



UNIVERSIDADE ESTADUAL DE CAMPINAS
FACULDADE DE ODONTOLOGIA DE PIRACICABA

CAIO VINÍCIUS SIGNORELLI GROHMANN

**EFEITO DO TEMPO DE EXPOSIÇÃO À LUZ DO REFLETOR
SOBRE A CONSISTÊNCIA E AVALIAÇÃO DE PROPRIEDADES
MECÂNICAS DE COMPÓSITOS EXPERIMENTAIS CONTENDO
DIFERENTES CONCENTRAÇÕES DE INIBIDOR DE
POLIMERIZAÇÃO**

**EFFECT OF TIME EXPOSITION TO THE REFLECTOR LIGHT ON
CONSISTENCY AND EVALUATION OF MECHANICAL
PROPERTIES OF EXPERIMENTAL RESIN COMPOSITES
CONTAINING DIFFERENT CONCENTRATION OF
POLYMERIZATION INHIBITOR**

Piracicaba

2017

CAIO VINÍCIUS SIGNORELLI GROHMANN

**EFEITO DO TEMPO DE EXPOSIÇÃO À LUZ DO REFLETOR
SOBRE A CONSISTÊNCIA E AVALIAÇÃO DE PROPRIEDADES
MECÂNICAS DE COMPOSTOS EXPERIMENTAIS CONTENDO
DIFERENTES CONCENTRAÇÕES DE INIBIDOR DE
POLIMERIZAÇÃO**

**EFFECT OF TIME EXPOSITION TO THE REFLECTOR LIGHT ON
CONSISTENCY AND EVALUATION OF MECHANICAL
PROPERTIES OF EXPERIMENTAL RESIN COMPOSITES
CONTAINING DIFFERENT CONCENTRATION OF
POLYMERIZATION INHIBITOR**

Tese apresentada à Faculdade de Odontologia de Piracicaba, da Universidade Estadual de Campinas, como parte dos requisitos exigidos para obtenção do título de Doutor em Materiais Dentários.

Thesis presented to the Piracicaba Dental School of the University of Campinas in partial fulfillment of the requirements for the degree of Doctor in Dental Materials.

Orientador: Prof. Dr. Mário Alexandre Coelho Sinhoreti

ESTE EXEMPLAR CORRESPONDE À VERSÃO
FINAL DA TESE DEFENDIDA PELO ALUNO
CAIO VINÍCIUS SIGNORELLI GROHMANN E
ORIENTADA PELO PROF. DR. MÁRIO
ALEXANDRE COELHO SINHORETI.

Piracicaba

2017

Agência(s) de fomento e nº(s) de processo(s): CAPES; CNPq

Ficha catalográfica
Universidade Estadual de Campinas
Biblioteca da Faculdade de Odontologia de Piracicaba
Marilene Girello - CRB 8/6159

G894e Grohmann, Caio Vinícius Signorelli, 1987-
 Efeito do tempo de exposição à luz do refletor sobre a consistência e
 avaliação de propriedades mecânicas de compósitos experimentais contendo
 diferentes concentrações de inibidor de polimerização / Caio Vinícius Signorelli
 Grohmann. – Piracicaba, SP : [s.n.], 2017.

 Orientador: Mario Alexandre Coelho Sinhoreti.
 Tese (doutorado) – Universidade Estadual de Campinas, Faculdade de
 Odontologia de Piracicaba.

 1. Resinas compostas. 2. Propriedades mecânicas. 3. Hidroxitolueno
 butilado. I. Sinhoreti, Mario Alexandre Coelho, 1969-. II. Universidade Estadual
 de Campinas. Faculdade de Odontologia de Piracicaba. III. Título.

Informações para Biblioteca Digital

Título em outro idioma: Effect of time exposition to the reflector light on consistency and evaluation of mechanical properties of experimental resin composites containing different concentration of polymerization inhibitor

Palavras-chave em inglês:

Composite resins

Mechanical properties

Butylated hydroxytoluene

Área de concentração: Materiais Dentários

Titulação: Doutor em Materiais Dentários

Banca examinadora:

Mario Alexandre Coelho Sinhoreti [Orientador]

Alysson Noriyuki Kajishima Konno

Adriano Fonseca de Lima

Regina Maria Puppin Rontani

Americo Bortolazzo Corrêa

Data de defesa: 23-02-2017

Programa de Pós-Graduação: Materiais Dentários



UNIVERSIDADE ESTADUAL DE CAMPINAS
Faculdade de Odontologia de Piracicaba



A Comissão Julgadora dos trabalhos de Defesa de Tese de Doutorado, em sessão pública realizada em 23 de Fevereiro de 2017, considerou o candidato CAIO VINÍCIUS SIGNORELLI GROHMANN aprovado.

PROF. DR. MARIO ALEXANDRE COELHO SINHORETI

PROF. DR. ALYSSON NORIYUKI KAJISHIMA KONNO

PROF. DR. ADRIANO FONSECA DE LIMA

PROFª. DRª. REGINA MARIA PUPPIN RONTANI

PROF. DR. AMERICO BORTOLAZZO CORRER

A Ata da defesa com as respectivas assinaturas dos membros encontra-se no processo de vida acadêmica do aluno.

Dedico este trabalho

Aos meus dois amores... Isabela, que é a Periodontista que mais entende de canforoquinona, amina terciária, BHT, Grau de Conversão e radicais livres. Sua facilidade em lidar com pós-graduação me ajudou demais nesta empreitada. Eu não te amo “mais que o infinito x 2”. Eu te amo “mais que o infinito x infinito”! Você me deu o melhor (atualmente falando) presente que eu poderia esperar: FELIPE! É um anjo de menino, lindo, maravilhoso, gostosão, igual o pai! Você possibilitou a realização do meu maior sonho, começar a constituir uma família.

Aos meus pais, Maria Raquel Rodrigues Signorelli Grohmann e Fernando José Pércico e Grohmann, cirurgiões-dentistas, que seguraram a onda e não medem esforços para que eu tenha sucesso profissional e pessoal. A saliva “gasta” até hoje parece ter valido a pena. Espero um dia poder retribuir, de alguma forma, tudo o que fizeram e tem feito por mim. Amo vocês!!!

