

Simone Xavier Silva Costa

**Influência dos Métodos de Fotoativação e
Fontes de Luz nas Propriedades
de Diferentes Resinas Compostas**

Tese apresentada ao Programa de Pós-Graduação em Ciências Odontológicas-Área Dentística Restauradora, da Faculdade de Odontologia de Araraquara-Universidade Estadual Paulista, para o título de Doutor em Ciências Odontológicas.

Orientador: Prof. Dr. Marcelo Ferrarezi de Andrade
Co-orientadora: Prof^a Dr^a Alessandra Nara de Souza Rastelli

Araraquara

2010

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Comissão julgadora

Tese para obtenção do grau de Doutor

Presidente e orientador: Prof. Dr. Marcelo Ferrarezi de Andrade

2º examinador: Profª Drª Silmara Aparecida Milori Corona

3º examinador: Profª Drª Denise Pedrini

4º examinador: Prof. Dr. Osmir Batista de Oliveira Júnior

5º examinador: Prof. Dr. José Roberto Cury Saad

Dados curriculares

Simone Xavier Silva Costa

Data de nascimento: 26/04/1976

Naturalidade: Vitória de Santo Antão-PE

Filiação: Elenildo Xavier Costa
Maria do Socorro Silva Costa

1995-1998: Graduação em Odontologia – Associação Caruaruense de Ensino Superior – Faculdade de Odontologia de Caruaru.

1999-2000: Especialização em Dentística Restauradora – Universidade Federal de Pernambuco.

2001-2003: Mestrado em Dentística – Universidade de Pernambuco – Faculdade de Odontologia de Pernambuco.

2006-2010: Doutorado em Ciências Odontológicas, área de concentração Dentística – Universidade Estadual Paulista “Júlio de Mesquita Filho” – Faculdade de Odontologia de Araraquara.

Dedicatória

Dedico este trabalho aos meus pais, **Elenildo Costa** (*in memorian*) e **Maria do Socorro S. Costa**, ao meu marido **Luiz Mantovani** e ao meu irmão **Hugo Costa**.

Painho, eis mais uma conquista em que infelizmente não tenho a sua presença física, porém não tenho a menor dúvida da sua presença e participação em outro nível. Obrigada pelo amor, carinho, dedicação, educação, enfim, pela participação fundamental na construção do meu caráter. A sua presença ao meu lado foi breve, mas de uma intensidade inigualável e insubstituível. Saudades...

Mainha, jamais esquecerei o dia que eu estava começando a arrumar as malas para vir à Araraquara, ainda um pouco ansiosa sobre a possibilidade real de vinda, e você ter dito que “sem dúvidas eu viria”. Neste dia recebi um abraço que reunia toda a força e a certeza de que eu ocuparia o lugar conquistado por mim no processo seletivo. Mesmo que você estivesse com o coração apertado, pois eu estaria a muitos quilômetros de distância, longe dos seus olhos pela primeira vez, você foi totalmente desprendida e me disse “vá”. Então, agora, etapa concluída, conquista obtida e compartilho-a com você. Afinal, a sua participação foi essencial em mais esta vitória. Obrigada pelo amor, dedicação, carinho, educação, paciência, enfim, por tudo. Afinal, desde os meus 14 anos a sua jornada foi em dose dupla, quando assumiu o papel presencial de pai e mãe. Tenho um orgulho imenso de você, pois apesar da grande perda que sofremos, eu e meu irmão somos a prova do quanto você foi competente e completa nesta dupla função.

Lu, olha o que vir fazer o doutorado em Araraquara trouxe para mim: você! Parece que estava escrito, sim, não tenho dúvidas de que estava escrito. Obrigada pelo amor, carinho, companheirismo, parceria, amizade, apoio, segurança e, acima de tudo, pela admiração. É fundamental e reconfortante ter um porto-seguro e você é o meu porto-seguro. Admiro e amo imensamente você, continuemos agora na construção diária da nossa história...

Hugo, o meu único irmão que, apesar de mais novo, por tantas vezes foi parceiro e companheiro presente na resolução dos problemas. Tenho tanto orgulho de você! Sua maturidade, segurança, competência, determinação, inteligência..., enfim, admiro imensamente este grande homem que você se tornou. Conte sempre e para o que for preciso comigo, a qualquer hora, em qualquer lugar.

A vocês, que são as pessoas mais importantes da minha vida.

Amo infinitamente vocês!

Aos orientadores

Um agradecimento especial ao Prof. Dr. **Marcelo Ferrarezi de Andrade** pelo apoio, incentivo, carinho e dedicação. Gradativamente, ao longo destes quatro anos, pude conhecê-lo melhor. Hoje, o que tenho por você é admiração e respeito, especialmente por sua simplicidade, disponibilidade, alto astral e alegria. Valeu a pena ter trabalhado com você. Obrigada!

À Prof^a Dr^a **Alessandra Nara de Souza Rastelli**, co-orientadora deste trabalho, minha gratidão, admiração e respeito. Você desempenhou um importante papel na condução e direcionamento dos meus passos como pesquisadora. Obrigada pela confiança, apoio e dedicação.

Agradecimentos especiais

Aos amigos **Alexandre Batista Lopes do Nascimento** e **Hílcia Mezzalira Teixeira**, ex-alunos da pós-graduação e graduação desta Instituição, por serem os responsáveis diretos para que eu escolhesse a Faculdade de Odontologia de Araraquara. Obrigada pelo incentivo, apoio e especialmente pela AMIZADE, no sentido integral que esta palavra representa.

À **Lizeti** e **Roberto Ramalho**, por me acolherem em sua casa desde a minha primeira vinda à Araraquara. A cidade me foi apresentada de forma muito acolhedora e prestativa por este casal. Um apoio e força equiparados aos que encontramos nas figuras do pai e da mãe.

À **Priscila Paiva Portero**, muito mais que uma colega de turma da pós-graduação, uma AMIGA, aliás, uma das minhas melhores amigas. Confidências, risadas (muitas risadas), tristezas, inseguranças e medos partilhados. Enfim, foram dois anos vividos intensamente, lado a lado, e ao todo quatro anos de amizade. Hoje distantes fisicamente, porém quando nos reencontramos parece que somos as mesmas que nos víamos e ainda nos telefonávamos todos os dias. Conte comigo sempre!

Ao casal mais do que querido **Alexandre Bier** e **Anne Becker**. Vocês foram um dos grandes presentes que recebi por morar em Araraquara. Quando penso em vocês, associo a nossa convivência a alegria, carinho, emoção, parceria, cuidado, além do melhor churrasco, claro! Admiro-os profundamente e, quando eu e Luiz crescermos ainda mais como marido e mulher, quero ser igual a vocês. Quero tê-los sempre por perto.

À **Carolina Chaves**, de ex-aluna, ex-monitora, à categoria de uma das minhas melhores amigas. Tenho muito orgulho de você, acho que sabe. Agradeço por tudo, especialmente por permitir que eu tivesse a sua casa como o meu lar araraquarense. Imprescindível e muito gostoso ter a sensação de, mesmo estando em Araraquara, estar em Recife toda vez que ouvia você falar com o sotaque igualzinho ao meu. Sempre que precisar, estarei pronta!

Aos amigos de pós-graduação **Marília Galvão, Sergei Caldas e Norberto Faria Jr**, pela convivência sempre alegre e prazerosa, típica do “ser nordestino”. Vocês são especialíssimos!

Agradecimentos

À Universidade Estadual Paulista e à Faculdade de Odontologia de Araraquara, representadas pelo Digníssimo Reitor **Herman Jacobus Cornelis Voorwald** e pelo Digníssimo Diretor **José Cláudio Martins Segalla**.

Ao Programa de Pós-Graduação em Ciências Odontológicas, representado pela Prof^ª Dr^ª **Josimeri Hebling** e pelo Prof. Dr. **Osmir Batista de Oliveira Jr.**

Aos **professores do Programa de Pós-Graduação da área de Dentística Restauradora**: José Roberto Cury Saad, Leonor de Castro Monteiro Loffredo, Marcelo Ferrarezzi de Andrade, Maria Salete Machado Candido (*in memorian*), Osmir Batista de Oliveira Júnior e Sizenando de Toledo Porto Neto, pelo conhecimento e experiência transmitidos, além dos momentos de convivência.

A todos os demais **professores do Programa de Pós-Graduação em Ciências Odontológicas** pelos conhecimentos e experiência compartilhados.

Aos amigos e colegas de pós-graduação **Benícia Ribeiro, Desirre Rossato, Milko Cortes, Priscila Portero, Renato Queiroz, Ubiraci Gaião, Adriano Mendonça, Cristiane Henriques, Darlon Lima, Esther Saad, Fábio Alvarenga, Fernando Florez, Gislaine Padovani, João Paulo Lima (JP), Juliana Boaventura, Martín Kreidler, Matheus Bandeca, Rafael Calixto, Victor Clavijo e William Kabbach** por todos os momentos vividos neste período. Espero encontrá-los em breve.

Aos funcionários do departamento de Dentística: **Creuza, Dona Cida (loira), Dona Cida (morena), Marinho, Vanderlei** e à ex-funcionária **Adriana** pelo apoio, colaboração, disponibilidade e, acima de tudo, pelos bons momentos compartilhados.

Aos funcionários da secretaria de pós-graduação: **Mara, Rosângela, José e Flávia** por serem sempre disponíveis, cordiais e solícitos no esclarecimento das dúvidas e prestação dos serviços.

Aos funcionários da biblioteca, em especial à **Ceres, Marlei e Maria Helena** pela prestabilidade, sempre com cordialidade, no atendimento e esclarecimento das dúvidas.

À **Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES)** pelo auxílio financeiro.

À **Maria Eugênia**, representante da 3M ESPE em Araraquara-SP, pela doação das resinas compostas para execução das pesquisas.

À **Regiane Pires** (consultora técnica da Labordental), **Milko Cortes** (Ivoclar-Vivadent) e ao **Marcelo** (representante da 3M ESPE em Florianópolis-SC) pela disponibilização dos aparelhos fotoativadores utilizados nas pesquisas.

Ao Grupo de Óptica e ao Grupo Crescimento de Cristais e Materiais Cerâmicos, nas pessoas do Prof. Dr **Vanderlei Salvador Bagnato**, Prof. Dr. **Antônio Carlos Hernandez**, Prof^ª Dr^ª **Maria Inês Basso Bernardi** e **Geraldo José M. Frigo** pela disponibilização de toda estrutura física e laboratorial para realização de alguns dos ensaios desta pesquisa, além do apoio técnico-científico, fundamentais para realização deste trabalho.

À Universidade Federal de Santa Catarina, especialmente ao Prof. Dr. **Luiz Henrique Maykot Prates** e à Prof^ª Dr^ª **Jussara Karina Bernardon** pela disponibilização da utilização do Laboratório de Ensaios do departamento de Odontologia e apoio técnico-científico, imprescindíveis para execução deste trabalho.

Ao Prof. Dr. **Paulo Afonso S. Francisconi** e, especialmente, ao doutorando **Leandro Martins**, pela disponibilização do laboratório do Centro Integrado de Pesquisa (CIP) da Faculdade de Odontologia de Bauru, além do apoio técnico-científico para realização de parte deste trabalho.

A todos aqueles que participaram direta ou indiretamente na execução deste trabalho. **Muito obrigada!**

*Se depender de mim,
Nunca ficarei plenamente maduro,
Nem nas idéias, nem no estilo,
Mas sempre verde, incompleto, experimental.*

Gilberto Freyre

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Resumo

Costa SXS. Influência dos métodos de foto-ativação e fontes de luz nas propriedades de diferentes resinas compostas [Tese de Doutorado]. Araraquara: Faculdade de Odontologia da UNESP; 2010.

