de resinas compostas reparadas com silano modificado com tiouretano, por meio do ensaio mecânico de microcisalhamento.

### **2.3 Capítulo 3) Artigo aceito para publicação no periódico *Brazilian Dental Journal*: “OXYGEN INHIBITION OF SURFACE COMPOSITES AND ITS CORRELATION WITH DEGREE OF CONVERSION AND COLOR STABILITY”**

O objetivo deste estudo foi avaliar os efeitos da inibição de oxigênio com glicerina e de procedimentos de acabamento/polimento sobre o grau de conversão, alteração de cor e opacidade de resinas compostas convencionais e de incremento único.

### **2.4 Capítulo 4) Artigo submetido ao periódico *Brazilian Oral Research*: “EFFECT OF LUTING PROTOCOL AND TIME TO PROSTHETIC PREPARATION ON BOND STRENGTH OF FIBER POSTS TO ROOT DENTIN”**

O objetivo deste estudo foi avaliar a influência de protocolos de cimentação e do momento para a realização do preparo protético na resistência de união de pinos de fibra de vidro à dentina do canal radicular de incisivos bovinos, por meio do ensaio mecânico de micro *push-out* e microscopia óptica.

# Capítulos

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Avaliação da composição química, do desafio bacteriano, do acabamento/polimento e de protocolos de cimentação de diferentes materiais restauradores – MARCELA GONÇALVES BORGES FARIA – Tese de Doutorado – Programa de Pós-Graduação em Odontologia – Faculdade de Odontologia – Universidade Federal de Uberlândia.

## 2.1 Capítulo 1

### **Referência do artigo segundo normas do programa de pós-graduação:**

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## Effect of the addition of thiourethane oligomers on the sol–gel composition of BisGMA/TEGDMA polymer networks

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### ABSTRACT

**Objectives.** Thiourethane oligomers have been shown to increase the fracture toughness and reduce the polymerization stress of methacrylate-based materials. However, network formation has not been elucidated in these materials yet. The aim of this study was to evaluate how the addition of a thiourethane oligomer (TU) influences the sol/gel composition and network structure of methacrylate-based materials using dynamic mechanical analysis and extraction methods.

**Materials and methods.** BisGMA/TEGDMA at systematically varied mass ratios (20/80 to 80/20 wt%) were mixed with pre-polymerized thiourethane oligomers at 0 (control) or 20 wt%, synthesized by combining pentaerythritol tetra-3-mercaptopropionate with dicyclohexylmethane 4,4'-Diisocyanate, at 1:2 isocyanate:thiol. 0.1 wt% of 2,2-Dimethoxy-2-phenylacetophenone was added as the photoinitiator and 0.3 wt% of 2,6-di-*tert*-butyl-4-methylphenol was added as a free radical inhibitor. Disk specimens (0.8 × 10 mm in diameter, n = 3) were photoactivated at 270 mW/ (320–500 nm) for 1 min. The degree of conversion (DC) was measured in near-IR (6165 cm<sup>-1</sup>). Specimens were immersed in two different solvents (water for 7 days or dichloromethane for 48 h). Water sorption (WS) and solubility (SL) were obtained according to ISO 4049. The leachates for both solutions were analyzed with <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>). Bar specimens (1 × 3 × 25 mm, photocured and then post-processed at 180 °C for 8 h to DC > 95%) were subjected to dynamic mechanical analysis (–30 to 230 °C) to obtain glass transition temperature (T<sub>g</sub>), tan delta curves and crosslinking density (ν). Data was analyzed with two-way ANOVA/Tukey's test (95%).

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**Results.** In general, the presence of TU increased the overall conversion. The WS was similar for all groups, but the SL decreased by 2-fold with the addition of the TU oligomer for all compositions, except BisGMA/TEGDMA 80/20. The BisGMA concentration of the leachates increased with increasing BisGMA in the initial mixture, and with the presence of thiourethane. This compositional drift of the gel with the presence of TU was attributed to the preferential dissolution of TEGDMA into the TU network.  $T_g$  and  $\nu$  decreased with the addition of TU, as expected. The addition of TU produced more homogeneous networks, as evidenced by narrower breadth of the tan delta curve.

**Conclusion.** The addition of TU affected the composition of the sol/gel in crosslinked networks, which were more homogeneous and presented 2-fold less potentially toxic leachates than the methacrylate controls.

**Clinical significance.** The addition of TU may produce less cytotoxic materials based on the increased conversion and reduced amount of unreacted extractables from its network after water storage.

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## 1. Introduction

Typical resin composites used in dental restorative applications are composed of a mixture of dimethacrylate monomers with inorganic fillers [1]. The most common dimethacrylate used in such materials is Bisphenol A diglycidyl ether dimethacrylate (BisGMA), combined with lower viscosity diluent monomers to improve the degree of conversion, inorganic filler content in the composite and also reduce leachable components [2]. The most common diluent is triethylene glycol dimethacrylate (TEGDMA), but urethane dimethacrylate (UDMA) and ethoxylated bisphenol-A dimethacrylate (BisEMA) are also commonly used. The co-polymerization of these methacrylates is complex, and the relative participation of each monomer in different phases of the reaction (pre-gel, autoacceleration and vitrification) depends on the diffusional capabilities of each monomer, as well as on the reactivity of its vinyl bonds [3]. One study has demonstrated that BisGMA participates in the gel formation early in conversion, but as polymerization progresses, the composition of the gel becomes richer in TEGDMA [4]. In fact, by analyzing the sol phase (unreacted monomers) at various stages of polymerization, the increased contribution of TEGDMA to the polymer network in co-polymerizations with BisGMA has been demonstrated, pointing to a compositional drift during polymerization reactions [4,5]. It is expected that the inclusion of additional monomers or oligomers will alter this balance, and therefore, any proposed modifications in the composition must also evaluate and take into account the possible compositional shifts during polymerization.

Recently, additives based on thiourethane oligomers have been proposed as modifiers in highly filled dental composites, with several advantages including significantly increased fracture toughness and decreased polymerization stress [6]. These additives are synthesized by combining excess multifunctional thiols with diisocyanates, forming a network loosely crosslinked by thiourethane bonds, which are thought to facilitate crack arrest, increase abrasion resistance and tear strength, aided by stable and strong intermolecular hydrogen bonds [7]. In the case of thiourethane oligomers, pendant

thiols impart chain-transfer capability to the polymerizing methacrylate networks, delaying gelation/vitrification and thus reducing polymerization stress while at the same time increasing the limiting conversion [6]. Due to their effects on network formation, it is reasonable to assume that the addition of thiourethanes may affect the compositional drift in dimethacrylate co-polymerizations.

Since the compositional drift directly affects the resulting network, final conversion and the type and concentration of monomers that can potentially be extracted from the polymer while in service, this study aimed at investigating the sol/gel composition of systematically varied BisGMA/TEGDMA networks modified by the addition of thiourethane oligomers. Extractions were conducted in water or organic solvents, and the composition of the extracts was evaluated using nuclear magnetic resonance. Water was used to conform to ISO 4049 (water sorption and solubility tests - [8]) and dichloromethane was used as the organic solvent capable of extracting the quasi-totality of unreacted monomers (sol portion) from polymerized specimens [4]. In addition, the resulting network was characterized with dynamic mechanical analysis, to obtain glass transition temperature and degree of crosslinking. The hypotheses to be tested were that composites formulated with TU will increase degree of conversion, and affect the amount and composition of the leachates.

## 2. Material and methods

### 2.1. Composite formulation

All reagents were purchased from Sigma–Aldrich (Milwaukee, WI, USA) and used without further purification. The commercial monomers used to prepare the composites were all obtained from ESSTECH (Essington, PA, USA). The thiourethane oligomer used in this study was synthesized as previously described [6] by combining pentaerythritol tetra-3-mercaptopropionate (PETMP) with dicyclohexylmethane 4,4'-Diisocyanate (HMDI) at a 1:2 molar ratio of isocyanate:thiol to avoid gelation and allow for pendant thiols. This produces a loosely crosslinked oligomer, with average molecular weight

of 5 kDa and average pendant thiol concentration of 58 mM/g, as demonstrated in a previous study [6]. BisGMA/TEGDMA was used as the organic resin matrix, mixed at 20/80, 40/60, 50/50, 60/40 and 80/20 mass ratios. Thiourethanes were added at 0 (control) or 20 wt%, since this concentration was previously demonstrated to produce increased conversion and fracture toughness and reduced polymerization stress [6]. 0.1 wt% of 2,2-Dimethoxy-2-phenylacetophenone (DMPA) was added as a single component photoinitiator and 0.3 wt% of 2,6-di-tert-butyl-4-methylphenol (BHT) was added as a freeradical inhibitor.

## 2.2. Curing conditions and degree of conversion

Disk specimens (10 mm diameter and 0.8 mm thickness  $n = 10$ ), were made using a rubber mold sandwiched between glass slides, and photocured with a mercury arc lamp (320–500 nm at 270 mW/cm<sup>2</sup>) for 1 min. The irradiance was recorded at the surface of the specimen, which was kept at a distance of 7 cm from the tip of the light guide to minimize the effects of heat generation and to ensure uniform curing. The irradiance was checked daily with a power meter, and the light emission spectrum was characterized using the MARC resin calibrator (BlueLight analytics, Halifax, Nova Scotia, Canada). The degree of conversion (DC - %) was measured in near-IR using the vinyl overtone peak at 6165 cm<sup>-1</sup>, with 32 scans per spectrum at 4 cm<sup>-1</sup> resolution [9].

The DC was calculated based on the ratio of the vinyl peak before (npol) and after (pol) photoactivation as follows:

$$DC = \left(1 - \frac{pol}{npol}\right) \times 100$$

All specimens were stored dry for 24 h after photoactivation and individual masses were recorded (m1) prior to being stored in the two extraction solvents (water or dichloromethane), as described below.

## 2.3. Water sorption and solubility and extraction with an organic solvent

Half of the disks were stored in water (5 mL) for 7 days at room temperature. Excess water was then removed with absorbent paper and the mass (m2) was subsequently recorded. The discs were then dried to constant mass (m3) in a vacuum desiccator. Water sorption (Wsp) and solubility (Wsl) (μg/mm<sup>3</sup>) were calculated based on standard ISO 4049 [8], according to the equation, where V<sub>0</sub> is the volume of the specimen (2πr<sup>2</sup>h):

$$Wsp = (m2 - m1)/V_0$$

$$Wsl = (m3 - m1)/V_0$$

The remaining half of the specimens were stored in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, 5 mL) for 48 h, and the weighing procedure described above was repeated to obtain the amount of mass extracted with the organic solvent.

The leachates in the storage solutions were lyophilized and re-suspended in deuterated chloroform for <sup>1</sup>H-NMR analysis (400 MHz, CDCl<sub>3</sub>). Relative concentrations of BisGMA and TEGDMA in solution were calculated based on the signals for the different methyl protons in the <sup>1</sup>H-NMR spectra, as shown

in the representative spectrum in Fig. 1. In summary, BisGMA contains two types of methyl groups: at 1.93 and 1.61 ppm, respectively, each with a relative integration of 6 protons (12 methyl protons total). TEGDMA contains one type of methyl group at 1.93 ppm, with a relative integration of 6 protons. In a mixture of the two monomers, the 1.93 ppm peak corresponds to the sum of protons of each molecule, but the 1.61 ppm peak contains only the BisGMA protons. Therefore, the molar percentage of BisGMA in each extracted mixture was calculated as follows:

$$\text{BisGMA \%} = \frac{\text{integration of 1.61 ppm}}{\text{integration of 1.93 ppm}} \times 100$$

## 2.4. Dynamic mechanical analysis (DMA)

Bar specimens measuring 1 × 3 × 25 mm were produced following the same curing protocol described for the water sorption and solubility specimens. The specimens were thermally post-cured at 180 °C (above the expected glass transition temperature of the materials) for 8 h prior to testing. This was done to avoid additional curing during DMA testing. Dynamic mechanical analysis (Q800, TA Instruments, New Castle, DE, USA) was performed in tension mode at constant amplitude of 5 μm with 1% strain rate at a frequency of 1 Hz. A temperature sweep was conducted from -30 to 230 °C, at a heating rate of 3 °C/min. Storage modulus (E'), loss modulus (E'') and tan delta values were recorded during the heating cycle and plotted as a function of temperature. The glass transition temperature (T<sub>g</sub>) was defined as the peak maximum of the tan delta curve. Network heterogeneity was estimated using the breadth of the tan delta curve, from which the width at half height was calculated. The crosslinking density was calculated from the rubbery plateau of the E' curve [10], using the equation

$$E = 3\nu dRT$$

where E is the elastic modulus at the rubbery plateau (in MPa), ν is the concentration of active strands (crosslinking density in mol/kg), d is the density (kg/m<sup>3</sup>), R is the gas constant (8.314472 J/(mol·K)) and T is the temperature (K).

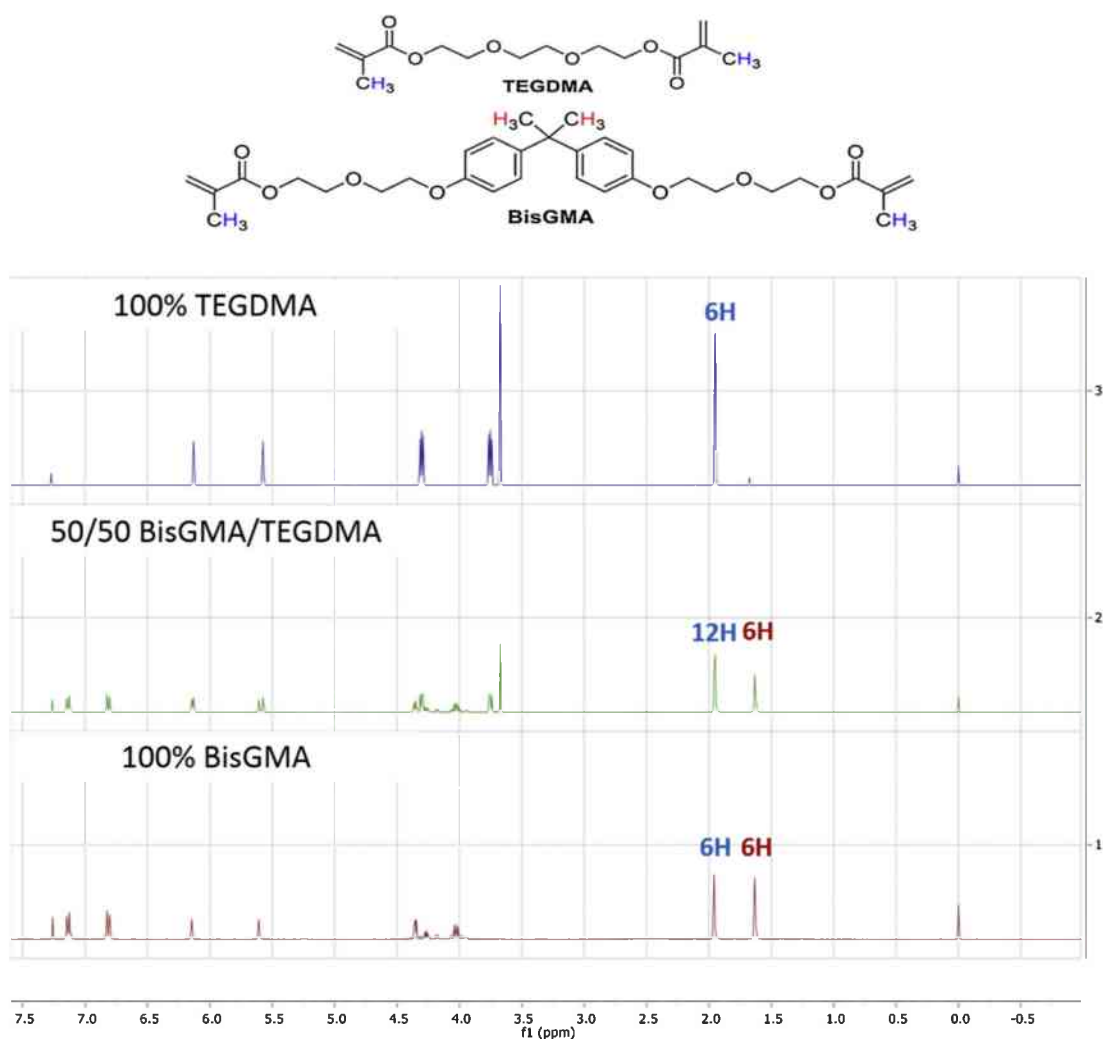
## 2.5. Statistical analysis

Sample sizes were based in previous studies or followed ISO recommendations, and were confirmed to provide power of 90% or better. The data were tested for normal distribution (Anderson-Darling) and homoscedasticity (Levene's test), followed by parametric statistical tests. A two-way analysis of variance (ANOVA) was performed and multiple comparisons were made using Tukey's test (95%). All analyses were carried out using statistical package Sigma Plot version 13.1 (Systat Software Inc.).