A minha fiel e super companheira... Bela. Foram curtos, mas muito intensos, os 2 anos em que você entrou na minha vida e mudou a minha concepção do que é **ser** e **ter** uma cachorra. JAMAIS vou te esquecer.

Agradecimentos Especiais

A Deus, que me deu saúde e força pra cumprir mais esta etapa.

Ao meu orientador, Prof. Dr. Mário Alexandre Coelho Sinhoreti, um grande exemplo de professor e ser humano. Disse na dissertação de mestrado, e reforço: EU SOU SEU FÃ NÚMERO 1!

A “Elevine” (Eveline) que, com muita paciência, me ajudou na manipulação das resinas da minha tese e nos testes realizados em Guarulhos. Porpeta, te devo todo o bacon do mundo!!!

Ao Robson, que também participou de parte deste projeto, me ajudando na tabulação dos dados, e dando algumas risadas com a gente em Guarulhos também.

Ao amigo William Brandt, idealizador das pesquisas que realizei no Mestrado e Doutorado.

Agradecimentos

A Faculdade de Odontologia de Piracicaba da Universidade Estadual de Campinas. Foram 10 anos incríveis (Graduação-Mestrado-Doutorado), em que vivi coisas que vou contar para meus filhos e netos: “Rep.” da Márcia, Rep. kaRkavaRa, Dumont & Taquaral, kRRkSamba, mil exames, festas, jogos do Guarani, iniciações científicas (Puppin s2), InterOdonto, Atlético, namoro, 4º ano (2010), convulsão do Pacheco, meu branco no 1º seminário do Mestrado (aí, Américo!), qualificações (Profs. Simonides duplamente, Pascon, Bolzan, Giovana Araújo e Ana Rosa) e defesas (Profs. Adriano Lima e Américo duplamente, Puppin e Alysson Konno), madrugadas no laboratório pra fazer a tese do amigo, **AMIZADES ETERNAS**.

A CAPES e CNPq pelo apoio financeiro durante o curso do doutorado.

Ao meu parceiro, Eduardo Souza Junior, que, mesmo de longe, me ajudou neste projeto, sempre compartilhando seus conhecimentos.

Aos funcionários do Laboratório de Materiais Dentários, Selma e Marcão, sempre tornando o ambiente de trabalho alegre e menos estressante (até quando o Marcão me dava sustos com sua formiga).

A Tia Sílvia, que cedeu seu refletor antigo do consultório, para que eu trouxesse pra Piracicaba. Só espero que você não o queira de volta, pois está, literalmente, chumbado na parede do laboratório!

A todos os amigos que acompanham meu crescimento pessoal e profissional. Tenho o privilégio de ter amigos que considero irmãos.

Resumo

O objetivo neste estudo foi estabelecer a concentração de butil-hidroxitolueno (BHT) para obter o máximo de tempo de trabalho sob exposição à luz do refletor, sem afetar propriedades mecânicas e grau de conversão de compósitos experimentais. Para, isso, seis formulações de compósitos experimentais contendo diferentes concentrações do inibidor BHT foram testadas: C1 – 0% de BHT; C2 – 0,01% de BHT; C3 – 0,025% de BHT; C4 – 0,05% de BHT; C5 – 0,1% de BHT e C6 - 0,5% de BHT. Foram avaliados o grau de conversão (GC), resistência à flexão (RF), módulo flexural (MF) e microdureza Knoop (MK), além de determinar a consistência (C) dos compósitos após diferentes tempos de exposição à luz do refletor (20, 40 ou 60 segundos). Os dados de GC, RF, MF e MK foram submetidos a ANOVA 1 fator e de C foi submetido a ANOVA 2 fatores. As médias foram comparadas pelo teste de Tukey, considerando a significância de 5% ($\alpha=0,05$). Para GC, RF e MF, todos os compósitos mostraram valores semelhantes em cada avaliação. Para os valores de MK, C1 representou o mais alto, não apresentando diferença estatística com C3. Este grupo apresentou valor estatisticamente maior que C4 e C5, mas não apresentou diferença estatística quando comparado a C2 e C6. Para o teste de C, em 20 segundos de exposição à luz do refletor, C4, C5 e C6 obtiveram os maiores valores, e diferiram dos demais grupos. Quando expostos por 40 s, somente C5 e C6 obtiveram valores para comparação, sendo que C6 apresentou média estatisticamente diferente de C5 ($p\leq0,05$). Somente C6 obteve média para o teste de consistência no tempo de 60 s. A comparação entre os tempos de exposição para cada compósito foi somente possível para C5 e C6, onde houve aumento estatisticamente significativo da consistência do material em função do aumento do tempo de exposição ($p\leq0,05$). Em conclusão, concentrações mais elevadas de BHT não influenciaram na maioria das propriedades mecânicas dos compósitos; no entanto, promoveram maior tempo de trabalho frente à exposição à luz do refletor. Desta forma, C6 apresentou as melhores propriedades após a realização dos testes.

Palavras-chave: butil-hidroxitolueno, resina composta, propriedades mecânicas.

Abstract

The aim of this study was to establish the concentration of butylatedhydroxytoluene (BHT) to obtain the maximum working time under exposure to reflector light, without affecting the mechanical properties and degree of conversion of experimental composites. For this, six formulations of experimental composites containing different concentrations of BHT were tested: C1 0% BHT; C2 - 0.01% BHT; C3 - 0.025% BHT; C4 - 0.05% BHT; C5 - 0.1% BHT and C6 - 0.5% BHT. The degree of conversion (DC), flexural strength (FS), flexural modulus (FM) and Knoop microhardness (KH) were evaluated, besides determining the consistency (C) of the composites after different exposure times to dentistry light reflector (20 , 40 or 60 s). Data from DC, FS, FM and KH were submitted to 1-way ANOVA and C was subjected to 2-way ANOVA. The means were compared by the Tukey's test, considering the significance of 5% ($\alpha = 0.05$). For DC, FS and FM, all composites showed similar values in each evaluation. For the KH values, C1 represented the highest, presenting no statistical difference with C3. This group had statistically higher value than C4 and C5, but did not present statistical difference when compared to C2 and C6. For the C test, in 20 s of exposure to the reflector light, C4, C5 and C6 obtained the highest values, and differed from the other groups. When exposed for 40 s, only C5 and C6 obtained values for comparison, and C6 presented a statistical different mean of C5 ($p \leq 0.05$). Only C6 obtained the mean for the 60 s time consistency test. The comparison between exposure times for each composite was only possible for C5 and C6, where there was a statistical significant increase in material consistency as a function of the increase in exposure time ($p \leq 0.05$). In conclusion, higher concentrations of BHT did not influence most of the mechanical properties of the composites; however, they promoted higher working time when exposed to reflector light. Thus, C6 showed better properties after tests.

