Universidade Federal de Uberlândia
Faculdade de Odontologia
Programa de Pós-Graduação em Odontologia

Luciana Mendes Barcelos

Propriedades fisícas e mecânicas de resinas compostas convencionais e bulk fill – efeito da composição e do modo de fotoativação

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

Uberlândia, 14 de novembro de 2020

Luciana Mendes Barcelos

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Banca Examinadora
Orientador: Prof. Dr. Carlos José Soares - UFU
Prof. Dr. Paulo Sérgio Quagliatto - UFU
Prof. Dr. Paulo César de Freitas Santos Filho - UFU
Prof. Dr. Cesar Penazzo Lepri - UNIUBE
Prof. Dr. Renata Afonso Pereira da Silva - UNITRI

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Uberlândia, 14 de novembro de 2020

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B242
2020

Barcelos, Luciana Mendes, 1977-
Propriedades físicas e mecânicas de resinas compostas convencionais e bulk fill - efeito da composição e do modo de fotoativação [recurso eletrônico] / Luciana Mendes Barcelos. - 2020.

Orientador: Carlos José Soares.
Tese (Doutorado) - Universidade Federal de Uberlândia, Pós-graduação em Odontologia.
Modo de acesso: Internet.
Disponível em: http://doi.org/10.14393/ufu.te.2020.836
Inclui bibliografia.

1. Odontologia. I. Soares, Carlos José ,1965-, (Orient.). II. Universidade Federal de Uberlândia. Pós-graduação em Odontologia. III. Título.

CDU: 616.314

Bibliotecários responsáveis pela estrutura de acordo com o AACR2:

Gizele Cristine Nunes do Couto - CRB6/2091

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Coordenação do Programa de Pós-Graduação em Odontologia
Av. Pará, 1720, Bloco 4L, Anexo B, Sala 35 - Bairro Umuarama, Uberlândia-MG, CEP 38400-902
Telefone: (34) 3225-8115/8108 - www.ppgoufu.com - copod@umuarama.ufu.br

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Programa de Pós-Graduação em:	Odontologia				
Defesa de:	Tese Doutorado, número 55, PPGODONTO				
Data:	Quatorze de Dezembro de Dois Mil e Vinte	Hora de início:	14:00	Hora de encerramento:	[17:15]
Matrícula do Discente:	11613ODO009				
Nome do Discente:	Luciana Mendes Barcelos				
Título do Trabalho:	Propriedades físicas e mecânicas de resinas compostas convencionais e bulk fill – efeito da composição e do modo de fotoativação				
Área de concentração:	Clínica Odontológica Integrada				
Linha de pesquisa:	Biomecânica Aplicada à Odontologia				
Projeto de Pesquisa de vinculação:	Biomecânica Aplicada à Odontologia				

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DEDICATÓRIA

Dedico este trabalho ao meu esposo Wendell por nunca medir esforços para que eu pudesse seguir o caminho que escolhi, e mesmo diante as dificuldades foi, o acolhimento e a força necessária para que eu pudesse seguir sempre em frente!

A você minha gratidão!

AGRADECIMENTOS ESPECIAIS

À Deus,

Gratidão Senhor por mais este dia especial, feliz e memorável em minha vida! Gratidão por me conceder serenidade para aceitar tudo que não pude mudar, coragem para mudar o que era possível, e sabedoria por me ensinar a discernir entre as duas coisas. E assim aprender a viver um dia de cada vez! Obrigada Senhor, por sempre me proteger guiando meu caminho ao encontro das melhores oportunidades e pessoas!

Gratidão Senhor pelas bênçãos diárias!

À minha mãe Marcia Helena, e ao meu pai Adalberto (In memorian)

A minha honra e gratidão a vocês por tudo!

Gratidão por me propiciarem uma vida digna, acreditando que tudo é possível desde que sejamos honestos, íntegros e de caráter! Obrigada por sempre me ensinarem a caminhar por mim mesma, por me apoiarem nos meu sonhos, e que sonhar e concretizar os sonhos só dependerá de nossa vontade! Mãe gratidão por todo apoio, compreensão e paciência durante a minha ausência! Você é um grande exemplo pra mim! Pai, digo sempre... você foi e é exemplo de pessoa e generosidade constantes na minha vida, sempre presente no meu coração, sei que está orgulhoso das minhas conquistas! Gratidão por tudo, por me ensinarem os grande valores e essência da vida! Amo vcs infinitamente!

Ao Wendell meu esposo, companheiro e amigo

A você darling minha imensa gratidão pelo amor, paciência, respeito, confiança, e acima de tudo por me por me apoiar nas minhas escolhas! Se cheguei até aqui, foi por todo incentivo e suporte que você me deu, que foram essenciais para as tomadas de decisões! Obrigada por acreditar em mim, e me mostrar que eu era capaz! E mais uma vez digo: você fez dos meus sonhos os seus... essa conquista também é sua! Gratidão por toda sua ajuda na concretização de mais um sonho! I love you Darling!

As minhas ***irmãs Daniela e Fernanda***

Gratidão por serem parte da minha base, pela tolerância e paciência compreendendo minha ausência mesmo nos momentos mais difíceis, e mesmo assim apoiando as minhas escolhas! Amo vocês!

A todos os meus ***Sobrinhos, sobrinhas e afilhados***

Vocês são minha alegria de viver! Gratidão por fazerem meus dias mais felizes a cada encontro! O sorriso, e a alegria de vocês me contagia! Gratidão imensa pela grandeza e pureza de sentimentos, superando a minha ausência.

Amo vocês!

À toda minha ***família – avós, tios, tias e primos***

Gratidão por toda palavra de incentivo e por estarem sempre ao meu lado, apoiando e motivando a caminhada diante os desafios! Cada um do seu jeito, mas com todo amor demonstrado incondicionalmente. Só tenho a agradecer! Sou abençoada pela família que Deus me deu! Amo vocês!

Aos meus sogros - Luzia e José

Gratidão por tudo! Vocês sempre prestativos e disponíveis a ajudar em qualquer situação! Obrigada por compreenderem as minhas ausências e por estarem presente nos momentos que mais precisei!

AGRADECIMENTOS

Ao meu orientador ***Prof. Dr. Carlos José Soares***
Querido professor Carlos, mais uma vez registro aqui a minha sincera gratidão por tudo! Posso dizer com certeza que tive o grande privilégio de ser sua orientada! Muito obrigada por cada oportunidade, por acreditar em mim, por me incentivar cada novo passo... Obrigada por cada novo aprendizado, por toda confiança em mim creditada e por todo o suporte para que eu pudesse trilhar este caminho! Obrigada pela maneira como me orientou, sempre me direcionando da melhor maneira para que pudesse seguir sozinha, sempre visando contribuir com o meu crescimento.
A minha gratidão por todo esforço realizado para que eu pudesse realizar o período de estágio sanduíche no exteriror... Realizei um grande sonho! Obrigada por nunca medir esforços e por sempre me dar todo o amparo necessário frente às mais diversas dificuldades. Posso dizer que com certeza foi uma experiência única tanto na minha vida pessoal e profissional. Gratidão por tudo professor!

À minha orientadora no exterior ***Profª. Drª Carmem Silvia Costa Pfeifer***
Querida professora minha gratidão pela oportunidade de conviver e aprender muito com você! Durante todo estágio no Pfeifer lab's na Oregon Health & Science University, pude ter uma experiência única, tanto profissional quanto pessoal. Gratidão por muito me ensinar com toda humildade, amor a pesquisa e ciência. Sua dedicação à profissão e ideais de crescimento foram grandes ensinamentos, ficam como exemplo e inspiração para mim! Gratidão!

Ao ***Prof. Dr. Jack Farracane***
Gratidão por junto a Professora Carmem me acolher tão bem! Muito obrigada por todo conhecimento compartilhado, cada ensinamento que levo pra vida! Querido professor o senhor é um grande exemplo de gentileza e humildade. Gratidão!

À ***Profª. Drª Ana Paula Piovezan Fugolin***

Querida Aninha, gratidão por ter conhcecido você durante essa jornada, sempre amiga, atenciosa e prestativa. Muito obrigada por toda disponibilidade em tudo que precisei, sua dedicação e profissionalismo são exemplos pra mim!

Aos ***professores da Faculdade de Odontologia da UFU***

Aos Professores do Programa de Pós-graduação em Odontologia, muito obrigada pela grande contribuição na minha formação acadêmica e científica, bem como pela convivência durante os anos de Pós-Graduação, vocês foram essenciais para minha formação.

Ao ***Prof. Dr. Marcio Teixeira,***

Obrigada por ser um grande exemplo de gestão e amor ao trabalho!

Aos ***Professores da banca***

Agradeço por aceitaram o convite e me presentearem com a oportunidade de fazer parte desse momento tão especial para mim e engrandecer este trabalho! Vocês são exemplos! A vocês muito obrigada!

Aos ***funcionários da FOUFU***

Aos amigos Sr. Advaldo, John Douglas, Bruno, Eliete, Auxiliadora, e demais funcionários, o meu muito obrigada pela amizade, presteza e orientações em tudo que precisei. Obrigada pela disponibilidade, me auxiliando nessa trajetória, cada um do seu jeito, mas sempre com aquele sorriso no rosto, agradeço a amizade!

Ao ***Programa de Pós-graduação da FOUFU***, hoje coordenado pela Professora Dra. Priscilla Barbosa Ferreira Soares, e às secretárias Graça, Brenda e Laís, agradeço a todas pela presteza, gentileza e disponibilidade frente às minhas demandas! Os meus sinceros agradecimentos por tudo! Vocês foram essenciais nesse processo!

Às ***minhas amigas Aline, Ana Luiza e Renata***

Minhas queridas, vocês são essênciais e fizeram a diferença durante toda a minha trajetória nesse doutorado. A jornada foi mais leve, compartilhamos conquistas, perdas, mas sempre com o apoio dos grandes amigos somos mais fortes! E vocês são grandes amigas... Cada uma com sua singularidade têm um lugar especial no meu coração! Amo vocês!!

Aos ***meus queridos amigos Victor e Camila***

A amizade de vocês levo pra vida! Um presente que a Pós-graduação me deu! Com vocês dei as melhores risadas, também demonstrei fragilidade, e chorei quando precisei... E vocês me deram força pra juntos contiuarmos! Gratidão por todos os momentos juntos e por fazerem parte da minha vida!

Ao ***meu amigo de doutorado Marcio Alex***

Gratidão pela amizade construída ao longo desses anos! Você se tornou um grande amigo, e foi importante nessa jornada! Muito obrigada por todo aprendizado durante os momentos das clínicas de hibiatria, e também dos momentos compartilhados em sala de aula. Sua amizade levo pra vida!

À ***amiga de doutorado Stella***

Gratidão por toda ajuda, que foi essencial nesse trabalho! Obrigada pela paciência e por me ensinar muito sobre fontes de luz e ftir. Você o fez brilhantemente! Obrigada por tudo!

À ***amiga de doutorado sanduíche Marcela***

Gratidão por fazer parte dessa história e por ter se tornado uma pessoa amiga! Com você muito aprendi ao longo desses anos, em especial no sanduíche! Você é muito especial! Obrigada por tudo!

Aos ***amigos do doutorado da UFU,***

Livia, Guilherme, Camilinha, Jéssica, Predro, Frederick, Obrigada pelo convívio, e por todos os momentos que ficarão para sempre em minha memória! Vocês foram essenciais nessa trajetória e tornaram-se amigos especiais! Obrigada por tudo!

Aos ***amigos do doutorado sanduíche da OHSU***

Vocês foram essenciais durante esse período! Foi o apoio necessário em dias difíceis, e o riso facil na hora do café! Gratidão a cada um que fez parte desse momento! Amizade que levo pra vida!

À ***outros amigos***

Gabriela Mesquita, você é uma pessoa ímpar, de um coração de ouro, sempre disposta a ajudar no que preciso for! Obrigada por tudo! Te love! **Suely**, você é um grande exemplo, pessoa boa, de um coração gigante! Obrigada por todo apoio sempre, e por ser essa sido uma amiga durante todo o meu período de Pos Graduação. **Laís**, minha querida amiga, por você tenho um grande carinho, obrigada por tudo! **Monise**, voce é um grande presente que a Ufu me deu! Sou muito feliz e abençoada por ter amigos como você! **Maria Teresa** obrigada pela amizade sincera e por estar sempre disposta a ajudar! Muito obrigada por tudo! **Raissa, Júlia, Ludmilla**, **Andomar**, **Gabriel**, Obrigada a vocês que foram sempre solicitos em tudo que precisei! obrigada por tudo, por toda ajuda e amizade! Vocês são muito especiais!!!!

Ao ***ex-aluno de Pós-doutorado Tales Cândido***

Querido Tales, muito obrigada pela troca de experiências durante o tempo que esteve conosco em Uberlândia! Gratidão por toda ajuda, e pela amizade que fica com lembranças de muitos bons momentos!

Ao ***ex-aluno de graduação e iniciação científica João Vitor***

Querido João, obrigada por tudo! Com você aprendi do início ao fim o que é o gostinho de co-orientar um trabalho. Com você aprendi e ensinei! Obrigada pela disponibilidade e paciência durante a minha trajetória!

À ***Universidade Federal de Uberlândia e a Faculdade de Odontologia***

Instituição que me possibilitou o acesso à Pós–graduação, onde fui bem recebida e posso dizer com grande alegria que foi minha segunda casa pelos últimos 7 anos. Permitiu adquirir e compartilhar conhecimento. Muito obrigada FOUFU, sempre levarei seu nome onde quer que eu vá!

À ***CAPES, FAPEMIG e CNPq***

Sou imensamente grata a todo apoio financeiro que me foi cedido pela Capes, que foi de extrema importância para que eu pudesse cursar o estágio sanduíche no exterior. Muito obrigada também a Fapemig pelo apoio financeiro que muito me auxiliou enquanto não tinha trabalho.
Ao CnPQ muito obrigada a todo apoio financeiro cedido para colaboração na execução desse trabalho.

A ***todos os amigos de trabalho e coordenadores da Saúde Bucal de Uberlândia, onde exerço minha profissão nos últimos dois anos...***
Em especial aos amigos Ana Carla, Ana Márcia, Daiane, Fabiane, Kellen, Laura, Paula, Ondina, e a todos aqueles que fazem parte da minha rotina diária de trabalho, muito obrigada por acreditarem que o conhecimento é o que transforma, melhorando a qualidade de vida da população, e por me apoiarem nos momentos que mais precisei!

Aos ***inúmeros amigos que a vida me deu***

Gratidão a Deus por tantos amigos! Me sinto abençoada pois são tantos e cada um com o seu jeito especial transformam a minha vida!

Sou feliz por tê-los na minha vida!

EPÍGRAFE

"Suba o primeiro degrau com Fé. Não é necessário que você veja toda a escada. Apenas dê o primeiro passo."

Martin Luther King

SUMÁRIO

Resumo

RESUMO

As resinas compostas tornaram-se a primeira escolha para restaurações diretas tanto para dentes anteriores quanto para posteriores. A grande popularidade para do uso desses materais está relacionada à aparência estética e a possibilidade preparos menos invasivos, reduzindo a necessidade de remoção de tecidos sadios. Resinas composta viabiliza ainda reconstituição coronária, promovendo a reabilitação e estética de forma mais acessível. O desempenho clínico das resinas compostas é influenciado por diversos fatores, como biológicos, mecânicos e estéticos. Este estudo teve por objetivo geral avaliar características inerentes aos materiais que interferem na polimerização. Três objetivos integram esse estudo; **objetivo específico 1:** investigar a influência do sistema fotoiniciador na cinética de polimerização de monômeros à base de metacrilamida como alternativa aos metacrilatos em materiais dentários adesivos; **objetivo específico 2:** desenvolver um dispositivo de laboratório para padronização de radiografias usando filmes convencionais e sensores digitais, validando o mesmo por meio de análise de radiopacidade de resinas compostas; **objetivo específico 3**: avaliar o efeito de fontes de luz de espectro único ou multi-espectros nas propriedades mecânicas expresso pela dureza Knoop, grau de conversão e módulo de elasticidade de resinas compostas convencional e bulk fill com diferentes fotoiniciadores. Em conclusão, a cinética de polimerização foi afetada pelos fotoiniciadores para ambos os monômeros testados. A viscosidade aumentou significativamente com a incorporação de metacrilamida secundária. Este trabalho demonstrou a viabilidade do uso de monômeros de metacrilamida recém sintetizados em conjunto com sistemas iniciadores já usados em materiais comerciais. Resinas compostas convencionais e bulk fill exibiram nível de radiopacidade adequado. Os métodos radiográficos digitais e os processos de imagem testados mostraram capacidade de classificação de similaridade para todas as resinas compostas testadas. O dispositivo desenvolvido foi capaz de padronizar os métodos radiográficos usados para avaliar a radiopacidade dos materiais restauradores. As resinas compostas Vittra APS, Opus Bulk Fill APS e Tetric Evoceram Bulk Fill apresentaram valores adequados de dureza Knoop, grau de conversão e módulo de elasticidade nas análises realizadas na superfície e na profundidade de 2,0mm. As fontes de luz Bluephase e VALO Cordless, resultaram em maiores valores de dureza Knoop, grau de conversão e módulo de elasticidade quando comparadas às fontes de radiical plus e optilight max independente da resina testada. O sistema fotoiniciador tende a influenciar menos os resultados do que o desempenho das fontes de luzes.