## 3. Results

The results for degree of conversion for the disc specimens prior to storage in water for all materials (with and without TU) are shown in Fig. 2. Both factors and the interaction were significant ( $p < 0.001$ ). For the materials not containing TU, the lowest conversion values were observed for the 50/50





**Fig. 1** –  $^1\text{H-NMR}$  spectra for BisGMA, TEGDMA and BisGMA/TEGDMA 50/50 mixtures, highlighting the methyl proton region used to calculate the relative concentration of each monomer in the extracted products after storage in water or dichloromethane.

and 60/40 BisGMA/TEGDMA groups, statistically similar to the 20/80 group. For the TU-containing materials, there was no statistical difference among the different TEGDMA concentrations. The presence of TU led to statistically higher conversion for all groups, except BisGMA/TEGDMA 80/20.

The results for water sorption and solubility are shown in Fig. 3. For water sorption, the monomer composition was significant ( $p = 0.007$ ) but the presence of TU and the interaction were not ( $p = 0.572$  and  $p = 0.087$ , respectively). For solubility in water, neither the factors nor the interaction were significant ( $p = 0.001$  for all). The results for mass loss after storage in dichloromethane and water (same as the water solubility results shown in Fig. 3, but with adjusted Y scale) are shown in Fig. 4. For mass loss after storage in dichloromethane, the factor “monomer composition” and the interaction were significant ( $p = 0.001$ ) while the factor “TU concentration” was not ( $p = 0.058$ ). The mass loss with the organic solvent was much greater than that observed with water. The sol extracted

increased with the concentration of BisGMA in the mixture for materials both with and without TU. TU-containing groups showed a significant increase in the amount of mass extracted for 40/60, 60/40 and 80/20 BisGMA/TEGDMA groups, and a decrease in the mass extracted for 50/50 BisGMA/TEGDMA groups in relation to the materials without TU. The 20/80 BisGMA/TEGDMA composition showed statistically similar mass loss for materials, regardless of the presence of TU.

Fig. 5 shows the sol composition after extraction for materials with or without TU in the original monomer mixtures. For this test, no statistical analysis was performed, since the leachates of each of the 5 specimens stored in water or dichloromethane were combined, and only one qualitative  $^1\text{H-NMR}$  spectra were obtained for each group. For the leachates extracted with water, there was no detectable presence of BisGMA in the leachates, meaning that 100% of what was extracted was made up of TEGDMA monomers. For the dichloromethane extractions, both BisGMA and TEGDMA were

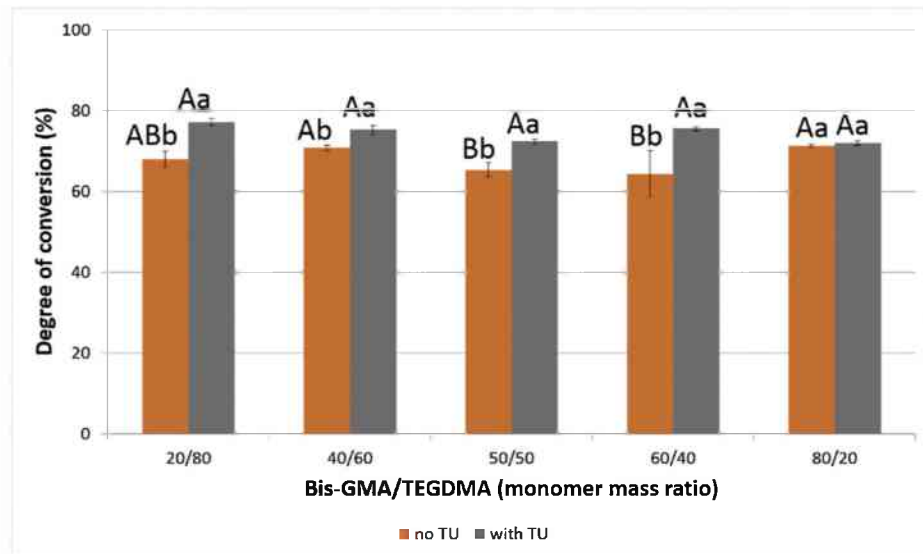


Fig. 2 – Degree of conversion (%) as a function of Bis-GMA/TEGDMA mass ratio. Upper case letters refer to comparisons within TU or non-TU containing groups, and lower case letters refer to comparisons within each BisGMA/TEGDMA ratio.

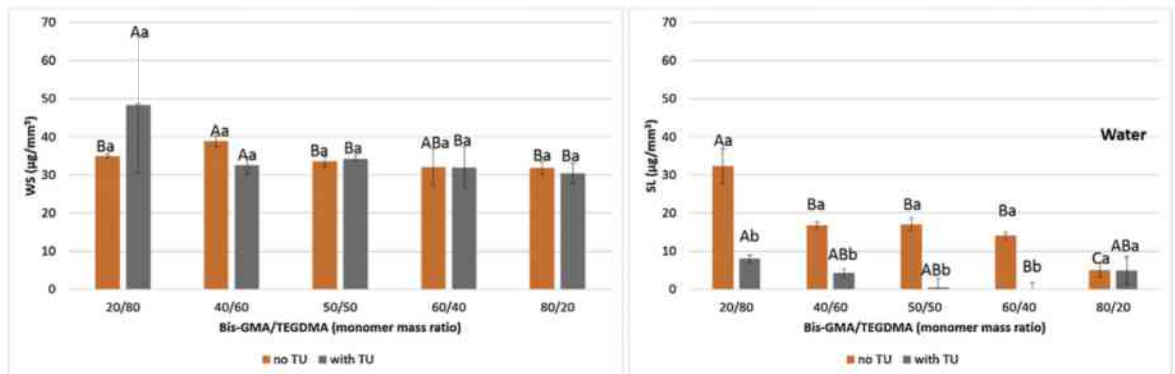


Fig. 3 – Water sorption and solubility ( $\mu\text{g}/\text{mm}^3$ ) as a function of Bis-GMA/TEGDMA mass ratio. Upper case letters refer to comparisons within TU or non-TU containing groups, and lower case letters refer to comparisons within each BisGMA/TEGDMA ratio.

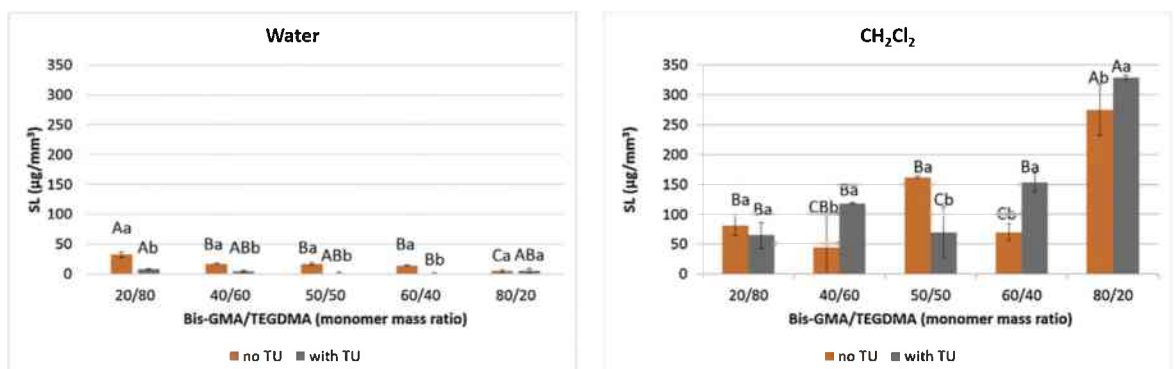
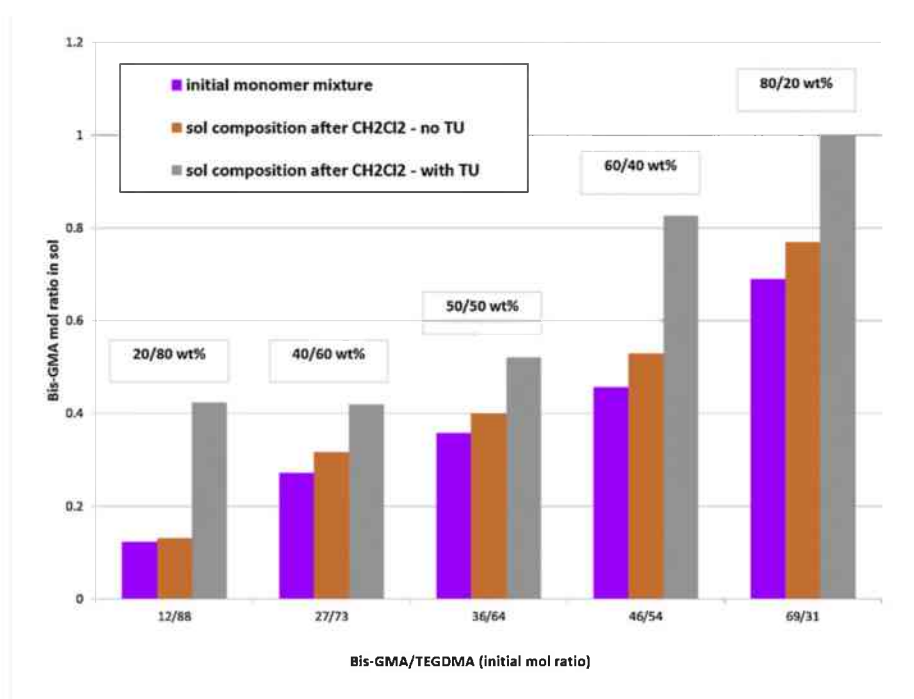


Fig. 4 – Solubility (or final mass extracted -  $\mu\text{g}/\text{mm}^3$ ) after storage in water or dichloromethane as a function of Bis-GMA/TEGDMA mass ratio. Upper case letters refer to comparisons within TU or non-TU containing groups, and lower case letters refer to comparisons within each BisGMA/TEGDMA ratio.



**Fig. 5 – Composition of the sol after extraction in dichloromethane for the different BisGMA/TEGDMA ratios with or without addition of thiourethanes. The composition is shown in mols in the graph axis, and in weight in the insert boxes. The left-most bars on the data set refer to the initial molar concentration of BisGMA in the monomer mixture, and the subsequent bars show the composition of the sol (extracted from the disks).**

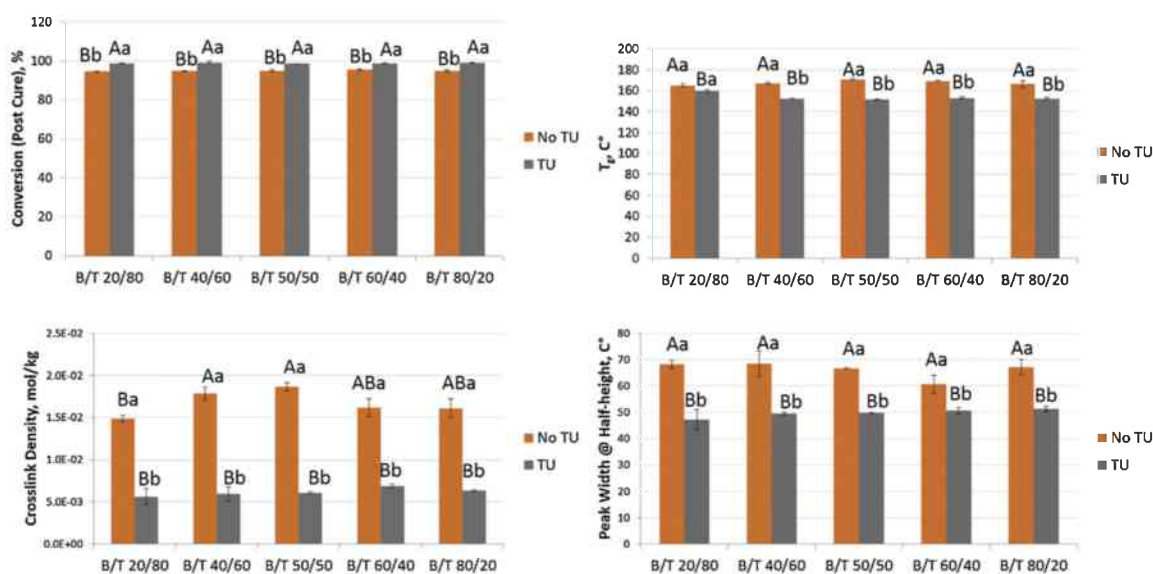
detected. The molar concentration of the BisGMA in the sol increased as the initial BisGMA concentration increased. Except for the 20/80 BisGMA/TEGDMA group, the concentration of BisGMA in the sol was higher than the initial concentration for all groups. The presence of TU led to even higher BisGMA concentrations in the sol.