Keywords: butylatedhydroxytoluene, composite resin, mechanical properties.

SUMÁRIO

1. INTRODUÇÃO	11
2. ARTIGO: Influence of different concentration of polymerization inhibitor on the mechanical properties and consistency of experimental resin composites	13
3. CONCLUSÃO	26
REFERÊNCIAS	27
APÊNDICE 1 – Metodologia ilustrada	29
ANEXO 1 – Comprovante de submissão do artigo	33

1. INTRODUÇÃO

Os compósitos resinosos são os materiais restauradores mais utilizados para restaurações diretas em dentes anteriores e posteriores. Essa preferência se deve às características estéticas e também às facilidades de manipulação (Nash et al., 2001; Bernardo et al., 2007). Esse tipo de material é fotoativado, em que se utiliza luz de alta intensidade, que converte o monômero em polímero e que, por sua vez, produz uma transformação de uma massa viscosa para um produto final sólido (Bolhuis et al., 2006; Alpoz et al., 2008; Brandt et al., 2008). Após irradiação de luz, inicia-se a polimerização por radicais livres do monômero, que é acompanhada pela reticulação da cadeia polimérica (Abate et al., 2001).

A tecnologia de polimerização dos compósitos atuais está baseada no uso do sistema fotoreativo (fotoiniciador e co-iniciador), adequado para a absorção da luz de irradiação de comprimento de onda específico, o qual produz radicais livres capazes de converter um monômero em uma rede de ligações lineares e cruzadas (Cowie, 1991; Craig, 2003). Tecnicamente, os compósitos já iniciam a polimerização desde o momento em que são expostos à luz do refletor ou à luz ambiente. Isso pode dificultar a aplicação do material pelo profissional devido à redução do tempo de trabalho, além de, potencialmente, influenciar negativamente nas propriedades mecânicas do material (Al-Shammari, 2007). Os inibidores de polimerização são moléculas antioxidantes adicionadas à base monomérica para neutralizar os radicais livres que ativam os fotoiniciadores, impedindo a polimerização precoce e espontânea. O inibidor mais utilizado nos compósitos comerciais é o butil-hidroxitolueno (BHT) (Swartz et al., 1982; Katona et al., 1994). O BHT tem sido utilizado como inibidor no compósito resinoso em concentração ao redor de 0,01% em peso (Anusavice, 2003; Van Landuyt et al., 2007). Quando a concentração dos inibidores se torna baixa, a polimerização e a propagação da reação tornam-se competitivas com a reação de inibição. Para que os inibidores sejam eficazes, devem reagir com o radical livre a uma taxa mais rápida do que a do radical livre com o monômero. Além disso, com a presença dos inibidores, a polimerização será inexistente até que a sua concentração seja substancialmente reduzida (Oadian, 2004).

Existe tendência para a diminuição no grau de conversão, pela fotoativação, com o aumento na concentração de inibidor (Braga & Ferracane, 2002). Porém, os efeitos dos inibidores sobre as propriedades mecânicas não foram avaliados. Al-Shammari (2007) observou em seu estudo resultados promissores na variação da concentração dos inibidores nas características de polimerização de compósito resinoso fotopolimerizável. Verificou-se também que o ajuste fino dos níveis de inibidor pode ser um método eficaz para retardar a polimerização precoce do material, sem comprometer o grau de conversão da reação. O autor inferiu ainda, que o nível ideal de inibidor permitiria uma taxa de polimerização adequada, o que não prejudicaria as propriedades mecânicas do compósito (Al-Shammari, 2007).

Os estudos que verificaram a variação da concentração dos inibidores na composição dos compósitos tinham como objetivo principal controlar e minimizar a tensão de contração de polimerização (Al-Shammari, 2007, Karunagaran & Chu, 2013). No entanto, muitos profissionais encontram dificuldade no momento de aplicar, adaptar e modelar o compósito na cavidade, devido à polimerização precoce do material pela exposição à luz do refletor, muitas vezes tendo que fazer esse processo com a luz do refletor apagada ou utilizando refletores com luz na cor laranja. Assim, a obtenção de tempo de trabalho adequado é desejável pelos profissionais durante a prática clínica, sendo a correta concentração de BHT mais uma etapa para alcançar sucesso nesse quesito.

Dessa maneira, o objetivo neste estudo, composto por um capítulo, foi avaliar a influência de diferentes concentrações do inibidor de polimerização (BHT) em compósitos experimentais sobre o grau de conversão (GC), resistência à flexão (RF), módulo flexural (MF) e microdureza Knoop (MK), além de determinar a consistência (C) dos compósitos após diferentes tempos de exposição à luz do refletor (20, 40 ou 60 segundos). As hipóteses testadas foram que: 1- a concentração de BHT não influenciaria nas propriedades mecânicas e grau de conversão dos compósitos; 2- quanto maior a concentração de BHT, menor a consistência do material em função à exposição à luz.