Palavras – Chave: monômeros alternativos, resinas compostas bulk fill, fotoiniciador, propriedades mecânicas, radiopacidade, fontes de luz, dureza koop, grau de conversão.

Abstract

ABSTRACT

Resins composites have become the first choice for direct restorations for anterior and posterior teeth. The great popularity for the use of these materials is related to the aesthetic appearance and the possibility of less invasive procedure, reducing the need of removal of healthy tissues. Resins composite also enable coronary reconstruction, promoting rehabilitation and aesthetics in a more accessible way. The performance of resin composites can be influenced by several factors, such as biological, mechanical and aesthetic. The general objective of this study was to evaluate characteristics inherent to materials that can interfere with the polimerization. Three objectives are part of this study; **specific objective 1:** to investigate the influence of the photoinitiator system on the polymerization kinetics of methacrylamide-based monomers as an alternative to methacrylars in adhesives of dental materials; **specific objective 2:** to develop a laboratory device for standardization of radiographs using conventional films and digital sensors, validating it through radiopacity analysis of composite resins; **specific objective 3**: to evaluate the effect of single spectrum or multi-spectrum light sources on the mechanical properties expressed by Knoop hardness, degree of conversion and modulus of elasticity of conventional and bulk fill resins composite with different photoinitiators systems. In conclusion, polymerization kinetics was affected by photoinitiators for both monomers tested. Viscosity increased significantly with the incorporation of secondary methacrylamide. This work demonstrated the viability of using newly synthesized methacrylamide monomers in conjunction with primer systems already used in commercial materials. Conventional and bulk fill resins composite exhibited adequate radiopacity level. The digital radiographic methods and imaging processes tested showed similarity classification capacity for all resins composite tested. The developed device was able to standardize the radiographic methods used to evaluate the radiopacity of restorative materials. The composite resins Vittra APS, Opus Bulk Fill APS and Tetric Evoceram Bulk Fill showed adequate values of Knoop hardness, conversion gradu and modulus of elasticity in the analyses performed on the surface and at the depth of 2.0mm. The Light Sources Bluephase and VALO Cordless resulted in higher values of Knoop hardness, degree of conversion and modulus of elasticity when compared to the sources independent of the tested resin. The photoinitiator system tends to influence the results less than the performance of light sources.

Keywords: alternative monomers, bulk fill resin composite, photoinitiator, mechanical properties, radiopacity, light sources, koop hardness, degree of conversion.

Introdução e Referencial Teórico

1. INTRODUÇÃO E REFERENCIAL TEÓRICO

Restaurações adesivas realizadas com resinas compostas vêm sendo amplamente utilizadas na prática clínica (Demarco *et al.* 2012; Sabbagh *et al.,* 2016). Muito se deve a evolução de suas propriedades químicas, físicas e mecânicas que mimetizar cada vez mais a estrutura dental (Soares *et al.,* 2017), melhorando a longevidade dos materiais restauradores adesivos (van Dijken & Pallesen 2015; Alkurdi & Abboud 2016). Desde que as resinas compostas foram desenvolvidas há mais de 60 anos muitas mudanças aconteceram com intuito de aperfeiçoar suas propriedades, principalmente nos sistemas de carga, e eficiência do sistema fotoiniciador (Ferracane, 2011; Fugolin & Pfeifer, 2017). Ao mesmo tempo avanços tecnológicos vêm sendo alcançados nas fontes luz que induzem a polimerização (Rueggeberg 2011; Shimokawa *et al.,* 2018). Esses avanços tornaram os materiais restauradores adesivos opção popular para restaurações em dentes posteriores e anteriores para restaurações diretas (Demarco *et al.*, 2012). No entanto, a durabilidade clínica de materiais diretos adesivos ainda é desafior, e pode levar a substituições de restaurações mais frequente quando se negligência pontos importantes como por exemplo a fonte de luz a ser utilizada (Demarco *et al.,* 2012).

Nos dias atuais, um dos protocolos mais utilizados para restaurações com resinas compostas convencionais é definido pela técnica incremental. Porém, com o objetivo de simplificar procedimentos bem como melhorar desempenho clínico das restaurações em resinas compostas, foram desenvolvidas as resinas composta do tipo *Bulk fill* que propiciam o seu uso em incremento de até 4 a 5mm (Ilie & Stark 2014; Leprince *et al.,* 2014).

As características inerentes às resinas compostas como dureza e grau de conversão, são propriedades que impactam no sucesso clínico das restaurações em dentes posteriores (Fronza *et al.,* 2015). Materiais com baixa dureza de superfície são mais suscetíveis ao desgaste e geram superfícies rugosas o que compromete a resistência à fadiga do material, e pode sugerir falhas clínicas prematuras das restaurações (Monterubbianesi *et al.,* 2016). O desempenho de restaurações em resinas compostas pode ser afetado negativamente por parâmetros como grau de conversão e dureza (Da Silva *et al.,* 2008a). Alto grau de conversão pode refletir em boas propriedades mecânicas, estabilidade química, além de boa longevidade da restauração (Miyazaki *et al.,* 2003; Da Silva *et al.,* 2008b). Outra propriedade importante é a radiopacidade, propriedade essencial dos materiais restauradores, que permite avaliar a integridade das restaurações, detecção de cárie secundária, espaços vazios, e até mesmo desadaptação nas margens e também contato com dentes adjacentes (Ferracane, 2017; Gul *et al.,* 2017). As resinas compostas precisam ser suficientemente radiopacas para permitir a diferenciação entre esmalte e dentina (Dukic *et al.*, 2012). Diversos sistemas convencionais e digitais vem sendo utilizados para testar essas propriedades em técnicas incremental e bulk fill (Soares *et al.,* 2017; Berti et al., 2020).

Sugere-se que um dos principais requisitos para garantir o sucesso clínico das resinas compostas é a fotoativação com a fonte de luz adequada (Santini & Turner, 2011; Price *et al.,* 2015). Considera-se que a ativação da polimerização das resinas compostas por meio da luz é um processo complexo dependente também do tipo de fotoiniciadores (Rueggeberg, 2017; Gan *et al.,* 2018). Durante o processo restaurador é importante ter certeza de que todo o material está recebendo luz suficiente nos comprimentos de onda corretos que reflita em polimerização satisfatória (Leprince *et al.,* 2013; Braga *et al.,* 2020). O fotoiniciador é capaz de absorver luz e consequentemente de forma direta ou indiretamente iniciar o processo de polimerização dos monômeros resultando na formação de cadeias poliméricas (Pfeifer *et al.*, 2009). A forma como os fotoiniciadores convertem monômeros em polímeros, são influenciados por variedade de fatores, como composição do material, tipo e concentração de fotoiniciador presente, assim como no espectro e na transmissão de luz através do material (Stansbury, 2000; Santini *et al.,* 2013).

Importante evidenciar que na composição da matriz orgânica, os monômeros têm a função de estruturar um material que possa ser adaptado no interior da cavidade, restaurando a estrutura dental perdida após sua polimerização. Dentre os monômeros mais utilizados, destacam-se o Bis-GMA (Bisfenol glicidil dimetacrilato) e o UDMA (uretano dimetacrilato), denominados monômeros de alto peso molecular, e os monômeros diluentes como TEGDMA (trietilenoglicol dimetacrilato) e EGDMA (etilenoglicol dimetacrilato), de baixo peso molecular (Emami *et al*., 2003). Uma alternativa adequada para superar esse problema depende da incorporação de monômeros livres de éster na formulação da matriz orgânica. As methacrilamidas têm se mostrado opções promissoras para formulações de adesivos dentários no intuito de melhorar assim o desempenho das restaurações adesivas (Rodrigues *et al.*, 2018; Fugolin *et al.* 2019; Barcelos *et al.,* 2020)

Diante o exposto, o objetivo geral deste trabalho foi avaliar o comportamento de monômeros alternativos com diferentes sistemas fotoinicadores durante o processo de polimerização, assim como a influência de diferentes tipos de fontes de luz nas propriedades de resinas compostas disponíveis comercialmente.

Objetivos

2. OBJETIVOS

2.1 Objetivo Geral

Avaliar o comportamento de monômeros alternativos com diferentes sistemas fotoinicadores durante o processo de polimerização, assim como a influência de diferentes tipos de fontes de luz e o efeito da composição nas propriedades de resinas compostas disponíveis comercialmente.

2.2 Objetivos Específicos

Objetivo específico 1

Capítulo 1 - *Effect of the photoinitiator system on the polymerization of secondary methacrylamides of systematically varied structure for dental adhesive applications*

O objetivo deste estudo foi investigar a influência do sistema fotoiniciador na cinética de polimerização de monômeros à base de metacrilamida como alternativa aos metacrilatos em adesivos de materiais dentários.

Objetivo específico 2

Capítulo 2 - *Development of device for radiopacity analysis of resin composites using different radiographic methods.*

Este estudo teve como objetivo desenvolver um dispositivo de laboratório para padronização de radiografias usando filmes convencionais e sensores digitais, validando o mesmo por meio de análise de radiopacidade das resinas compostas.

Objetivo específico 3

Capítulo 3 - *Bulk fill or conventional resin composites – interaction between mono and multi-peak light-curing units and photoinitiator are a concern in nondeep posterior cavities?*

Avaliar o efeito de fontes de luz de espectro único ou multi-espectros nas propriedades mecânicas expresso pela dureza Knoop, grau de conversão e módulo de elasticidade de resinas compostas convencional e bulk fill com diferentes fotoiniciadores.

Capítulos

Capítulo 1

3.1 CAPÍTULO 1

Effect of the photoinitiator system on the polymerization of secondary methacrylamides of systematically varied structure for dental adhesive applications

Artigo publicado no periódico **Dental Materials**

DENTAL MATERIALS 36 (2020) 468–477

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.intl.elsevierhealth.com/journals/dema

Effect of the photoinitiator system on the polymerization of secondary methacrylamides of systematically varied structure for dental adhesive applications

L.M. Barcelos[a], **M.G. Borges**[a], **C.J. Soares**[a], **M.S. Menezes**[a], **V. Huynh**[b], **M.G. Logan**[b], **A.P.P. Fugolin**[b], **C.S. Pfeifer**[b],*

[a] *Department of Operative Dentistry and Dental Materials, School of Dentistry, Federal University of Uberlandia, Brazil*

[b] *Department of Restorative Dentistry, Biomaterials and Biomechanics, School of Dentistry, Oregon Health & Science University, United States*

ARTICLE INFO

Article history:
Received 23 August 2019
Received in revised form
8 January 2020
Accepted 19 January 2020

Keywords:
Photoinitiator
Polymerization kinetics
Methacrylamide-based monomers
Methacrylates monomers
Adhesive system

ABSTRACT

Objective. The aim of this study was to investigate the influence of the photoinitiator system on the polymerization kinetics of methacrylamide-based monomers as alternatives to methacrylates in adhesives dental-based materials.

Methods. In total, 16 groups were tested. Monofunctional monomers (2-hydroxyethyl methacrylate) – HEMA; (2-hydroxy-1-ethyl methacrylate) –2EMATE, (2-hydroxyethyl methacrylamide) – HEMAM; and (N-(1-hydroxybutan-2-yl) methacrylamide) –2EM; were combined with bifunctional monomers containing the same polymerizing moieties as the monofunctional counterparts (HEMA-BDI; 2EMATE-BDI; HEMAM-BDI; and 2EM-BDI) at 50/50 M ratios. BHT was used as inhibitor (0.1 wt%) and the photoinitiators used were: CQ + EDMAB (0.2/0.8), BAPO (0.2), IVOCERIN (0.2), and DMPA (0.2), in wt%. The polymerization kinetics were monitored using Near-IR spectroscopy (~6165 cm^{-1}) in real-time while the specimens were photoactivated with a mercury arc lamp (Acticure 2; 320–500 nm, 300 mW/cm^{2}) for 5 min, and maximum rate of polymerization (Rp$_{max}$, in %.s^{-}–^{1}), degree of conversion at Rp$_{max}$ (DC@Rp$_{max}$, in %), and the final degree of conversion (Final DC, in %) were calculated (n = 3). Initial viscosity was measured with an oscillating rheometer (n = 3). Data were analyzed using Two-way ANOVA for the polymerization kinetics and one–way ANOVA for the viscosity. Multiple comparisons were made using the Tukey's test (∝ = 0.05).

Results. There was statistically significant interaction between monomer and photoinitiator ($p < 0.001$). For the methacrylates groups, the highest Rp$_{max}$ was observed for HEMA + DMPA and 2EMATE + BAPO. For methacrylamides groups, the highest Rp$_{max}$ were observed for HEMAM and 2EM, both with DMPA. Final DC was higher for the methacrylate groups, in comparison with methacrylamide groups, independent of the photoinitiators. However, for the methacrylamide groups, the association with BAPO led to the lowest values of DC. In terms of DC@Rp$_{max}$, methacrylate-based systems showed significantly higher values than

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* *Corresponding author at*: Biomaterials and Biomechanics, OHSU, 2730 SW Moody Ave, Portland, OR, 97201, United States.
E-mail address: pfeiferc@ohsu.edu (C.S. Pfeifer).

https://doi.org/10.1016/j.dental.2020.01.020

methacrylamide formulations. DMPA and Ivocerin led to higher values than CQ/EDMAB and BAPO in methacrylamide-based compounds. BAPO systems showed de lowest values for both HEMA and HEMAM formulations. For the viscosity (Pa.s), only 2EM had higher values (1.60 ± 0.15) in comparison with all monomers. In conclusion, polymerization kinetics was affected by the photoinitiators for both monomers. Viscosity was significantly increased with the use of secondary methacrylamide.

Significance. this work demonstrated the feasibility of using newly-synthesized methacrylamide monomers in conjunction with a series of initiator systems already used in commercial materials.

1. Introduction

The composition of the vast majority of dental adhesive systems available on the market includes methacrylates, mainly because their chemical and mechanical properties have shown satisfactory results in this application [1]. The mono-methacrylate 2-Hydroxyethyl (HEMA) was incorporated in the composition in the late 1960's due to its "water-chasing" capabilities, which in turn allowed for wet bonding to the dentin substrate using total etch techniques [1]. Until the introduction of more hydrophilic adhesive compositions, the bonding could only be reliably performed within enamel margins, so the introduction of bonding to dentin and the novel description of the hybrid layer were revolutionary [2]. However, since that time, in spite of active research in the area [3,4], very few products with monomers different from HEMA have been introduced in the market. The clinical studies that followed this products have demonstrated acceptable performance [5,6], in spite of lower in vitro results compared to other commercial products [7]. There is interest in pursuing alternatives to HEMA, since this monomer imparts significant water sorption and solubility to the adhesive, and contains ester bonds that make it prone to hydrolysis in the oral environment [4,8,9]. In addition, studies have shown that the degradation of methacrylates is accelerated at low pH, a common condition in some adhesive compositions and also when caries-forming biofilm is present mainly in gingival margins at proximal surfaces [10–13]. As a result, polymer properties can be compromised, resulting in premature bonding degradation, secondary decay or restoration de-bonding [14,15]. The degradation of the adhesive can also pose toxicity to pulp cells through the dentinal tubules or even to adjacent soft tissues in regions of the restoration close to gingival margins [16].

Since the maintenance of the integrity of the bonded interface is crucial to the longevity of the restoration, novel monomer alternatives such as acrylamides and methacrylamides have been proposed [4,17]. Methacrylamides and acrylamides have an amide group instead of an ester group, which makes them less prone to degradation in the oral environment. This is due to the fact that the electronegativity of the nitrogen is greater than the oxygen present in the methacrylate, which stabilizes the bond via resonance with the lone pair [18]. The energy required to break the bond between the carbon in the carbonyl and the nitrogen in the amide is much greater than the energy required to break the bond with the oxygen in the methacrylate [19]. Therefore, it can be envisioned that these monomers will be less prone to the hydrolysis via acid-base reactions in aqueous environment, and even through the great advantage from the bond preservation standpoint. Also it means that the vinyl bond attached to the methacrylamide is more stable, which leads to concerns over the reactivity of acrylamides and methacrylamides [17]. Previous study has demonstrated that steric constraints such as the ones observed in tertiary methacrylamides significantly reduce monomer reactivity [20].