Resumo

O objetivo deste trabalho, dividido em três estudos, foi avaliar: (1) a influência da utilização de diferentes fontes de luz e métodos de fotoativação sobre o grau de conversão e a contração de polimerização de uma resina composta nanoparticulada; (2) a influência da utilização dos diferentes métodos de fotoativação, disponibilizados por aparelhos LED de 2ª geração, sobre a contração volumétrica das resinas compostas microhíbrida e nanoparticulada e (3) as propriedades térmicas e o grau de conversão das resinas compostas microhíbrida e nanoparticulada, submetidas aos diferentes métodos de fotoativação disponibilizados por aparelhos LED de 2ª geração. No primeiro estudo, o grau de conversão (GC) foi avaliado pelo método da espectroscopia infravermelha transformada de Fourier (FT-IR) e as forças de contração (C) mensuradas em máquina de ensaios universal (EMIC). Os dados obtidos para o GC e C foram analisados estatisticamente pelo teste da análise de variância (ANOVA), sendo que para as forças de contração, a correção de *Welch* e o teste *Tamhane* também foram empregados. No segundo estudo, a contração volumétrica foi avaliada por um mecanismo de vídeo e imagem (Acuvol[®]/Bisco) e os dados obtidos foram analisados estatisticamente pelos testes ANOVA e *Tukey*. No terceiro estudo, o método da calorimetria exploratória diferencial foi empregado para avaliar a temperatura de transição vítrea (*Tg*) e de degradação dos materiais e o GC por FT-IR. Os dados relativos ao GC foram analisados estatisticamente pelos testes ANOVA e *Tukey*. Os resultados demonstraram diferenças na contração de polimerização de acordo com o método de fotoativação empregado. No primeiro e segundo estudos, mesmo empregando diferentes metodologias, o método de fotoativação contínuo apresentou os maiores valores de contração. Por outro lado, o GC não foi influenciado pelo método de fotoativação, mas sim pelo tipo de luz

empregada. Os menores valores do GC foram verificados para o aparelho a base de luz halógena. No segundo estudo, além da influência exercida pelo método de fotoativação sobre a contração volumétrica dos materiais, diferenças foram encontradas entre as resinas compostas. A resina composta microhíbrida apresentou menor contração volumétrica. No terceiro estudo, a resina microhíbrida apresentou a maior estabilidade térmica, apresentando os maiores valores T_g e de degradação. Os métodos de fotoativação graduais apresentaram valores T_g e de degradação semelhantes ou até superiores aos verificados para os métodos contínuos. Mais uma vez, no terceiro estudo, o GC não foi influenciado pelo método de fotoativação. No entanto, o tipo de aparelho LED e a categoria da resina composta exerceram influência sobre o GC. O aparelho Elipar Freelight 2TM (3M ESPE) e a resina composta microhíbrida exibiram as menores taxas de conversão. Também foram observados menores valores T_g para os grupos fotoativados com o aparelho Elipar Freelight 2TM (3M ESPE). Assim, baseados nos resultados apresentados nos três estudos, podemos concluir que a utilização dos métodos graduais de fotoativação, aliados à luz halógena ou tecnologia LED, minimizam as tensões decorrentes da contração de polimerização. O aparelho de luz halógena (densidade de potência=570mW/cm²), no entanto, apresentou menores taxas de conversão para as resinas compostas quando comparado ao aparelho LED (densidade de potência=860mW/cm²). Os aparelhos LED de 2^a geração e os métodos de fotoativação graduais disponibilizados por estes aparelhos apresentaram taxas de conversão aceitáveis, sem alterar a configuração polimérica final das resinas compostas. Porém, o tipo de aparelho empregado e a categoria da resina composta podem interferir no comportamento térmico e estrutural dos materiais.

Palavras-chave: Resinas compostas; luzes de cura dental; espectroscopia infravermelho transformada de Fourier; propriedades físicas e químicas.

Abstract

Costa SXS. Influence of photo-activation methods and light sources on the properties of different composite resins [Tese de Doutorado]. Araraquara: Faculdade de Odontologia da UNESP; 2010.

Abstract

The aim of this work, divided into three studies, was evaluate: (1) the influence of different light sources and photo-activation methods on degree of conversion and polymerization shrinkage of a nanocomposite resin; (2) the influence of different photo-activation methods, available by the 2nd generation LED light-curing units, on the volumetric shrinkage of microhybrid and nanocomposite resins and (3) thermal properties and degree of conversion of microhybrid and nanocomposite resins submitted to different photo-activation methods available by 2nd generation LED light-curing units. In the first study, degree of conversion (DC) was evaluated by Fourier transform infrared spectroscopy (FT-IR) and shrinkage forces (S) were measured in a universal testing machine (EMIC). The data obtained for DC and S were analyzed by Analysis of Variance test (ANOVA) and for S *Welch's* correction and *Tamhane's* tests were also employed. In the second study, volumetric shrinkage was evaluated by video-imaging device (Acuvol[®]/Bisco) and data were analyzed by ANOVA and *Tukey's* test. In the third study, differential scanning calorimetry was used in order to observe glass transition temperature (*Tg*) and degradation peak of the materials and DC was evaluated for FT-IR. The DC data were analyzed by ANOVA and *Tukey's* test. The results showed differences in the polymerization shrinkage according to photo-activation method employed. In the first and second studies, the continuous photo-activation methods presented the highest values for shrinkage even though different methodologies were used to assess. Moreover, DC was not influenced by the photo-activation method but was influenced by light sources. The lowest DC values were observed for halogen light-curing unit. In the second study beyond the influence of the photo-activation method on the volumetric shrinkage of materials, differences were found between the composite resins. Microhybrid

composite resin showed the lowest volumetric shrinkage. In the third study, microhybrid composite resin presented the best thermal stability with highest T_g and degradation temperature values. Gradual photo-activation methods showed T_g and degradation temperature values higher or similar to those found for the continuous methods. Once more, in the third study, DC was not influenced by the photo-activation method. However, the kind of LED light-curing unit (LCU) and composite resin influenced the DC. The Elipar Freelight 2TM (3M ESPE) LCU and microhybrid resin showed the lowest DC values. Were also observed lower T_g values for groups light-cured with Elipar FreeLight 2TM (3M ESPE) LCU. Thus, based on results presented in the three studies concluded that the use of gradual photo-activation methods, either halogen or LED technologies, minimize the stress of shrinkage. The halogen LCU (power density=570mW/cm²) presented lowest conversion rates for composite resins when compared to LED LCU (power density=860mW/cm²). LED LCU and gradual photo-activation methods provided by these devices provide adequate degree of conversion without promoting changes in the polymer chain of composite resins. Notwithstanding, the kind of LCU and composite resin may influence the thermal and structural properties of the materials.

Key-words: Composite resins; curing lights, dental; spectroscopy Fourier transform infrared; physical and chemical properties.

Introdução

1 Introdução

Desde o desenvolvimento e introdução das resinas compostas por Bowen, em 1963, as pesquisas odontológicas têm por objetivo minimizar os problemas associados a estes materiais, especialmente a contração de polimerização. A contração é um evento inerente aos materiais resinosos devido à conversão dos monômeros em polímeros durante o processo de polimerização. Por sua vez, esta contração é decorrente da aproximação dos monômeros durante a formação das cadeias poliméricas, as quais ocupam um volume final menor que o inicial devido à aproximação destas moléculas^{34,43}.

As tensões geradas pelo fenômeno da contração podem gerar fendas na interface adesiva, além de trincas no substrato dental^{41,104}, os quais estão comumente associados aos principais problemas pós-operatórios das restaurações em resina composta. Duas abordagens podem ser utilizadas para controlar o problema da contração de polimerização: alteração da química e/ou composição das resinas compostas, além do emprego de artifícios técnicos como inserção incremental do material e métodos de fotoativação graduais que procuram tornar a conversão dos monômeros em polímeros mais lenta⁷⁰.

Desde o final da década de 70, a Odontologia baseia-se na utilização de resinas compostas que têm o processo de polimerização ativado por luz visível. Quatro décadas depois, os aparelhos que utilizam as lâmpadas halógenas convencionais de quartzo-tungstênio (QTH) ainda continuam sendo os mais usados na clínica. No entanto, algumas desvantagens estão associadas a este sistema de luz, especialmente a produção de um amplo espectro, com comprimentos de onda que geram calor, degradando o bulbo halógeno e seu refletor. Estas propriedades da luz halógena ocasionam diminuição da densidade de potência dos aparelhos com o tempo¹⁰¹.

A tecnologia dos diodos emissores de luz (LEDs) foi introduzida no mercado odontológico no final da década de 90 devido às suas vantagens quando comparada ao tradicional sistema halógeno⁴⁶. Os LEDs combinam semicondutores de nitreto de gálio e índio (InGaN) que produzem luz azul dentro

de uma faixa espectral estreita (450 a 490nm), com pico em torno de 470nm, o qual está idealmente apropriado para excitar o foto-iniciador primário mais comumente usado nas resinas compostas, a canforoquinona. Outras vantagens incluem vida útil extensa, estimada em cerca de 10 mil horas (os bulbos de lâmpada halógena duram apenas de 50 a 100 horas) e a não necessidade do uso de refletores e filtros, o que faz com que a luz produzida pelos LEDs tenha densidade de potência constante e maior estabilidade^{29,84-85,87}.

Os primeiros aparelhos à base de LED (1ª geração) possuíam densidade de potência ou intensidade luminosa baixa, aproximadamente 75 mW/cm², o que produziu resultados laboratoriais e clínicos iniciais insatisfatórios. Estes aparelhos de 1ª geração eram constituídos por um arranjo de LEDs para concentrar a radiação e gerar intensidade luminosa capaz de fotoativar os materiais resinosos⁴⁷. Na segunda geração, os diodos emissores de luz convencionais foram substituídos por diodos com maior área de superfície, emitindo luz com maior densidade de potência. Tais aparelhos não requerem o uso de vários diodos, atingindo densidades de potência de 800 mW/cm² ou mais^{17,21,67,96}.

Com o aumento da densidade de potência, o desempenho obtido por estes aparelhos de 2ª geração assemelhou-se ou superou os tradicionais aparelhos de luz halógena^{8,45,94}. No entanto, surge outra discussão: a não capacidade que estes aparelhos possuem para fotoativar efetivamente as resinas compostas que não apresentam a canforoquinona como foto-iniciador primário. Assim, são introduzidos os aparelhos de 3ª geração, os quais operam em diferentes comprimentos de onda, com o objetivo de ampliar o número de foto-iniciadores ativados^{24,63}.

A utilização de métodos de fotoativação graduais, os quais promovem lenta velocidade de polimerização inicial, tem sido sugerida como forma de minimizar as tensões geradas durante o processo de conversão dos monômeros em polímeros. Tanto os aparelhos à base de luz halógena como os à base de LED podem ser utilizados com baixa densidade de potência nos primeiros segundos de fotoativação, aumentando-se nos segundos restantes⁵⁶⁻⁵⁷.

O processo de fotoativação pode incluir, resumidamente, três métodos: contínuo, *pulse-delay* e a irradiação por etapas, sendo estes últimos também referidos como métodos *soft-start* ou de fotoativação gradual. No método contínuo, a mesma densidade de potência é empregada ininterruptamente durante todo o período de irradiação; no método *pulse-delay*, há uma exposição inicial de poucos segundos, seguida por uma interrupção da irradiação por um ou mais minutos e nova irradiação; no método por etapas, o início da fotoativação é realizado com baixa densidade de potência, havendo posteriormente o aumento gradual da mesma¹⁰.

Existe na literatura um questionamento sobre a possibilidade dos métodos de fotoativação graduais produzirem alterações na cadeia polimérica das resinas compostas, aumentando a quantidade de ligações lineares na estrutura final do polímero. Tal estrutura é mais susceptível aos efeitos das substâncias presentes nos alimentos e ao ataque enzimático, degradando os materiais e, conseqüentemente, reduzindo a longevidade das restaurações^{4,51,53,58,107}.

Assim, se por um lado as técnicas graduais de fotoativação propõem o controle da contração de polimerização e a conseqüente geração de tensões na interface adesiva, qual seria a influência exercida por estas técnicas nas propriedades finais das resinas compostas caso a estrutura polimérica seja alterada?

Os aparelhos LED de última geração operam com elevadas densidades de potência e alguns fabricantes já disponibilizam métodos graduais de fotoativação nestes aparelhos com o objetivo de minimizar o estresse gerado durante a polimerização. Estes métodos graduais também podem alterar as propriedades físico-mecânicas das resinas compostas, como já relatado na literatura^{4,51,53,58,107}. Dessa forma, haverá repercussão direta sobre o desempenho clínico das restaurações, apesar do benefício associado a estes métodos.

Compreender como estes métodos graduais podem interferir nas propriedades finais dos materiais resinosos pode auxiliar o profissional quando da seleção do melhor método de fotoativação para uma determinada aplicação clínica. Assim, esta pesquisa se propôs a avaliar a influência da utilização dos

métodos de fotoativação gradual e contínuo, disponibilizados em aparelhos fotoativadores de alta densidade de potência à base de luz halógena e LED, sobre as propriedades de diferentes resinas compostas.

Proposição

2 Proposição

Os objetivos deste estudo foram:

1. Avaliar o efeito dos métodos de fotoativação contínuo e gradual, utilizando diferentes fontes de luz (halógena e LED de 2ª geração), sobre a contração de polimerização e o grau de conversão de uma resina composta nanoparticulada;
2. Avaliar o efeito dos métodos de fotoativação contínuo e gradual, disponibilizados por aparelhos de fotoativação à base de LED de 2ª geração, sobre a contração volumétrica de uma resina composta microhíbrida e uma nanoparticulada;
3. Avaliar o efeito dos métodos de fotoativação contínuo e gradual, disponibilizados por aparelhos de fotoativação à base de LED de 2ª geração, sobre o grau de conversão e estrutura polimérica de uma resina composta microhíbrida e uma nanoparticulada.