2. ARTIGO

**Influence of different polymerization inhibitor concentration on
the mechanical properties and consistency of experimental resin
composites**

Abstract

The aim of this study was to establish the concentration of butylatedhydroxytoluene (BHT) to obtain the maximum working time under exposure to reflector light, without affecting the mechanical properties and degree of conversion of experimental composites. For this, six formulations of experimental composites containing different concentrations of BHT were tested: C1 0% BHT; C2 - 0.01% BHT; C3 - 0.025% BHT; C4 - 0.05% BHT; C5 - 0.1% BHT and C6 - 0.5% BHT. The degree of conversion (DC), flexural strength (FS), flexural modulus (FM) and Knoop microhardness (KH) were evaluated, besides determining the consistency (C) of the composites after different exposure times to dentistry light reflector (20 , 40 or 60 s). Data from DC, FS, FM and KH were submitted to 1-way ANOVA and C was subjected to 2-way ANOVA. The means were compared by the Tukey's test, considering the significance of 5% ($\alpha = 0.05$). For DC, FS and FM, all composites showed similar values in each evaluation. For the KH values, C1 represented the highest, presenting no statistical difference with C3. This group had statistically higher value than C4 and C5, but did not present statistical difference when compared to C2 and C6. For the C test, in 20 s of exposure to the reflector light, C4, C5 and C6 obtained the highest values, and differed from the other groups. When exposed for 40 s, only C5 and C6 obtained values for comparison, and C6 presented a statistical different mean of C5 ($p \leq 0.05$). Only C6 obtained the mean for the 60 s time consistency test. The comparison between exposure times for each composite was only possible for C5 and C6, where there was a statistical significant increase in material consistency as a function of the increase in exposure time ($p \leq 0.05$). In conclusion, higher concentrations of BHT did not influence most of the mechanical properties of the composites; however, they promoted higher working time when exposed to reflector light. Thus, C6 showed better properties after tests.

Keywords: butylatedhydroxytoluene, composite resin, mechanical properties.

Introduction

Resin composites are the most commonly used restorative materials for restorations on anterior and posterior teeth. This preference is due to the aesthetic characteristics and also to manipulation easiness (Nash et al., 2001; Bernardo et al., 2007). This type of material is photoactivated, where a light of high intensity is employed converting monomers to polymers, which transforms a viscous mass to a solid final product (Bolhuis et al., 2006; Alpoz et al., 2008; Brandt et al., 2008). After light irradiation, monomer polymerization is initiated with free radicals formation, which is accompanied by molecule cross-linking (Abate et al., 2001).

The polymerization technology of current composites is based on the application of photoactive systems (photoinitiator and co-initiator), suitable for the absorption of specific wavelength irradiation light, which produces free radicals capable of converting a monomer into a network of linear and cross connections (Cowie, 1991; Craig, 2003). Technically, composites start polymerization at the moment when it is exposed to light either from the reflector or from room environment light. This may hinder the manipulation of the material by the professional due to the reduction of working time, as well as can negatively influence the mechanical properties of the material (Al-Shammari, 2007). Polymerization inhibitors are antioxidant molecules added to monomeric base to inhibit the premature polymerization, preventing premature and spontaneous polymerization. The most commonly used inhibitor in commercial composites is butylatedhydroxytoluene (BHT) (Swartz et al., 1982; Katona et al., 1994). BHT has been used as an inhibitor in the resinous composite at concentration around 0.01% by weight (Anusavice, 2003; Van Landuyt et al., 2007). When the inhibitors are present, the polymerization will be nonexistent until its concentration is substantially reduced. When the inhibitor concentration becomes low, reaction polymerization and propagation becomes competitive with the inhibition reaction. To ensure inhibitors effectiveness, they must react with free radicals faster than that of free radicals with the monomer (Oadian, 2004).

There is a tendency for the decrease in the degree of conversion with the increase in inhibitor concentration (Braga & Ferracane, 2002). However, the effects of the inhibitors on the mechanical properties were not evaluated. Al-Shammari, (2007) observed in his study promising results in the variation of inhibitor concentration in the polymerization

characteristics of photo-polymerizable resinous composite. It has also been found that fine-tuning inhibitor levels may be an effective method of avoid early polymerization of the material without compromising its degree of conversion. The authors also infer that the ideal inhibitor level would allow a suitable rate of polymerization, which would not impair the composite mechanical properties (Al-Shammari, 2007).

The studies that verified the variation of inhibitor concentration in the composition of the composite had a main objective to control and minimize their polymerization shrinkage stress (Al-Shammari, 2007, Karunagaran & Chu, 2013). However, many professionals find difficult to apply, adapt and model the composite into the cavity due to early material polymerization by exposure to the light from the reflector, often having to do this under switched off light reflector or using reflectors with orange color light. Thus, obtaining adequate working time is a desirable issue for professionals during clinical practice, and the correct concentration of BHT is another step to achieve success in this area.

The aim of this study was to evaluate the influence of different polymerization inhibitor (BHT) concentrations on experimental designed composites on the degree of conversion (DC), flexural strength (FS), flexural modulus (FM) and microhardness Knoop (KH), in addition to determining the consistency (C) of the composites after different exposure times to the light reflector (20, 40 or 60 s). The hypotheses tested were that: 1- the concentration of BHT would not influence the mechanical properties and degree of conversion of the composites; 2- the higher the concentration of BHT, the lower the consistency of the material as a function of light exposure.

Material and methods

Resin preparation

Six experimental resin composites formulations were tested in this study. The resin matrix for all formulations consisted of a blend of bisphenolglycidyl methacrylate – 30 wt% (BisGMA – Sigma-Aldrich Inc, St Louis, MO, USA); urethane dimethacrylate – 30 wt% (UDMA - Sigma-Aldrich Inc); bisphenolethoxylatedimethacrylate – 30 wt% (BisEMA - Sigma-Aldrich Inc); and triethyleneglycoldimethacrylate – 10 wt% (TEGDMA - Sigma-Aldrich Inc). The photoinitiator and co-initiator used were camphorquinone (0.25

wt%) and ethyl-dimethylaminobenzoic (DABE - 0.5 wt%), respectively. Composites were loaded at 75% by volume with silanized filler (20 wt% of 0.05 μ m fumed silica (Nippon Aerosil Co. Ltd., Yokkaichi, Tokyo, Japan) and 80 wt% of 0.7 μ m Ba-Al-silicate glass (Esstech Inc., Essington, PA, USA). The inhibitor, BHT (butylatedhydroxytoluene, - Sigma-Aldrich Inc) was the only difference among the experimental composites added to the organic matrix, in different concentration, according Table 1.

Table 1. Inhibitor system different concentrations of the experimental composites used in the study.