Fig. 6 shows the dynamic mechanical analysis results. All specimens showed conversion greater than 95% (without TU) or greater than 99% (with TU) after post-curing and prior to DMA testing. Two-way ANOVA indicated that the monomer composition and the interaction were not significant ( $p=0.393$  and  $p=0.248$ , respectively), while the presence of TU was significant ( $p=0.001$ ), with all TU-containing materials presenting higher conversion even at those levels. For glass transition temperature ( $T_g$ ), the factors and the interaction were significant ( $p=0.001$ ). For the materials not containing TU, there was no statistical difference among the different BisGMA/TEGDMA compositions. For the TU-containing materials, the 20/80 BisGMA/TEGDMA group presented  $T_g$  statistically higher than the other groups. Except for 20/80 BisGMA/TEGDMA, all TU-containing materials showed lower  $T_g$  values compared to the non TU-containing counterpart. For crosslinking density ( $\nu$ ), the factors and the interaction were significant ( $p=0.001$ ). For materials without TU, the highest  $\nu$  values were observed for 40/60 and 50/50 BisGMA/TEGDMA groups, which were statistically higher than the rest. The TU-containing materials led to consistently lower crosslinking density, and all values within that group were statistically similar to each other. For width at half height of tan delta peak

(WHH, indirect measure of polymer heterogeneity), the TU concentration and the interaction were significant ( $p=0.001$  and  $p=0.014$ , respectively) while the monomer composition was not ( $p=0.145$ ). All materials without TU were statistically similar to each other, and all materials with TU were statistically similar to each other. The addition of TU led to statistically lower WHH for all BisGMA/TEGDMA compositions.

#### 4. Discussion

The BisGMA/TEGDMA monomers were used as models in this study to identify any potential effect of the addition of thiourethanes on the sol/gel composition of methacrylate networks. In general terms, the gel portion of the material contains the monomer units that are involved in the actual network, either as crosslinks, or otherwise part of polymeric chains, and includes partially reacted multifunctional monomers [3]. Conversely, the sol represents the portion that can be extracted, and includes unreacted monomers and small oligomers [4]. The leachates (sol) of fully cured specimens were analyzed with nuclear magnetic resonance and the relative BisGMA/TEGDMA composition of the sol was compared to the initial composition of the monomer mixtures, with or without the addition of thiourethanes. The selection of BisGMA/TEGDMA was based on the fact that these are commonly used monomers to formulate dental composites, which have been extensively characterized in the literature [11]. The participation of BisGMA in network formation has



**Fig. 6** – Results for the dynamic mechanical analysis (–30 to 230 °C) of all groups tested. From top left, clockwise: degree of conversion of the tested specimens after heat treatment in the oven and prior to DMA testing; glass transition temperature (T<sub>g</sub>); breadth of tan delta curve (reported as the width at half height); and crosslinking density calculated from the rubbery plateau of the storage modulus). Upper case letters refer to comparisons within TU or non-TU containing groups, and lower case letters refer to comparisons within each BisGMA/TEGDMA ratio.

been demonstrated to be predominant at the early stages of conversion, while TEGDMA contributes at the later stages in conversion [4]. The addition of any compounds to this mixture is expected to alter the balance of reactivity of the dimethacrylate components [12], and in this particular study, this was hypothesized to affect the amount and composition of the sol/gel in crosslinked networks. Thiourethane oligomers were selected for this study due to recent reports in the literature demonstrating their ability to significantly improve dimethacrylate networks, specifically the ones used in dental cements and composites [6,13]. These oligomers take advantage of thio-carbamate bonds to increase fracture toughness, and of chain-transfer reactions afforded by the pendant thiols to delay gelation and vitrification, and ultimately reduce polymerization stress and increase limiting conversion [6,7]. However, the effect of the addition of these chain-transfer compounds on the sol/gel composition of dimethacrylate networks had not been investigated to date.

The conversion was greater than 65% for all groups tested, and, in general, the presence of TU increased the overall values by about 10% on average, as previously demonstrated [6,14]. This increase in conversion has been attributed to delayed gelation/vitrification of the network via chain-transfer reactions afforded by the pendant thiols from the thiourethane within the polymerizing methacrylate network [7,15]. Chain-transfer is a chain-breaking mechanism [16,17], expected to decrease the crosslinking density, as was indeed confirmed in this study and will be discussed in more detail later. The increase in conversion was not sufficient to influence the water sorption of the materials containing TU, regardless of the BisGMA/TEGDMA composition. However, the solubility in

water was severely diminished by the presence of TU for every BisGMA/TEGDMA ratio, except for 80/20. This decrease can be explained by two overlapping factors. (1) The increase in conversion is expected to decrease the amount of unreacted monomers available to be extracted [18]; (2) The addition of a high molecular weight oligomer to the network hampers diffusion of molecules out of the material. For the 20/80 BisGMA/TEGDMA composition, the solubility decreased by over 70%, from 32 to 9  $\mu\text{m}^3/\text{mm}^3$ , which was a statistically significant difference. For other groups, the reduction in solubility brought by the presence of TU in the composition varied from 75 to 99%. BisGMA/TEGDMA 80/20 was the only group where the presence of TU did not affect the solubility, which is likely due to the same reason that the conversion did not increase: at that composition, the increase in viscosity given by the BisGMA-predominant composition combined with a viscous oligomer might have created limitations to diffusion of polymerizing species, in turn leading to less homogeneous network formation, ultimately facilitating the leaching of components. This was not corroborated by the tan delta width at half-height results, however, as will be explored in more detail later. It is noteworthy that for the 50/50 and 60/40 BisGMA/TEGDMA compositions virtually no leachates were present after immersion in water when the TU was included in the composition. Finally, the analysis of <sup>1</sup>H-NMR spectra revealed that, for the groups where leachates were detected, the composition of the sol contained only trace amounts of BisGMA, with TEGDMA being by far the predominant species. This was true even for the compositions where BisGMA was the main component, suggesting that the extraction solvent used (water) was not capable of extracting any potentially



unreacted BisGMA due to its large molecular weight and relatively lower hydrophilicity ( $\log P = 5.09$ ) compared to TEGDMA ( $\log P = 1.42$ ) [19]. In fact, the overall solubility decreased with the increase in BisGMA concentration in the initial composition. This agrees with previously reported data showing that the amount of the more hydrophobic BisGMA is dramatically underestimated with the use of aqueous extraction solutions [18].

It is important to highlight, therefore, that the amount of leachates extracted by immersion in pure water does not correspond to the total sol composition of the material [4]. For that reason, a separate series of extractions was conducted using dichloromethane as a strong organic solvent. While the extraction in water more closely approximates the clinical scenario, the extraction in dichloromethane allows us to analyze the quasi-totality of the sol composition, or a worst-case scenario. The amount of sol extracted from the polymerized discs increased by one order of magnitude with the use of dichloromethane compared to water. Importantly, this increase was more pronounced for the groups containing higher concentrations of BisGMA, in contrast with what was observed in the water immersions. This shows that the dichloromethane was indeed able to extract even the most hydrophobic, highest molecular weight species in the sol. In this case, the  $^1\text{H-NMR}$  analysis showed that the initial composition and the presence of TU significantly influenced the composition of the sol. For all materials, as the mol ratio of BisGMA increased in the initial monomer mixture, the overall BisGMA concentration on the sol increased, as expected. Also the BisGMA/TEGDMA ratio also increased for the higher initial BisGMA concentrations — for example, in the BisGMA/TEGDMA 80/20 weight ratio, the mol ratio of the initial mixture is 69/31 (based on molecular weights of 512 and 286 g/mol for BisGMA and TEGDMA, respectively), whereas the mol ratio of BisGMA/TEGDMA in the sol was 77/23. This demonstrates that the participation of TEGDMA in the gel was greater than BisGMA, which is explained by TEGDMA's greater flexibility as well as lower viscosity. This compositional drift at limiting conversions has been previously demonstrated for dimethacrylate networks [4].

Interestingly, for the materials containing TU, the participation of BisGMA in the sol is even more pronounced. This is true for all compositions, with increased participation in the sol ranging from 28 to 70 mol% in relation to the initial composition. For example, in the case of BisGMA/TEGDMA 80/20 weight ratio (mol ratio of 69/31 in the initial monomer mixture), the concentration of BisGMA in the sol when TU is present increases to close to 100 mol%, a 31% increase in relation to the initial composition (69 mol%). This shows that in the TU-containing materials, TEGDMA has a much greater participation in the gel. Possible explanations for this finding are the lower viscosity and greater hydrophilic character of TEGDMA, which likely facilitate its solvation into the hydrogen bonding-rich TU oligomer “pre-network”. It is then possible that most of the TEGDMA is entrapped within the TU oligomer, possibly also forming shorter chains with reduced crosslinking, and creating BisGMA-rich regions elsewhere in the polymer. This also partially explains the increased overall solubility of the TU-containing materials in dichloromethane, since greater heterogeneity and shorter

chains facilitate molecular diffusion and extraction of unreacted monomers and other low molecular weight species.

Dynamic mechanical analysis was used in this study to elucidate network structure. Post-photoactivation heat treatment was used to ensure that the maximum conversion was achieved before the specimens were subjected to the temperature sweep required by the test, without causing further polymerization. This is required to obtain accurate measurements of the glass transition temperature ( $T_g$ ), elastic modulus and tan delta curves [10]. Due to the increased level of conversion, these networks are not exactly the same as the ones discussed in the extraction studies, which would have warranted the use of thermal stabilizers, such as iniferters [20], not used here. The use of iniferter-containing materials and partial cure specimens will be the subject of future investigations. With those caveats, and using specimens with conversion levels greater than 98% for all materials, no statistical differences were found in terms of  $T_g$  among the materials without TU, regardless of the BisGMA concentration. This was not expected, since at the same conversion, the higher monomeric  $T_g$  of BisGMA ( $-10^\circ\text{C}$  compared to  $-80^\circ\text{C}$  for TEGDMA) [21], given by strong hydrogen bonding and rigidity of the BPA core [22], was anticipated to increase the polymeric  $T_g$ . The explanation is likely a combination of the crosslinking density and the polymeric heterogeneity, estimated in this study by the breadth of tan delta peak [23] and quantified as the peak width at half-height — the wider the peak, the more heterogeneous the material [10]. In general, the compositions with the lowest crosslinking density were also the ones with the broadest tan delta peaks (less homogeneous), which are both related to polymer packing and free volume distribution. In the case of the 20/80 BisGMA/TEGDMA compositions, the lower crosslinking density/greater heterogeneity is explained by the high tendency to cyclization presented by TEGDMA [23]. On the other side of the spectrum, as already explained, the 80/20 BisGMA/TEGDMA composition presents much greater diffusion limitations due to BisGMA's viscosity and lack of flexibility [3]. When TU was added to the mixtures, the  $T_g$ , the crosslinking density and the breadth of tan delta decreased, regardless of the initial BisGMA/TEGDMA composition. The decrease in  $T_g$  was expected and is previously reported [6], and is based on the inclusion of a lower  $T_g$  “pre-network” in the mixture. The  $T_g$  of the TU used in this study is  $-5^\circ\text{C}$ . The only group where the addition of TU did not lead to a statistically significant reduction in  $T_g$  was the 20/80 BisGMA/TEGDMA composition. In that particular case, the low  $T_g$  of the TU was likely counteracted by the increase in initial viscosity. The low viscosity of TEGDMA-rich systems leads to predominance of termination-controlled reactions and cyclization early in conversion, thus decreasing the overall conversion [24]. That way, by increasing the initial viscosity beyond a certain threshold, the addition of TU acted synergistically and increased the overall conversion of the system, partially counteracting the effect of its low  $T_g$  on the overall  $T_g$  of the network. The decrease in crosslinking density was expected also, since the chain-transfer reactions afforded by the pendant thiols in the TU backbone are chain-breaking [16], as already mentioned. Previous reports have demonstrated, however, that this does not affect other mechanical properties, which actually increase with the presence of TU, for reasons

beyond the scope of this present study [6,13,14]. Those same chain-breaking reactions, however, have been shown to produce more homogeneous polymer networks [7], as was indeed shown here. All TU-containing groups presented narrower tan delta peaks, for all compositions. Again, the 20/80 Bis-GMA/TEGDMA was the composition to benefit the most from the addition of TU in obtaining more homogeneous networks, also likely due to the increased conversion and decreased degree of cyclization, as already discussed.

## 5. Conclusion

In conclusion, this study demonstrated that the presence of thiourethane additives affects network formation and ultimately the composition of the sol/gel in dimethacrylate networks. The presence of thiouretanes favored the contribution of TEGDMA to the overall network formation, as evidenced by the increase in BisGMA concentrations after extraction with dichloromethane.

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# Capítulos

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Avaliação da composição química, do desafio bacteriano, do acabamento/polimento e de protocolos de cimentação de diferentes materiais restauradores – MARCELA GONÇALVES BORGES FARIA – Tese de Doutorado – Programa de Pós-Graduação em Odontologia – Faculdade de Odontologia – Universidade Federal de Uberlândia.

## 2.2 Capítulo 2

### **Effect of bacterial challenge on the micro-shear bond strength of dental composites repaired using a thiourethane-based silane**

**Running title:** Aging effects on the dental composites repaired using thiourethane-silanes

#### **Clinical Relevance**

TU-based silanes may be an alternative with good mechanical and chemical properties for repair of composite restorations.



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## **SUMMARY**

**Objectives:** The aim of this study was to evaluate the effect of bacterial challenge on the micro-shear bond strength of dental composites repaired with thiourethane-modified silanes.

**Methods and Materials:** Disk specimens (Filtek Supreme A3 Body - 3M ESPE) with 10 mm in diameter and 5 mm in thickness were sandwiched between glass slides and photo-polymerized for 20 s. The groups were divided according to the silane used in the surface treatment of the composite resin restorations: commercial control (RelyX Ceramic Primer – 3M ESPE), experimental control (3-(trimethoxysilyl)propyl methacrylate), three different thiourethane-silanes synthesized in house (TU: PETMP-BDI, PETMP-HDDI or PETMP-HMDI). For all groups, the silane was added at 2 wt% to 75/25 vol ethanol/water. The surface was roughened and acid etched prior to silane and adhesive application, followed by photo-polymerization for 10 s. Repairs (2 x 2 mm) were built using tygon tubing. Specimens were kept in water for 24 h at room temperature, before being tested for micro-shear bond strength ( $\mu$ SBS) at 0.5 mm/min. Selected groups were aged in media containing *S. mutans* cultures during 7 days. Data was analyzed with one-way ANOVA/Tukey's test (95%). Student's t-tests were used to contrast the micro-shear bond strength results before and after aging within the same group.

**Results:** There was statistical difference among the groups before aging ( $p < 0.001$ ). The experimental control was statistically similar to the commercial control and the group containing the PETMP-BDI silane. The groups containing TU were all statistically similar to the commercial control. After aging, the group containing TU had statistically higher bond strength than either control group. While the controls showed a 50% reduction with aging, the TU-containing groups were able to maintain the bond strength to the same level as before aging.