Capítulo 1

3 Capítulos

3. 1 Capítulo 1

Influence of Different Light Sources and Photo-Activation Methods on Degree of Conversion and Polymerization Shrinkage of a Nanocomposite Resin*

Authors: ^aS. X. S. Costa, ^bL. M. Martins, ^bP. A. S. Franscioni, ^cV. S. Bagnato, ^aJ. R. C. Saad, ^{a,c**}A. N. S. Rastelli, ^aM. F. Andrade

^aUniversity of São Paulo State-UNESP, Araraquara School of Dentistry, Department of Restorative Dentistry, Araraquara, SP, Brazil.

^bUniversity of São Paulo-USP, Bauru School of Dentistry, Bauru, SP, Brazil.

^cUniversity of São Paulo, São Carlos Physics Institute, São Carlos, SP, Brazil.

* Artigo publicado no periódico *Laser Physics* (Anexo 2).

**Corresponding author: Prof. Dra. Alessandra Nara de Souza Rastelli, University of São Paulo State-UNESP, Araraquara School of Dentistry, Department of Restorative Dentistry, 1680 Humaitá St. ZipCode: 14801-903. Telephone: +55 16 3301-6389. Fax:

e-mail address: alerastelli@yahoo.com.br

ABSTRACT

The purpose of this study was to evaluate the influence of different light sources and photo-activation methods on degree of conversion (DC%) and polymerization shrinkage (PS) of a nanocomposite resin (Filtek™Supreme XT, 3M/ESPE). Two light-curing units (LCUs), one halogen-lamp (QTH) and one light-emitting-diode (LED), and two different photo-activation methods (continuous and gradual) were investigated in this study. The specimens were divided in four Groups: Group 1– power density (PD) of 570mw/cm² for 20s (QTH); Group 2–PD 0 at 570mw/cm² for 10s + 10s at 570mw/cm² (QTH); Group 3–PD 860mw/cm² for 20s (LED) and

Group 4–PD 125mw/cm² for 10s + 10s at 860mw/cm² (LED). A testing machine EMIC with rectangular steel bases (6x1x2mm) was used to record the polymerization shrinkage forces (MPa) for a period that started with the photo-activation and ended after two minutes of measurement. For each Group, ten repetitions (n=40) were performed. For DC% measurements, five specimens (n=20) for each Group were made in a metallic mold (2mm thickness and 4mm diameter, ISO 4049) and them pulverized, prensed with bromide potassium (KBr) and analysed with FT-IR spectroscopy. The data of PS were analysed by Analysis of Variance (ANOVA) with *Welch's* correction and *Tamhane's* test. The PS means (MPa) were: 0,60 (G1); 0,47 (G2); 0,52 (G3) and 0,45 (G4), showing significant differences between two photo-activation methods, regardless of the light source used. The continuous method provided the highest values for PS. The data of DC% were analyzed by Analysis of Variance (ANOVA) and shows significant differences for QTH LCUs, regardless of the photo-activation method used. The QTH provided the lowest values for DC%. The gradual method provides lower polymerization contraction, either with halogen lamp or LED. Degree of conversion (%) for continuous or gradual photo-activation method was influenced by the LCUs. Thus, the presented results suggest that gradual method photo-activation with LED LCU would suffice to ensure adequate degree of conversion and minimum polymerization shrinkage.

PACS numbers: 42.55.-f, 42.62.-b, 42.62.Be

1. INTRODUCTION:

The polymerization process of a composite resin occurs by the conversion of the monomer molecules of the matrix into a polymer chain, followed by a reduction of the space between these molecules, which then occupy a smaller volume than the initial. This reduction in the total volume of the material is known as the polymerization shrinkage [1]. Although the composite resin is considered the best esthetic direct restorative material, excessive shrinkage of polymerization is one of the main factors that contribute to the failure of restorations [2]. The magnitude of the stress is influenced by several factors,

including the overall shrinkage, the curing rate, the elastic modulus, and the stress relieving characteristics of the composite restoration [3].

The determining factors of the polymerization quality is the light power density (mW/cm^2) produced by the light curing unit (LCU). The power density represents the amount of photons emitted in the light guide. A minimal power density of $300 \text{ mW}/\text{cm}^2$ is required to effectively polymerize a 2 mm deep increment with a light-curing unit conventional halogen (QTH) and light emitting-diode (LED) [4].

LCUs are an integral part of the daily practice of restorative dentistry. Quartz-tungsten- halogen (QTH), plasma-arc (PAC), argon laser and light-emitting diode (LED) curing lights are currently commercially available and different light sources may also influence the development of physical properties. The QTH curing light has a long, established history as a workhorse for composite resin polymerization in dental practices and remains the most common type of light in use today [5]. The light emitted by these units is generated when the tungsten filament is heated emitting a visible blue light in a large spectrum. A filter limits the interval of the wavelength in the range from 400 to 500 nm (nanometer). Consequently, the use of QTH LCUs to polymerize dental composites has several limitations as the halogen bulbs, reflector and filter degrade over time due to high operation temperatures and heat produced, resulting in a limited effective lifetime of about 40 to 100 hours [6-11].

The LCUs using blue light-emitting diode (LED) has the advantage of a narrower spectral range than the QTH light and a better match of light emitted with the absorption spectrum of the photoinitiator camphorquinone [12-13]. Additionally, LED units do not use filters, which are required with halogen units for wavelength selection. Thus, LED units represent an improvement over halogen lamps [14-18]. According to Aravamudhan et al. (2006) [19] and Calixto et al. (2008) [11], in general, there were no differences between the halogen and LED light-curing units with the same parameters.

In spite of the mechanical properties of current composite resins have been improved, polymerization shrinkage is still an inevitable problem. Polymerization

shrinkage and degree of conversion (DC) of resin composites are closely related manifestations of the same process. Ideal dental composite would show an optimal degree of conversion and minimal polymerization shrinkage. These seem to be antagonistic goals, as increased monomer conversion invariably leads to high polymerization shrinkage values [20].

The marginal integrity of composite resins restorations depends on many factors among them the difference between the thermal expansion coefficient of the tooth and the restorative material, however especially the polymerization shrinkage related to the dimethylacrylate-based matrix of these materials. In the polymerization process, composite resins shrink due to their passage from a liquid to solid state and the shrinkage is the result of the reduction in the intermolecular distance between monomeric units. The polymerization shrinkage should be considered as the principal mechanism responsible for problems concerning the interface failures [21-22].

If shrinkage forces exceed the bonding strength at the interface, the resulting interfacial gap can lead to staining, marginal leakage [23], post-operative sensitivity [24] and recurrent caries [25-26]. Moreover, the contraction forces can be transferred to neighboring dental structures causing cuspal deflection or fractures in the enamel [27]. The clinical consequences of polymerization shrinkage constitute the main reasons for premature replacement of composite resin restorations [28]. This explains why it is regarded as the main limitation of present-day resin composites and why its elimination or minimization is one of the most important research tasks in this field.

Volumetric contraction and elastic modulus are directly related to the composite degree of conversion [29]. Because higher degree of conversion is also associated with improved mechanical properties [30], there is an idea that high degree of conversion would improve the performance of composite restorations over time. However, it seems reasonable to expect that higher degree of conversion will also lead to higher contraction stresses, therefore, increasing the risk of bonding failure. In fact, a previous study assessing the relationship

between degree of conversion and contraction stress in an experimental composite found that the stress development rate increases at higher conversion levels [31].

As a consequence of the dependence of volumetric shrinkage and elastic modulus on degree of conversion (DC), a direct relationship between DC and polymerization shrinkage (PS) exists. Consequently, at this late stage into the polymerization reaction, small increments in DC produce significant increases in PS [31-33]. Furthermore, *in vitro* studies verified that insufficient conversion may cause allergic reactions and stimulate bacterial growth around restoration margins [34-35]. Also, residual monomers can act as plasticizers and compromise a composite's mechanical properties [36].

The contraction forces development and relaxation are related to local conditions such as the C-factor corresponding to the bonded/unbonded surface area ratio, structure that dentin exhibits [37, 38, 39, 40], the compliance of the substrate corresponding to the surrounding tooth structure and the thickness of the adhesive layer. Also they depend to the composite itself (filler content) [41], ratio and type of comonomers, concentration and system of photoinitiators and finally, to the type of technique used (incremental technique) [42-43] and parameters of photo-activation (light sources, power densities, photo-activation method) [44].

The photo-activation method has a profound influence on shrinkage stress. High intensity lights provide higher values for degree of conversion, but they also produce higher contraction stress. As lower curing process that permits composite flow may allow for stress relaxation during polymerization [45].

With the objective of to reduce polymerization shrinkage stress different photo-activation methods have been suggested. Commonly, QTH and LED lights have been used in a continuous output mode while emitting a fairly high irradiance [46-47]. However, radiation from this type of source can also be applied for different methods. The soft-start method, i.e, employs an initial low irradiance for a specific duration followed by a high one equivalent in value to that of the continuous phase [48]. Some studies have associated this method with better marginal integrity of composite resins [47, 49-51].

Manufacturers have recommended high light intensity to provide a higher degree of monomer conversion into polymer, thus improving the mechanical properties of composite resins. However, the degree of conversion is always proportionally associated with shrinkage and a high rate of polymerization [52-53]. Clinically, the effect of post-gel shrinkage and contraction stress can be minimized by flow during setting by applying short pulses of energy (pulse activation) or pre-polymerization at low-intensity light followed by a final cure at high intensity (soft-start techniques) [8, 54], as these methods promote a longer pre-gel phase in light-cured composites. Curing methods using lower irradiance levels were shown to be effective in reducing the rate of stress generation without compromising the conversion of the restorative composite [55].

Some studies have shown that the polymerization rate influences the polymer structure. Thus, so-called soft-start curing may reduce the degree of conversion and, at a given degree of conversion, the crosslink density [56-57]. It was hypothesized that gradual photo-activation methods would exhibit a reduced crosslink density, in despite the reduction of the shrinkage. The degree of polymerization in crosslinked polymeric systems plays a potentially large role in determining the ultimate physical and mechanical properties of the material [8].

Thus, in this study it was hypothesized that different light sources and photo-activation methods could lead to different polymer structures and lowest degree of conversion. Since DC and shrinkage properties are correlated, the aim of the present study was to measure the degree of conversion and polymerization shrinkage of a nanocomposite resin photo-activated by QTH and LED LCUs.

2. MATERIALS AND METHODS:

2.1. Composite resin used in this study:

In the present study, the nano-filled composite resin Filtek™ Supreme XT (shade A2B) was selected. The Table 1 shows the main composition the dental composite resin used.

2.2. Light-curing units used (LCUs):

Two light-curing units one QTH (Optilux 501/Demetron) and one blue LED (Bluephase/Ivoclar-Vivadent), were used in this study. Two different light-curing methods (continuous and gradual) were tested (Table 2).

Prior to the curing procedures, the output power of the LCUs was measured with a calibrated power meter (Fieldmaster Power Meter, Coherent-model n° FM, set n° WX65, part n° 33-0506, USA) and the diameter of the light guide tip with a digital caliper (Mitutoyo, Tokyo, Japan). Power density (mW/cm^2) was computed as the ratio of the output power and the area of the tip with the following formula: $I = P/A$, where P is the power in milliwatts and A is the area of the light tip in squared centimeters.

Figure 1 shows the emission spectrum of the two LCUs obtained using a spectrophotometer USB 2000 (Ocean Optics).

2.3. Samples Preparation:

For degree of conversion measurements, the samples ($n=20$) were made with a metallic mould (4 mm in diameter and 2 mm in thickness). The metallic mould was positioned in a glass plate of 10 mm thickness. The composite resin was packed in a single increment and the top and base surfaces were covered by a mylar strip. A glass sheet with 1mm thickness was positioned, and the 1 Kg weight (kilogram) was used to pack the composite resin. The top surface of the samples was placed in contact with the curing light tip. The samples were photo-activated for 20s of irradiation times (manufacturer's instructions).

After 24 hours, the composite resin was pulverized into fine powder. Five milligrams of the composite powder was thoroughly mixed with one hundred milligrams of KBr (bromide potassium) powder salt. This mixture was placed into a pelleting device and then pressed in a press with a load of 10 tons during 1 minute to obtain a pellet. The table 3 shows the division of the groups.

2.4. Determination of the degree of conversion (% DC):

The number of double carbon bonds which are converted in single bonds provides the degree of conversion (%DC) of composite resin. To measure the degree of conversion the pellet was then placed into a holder attachment into the spectrophotometer (Nexus-470 FT-IR, Thermo Nicolet, E.U.A). FT-IR spectra of both uncured and cured samples were analyzed using an accessory of reflectance diffuse. The measurements were recorded in absorbance operating under the following conditions: 32 scans, 4 cm⁻¹ resolution, 300 to 4000 cm⁻¹ wavelength. This experiment was carried out in triplicate. The degree of conversion was determined by subtracting the % C=C from 100%, according to the formula:

$$(\%)DC = 1 - \frac{\left(\frac{1638\text{cm}^{-1}}{1608\text{cm}^{-1}}\right)_{\text{cured}}}{\left(\frac{1638\text{cm}^{-1}}{1608\text{cm}^{-1}}\right)_{\text{uncured}}} \times 100$$

The percentage of unreacted carbon-carbon double bonds (% C=C) was determined from the ratio of absorbance intensities of aliphatic C=C (peak at 1638 cm⁻¹) against internal reference aromatic C-C (peak at 1.608 cm⁻¹) before and after curing of the specimen.