Experimental group	BHT wt%
Composite 1 (C1)	0
Composite 2 (C2)	0.01
Composite 3 (C3)	0.025
Composite 4 (C4)	0.05
Composite 5 (C5)	0.1
Composite 6 (C6)	0.5

Degree of conversion (DC)

For the degree of conversion (DC) analysis, 5 specimens per group, with 7 mm length x 2 mm width x 1 mm thickness, were made in rubber molds and photo-activated by a LED curing unit (Radii Cal, SDI, Victoria, Australia – 800 mW/cm²), for 20s. The total energy dose was standardized at 20 J/cm². After polymerization, the specimens were removed from the molds and stored dry in light-proof containers at 37°C, for 24 h. DC was measured on the top surface of each specimen using Fourier transformed infrared spectroscopy with attenuated total reflectance (FTIR/ATR - Spectrum 100, PerkinElmer, Shelton, CA, USA).

The absorption spectra of non-polymerized and polymerized composites were obtained from the region between 4000 and 650 cm⁻¹ with 32 scans at 4 cm⁻¹. The aliphatic

carbon-carbon double-bond absorbance peak intensity (located at 1638 cm^{-1}) and that of the aromatic (C–C) (located at 1608 cm^{-1} ; reference peak) were collected. The DC was calculated using the following equation: $DC = 100 \times [1 - (R_{\text{polymerized}}/R_{\text{non-polymerized}})]$, where R represents the ratio between the absorbance peak at 1638 cm^{-1} and 1608 cm^{-1} .

Flexural strength (FS) and flexural modulus (FM)

Immediately of DC analysis, the same bar-shaped specimens of DC analysis (n=5) were used for the three-point bending flexural test, accordingly to ISO 4049, except specimen dimensions. The three-point bending test was performed in an universal testing machine (Instron, Canton, USA – span between supports = 5 mm) at a cross-head speed of 0.5 mm/min. The maximum load for the specimens at fracture was recorded and the flexural strength (FS) calculated using the following equation: $FS = 3.F.L/2.B.H^2$, where F was the maximum load (N) exerted on the specimens; L, the distance (mm) between the supports; B, the width (mm) of the specimens and H was the height (mm) of the specimens measured immediately prior testing.

The flexural modulus was measured as the slope of the stress x strain curve in the linear portion, using the following equation: $E = L1.D^3.10^{-3}/4.B.H^3.d$, where L1 was the load (N); D, distance (mm) between the supports; B, width (mm); H, height (mm) and d was the deflection due to the load (mm).

Microhardness Knoop (KH)

Specimens were prepared in a rubber mold with a central circular orifice, where resin composite was inserted in a single increment and activated for 20 s using Radii Cal LED (800 mW/cm^2). The height of the die orifice was 2 mm and the diameter 5 mm. All samples were prepared in controlled temperature environment. For each group tested, five samples were prepared (n=5).

After this, the surfaces that have been exposed to LED unit were submitted to the Knoop microhardness test, performed after 24 h storage in an incubator at 37°C , in dry and protected from the light environment. The assay was performed in a micro-durometer (HMV-2000, Shimadzu, Tokyo 101, Japan), applying a load of 50g for 15 s (three

indentations were performed for each sample). The values obtained, in micrometers, were transformed into Knoop hardness values (KHN) through micro-durometer software.

Consistency testing (C)

The consistency testing was performed using the ADA (American Dental Association) Specification N°.8. A volume of 0.5 mL of composite resin was placed in spherical rubber molds. Each composite sphere was taken on a glass plate and exposed to the light emitted by the lamp (150 W, Osram, Berlin, Germany) of the reflector for a predetermined time (20, 40 or 60 s of light exposure, at a distance of 50 cm). For each group of experimental composite resin, 5 samples were taken for each time. Next, another glass plate, with 20 g weight, together with a 100 g weight, was placed over the composite sphere for 30 seconds – to form a disc.

After this, the load was removed and the composite resin was activated for 20 s with the Radii Cal LED curing unit (SDI). Disc shape samples were removed from the glass plate, and their larger and smaller diagonals were measured (mm), with a digital electronic caliper (Mitutoyo Corporation, Tokyo, Japan). The mean of the diagonals of each sample was calculated and, in each group, the mean of these values was also calculated.

Statistical analysis

The DC, FS, FM and KH outcomes were analyzed by 1-way ANOVA and C outcomes by 2-way ANOVA. The means were compared by Tukey's test with statistical significance established at $\alpha=0.05$ for all tests.

Results

The flexural strength (FS), flexural modulus (FM), degree of conversion (DC) and microhardness Knoop (KH) values are shown in Table 2. All composites showed similar values ($p \geq 0.05$) for FS, FM and DC, for each evaluation. For the KH values, the composite C1 showed the highest values, presenting no statistical difference with C3. This group had higher statistically value than C4 and C5, but did not present statistical differences compared to C2 and C6 ($p \leq 0.05$).

Table 2. Means (standard-deviation) of flexural strength (FS), flexural modulus (FM), degree of conversion (DC) and microhardness Knoop (KH) for the experimental composites.

Composite	FS (MPa)	FM (GPa)	DC (%)	KH (KHN)
C1	96.85 (12.82) a	1.65 (0.1) a	44.9 (5.7) a	22.6 (1.7) a
C2	82.36 (10.19) a	1.42 (0.27) a	44.0 (2.8) a	19.9 (0.7) bc
C3	97.74 (15.96) a	1.63 (0.2) a	43.9 (2.7) a	20.5 (0.9) ab
C4	94.89 (10.37) a	1.6 (0.2) a	44.1 (1.2) a	17.9 (0.8) c
C5	93.42 (6.7) a	1.52 (0.21) a	43.5 (0.7) a	17.7 (0.9) c
C6	94.77 (15.09) a	1.77 (0.16) a	39.6 (2.0) a	18 (0.8) bc

Means followed by same small letter in the same column are not statistically different at 5%, by Tukey's test.

The results for consistency testing (C) are shown in the Table 3. For the groups with 20 s of exposure to the reflector light, C4, C5 and C6 obtained the highest mean values, and were statistically different from the groups C1, C2 and C3. When exposed for 40 s to the reflector light, only C5 and C6 obtained values for comparison, with C6 presenting statistically higher values than C5 ($p \leq 0.05$). Only C6 obtained consistency at 60 s of exposure to the reflector light. The comparison of exposure times for all experimental composites was only possible for C5 and C6. There was a statistical difference ($p \leq 0.05$) between the exposure times with an increase in the consistency of the material as a function of the increase in exposure time. For other materials, only in 20 s of exposition to reflector light was possible to measure the consistency of the material.