**Conclusion:** The use of TU silanes was able to maintain the bond strength of repaired interfaces of composites.

**Keywords:** dimethacrylates; thiourethane; silane; composite repair; microshear bond strength

## INTRODUCTION

Composite resin restorations achieve acceptable survival, with annual rate of failure between 1.8 and 2.5%.<sup>1,2</sup> However, a number of cohort studies has demonstrated that the average life span of those restorations is about 7-10 years.<sup>3</sup> Such restorations become less stable due to the prolonged exposure to organic solvents and mechanical loads in the oral cavity,<sup>4,5</sup> which can lead to hydrolytic degradation in methacrylate-containing materials. Factors such as the action of salivary enzymes, variations in pH, presence of cariogenic diet, accumulation of biofilm, wear by abrasive toothpastes and tooth-brushing and occlusal fatigue can accelerate this process.<sup>6, 7</sup> Combined, these factors contribute mainly to the development of sensitivity, marginal infiltration, secondary caries and fractures, ultimately leading to the need for replacement of restorations.<sup>8,9</sup> Upon removal of those restorations, inevitably some sound tooth structure is lost. Therefore, the ability to repair restorations represents a more conservative approach, as part of a minimally invasive dentistry philosophy.<sup>10, 11</sup>

The advantages of restoration repair for patients and professionals include time-saving,<sup>12</sup> cost-effectiveness, tooth conservation, local anesthesia may not be required and avoidance of the repetitive restorative cycle.<sup>9</sup> One of the difficulties in performing repairs is that pre-existing restorations have limited residual C=C bonds available for cross-linking with monomers on the fresh composite resins used in the repair.<sup>13</sup> The intraoral aging process also causes water sorption and loss of components, leading to up to 80% reduction of cohesive strength and challenging the adhesion between aged and new increments of the composite resin repair.<sup>13, 14</sup> When repairing composite resin restorations, a durable bond strength to the original material is important.<sup>15</sup> In fact, one study has demonstrated that the bond strength of a fresh composite increment is lower when placed over composites aged with water for 1 year<sup>15</sup> or for 1 month at 37°C,<sup>16</sup> compared to the placement over a virgin composite surface. This could be due to several factors, mainly related to monomer composition, which regulate water uptake and degradation, among other things, as well as factors controlled by the clinician, which are relevant in this technique-sensitive procedure. All of those influence the adhesion of the repair to resin matrix of the water-aged composite.<sup>16</sup> In addition, the interfacial margin of the

repair itself is also subject to the environmental challenges in the oral cavity, but fewer reports in the literature have investigated the durability of the repairs, simulating clinical situations.<sup>16</sup> Therefore, the immediate bond strength of the repair depends on the chemical composition of the composite, the conditions of the original and/or repaired surface, as well as on the protocol utilized in the repair.<sup>16, 17</sup>

The most common surface treatments for repairs consist of sandblasting with aluminum oxide powder or silica coating and subsequent application of first a silane and then a bonding agent as an effective adhesive pre-treatment, which has been reported to result in about 60% of the original cohesive strength of the material when tested after the repair procedure.<sup>18</sup> In every report in the literature, the silane used on the repair is a conventional 3-(trimethoxysilyl)propyl methacrylate.<sup>19</sup> In recent years, silanes based in thiourethane oligomers (TU) have been developed, showing improved fracture toughness and reduced polymerization stress when used as surface treatment for filler particles.<sup>20, 21</sup> The use of TU silanes as a surface treatment prior to repair procedures has not been explored in the literature, but it can be envisioned as an alternative due to the potential for toughening of the repair interface, potentially increasing the long-term bond strength of the repair. In this context, bearing in mind the need for longevity of restorations and conservative treatment approaches, this study proposes to combine conventional mechanical asperization procedures with TU silanes, test the bond strength of repairs both immediately and after aging under bacterial challenge. The null hypothesis was that the silanes formulated with TU will not affect the micro-shear bond strength of the repair, independent of the time of aging.

## **METHODS AND MATERIALS**

### Experimental design and silane formulation

The study design comprised five groups (n=10), according the silane used in the repair protocol of the composite resin restorations: commercial control (RelyX Ceramic Primer – 3M ESPE, St. Paul, MN, USA, used as received), experimental control (3-(trimethoxysilyl)propyl methacrylate), or one of the

following TU-silanes: TU PETMP BDI, PETMP HDDI or PETMP HMDI. The TU silanes were synthesized as previously described (22) by combining pentaerythritol tetra-3-mercaptopropionate (PETMP) with different di-isocyanates – 1,3-Bis(isocyanato-1-methylethyl) benzene (BDI), 1,6-Hexanediol-diisocyanate (HDDI) or dicyclohexylmethane 4,4'-Diisocyanate (HMDI), and 3-(Triethoxysilyl)propyl isocyanate at 1:2:1 isocyanate:thiol, leaving pendant thiols. For all experimental groups, the silane was added at 2 wt% to a mixture of water/ethanol (25/75 vol%). All reagents used in this work were purchased from Sigma-Aldrich (Milwaukee, WI, USA) and used without further purification.

### Repair techniques

Disk specimens (Filtek Supreme A3 Body - 3M ESPE, St. Paul, MN, USA) with 10 mm in diameter and 5 mm in thickness were fabricated using a silicon mold sandwiched between glass slides. Photoactivation was carried out using a light curing unit (Elipar Depp Cure S – 3M ESPE, St. Paul, MN, USA) positioned directly on the surface of the glass, delivering 710 mW/cm<sup>2</sup>, during 20 seconds. The irradiance was checked daily using the MARC resin calibrator (BlueLight Analytics Inc., Halifax, NS, CAN). These disks were used as the substrate for repair, which was performed immediately after the discs were produced. The intent here was to test the resistance of the repair itself, independent on the form of aging on the surface. For all groups, the surface treatment consisted of asperization with sandpaper #320, acid etching with phosphoric acid at 37% (Ultra-Etch – Ultradent Products, Inc, South Jordan, UT, USA) during 1 minute, rinsing and drying during the same time, silane application, bond application (Clearfil SE Bond – Kuraray Noritake Dental Inc., New York, NY, USA) and photopolymerization during 10 seconds.

Tygon tubing (Embramac, Campinas, SP, Brazil) with 2 in diameter x 2 mm in thickness was used to build new composite stubs onto the surface, photopolymerized as previously described. After polymerization, the tygon tube was removed by scalpel blade. Specimens were kept in water during 24 hours at room temperature. After this storage, the specimens were tested for microshear bond strength, as described below. The groups with the best performance were further tested under harsher conditions, after aging in the presence of caries-forming bacteria.

### Inclusion and micro-shear bond strength test

The specimens were embedded in epoxy resin (Epoxy Cure™ 2 – Buehler, Lake Bluff, IL, USA), leaving the repair interface exposed. The Ultradent micro-shear device (Test Base Clamp, Ultradent Products, Inc, South Jordan, UT, USA) was used to position the specimen on a universal testing machine (Criterion, MTS Systems Corp, Eden Prairie, WI, USA), which were tested until failure at 0.5 mm/min crosshead speed. The diameter (mm) of each specimen was measured with a digital caliper to the second decimal place, and the bonded area was used to calculate the peak stress data in MPa. Three groups were selected based on these results for further testing, after aging by bacterial challenge.

### Bacterial challenge

Additional specimens of the selected group and the commercial and experimental controls were produced and exposed to the bioluminescent *S. mutans* strain IdhRenGSm, a derivative of wild type UA159.<sup>23</sup> Starting from a frozen stock, bacteria were streaked onto an agar plate and grown overnight in a CO<sub>2</sub> incubator at 37°C. IdhRenGSm planktonic cultures<sup>24</sup> were grown in TH culture medium supplemented with 0.3% yeast extract for 16 hours at the same incubation conditions described above. At the end of this period, 1:500 dilution of the inoculum was added to TH biofilm growth medium supplemented with sucrose (1.0% (w/v)). 1.0 mL aliquots were dispensed into the wells of sterile 48-well plates (Falcon, Corning, USA) containing the specimens previously sterilized by immersion in isopropyl alcohol for 20 minutes. As sterility control, representative specimens were incubated in media without inoculum. The plates were incubated for 7 days in a CO<sub>2</sub> incubator at 37°C. Culture medium was changed daily. After the incubation period, specimens were carefully moved to 24-well black plates (Black Visiplat TC, Wallac Oy Perkinelmer, Torku, Swedish Åbo, Finland) containing 0.5 ml of fresh media per well and incubated at 37°C for 1 hour.

### Statistical analysis

The data were tested for normal distribution (Anderson-Darling) and homocedasticity (Levene's test), followed by parametric statistical tests. One-way analysis of variance (ANOVA) followed by multiple comparisons test (Tukey) at

95% significance level were used to analyze the data for micro-shear bond strength in each of the aging conditions. Student's t-tests were used to contrast the micro-shear bond strength results before and after aging within the same group. All analyses were carried out using statistical package Sigma Plot version 13.1 (Systat Software Inc.).

## RESULTS

The results of micro-shear bond strength before and after bacterial challenge are shown in Figure 1. Before bacterial challenge, there was statistical difference among the groups ( $p < 0.001$ ). The experimental control presented the highest value, statistically similar to the commercial control and the group containing as the TU silane, all statistically similar. All silane groups (PETMP-BDI, PETMP-HDDI and PETMP-HMDI) were statistically lower than the experimental control, but statistically similar to the commercial control.

The micro-shear bond strength after bacterial challenge (Figure 1) for the group where PETMP-BDI was used as the silane in the repair protocol was statistically higher than either control ( $p = 0.002$ ). The asterisk indicates statistical differences within the same treatment group before and after aging. The micro-shear bond strength was statistically lower for both controls after aging, with 27% reduction for the commercial control ( $p = 0.018$ ) and 56% reduction for the experimental control ( $p < 0.001$ ). For the group containing PETMP-BDI as the TU silane, the results were not affected by the aging ( $p = 0.340$ ).

## DISCUSSION

The null hypothesis of this study was rejected. The silanes formulated with TU affected the micro-shear bond strength of the repair and were able to maintain the bond strength to the same level as before aging. Replacement of restorations still accounts for more than half of dental restorative procedures, and this proportion continues to increase.<sup>25</sup> 'Big data' on restoration repair vs. replacement is scarce, as are randomized controlled investigations on the subject.<sup>25</sup> Previous *in vitro* studies reported that the bond strength of nanohybrid composites repairs fell short of the cohesive strength of the original material itself

by about 80%.<sup>17, 26</sup> Clinical studies have followed up that ten-year mean annual failure rates (mAFR) of composite restorations were reported to amount to 3.1% for anterior<sup>27</sup> and 4.1% for posterior restorations.<sup>28</sup> When repaired restorations were performed, mAFR were lowered to 2.6%<sup>27</sup> and 2.9%,<sup>28</sup> respectively. Twelve-year mAFR of composite posterior restorations was reduced from 1.8% to 0.7%, by performing repairs.<sup>29</sup> On the other hand, for clinicians and patients facing with a partially defective restoration it might not only be important if repairs increase the longevity of the original restoration, but rather if the repaired restoration will last as long as a replacement restoration.<sup>30</sup> Thus, information on the longevity of both decisions (repair vs. replacement) is highly relevant.<sup>30</sup> So far, only one study assessed the survival of repaired restorations (4-year mAFR: 5.7%),<sup>30</sup> but compared longevity to “newly” placed (i.e. initial restorations) rather than truly replaced restorations. Longevity of repaired restorations was lower than of newly placed restorations.<sup>29</sup>

The causes for the failures are confounded by many factors, such as the size of the restoration, presence of para-functional habits or premature contacts, the type of surface treatment, marginal opening with secondary caries, fracture, marginal deterioration, discoloration or wear.<sup>31</sup> Meta-analysis studies are very rare, but the few that exist seem to agree with the general consensus that repairs are relatively safe, and represent a more conservative option for the total replacement of the restoration.<sup>32</sup> In addition, individual circumstances, operator knowledge of the repair technique and what constitutes a failed restorations and patients' preferences are indicate for clinicians' interventions based on evidence of existing defective restorations.<sup>32</sup> The treatment of the surface of the restoration to be repaired can include mechanical roughening, acid etching and silane application, followed by adhesive resin application.<sup>18</sup> These procedures were found to be quite efficient in the repair of microhybrid resins, although not for nanohybrid composites.<sup>19, 33</sup> This has been explained based on the higher degree of conversion achieved by nanohybrids, limiting the number of carbon double bonds available to co-polymerize with the fresh layer of composite.<sup>34</sup> It is generally agreed upon that the repair bond strength of composites currently relies mainly on micro-mechanical retention between old and new composite layers.<sup>26</sup> Studies comparing repair procedures carried out with and without mechanical



roughening of the surface have shown that the use of sandblasting with alumina particles or silica coating prior to the repair increases the flexural strength.<sup>35</sup> The reliance on mechanical retention justifies the roughening of the surface used in this study. Before aging, the substrate surfaces were wet-ground with 320-grit abrasive paper corresponding to the roughness obtained by diamond bur grinding in order to remove the resin-rich superficial layer of specimens, and also to create standardized repair surfaces.<sup>35, 36</sup> This mechanical surface treatment simulated a common repair technique.<sup>37</sup> The abraded surfaces of the aged specimens were etched to clean the debris and remove dust from the surface, also according to the recommended in the literature.<sup>38, 39</sup>

The use of a silane coat during resin repair procedures basically aims to promote chemical bonding by forming siloxane bonds between silicate-containing filler particles exposed on the repair surface and the resin matrix of fresh resin layer.<sup>40</sup> It has also been demonstrated that surface wettability increases with this procedure, which can improve the adaptation of the fresh composite layer, and ultimately increase the micro-mechanical interlocking in the repair interface.<sup>19, 41</sup> In most of the studies dealing with restoration repair, including composites and ceramics, a conventional methacrylate silane is used.<sup>42</sup> This is justified by the simplicity of use, the availability of a commercial material and the possibility of covalent bonding both with the silica component of the surface to be repaired, as already mentioned, but also potentially by co-polymerization with available carbon double bonds.<sup>43</sup> However, these materials are still prone to hydrolysis over time, via degradation of the silanol bonds as well as of the ester bonds in the methacrylate,<sup>44</sup> leading to weakening of the organic matrix and silica interfaces, both in the aged and fresh composites. This has been demonstrated to facilitate crack propagation and premature failures.<sup>45</sup> For those reasons, this study proposed to use a modified silane agent, based on thiourethane oligomers – TU.<sup>21</sup> TU-silanes have been demonstrated to improve fracture toughness and reduce stress when used as the surface treatment for filler particles added to composite materials,<sup>21, 44, 45</sup> and therefore, could potentially reinforce the interface between aged and fresh composite layers in repaired restorations.

Before the bacterial challenge, the use of TU silanes did not improve the shear bond strength compared to the commercial control, and in fact led to lower

bond strengths compared to the commercial control. This may have been due to a more flexible interface, since the glass transition temperature of the oligomer itself lays below room temperature, at about 5 °C.<sup>22</sup> Therefore, in the absence of water or bacterial enzymes and acidic metabolic products, the flexibility of the interface probably led to reduced bond strength. It is important to note, however, that even still, the bond strength of the TU-silanes was statistically similar to the commercial control. Since the objective of this study was to improve the long-term stability of the bond, the fact that the TU-modified material presented the same bond strength as the commercial control was encouraging. In this study, the initial surfaces of the composite were treated the same way for the groups with and without exposure to the bacterial challenge.