2.5. Polymerization Shrinkage:

The polymerization shrinkage was recorded by a universal testing machine (EMIC, DL 500 BF-NO5775-NS168, São José dos Pinhais, PR, Brazil). Two opposite and parallel stainless steel plates were used (6x1x2mm). The bottom plate (cylindrical) was fixed and connected to a Bencor Multitest device especially adapted for this test. The top plate (rectangular) was connected to a 20 kgf load cell of a computerized testing machine (Figure 2).

The dental composite resins were placed between the plates (Figure 3) and the test was performed simultaneously to the composite resins photo-activated record the shrinkage forces for a period that started with the photo-activation and ended after two minutes of measurement. The LCUs was positioned in a device for maintaining a stable position and distance during the test. For each group, 10 repetitions were performed (Table 3).

The tip of the light curing units (LCUs) were placed perpendicularly to the long axis and centred on the middle of the specimen. The distance between the light tip and the composite surface was 1mm.

During test, the shrinkage stress generated by polymerizing caused a minimal deflection in load cell, which was transmitted to the universal testing machine. Each measurement produced a graph (force, in Newton X time, in seconds). The maximum shrinkage stress obtained for each group was recorded.

2.6. Statistical analysis:

The data of polymerization shrinkage were statistically analyzed by Analysis of Variance (ANOVA) with Welch's correction and Tamhane's test. The DC's data were analysed by Analysis of Variance (ANOVA), using a confidence interval of 95%

3. RESULTS:

3.1. Degree of conversion:

The Table 5 shows the degree of conversion (DC%) mean values promoted by different light-curing units (LCUs) and photo-activation methods. The Analysis of Variance (ANOVA) showed that the DC% was not influenced by photo-activation methods ($p < 0,05$), but differences were observed for light sources. Significant differences were found only when QTH LCU was used, ie, the QTH provided the lowest values for DC% (Figure 4).

The DC (%) values varied from 46,21% ($\pm 3,03$) to 49,35% ($\pm 2,28$) for QTH LCU photo-activated for continuous and gradual methods, respectively. For LED LCU, the DC (%) values varied from 52,32% ($\pm 0,67$) to 52,30% ($\pm 1,14$) when continuous and gradual methods were used.

After 24 hours, using the irradiation time recommended by the manufacturers, QTH (20 seconds) and LED (20 seconds) were statistically different ($p > 0.001$). Therefore, the results revealed that the light source used had a significant ($p < 0.05$) impact on the degree of conversion.

3.2. Polymerization Shrinkage:

Mean values and standard deviations (SD) for polymerization shrinkage (PS) are shown in Table 4. It was observed that there is greater variability of the values of PS for the QTH in relation to those obtained with LED.

The Analysis of Variance (ANOVA) with Welch's correction showed that the polymerization shrinkage was not influenced by LCUs (QTH or LED), but significant differences were found between the two photo-activation methods ($p < 0,001$). The Tamhane's test indicates that the gradual photo-activation method provided the lowest values for polymerization shrinkage, regardless of the LCU used (Figure 3).

4. DISCUSSION:

Adequate polymerization or high degree of conversion is a crucial factor in obtaining optimal physical properties and the clinical performance of composite resins. Thus, inadequate polymerization leads inferior physical properties, the solubility in the oral environment, and an increased microleakage with a resultant recurrent decay and pulpal irritation [58]. On the other hand, polymerization shrinkage is considered a major problem with resin-based materials because it creates destructive stresses when the material is bonded to cavity walls [59].

Polymerization shrinkage and degree of conversion of composites are closely related manifestations of the same process. Ideally, composite resins would show a high degree of conversion and minimal polymerization shrinkage. These seem to be antagonistic goals, as increased monomer conversion invariably leads to high polymerization shrinkage values [60].

The contraction stress developing in composites during polymerization depends on many factors such as: the chemical composition of the polymer matrix, filler particles and silane, the rheology and viscosity of the paste, the flow behavior of the material during the pre-gel phase as well as the duration of the pre-gel phase and the initiator systems. In the pre-gel phase, the polymer chains formed are very flexible so that material of the free surface of the cavity can flow. The viscosity of the developing polymer is still low, so that shrinkage stress can

be compensated. The time at which the material is no longer able to compensate for polymerization shrinkage (time until gelation) therefore, determines the final stress in the material [61].

A higher degree of conversion, which is primarily related to curing light intensity and irradiation time, conflicts with the objective of achieving optimal marginal integrity, because of increased shrinkage [62]. To minimize shrinkage stress, “soft cure” or “soft-start” methods were suggested. These photo-activation methods have the option of operating with an initial period of low intensity illumination, which should reduce stress development during composite curing [29, 63].

The use of gradual photo-activation methods to reduce shrinkage stress has become widespread in restorative dentistry. However, an increased susceptibility to ethanol degradation of polymers formed by gradual photo-activation was reported. Asmussen, Peutzfeldt (2001, 2003) [56, 63] and Benetti et al. (2009) [64] explains that a slow polymerization start with low intensity is associated with relatively few centers of polymer growth, resulting in a more linear polymer structure with relatively few cross-links. On the other hand, a high intensity during the initial phase of the irradiation period will initiate a multitude of growth centers and a polymer with higher cross-link density results.

In agreement with previous observation, the results obtained for Gonçalves, Calheiros, Witzel, Kawano, Braga (2006) [65] suggest that when low irradiances or gradual methods are used, a relatively high radiant exposure is necessary to originate a polymer network structure similar to that obtained by continuous high irradiance photo-activation.

In the present study, both degree of conversion and polymerization shrinkage were used to estimate crosslinking density of a resin composite photo-activated by two different light sources (QTH and LED) and photo-activation methods (continuous and gradual). For the polymerization shrinkage (PS), statistical difference was observed among the curing methods, independently of the light source used. The continuous method provided the highest values for PS. These findings coincide with the results of Cunha, Alonso, Sobrinho, Sinhoreti

(2006) [66] and Lopes, Franco, Pereira, Mondelli (2008) [10], which found that the conventional mode with QTH and LED LCUs produced the higher stress means. Several authors have reported the efficacy of low intensity or pulse-delay methods in reducing the polymerization contraction stress of composites [10, 54, 60, 67].

For Visvanathan, Ilie, Hickel, Kunzelmann (2007) [68] it is probable that the effects of soft-start method depends on the type of the device used, i.e. LED or QTH and the light intensity, which was not found in this study. This is probably associated to the similar power density between the LCUs, a fact that was not seen in the first LED generations, which had a much lower power density when compared to the halogen-lamp devices. The high light intensity or power density of LCUs used in this study caused fast polymerization with a very short pre-gel phase. As a consequence, the contraction strain occurring in the material during polymerization could not be compensated for by flow and therefore, allowed the development of contraction stress. This statement is in accordance with Ilie, Felten, Trixner, Hickel, Kunzelmann (2005) [61] and Tonegawa et al. (2009) [69].

Photo-activation methods tested in the present study did not affect the degree of conversion of the composite resin, in accordance with results of other studies [49, 54, 60, 70-71].

In this research, the Fourier Transformer Infra-red Spectroscopy analyzes (FT-IR) was used to evaluate a possible interference in the DC% of composite resin produced by the light source and photo-activation method (continuous and gradual). Techniques such as Fourier Transform Infra-red spectroscopy (FT-IR) [29, 72], spectroscopy RAMAN [73], electron paramagnetic resonance (EPR) [74], nuclear magnetic resonance (NMR) [75], differential scanning calorimetry (DSC) [76] and differential thermal analysis (DTA) [77] have been used to determine the DC. Among these, FT-IR is the most frequently used technique.

Asmussen, Peutzfeldt (2003) [63] showed that a lower DC is associated with softer polymers after storage in ethanol. This is in accordance with earlier work [78-79]. Low DC implies a less dense structure of the polymer and therefore easier penetration of plasticizing substances such as ethanol. Lovell et al. (2001)

[80], however, showed contradictory results. They found that the mechanical properties were insensitive to the rate of polymerization but strongly dependent on the final double bond conversion.

However, the DC was influenced by light source. The QTH provided the lowest values for DC. Similar results from a study of Bala, Olmez, Kalayci (2005) [81], where a LED LCU polymerization was superior to that of QTH LCU. This result can be explained because the blue LED is almost totally absorbed by the material along the polymerization procedure, producing uniform curing without compromising the physical and chemical properties of the material through time [82].

Several studies reported that the DC of composite resin produced by the QTH was higher than that produced by LED LCUs due to higher light intensities [6, 63]. Other studies reported that LED LCU cured better than did the QTH LCU [14, 83]. However, those studies did not investigate DC in the soft-start method produced by high powered LED LCUs. In this study, DC produced by QTH LCU show a significant statistical difference for both photo-activation methods ($p > 0.001$). However, polymerization produced by high power LED (continuous or gradual photo-activation methods) produced the highest DC. Calixto et al. (2008) [11] showed that, in general, there were no differences in the curing depth between the QTH and LED light-curing units used with the same parameters.

For dental resins cured under clinical conditions, final conversion is typically between 55 and 75% [73, 84], which also agrees with the DC observed in this study, except for the gradual method. Under these circumstances, the DC were 47% and 45% when QTH (gradual method) and LED (gradual method) were used, respectively. Nevertheless, according Soares, Liporoni, Martin (2007) [85] and Rastelli, Jacomassi, Bagnato (2008) [58] the minimum DC for a clinically satisfactory restoration has not yet been precisely established. A negative correlation of *in vivo* abrasive wear depth with DC has been found for values in the range of 55%-65%. This suggests that, at least for occlusal restorative layers, DC values below 55% may be contraindicated [29]. From our experiment, the DC ranged from ± 46 to $\pm 52\%$.

In this study, composite polymerization by QTH LCU in the continuous photo-activation method produced a DC of 46,21% and 49,35% for gradual photo-activation method, with possible influence on composite physical properties. However, composite polymerization by LED produced DC of 52,32% (continuous method) and 52,30% (gradual method). Thus, according to these results, it seems that the LED-based devices allow for a better conversion from monomers to polymers.

The high power LED LCU is an alternative to the halogen light LCU, because the LED is more compact, wireless and has a working lifetime of more than 10,000 hours, which is a significantly lower thermal emission, and LEDs have wavelength peaks of around 470 nm, which match the absorption peak of the most commonly used photo initiator camphoroquinone [7, 86].

A lower degree of conversion could affect the longevity of the composite restoration, because an incomplete conversion may result in unreacted monomers, which might dissolve in a wet environment. In addition, reactive sites (double bonds) are susceptible to hydrolyzation or oxidation and, thereby, lead to a degradation of the material [58]. Additionally, this fact could directly affect biocompatibility of the composite restoration [87], since increasing the DC number of methacrylate pendant groups available for hydrolytic degradation decreases. Hydrolytic degradation and oxidation of composites may lead to the leaching of different degradation products from composite resin. Formaldehyde has been identified as one of the degradation products. Methacrylic acid has also been identified as an eluted species that can cause irritation of the mucosa membrane and is cytotoxic [58].

The degree of conversion is an important parameter in determining the final physical, mechanical and biological properties of composite resins, since it has been demonstrated that resin composite properties tend to improve as the degree of conversion attained during photo-activation is increased. However, constrained shrinkage during polymerization densification generates polymerization shrinkage stress, which is one of the most significant concerns during the highly technique-sensitive clinical placement of composite restorations.

5. CONCLUSIONS:

The results obtained for this study indicate that the photo-activation methods (continuous and gradual) evaluated promoted differences in the polymerization shrinkage, regardless of the light source used. The gradual photo-activation method provided the lowest polymerization shrinkage. However, the degree of conversion was influenced by light source. The light-curing unit based halogen lamp provided the lowest values for degree of conversion, either continuous or gradual photo-activation methods.

Based on the results of this study may be suggested that LED LCU promotes better conversion of the nanocomposite. Additionally, the gradual photo-activation method should be used to minimize the polymerization shrinkage of the material when the LED LCUs second generation are selected due to the high power density.

6. ACKNOWLEDGMENTS:

We would like to thank:

- 3M/ESPE Brazil for providing the nanofilled composite resin used in this study;
- Labordental Brazil for providing the light-curing unit (Optilux 501/Kerr) used in this study;
- Dr Milko Javier Villarroel Cortes for providing the light-curing unit (Bluephase/Ivoclar-Vivadent) used in this study;
- The Physics Institute of São Carlos, University of São Paulo/Brazil and Bauru School of Dentistry, University of São Paulo/Brazil by the use of equipments.

This study was supported by the CAPES/Brazil and São Paulo State University, UNESP, Araraquara School of Dentistry, Brazil.