Table 3. Means in mm (standard-deviation) of the Consistency (C) for the experimental composites.

Composite	Time (s)		
	20	40	60
C1	12.67 (1.16) b, A	0.0 (0.0) c, B	0.0 (0.0) b, B
C2	12.77 (0.48) b, A	0.0 (0.0) c, B	0.0 (0.0) b, B
C3	13.05 (0.62) b, A	0.0 (0.0) c, B	0.0 (0.0) b, B
C4	13.78 (0.47) a, A	0.0 (0.0) c, B	0.0 (0.0) b, B
C5	13.11 (0.66) a, A	8.42 (0.38) b, B	0.0 (0.0) b, C
C6	14.23 (0.19) a, A	13.49 (0.44) a, B	8.96 (0.39) a, C

Means followed by same small letter in the column and capital letter in row are not statistically different at 5%, by Tukey's test.

Discussion

The first hypothesis that the concentration of BHT would not influence the degree of conversion and mechanical properties of the composites was rejected, since it did present an influence in microhardness Knoop test. The higher the concentration of BHT, the material flow would remain in function underlight exposure; therefore, the second hypothesis in this study was accepted. The highest concentration of BHT did not influence the degree of conversion and the major part of the mechanical properties evaluated conceding longer working time, even under light reflector exposition. The optimum concentration of BHT molecules should be defined as essential to ensure longer composite life, as well as optimum working time for the operator during handling. It is also a fundamental parameter that determines the polymerization characteristics of a composite. This concentration is variable among commercial composites and its effects on polymeric structure of composites are not still completely elucidated. In order to guarantee a satisfactory handling time of the composites, many concentration of BHT is included in the composite formulation. It is very important to understand the outcomes of including a higher or lower concentration of BHT in the actual composite formulations.

Braga and Ferracane (2002) reported that increase the inhibitor concentration results in a lower curing rate and in a decrease in contraction stress without compromise conversion rate. However, they found a tendency towards degree of conversion decrease when inhibitor concentration increased. But, the effects of inhibitors on mechanical properties were not evaluated in that study. Al-Shamari (2007) has shown that the optimum level of inhibitor promotes a rate of polymerization slow enough to reduce contraction stress, but sufficient to achieve a degree of conversion that does not impair the mechanical properties of the resin composite.

In attempt to find a method to increase the useful life and delay the polymerization of the resinous composites, researchers studied the effects of the inhibitor concentration (Braga & Ferracane, 2002; Al-Shammari, 2007) on these materials. Polymerization inhibitors are molecules added into composite resin to prevent formed free radicals from prematurely activate photoinitiators, preventing spontaneous initiation of the polymerization reaction (Shaabin, 2009).

The study of Al-Shammari (2007) evaluated the effect of variation of BHT concentration on mechanical properties. It was shown that flexural strength and flexural modulus were not affected by the increase in BHT level up to 1.2%. On the other hand, it showed a significant decrease when the concentration reached 1.4%. Another study (Ferracane & Greener, 1986) showed that increase inhibitor concentration reduces flexural strength and flexural modulus, which was attributed to fewer cross-links that were found. It was concluded that the lower degree of conversion was responsible for the reduction of the mechanical properties.

In the present study, the concentration of BHT ranged from 0 to 0.5 wt% into monomer and this values did not affect the tested mechanical properties and degree of conversion. It probably occurred due to the amount of photoinitiator system that was able to promote the monomer conversion, even using higher concentration of BHT (0.5%). The curing kinetics of these materials allows a satisfactory degree of conversion, flexural strength and flexural modulus of the tested composites.

Besides this, microhardness measurements have been shown to have a good correlation with the degree of conversion of resinous materials, which did not have different formulations, with the exception of BHT, in this study. For this reason,

microhardness was used by some authors in order to study composite cure in different depths (Uhl et al., 2003; Baharav et al., 1988).

Physical characteristics are of great importance to choose appropriate materials. Hardness evaluation may determine their abrasion resistance compromising the clinical behavior of the resin composite, which leads it to failure (Ferracane, 1985). Results of this study confirm that multiple laboratorial tests are of great concern to characterize correctly the effect of BHT concentration on the polymeric network of resin-based dental materials.

In relation to consistency test, the higher the concentration of BHT, the material flow level would remain in function when light exposed for a longer time. In this sense, this study showed that the most favorable concentration of BHT was C6 (0.5% of polymerization inhibitor), which exhibited satisfactory properties and lower consistency, even after a light exposure of 60 s. Thinking in a clinical possibility, the dentist will work with the composite with a more interesting time to adapt and model the composite into the cavity. It is well known that the clinical should put away the light reflector during the procedure of sculpture of the composites in order to avoid an early polymerization. Therefore, in some places in mouth, the light reflector is required for a better view. Thus, it is important that the composite might have a good working time for placement and sculpture.

Thus, further studies evaluating other mechanical and physical properties, such as color stability, sorption and solubility, still needs to be conducted. Based on the outcomes of this study, the composite with 0.5 wt% of BHT concentration is the most indicated for application due its better of manipulation under light reflector added to a maintained characteristic of less sensitive to early photocuring.

Conclusion

All concentrations of BHT in experimental composites did not negatively influence mechanical properties and degree of conversion, except for microhardness Knoop. Higher concentrations of BHT promoted longer working time when exposed to light reflector. Thus, C6 showed better properties after tests.