Aging is one of the important factors limiting the longevity of adhesive restorations. As the restoration ages under service in the oral environment, water molecules absorbed by the resin structure both plasticize the polymer matrix and also diffuse into silane treated filler-matrix interface, resulting in the hydrolysis within the resin matrix and/or at the resin-filler interface.<sup>46-48</sup> In addition, emerging stresses caused by the recurring thermal expansion and contractions undermine the durability of adhesive interfaces.<sup>49</sup> Importantly, the presence of acidogenic biofilms at the repaired interface must also play a role in the longevity of this procedure, as the by-products of methacrylate degradation have been shown to up-regulate the activity of *S. mutans*.<sup>50</sup> Rather than pre-aging the composite itself, the rationale here was to provide an unbiased design to assess the effect of the bacterial challenge on the bonded interface itself. In other words, the biofilm challenge was equal for all materials. Since all TU silanes were statistically similar prior to the bacterial challenge, only one group was selected for comparison with the commercial and experimental controls after exposure to single species biofilms. The TU silane presented higher shear bond strength than either control group. Perhaps more importantly, while the controls showed 27 and 56% reduction in shear bond strength (commercial and experimental, respectively), the TU-silane stayed stable after bacterial challenge. This may be explained by potentially less degradation of the TU-containing materials, as previously demonstrated,<sup>51</sup> due to the reduction of ester bond concentration, as well as the higher molecular weight of the TU silane compared to the methacrylate controls.

Moreover, the presence of thio-carbamate bonds likely led to the toughening of the interface, decreasing the likelihood of crack propagation.<sup>52</sup> That, allied with the greater resistance to hydrolysis of the same bonds, led to improved stability of the bonded interface.

This study demonstrates encouraging results with the use of TU silanes for repair procedures, though not without limitations. The use of pre-aged surfaces and longer incubation times, potentially combined with mechanical loading in fatigue mode, are logical next steps for further investigation to provide an unbiased design to assess the effect of the bacterial challenge on the bonded interface itself and to improve bond stability.

## **CONCLUSION**

Within the limitations of this study, it can be concluded that the use of TU silanes was able to maintain the bond strength of repaired interfaces of composites, while the controls showed a 50% reduction with aging.

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Figure

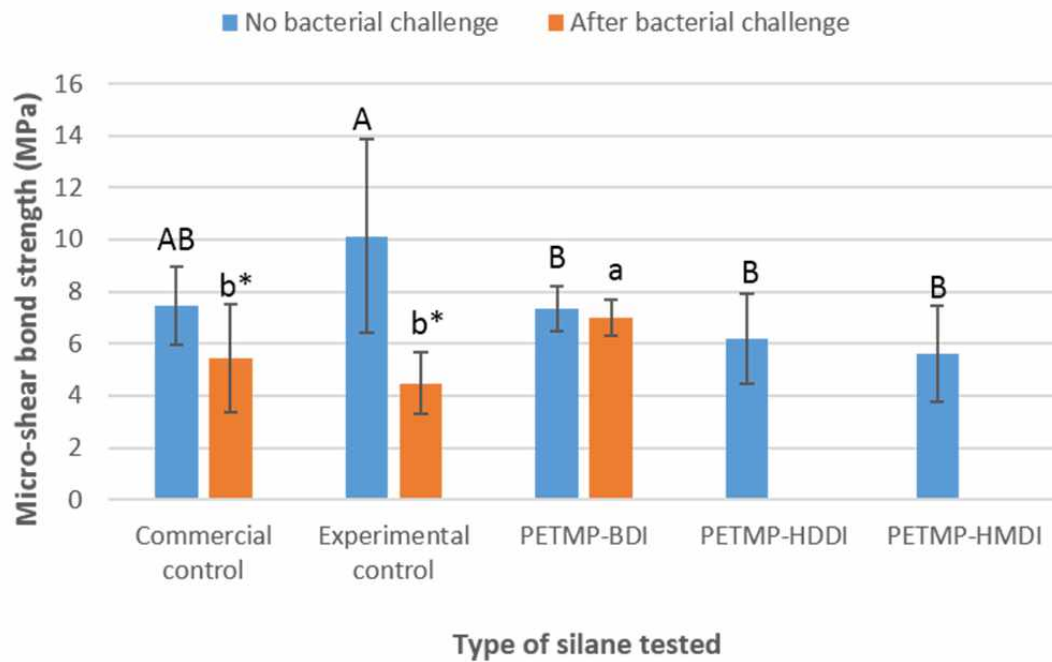


Figure 1: Results for micro-shear bond strength for the repaired groups tested before and after bacterial challenge. The same superscript within each aging condition indicates statistical similarity among groups. The asterisks indicate statistical difference within the same group before and after bacterial challenge. The overall level of significance was 95%.

# Capítulos

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Avaliação da composição química, do desafio bacteriano, do acabamento/polimento e de protocolos de cimentação de diferentes materiais restauradores – MARCELA GONÇALVES BORGES FARIA – Tese de Doutorado – Programa de Pós-Graduação em Odontologia – Faculdade de Odontologia – Universidade Federal de Uberlândia.

## **2.3 Capítulo 3**

Oxygen inhibition of surface composites and its correlation with degree of conversion and color stability

Oxygen inhibition effects of composite resins

Oxygen inhibition of surface composites and its correlation with degree of conversion and color stability

Oxygen inhibition effects of composite resins

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## Summary

This study investigated the effects of oxygen inhibition and finishing/polishing procedures on the composite resin properties. One bulk-fill and two conventional composite resins (nanoparticle and microhybrid) were evaluated. Specimens were prepared using 4 surface treatments: control, no treatment; Gly, oxygen inhibition with glycerin; FP, finishing and polishing; Gly + FP, glycerin followed by finishing and polishing. The degree of conversion (DC) was measured using Fourier Transformed Infrared Spectroscopy (FTIR) immediately and after 15 days (n=5). Color stability ( $\Delta E_{ab}$ , and  $\Delta E_{00}$ ) and opacity were evaluated using a spectrophotometer after 15 days of immersion in coffee, using the CIELAB system (n=5). Data were analyzed by two-way ANOVA and Tukey tests ( $\alpha=0.05$ ) and opacity by two-way repeated-measures ANOVA. Glycerin usage increased significantly the DC however had no influence on the  $\Delta E_{ab}$ ,  $\Delta E_{00}$  and, opacity values. Finishing and polishing reduced  $\Delta E_{ab}$  and  $\Delta E_{00}$  values, regardless of composite resins. Microhybrid showed higher opacity, followed by the nanoparticle and bulk fill, regardless of surface treatment. Post-polymerization polishing procedures resulted in lower conversion than using an oxygen inhibitor agent (Gly condition), but similar staining caused by coffee.

Keywords: composite resin, oxygen inhibition, finishing and polishing, color change, degree of conversion

## 1. Introduction

Composite resins are materials widely used in daily practice that need adequate polymerization for good clinical performance (1). These materials are undergoing chemical degradation processes in the oral cavity due to diets that contain staining solutions, as well as acidic foods and drinks. (2,3) Degradation of composite resin, including color alteration, may result in additional costs due to early replacement of restorations. The degree of conversion (DC) of monomers is measured by the percentage of double bonds of carbon consumed during the polymerization reaction. (1) The DC depends on the emission spectra of light curing units to match the absorption spectra of the photoinitiators used in these materials. Additionally, the light must actually reach all area of the restoration. (4)

During composite light-curing, the contact of oxygen produces a surface layer of uncured resin. (5,6) The oxygen inhibits the polymerization reaction, resulting in the formation of a polymer chain more prone to staining and wearing. (5) The oxygen-inhibited layer thickness for composite resins ranges from 4  $\mu\text{m}$  to 40  $\mu\text{m}$ . (5) The thickness of the oxygen-inhibited layer depends on the type of monomer, initiator-activator systems, particle morphology, concentration of free radicals, and the oxygen consumption rate. (5,6) Some clinicians have applied glycerin gel or water-soluble gel over the last increment light-curing through the transparent layer avoiding the oxygen inhibition of composite resin surface. (5,6)

Nowadays, microhybrid and nanoparticle composites are considered universal resin-based restorative materials suitable for the restoration of anterior and posterior teeth due to their excellent aesthetic properties. These nanomaterials use submicrometre particles to further enhance the optical and physical properties of the resins. (3) Bulk fill composite resin, flowable and higher viscosity, claim to enable the posterior restoration of build-up in thick layers, 4 to 5 mm, reaching adequate polymerization in deeper regions. (4,7–9) Sufficient depth of cure may be achieved by using specific polymerization modulators, by improving the translucency, or by using more potent initiator systems. Restoring posterior cavities using bulk-fill composite resins can result in reduced shrinkage stress and cusp deflection, which might improve the clinical performance of the restoration. (10)

To the best of our knowledge, the literature is scarce in terms of the ideal moment to perform surface finishing and polishing procedures of composite

resins modulated by presence of unpolymerized monomers on the surface. This condition could absorb pigments, especially on the difficult to access areas such as the proximal surface or occlusal surface of posterior teeth. Moreover, the effects of glycerin use over composite resin surfaces are not clear in relation the mechanical properties improvement. Therefore, the aim of this study was to investigate the effects of oxygen inhibition and finishing/polishing procedures on the degree of conversion (DC) and color stability ( $\Delta E_{ab}$ ,  $\Delta E_{00}$  and opacity) of bulk-fill and conventional composite resins. The null hypothesis was that the use of the glycerin oxygen inhibitor gel or its association with immediate finishing and polishing would not improve the color stability and the degree of cure of bulk-fill or conventional composite resins.

## 2. Material and Methods

### 2.1 Experimental design

This in vitro investigation was conducted using a 3x4x2 factorial study design to evaluate the factors “composite resin – bulk-fill, conventional nanoparticle and microhybrid”, “protocols of surface treatments- no treatment, oxygen inhibition with glycerin, finishing and polishing, and glycerin + finishing and polishing” and “assessment time – immediate and mediate analysis”. The main response variables included in this study were (1) degree of conversion and (2) color change.

### 2.2 Specimen preparation

One bulk-fill (Filtek Posterior Bulk-Fill, 3M ESPE, St, Paul, MN, USA), and two conventional nanoparticle (Filtek Z350 XT, 3M ESPE) and microhybrid (Filtek Z250, 3M ESPE) composite resins were evaluated in this study. The compositions of materials used are described in Table 1. To measure the DC, according to the International Standards Organization (ISO) 4049, the composite resins were inserted into a silicone mold (HydroXtreme, Vigodent, Rio de Janeiro, Rio de Janeiro, Brazil) with internal dimensions of 4 mm in diameter x 2 mm of thickness. Specimens for color measurement (ISO/TR 28642) were built-up using a Teflon mold (8 mm of diameter x 2 mm of depth).

A halogen-light-based curing unit (OptiLux 501, Demetron, Danbury, CT, USA - 600 mW/cm<sup>2</sup>) was fixed in a standard device in order to maintain a fixed



distance between the light-curing tip and sample surface. After placing the material into the mold, a polyester strip was pressed over the surface with a glass slab to obtain a flat surface. After the glass slab and the strip were removed and the photoactivation was made for 20 s, perpendicular and directly on the top of the specimens, at the shortest possible standardized position between the tip and the mold. Specimens were prepared according to different surface treatments: *Control group (Control)*: the composite resins were light-cured for an additional 20 s.

*Glycerin surface treatment (Gly)*: glycerin (Biopharma, Uberlândia, MG, Brazil) was applied on the surface of composite resin specimens followed by additional light activation for 20 s.

*Finishing and polishing (FP)*: the composite resin specimens were light-cured for an additional 20 s, followed by finishing and polishing with abrasive disc Sof-Lex Pop-On (3M/ESPE) used sequentially according to the abrasiveness (medium, fine, and extra-fine discs). Ten movements were performed for each disc. The surface of the specimen was cleaned with distilled water and the composite resin surface was polished with a polishing paste Fotoacrill (Dhpro, Paranaguá, Paraná, Brazil) associated with a felt disk Diamond (FGM, Joinville, Santa Catarina, Brazil). The felt disk was wiped on the surface of the sample with alcohol 70% (Itajá, Goianésia, Goiás, Brazil) with friction and dried with an air-stream for 10 s following each procedure.

*Glycerin + finishing + polishing (Gly + FP)*: after glycerin surface application and light activation for 20 s, the finishing and polishing were performed using the previously described protocol.

Five specimens were produced with the same finishing/polishing instrument. Before DC analysis, 70% alcohol with gauze was used with on the specimens to remove the glycerin and post polishing compounds. The same clean protocol was used for control group.

### 2.3 Degree of conversion measurement

The specimens were placed on the ATR crystal directly with standardized pressure by the ATR device. The DC was measured immediately after the finishing and polishing surface procedures and again after 15 days using Fourier Transformed Infrared Spectroscopy (FTIR- Vertex 70, Bruker Optik GmbH,

Ettlingen, Germany). For the evaluation after 15 days, specimens were stored in a dry and dark container at 37 °C. The DC was assessed using FTIR with attenuated total reflectance (ATR crystal) sampling, mid-infrared (MIR) and deuterated triglycine sulfate (DTGS) detector elements (Bruker Optik), with a 4cm<sup>-1</sup> resolution and coaddition of 32 scans. All analyses were performed under controlled temperature (25±1 °C) and humidity (60±5%) conditions. The DC was calculated from the equivalent aliphatic (1640 cm<sup>-1</sup>) and aromatic (1610 cm<sup>-1</sup>) of cured (C) and uncured (U) composite resin specimens according to the following equation:  $DC = (1 - C/U) \times 100$ .

#### 2.4 Immersion of coffee and color stability measurement (n=5)

The color analysis was carried out immediately after specimen preparation. After 24 h of specimens being stored in a dry and dark container at 37 °C, they were individually immersed in 1 mL of coffee solution (Nestlé, São Paulo, SP, Brazil) for 15 days at 37°C. (9) The solution was replaced daily. After storing, the excess of the solution was removed, and the specimens were ultrasonically (Ultrasonic Cleaner, Thornton – INPEC, Vinhedo, SP, Brazil) washed in distilled water for 10 minutes and dried.

The readings assessed at baseline were used to calculate the color changes caused by coffee immersion. The baseline color coordinates were assessed in standard conditions by means of a reflectance spectrophotometer (Ci64UV, Xrite, Chandler, Arizona, USA). The device was adjusted for the D65 light source, with 100% ultraviolet and specular reflection included. The observer angle was set at 10 degrees, and the device was adjusted to a small reading area (SAV), with a total area of 4 mm<sup>2</sup>. The color parameters were measured over white background (L\*white 85.6, a\*white 1.28, b\*white 6.83) while the opacity was directly measured by the device. To measure opacity, samples were made against white, black (L\*black 26.32, a\*black -38, b\*black 0.53), and white backgrounds again. (11) The spectrophotometer was adjusted for three consecutive readings, which were later averaged.

The results of the color readings were quantified in terms of the L\*, a\*, and b\* coordinate values established by the Commission Internationale de l'Eclairage (CIELAB system). The color difference of the same specimen was calculated by the use of two different equations. The first one is the CIELAB color difference

( $\Delta E_{ab}$ ) equation, which was calculated as follows:  $\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$  where  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  refers to lightness, green-red, and blue-yellow differences of baseline and post coffee immersion color measurements. The second is the CIEDE2000 color difference ( $DE_{00}$ ), and it was calculated as follows:  $\Delta E_{00} = [(\Delta L/K_L S_L)^2 + (\Delta C/K_C S_C)^2 + (\Delta H/K_H S_H)^2 + R_T (\Delta C/K_C S_C) (\Delta H/K_H S_H)]^{1/2}$  where  $\Delta L$ ,  $\Delta C$  and  $\Delta H$  are considered lightness, chroma, and hue differences between color measurements.  $K_L$ ,  $K_C$ , and  $K_H$  are the parametric factors for viewing conditions and illuminating conditions influence.  $R_T$  is the function for the hue and chroma differences interaction in the blue region.  $S_L$ ,  $S_C$ , and  $S_H$  are the weighting functions for the color difference adjustment considering the location variation of  $L^*$ ,  $a^*$ , and  $b^*$  coordinates. (12)

## 2.5 Statistical Analysis

DC data was tested by normal distribution (Shapiro-Wilk test) and homoscedasticity (Levine test) followed by two-way ANOVA and Tukey tests ( $\alpha=0.05$ ). The color alteration data were tested by normal distribution (Shapiro-Wilk test) and homoscedasticity (Levine test) followed by two-way ANOVA and Tukey tests ( $\alpha=0.05$ ). For opacity data, two-way repeated measures ANOVA were applied for each composite resin ( $\alpha=0.05$ ). Linear regression for  $\Delta E_{ab}$  and immediate and mediate composite DC data set were calculated.