One approach to circumvent the lower reactivity of methacrylamides is to use initiator systems with greater quantum yields than what is observed for the conventional camphorquinone/amine pair [21]. The efficiency of this Norrish-type photoinitiator system can be improved by the addition of electron acceptors such as diphenyl iodonium salts [22]. Studies with methacrylate monomers have shown significantly improved rates of polymerization and conversion with the addition of iodonium salt concentrations of around 1 mol% [22]. In addition, the use of cleavage-type photoinitiators such as phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide (BAPO) and 2,2-dimethoxy-2-phenylacetophenone (DMPA) can also improve reactivity, since they rely on a single electron transfer event to generate twice the amount of radicals compared to CQ/amine [23]. In fact, their quantum yields of conversion are two to four-fold that of the CQ/amine pair [23]. More recently, photoinitiators based on germanium chemistry have also been described [24]. These are also cleavage-type initiators, and have been shown to be suitable for the polymerization of methacrylates and methacrylamides [25]. Bis-(4-methoxybenzoyl)diethyl germane (brand name Ivocerin, Ivoclar-Vivadent, Liechtenstein) and BAPO can be activated by visible light, at a slightly shorter wavelengths compared to CQ (405 and 470 nm, respectively), which also improves light penetration through the bulk of the material [26].

The present study had two distinct aims: firstly was to develop alternative monomers to BisGMA and HEMA, based on secondary methacrylamides, for future potential use as adhesive monomers. The monomers were prepared with systematically varied structures to allow for the assessment of the effect of steric hindrance on the kinetics of polymerization. Methacrylate analogs with similar steric constraints were also synthesized to allow for direct comparisons with the novel methacrylamides. Secondly was to evaluate the polymerization kinetics of these monomers when in combination with different types of initiators, including the conventional CQ/amine and three other examples of cleavage-type initiators. The null hypotheses of this study were: (1) the methacrylamide-based monomers would have the same polymerization kinetics behavior as the methacrylate-based monomers, and (2) the polymerization kinetics would not be influenced by the type of initiator used.

2. Material and methods

2.1. *Monomer synthesis, material composition, and specimen preparation*

Unless otherwise noted, all commercially-available materials were obtained from Sigma-Aldrich (Milwaukee, WI, USA). The synthesis procedures for the materials produced *de novo* are described in the supplemental materials. Four different monofunctional monomers were used: two commercially available (2-hydroxyethyl methacrylate (HEMA); and N-hydroxyethyl methacrylamide (HEMAM)) and two synthesized *de novo* (α-substituted methacrylate 2-hydroxy-1-ethyl methacrylate (2EMATE); and 2-hydroxy-1-ethyl methacrylamide (2EM)). The OH-bearing monofunctional monomers were then reacted with a difunctional isocyanate (1,3-bis (1-isocyanato-1-methylethylbenzene) – BDI) at 2:1 mol ratio, resulting in difunctional urethanes. The structures of all monomers used in this study are shown in Fig. 1.

Each monofunctional monomer was combined at 50:50 mass ratio with the corresponding difunctional urethane, resulting in four different monomer systems – HEMA+HEMA-BDI, 2EMATE+2EMATE-BDI, HEMAM+HEMAM-BDI and 2EM+2EM-BDI. For simplicity's sake, throughout the manuscript, the groups containing a pair of monofunctional monomer plus its analogous difunctional monomer with the BDI core will be referred to by the name of the monofunctional monomer. For example, HEMA+HEMA-BDI will be referred to as HEMA. These were made photopolymerizable by the addition of one of the following four photoinitiator systems: 0.2/0.8 wt% dl-camphoroquinone/ethyl 4-dimethylaminobenzoate (CQ/EDMAB – λ_{max} = 470 nm), 0.2 wt% phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide (BAPO – λ_{max} = 380 nm); 0.2 wt% 2,2-dimethoxyphenoxy acetophenone (DMPA – λ_{max} = 365 nm); or 0.2 wt% bis-(4-methoxybenzoyl)diethyl germane (IVOCERIN^{TM}, donated by Ivoclar-Vivadent, Schaan, Liechstein – λ_{max} = 405 nm). 0.1 wt% 2,6-di-tert-butyl-4-methylphenol (BHT) was used as inhibitor. Materials were formulated under filtered yellow lights. Molecular structures for photoinitiator systems are shown in Fig. 2.

2.2. *Viscosity*

The initial viscosity in Pa.s n = 3 was measured with an oscillating rheometer DH-R1, TA Instruments, New Castle, DE, USA. Approximately 20 mg of each monomer mixture were placed between 20-mm diameter plates separated by a 300 μm gap, and tested at room temperature with strain rate ranging from 10 to 1000 Hz flow sweep mode.

2.3. *Photopolymerization reaction kinetics and degree of conversion*

Specimens were made using a rubber mold 10 mm in diameter and 0.8 mm thick, laminated between two glass slides. Polymerization kinetics (n = 3) was monitored using near–infrared (NIR) spectroscopy in real time. The vinyl overtones for the methacrylate and methacrylamide (6165 and 6135 cm^{-1}, respectively) were followed with 2 scans per spectrum at 4 cm^{-1} resolution, resulting in 2 Hz data acquisition rate. The test was recorded continuously during 300 s of irradiation with a mercury arc lamp filtered to 320–500 nm (Acticure 4000, EXFO, Mississauga, ON, Canada). The tip of the light guide was positioned 1.5 cm away from the surface of the specimen, so to deliver approximately 300 mW/cm^2. Selected groups (HEMA and HEMAM-containing materials) were also evaluated using a mono-wave LED light source (Elipar, 3M-ESPE, St. Paul, MN, USA), centered at 470 nm and delivering an irradiance of 840 mW/cm^2 to the surface of the specimen for 60 s. Polymer conversion was calculated based on the area of the overtone peak before and during polymerization [27], and the rate of polymerization was calculated as the first derivative of the conversion vs. time curve.

2.4. *Characterization of the light curing units*

The emission spectra and irradiance of all light curing units (LCU) used in this study were obtained using a UV–vis detector (MARC Resin Calibrator, Blue Light Analytics Inc., Halifax, NS, Canada). The tip of the LCU was positioned parallel to the surface of the top detector, separated by 1.5 cm to mimic the conditions of the polymerization kinetics on the IR chamber. Spectra were recorded after light stabilization, 5 s after power up. The irradiance for each individual wavelength band was calculated in mW/cm^2.

2.5. *Characterization of the absorption spectra of each photosensitizer*

Each initiator (0.008 g of EDMAB and 0.002 g of the others) was dissolved in 1 ml of ethanol. These concentrations were selected to match the mass ratio of initiators in the materials as tested. Therefore, the results are reported in arbitrary units, rather than in molar absorptivity units. The solutions were placed in UV-transparent cuvettes and UV–vis spectra (300–540 nm) were obtained using a UV–vis spectrophotometer (Evolution 201, Thermo Fisher Scientific, Waltham, MA), with 1 nm sampling interval.

2.6. *Statistical analysis*

The data was tested for normality (Anderson-Darling) and homoscedasticity (Bartlett/Levene). Degree of conversion, maximum rate of polymerization and conversion at rate maximum data were analyzed with two-way ANOVA (monomer type and photoinitiator system). The data for initial monomer viscosity failed the normality and homocedasticity tests, so one-way ANOVA was performed on ranks (Kruskall-Wallis). Multiple comparisons were done using Tukey's test. The significance level of 95% was used for all tests.

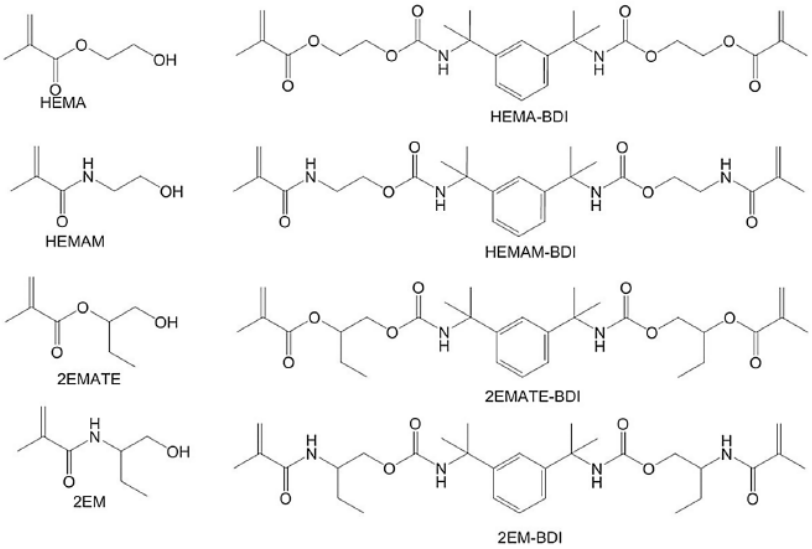

Fig. 1 – Molecular structure of all monomers used in this study. The monofunctional monomers were HEMA (2-hydroxyethyl methacrylate), HEMAM (2-hydroxyethyl methacrylamide), 2EMATE (2-hydroxy-1-ethyl methacrylate) and 2EM (2-hydroxy-1-ethyl methacrylamide) – the latter two bearing one ethyl substituent on the alpha-carbon. The di-functional monomers were produced by reacting 2 mols of each of the monofunctional monomers with 1 mol of BDI (1,3-bis (1-isocyanato-1-methylethylbenzene)). The monomethacrylate monomers were used in combination with dimethacrylate monomers of analogous polymerizable structure, at a mass ratio of 50–50.

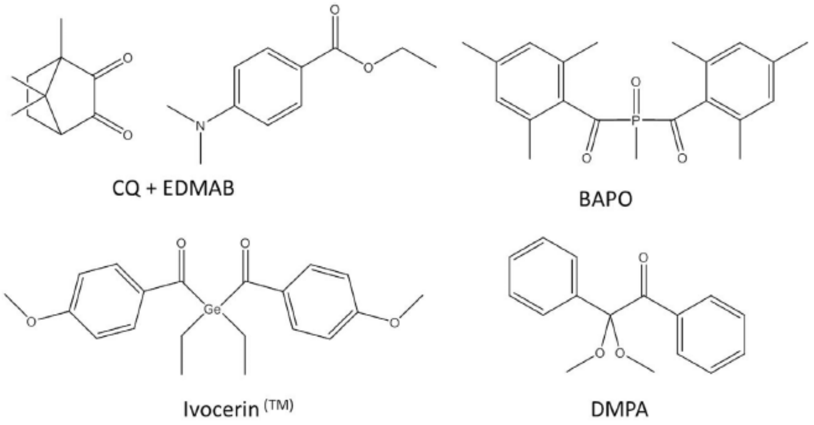

Fig. 2 – Photoinitiator systems used in this study: CQ + EDMAB (dL-camphorquinone + Ethyl 4-dimethylaminobenzoate), BAPO (phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide), DMPA (2,2-dimethoxyphenoxy acetophenone) and Ivocerin ^{TM} (bis-(4-methoxybenzoyl)diethyl germane, kindly donated by Ivoclar-Vivadent).

3. Results

3.1. Viscosity

Results for viscosity are presented in Table 1. Both methacrylate-based formulations were statistically similar to each other (HEMA = 0.067 and 2 EMATE = 0.05 Pa.s), and showed statistically lower viscosity than the methacrylamide systems (HEMAM = 3.567 and 2 EM =40.0 Pa.s). The methacrylamide 2 EM monomer system presented the highest viscosity of all materials (p = 0.001; F = 874.7).

3.2. *Light source and photoinitiator spectra*

The emission spectra of the two light curing units used in this study are shown in Fig. 3. The Acticure presents three distinct emission peaks, centered at 365, 405 and 435 nm, with approximately 157, 53 and 90 mW/cm^2 absolute irradiance, respectively. These values were calculated by integrating

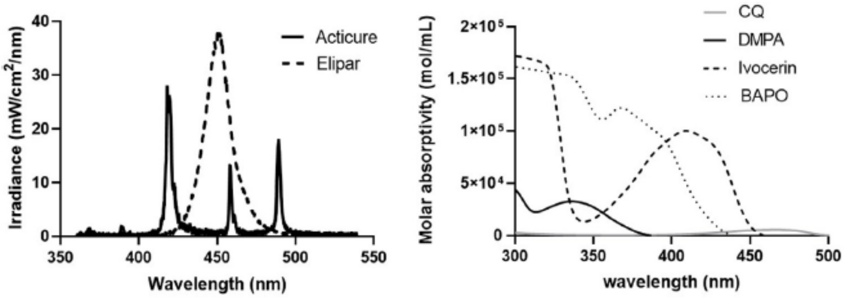

Fig. 3 – Left – Emission spectra for the mercury arc lamp (Acticure) and the commercial LED (Elipar) light sources, obtained with the MARC resin calibrator (values expressed in mW/cm^2/nm). Right – Absorption spectra for each photosensitizer utilized in this study (CQ: camphorquinone; DMPA: 2,2-dimethoxyphenhoxy acetophenone; BAPO: phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide and Ivocerin TM: bis-(4-methoxybenzoyl)diethyl germane.

Table 1 – Mean ± standard deviation for viscosity (Pa s) for the monomer systems tested in this study (HEMA/HEMA-BDI, HEMAM/HEMAM-BDI, 2EMATE/2EMATE-BDI, 2EM/2EM-BDI). Values followed by the same superscript are statistically similar (α = 5%), according to one-way ANOVA on ranks (F = 874.7 and p < 0.001).

Monomer system	Viscosity (Pa s)
HEMA	0.067 ± 0.006 c
2EMATE	0.050 ± 0.007 c
HEMAM	3.567 ± 0.303 b
2EM	40.0 ± 12.578 a

the area under those peaks. The Elipar is a mono-wave LED, with emission spectra centered at 450 nm and irradiance of 840 mW/cm^2. Irradiance for each individual peak is shown in Table 2.

The absorption spectra of the four different photosensitizer molecules are shown in Fig. 3. Absorption maxima and absorption ranges for each photoinitiator system is shown in Table 2.

3.3. *Photopolymerization reaction kinetics and degree of conversion*

Results for degree of conversion and polymerization kinetics obtained with the Acticure are presented in Table 3 and Figs. 4a/b and 5 . In terms of degree of conversion (final DC), two-way ANOVA showed that both factors (monomer and photoinitiator) as well as the interaction between them were statistically significant ($p < 0.001$). The methacrylamide formulations presented lower conversion than the methacrylate counterparts for all photoinitiator systems tested. Within each polymerizing functionality (methacrylate or methacry-

Table 2 – Top — Maximum emission wavelength (nm), range of emission (nm) and irradiance at range (mW/cm^2) for the mercury arc lamp (Acticure) and the commercial LED (Elipar) light sources. Bottom — Maximum absorption wavelength (nm), range of absorption (nm) and potential useful irradiance from the Acticure (calculated as the sum of irradiances at the wavelengths overlapping the absorption ranges of the initiators).

Light source characterization

Light source	Maximum emission wavelength (nm)	Range of emission (nm)	Irradiance at range (mW/cm^2)	
Acticure	365	345–380	157	300
	405	380–410	53	
	435	430–460	90	
Elipar	450	430–480	840	

Photosensitizer characterization

Initiator	Lambda max (nm)	Range of absorption (nm)	Useful irradiance from Acticure (mW/cm^2)
CQ	471	400–500	143
EDMAB	320	300–450	300
DMPA	365	300–390	157
BAPO	380	300–435	236*
Ivocerin TM	405	300–340/340–460	300

* The Acticure provides 26 mW/cm^2 up to 435 nm.

Table 3 – Mean ± standard deviation for degree of conversion (Final DC, %), maximum rate of polymerization (RP_{MAX}, % s^{-1}) and degree of conversion at rate maximum ($DC@RP_{MAX}$, %) for the monomer systems tested in this study (HEMA/HEMA-BDI, HEMAM/HEMAM-BDI, 2EMATE/2EMATE-BDI, 2EM/2 EM-BDI), as a function of the photoinitiator system (CQ/EDMAB, DMPA, BAPO and Ivocerin™). Values followed by the same uppercase letter on the same column or lowercase letter on the same row are statistically similar, according to two-way ANOVA (α = 5%).