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FIGURES AND TABLES

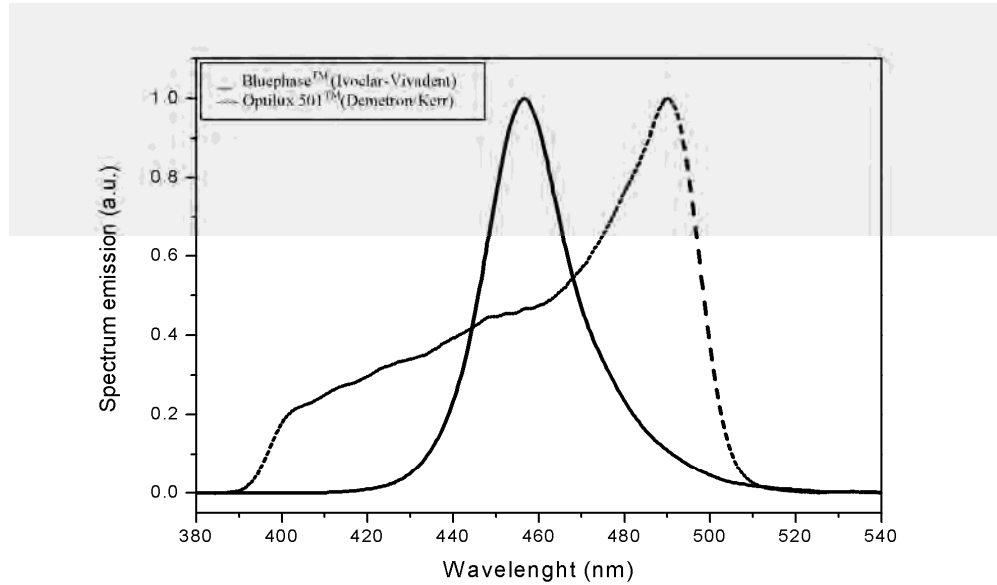


Figure 1: Emission spectrum of the LCUs.

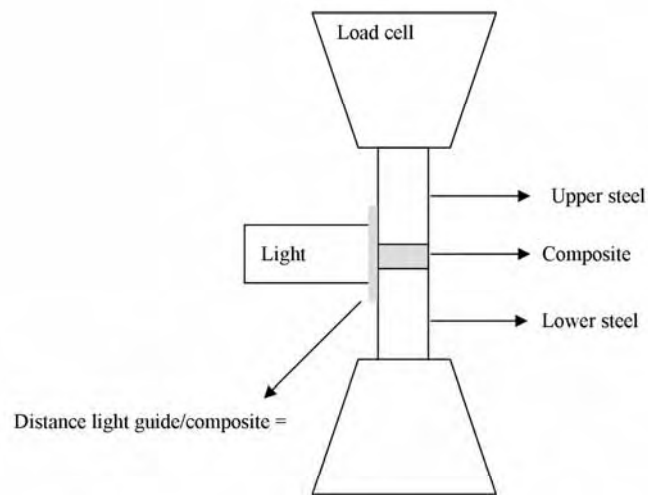


Figure 2. Schematic illustration of the steel bases EMIC test system and the light guide of the curing system device.

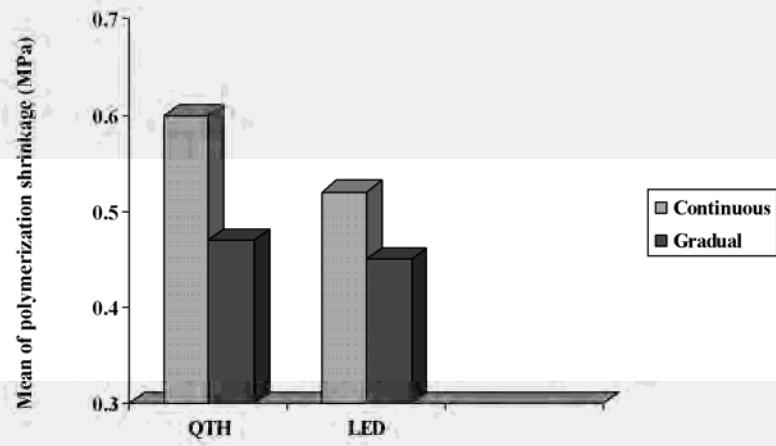


Figure 3: Averages of the polymerization shrinkage depending on the light source and photo-activation method.

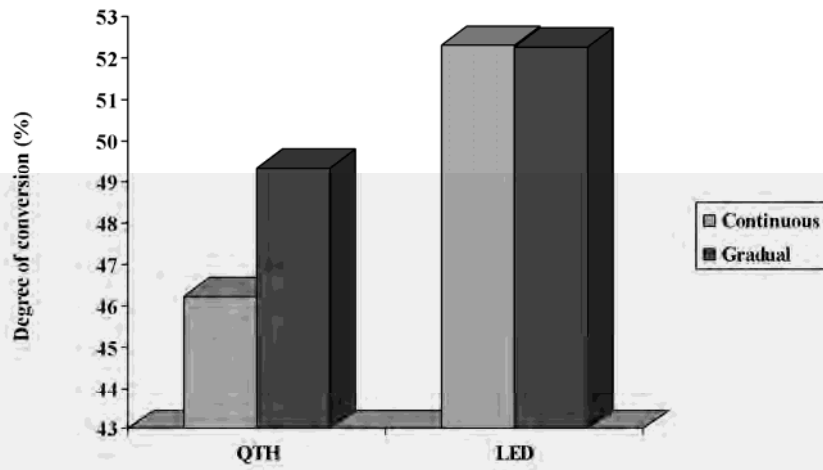


Figure 4: Averages of the degree of conversion depending on the light source and photo-activation method.

Table 1. Characteristics of restorative material used in the study (manufacturers' data)

Material	Manufacturer	Shade	Material type	Matrix	Filler size	Filler Volume	Lote number
Filtek™ Supreme XT	3M/ESPE	A2B	Nanofilled composite	Bis-GMA, Bis-EMA, UDMA, TEGDMA	Agglomerated/non-aggregated of 75 nm silica nanofiller and a loosely bound agglomerate silica nanocluster consisting of agglomerates of primary silica nanoparticles of 75 nm size fillers. The cluster size range is 0.6 to 1.4	72.5%	6ER

Table 2. Characteristics of light curing units used in the study (manufacturers' data)

Light curing unit/ serial number	Manufacturer	Light source	Light curing method (LCM)	Description of LCM
Optilux 501/ 5817562 USA	Demetron- Kerr	Halogen lamp	Continuous	Power density (PD) of 570mw/cm ² for 20s
			Gradual	PD of 0 at 570mw/cm ² for 10s + 10s at 570mw/cm ²
Bluephase/ 2124 Norway	Ivoclar- Vivadent	LED	Continuous	PD of 860mw/cm ² for 20s
			Gradual	PD of 125mw/cm ² for 10s + 10s at 860mw/cm ²

Table 3: Division of the investigated Groups

Group	Light source	Photo-activation methods
1	QTH (Optilux 501-Kerr)	Continuous (570mW/cm ² for 20s)
2	QTH (Optilux 501-Kerr)	Gradual (0 at 570mW/cm ² for 10s + 10s at 570mW/cm ²)
3	LED (Bluephase-Ivoclar)	Continuous (860mW/cm ² for 20s)
4	LED (Bluephase-Ivoclar)	Gradual (125mW/cm ² for 10s + 10s at 860mW/cm ²)

Table 4: Mean (M) and Standard deviation for PS

Light source	Photo-activation method	Mean		SD
			b	
Halógena	Continuous	0,60	a	0,07
	Gradual	0,47	b	0,04
LED	Continuous	0,52	a	0,01
	Gradual	0,45		0,01

* Different letters denotes a significant difference ($p < 0.05$).

Table 5: Mean (M) and standard deviation (SD) for degree of conversion.

Light source	Photo-activation methods	M	*	SD
QTH	Continuous	46,21	a	3,03
	Gradual	49,35	a	2,28
LED	Continuous	52,32	b	0,67
	Gradual	52,30	b	1,14

* Different letters denotes a significant difference ($p < 0.05$).

Capítulo 2

3.2 Capítulo 2

Volumetric Shrinkage of Composites Using Video-Imaging: Influence of Photo-Activation Methods in Light-Cured Units Based on Light-Emitting-Diode*

Simone X. S. Costa¹, Jussara K. Bernardon², Luiz H. M. Prates², Osmir B. Oliveira Júnior¹, Alessandra N. S. Rastelli^{1}, Marcelo F. Andrade¹**

¹ Department of Restorative Dentistry, São Paulo State University/UNESP, Araraquara School of Dentistry, Araraquara, São Paulo, Brazil

² Federal University of Santa Catarina/UFSC, Department of Restorative Dentistry, Florianópolis, Santa Catarina, Brazil

* Enviado para publicação no periódico *Journal of Biomedical Materials Research Part B: Applied Biomaterials* (Anexo 3).

**Corresponding author: Alessandra Nara de Souza Rastelli, 1680 Humaitá St., Araraquara, São Paulo, Brazil, 14.801-903, e-mail: alerastelli@yahoo.com.br

ABSTRACT

The aim of this study was to evaluate the influence of photo-activation methods (PM) on the volumetric shrinkage (VS) of composite resins (CRs) using video-imaging devices AcuVol[®] (Bisco). Two light-curing units (LCUs) based on light-emitting-diodes (LEDs), two CRs (microhybrid, nanocomposite) and two different PM (continuous, gradual) were divided in eight Groups (n=80): G1=microbryd resin + Elipar Freelight 2TM/3M ESPE (EFL2) + continuous method (CM); G2= microbryd resin + EFL2 + gradual method (GM); G3=nanocomposite + EFL2 + CM; G4=nanocomposite + EFL2 + GM; G5=microbryd resin + Bluephase[®]/Ivoclar-Vivadent (B) + CM; G6= microbryd resin + B + GM; G7=nanocomposite + B + CM; G8=nanocomposite + B + GM. The VS was measured for a period that started seconds before the photo-activation and ended after ten minutes. The data were analyzed by Analysis of Variance (ANOVA) and

Tukey's test ($p < 0.05$), showing significant differences between the initial and post photo-activation periods. Significant differences were also found between PM and CRs during photo-activation. The mean and standard deviation for VS was: G1-17.58% (± 0.37); G2-17.47 (± 0.35); G3-19.80 (± 0.64); G4-17.91% (± 0.44); G5-17.05% (± 0.30); G6-17.44% (± 0.58); G7-18.24% (± 0.32); G8-17.94% (± 0.46). The results suggest that GM promote lowest VS, especially when microhybrid resins were used.

KEY-WORDS: Volumetric shrinkage, Light-curing units, Light-emitting-diodes, Photo-activation, Composite resin.

INTRODUCTION

Due to their conservative and aesthetic properties, composite resins have found widespread application in restorative dentistry. The properties of these materials have been improved significantly over the last few decades. Dental composites, however, still have several drawbacks, these include their polymerization shrinkage. Therefore, the reduction of polymerization shrinkage presents an important goal in biomaterials research. ¹

The polymerization process of a composite resin occurs by the conversion of the monomer molecules of the matrix into a polymer chain, followed by a reduction of the space between these molecules, which then occupy a smaller volume than the initial. This reduction in the total volume of the material is known as the shrinkage of polymerization. ²

Forces are generated by the polymerization shrinkage of bonded dental resin composite. These forces may result in stresses within the composite, at the interface between the composite and the surrounding enamel and dentin, and in the surrounding enamel and dentin. The stresses may induce several phenomena including deformation of the composite³ and tooth ⁴, formation of contraction gaps⁵, and cracking in the surrounding substrate. ⁶ The contraction stress may be one of the factors causing postoperative problems with composite restorations. ⁷

The properties of a light-curing composite resin are mainly influenced by the amount of energy delivered to the composite during irradiation, i.e. the energy density.^{8, 9, 10, 11,12} For a given energy density, different combinations of curing time and power density may be used to cure the composite materials. Moreover, the light can be delivered in different methods: continuous, pulse-delay or stepped irradiation. The continuous mode delivers the same power density uninterruptedly throughout the entire exposure period. The pulse-delay method initiates cure with a short exposure, which is interrupted for one or more minutes, and is then completed. The stepped mode operates at low power density at the beginning and at higher power density at the end of the irradiation. The pulse delay and the stepped mode of cure are so-called soft-start modes of cure.¹³

The different photo-activation methods and different combinations of power density and exposure duration may influence the properties of light-curing composite resins. Despite polymerization shrinkage of composite resin decreased with gradual photo-activation methods, different curing methods such as pulse-delay^{14, 15} and two-step curing^{16, 17} led to polymers of increased susceptibility to softening in ethanol. It has been speculated that a slow start of the polymerization may result in more linear polymer structures with fewer crosslinks when compared to a rapid reaction promoted by the irradiation with high power density.^{14, 16} On the other hand, a rapid initial polymerization may lead to shorter chain length.^{18, 19}

It is important that straightforward and simple methods be found to accurately measure resin composite polymerization shrinkage. Several methods have been used, such as: mercury dilatometry^{20, 21}, water dilatometry²², strain gauge^{20, 23}, linear contraction using a universal testing machine^{2, 24}, linear contraction polymerization using digital laser interferometry²⁵, digital video-imaging^{26, 27, 28}, 3D mapping using X-ray micro-computed tomography²⁹ and as well as others.