References

1. Nash RW, Lowe RA, Leinfelder K. Using packable composites for direct posterior placement. *J Am Dent Assoc* 2001;132(8):1099-104.
2. Bernardo M, Luis H, Martin MD, et al. Survival and reasons for failure of amalgam versus composite posterior restorations placed in a randomized clinical trial. *J Am Dent Assoc* 2007;138(6):775-83.
3. Bolhuis PB, de Gee AJ, Kleverlaan CJ, El Zohairy AA, Feilzer AJ. Contraction stress and bond strength to dentin for compatible and incompatible combinations of bonding systems and chemical and light-cured core build-up resin-matrix composites. *Dent Mater* 2006;22(3):223-33.
4. Alpoz AR, Ertugrul F, Cogulu D, Ak AT, Tanoglu M, Kaya E. Effects of light curing method and exposure time on mechanical properties of resin based dental materials. *Eur J Dent* 2008;2(1):37-42.
5. Brandt WC, de Moraes RR, Correr-Sobrinho L, Sinhoreti MA, Consani S. Effect of different photo-activation methods on push out force, hardness and cross-link density of resin-matrix composite restorations. *Dent Mater* 2008;24(6):846-50.
6. Abate PF, Zahra VN, Macchi RL. Effect of photopolymerization variables on composite hardness. *J Prosthet Dent* 2001;86(6):632-5.
7. Cowie JMG C. *Polymers: chemistry and physics of modern materials*. New York: Chapman and hall; 1991.
8. Craig RG PJ. *Restorative dental materials*. St Louis: C.B. Mosby; 2003.
9. Al-Shammari M. The effect of inhibitor concentration on polymerization characteristics of light-cured resin composites. Indianapolis: Indiana University School of Dentistry; 2007.
10. Swartz ML, Moore BK, Phillips RW, Rhodes BF. Direct restorative resins-a comparative study. *J Prosthet Dent* 1982;47(2):163-70.
11. Katona TR, Winkler MM. Stress analysis of a bulk-filled Class V light-cured composite restoration. *J Dent Res* 1994;73(8):1470-7.

12. Anusavice K. Phillips' science of dental materials. Philadelphia: W. B. Saunders Company; 2003.
13. Van Landuyt KL, Snauwaert J, De Munck J, et al. Systematic review of the chemical composition of contemporary dental adhesives. *Biomaterials* 2007;28(26):3757-85.
14. Odian G. Principles of polymerization. New Jersey: John Wiley and sons, INC.; 2004.
15. Braga RR, Ferracane JL. Contraction stress related to degree of conversion and reaction kinetics. *J Dent Res* 2002; 81:114-8.
16. Karunagaran S, Chu TMG. The effect of inhibitor concentrations on the chemical and mechanical properties of Bis-GMA-based resin dental composites. *Journal of Materials Science Research* 2013; 2(2):118-25.
17. Shaabin M. The effect of inhibitor and initiator concentration on degree of conversion, flexural strength and polymerization shrinkage stress on resin-matrix composite. Indianapolis: Indiana University School of Dentistry; 2009.
18. Ferracane JL, Greener EH. The effect of resin formulation on the degree of conversion and mechanical properties of dental restorative resins. *J Biomed Mater Res* 1986;20(1):121-31.
19. Uhl A, Mills RW, Jandt KD. Photoinitiator dependent composite depth of cure and Knoop hardness with halogen and LED light curing units. *Biomaterials* 2003; 24(10):1787-95.
20. Baharav H, Abraham D, Cardash HS, Helft M. Effect of exposure time on the depth of polymerization of a visible light-cured composite resin. *J Oral Rehab* 1988; 15(2):167-72.
21. Ferracane JL. Correlation between hardness and degree of conversion during the setting reaction of unfilled dental restorative resins. *Dental Materials* 1985; 1(1):11-14.

3. CONCLUSÃO

As concentrações de BHT nos compósitos experimentais não influenciaram negativamente nas propriedades mecânicas e grau de conversão, exceto para microdureza Knoop. Maiores concentrações de BHT promoveram maior tempo de trabalho das resinas quando expostas à luz do refletor. Portanto, o compósito 6 obteve os melhores resultados nos testes realizados.

REFERÊNCIAS

1. Nash RW, Lowe RA, Leinfelder K. Using packable composites for direct posterior placement. *J Am Dent Assoc* 2001;132(8):1099-104.
2. Bernardo M, Luis H, Martin MD, et al. Survival and reasons for failure of amalgam versus composite posterior restorations placed in a randomized clinical trial. *J Am Dent Assoc* 2007;138(6):775-83.
3. Bolhuis PB, de Gee AJ, Kleverlaan CJ, El Zohairy AA, Feilzer AJ. Contraction stress and bond strength to dentin for compatible and incompatible combinations of bonding systems and chemical and light-cured core build-up resin-matrix composites. *Dent Mater* 2006;22(3):223-33.
4. Alpoz AR, Ertugrul F, Cogulu D, Ak AT, Tanoglu M, Kaya E. Effects of light curing method and exposure time on mechanical properties of resin based dental materials. *Eur J Dent* 2008;2(1):37-42.
5. Brandt WC, de Moraes RR, Correr-Sobrinho L, Sinhoreti MA, Consani S. Effect of different photo-activation methods on push out force, hardness and cross-link density of resin-matrix composite restorations. *Dent Mater* 2008;24(6):846-50.
6. Abate PF, Zahra VN, Macchi RL. Effect of photopolymerization variables on composite hardness. *J Prosthet Dent* 2001;86(6):632-5.
7. Cowie JMG C. *Polymers: chemistry and physics of modern materials*. New York: Chapman and hall; 1991.
8. Craig RG PJ. *Restorative dental materials*. St Louis: C.B. Mosby; 2003.
9. Al-Shammari M. The effect of inhibitor concentration on polymerization characteristics of light-cured resin composites. Indianapolis: Indiana University School of Dentistry; 2007.
10. Swartz ML, Moore BK, Phillips RW, Rhodes BF. Direct restorative resins-a comparative study. *J Prosthet Dent* 1982;47(2):163-70.
11. Katona TR, Winkler MM. Stress analysis of a bulk-filled Class V light-cured composite restoration. *J Dent Res* 1994;73(8):1470-7.