Photoinitiator systems	Final DC (%)				RP_{MAX} (% s^{-1})				DC @ RP_{MAX} (%)			
	Methacrylates		Methacrylamides		Methacrylates		Methacrylamides		Methacrylates		Methacrylamides	
	HEMA	2EMATE	HEMAM	2EM	HEMA	2 EMATE	HEMAM	2EM	HEMA	2 EMATE	HEMAM	2EM
CQ/EDMAB	86.2 ± 2.2 ABb	94.6 ± 3.3 Aa	63.8 ± 1.6 Ac	56.1 ± 1.96 Ad	2.1 ± 0.3 Da	1.2 ± 0.2 Dab	0.6 ± 0.1 Cb	1.8 ± 0.2 Cab	42.1 ± 2.4 Aa	48.4 ± 5.3 Aa	1.0 ± 0.1 Cc	8.9 ± 1.5 Bb
DMPA	89.5 ± 2.5 Ab	93.0 ± 0.6 Aa	65.2 ± 3.0 Ac	59.8 ± 4.4 Ad	14.0 ± 0.6 Aa	4.3 ± 0.2 Cb	3.6 ± 0.2 Ab	3.5 ± 0.6 Bb	41.9 ± 2.9 Aa	43.9 ± 1.1 Aa	8.1 ± 1.4 Ac	11.8 ± 0.8 Ab
BAPO	81.1 ± 1.7 Bb	88.3 ± 0.2 Aa	41.7 ± 2.3 Cc	43.8 ± 5.4 Bc	10.6 ± 1.6 Cb	15.1 ± 0.6 Aa	2.2 ± 0.1 Bc	0.9 ± 0.5 Cc	25.5 ± 6.8 Ba	30.2 ± 3.4 Ca	3.9 ± 0.4 Bb	4.0 ± 3.5 Bb
Ivocerin ™	81.4 ± 1.7 ABb	90.9 ± 1.8 Aa	52.2 ± 4.3 Bc	58.7 ± 3.2 Ac	12.4 ± 0.3 Ba	8.9 ± 0.4 Bb	3.6 ± 0.2 Ad	6.7 ± 1.2 Ac	38.0 ± 1.7 Aa	38.7 ± 0.6 Ba	7.4 ± 0.9 Ac	13.0 ± 2.3 Ab
p (monomer)	0.001				0.001				0.001			
p (photoinit.)	0.001				0.001				0.001			
p (interaction)	0.001				0.001				0.001			

lamide), the presence of the ethyl substituent on the alpha carbon led to statistically lower conversion (except for BAPO and Ivocerin with the methacrylamides). The type of initiator system did not affect the conversion outcomes for the alpha-substituted methacrylate. For all the other monomers, BAPO consistently led to the lowest values of conversion.

In terms of maximum rate of polymerization (RP_{MAX}), two-way ANOVA showed that both factors (monomer and photoinitiator) as well as the interaction between them were statistically significant ($p < 0.001$). In general, methacrylamide monomers presented lower rates of polymerization compared to the analogous methacrylate monomers. In general, CQ/amine systems led to the lowest rates of polymerization, but the behaviour of the other three initiators varied widely with the monomer system. For HEMA, the rate of polymerization increased in the order CQ < BAPO < Ivocerin < DMPA. For 2EMATE, the ranking was: CQ < DMPA < Ivocerin < BAPO. For HEMAM, the ranking was: CQ < BAPO < DMPA = Ivocerin. For 2EM, the ranking was CQ = BAPO < DMPA < Ivocerin. In general, the degree of conversion at Rp_{max}, used in this study as an indication of the conversion at the onset of vitrification [28] was statistically lower for the methacrylamides compared to the methacrylate counterparts (Table 3). For BAPO, Rp_{max} was observed earlier in conversion compared to all other adhesives.

For the two materials photoactivated with the commercial LED light source, the final conversion values were 73.3 ± 0.7 and 17.7 ± 3.3 % for HEMA- and HEMAM-based materials, respectively, and the maximum rate of reaction values were 2.2 ± 0.1 and 1.0 ± 0.1% s^{-1} for HEMA- and HEMAM-based materials, respectively (Fig. 4b).

4. Discussion

The use of methacrylamide monomers as replacements for methacrylate counterparts in dental material compositions was evaluated in this study. The rationale is the absence of hydrolytically unstable ester bonds in methacrylamides, which has shown potential for decreased degradation in aqueous environments and in the presence of enzymes [19,29]. Methacrylamides have also been demonstrated to be less reactive when polymerized via radical-mediated methods [17], and therefore, the objective of this study was to evaluate the effect of different photoactivated radical initiator systems on the polymerization kinetics of methacrylamides. The study design included monomers with alkyl substituents on the alpha carbon, which has been shown to increase reactivity [30] and decrease the likelihood for hydrolytic degradation [31]. In general, based on the results obtained, the null hypotheses of the study were rejected, as methacrylates and methacrylamides presented distinct behaviors, which were influenced by the initiator used.

In general, both methacrylamide monomers polymerized at a slower rate and to a lesser extent compared to the methacrylate counterparts. The presence of the lone pair on the nitrogen provides resonance stabilization to the methacrylamide bond, and while this is advantageous from the standpoint of potentially protecting it from hydrolytic degradation, it also causes the vinyl bond to be more sta-

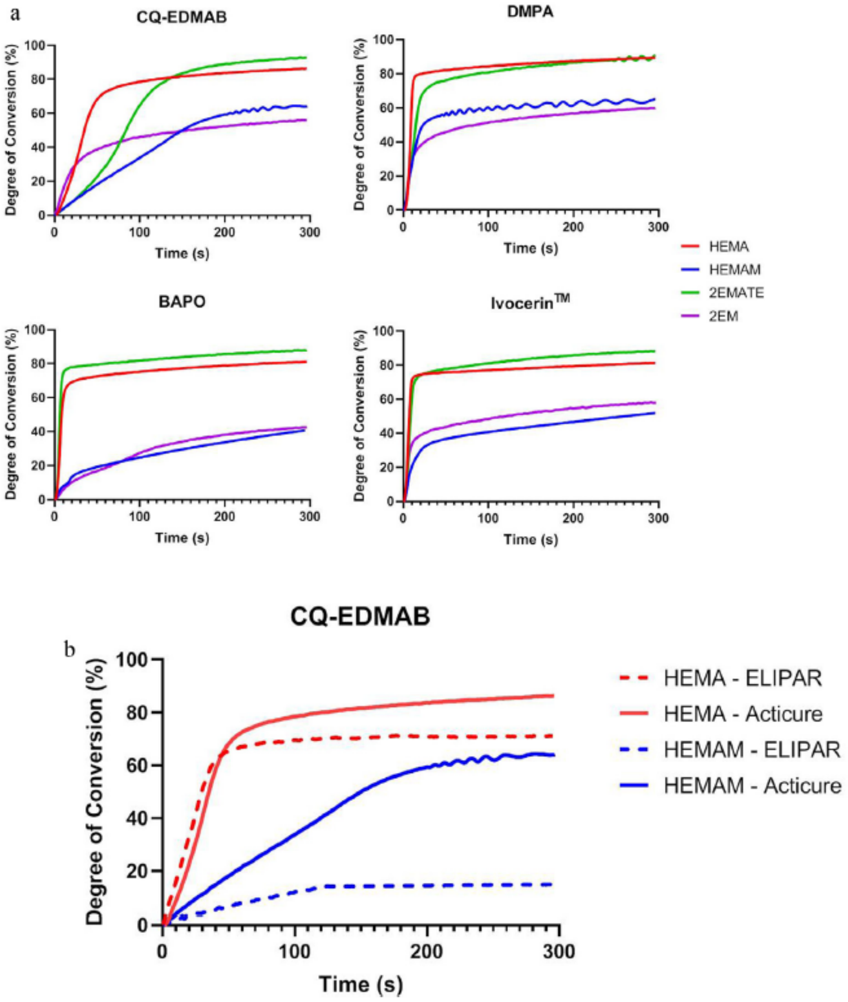

Fig. 4 – (a) Polymerization kinetic profiles (degree of conversion as a function of time) for the methacrylate- (HEMA and 2 EMATE) and methacrylamide-terminated (HEMAM and 2EM) monomers used in this study. Photoinitiator systems used in this study: CQ + EDMAB (dL-camphorquinone + Ethyl 4-dimethylaminobenzoate), BAPO (phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide), DMPA (2,2-dimethoxyphenoxy acetophenone) and Ivocerin ™ (bis-(4-methoxybenzoyl)diethyl germane, kindly donated by Ivoclar-Vivadent). Photopolymerization kinetics was followed in near-IR in real time, while the materials were exposed to 300 mW/cm^2 (320–500 nm) for 5 min. (b) Polymerization kinetic profiles (degree of conversion as a function of time) for one methacrylate- (HEMA) and one methacrylamide-terminated (HEMAM) combined with CQ + EDMAB (dL-camphorquinone + Ethyl 4-dimethylaminobenzoate) as the photoinitiator system. Photopolymerization kinetics was followed in near-IR in real time, while the materials were exposed to 300 mW/cm^2 (320–500 nm) for 5 min with a mercury arc lamp (Acticure) or to 840 mW/cm^2 (440–480 nm) for 60 s with a mono-wave LED light source (Elipar, 3M-ESPE).

ble and less susceptible to propagation in the presence of free radicals [20]. In addition, the methacrylamides produced higher viscosity mixtures, which affects the initial kinetics of polymerization [28]. In higher viscosity systems, diffusional limitations to termination, and subsequently, to propagation, take place earlier in conversion, as evidenced by the much lower conversion at Rp_{max}, used in this study as a proxy for the onset of vitrification [28]. This helps explain both the lower rate and lower limiting conversion achieved by methacrylamides in this study.

The effect of the presence of alkyl substituents was less pronounced, but statistical differences in final conversion were found within the same polymerizable functionality (methacrylate or methacrylamide) for a given initiator system. In general, conversion was lower for all alpha-substituted monomers, with only two exceptions (methacrylamides polymerized with BAPO and Ivocerin), when the conversion values were statistically similar for HEMAM and 2EM, within the same initiator. The decreased conversion is explained by steric hindrance around the vinyl functionality [30]. That same sta-

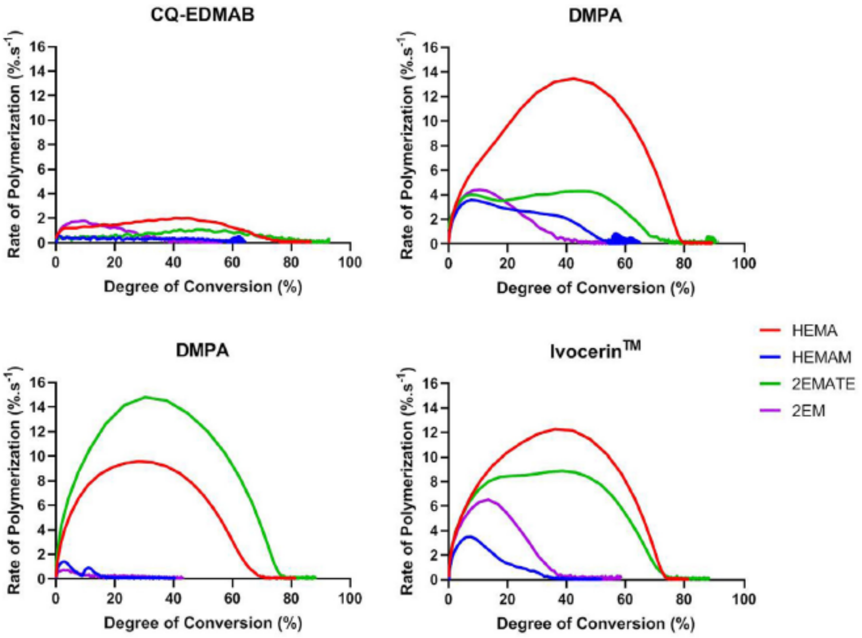

Fig. 5 – Polymerization kinetic profiles (rate of polymerization as a function of conversion) for the methacrylate- (HEMA and 2EMATE) and methacrylamide-terminated (HEMAM and 2EM) monomers used in this study. Photoinitiator systems used in this study: CQ + EDMAB (dL-camphorquinone + Ethyl 4-dimethylaminobenzoate), BAPO (phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide), DMPA (2,2-dimethoxyphenoxy acetophenone) and Ivocerin ™ (bis-(4-methoxybenzoyl)diethyl germane, kindly donated by Ivoclar-Vivadent). Photopolymerization kinetics was followed in near-IR in real time, while the materials were exposed to 300 mW/cm^2 (320–500 nm) for 5 min.

bilization is hypothesized to increase stability of the amide and ester bonds when the resulting polymeric network is presented with hydrolytic challenges, which will be the subject of a separate study. In summary, the two mechanisms that increase the hydrolytic stability (lone pair on the nitrogen on the amide bond and the alpha substitution on either monomer type) also lead to decreased monomer reactivity (lower polymerization rates). The effects of the substituent on the rate of polymerization were more complex, and dependent on the initiator system. For CQ/EDMAB, all rates of polymerization were very low, ranging from 0.6 to 2.1% s^{-1}. HEMAM presented the lowest result, but it was only statistically lower than HEMA, showing that even at low rates, it was possible to notice the effect of the stabilization of the vinyl by the resonance provided by the lone pair on the nitrogen of the amide bond. At those lower rate levels, the presence of the alkyl substitution did not affect the results. All other initiators led to much higher rates of polymerization, and in general, the methacrylamides presented lower rates than the methacrylates, as already mentioned. For the methacrylates, DMPA and Ivocerin led to higher rates in the non-substituted monomer (HEMA), while BAPO led to lower rates for HEMA. For the methacrylamides, there was either no difference between HEMAM (non-substituted) and 2EM (bearing the alkyl side chain), as was the case for DMPA and BAPO, or the rate was higher for 2EM, as was the case for Ivocerin.

The differences among initiator systems were due to two well-explored factors: the quantum yield of conversion of each molecule and the irradiance at the wavelength of maximum absorption (λ_{max}) [23,28]. In terms of quantum yield of conversion, CQ has been reported to present the lowest initiator efficiency by each packet of photons absorbed. This is in part due to the fact that CQ is a Norrish-type initiator, whose radical-generating events are dependent both on the bleaching of CQ and on the successful abstraction of a proton from a co-initiator [23]. The band of absorption for CQ is broad, ranging from 400 to 500 nm. At the λ_{max}, centered at 470 nm, the absorption efficiency is maximized, and outside of 470 nm, excitation of the initiator is still possible, albeit less efficient. The light source used in this study was a mercury arc lamp, with three distinct peaks of irradiance, centered at 365, 405 and 435 nm, each with an absolute irradiance of approximately 157, 53 and 90 mW/cm^2, respectively. Of those peaks, CQ overlaps with the ones centered at 405 and 435 nm, and therefore, received useful irradiance totaling approximately 143 mW/cm^2. However, the irradiance at 470 nm was very low. In other words, on top of being the least efficient initiator, the mercury arc lamp did not efficiently overlap CQ's λ_{max}, both of which explain the low rate of polymerization. The degree of conversion was still greater than 50% for all monomers, due to the extended exposure time (5 min), resulting in 50 J/cm^2 radiant exposure. Since the low rates of polymerization obtained did not allow for the assessment of the potential differences among the monomers, HEMA and HEMAM were selected to be tested using a commercial dental mono-wave LED light source, with emission spectrum centered at 450 nm and effective irradiance of 840 mW/cm^2. For HEMA, the rate of polymerization increased as expected, and the final conversion was lower to what was obtained with the mercury arc lamp, also as expected due to the shorter exposure time and consequently lower radiant exposure. Interestingly and unexpectedly, for HEMAM, both the rate and the conversion significantly decreased with the use of the mono-wave LED compared to what was obtained with the mercury arc. This was unexpected because of the direct and exponential relationship between rate of polymerization and irradiance [28], and especially because the wavelengths delivered by the LED light more closely match the absorption spectrum of the photosensitizer CQ [32]. One possible explanation for the higher conversion of HEMAM materials when polymerized with the light source extending to the UV is the fact that the amine co-initiator also has absorption in that range (300–450 nm). Previous reports have demonstrated that when exposed to light at those wavelengths, organic bases (electron donors in this case) can potentially aid in direct radical generation [32]. Therefore, the presence of the amine in Acticure polymerizations helped improve the conversion, while for the mono-wave LED light source, centered at 470 nm, the same was not observed. Another possible explanation relates to the high initial viscosity of HEMAM. This initially hampered the diffusion of polymerizing species, and as a consequence, delayed the onset of diffusion-controlled termination and propagation, keeping the overall rate of polymerization low. For the lower intensity combined with longer exposure (Acticure polymerizations), the final conversion was not affected because the final radiant exposure was much higher. However, for the shorter exposure at higher irradiance (Elipar polymerization), it is likely that most of the radicals generated decayed before any meaningful chain growth could take place, keeping both the rate and the final conversion low.