A simple and easy method has recently been developed to measure volumetric shrinkage of resins using video imaging (AcuVol[®]/Bisco). This method, in addition to having several practical advantages, has been shown to

yield results comparable to those observed using mercury dilatometry. However, because it is a relatively new piece of equipment, few laboratories have this equipment.^{26, 27, 30} This method enables quantitative measurements providing data for the continuous shrinkage evolution pre, during and after photo-activation.

Sharp et al (2003)²⁶ made a study to describe and validate volumetric shrinkage measurements, both static and dynamic, for various commercial and experimental composites using an instrument based on a video comparison technique (AcuVol[®]/Bisco). The authors concluded that the video-imaging technique gives reproducible results for volumetric shrinkage of composites comparable to those measured by dilatometry. Unfortunately, very little information is available that explains the specific method by analysis of polymerization shrinkage.

Over the past 10 years, manufacturers have introduced light-curing units of various types and ever-increasing power: quartz-tungsten-halogen (QTH); high power QTH, argon laser; plasma arc (PAC); light emitting diode (LED); and high intensity LED units.³¹

LED curing light-units were introduced to the dental profession in 2001. LEDs are special semiconductors that produce electroluminescence of light in a manner completely unlike the hot filament found in QTH lights. This difference reportedly provides a longer life span, more consistent output, lower power consumption, and reduced induced. The energy from the LED is clearly defined by the semiconductor and most of the emitted light is concentrated in a narrow band around 470 nanometers, which is ideally suited for composite resins that use the camphorquinone photo-initiator.³²

In according to Leonard (2007)³³ second-generation LED LCUs are now similar in output and performance to high-intensity QTH curing lights and are actually superior to standard QTH curing lights. From all indications, LED curing lights are the wave of the future in visible light curing.

The second generation LED-based LCUs presents high power density and, usually, these new devices make it possible to have gradual photo-activation methods, thus reducing the polymerization shrinkage (typical of composite

resins). However, many authors^{13, 14, 16} discuss if the usage of these methods changes the polymer structure of composite resins.

The aim of this paper is to evaluate if the photo-activation methods, available in these devices, influences on volumetric shrinkage of composite resins using of video-imaging devices. If a positive influence in the usage of the gradual photo-activation methods is not found, its usage should be avoided, considering that literature has not yet defined if there is a direct influence over polymer structure this material.

MATERIAL AND METHODS

The composite resins used in this study are listed in Table 1. Each represents one of two different categories of composites: microhybrid and nanocomposite. The light-curing units (LCUs) used in this study were Elipar Freelight 2TM (3M/ESPE) and Bluephase[®] (Ivoclar/Vivadent). For each LCUs, two photo-activation methods: continuous and gradual, pre-programmed by their manufacturers were used (Table 2). The method chosen to measure the volumetric shrinkage (VS) was a video-imaging device specifically developed for shrinkage measurement AcuVol[®]/Bisco (RefX-81100P, Schaumburg, EUA).

The AcuVol[®] Bisco, a video-imaging device, captures and analyzes specimen images using a black and white CCD video camera fitted with a 45-mm Macrolens with a 1.0-cm aperture. The resin specimen, illuminated by red light-emitting-diodes, is imaged from a 10-cm distance. A video processor then digitizes the image to a resolution of 512 pixels wide by 486 pixels high and 8 bits per pixel. Image analysis software is used to calculate the specimen's volume by dividing the captured image into hundreds of horizontal slices, each with a height of 1 pixel. The software then employs a boundary-detection method in which the computer determines the location of the specimen's left and right boundaries by comparing pixel brightness against a manufacturer-recommended threshold value which is significantly brighter than the intensity levels of the background pixels. The boundary values are then subtracted to yield the width of the slice in pixels.

The image analysis software calculates the specimen volume by adding the volume values of all the horizontal slices.^{26, 27}

To measure shrinkage, approximately 15 μl (± 1) of the composite resins (Table 1) was manually shaped into a semi-sphere and placed on a 4.2-mm-diameter polytetrafluoroethylene (PTFE) pedestal in front of the machine's charge-coupled device (CCD) camera. The obtained image was captured and scanned by the software AcuVol[®] Bisco (MIOD Detection) and after a two minute flowing of material, the samples perimeter was measured by a virtual dotted line. The measured size was stored in the program, as an initial volume of the sample. Then, the composite resin was cured for 20 s (Table 2). The tip of the LCUs wand was positioned 1 mm from the top of the composite resin.

Prior to the curing procedures, the output power of the LCUs was measured with a calibrated power meter (Fieldmaster Power Meter, Coherent-model n° FM, set n° WX65, part n° 33-0506, USA) and the diameter of the light guide tip with a digital caliper (Mitutoyo, Tokyo, Japan). Power density (mW/cm^2) was computed as the ratio of the output power and the area of the tip with the following formula: $I = P/A$, where P is the power in milliwatts and A is the area of the light tip in squared centimeters.

The VS was recorded in single-view mode during 10 min after light activation in order to let the temperature of the specimen equilibrate to room temperature. Five samples of each resin composite were tested (Table 3).

After photo-activation, another virtual dotted line circumvented the perimeter of the final volume achieved by the material. Since the initial and final lines were represented in the same image, it was possible to visualize the contraction of the sample by analyzing the difference between them. At the same time, the shrinkage percentage, automatically calculated by the software, was numerically recorded each second, during 10 minutes. The data were also provided by the program as a text file (doc), containing the shrinkage percentage for each second.

The data obtained were analyzed by linear regression analysis and analysis of variance (ANOVA). The ANOVA was complemented by multiple comparisons of means of Tukey's test at significance level of 0.05.

RESULTS

Mean (M) values and standard deviations (\pm sd) are shown in Table 4. These values represent the VS in four periods of time (initial, during photo-activation, post photo-activation and final). Analysis of the data showed significant difference between the time frame comprising the initial time and post photo-activation for any of the groups. No significant differences were found in the values of VS among post photo-activation and final period.

Statistically significant differences in VS values were noted among composite resins in post photo-activation period ($p < 0.046$). The lowest stress values were recorded for the microhybrid resin (Filtek™ Z-250/3M ESPE).

Three way ANOVA analysis of variance (ANOVA) was applied to evaluate the behavior of the VS in the photo-activation period. The three factors (composite resin, LCU and photo-activation method) reveal significant differences in the VS. Interactions between photo-activation method and resin, and photo-activation and LCUs showed strong dependence between the three factors. The results obtained by Tukey's test were shown in the Table 4.

The highest VS values were recorded for the composite Filtek™ Supreme XT (3M/ ESPE) using the continuous method with Elipar Freelight 2™ (3M/ESPE). Trippingly, the same composite using the continuous method with Bluephase® (Ivoclar/Vivadent) presented high VS values, significantly different only when compared to the Filtek™ Z-250 (3M/ESPE) using the continuous method with Bluephase® (Ivoclar/Vivadent). The Figure 1 displays the percent means of VS for each Group during the photo-activation period.

DISCUSSION

The build-up of shrinkage stresses in dental composite restorations during the polymerization is a complicated physical and chemical process. It is

influenced by the mechanical properties of the restorative material, tooth geometry, cavity shape and size, and curing history.^{26, 33} The relationships between these factors and the polymerization shrinkage have been widely studied, with the aim being to minimize the latter by optimizing the relevant parameters.^{3, 21, 34} Several efforts have been focused on reducing the polymerization shrinkage of composite resins as well as developing methods to prevent microleakage by improving or optimizing the tooth-composite bonding.³⁵

One way of reducing polymerization shrinkage consists of the use of specific layering techniques or flexible adhesive layers.³⁶ Another way, sometimes in combination with the use of flexible adhesive layers, is the modification of light-curing protocols³⁷ for gradual methods, such as the soft-start or ramped light polymerization³⁸, the variable light intensity protocol³⁹, the intermittent polymerization or the pulse delay polymerization.⁴⁰

Nevertheless, the different photo-activation methods and different combinations of power density and exposure duration may influence the properties of composite resins.^{10, 11, 14, 15, 16, 41} It is known that polymerization shrinkage of resins increased with increasing levels of energy density, and, for each level of energy density, the contraction increased with increasing power density.^{25, 11, 42, 43, 44} In other hand, Lu, Stansbury, Bowman (2005)⁴² observed that soft-start or pulse photo-activation methods led to decreased shrinkage stress, however, significantly decreased final conversion was also produced.

Gonçalves et al. (2006)⁴⁵ suggest that when low irradiances or pulse-delay methods are used, a relatively high radiant exposure is necessary to originate a polymer network structure similar to that obtained by continuous high irradiance photo-activation. Other studies indicated that reduced shrinkage stress can be achieved with soft-start curing, while the same final conversion can still be achieved.^{25, 46} Otherwise, Visvanathan et al (2007)⁴⁴ say that soft-start regimes have no paramount benefit in a LED regarding stresses in the clinical situation. The soft-start polymerization does not provide any added advantage based on the stress and mechanical properties.

Our findings suggest that the volumetric shrinkage (VS) decreased for contraction with the use of continuous photo-activation methods, in agreement with others studies.^{11, 25, 42, 43, 44} One major hypothesis supporting gradual photo-activation methods is that the initial lower light intensity would allow for polymer chain relaxation, so that shrinkage stress can be partly relaxed before the vitrification stage is reached.^{20, 25, 42, 46, 47} However, other studies raise the question that this reduction in shrinkage can be obtained at the expense of lower conversion, change of polymer structure, and consequent reduction of the physical-mechanical properties.^{10, 11, 14, 15, 16, 41, 42} In the present study was not possible to make this correlation, it was evaluated only the effect of these methods on the volumetric shrinkage.

The highest values of VS were observed for nanofilled resin (Filtek™ Supreme XT/3M ESPE) when Elipar Freelight 2™ (3M/ESPE) LCU and continuous photo-activation method were used. This LCU presented power density of 996mW/cm², ie, higher than the other device evaluated (Bluephase®=860mW/cm²). Moreover, when the same resin was photo-activated by Bluephase® (Ivoclar/Vivadent) using the continuous photo-activation method, were also found high VS values. These observations reinforce that the contraction increased with increasing power density.

Adicionally, the chemical composition of composite resins is directly related to their viscoelastic properties. Properties, such as elastic modulus and shrinkage, have an important relationship with stress development.^{36, 48} Therefore, the material capacity to flow during polymerization is another important characteristic to compensate shrinkage. Either the modulus of elasticity or the flow capacity depends on the material's monomer composition and inorganic filler loading.⁴⁹

Higher stiffness leads to increased stress for a given shrinkage strain. The opposite is also true, as the amount of shrinkage strain also plays an important role in generating stress in dental composite restorations. The increase in the filler level will contribute to a reduced shrinkage strain because the overall polymerization shrinkage depends on the amount of polymer matrix.³⁶

In this study, the behavior of Filtek™ Z-250 (3M/ESPE), which presents 78% weight of filler loading and a modulus of elasticity of 11.70 MPa, according to manufacturer's information, could suggest a proper balance between filler loading and material rigidity. Our results indicate that there is influence of composite modulus of elasticity on the tension generated during volumetric shrinkage. Thus, the present results suggest that a material with high filler loading and high modulus of elasticity presents low free shrinkage.

Other authors may disagree our findings; Pereira et al. (2008)⁴⁹ and Cadenaro et al. (2008)⁵⁰ not found significant differences in the VS among microhybrid (Filtek™ Z-250, 3M/ESPE) and nanocomposite (Filtek™ Supreme, 3M/ESPE).

The selection of two different restorative materials, in this study, was to address whether their different compositions and formulations would interfere with polymerization shrinkage and the generation of tensions, which was observed in this study. As the Pereira et al., 2008⁴⁹ and Ellakwa, Cho, Lee, 2007⁵¹, properties, such as modulus of elasticity, polymerization shrinkage, coefficient of linear thermal expansion and water sorption, correlate directly to each material's type and composition. According to the same authors, in the resins where nanotechnology is present, the particles type (spherical, microhybrid or nanoclustered, respectively) could apparently lead to increased creep during shrinkage, allowing to tension releases.

Ernst et al. (2000)⁵² and Ernst et al. (2003)⁵³ said that the effect of gradual photo-activation methods depends on the material itself, with the most effective response from hybrid resin-based composites. These observations are similar results from this study.

In the present study, significant differences in the VS values were verified between the time frame comprising the initial time and post photo-activation periods for any of the groups. However, no significant differences were found in the VS values between post photo-activation (2 minutes) and final periods (10 minutes).