12. Anusavice K. Phillips' science of dental materials. Philadelphia: W. B. Saunders Company; 2003.
13. Van Landuyt KL, Snauwaert J, De Munck J, et al. Systematic review of the chemical composition of contemporary dental adhesives. *Biomaterials* 2007;28(26):3757-85.
14. Odian G. Principles of polymerization. New Jersey: John Wiley and sons, INC.; 2004.
15. Braga RR, Ferracane JL. Contraction stress related to degree of conversion and reaction kinetics. *J Dent Res* 2002; 81:114-8.
16. Karunagaran S, Chu TMG. The effect of inhibitor concentrations on the chemical and mechanical properties of Bis-GMA-based resin dental composites. *Journal of Materials Science Research* 2013; 2(2):118-25.
17. Shaabin M. The effect of inhibitor and initiator concentration on degree of conversion, flexural strength and polymerization shrinkage stress on resin-matrix composite. Indianapolis: Indiana University School of Dentistry; 2009.
18. Ferracane JL, Greener EH. The effect of resin formulation on the degree of conversion and mechanical properties of dental restorative resins. *J Biomed Mater Res* 1986;20(1):121-31.
19. Uhl A, Mills RW, Jandt KD. Photoinitiator dependent composite depth of cure and Knoop hardness with halogen and LED light curing units. *Biomaterials* 2003; 24(10):1787-95.
20. Baharav H, Abraham D, Cardash HS, Helft M. Effect of exposure time on the depth of polymerization of a visible light-cured composite resin. *J Oral Rehab* 1988; 15(2):167-72.
21. Ferracane JL. Correlation between hardness and degree of conversion during the setting reaction of unfilled dental restorative resins. *Dental Materials* 1985; 1(1):11-14.

APÊNDICE 1

Metodologia ilustrada



Figura 1 – Compósito experimental.



Figura 2 – Confeção das amostras para os testes de Grau de Conversão, Resistência à Flexão e Módulo Flexural.

- A. Adaptação da tira de poliéster e lâmina de vidro sobre o compósito
- B. LED Radii Cal (SDI, Victoria, Australia - 800 mW/cm²)



Figura 3 – Espectrofotômetro utilizado para o teste de Grau de Conversão.



Figura 4 – Máquina de Ensaio Universal Instron, utilizada para os testes de Resistência à Flexão e Módulo Flexural.

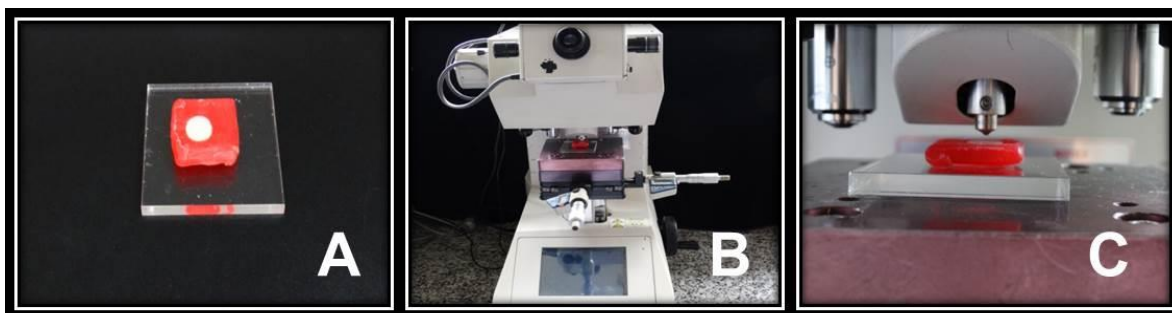


Figura 5 – Sequência do teste de Microdureza Knoop:

A. Planificação da amostra no conjunto placa de acrílico e cera utilidade

B. Colocação da amostra no Microdurômetro HMV-2000

C. Aplicação da carga de 50 g por 15 segundos (foram realizadas 3 indentações por amostra)

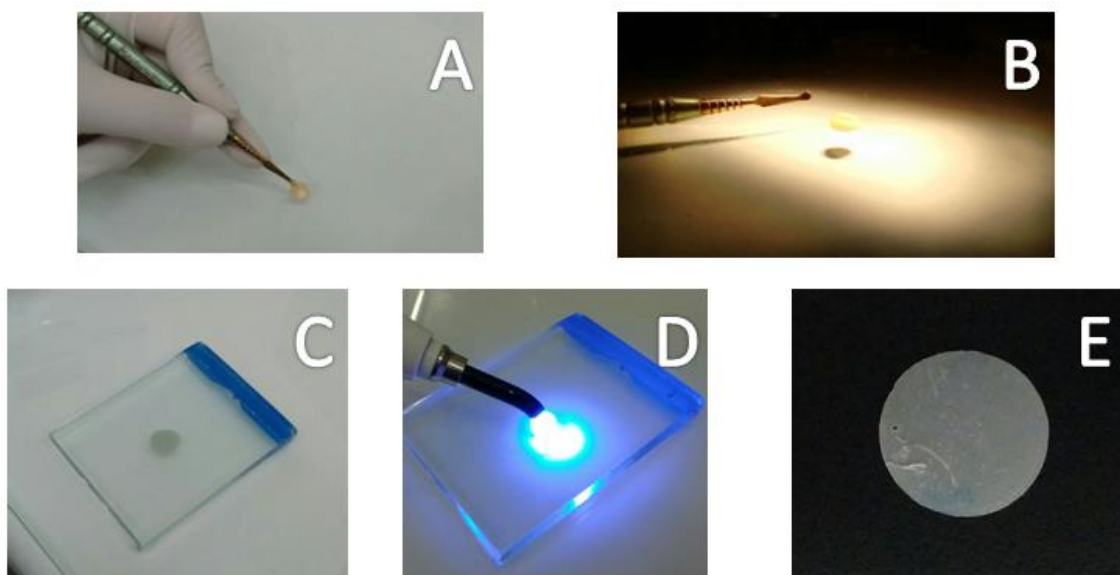


Figura 6 – Confecção das amostras para o teste de Consistência

- A.** Colocação de 0,5 mL de resina composta sobre uma placa de vidro
- B.** Incidência da luz do refletor, a uma distância de 50 cm
- C.** Amostra não-polimerizada, após aplicação da carga de 120 g por 30 segundos
- D.** Polimerização da amostra por 20 segundos
- E.** Disco de resina composta

ANEXO 1

Comprovante de submissão do artigo

ScholarOne Manuscripts™

Mário Sinhoreti ▾Instructions & FormsHelpLog Out

 Brazilian Dental Journal

[Home](#) [Author](#) [Review](#)

[Author Dashboard](#) / [Submission Confirmation](#)

Submission Confirmation

[Print](#)

Thank you for your submission

Submitted to	Brazilian Dental Journal
Manuscript ID	BDJ-2017-1644
Title	Influence of polymerization inhibitor concentration on the physical properties of experimental composites
Authors	Sinhoreti, Mário Grohmann, Caio
Date Submitted	21-Apr-2017