For all other initiators, the effective irradiance (within the absorption range of each molecule) ranged from 150 mW/cm^2, and that contributed to higher rates of polymerization, as expected [28]. In addition, the increase in comparison with CQ is due to the fact that BAPO, DMPA and Ivocerin are cleavage type initiators, with higher quantum yields of conversion [21]. For those initiators, each photon absorbed has the potential to generate 2 radicals per molecule of initiator, independent of the interaction with a co-initiator. In contrast, for camphorquinone/amine pairs, each photon absorbed can potentially take one CQ molecule to a triplex state, which then has a very short time to interact with the amine to generate one radical [23]. Therefore, the process is expected to be much more efficient for cleavage-type initiators, as long as they are exposed to wavelengths at or close to their lambda max [23]. This was indeed observed for almost all monomer/initiator pairs, with the exception of the 2EMATE combined with DMPA and 2EM combined with BAPO – therefore, both exceptions involve an alpha-substituted monomer. These aspects are likely explained by a complex interplay between the size of the formed radical for each initiator and the steric hindrance around the vinyl radical for the acrylate/acrylamide monomer, as well as possibly due to other electronic effects [30]. Within the limitations of this study, it is not possible to confidently determine which factor was prevalent in explaining these exceptions. However, for the non-substituted monomers, the rate of polymerization was consistently higher for the cleavage-type initiators compared to CQ/amine, as already mentioned.

5. Conclusion

In conclusion, this exploratory study demonstrated that the polymerization of methacrylamides is less efficient and progresses to a lesser extent compared to methacrylate analogues, regardless of the presence of alkyl substitutions on the alpha carbon. Cleavage-type initiators led to faster rates of polymerization compared to CQ/amine, with two exceptions, but that did not translate into higher conversion for any of the monomers tested. Conversion values with CQ/amine, a clinically-relevant initiator system, were above 55% for all materials. Future studies will evaluate monomer and resulting polymer stability to determine whether methacrylamides are a suitable alternative for dental materials applications.

Acknowledgements

The authors thank NIH-NIDCR for the research support to CSP (R15-DE023211; U01-DE023756; R01-DE025280; K02-DE025280), and CAPES (Coordenação de Aperfeiçoamento de Pessoal em Nível Superior) for the scholarship and research support to LMB (88881.135168/2016-01) and FAPEMIG for the scholarship support to MGB (conv. 5.313/15, #11311). The authors thank BlueLight Analytics for making the MARC Resin Calibrator available for this study. The donation of Ivocerin^{TM} (photinitiator) by Ivoclar-Vivadent is also greatly appreciated.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.dental.2020.01.020.

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Capítulo 2

3.2 CAPÍTULO 2

Development of device for radiopacity analysis of resin composites using different radiographic methods.

Artigo a ser submetido para publicação no periódico **Brazilian Oral Research**

Development of device for radiopacity analysis of resin composites using different radiographic methods.

Luciana Mendes Barcelos, João Vitor Goulart, Renata Afonso da Silva Pereira, Tales Candido Garcia da Silva, Gabriella Lopes de Rezende Barbosa, Carlos José Soares

Luciana Mendes Barcelos, DDS, MSc, PhD Student, Department of Operative Dentistry and Dental Materials, Dental School, Federal University of Uberlândia, Uberlândia, MG, Brazil. Phone: +55 34 991063077, e-mail: lucianabarcelos@hotmail.com

João Vitor Goulart, DDS, Department of Operative Dentistry and Dental Materials, Dental School, Federal University of Uberlândia, Uberlândia, MG, Brazil. Phone: +55 34 992521443, e-mail: jvgoulartg@gmail.com

Tales Candido Garcia da Silva, Department of Operative Dentistry and Dental Materials, Dental School, Federal University of Uberlândia, Uberlândia, MG, Brazil. Phone: +55 17 981215107, e-mail: tales_candido@hotmail.com

Renata Afonso da Silva Pereira, DDS, MSc, PhD, Department of Operative Dentistry and Dental Materials, Dental School, Federal University of Uberlândia, Professor, Dental School UNITRI, Uberlândia, MG, Brazil. Phone: +55 34 9978; renatjvalafonso@hotmail.com

Gabriella Lopes de Rezende Barbosa, DDS, MSc, PhD, Professor at Department of Oral Diagnosis, Dental School, Federal University of Uberlândia, Uberlândia, MG, Brazil. Phone: +55 34 993427191, e-mail: gabriellalopes@ufu.br

Carlos José Soares, DDS, MSc, PhD, Professor and Chair at Department of Operative Dentistry and Dental Materials, Dental School, Federal University of Uberlândia, Uberlândia, MG, Brazil. Phone: +55 34 999713472, e-mail: carlosjsoares@ufu.br

Running title: Imaging methods to analyse radiopacity of composite resins.

Corresponding author
Dr. Carlos José Soares
Federal University of Uberlândia, School of Dentistry
Avenida Pará, 1720, Bloco 4L, Anexo A, sala 42, Campos Umuarama.
Uberlândia - Minas Gerais - Brazil CEP. 38400-902
E-mail: carlosjsoares@ufu.br; Phone: +55 34 3225 8106; +55 34 999713472

Original Research: Dental Materials

Development of device for radiopacity analysis of resin composites using different radiographic methods.

Abstract

This study aimed to develop a laboratory device for standardization of radiographs using conventional films and digital sensors for testing the radiopacity of composites resins. To validate the developed device, the radiopacity analysis of composite resins was performed. Specimens with 6.0mm in diameter and 2.0mm in thickness of 6 composite resins: 2 nanohybrid: Z350 - Filtek Z350XT, 3M-ESPE; and VIT- Vittra APS, FGM; and 4 bulk fill: POST - Filtek Bulk fill Posterior, 3M-ESPE; OPR - Opus Bulk Fill Regular, FGM; OPF - Opus Bulk fill flow, FGM; and TET-Tetric Evoceram Bulk fill, Ivoclar, Vivadent. The radiographs were obtained of 6 composite resins and aluminium step wedge on 2 imaging receptors: CMOS sensor (FIT, Acteon); and PSP Plate (VistaScan). Image J and DBSWIN softwares were used to calculate the radiopacity values. Data were analysed by 3-way ANOVA followed by Tukey test (α=0.05). The developed device showed adequate performance to standardize the radiographs. All composites resins showed adequate radiopacity. TET had the highest radiopacity values, followed by POST, Z350 and OPR, which had similar values among them. VIT had the lowest radiopacity level. When PSP system was associated with DBSWIN software, the radiopacity order values for composite resins was the opposite, maintaining the same significant differences. Bulk fill and conventional composite resins exhibit proper radiopacity level. Digital radiographic methods and imaging process tested showed similarity ranking capacity for all composite resins. The developed device was able to standardize the radiographic methods used to assess radiopacity of restorative materials.

Keywords: Resin composites, Radiography, Radiology, In Vitro Techniques.

Introduction

Radiopacity is an essential property of dental restorative materials, allowing to assess the integrity of restorations, detection of secondary caries, voids, overhangs or open margins, and adaptation and its contact with adjacent teeth.[1,2] Resins composites need to be sufficiently radiopaque to allow the differentiation between enamel and dentin.[3] The literature is controversial regarding the most effective level of radiopacity of resins composites to distinguish secondary caries from normal adjacent tooth structure or the restoration.[1] Some studies have reported that the adequate radiopacity level of composite resins should be close to dentin.[4] Others studies reported that it should have equal or slightly greater radiopacity than enamel to accurately distinguish the tooth-restoration margin.[5,6] The International Organization for Standardization (ISO) 4049, defines that the radiopacity of a material must be equal or greater than the same thickness of aluminium wedge step and should not be less than 0.5 mm of any claimed value by the manufacturer.[6] Aluminium is the reference of choice as it is specified to have similar radiopacity when compared to same thickness of dentin, and two times more radiopaque when compared to the enamel .[2,6]

The modification of resin composites over the years include reduction on particle size and increase of the filler content.[7] Moreover, the use of particles with high atomic numbers, such a barium, strontium, and zirconium have been recommended to produce more radiopaque materials.[8] Otherwise, if the material has low radiopacity it could mislead to an inappropriate analysis of adaptability and caries diagnosis.[9]

Digital imaging systems in oral and maxillofacial radiology was introduced in 1989 and gained popularity for its use in dental practice.[2] Digital radiographic analysis can be performed using different softwares available in the market that can be included in the purchased system, free, open-source for download or paid.[10] Digital imaging systems have been widely used for evaluating radiopacity of restorative materials and have advantages as the reduction of x-ray exposure time and no need of film processing.[1,12-14] Additionally, the image manipulation can be improved through basic and advanced softwares that allows a dynamic analysis of the produced images by working with the gray scale and image density and contrast.[12,14] The direct digital sensor (CMOS - Complementary metal – oxide – semiconductor) and the semi-direct plates (PSP - photostimulable phosphor plate) systems can be used in association with different softwares for image assessment.[7,11,14] The standardization of the distance between the x-ray source and specimen for *in vitro* studies should be preserved to create regular exposure during image acquisition. The development of a laboratory device for *in vitro* studies that allows handling different conventional x ray films or digital detectors maintaining the position of the specimen, can deliver more standardized images, more accurate analysis, as well as time saving lab procedures. Therefore, the aim of this study was to develop a laboratory device for obtaining standardized x-ray images of *in* vitro studies as well as to evaluate the radiopacity of conventional and bulk-fill composite resins by radiographs obtained with direct (CMOS) and semi direct (PSP) imaging systems analysed by Image J and DBSWIN softwares. The null hypotheses were: 1) the composition and type of composite resin would not influence their radiopacity values; and 2) the CMOS and PSP digital imaging systems used in combination with Image J and DBSWIN softwares would not modify the values and the ranking of the tested composite resins.

Methodology

Radiograph standardization device development

The radiographic standardization device was designed and produced as demonstrated in Figure 1. The device was proposed in order to promote safety and adequate standardization on the position during the x ray exposure, improving the accuracy on the methodology.

The device construction started with a lead shielding box with 3.0mm of lead barrier and lead glass window. A mechanism was designed and fixed inside the box to support the specimens avoiding the operator exposition to secondary radiation. The mechanism is based on a platform that fits different imaging sensors, plates and conventional films. The device mechanism attached internally to the lead shielding box is a milled Teflon block that slides through two metal guides to adjust the distance of the sample and image receptor. The milled

Teflon block has support to fit different sizes of imaging receptors: sizes #0, 1, 2 or 4.

Specimen preparation

Six different resin composites as shown in Table 1, were selected: Z350 - Filtek Z350 3M ESPE (St Paul, MN, USA); POST - Filtek Posterior Bulk fill 3M ESPE (St Paul, MN, USA); OPR - Opus Bulk fill regular (FGM, Joinville, SC, Brazil); OPF - Opus Bulk fill flow FGM (Joinville, SC, Brazil); VIT - Vittra APS (FGM, SC, Joinville, Brazil); and TET - Tetric Evoceram Bulk fill (Ivoclar, Vivadent, Schaan, Liechtenstein).

The specimens with 6 mm in diameter and 2 mm in thickness were produced (n=5), using Teflon mold and light cured using broad wave light curing unit (Bluephase G2, Ivoclar Vivadent Schaan, Liechtenstein). The light curing unit tip has 9.0mm covered all the diameter of the specimen. The irradiance (1.390 mW/cm^2) was checked using MARC Resin Calibrator (BlueLight Analytics, Halifax, Canada). The mold was positioned over a glass plate and covered by polyester matrix aiming to minimize the bubbles and irregularities, a second glass plate was positioned over the polyester matrix pressing the material in order to standardize the specimen thickness. The light curing tip was positioned touching the polyester matrix and the composite resin was light activated for 20 seconds.

Radiographic procedures and imaging process

Specimens were radiographed using two methods: digital intraoral sensor - CMOS (Complementary metal – oxide – semiconductor) (FIT, size 1, Acteon; Indaiatuba, São Paulo, Brazil); and photostimulable phosphor plate - PSP (VistaScan #2; Durr Dental, Bietigheim Bissingen, Germany). Specimens were properly positioned on the detector next to the aluminium step wedge for both imaging methods inside the device as shown in Figure 1.

The X ray exposure for both methods was performed using an x-ray machine Timex 70 E (Gnatus, Ribeirão Preto, São Paulo, Brazil) 20cm from the specimen with exposure time of 0.10s and operating at 70kV and 7.0 mA. Radiopacity was analysed by two different softwares: ImageJ (version 1.48 software of public domain, Wayne Rasband, National Institutes of Health, USA) and DBSWIN (VistaScan, Dürr Dental, Bietigheim-Bissingen, Germany). Five measuring points were defined on each specimen where the mouse cursor was positioned to indicate the gray value of the selected point as shown in Figure 1. The mean value of the 5 measurements was used as radiopacity values for each composite resin specimen.

Statistical Analysis

Data of the radiopacity level of composite resins were analyzed for normal distribution (Shapiro-Wilk test) and homoscedasticity (Levene's test). Data were analyzed by using three-way analysis of variance ANOVA (2 x-ray systems, 2 softwares and 6 composite resins). All tests used $\alpha = 0.05$ significance level and all analyses were carried out with the statistical package Sigma Plot version 13.1 (Systat Software Inc, San Jose, CA, USA).

Results

Radiopacity of different composite resins evaluated by the 2 imaging receptors and the 2 softwares are shown in Table 2. Three-way ANOVA showed significant influence of composite resin ($P < 0.001$), imaging detector ($P < 0.001$) and software used ($P < 0.001$), however no significance was observed for the interaction between the two factors: composite resin type and software used ($P = 0.342$), composite resin type and imaging detector ($P = 0.412$), software used and imaging detector ($P = 0.118$), and between three study factors ($P = 0.156$). TET had the highest radiopacity values, followed by POST, Z350 and OPR, which had similar radiopacity values between them, OPF and VIT that had the lowest radiopacity values measured using CMOS method associated with both software and with PSP associated with Image J. However, when PSP system was used in association with DBSWIN, the order of the composite was inverse, maintaining the same significant differences among materials. The developed device contributed for great reproducibility of the radiopacity data and the low coefficient of variation of all tested combination CMOS/ImageJ (2.5 – 8.3%), CMOS/DBSWIN (2.9 – 10.0%), PSP/ImageJ (1.5 – 10.6%), PSP/ImageJ (4.4 – 15.1%). The composites resins compared to aluminium step wedge presented equal or higher grey values when compared to 4mm reference value, demonstrating adequate radiopacity according to the ISO 4049 guidelines.

Discussion

The standardization on specimen preparation and methodology reproduction in order to better answer tested hypothesis is essential to avoid risks of bias in laboratory experiments. This study showed that the device developed for standardization of *in vitro* studies that requires a radiographic test was a valuable and reliable setting. The reproducibility of the protocols was observed without any secondary external radiation, demonstrating important safety performance. The developed device was validated analysing radiopacity of composite resins used for restoring posterior cavities using incremental or bulk fill techniques. The conventional and bulk fill composite resins showed significant difference for radiopacity levels irrespective of the imaging receptor and software used for gray values measurement. Therefore, the first null hypothesis was rejected.

Radiopacity is related to the chemical composition of the materials,[9] allowing the differentiation between dental structures and restorative materials.[3,15] The radiopacity of the materials also allows the radiographic evaluation of inadequate proximal contours, marginal adaptation and possible gaps between material and tooth structure.[1] The method used to evaluate the radiopacity of different material specimens and the aluminium step wedge on the radiograph , allows the operator to compare the radiopacity of the each specimen to an aluminium step of equal radiopacity. [5,10]

The addition of certain elements with high atomic number in the material such as zirconia, aluminium, barium, silicon, strontium, zinc, and ytterbium can increase the material's absorption of x rays making it more radiopaque.[7] The greater the quantity of these elements in the composition of the material, the greater its radiopacity.[7,9,18] The fact that Tetric Evo BKF composite resin showed the highest radiopacity in all tests can be justified by its filler composition. There are some chemical elements of high atomic number such as Ytterbium (atomic number 70), Ytrium (atomic number 39) and Barium (atomic number 56) which is the most commonly used element to increase radiopacity on composites resin.[2]

Since the presence of bubbles in the material may change radiopacity, the selection of five different measuring points was used to provide a mean gray value correspondent to the radiopacity of each specimen. The coefficient of variations observed in same materials are probably related to the bubbles into the specimen, however this parameter had no great influence in the present study.[8] Image J software tested in this study is a reliable open-source software of public domain that appears to be an interesting alternative for researchers as well as for clinicians in their radiographic evaluation.