Some of the shrinkage occurs during the predominantly viscous phase, prior to the development of elastic properties in the resin, and some after elastic behavior dominates. Total contraction refers to measurement of shrinkage throughout the polymerization reaction—from a viscous fluid state (pre-gel), through gelation, to post-gel, and, finally, vitrification.²⁰ The initial low intensity light exposure is characterized by the formation of linear polymers, with few cross links, and, thus, more susceptible to movement and structural rearrangement.⁴⁶

The results of the present study showed that a total time of 10 minutes volumetric shrinkage's measurement (initial, during and post photo-activation), the highest VS values occurred in time of one minute. This finding suggests that, within the methodology used in this study, the maximum time of two minutes is sufficient to measure of the VS before, during and after the curing of composite resins.

In according to Zanchi et al. (2006)²⁴, all composites continued generating shrinkage forces after interruption of the light exposure, which was already identified in literature^{20, 54, 55} as post gel shrinkage. For these authors, the shrinkage reaction continues occurring with the progressive formation of cross links initiated immediately after the light activation and with the thermal contraction resulting from the exothermic reaction.⁵⁶ Cunha et al. (2008)⁵⁷, verified a significant increase in the stress level was observed during the post-curing period up to 5 min, for all evaluated methods. Although, the authors used xenon plasma arc (PAC) light and a quartz-tungsten-halogen (QTH) light with three light-curing regimens: continuous exposure, soft-start and intermittent light. In other hand, our findings verified that the VS occurred post photo-activation no is significant after 2 minutes of measurement.

A new method that is purportedly faster and easier than other techniques has recently been described (AcuVol[®]/Bisco). This technique, in addition to having several practical advantages, has been shown to yield results comparable to those observed using mercury dilatometry, which represents a methodology already established in the literature. In addition, to its ease of use and ability to follow polymerization shrinkage during the entire curing process. Its software has

several useful features, including automatic, real-time calculation of polymerization shrinkage, i.e., no calculations need to be done by the operator. The software also allows the operator to view pre- and post-polymerization images superimposed on each other, which provides a visual sense of the amount of shrinkage that has occurred.^{27, 28, 29} Considering these advantages, this technique was selected for this study. Unfortunately, very little information is available that explains this specific method by video-imaging for calculates volumetric shrinkage.

Among its limitations has been that difficult to position the specimen in pedestal, because of small dimensions; there is no way to measure shrinkage under controlled temperature conditions because the specimen is exposed to the ambient environment and finally, the AcuVol[®]/Bisco is only used for measuring polymerization shrinkage; it is not a multifunctional piece of equipment.^{28, 29}

The AcuVol[®]/Bisco reconstructs volume using two different modes: single view mode (single view volumetric reconstruction- SVVR) and multiple view mode (multiple view volumetric reconstruction-MVVR). In SVVR mode, the sample is not rotated, images from only a single view of the sample is reconstructed, the outline of the sample is determined from the single view and the volume of the sample is reconstructed if the sample where spherically symmetrical. In MVVR mode, the sample is rotated through 360°, images of the sample are recorded at regular degree intervals, the outline of the sample is determined in each image, and the volume is reconstructed (instruction's manual of the equipment).²⁷

The single-view mode of measurement is faster and simpler to use than the multi-view mode, therefore was chosen for this study. It may be perceived as less accurate than the latter since in the multi-view mode, various camera angle shots can be averaged to handle the possible asymmetry problem of the sample shape. However, the experimental results found by Sharp et al. (2003)²⁷ shows that both modes give the same shrinkage values with similar data scatter as evidenced by the standard deviations.

The results of the present study show that high power density of LCUs produces high values for volumetric shrinkage (VS). When a LED LCU Elipar Freelight 2™ (3M/ESPE) were used, differences in the contraction behavior of nanocomposite by different photo-activation methods were observed. The continuous photo-activation method produces the highest values of VS. Differences of VS were also found between the composite resins. The nanocomposite showed the highest values of volumetric shrinkage. Thus, our findings suggest that the gradual photo-activation method and microhybrid resins produces the lowest volumetric shrinkage.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to the Federal University of Santa Catarina/UFSC for the opportunity of using AcuVol®/Bisco device. Also, the authors would like to thank for 3M ESPE Brazil for providing the composite resins and LCU used in this study. Special thanks to Milko Javier Villarroel Cortes for the availability of the Bluephase® (Ivoclar/Vivadent) LCU. This study was funded by CAPES and São Paulo State University-UNESP, Araraquara School of Dentistry.

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FIGURES AND TABLES LEGENDS

Table 1. Characteristics of restorative material used in the study (manufacturers' data)

Table 2. Light-curing units and photo-activation methods used in the study

Table 3. Experimental Groups investigated in this study

Table 4. Mean values (M) and standard deviations (\pm sd) of the volumetric shrinkage (VS) at four periods (initial, during and post photo-activation, final).

Figure 1. Mean values of percent volumetric shrinkage for each group during the photo-activation period

SHORT TITLE: Shrinkage of composites submitted to different curing methods.

Table 1. Characteristics of restorative material used in the study (manufacturers' data)

Material	Manufacturer	Shade	Material type	Matrix	Filler size	Filler Volume	Lote number
Filtek Supreme XT™	3M/ESPE	A2B	Nanofilled composite	Bis-GMA, Bis-EMA, UDMA, TEGDMA.	Agglomerated/non-aggregated of 75 nm silica nano-filler and a loosely bound agglomerate silica nano-cluster consisting of agglomerates of primary silica nanoparticles of 75 nm size fillers. The cluster size range is 0.6 to 1.4 microns.	72.5%	6ER
Filtek Z-250™	3M/ESPE	A2	Microhybrid	Bis-GMA, TEGDMA, UDMA and Bis-EMA 6	Zirconia/silica (medium size of 0.19×3.30µm)	60%	6TU

Table 2. Light-curing units and photo-activation methods used in the study

Light curing unit/ serial number	Manufacturer	Continuous photoactivation method	Gradual photoactivation method
Elipar Freelight 2 TM / 939820018167 Germany	3M/ESPE	Power density (PD) of 996mw/ cm ² for 20s	PD 0 at 996mw/cm ² for 10s + 10s at 996mw/cm ²
Bluephase TM /2124 Norway	Ivoclar-Vivadent	PD 860mw/cm ² for 20s	0 at 860mw/cm ² for 10s + 10s at 860mw/cm ²

Table 3. Experimental Groups investigated in this study

Group	Composite resin	LCU	Photo-activation methods
1 - Control	Z-250/3M ESPE TM	Elipar Freelight 2 TM 3M/ESPE	Continuous
2	Z-250/3M ESPE TM	Elipar Freelight 2 TM 3M/ESPE	Gradual
3	Filtek Supreme XT/3M ESPE TM	Elipar Freelight 2 TM 3M/ESPE	Continuous
4	Filtek Supreme XT/3M ESPE TM	Elipar Freelight 2 TM 3M/ESPE	Gradual
5 - Control	Z-250/3M ESPE TM	Bluephase [®] Ivoclar/Vivadent	Continuous
6	Z-250/3M ESPE TM	Bluephase [®] Ivoclar/Vivadent	Gradual
7	Filtek Supreme XT/3M ESPE TM	Bluephase [®] Ivoclar/Vivadent	Continuous
8	Filtek Supreme XT/3M ESPE TM	Bluephase [®] Ivoclar/Vivadent	Gradual

Table 4. Mean values (M) and standard deviations (\pm sd) of the volumetric shrinkage (VS) at four periods (initial, during and post photo-activation, final).

Composite resin	LCUs	Photo-activation methods	Periods				
			Initial	During photo-activation	Post photo-activation	Final	
Filtek™ Supreme XT	Bluephase®	Continuous	M	17,21	18,24	16,85	16,77 ^b
			sd	0,67	0,32	0,64	0,65
		Gradual	M	17,35	17,94	17,00	16,92 ^{ab}
			sd	0,33	0,46	0,32	0,34
	Elipar Freelight 2™	Continuous	M	17,64	19,80	17,26	17,19 ^c
		sd	0,30	0,64	0,30	0,33	
Filtek™ Z-250	Bluephase®	Continuous	M	16,83	17,05	16,49	16,43 ^a
			sd	0,26	0,30	0,24	0,24
		Gradual	M	17,27	17,44	16,88	16,85 ^{ab}
			sd	0,59	0,58	0,58	0,57
	Elipar Freelight 2™	Continuous	M	17,31	17,58	16,95	16,89 ^{ab}
			sd	0,43	0,37	0,42	0,41
		Gradual	M	17,18	17,47	16,84	16,77 ^{ab}
			sd	0,26	0,35	0,24	0,25

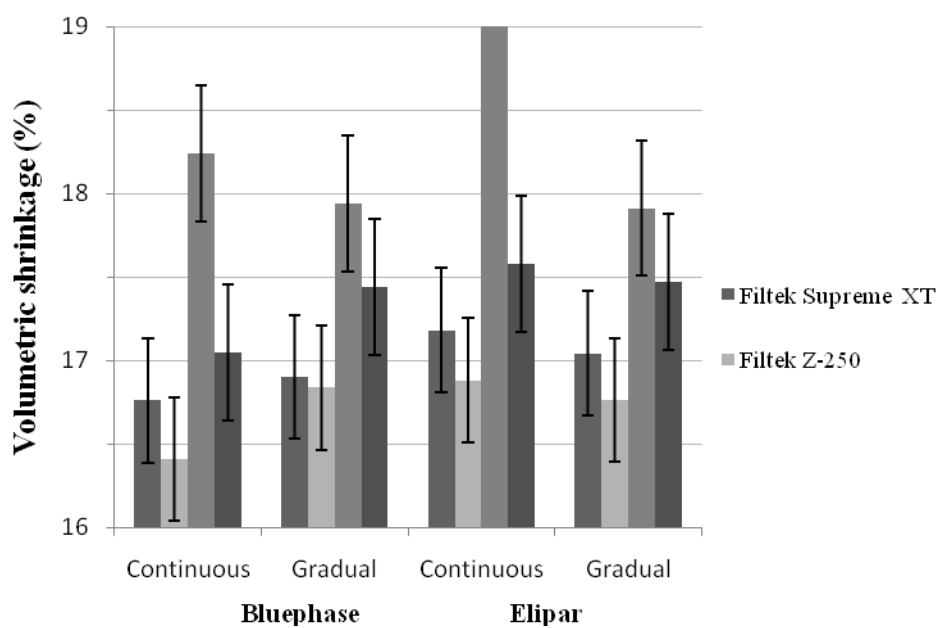


Figure 1. Mean values of percent volumetric shrinkage for each group during the photo-activation period

Capítulo 3

3.3 Capítulo 3

Continuous and gradual photo-activation methods: influence on degree of conversion and crosslink density of composite resins *

S. X. S. Costa,¹ M. R. Galvão,¹ D. P. Jacomassi,² M. I. B. Bernardi,² A. C. Hernandez,² A. N. S. Rastelli,^{1,2,3**} M. F. Andrade¹

¹São Paulo State University-UNESP, Araraquara School of Dentistry, Department of Restorative Dentistry, Araraquara, SP, Brazil. Humaitá St., 1680, ZipCode: 14801-903, Araraquara, São Paulo, Brazil. Telephone: +55 16 3301-6389. Fax: +55 16 3301-6393.

²Universidade de São Paulo, Instituto de Física de São Carlos, Grupo de Óptica, Laboratório de Biofotônica, São Carlos, SP, Brazil.

³Universidade de São Paulo, Instituto de Física de São Carlos, Grupo de Crescimento de Cristais e Materiais Cerâmicos.

* Enviado para publicação no periódico *Journal of Thermal Analysis and Calorimetry* (Anexo 4).

****Corresponding author:** Prof. Dra. Alessandra Nara de Souza Rastelli, Humaitá St., 1680, ZipCode: 14801-903, Araraquara, São Paulo, Brazil. Telephone: +55 16 3301-6389. Fax: +55 16 3301-6393. e-mail address: alerastelli@yahoo.com.br

ABSTRACT

Thermal properties and degree of conversion (DC%) of two composite resins (microhybrid and nanocomposite) and two photo-activation methods (continuous and gradual) displayed by the light-emitting-diode (LED) light-curing units (LCUs) were investigated in this study. Differential Scanning Calorimetry (DSC) thermal analysis technique was used to investigate the glass transition temperature (T_g) and degradation temperature. DC% was determined by Fourier Transform Infrared Spectroscopy (FT-IR). The results showed that the microhybrid

composite resin presented highest T_g and degradation temperature values, i.e., the best thermal stability. Gradual photo-activation methods showed higher or similar T_g and degradation temperature values when compared to continuous method. The Elipar Freelight 2TM LCU showed the lowest T_g values. With respect to the DC%, the photo-activation method did not influence the final conversion of composite resins. However, Elipar freelight 2TM LCU and microhybrid resin showed the lowest DC values. Thus, the presented results suggest that gradual method photo-activation with LED LCUs would suffice to provide adequate degree of conversion without promoting changes in the polymer chain of composite resins. However, the thermal properties and final conversion of composite resins can be influenced by the kind of composite resin and LCU.