## 3. Results

The DC (%) mean and standard deviation values of the all tested composite resins are shown in Table 2. Two-way ANOVA showed that the composite resin ( $P<0.01$ ) and surface treatment ( $P<0.01$ ) and the interaction between both study factors ( $P=0.005$ ) were significant for DC values. The moment of analysis had no influence in the DC values. Glycerin usage increased significantly ( $P<0.001$ ) the DC values for all composite resins.

The mean and standard deviation values of opacity before and after coffee storage, are shown in Table 3. Two-way ANOVA showed that the composite resin ( $P=0.007$ ), and moment of analysis ( $P<0.001$ ) influenced significantly the opacity but not the interaction of them. ( $P=0.803$ ). Microhybrid composite resin showed

higher opacity, followed by the nanoparticle and bulk-fill composite resins, regardless of surface treatment.

The color changes for  $L^*$ ,  $a^*$  and  $b^*$  parameters are shown in Figure 1 and the mean and standard deviation values of  $\Delta E_{ab}$  and  $\Delta E_{00}$  after coffee storage, are shown in Table 4. Two-way ANOVA showed that the composite resin ( $\Delta E_{ab}:P<0.001/\Delta E_{00}:P<0.001$ ) and surface treatment factor ( $\Delta E_{ab}:P<0.001/\Delta E_{00}:P=0.003$ ) were significant; however, the interactions between both factors ( $\Delta E_{ab}:P=0.167/\Delta E_{00}:P=0.38$ ) were not significant. In general, glycerin usage had not influence on the surface coffee staining for all composite resins. Finishing and polishing caused lowest  $\Delta E_{ab}$  and  $\Delta E_{00}$  values, regardless of composite resins. Linear regression showed a very weak correlation between  $\Delta E_{00}$  and DC ( $R^2 = 0.00548$ ).

#### 4. Discussion

In the present study, the DC of bulk-fill and conventional composite resins was affected by the glycerin usage and the color stability was influenced by the finishing and polishing procedures. Therefore, the null hypothesis of this study was rejected.

DC is the proportion of single carbon-carbon bonds in a polymer matrix to double carbon bonds between monomers. (1) It has been shown that the clinical performance (13) of dental composites can be affected by mechanical properties that are influenced mainly by the DC (14), filler content and type of matrix. (13,15) Low DC values might have negative influence on fracture resistance, wear resistance, compressive strength and can lead to early replacement of long-term restorations caused by detachment or discoloration around the adhesive interfaces. (16) Low DC values can also increase the release of toxic monomers and initiators in the oral environment. (5,17) In this study, a higher DC was observed for groups with oxygen inhibition surface treatment by glycerin, regardless of composite resins tested. During polymerization, oxygen reacts rapidly with free oxidized radicals and its presence slows the reaction. Oxygen inhibition improved polymerization of the surface layer. (6) This aspect could also have impact on the surface hardness when the matrix band for making a direct restoration is removed after the light curing procedure. (5,6)

Low DC was observed in the control group and when composite materials were submitted only to finishing and polishing protocol. Also, these data were lower than the literature reports. (3,1) In this research, one possible explanation for this phenomenon may be related to the fact that a polyester strip was used to obtain a flat surface but it was removed before photoactivation, allowing contact between the resin and oxygen. Additionally, maybe finishing and the polishing protocol was not able to completely remove the unpolymerized resin layer, resulting in a lower DC in the resin composite surface.

However, finishing and polishing (5) surface procedures can reduce color variation ( $\Delta E_{ab}$  and  $\Delta E_{00}$ ) after immersion in coffee. The esthetic features of restorations should not be defined as a factor indicating some intervention in posterior restorations. However, it is well-known that resin staining remains a cause of re-intervention even in posterior teeth, and more color-stable composites can prevent over-interventions. In case finish and polish procedures are awkward to achieve in posteriors composite restoration, light-curing in the absence of oxygen should be considered, especially when performing composite restoration in esthetic areas or in areas difficult to access such as the proximal surfaces.

Instrumental techniques for measuring color alteration include colorimetry and spectrophotometry, with good reliable performance for dental materials. Spectrophotometry is more accurate than measuring by using colorimeter, which is not influenced by ambient light. (2) For the objective color difference measurement in dentistry, the CIELAB color difference formula has been extensively used, allowing for comparison with previous similar studies on dental composites. It assumes the uniformity of CIELAB color space and the equal importance of CIELAB individual parameters ( $L^*$ ,  $a^*$ , and  $b^*$ ). However, a discrepancy sensitivity on the  $L^*$ ,  $a^*$ , and  $b^*$  parameters has been demonstrated concerning visual perceptibility and acceptability thresholds.(12,19) The CIEDE2000 metrics have also been then proposed due better indicative of human visual thresholds, even closer with the adjustment of parametric factor  $KL$ ,  $KC$ , and  $KH$  set (2:1:1) (12). Similar results were observed for both color difference parameters in this research.

In the present study, microhybrid composite resin storage for 15 days in coffee had different performance, in terms of color change than conventional

nanoparticle or bulk-fill composite resins, regardless of surface treatment. The difference in staining may be attributed to the composition of the materials and the characteristics of the particles. The hydrophilicity and degree of water sorption of a resin matrix could affect the staining susceptibility of resin composites. Although the particle sizes of nanoparticle resin composite smaller than microhybrid, it is expected to show less water sorption, thus less  $\Delta E$ . The discrepancy could be due to resin matrices and additives such as dyes, photosensitizer molecules, and other chemicals in these materials. Moreover, both bulk-fill and nanoparticle (enamel shade) have high translucency and high-translucent materials had the lowest color stability. (19)

The aging process was simulated to examine changes in the color alteration of the composite resins over time. (14,16,20) In vitro studies evaluating color stability have examined composite specimens immersed in staining solutions over a particular period of time. (9,14,16) Some beverages can alter the color of composite resins through the absorption and/or adsorption of colorants during the period of exposure. (9,21) In most studies, the specimens have been immersed in coffee, grape juice, wine, and other beverages continuously for long periods of time (hours or days). (3,9) However, the exposure of composite restorations to beverages in vivo occurs through several cycles of a few seconds each. The temperature of a beverage can also increase its staining effect, as volumetric changes caused by heat or cold affect possible specimen defects. (22)

For most restorative materials, there is a complex process in the oral environment that includes disintegration and dissolution in saliva and other types of physical/chemical degradation, such as wear and erosion caused by food and drinks, chewing, and bacterial activity. (9,17) This study demonstrated that bulk-fill composite resin storage for 15 days in coffee had different performance, in terms of opacity, than conventional composite resins, regardless of surface treatment. While there is a less evident change in the chemical composition in bulk-fill and conventional composites, the enhanced depth of cure in several bulk-fill is not a result of an improved refractive index mismatch between resin and filler but seems rather have been carried out by reducing the amount of pigments and enlarging the filler size. The higher level of translucency already characteristic of bulk-fill and nanoparticle resins may be responsible for the lower opacity values than microhybrid resin.

More studies are still necessary, especially clinical trials, with real time follow-up. Additionally, in laboratorial study should perform thermal/mechanical fatigue, wettability, water sorption and solubility, the thickness of the unpolymerized surface layer, biofilm presence for degradation and cumulative deleterious effects, to better respond to the dilemma of long-term maintenance of restorative materials after oxygen inhibition and also the consequence of the finishing and polishing procedures. The degradation can be prolonged by the maintenance of a low pH in the oral cavity. (9,23) Associated with stains produced by immersion in drinks such as coffee, this aspect may also contribute to marginal discoloration, which is wrongly defined as the main reason for the replacement of esthetics restorations. (18,24,25)

In this study, it was simulated the effect of intermittent usage of coffee on the composite resins. The immersion of coffee negatively influenced the physical and chemical properties of the composite resins tested. To maintain the esthetic performance of composite resin restoration, it is suggested to make finishing and polishing surface procedures after conclude the restorative procedure. It is an important indicator to reduce the possibility of changing color parameters and could prevent degradation and darkening of composite resins. Furthermore, patients should be informed about the deleterious effects caused by the abusive use of coffee solutions on composite resin restorations.

The clinical significance of this study is that the degree of conversion of the composite resins surface can be improved by using glycerin to reduce the oxygen presence and the surface staining can be reduced if this previous procedure is associated with immediate finishing and polishing procedures. Within the limits imposed in the experimental design, it is possible to conclude that the glycerin usage increased the degree of conversion and had no effect on the surface coffee staining of tested composite resins and the finishing and polishing surface procedures reduced significantly the color variation ( $\Delta E_{ab}/ \Delta E_{00}$ ) on the surface of bulk-fill and conventional composite resins.

## Resumo

Este estudo investigou os efeitos da inibição de oxigênio e dos procedimentos de acabamento/polimento nas propriedades das resinas compostas. Foram avaliadas uma resina composta bulk fill e duas resinas convencionais (nanoparticulada e microhíbrida). Os espécimes foram confeccionados, variando o tratamento de superfície: controle, sem tratamento; glicerina (inibidor de oxigênio); acabamento e polimento; glicerina + acabamento e polimento. O grau de conversão (GC) foi medido pela Espectroscopia de Infravermelho Transformada de Fourier (FTIR) imediatamente e após 15 dias da confecção dos espécimes (n=5). Os índices de alteração de cor  $\Delta E_{ab}$ ,  $\Delta E_{00}$  e opacidade foram avaliados por meio de espectrofotômetro, após 15 dias de imersão no café, utilizando o sistema CIELAB (n=5). Os dados da alteração da cor foram analisados pelos testes ANOVA de dois fatores e Tukey ( $\alpha=0,05$ ) e a opacidade por ANOVA de medidas repetidas. O uso de glicerina aumentou significativamente o GC, no entanto, não teve influência sobre os valores  $\Delta E_{ab}$  e  $\Delta E_{00}$ . O acabamento e o polimento reduziram os valores de  $\Delta E_{ab}$  e  $\Delta E_{00}$ , independentemente da resina composta. A resina microhíbrida apresentou maior opacidade, seguida pela nanoparticula e bulk-fill, independentemente do tratamento de superfície. O acabamento e polimento resultou em menor grau de conversão das resinas compostas se comparado ao uso de um agente inibidor de oxigênio (glicerina), porém apresenta resultados similares para a pigmentação pelo café.



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Figure

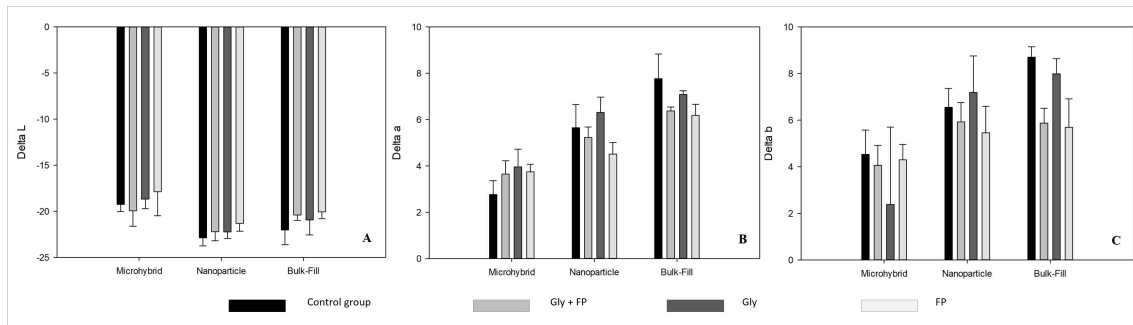


Figure 1: Color changes of composite resins after storage in coffee, according surface treatments. A = represents the change lightness within a specimen and ranges from 0 (black) to 100 (white). B = represents the change of degree of green/red measurement and C = represents the degree of blue/yellow color change of composite resins after the storage in coffee.

## Tables

Table 1. Materials used (information provided by the manufacturers)

<b>Composite resin</b>	<b>Type</b>	<b>Composition*</b>
Filtek Posterior Bulk-Fill	Bulk-Fill	Aromatic UDMA, UDMA, silica, DDDMA, silane treated ceramic, pentanedioic acid, 2,2-dimethyl-4-methylene-reaction products with glycidyl methacrylate, EDMAB, benzotriazol, titanium dioxide. Shade A3
Filtek Z350 XT	Conventional Nanoparticle	Bis-GMA, UDMA, Bis-EMA, PEGDMA, TEGDMA resins, combination of 20 nm silica filler, 4 to 11 nm zirconia filler, zirconia/silica cluster filler. Shade A3E
Filtek Z250XT	Conventional Microhybrid	Bis-GMA, TEGDMA, UDMA, Bis-EMA, aluminum oxide, EDMAB, silane treated ceramic, initiators, stabilizers, pigments. Shade A3

*\*Bis-GMA: bisphenol glycidyl methacrylate; UDMA: urethane dimethacrylate; TEGDMA: triethylene glycol dimethacrylate; PEGDMA: polyethylene glycol dimethacrylate; Bis-EMA: ethoxylated bisphenol-A dimethacrylate; DDDMA—1,12-dodecane dimethacrylate; EDMAB—ethyl 4-dimethyl aminobenzoate. All composite resin was manufactured by 3M/ESPE.*

Table 2. Mean and standard deviation of the degree of conversion (%) for all composite resins, according to surface treatments and assessment time.

Surface treatment	<i>Composite resins</i>					
	Bulk-fill		Nanoparticle		Microhybrid	
	<i>Immediate</i>	<i>Mediate</i>	<i>Immediate</i>	<i>Mediate</i>	<i>Immediate</i>	<i>Mediate</i>
Control	45.5 ± 6.1 <sup>Ba</sup>	52.0 ± 2.4 <sup>Ba</sup>	31.0 ± 3.8 <sup>Bb</sup>	31.4 ± 7.9 <sup>Bb</sup>	43.5 ± 7.4 <sup>Ba</sup>	44.0 ± 9.1 <sup>Ba</sup>
Gly	70.0 ± 8.4 <sup>Ac</sup>	69.8 ± 8.0 <sup>Aa</sup>	72.5 ± 2.2 <sup>Abc</sup>	70.4 ± 5.8 <sup>Aa</sup>	74.5 ± 4.2 <sup>Aa</sup>	81.6 ± 1.7 <sup>Aa</sup>
Gly + FP	72.7 ± 5.3 <sup>Aa</sup>	83.4 ± 2.9 <sup>Aa</sup>	67.9 ± 5.6 <sup>Ab</sup>	64.7 ± 6.9 <sup>Aa</sup>	72.1 ± 5.0 <sup>Aa</sup>	70.0 ± 6.9 <sup>Aa</sup>
FP	43.4 ± 9.1 <sup>Ba</sup>	45.3 ± 4.3 <sup>Ba</sup>	28.6 ± 6.9 <sup>Bb</sup>	28.1 ± 1.2 <sup>Ba</sup>	39.7 ± 8.7 <sup>Bb</sup>	39.0 ± 9.5 <sup>Ba</sup>

*Means followed by the different letters (uppercase for comparing the “surface treatment within assessment time for each composite resin – in columns”; lowercase for comparing the “resins within each assessment – in rows”) indicate significant difference at Tukey’s test (P<0.05). Gly: glycerin; FP: finishing and polishing.*

Table 3. Mean and standard deviation of opacity (%) for all composite resins before and after coffee storage, according to surface treatments.