The present study showed that all tested composite resins had adequate radiopacity, with higher radiopacity than the 4.0mm aluminium step when compared to the step aluminium wedge.[3,6,16] The use of the aluminium step wedge is highly recommended for studies of radiopacity.[6] However, for a better effectiveness the aluminium step wedge must have at least 98% of pureness.[4,6,17] The 10 steps wedge used in this study had 99.7% pureness and it is important to mention that the aluminum radiopacity is a commonly used threshold value used by manufactures to identify whether their material is sufficiently radiopaque.[19]

The imaging detectors and softwares used demonstrated different ranking of tested materials, therefore the second hypothesis was also rejected. The results showed that when radiopacity was evaluated by ImageJ software, the grayscale values ranged from 0 to 256, showing that the higher the value obtained the higher the radiopacity of material. On the other hand, when the images obtained by PSP plates radiographs were evaluated by DBSWIN software the grayscale pattern was different, with numbers ranging from 631 to 1273; where the lower the value, the higher the radiopacity of material. Therefore, when using any type of software analyses, it is important to pay attention in the way the results are expressed, as they can be equivalents, though in different or contrary position, and even in need of previous calibration. However, even with different values for PSP/DBSWIN, the order of radiopacity levels for all composites resins was similar. Tetric Evo BKF was always the most radiopaque and Vittra APS was the less radiopaque, irrespective of radiographic method and software used. Radiographic visualization of composite resin restoration and dental structures is essential for establishing a correct diagnosis and treatment plan. A composite resin may be within the established requirements for radiopacity, however on radiographic evaluation it might not be differentiated from mineralized dental tissues.[20] The radiopacity of the dental materials is an important property and can justify the incorporation of nanoparticles improving radiopacity of restorative dental resins, easing the tracking of actual remineralization effects and enabling diagnosis of recurrent caries.[21]

Standardization of the distance between imaging receptor, specimens and aluminum step wedge by the developed device was guaranteed. The device proved to be viable, maintaining the position during the tests leading to higher standardization and accuracy of the images and analysis. Additionally, the mechanism of the construction of the device provided a safety using because no secondary external radiation was observed. Overall, it was demonstrated that bulk fill and conventional composites have sufficient radiopacity to facilitate its detection when measured with different radiographic methods and processed by different software.

Conclusion

Within the limitations of this laboratorial study, the following conclusions can be drawn:

1. The developed device for *in vitro* studies showed adequate standardization on the radiographic acquisition and analysis;
2. All tested bulk fill and conventional composite resins exhibit appropriate radiopacity;
3. Both softwares used in the evaluation of radiopacity were reliable and worthwhile to be used, however they presented different sequence of the radiopacity level, requiring careful assessment when comparing data from different studies.

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Tables and Figures

Table 1. Composites resins tested.

Material	Composite type	Light activation time	Basic composition: Organic matrix/Filler	Filler % w/vol	Manufacture
Z350, Filtek Z350	Conventional	20 s	Bis-GMA, UDMA, TEG-DMA/ Silica and zirconia nanofillers, agglomerated zirconia silica nanoclusters.	78.5/59.5	3M-ESPE (St. Paul, MN, USA)
VIT, Vittra APS	Conventional	20 s	Methacrylate monomers mixtures, photoinitiators composition (APS), co-initiators, stabilizer and silane/Particles of zirconia, silica and pigments.	72/52	FGM (Joinville, SC, Brazil)
POST, Filtek Posterior Bulk fill	High Viscosity Bulk fill	20 s	AUDMA, UDDMA, UDMA/ Silica, zirconia, and YbF3.	76.5/59.5	3M-ESPE (St. Paul, MN, USA)
OPR, Opus Bulk Fill APS	High Viscosity Bulk fill	20 s	Urethane-dimetacrylic monomers, stabilizers, photoinitiations and co-initiators/ Inorganic load of silanized silicon dioxide (silica), stabilizers and pigments	79/ -	FGM (Joinville, SC, Brazil)
TET, Tetric Evoceram Bulk Fill	High Viscosity Bulk fill	20 s	UDMA, Bis-GMA/ Barium glass, ytterbium trifluoride, mixed oxide prepolymer	79/61	Ivoclar (Vivadent, Schaan, Liechtenstein)
OPF, Opus Bulk Fill Flow APS	Low Viscosity Bulk fill	20 s	Urethane dimetrhacrylate monomers, stabilizers, canforoquinone and coinitiators/ salinized silica dioxide, salinized barium glass, YbF3.	68/ -	FGM (Joinville, SC, Brazil)

Table 2. Mean and standard deviation radiopacity values of composite resins analyzed by different methods and software.

Resin composites	CMOS sensor		Phosphorus plate	
	ImageJ	**DBSWIN**	**ImageJ**	**DBSWIN**
Tetric Evoceram Bulk Fill	234.0 ± 6.0 Aa	225.0 ± 9.0 Aa	193.2 ± 6.7 Ba	773.4 ± 34.3 Aa*
Filtek Bulk fill Posterior	208.2 ± 9.7 Ab	199.0 ± 7.8 Ab	171.7 ± 6.0 Bb	1035.4 ± 124.1 Ab*
Filtek Z350	200.3 ± 7.9 Ab	195.2 ± 5.7 Ab	163.0 ± 4.9 Bb	1145.2 ± 63.3 Ab
Opus Bulk fill Regular	197.3 ± 7.8 Ab	192.4 ± 7.58 Ab	168.6 ± 2.6 Bb	1057.2 ± 159.9 Ab
Opus Bulk Fill Flow	152.1 ± 12.6 Ac	151.0 ± 15.1 Ac	147.0 ± 15.7 Bc	1313.2 ± 94.0 Ac
Vittra APS	96.2 ± 5.8 Ad	93.6 ± 6.5 Ad	112.2 ± 2.4 Bd	1819.0 ± 112.2 Ad

Different letters indicate a significant difference – upper caser used for comparing the composites resins and lower-case letters used for comparing radiographic methods and software analyses ($P < 0.05$).

Figures

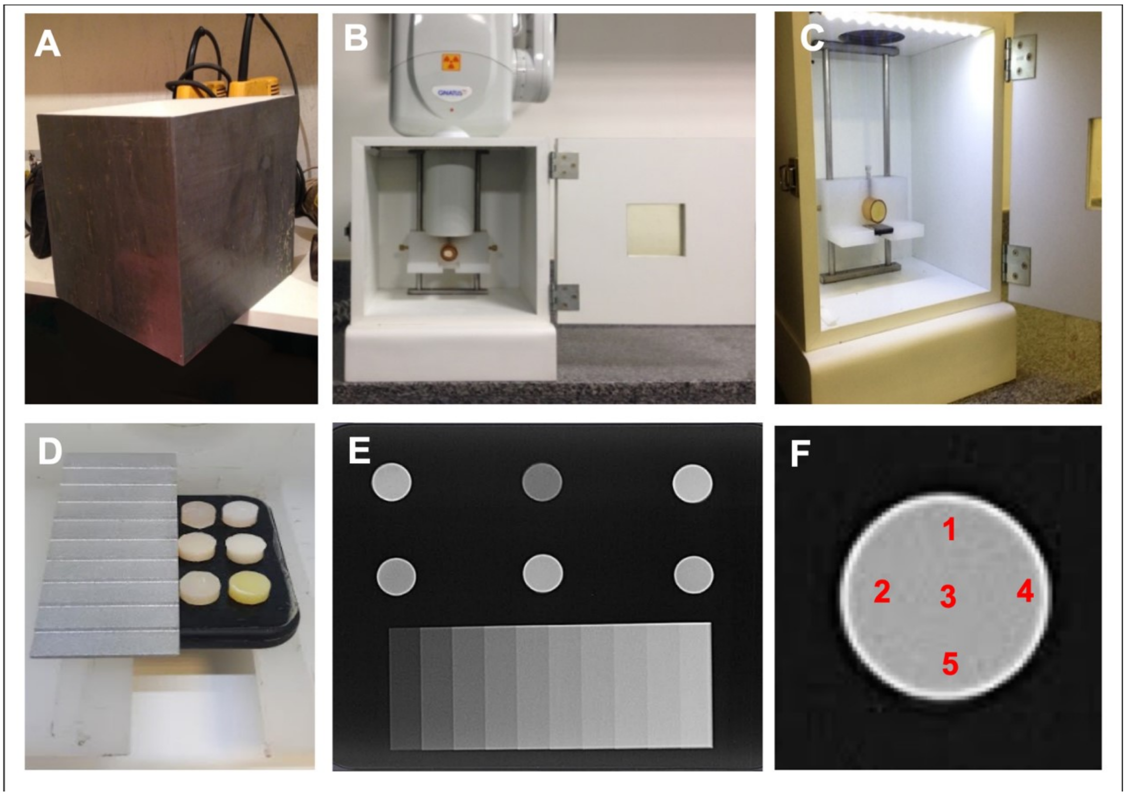

Figure 1. A: Construction of the developed device for the radiography standardization for in vitro test; B: Device developed stabilizing the x ray tube; C: Internal support for sample of *in vitro* studies and illumination**;** D: Composite resin samples and step wedge over the CMOS sensor. E: Radiography image of all composite resin samples and step wedge. F: Radiography image of 5 measuring points for radiopacity level of composite resin samples.

Acknowledgements

This project was funded by grants from the CAPES Grants 001; CNPq-National Council for Scientific and Technological Development, grants 434598/2018-6; and FAPEMIG, grants APQ-02105-18. This research was performed at CPbio-Biomechanics, Biomaterials and Cell Biology Research Center, School of Dentistry, Federal University of Uberlândia - UFU.

JUSTIFICATION FOR THE PARTICIPATION OF EACH AUTHOR - BOR

- The author **Luciana Mendes Barcelos** collaborate with design of the study, performed the experimental stages, and writing of the paper.
- The co-author **João Vitor Goulart** outlined the experiments, collaborated with the experimental stages and collaborate with the paper.
- The co-author **Tales Cândido Garcia da Silva** outlined the experiments, collaborated with the experimental stages and collaborate with the paper.
- The co-author **Renata Afonso da Silva Per**eira worked in the experimental stage, preparing samples, collaborated with experimental procedures, data analysis and writing of the paper.
- The co-author **Gabriella Lopes de Rezende Barbosa** designed the study, contribute with device develop design, collaborated with the experimental stages, and writing of the paper.
- The Co-author Carlos José Soares designed the study, obtained funding, outlined the experiments, collaborated with the experimental stages, data analysis and writing and submission of the paper.

Capítulo 3

3.3 CAPÍTULO 3

Bulk fill or conventional resin composites – interaction between mono and multi-peak light-curing units and photoinitiator are a concern in nondeep posterior cavities?

Artigo a ser submetido para publicação no periódico **Operative Dentistry**

Bulk fill or conventional resin composites – interaction between mono and multi-peak light-curing units and photoinitiator are a concern in nondeep posterior cavities?

Luciana Mendes Barcelos[1], Stella Sueli Lourenço Braga[1], Renata Afonso da Silva Pereia[1], Richard B Price[2], Carlos José Soares[1]

[1]Luciana Mendes Barcelos, DDS, MSc, PhD student, Department of Operative Dentistry and Dental Materials, School of Dentistry, Federal University of Uberlândia, Minas Gerais, Brazil. (*Statement of contribution:* collaborated with methodology, collected data, formal analysis and writing the original draft).

[1]Stella Sueli Lourenço Braga, DDS, MSc, PhD student, Department of Operative Dentistry and Dental Materials, School of Dentistry, Federal University of Uberlândia, Minas Gerais, Brazil. (*Statement of contribution:* collaborated with methodology, collected data, formal analysis and writing the original draft).

[1]Renata Afonso da Silva Pereira, DDS, MSc, PhD, Department of Operative Dentistry and Dental Materials, School of Dentistry, Federal University of Uberlândia, Minas Gerais, Brazil. (*Statement of contribution:* collaborated with methodology, collected data, formal analysis and writing the original draft).

[2]Richard Bengt Price, DDS, MSc, PhD, DDS, MSc, PhD, Professor at Department of Dental Clinical Sciences, Dalhousie University, Halifax, Nova Scotia, Canada. E-mail address: richard.price@dal.ca (*Statement of contribution:* contributed with conceptualization, supervision, project administration, methodology, funding acquisition, resources, writing review, editing and submission of the manuscript).

[1]Carlos José Soares, DDS, MSc, PhD, Professor and chair Department of Operative Dentistry and Dental Materials, School of Dentistry, Federal University of Uberlândia, Minas Gerais, Brazil. (*Statement of contribution:* contributed with conceptualization, supervision, project administration, methodology, funding acquisition, resources, writing review, editing and submission of the manuscript).

Running title: Light curing and mechanical properties of resin composites.

Keywords: resin composite, light curing unit, light spectrum, photoinitiator, degree of conversion, microhardness.

Corresponding author:

Dr. Carlos José Soares

Department of Operative Dentistry and Dental Materials

Dental School, Federal University of Uberlândia

1720 Pará Ave., Block 4L, Annex A, Campus Umuarama

Uberlândia, Minas Gerais, Brazil

Zip Code: 38400-902

E-mail address: carlosjsoares@ufu.br - Phone: +55 34 999713472

Abstract

Objectives: To analyze the effect of monowave and multiple peak light curing units (LCU) on Knoop hardness (KH), elastic modulus (E) and degree of cure (DC), of conventional and bulk fill resin-based composites (RBCs) with different photoinitiators systems.

Methods: Three commercially available Resin Based Composites (RBCs) were tested in this study: Tetric EvoCeram Bulk Fill (Ivoclar Vivadent, Schaan, Liechtenstein) and Opus Bulk Fill APS (FGM); and 1 conventional RBC: Vittra APS (FGM), were tested after light activation of four light curing units: 2 single peak (Optilight Max and Radii-Cal) and 2 mult peak (VALO Cordless and Bluephase G2) were used in this study. The effect of both study factors was tested regarding the Irradiance reaching the bottom surface (n = 3), Knoop hardness and Elastic modulus (n = 5), and Degree of conversion (%) at the top and bottom surfaces of specimens. Data of KH, E and DC values were analyzed by 2-way ANOVA followed by a Tukey test ($\alpha = 0.05$).

Results: The irradiance (mW/cm^2), emission spectrum (mW/cm^2/nm) emitted by the four LCUs reduced significantly when measured thought 2.0mm of all tested composite resin ($P < 0.001$). The KH and E values at top surface were always significantly higher than at the bottom surface, irrespective of RBC and LCU tested ($P < 0.001$). The DC values of Vittra APS were more influence by the depth of the restoration than both bulk fill resin composites. Optilight Max and Radii-Cal were less efficient regarding the KH and DC values than VALO Cordless and Bluephase G2 ($P < 0.001$).

Conclusions: all RBCs showed adequate KH, DC and E values at the top and bottom analyses. Bluephase and Valo, resulted in higher values of KH, E and DC regardless of the tested resin. The photoinitiator system tend to influence less the outcomes than the LCU performance.

Clinical relevance: *Clinician should be aware that in cases of restoring small conservative cavities, both conventional and Bulk fill RBC could be the material of choice, irrespective of the type of the light curing unit used, since it offers a good irradiance, however, in the use of a bulk fill composite less error in thechique can be avoided, improving restoration longevity.*

1. Introduction

Over the years resin-based composites (RBC) have been widely used as the primary option for restoring anterior and posterior teeth.[1] Mechanical properties of RBC, such as degree of conversion (DC) and Knoop microhardness (KH) are important parameters that can reflect the polymerization process of RBC.[2,3] Higher DC can determine good mechanical properties, chemical stability, and longevity of the restoration.[4] The RBC's DC has direct correlation with biocompatibility of restorations.[5] Microhardness is defined as the resistance of solid structures to permanent indentation or penetration and changes in hardness may reflect the state of the polymeric network of the resinous material.[6] Low surface microhardness tends to be correlate with more susceptibility to roughness, and consequently can lead to a low fatigue resistance causing premature failure of the restoration.[7-9] When the RBC polymerizes the elastic modulus (E) is generated by vitrification of the material.[10] The KH method is a convenient test to determine at the same time KH and E of RBCs influenced by different light activation process.[10]

The polymerization process of RBCs is mediated by light photons with the ability to activate free radicals, via interaction with photoinitiator molecules.[11] The relationship between wavelength of radiation within specific light spectrum and the activation energy of the different photoinitiators is essential for efficiency of polymerization process.[11] Light intensity, wavelength and exposure time can have influence in the conversion of monomers into polymers.[12] Consequently, the mechanical properties of a RBC can be compromised by an inadequate light activation, which might be influenced by the amount and spectrum of energy emitted by different light-curing unit (LCU).[13] Other characteristics of LCU such as irradiance, power and exposure time can also influence the mechanical properties of a RBC.[14,15] If RBC receives lower and no specific wavelength energy required by the manufacture recommendation, improperly polymerization is generated, leading to lower mechanical properties.[16] LCUs have been evaluated delivering light in different spectrum with peak of the lights located in different wavelength.[15] The spectral radiant power, effective tip diameter, irradiance from these LCUs are often different and this may have a negative impact on the ability of these units to photo-cure RBCs with different photoinitiators.[11,15,17]

Additionally, most clinicians do not pay attention about the composition of a RBC, more specifically about the different photoinitiator systems, which might be influenced by the type of LCU.[18] Depending on the photoinitiator used, the compound must either react with an intermediary molecule (an amine), which then goes on to form free radicals (a Type 2 initiator), and cause polymerization, or can directly break down into one or more free radicals, which need no such secondary compounds to assist in initiating polymerization (Type 1 compounds).[11] The most commonly used photoinitiator system is camphorquinone (CQ) in combination with a tertiary amine as co-initiator (1,7,7-trimethylbicyclo [2.2.1] heptane-2,3-dione) Type 2 initiator system. CQ is bright yellow, resulting in restorations with the tendency to have a yellowish colour. Other new “amine-free” photoinitiator, Ivocerin® is the patented product only available in products from Ivoclar Vivadent. Ivocerin® is a Bis-(4-methoxybenzoyl) dibenzoyl germanium derivative photoinitiator, that provides an even broader spectrum of short-wave absorption.[19,20] Ivocerin® can be activated by visible light, at a slightly shorter wavelengths compared to CQ (405 and 470 nm, respectively), which has been described as an advantage for improving light penetration through the bulk of the material.[21,22] The APS system, Advanced Polymerization System, which is a patented combination of the CQ, and 2- (Dimethylamino) ethyl Benzoate (co-initiator), other patented Type I and II initiators and other special proprietary co-initiators present in conventional and bulk-fill RBC produced by FGM Company. The manufacturer reported that light activation of APS system-based resin composites does not requires any special LCU since the absorption peak of the proprietary initiators are between 400 and 500 nm. With the inclusion of the APS system, the CQ content is reduced minimizing the yellowing of the RBC.

Bulk fill composite resins have been gaining in popularity for restoring deep posterior cavities with good improvement on mechanical properties observed in in vitro evaluations.[23] However, the most of these studies are designed in deep cavities with 4-5mm in depth, then clinicians have presented the question about what protocol should be used in non-deep cavities, limited to 2.0mm in depth. Could the factors such as the LCU type and the composition of the bulk fill or conventional RBCs influence the performance of these restorations? Therefore, the aim of this study was to evaluate the effect of monowave and multiple peak LCUs on KH, E and DC, of RBCs with different photoinitiators systems in their composition. The null hypothesis was the interaction between different RBCs materials with different photoinitiators with monowave and multiple peak LCUs would not influence the KH, E and DC values.

2. Materials & Methods

2.1 Study Design

Three RBCs used for posterior restorations, 2 bulk-fill high viscosity: Tetric EvoCeram Bulk Fill (Ivoclar Vivadent, Schaan, Liechtenstein) and Opus Bulk Fill APS (FGM); and 1 conventional RBC: Vittra APS (FGM) were tested in this study. The chemical compositions of the RBCs are listed in **Table 1.** The RBCs were light activated using four LCUs: Two monowave LCU: Optilight Max (Gnatus, Ribeirão Preto, SP, Brazil) and Radii Cal (SDI, Basywater, Victoria, Australia); and two multiple peaks LCUs: Bluephase G2 (Ivoclar Vivadent); and VALO Cordless (Ultradent, South Jordan, UT, USA). LCU characteristics are listed in **Table 2.** The irradiance (mW/cm^2), emission spectrum (mW/cm^2/nm) and radiant exposure (J/cm^2) of emitted light delivered by each LCU were measured and mechanical properties of the RBCs, expressed by KH, E and DC were calculated.

2.2 Specimen Preparation

Specimens for all groups and tests were made using a plastic ring mold (Delrin Ring, DuPont, Mississauga, ON, Canada) of 6 mm inner diameter and 2 mm thickness. Specimens were prepared in a dark room with yellow light so that the room light would not influence the RBC polymerization. In order to minimize the presence of bubbles and obtain a smooth surface, the mold was covered with a Mylar strip (DuPont Teijin Films, Hopewell, VA, USA) and made flat by pressing between two glass slabs. All the RBCs were light activated by the four LCUs mentioned previously, accordingly to the manufacturer's instructions for each of them as shown in Table 1. Light activation was performed on MARC resin calibrator (MARC-RC, BlueLight Analytics Inc, Halifax, NS, Canada). The irradiance, emission spectrum, and radiant exposure of LCU were measured while photoactivating the RBCs. The specimens were stored dry at 37 °C, protected from light. After 24 hours, KH, E and DC for the RBCs specimens were tested at the top and bottom surfaces.

2.3 Irradiance, Emission Spectrum, and Radiant Exposure

The irradiance (mW/cm^2), emission spectrum (mW/cm^2/nm), and radiant exposure (J/cm^2) delivered by each LCU operating in the standard mode to the RBCs were measured using MARC-RC. The measurements were recorded three times under different conditions:

Control: the irradiance at the tip of each LCU was determined by placing the tip directly over and at a distance of 0 mm from the MARC-RC top sensor;

Through 2.0 mm of RBC: to estimate the irradiance, emission spectrum, and radiant exposure transmitted through each RBC during the light activation. The plastic ring mold previously described was filled with each RBC. A Mylar strip was placed over the MARC-RC bottom sensor, the ring matrix was centered over the sensor, and another Mylar strip was placed over the mold.

The same trained operator conducted all tests for the light exposures. The tip of the LCU was fixed as close as possible to the surface of the RBC with a rigid clamp. The MARC-RC software displayed the maximum irradiance (mW/cm^2), radiant exposure (J/cm^2), and the emission spectrum (mW/cm^2/nm) received by the sensor.

2 Knoop microhardness (KH) and Elastic Modulus (E)

After 24 hours of dry storage at 37ºC in the dark room, the specimens were submitted to KH test. Readings were taken in five locations on top and bottom surfaces.

The KH values (N/mm^2) and E, for each surface was calculated the average of five readings. The KH indentation values were determined with a microhardness tester (FM700; Future Tech Corp., Kawasaki, Japan) by applying a load of 500 g for 15 s. Five indentations were made on the middle of each surface (top/bottom) with interval of 1 mm between them to obtain an average value. The following formula was used: E= .25 KHN 14.2293 Load (Kg)/(long diagonal in mm). In addition to the microhardness determination, KH indentations were also used to determine the E.[24,25] The decrease in the length of the indentation diagonals caused by elastic recovery of a material is related to the microhardness: modulus ratio (H/E) by the equation where b/a is the ratio of the diagonal dimensions a and b in the fully loaded state, given by a constant 0.140647; b/a is the ratio of the altered dimensions when fully recovered; and ‘10.45 is a proportionality constant.

2.5 Degree of conversion (%)

The DC at the top and bottom of the RBCs specimens (n = 5) were assessed after 24 hours in 3 spots (2 mm distance from each measurement) using a LabRam HR Evolution Raman spectrometer (Horiba LabRam, Villeneuve d'Ascq, France) operating at an excitation power of 17 mW with radiation emitted by a He-Ne laser (633 nm). Raman signal was acquired using 600 line/mm grating centered on between 1000 and 2000 cm^{-1} with 200µm confocal hole. These settings enabled to acquire spectra of 1.05 cm^{-1}/pixel of resolution. The spectra were adjusted by polynomial function and by manual multiple point baseline correction. The Raman vibrational modes were analyzed in the area peaks: aliphatic (1638 cm^{-1}) and aromatic (1608 cm^{-1}), then calculated from polymerized (P) and unpolymerized (NP) RBCs specimens. The formula used for the calculation of the DC value was: DC (%) = (1 - P / NP) x 100. The test was done after 24 hours that the specimens were stored dry at 37 ^{o}C in a dark recipient.

2.6 Statistical Analysis

Data of KH, E and DC values were analyzed for normal distribution (Shapiro-Wilk test) and homoscedasticity (Levene’s test). Two-way analysis of variance (2-way ANOVA) was carried out, followed by a Tukey test for comparing KNH, E and DC data generated by different LCUs and composite resins. All tests used α = 0.05 significance level, and all analyses were carried out with the statistical package Sigma Plot version 13.1 (Systat Software, San Jose, CA, USA).

Results

3.1 Irradiance and Emission Spectrum Emitted by LCUs

The irradiance (mW/cm^2), emission spectrum (mW/cm^2/nm) emitted by the four LCUs when photocuring the three RBCs are reported in (Figure 1). The light transmission increased through Tetric EvoCeram Bulk fill and reduced through Opus Bulk Fill APS during the light activation (Figure 1). No alteration on light transmission through Vittra APS was verified, irrespective of LCU (Figure 1I, 1J). Optilight Max and Bluephase G2 had the highest irradiance values, VALO Cordless had intermediated values and Radii-Cal the lowest irradiance measured through Tetric Evoceram Bulk fill (Figure 1G, 1H). Optilight Max and Bluephase G2 had the highest, VALO Cordless and Radii-Cal the lowest irradiance measured through Opus Bulk fill APS (Figure 1K, 1L). The difference in the performance among LCU was better observed in for Vittra APS, which Optilight Max had the highest irradiance measured through Vittra APS, followed by Bluephase G2, VALO Cordless and Radii-Cal the lowest (Figure 2).

3.2 Knoop hardness and Elasticity Modulus

The KH (N/mm^2), of the RBCs when light activated using the four LCUs are shown in Figure 3. The KH values measured at top surface were always significantly higher those values measured at the bottom surface, irrespective of RBC and LCU tested ($P < 0.001$). Bluephase G2 and VALO Cordless resulted significantly higher KH values than Optilight Max and Radii-Cal, irrespective of tested surface and RBCs ($P < 0.001$). The KH values measured at top surface of Opus Bulk Fill APS and Vittra APS were significantly higher than Tetric EvoCeram Bulk fill when light cured with Bluephase G2 and VALO Cordless. The KH values measured at bottom surface of Vittra APS were significantly lower than

Opus Bulk fill APS and Tetric EvoCeram Bulk fill when light cured with Optilight Max and Radii-Cal.

The E values (MPa), of three RBCs when light activated using the four LCUs are shown in Figure 5. The E values measured at top surface were always significantly higher those values measured at the bottom surface, irrespective of RBC and LCU tested ($P < 0.001$). The LCU had no significant effect on the E values, irrespective of tested surface ($P = 0.328$) and RBCs ($P = 0.412$).

3.3 Degree of Conversion (%) of resin-based composites

The DC (%), of three RBCs when light activated using four LCUs are shown in Table 3. The DC values measured at top surface were significantly higher than those values measured at the bottom surface for Vittra APS light cured with all LCUs and Opus Bulk Fill light cured with Radii-Cal. Bluephase G2 and VALO Cordless resulted significantly higher DC values than Optilight Max and Radii-Cal for Opus Bulk Fill and Vittra APS, irrespective of tested surface ($P < 0.001$). LCU had no effect on the DC values for Tetric EvoCeram Bulk Fill, irrespective of tested surface. Opus Bulk Fill light activated with Bluephase G2 and VALO Cordless had significantly higher DC values than Tetric EvoCeram Bulk Fill irrespective of tested surface, and had also significantly higher DC values than Vittra APS at bottom surface.

3. Discussion

The effectiveness of monowave and multiple peak LCUs for polymerizing the RBCs with different composition and photoinitiator systems, have been studied in order to evaluate their effects on the mechanical properties. The null hypotheses were rejected, as KH, E and DC vales were influenced by the type of tested RBCs and by tested LCUs. A properly polymerization of RBCs is crucial to improve physicmechanical properties and consequently better clinical performance of composites restorations.[26] The polymerization efficiency of RBCs in 2.0 mm increment thickness or more are related to their translucency, which helps the light transmission through the material. Several studies have tested the effectiveness of bulk fill RBCs in 4-5mm increment thickness and have verified that the biomechanical properties of these materials are influenced by its behavior in depth of cavities.[27-30] We tested in this study the condition recommended for conventional RBC, increment of 2.0 mm, trying to verified if in this condition, often observed in posterior conservative restorations, the conventional or bulk fill resin composites perform similarly. Additionally, we also tested the effect of interaction between different LCUs with RBCs with different photoinitiator systems. The RBCs tested presented different performance in terms of polymerization, but they showed satisfactory performance irrespective of the type of LCU. Although, composition of RBCs might have influenced the light transmission, these parameters had no direct correlation with the performance of both study factors. The light transmission increased through Tetric Evoceram Bulk fill during the light activation time, however reduced through Opus Bulk Fill APS during the light activation, mainly when using Optilight Max, Bluephase G2 and VALO Cordless. These findings can suggest that the LCUs performed differently, depending on the quality and type of the emitted light. Other studies showed that, measured mechanicals properties of tested RBCs were influenced by the type of LCU, as well as by the distribution of emitted light at the LCU tip.[3,13] The three RBCs selected in this study were specifically chosen to verify the interaction amongst their composition with different photoinitiator systems and the emission spectra of the LCUs. Light transmission through the bulk fill RBCs is necessary to achieve good mechanical properties, however during and after curing if the material gains opacity, that can be benefit esthetical observed.[31] This aspect can result in esthetical impact when posterior restorations are visible to buccal surface.

Although, the two bulk fill RBCs used in this study have different photoinitiators systems that are known to be excited by different light spectrum, no significant difference was observed on their mechanical properties. However, it was observed that Tetric Evoceram Bulk fill was effectively polymerized but the KH values were significantly lower at the bottom when the monowaves LCU were used. This can suggest that Ivocerin when light activated PROPERLY by Optilight and Radii-Cal due to the absence of the violet light range was not activated as when used VALO Cordless and Bluephase G2. The KH values, although lower, they reach the satisfactory level.[32] As it was observed the Tetric Evoceram Bulk fill presented the highest light transmission, probably due its translucency, which can be justified by its filler composition. Some chemical elements such as Ytterbium, Yttrium and Barium, the most commonly elements to lead to higher radiopacity on RBCs, can increase translucency.[33] Additionally, it has been shown that light transmission is strongly linked to material opacity.[34]

The KH values followed the same tendency to all RBCs tested and LCUs evaluation. The KH where had higher values when the multiple peak LCU were used irrespective of the RBC. Although, KH measured at top surface of Opus Bulk Fill APS and Vittra APS were significantly higher than Tetric Evo Ceram Bulk fill when light cured with Bluephase G2 and VALO Cordless. These results could be elucidated by the composition for both RBCs and also by the high irradiance of the both LCUs multiple peak. However, the time activation for Opus and Vittra Aps was longer than the time activation for Tetric Evo Ceram Bulk fill, according to manufacturer's instructions and that could also have influenced these results. A study showed that longer light activation time can induce better polymerization of RBCs as long as the RBC has not reached the maximum conversion of monomers into polymers, so that mechanical properties can be improved.[35]

On the other hand, the KH values measured at bottom surface of Vittra APS were lower than Opus Bulk fill APS and Tetric EvoCeram Bulk fill when light cured with Optilight Max and Radii-Cal. This result can be explained by the presence of pre-polymer particles presented in Tetric Bulk Fill which showed results in inferior hardness values, agreeing with previous investigation studies.[36] Although Vittra APS and Opus Bulk fill APS have the same type of photoinitiator system, they are RBCs with different filler composition and light activation time, what can influence KH as mentioned before.

The E measured values, presented significantly higher values than those values at the bottom surface, irrespective of RBC and LCU tested. As E is a property that correlates with the filler content of RBC, as the top surface is near of the emitted light, consequently receive more energy that might explain the higher values.

The DC values measured at top surface were significantly higher than those values measured at the bottom surface, for Vittra APS light cured with all LCUs and Opus

Bulk Fill light cured with Radii-Cal. DC has a strong correlation with the organic matrix, what might explain Vittra APS results. Vittra is a free Bis-GMA composite, presenting monomers with lower viscosity, what can lead to greater mobility of the molecules, resulting in a higher DC as showed in studies about monomers behaviours.[20] Opus Bulk Fill APS also have a monomer with lower viscosity leading to the similar result as Vittra. In addition, Vittra APS and Opus are mention by the manufacture to have an advanced polymerization system with the absorbance peak around 470nm, another factor which probably have been an advantage for the two monowave LCUs in the case of RBCs with the necessity of absorbance at a short wavelength in the blue visible light. For Tetric Evoceram Bulk fill our study showed lower DC compared to the others RBCs of this study, and again it can be associated with the higher irradiance of. Other point to mention is that high irradiance can be associated with a production of more radicals quickly, and may cause an earlier termination of the polymers chains, resulting in lower degree of conversion of an RBC.[37]

Nonetheless, we noted in the present study that a 2mm increment of an RBC, either conventional or bulk fill can have a different behavior in polymerization due to the type of light as well as light activation time. Previous studies, have showed that to restore a cavity with conventional RBC the best choice it is to use 2mm increment in the correct technique.[38] However, in cases of conservative cavities, our study shows that is totally suitable to use a bulk fill RBC but paying special attention to the type of LCU to have better results and excellence of the clinical procedure. In the present study, it can be mention that the thickness of the specimen could be a limitation, however, studies have showed that in the analyse of KH, E and DC thickness would not influence in the investigation proposed. The RBCs with the new APS system showed encouraging outcomes, for esthetical and mechanical points.