Surface treatment	<i>Composite resins</i>					
	Bulk-fill		Nanoparticle		Microhybrid	
	<i>Immediate</i>	<i>Mediate</i>	<i>Immediate</i>	<i>Mediate</i>	<i>Immediate</i>	<i>Mediate</i>
Control	67.5 ± 1.2 <sup>b</sup>	81.4 ± 1.7 <sup>a</sup>	75.0 ± 0.8 <sup>b</sup>	88.6 ± 1.9 <sup>a</sup>	82.8 ± 0.4 <sup>b</sup>	92.9 ± 0.9 <sup>a</sup>
Gly	67.6 ± 2.1 <sup>b</sup>	80.5 ± 1.8 <sup>a</sup>	75.4 ± 1.0 <sup>b</sup>	88.7 ± 0.8 <sup>a</sup>	82.6 ± 0.9 <sup>b</sup>	92.2 ± 0.8 <sup>a</sup>
Gly + FP	68.7 ± 1.2 <sup>b</sup>	81.6 ± 1.0 <sup>a</sup>	75.2 ± 1.7 <sup>b</sup>	88.8 ± 2.1 <sup>a</sup>	83.0 ± 0.9 <sup>b</sup>	92.7 ± 1.0 <sup>a</sup>
FP	69.1 ± 1.1 <sup>b</sup>	81.0 ± 0.5 <sup>a</sup>	74.8 ± 2.3 <sup>b</sup>	87.9 ± 1.2 <sup>a</sup>	83.5 ± 0.5 <sup>b</sup>	93.7 ± 0.8 <sup>a</sup>
Pool average	C	C	B	B	A	A
	68.2 ± 1.4	81.1 ± 1.2	75.1 ± 1.4	88.5 ± 1.5	82.9 ± 0.9	92.8 ± 0.8

Means followed by the different letters (uppercase for comparing the “composite resins within assessment time”; lowercase for comparing the “assessment time within each resin”) indicate significant difference at Tukey’s test ( $P < 0.05$ ). There is not a statistically significant difference between surface treatments. Gly: glycerin; FP: finishing and polishing.



Table 4. Means and standard deviation of the color difference ( $\Delta E_{ab}$  and  $\Delta E_{00}$ ) after storage in coffee, according to surface treatments and composite resins.

Surface treatment	<i>Composite resins</i>					
	Bulk-fill		Nanoparticle		Microhybrid	
	$\Delta E_{ab}$	$\Delta E_{00}$	$\Delta E_{ab}$	$\Delta E_{00}$	$\Delta E_{ab}$	$\Delta E_{00}$
Control	24.9 ± 1.7 <sup>Bb</sup>	20.3 ± 1.6 <sup>Bb</sup>	24.4 ± 0.9 <sup>Bb</sup>	20.5 ± 1.0 <sup>Bb</sup>	19.9 ± 0.9 <sup>Ba</sup>	16.2 ± 0.7 <sup>Ba</sup>
Gly	23.5 ± 1.3 <sup>Bb</sup>	19.4 ± 1.0 <sup>Bb</sup>	24.2 ± 0.8 <sup>Bb</sup>	20.2 ± 0.6 <sup>Bb</sup>	19.4 ± 1.0 <sup>Ba</sup>	16.4 ± 1.2 <sup>Ba</sup>
Gly + FP	22.1 ± 0.5 <sup>ABb</sup>	18.4 ± 0.4 <sup>ABb</sup>	23.6 ± 1.0 <sup>ABb</sup>	19.6 ± 0.8 <sup>ABb</sup>	20.6 ± 1.7 <sup>ABa</sup>	17.0 ± 1.6 <sup>ABa</sup>
FP	21.7 ± 1.0 <sup>Ab</sup>	18.1 ± 0.8 <sup>Ab</sup>	22.4 ± 1.0 <sup>Ab</sup>	18.6 ± 0.8 <sup>Ab</sup>	18.7 ± 2.6 <sup>Aa</sup>	15.3 ± 2.3 <sup>Aa</sup>

*For values of color parameters ( $\Delta E_{ab}$  or  $\Delta E_{00}$ ) different letters (uppercase for comparing the surface treatment - in columns; lowercase for comparing composite resin - in rows) indicate significant difference at Tukey's test ( $P < 0.05$ ). Gly: glycerin; FP: finishing and polishing.*

# Capítulos

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Avaliação da composição química, do desafio bacteriano, do acabamento/polimento e de protocolos de cimentação de diferentes materiais restauradores – MARCELA GONÇALVES BORGES FARIA – Tese de Doutorado – Programa de Pós-Graduação em Odontologia – Faculdade de Odontologia – Universidade Federal de Uberlândia.

## **2.4 Capítulo 4**

EFFECT OF LUTING PROTOCOL AND TIME TO PROSTHETIC  
PREPARATION ON BOND STRENGTH OF FIBER POSTS TO ROOT DENTIN

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## ABSTRACT

The aim of this study was to evaluate the bond strength and failure modes of fiber posts luted to the root canal dentin of bovine incisors. Nine luting protocols (n=10) were defined according to the luting types: Single Bond Universal (SU) + RelyX Ultimate, Clearfil SE Bond (CS) + RelyX Ultimate, or RelyX U-200 (U-200); and time to prosthetic preparation: no preparation (control), immediate preparation or after 7 days. A micro push-out test was performed, and the failure mode was classified with 40x magnification as adhesive type I, adhesive type II, cohesive type I, cohesive type II, or mixed. Irrespective of the root third, the push-out bond strength values from the same root (experimental unit) were averaged in the data analysis. The data were transformed to ranks before being assessed by 2-way ANOVA. Multiple comparisons were performed by Tukey's post hoc test. Possible associations between the factors "time to prosthetic preparation" and "luting protocol" and the distribution of failure modes were assessed by the Chi-square test. Both factors, the "time to prosthetic preparation" ( $p = 0.239$ ) and "luting protocol" ( $p = 0.054$ ), did not affect the push-out bond strength values, but the interaction between the factors was significant ( $p = 0.035$ ). No cohesive failures were observed, and two adhesive failures in the interface between the post and dentin were found. In conclusion, both time to prosthetic preparation and luting protocol influenced the bond strength of the fiber post to the root dentin with combined effect.

Keywords: post and core technique, resin cements, dental bonding.

## INTRODUCTION

The rehabilitation of endodontically treated teeth is challenging for restorative dentistry professionals, especially when there is a substantial loss of coronary structure, which results in less coronary material remaining for oral rehabilitation (1). Cast metal posts have been indicated for oral rehabilitation for years due to its advantages, such as being able to replicate the internal anatomy of the root canal and adapt to the canal walls. However, cast metal posts are rigid and might induce concentrated areas of stress (2).

In recent decades, the use of glass fiber posts as an alternative to cast metal posts has increased due to some favorable characteristics. Most notably, the glass fiber posts allow the possibility of post cementation in a single session, satisfactory aesthetics and reduced overall stress in the root dentin, which reduces the risk of a catastrophic fracture of the restoration (3). However, the reduced occurrence of a root fracture by using a fiber post has been demonstrating effects on survival and success rate as well (4).

Bonding the fiber post to the root dentin by an adhesive procedure yields a homogeneous complex system (2) and reduces the likelihood of a root fracture (3). Therefore, the biomechanical behavior of the glass fiber post depends not only on the mechanical characteristics themselves but also on the bonds between the post, resin cement and dental structure (5).

The displacement of the post from the root canal and post/core fracture are frequent causes of clinical failure in fiber post-retained restorations (6), possibly due to the complexity of obtaining satisfactory adhesion between the fiber post, root dentin and composite resin (7). In addition, differences in the intraradicular dentin along the root depth (1) and the large cavity created for the whole post (8) are challenges for the bonding procedures performed in a root canal.

Thus, several studies have proposed different post surface treatments to increase chemical and micromechanical adhesion between the fiber post and composite resin (9-12). Most of the treatments the application of hydrogen peroxide or dichloromethane (13-16) involve selectively dissolving the epoxy matrix, exposing an enhanced amount of fibers (17). Chemical bonding could be promoted by silane coupling agents (10). A meta-analysis established that fiber

post silanization only has positive effects when appropriate surface pretreatment is created (18).

During the past several years, resin cements have been used as an adhesive system for luting fiber posts to root canals (19). Dual-cured resin cement is widely used because chemical activation can compensate for a lack of light reaching the deeper areas of the root canal and properly polymerize the cement (7). However, since the chemically activated polymerization process is slower in the beginning, complete polymerization of the dual resin materials only occurs after several hours (20,21). Thus, reduced mechanical strength of the resin cement and decreased bonding to the root canal is common, especially in the early stages after luting protocols (22).

However, an important advantage of the fiber post is that it allows direct restorations to be performed in the same clinical session, which reduces costs and is preferred by patients. Thus, several clinicians prefer to perform prosthetic preparation immediately after the post cementation and core build-up processes that is bonded to the remaining coronal dentin. In this scenario, the use of diamond burs results in vibration on the fiber post and induces stress in the bonding interface (19). This stress can be related with areas of debonding, compromising the longevity of the post-retained restoration (19). This early stress in the poorly polymerized adhesive interface can compromise the bond strength between the post, resin cement and root dentin.

The objective of this study was to evaluate the effect of the bonding procedure and the prosthetic preparation time on the bond strength and failure pattern of fiberglass posts luted into the root canal dentin, with different resin cements and adhesive systems. The null hypothesis is that both factors do not influence the bond strength or failure pattern.

## METHODOLOGY

### Study design

This in vitro investigation was conducted using a 3x3 factorial study design to evaluate the factors “time to prosthetic preparation” and “luting protocol”. Three levels of bonding procedures were used: a regular dual-cure resin cement (RelyX Ultimate, 3M ESPE, St Paul, MN, USA) in combination with a universal adhesive system (Single Bond Universal, 3M ESPE, St Paul, MN, USA) or a self-curing adhesive system (Clearfil SE Bond, Kuraray America Inc., Nova York, NY, USA) or a self-adhesive resin cement only (RelyX U-200, 3M ESPE, St Paul, MN, USA). Prosthetic preparation was performed immediately or 7 days after the fiber post luting procedure, while no preparation was performed in the control group.

### Sample preparation

Ninety bovine incisor roots (n=10) with similar dimensions and shapes were chosen for this study. Coronal portions of the teeth were removed 15.0 mm above the root apex using a diamond double-faced disk (KG Sorensen, Barueri, SP, Brazil) used in a slow-speed handpiece cooled with an air/water stream. The root canal was instrumented at a depth of 10 mm using #2, #3, and #4 Gates Glidden drills (TDKaFILES, PR, Brazil), #4 largo drills (MANI, Tochigi, Japão) and burs provided by the post manufacturer (White Post DC #3; FGM, Joinville, SC, Brazil), followed by irrigation with 2.5% NaOCl solution (Asfer Indústria Química Ltda, São Caetano do Sul, SP, Brazil) and 17% ethylenediaminetetraacetic acid (EDTA trissódico, Biodinâmica Química e Farmacêutica Ltda, Ibioporã, PR, Brazil) for 1 min to remove the smear layer.

Then, each root was included in a polystyrene resin cylinder (Cristal; Piracicaba, SP, Brazil) 2 mm below its cervical limit. For the periodontal ligament simulation, the external surfaces of the remaining portions of the roots were dipped in melted wax, resulting in a 0,2 to 0,3 mm thick wax layer. The wax-covered roots were placed in the acrylic resin cylinders. Following the resin polymerization process, the roots were removed from the cylinder, and wax was removed from the root surface to create a space in the resin cylinder. The polyether impression material (Impregum Soft; 3M ESPE, St Paul, MN, USA) was



mixed and placed in the space created in the resin cylinder. The tooth was reinserted into the cylinder, and the excess material was removed with a scalpel blade.

#### Fiber post surface treatment

Prior to cementation, the fiber posts were actively etched with 35% hydrogen peroxide for 1 min, rinsed with distilled water and air-dried for 1 min. A single layer of silane coupling agent (Prosil, FGM, Joinville, SC, Brazil) was applied for 60 s on the etched surface of the post and gently air-dried after 60 s. The adhesive system and resin cement were applied according to the conditions for each group (n=30).

#### Time to prosthetic preparation and luting protocol

Single Bond Universal + RelyX Ultimate: The adhesive system (Single Bond Universal, 3M ESPE) was actively applied on the root for 20 s with a microbrush, air-dried for 5 s and light-cured for 20 s. The resin cement pastes were mixed for 10 s and inserted into the root canal using a #35 K-file. Then, the post was inserted into the canal using light pressure for 10 s. After 1 min, the excess luting material was removed, and the resin cement was light-cured for 40 s on each face (mesial, distal, buccal, lingual and occlusal) after a 5 min delay.

Clearfil SE Bond + RelyX Ultimate: The primer of the adhesive system was actively applied on the root canal dentin with a microbrush for 20 s and air-dried. The bonding agent of the same system was applied and light-cured for 10 s after excess adhesive was removed. The mixed resin cement was inserted into the root canal, then the post was placed. The cement was light-cured according to the protocol that was described previously.

RelyX U-200: The pastes of the resin cement were mixed and inserted into the root canal, then the post was placed using light pressure for 10 s. After 1 min, the excess luting material was removed, and the resin cement was light-cured for 20 s after an additional 5 min delay.

All light activations were performed using a LED-based light-curing unit (Bluphase G2, Ivoclar Vivadent, Schaan, Liechtenstein) with approximately 2,300 mW/cm<sup>2</sup> of irradiance.

Immediately after post cementation, the core was confectioned with nanoparticulated composite resin (Filtek Z350 XT, 3M ESPE, St Paul, USA). The standardization of the build-up cores was achieved by using an acetate matrix obtained by BIO-CAD models (Computer Assisted Design, Rhino 3D, Rhinoceros, USA). A hydro-soluble gel (KY, Johnson & Johnson, São José dos Campos, SP, Brazil) was applied on the cut matrixes to form a thin insulating layer. The adhesive system (Single Bond Universal, 3M ESPE) was applied with a microbrush, air-dried for 5 s and light-cured for 20 s. The composite resin was applied to the matrix and around the post. The mold was positioned perpendicularly in the middle of the specimen, and the composite was light-cured for 20 s on each face. After polymerization, the matrix was removed. Then, prosthetic preparation was immediately performed or the specimens were stored in distilled water for 7 days before prosthetic preparation (n =10). Prosthetic preparation was performed with diamond burs (#2214, KG Sorensen, Cotia, SP, Brazil), and the bur diameter (1 mm) was used as a guide to standardize the thickness of the preparations. No preparations were performed for the control group (n=10).