Conclusion

Within the limitations of this in vitro study all investigated RBCs tested, showed adequate stability of KHN and E values between top and bottom. In general, Bluephase and Valo, resulted in higher values of KHN, E and DC regardless of the tested resin. Considering the thickness tested, irradiance tends to be more influential than the interaction between the light spectrum and the photoinitiator presented in the composite resin, and irrespective of the photoinitiator system the outcomes were satisfactory.

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Tables and Figures:

Table 1: Materials/Manufacturers, and Chemical Composition of Matrix and Filler.

Resin composites/ Manufacture	**Type**	**Shade**	**Organic matrix**	**Photoinitiator system**	**Filler**	**W/V(%)**	**Ligt activation time**
Tetric EvoCeram (Ivoclar Vivadent, Schaan, Liechtenstein)	Bulk fill – Regular paste	IVA	UDMA, Bis-GMA, mixed oxide prepolymer	Ivocerin*	Barium glass, ytterbium trifluoride, oxides and prepolymers	62.5%/60%	10 sec
Opus (FGM, Joinville, SC, Brazil)	Bulk Fill – Regular paste	A2	UDMA Monomers	APS System*	load of silanized silicon dioxide (silica), stabilizers and pigments	79%/ -	40 sec

Vittra APS (FGM, Joinville, SC, Brazil)	Conventional	A2	UDMA, TEGDMA	APS System*	Zircon load, silica and pigments.	72-82%/ 52-60%	20 sec

Composition provided by manufacturers. Abbreviations: Bis-GMA, bisphenol A diglycidylmethacrylate; Bis-EMA, bisphenol A polyethylene glycol diether dimethacrylate; UDMA, urethane dimethacrylate; TEGDMA, triethyleneglycol dimethacrylate; YbF3, ytterbium fluoride; EDMAB, tertiary amine ethyl-4-dimethylaminobenzoate; Ivocerin* - photoiniator dibenzoyl germanium derivative. APS system*- according to manufacture it is an Advanced Polymerization System.

Table 2. Information about the light-curing units used in this study, provided by manufacturers**.**

Light curing unit	Type	Wavelength (nm)	Irradiance (mW/cm²)	Manufacture
Optilight Max	Monowave	420-480	1200	Gnatus, Ribeirão Preto, SP, Brazil
Radii-Cal	Monowave	440-480	1200	SDI, Basywater, Victoria, Australia
Bluephase G2	Multiple peak	385-515	1394	Ivoclar Vivadent, Schaan, Liechtenstein
VALO Cordless	Multiple peak	395-480	1298	Ultradent, South Jordan, UT, USA

Table 3. Mean values and standard deviations of DC values of resins composites activated using different LCU are shown measured by Raman spectroscopy.

LCUs	**Tetric EvoCeram Bulk Fill**		**Opus Bulk Fill**		**Vittra APS**	
	Top	**Bottom**	**Top**	**Bottom**	**Top**	**Bottom**
Optilight Max	75.2 (1.5) Aa	71.8 (1.2) Aa	75.9 (1.7) Ba	73.3 (1.7) Ba	71.9 (0.4) Ba	64.6 (0.3) Bb*
Radii-Cal	72.8 (1.5) Aa	69.0 (1.1) Aa	76.3 (1.6) Ba	70.6 (2.3) Ba*	72.2 (2.5) Ba	66.5 (1.6) Ba*
Bluephase G2	74.0 (1.2) Ab	70.3 (1.7) Ab	83.6 (2.2) Aa	80.4 (1.6) Aa	80.2 (2.4) Aa	71.1 (5.9) Ab*
VALO Cordless	75.8 (2.2) Ab	72.6 (6.8) Ab	80.6 (0.7) Aa	78.3 (2.2) Aa	83.5 (1.6) Aa	66.1 (10.2) Bb*

Different letters indicate significant difference – uppercase letters used for comparison between LCU and lowercase letters used for comparison among resins composites ($P < 0.05$).

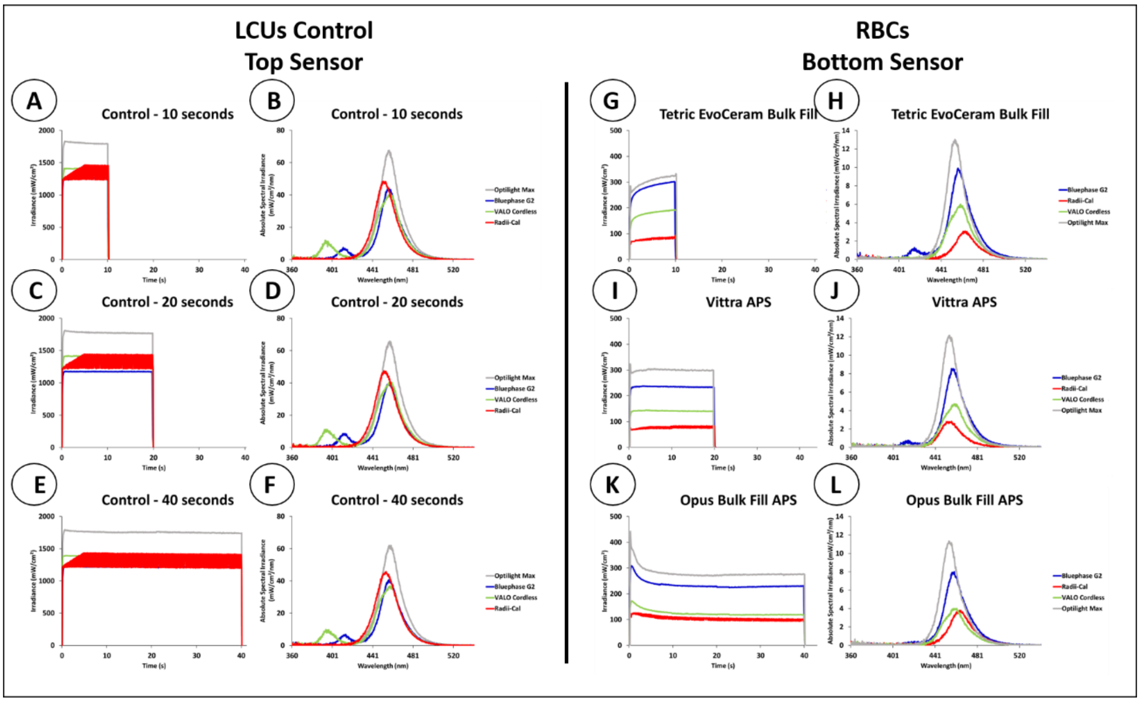

Figure 1. Irradiance (mW/cm²) and emission spectrum (mW/cm²/nm) from the LCUs. A, C and E: Irradiance of LCUs over the top sensor for 10, 20 and 40 seconds, respectively; B, D and F: Emission spectrum of LCUs over the top sensor for 10, 20 and 40 seconds, respectively; G, I and K: Irradiance of LCUs over the bottom sensor through the RBCs; H, J and L: Emission spectrum of LCUs over the bottom sensor through the RBCs. *Note the irradiance scales are different in A, C and E compared to G, I and K. The scales are also different in B, D and F compared to H, J and L.*

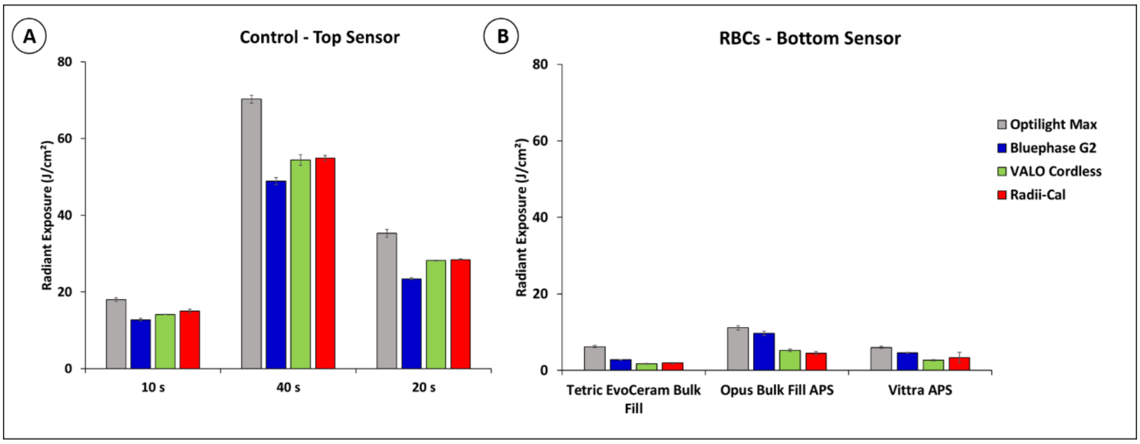

Figure 2. Mean and standard deviation of radiant exposure (J/cm²) of four LCUs for control condition and through three RBCs light activated. **A.** LCUs radiant exposure for three different exposure times tested without RBCs over the MARC-RC top sensor; **B.** LCUs radiant exposure through three RBCs over the MARC-RC bottom sensor.

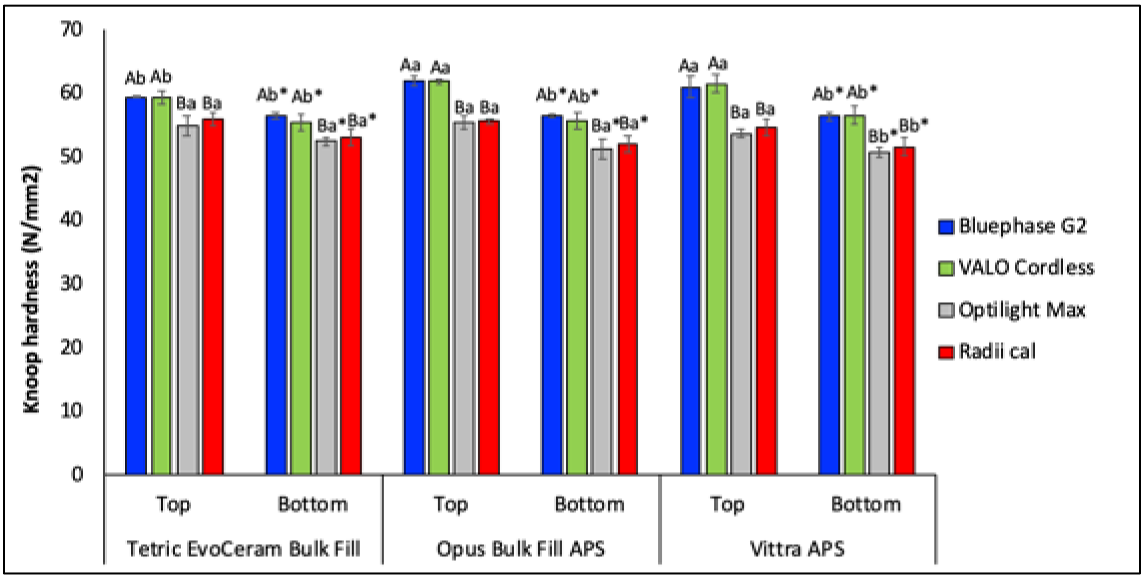

Figure 3. Mean and standard deviation of KH values (N/mm^2) for three RBCs light activated using 4 LCUs. Different letters indicate significant difference, uppercase letters used for comparison between LCU and lowercase letters used for comparison between composite resins; * indicate significant difference for tested surface, top or bottom ($P < 0.05$).

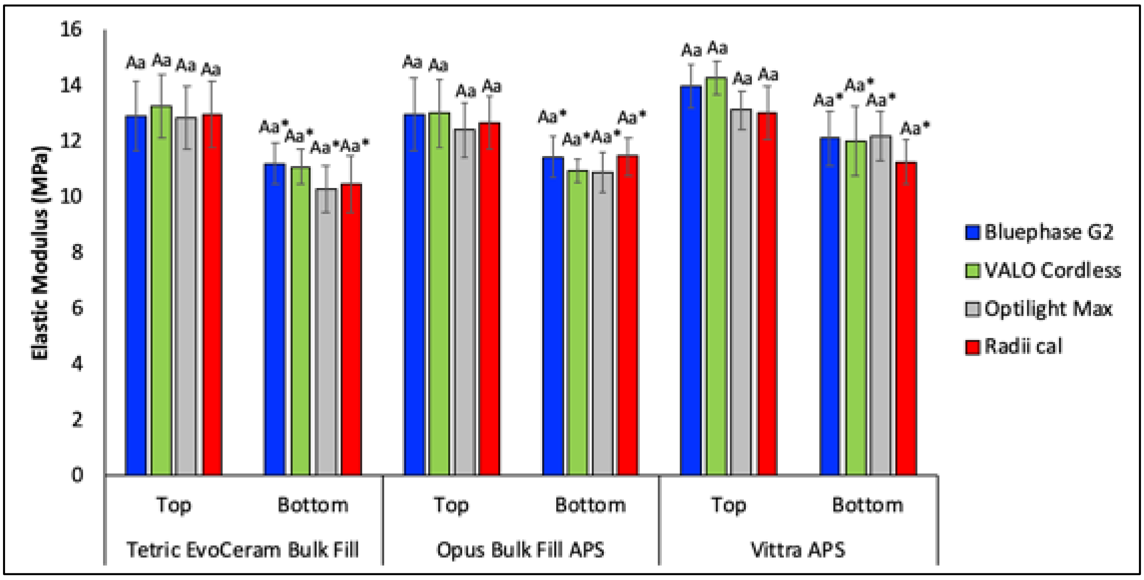

Figure 4. Mean and standard deviation of E values (MPa) for three RBCs, light activated using 4 LCUs. Different letters indicate significant difference, uppercase letters used for comparison between LCU and lowercase letters used for comparison between composite resins; * indicate significant difference for tested surface, top or bottom ($P < 0.05$).

Considerações Finais

4. CONSIDERACÕES FINAIS

A conjunção dos objetivos envolvidos nesse estudo demonstram que as resinas compostas convencionais e bulk fill apresentam propriedades adequadas e que a síntese de novos monômeros é promissora. No primeiro objetivo fica evidente que a cinética de polimerização dos compósitos experimentais testados foi afetada pelos fotoiniciadores. A incorporação de metacrilamida secundária aumentou significativamente a viscosidade desses materiais. Este trabalho demonstrou a viabilidade do uso de monômeros de metacrilamida recém-sintetizados em conjunto com sistemas iniciadores já usados em materiais comerciais. No segundo objetivo desse estudo foi demonstrado que as resinas compostas convencionais e bulk fill testadas exibiram nível de radiopacidade adequado. O dispositivo desenvolvido é uma importante ferramenta de pesquisa tendo demonstrado ser capaz de padronizar os métodos radiográficos usados para avaliar a radiopacidade dos materiais restauradores. No terceiro objetivo desse estudo, as resinas compostas Vittra APS, Opus Bulk Fill APS e Tetric Evoceram Bulk Fill utilizadas em incrementos de 2,0mm de espessura apresentaram valores adequados das propriedades mecânicas tanto na superfície como na região mais profunda. As fontes de luz Bluephase e VALO Cordless apresentaram desempenho superiores às fontes de luz Radii Cal e Optilight Max. O sistema fotoiniciador tende a influenciar menos os resultados do que o desempenho das fontes de luzes.

O horizonte de uso resinas compostas é promissoras, esse de material seja convencional ou bulk fill, busca aprimorar durabilidade e os trabalhos laboratoriais tem papel importante nesse cenário. A longevidade clínica das resinas compostas e da sua integração adesiva aos substratos dentais ainda é desafiador. A busca por novos monômeros, equilíbrio entre simplificação técnica e otimização de propriedades mecânicas de resinas compostas e a evolução de fontes de luzes para otimizar a fotoativação continua sendo o desafio a ser perseguido por pesquisadores para refletir no incremento de sucesso clínicos de protocolos restauradores adesivos diretos.

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Anexos

6.1 Normas dos periódicos

1. Dental Materials
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2. Brazilian Oral Research
   http://www.scielo.br/revistas/bor/iinstruc.htm

3. Operative Dentistry
   https://jopdent.com/author-review-for-journal/instructions-to-authors/