#### Micro push-out test

The roots were sectioned perpendicular to their long axis with a slow-speed diamond saw (Isomet 1000; Buehler, Lake Bluff, IL, USA) in 6 slides that were 1 mm thick. The specimens were analyzed using optical microscopy at 40x magnification (Mitutoyo, Kanagawa, Japan) to measure both the larger and shorter post diameters and to identify potential defects caused by the sectioning procedures. The specimens were positioned in a push-out jig and subjected to a compressive load (0.5 mm/min) in a mechanical testing machine (Emic DL 200: EMIC São Jose dos Pinhais PR, Brazil) until post dislodgement occurred. A load indenter with a tip diameter of 1.5 mm was used for the slices from the cervical and middle thirds, and a tip diameter of 1.0 mm was used for the slices

corresponding to the apical third. The maximum load at failure was recorded in Newtons (N) and converted into MegaPascals (MPa) by the bonded area (A), which was calculated by using the following formula:  $A = \pi (R1 + R2) \sqrt{(R1 - R2)^2 + h^2}$ , where  $\pi$  is a constant value of 3.14, r and R are the smallest and the largest radius, respectively, of the cross-sectioned tapered post, and h is the thickness of the section.

#### Failure mode classification

Fractured specimens were observed under stereoscopy with Leica MS 5 (Leica microsystems, Wetzlar, Alemanha) at 40x magnification to classify the failure modes. The extrusion side of the post was observed by two examiners with the system software, and the failure models were classified as follows: adhesive type I (failure between the post and cement), adhesive type II (failure between the dentin and cement), cohesive type I (failure in the post), cohesive type II (failure in the dentin) or mixed (adhesive and cohesive failures).

Irrespective of the root third, the push-out bond strength values from the same root (experimental unit) were averaged in the data analysis (n =10).

#### Statistical analysis

The significance level was set at 95%, and data analyses were performed using the Sigma-Stat v.3.5 statistical software package (Systat Software Inc., Chicago, IL, USA). The data on the push-out bond strength presented normal distributions (Kolmogorov-Smirnov test,  $P = 0.774$ ) but did not satisfy the assumption of equal variance (Levene`s test;  $p < 0.050$ ) for 2-way ANOVA. Therefore, the data were transformed to ranks before being assessed by 2-way ANOVA. The transformed data satisfied the assumptions of a normal distribution (Kolmogorov-Smirnov test,  $P = 0.640$ ) and equal variance (Levene`s test;  $p = 0.058$ ). Multiple comparisons were performed by Tukey`s post hoc test. Possible associations between the factors “time to prosthetic preparation” and “luting protocol” and the distribution of failure modes were assessed by the Chi-square test.

## RESULTS

Both factors, the “time to prosthetic preparation” ( $p = 0.239$ ) and “luting protocol”, ( $p = 0.054$ ) did not affect the push-out bond strength values, but the interaction between the factors was significant ( $p = 0.035$ ). The results of the push-out bond strength are presented in Table 1 and Figure 1. In the absence of prosthetic preparation, the highest values of bond strength were observed for posts cemented using Single Bond + RelyX Ultimate, and there was no difference between the other protocols. No differences among the protocols were found when the prosthetic preparations were performed immediately after post cementation. On the other hand, using Clearfil SE Bond + Relyx Ultimate yielded the lowest mean bond strength when the preparation was performed after 7 days of specimen storage. The two other protocols resulted in similar bond strength values for the delayed prosthetic preparation condition. The time to prosthetic preparation did not affect post retention when the Single Bond + RelyX Ultimate protocol was used. For Clearfil SE Bond + Relyx Ultimate, the highest values were observed for immediate preparation, and there was no difference between the other times. The lowest bond strength values were observed in the absence of preparation for RelyX U200, and the other times to prosthetic preparation resulted in similar values.

Figure 2 presents the results of the failure mode distributions according to the experimental conditions. No cohesive failures (neither in the post nor dentin) were observed, and only two adhesive failures in the interface between the post and dentin were found. Adhesive failures of types I and II were grouped for the statistical analysis (over 25% of the expected values in the contingency table must be more than 5). Thus, the contingency tables were arranged only by classifying the failure as adhesive or mixed. Both factors, the “time to prosthetic preparation” ( $p < 0.001$ ) and “luting protocol” ( $p = 0.005$ ), significantly affected the distribution of the failure modes.

## DISCUSSION

Fiber post systems present biomechanical properties that are similar to those of dentin (23), leading to a stress distribution that is more homogeneous than that with metal posts (24) and thus decreasing the risk of a root fracture (3). The use of glass fiber posts may also enhance aesthetic restorations and reduce the time required to finalize the restoration mainly due to the elimination of laboratory procedures (25). These effects are attributed to the fact that prefabricated posts are used; thus, the restorative procedures, including direct restorations, can be performed immediately after cementation of the post (26).

Fiber post usage reduces the risk of catastrophic fractures and the stresses accumulated on the dentin/cement interface to be restored or repaired (27). Therefore, an important finding of this study was that the diamond drill used in high rotation for prosthetic preparation was not able to generate tension build-up in the interfaces or significant failures. The time that elapsed between the light activation and the core build-up processes permits increased cement polymerization (28), thereby increasing the bonding stability (19). In addition, core reconstruction in the dental remnant can potentially increase post stabilization.

Proper bonding of the fiber posts to the intraradicular dentin is essential for the longevity of restorative procedures. Most failures of fiber post-retained restorations result from debonding (decementation), as the cement/dentin interface is the weakest link in the bonded assembly (29). Another commonly reported failure is a fracture of the post or core, which may result from an initial debonding of the luted post from the root canal (3).

Despite several advantages being associated with fiber posts, the coronal portion of these posts must be prepared so they can be used in various clinical situations. The core build-up with composite resin is important for the stabilization of fiber posts and creates a support area for prosthetic preparation (30). Although some resin cements present a gradual increase in the degree of conversion after complete polymerization (31), this aspect did not influence the fixation protocols evaluated and the prosthetic preparation time in this study. Thus, immediate prosthetic preparation can be favorable and recommended since its effectiveness in cementing has been demonstrated.

More recently, self-adhesive resin cements were introduced to facilitate luting procedures (32). The bonding mechanism of self-adhesive resin cements is attributed to both a chemical reaction between phosphate methacrylates and hydroxyapatite as well as the infiltration of these materials into the tooth tissues (28).

Various studies have demonstrated that self-adhesive resin cements exhibit a more stable bonding interface compared with regular resin cements (33). The use of dual-cured luting agents is preferable in this procedure to achieve proper cement polymerization along the entire root canal space and to obtain an initial stabilization of the fiber post (34). Once the chemically activated reaction is slowed, light activation of the cement promotes the polymerization of the cement in more cervical regions, thereby establishing post retention in the first minutes after post cementation (35). The results of this study can be related with the light-curing delay, that could be promoted less shrinkage stress for all resin cements used.

However, even when translucent fiber posts are used, a significant reduction in light intensity occurs in the deepest areas of the root canal, and only the slower chemically activated polymerization reaction occurs (20). Thus, reduced mechanical strength of the cement and decreased bonding to the dentin root canal is evident, particularly in the early stages after cementation procedures (22). The translucency of the glass fiber post allowed satisfactory transmission of light on the first 10 mm of the depth. However, whether the use of resin cements is essential to improve the long-term outcomes regarding the retention of fiber posts should be properly tested.

Clinicians should be aware that the interactions between irrigation protocols, types of self-adhesive resin cements or other cements used, and the moment of photoactivation can possibly influence the retention of fiber posts. Additional studies with additional resin cements and aged samples are required to confirm these findings.

## CONCLUSION

Based on the findings of this in vitro study, the following conclusions were drawn: the immediate prosthetic preparation did not influence the bond strength, the different luting protocols used had different influence on the fiber post bond strength to the root canal dentin, and only two adhesive failures in the interface between the post and dentin were found.

## ACKNOWLEDGMENTS

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## FIGURE LEGENDS

Figure 1. Box plot presenting the data distribution of the push-out bond strength values measured according to the time to prosthetic preparation and luting protocol (n = 10).

Figure 2. Distribution of the failure modes according to the time to prosthetic preparation and luting protocol (n = 60). Adhesive type I – between the post and cement; Adhesive Type II – between the cement and dentin.

Table 1. Means (standard deviations) of push-out bond strength according to the luting protocol and time of prosthetic preparation (n = 10).

# FIGURES

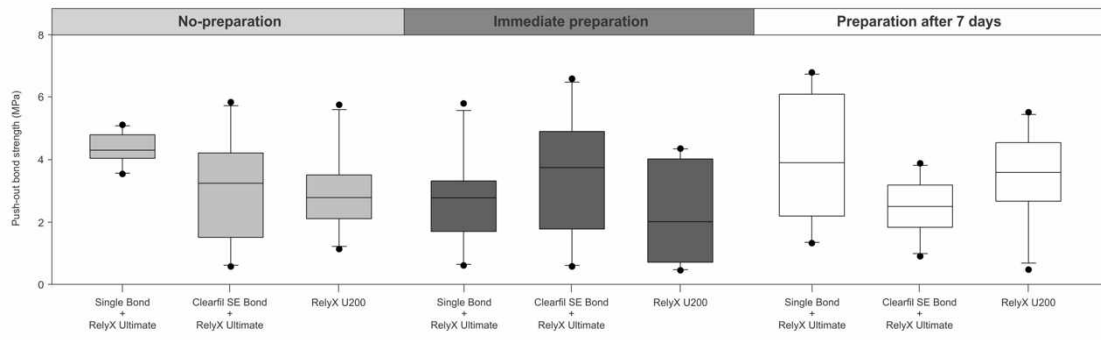


Figure 1

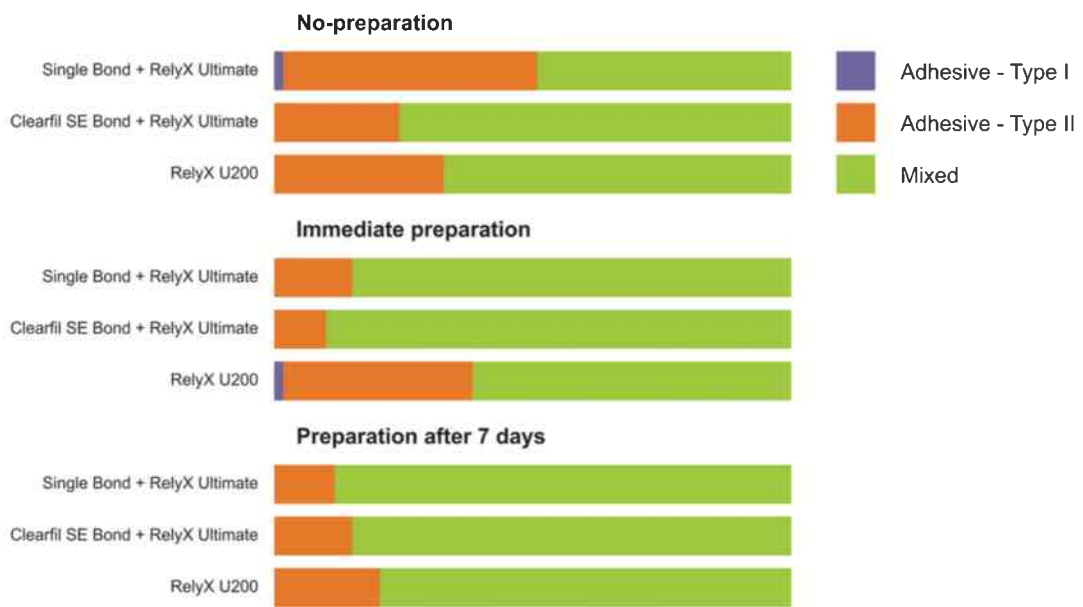


Figure 2

TABLE

Table 1

Luting protocol	Time to prosthetic preparation		
	No-preparation	Immediate	After 7 days
Single Bond + RelyX Ultimate	4.35 (0.48) <sup>Aa</sup>	4.02 (1.08) <sup>Aa</sup>	4.51 (1.71) <sup>Aa</sup>
Clearfil SE Bond + Relyx Ultimate	3.03 (1.69) <sup>Bb</sup>	4.62 (1.47) <sup>Aa</sup>	3.14 (0.75) <sup>Bb</sup>
RelyX U200	2.96 (1.31) <sup>Bb</sup>	3.67 (1.20) <sup>Aa</sup>	4.01 (1.25) <sup>Aa</sup>

Distinct letters (lowercase for columns, uppercase for lines) indicate significant differences ( $p < 0.05$ ).



# Considerações Gerais

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Avaliação da composição química, do desafio bacteriano, do acabamento/polimento e de protocolos de cimentação de diferentes materiais restauradores – MARCELA GONÇALVES BORGES FARIA – Tese de Doutorado – Programa de Pós-Graduação em Odontologia – Faculdade de Odontologia – Universidade Federal de Uberlândia.

### 3. CONSIDERAÇÕES GERAIS

A partir dos resultados obtidos nesse estudo, conclui-se que:

- A presença de aditivos de tiouretano nos metacrilatos afetou a formação da sua rede polimérica e da sua composição química. Além disto, o diluente TEGDMA contribuiu para a formação geral da rede, como evidenciado pelo aumento das concentrações de BisGMA após a extração dos lixiviados com solvente diclorometano;

- A adição de tiouretano pode produzir menos materiais citotóxicos devido ao aumento da conversão do material restaurador e à redução da quantidade de extração dos lixiviados com água;

- O uso do silano modificado com tiouretano pode ser uma alternativa com propriedades mecânicas e químicas promissoras para o reparo de restaurações com resina composta. Além disso, este material foi capaz de manter a resistência de união das interfaces reparadas;

- O grau de conversão das resinas compostas pode ser melhorado com o uso da glicerina como agente inibidor de oxigênio;

- O manchamento superficial pode ser reduzido se a inibição de oxigênio for associada com procedimentos imediatos de acabamento/polimento;

- O acabamento/polimento reduziu significativamente a variação de cor da superfície das resinas compostas convencionais e de incremento único (bulk-fill);

- A resina microhíbrida apresentou maior opacidade, seguida pela nanopartícula e bulk-fill, independentemente do tratamento de superfície;

- A realização imediata do preparo protético não influenciou na resistência de união de pinos de fibra de vidro à dentina do canal radicular;

- O momento para a realização do preparo protético e os protocolos de cimentação apresentaram efeitos combinados na resistência de união de pinos de fibra de vidro à dentina radicular;

- Apenas duas falhas adesivas foram encontradas na interface de união entre pino e dentina radicular.

# Referências

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Avaliação da composição química, do desafio bacteriano, do acabamento/polimento e de protocolos de cimentação de diferentes materiais restauradores – MARCELA GONÇALVES BORGES FARIA – Tese de Doutorado – Programa de Pós-Graduação em Odontologia – Faculdade de Odontologia – Universidade Federal de Uberlândia.

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