KEYWORDS: Spectroscopy Fourier Transform Infrared; Differential Scanning Calorimetry; LED, Dental Curing Lights; Composite resins.

1. INTRODUCTION

Due to their excellent aesthetics, adhesion to tooth structures and improvements in the chemical and mechanical properties, composite resins are extensively used in several dentistry applications in recent decades. However, one of the main problems is the polymerization shrinkage of the matrix phase [1-2].

Clinical failure of composite restorations is often the result of an incomplete sealing of the tooth/restoration interface. The role of polymerization shrinkage as one of the main causes of marginal integrity loss and consequent post-operative occurrences, such as hypersensitivity, microleakage and secondary caries [3-5]. Polymerization shrinkage is related to the restorative technique employed, as well as to the composite resin composition and degree of conversion [6].

Composite resins are set via exposure to light of a certain wavelength and an intensity that initiates the generation of free radicals that propagate polymerization, causing material hardening [7-9]. This light can be emitted by light curing units (LCUs), such as conventional quartz tungsten

halogen (QTH), xenon plasma arc (PAC), argon laser and light-emitting-diodes (LED) [10].

LED light-curing units were introduced to the dental profession in 2001. LEDs are special semiconductors that produce electroluminescence of light in a manner completely unlike the hot filament found in QTH lights. This difference reportedly provides a longer life span, more consistent output, lower power consumption, and reduced induced. The energy from the LED is clearly defined by the semiconductor and most of the emitted light is concentrated in a narrow band around 470 nanometers, which is ideally suited for composite resins that use the camphorquinone photo-initiator. The second-generation LED LCUs are now similar in output and performance to high-intensity QTH curing lights and are actually superior to standard QTH curing lights. From all indications, LED curing lights are the wave of the future in visible light curing [11].

In recent years, literature [12-16] has shown that the properties of composite resins are mainly influenced by the amount of energy delivered during irradiation. The total amount of energy per unit area, the so-called energy density is the product of the power per unit area (power density) by the duration of irradiation. For a given energy density, different combinations of power density and curing times may be used to cure the composite materials [17].

The light from dental light-curing units can be delivered in different methods: continuous, pulse-delay or stepped irradiation. The continuous method delivers the same power density (PD) uninterruptedly throughout the entire exposure period. The pulse-delay method initiates cure by a short flash of light followed by a delay of one or more minutes before the final photo-activation is performed. In the step-cure method, a low PD is used during the first part of the photo-activation period and a higher PD is used towards the end of the irradiation. The pulse-delay and the stepped mode of cure are so-called “soft-start” methods of cure [17-18].

The soft-start methods were introduced with the purpose of slowing down the polymerization reaction, which is inevitably accompanied by contraction of the material [19]. The different photo-activation methods and

different combinations of power density and exposure duration may influence the properties of light-curing composite resins [14-16, 20-23]. It has been shown that degree of conversion, flexural strength, and flexural modulus increased with increasing energy density, and, for each energy density level the degree of cure decreased with decreasing power density [14]. In the same way, polymerization shrinkage of composite resin increased with increasing levels of energy density, and, for each level of energy density, the shrinkage increased with increasing power density [15].

Some authors found that soft-start photo-activation methods were able to reduce microleakage with only a discrete reduction in the degree of conversion [24]. In the other hand, others studies demonstrate that soft start methods have resulted in either decreased degree of conversion (DC) as compared to the one of the continuous method, or similar DC but at the same time with polymers of lower crosslink density, reflecting on the mechanical properties [20-21, 25-26].

The soft-start methods of cure lead probably to the formation of relatively fewer growth centers, which may result in a more linear polymer, with decreased crosslinking. The increased concentration of crosslinks has been associated with increased physical properties and stability of polymers [25, 27].

The degree of conversion (DC) depends on the total light energy, the irradiation times, the correct wavelength of the light source, the material composition, and others factors [13, 23, 28-29]. All of these factors strongly influence the degree of conversion, which is the number of ethylene double carbon bonds that are converted into single bonds of the composite resin to obtain the optimal chemical–physical and clinical performance [30].

DC is an important parameter in determining the final physical, mechanical and biological properties of composite resins, since it has been demonstrated that composite properties tend to improve as the degree of conversion attained during photo-polymerization is increased [31]. Additionally, increased cure may result in a lower amount of uncured, potentially leachable monomer, leading to a more biocompatible restoration [22]. Moreover, uncured

functional groups can act as plasticizers, reducing the mechanical properties of the composite [26].

It has been shown that the extent of crosslinking of a polymer may be assessed by measurements of the glass transition temperature (T_g). T_g is an important parameter for polymer characterization as it marks a region of dramatic changes in the physical properties of the polymer [27, 32]. The T_g value represents the temperature region at which the polymer is transformed from a glassy material into a rubber like one. Crosslinking reduces molecular mobility and thus gives rise to increased apparent T_g . The curing procedure may influence the regularity of the network and the crosslink density, and this may be reflected in the T_g [17, 33].

It was hypothesized that gradual photo-activation methods would exhibit a reduced crosslink density, in despite the reduction of the polymerization shrinkage. In addition, lower conversion values can be obtained using this photo-activation method. Thus, the aim of this study was to investigate the effect of different photo-activation methods on degree of conversion and crosslink density of composite resins, using spectroscopy infrared (FT-IR) and differential scanning calorimetry (DSC) techniques. The tested hypotheses were: 1) the photo-activation methods (continuous or gradual) affect the degree of conversion; 2) the photo-activation methods (continuous or gradual) affect the concentration of crosslinks in the composite resins.

2. EXPERIMENTAL

The information about fillers and resins matrix of the commercial dental composite resins, used in this study, are summarized in Table 1. Each represents one of two different categories of composites: microhybrid and nanocomposite.

The light-curing units (LCUs) analysed in this study were Elipar Freelight 2TM/3M ESPE and Bluephase C8[®] /Ivoclar-Vivadent. For each LCUs were used two photo-activation methods: continuous and gradual, pre-programmed by their manufacturers (Table 2).

Tabela 1: Characteristics of restorative material used in this study

Material	Manufacturer	Shade	Material type	Matrix	Filler size	Filler Volume	Lote number
Filtek Supreme XT™	3M/ESPE	A2B	Nanofilled composite	Bis-GMA, Bis-EMA, UDMA, TEGDMA.	Agglomerated/non-aggregated of 75 nm silica nanofiller and a loosely bound agglomerate silica nanocluster consisting of agglomerates of primary silica nanoparticles of 75 nm size fillers. The cluster size range is 0.6 to 1.4 microns.	72.5%	6ER
Filtek Z-250™	3M/ESPE	A2	Microhybrid	Bis-GMA TEGDMA UDMA and Bis-EMA 6	Zircônia/silica (medium size of 0.19×3.30µm)	60%	6TU

Table 2: Characteristics of light curing units used in the study (manufacturers' data)

Light curing unit/ serial number	Manufacturer	Continuous photo-activation method	Gradual photo-activation method
Elipar Freelight 2™/ 939820018167 Germany	3M/ESPE	Power density (PD) of 996mw/cm ² for 20s	PD 0 at 996mw/cm ² for 10s + 10s at 996mw/cm ²
Bluephase®/2124 Norway	Ivoclar-Vivadent	PD 860mw/cm ² for 20s	PD at 125mw/cm ² for 10s + 10s at 860mw/cm ²

Prior to the curing procedures, the output power of the LCUs was measured with a calibrated power meter (Fieldmaster Power Meter, Coherent-model n° FM, set n° WX65, part n° 33-0506, USA) and the diameter of the light guide tip with a digital caliper (Mitutoyo, Tokyo, Japan). Power density (mW/cm^2) was computed as the ratio of the output power and the area of the tip with the following formula: $I = P/A$, where P is the power in milliwatts (mW) and A is the area of the light tip in squared centimeters (cm^2).

Samples preparation

For differential scanning calorimetry (DSC) and degree of conversion (DC) measurements, the samples ($n=24$ and $n=40$, respectively) were made with a metallic mould (4 mm diameter and 2 mm thickness – ISO 4049). The mould was placed on a glass plate of 10 mm of thickness. The composite resins were packed in a single increment and the top and base surfaces were covered by a mylar strip. A glass sheet with 1 mm thickness was positioned, and a 1 kg weight (kilogram) was used to pack the composite resin. After that, the top surface of the samples was placed in contact with the light-curing tip.

The samples were photo-activated for 20s (manufacturer's instructions) at room temperature, according to the group assessed (Table 3) and were stored in distilled water in light-proof containers at 37°C for 24h.

Table 3: Division of the investigated Groups

Group	Composite resin	LCU	Photoactivation method
1 (ZEC)	Z-250/3M ESPE™	Elipar Freelight 2™/3M ESPE	Continuous
2 (ZEG)	Z-250/3M ESPE™	Elipar Freelight 2™/3M ESPE	Gradual
3 (XTEC)	Filtek Supreme XT/3M ESPE™	Elipar Freelight 2™/3M ESPE	Continuous
4 (XTEG)	Filtek Supreme XT/3M ESPE™	Elipar Freelight 2™/3M ESPE	Gradual
5 (ZBC)	Z-250/3M ESPE™	Bluephase®/Ivoclar-Vivadent	Continuous
6 (ZBG)	Z-250/3M ESPE™	Bluephase®/Ivoclar-Vivadent	Gradual
7 (XTBC)	Filtek Supreme XT/3M ESPE™	Bluephase®/Ivoclar-Vivadent	Continuous
8 (XTBG)	Filtek Supreme XT/3M ESPE™	Bluephase®/Ivoclar-Vivadent	Gradual

Differential Scanning Calorimetry (DSC)

The DSC measurements were performed with a DSC 2910 (TA Instruments). The samples were heated at $10^{\circ}\text{C}/\text{min}^{-1}$ from 10°C to 350°C , under nitrogen flowing at 40 mL min^{-1} in order to observe the glass transition temperature (T_g) and degradation peak of the different groups. A mass of $\sim 18\text{ mg}$, calibrated in precision balance (Mettler AJ150), of the samples was used in an aluminum sample pan. The reference pan contained 5 mg of aluminum bulk. All samples were previously heated until 100°C in order to eliminate the thermal history of the resins and after that the DSC curves were performed.

Degree of conversion (DC)

After storage for 24h, the samples were pulverized into fine powder. Five milligrams of the composite powder was thoroughly mixed with one hundred milligrams of KBr (bromide potassium) powder salt. This mixture was placed into

a pelleting device and then compressed in a press with a load of 10 tons during 1 minute to obtain a pellet.

The number of double carbon bonds which are converted in single bonds provides the degree of conversion (%DC) of composite resin. To measure the DC the pellet was then placed into a holder attachment into the spectrophotometer (Nexus-470 FT-IR, Thermo Nicolet, and E.U.A). FT-IR spectra of both uncured and cured samples were analyzed using an accessory of reflectance diffuse. The measurements were recorded in absorbance operating under the following conditions: 32 scans, 4 cm^{-1} resolution, 300 to 4000 cm^{-1} wavelength. The DC was determined by subtracting the % C=C from 100%, according to the formula:

$$(\%)DC = 1 - \frac{\left(\frac{1638\text{cm}^{-1}}{1608\text{cm}^{-1}}\right)^{cured}}{\left(\frac{1638\text{cm}^{-1}}{1608\text{cm}^{-1}}\right)^{uncured}} \times 100$$

The percentage of unreacted carbon-carbon double bonds (% C=C) was determined from the ratio of absorbance intensities of aliphatic C=C (peak at 1638 cm^{-1}) against.

Statistical analysis

The DC data were analyzed by analysis of variance (ANOVA) at three factors and Tukey's test at the significance level of $\alpha = 0.05$.

RESULTS AND DISCUSSION

The influence of photo-activation methods provided by LED LCUs on the thermal characteristics and degree of conversion of composite resins were investigated by Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FT-IR) methods, respectively.

Studies have shown that energy density, power density, and photo-activation methods of cure influence the degree of conversion [20, 23-24, 34-36], volume shrinkage [37-38], elastic modulus and glass transition temperature [17], among other properties of composite resins. Thereby, in the present study, microhybrid (Filtek™ Z250) and nanocomposite (Filtek™ Supreme XT) composite resins were polymerized according to two photo-activation methods: continuous and gradual provided by two LED LCUs (Elipar Freelight 2™ and Bluephase® C8).

The Figures 1 and 2 displays the representatives DSC curves obtained for the different Groups investigated. The first thermal event that can be seen in the DSC curves refers to the glass transition temperature (T_g) of organic phase. The temperature of T_g was about 87–120°C, evidenced by the change in the baseline. The second thermal event refers to thermal degradation peak, which occurred in the 271-289°C range. It is known that this thermal event represents the decomposition of the composite resins [39].

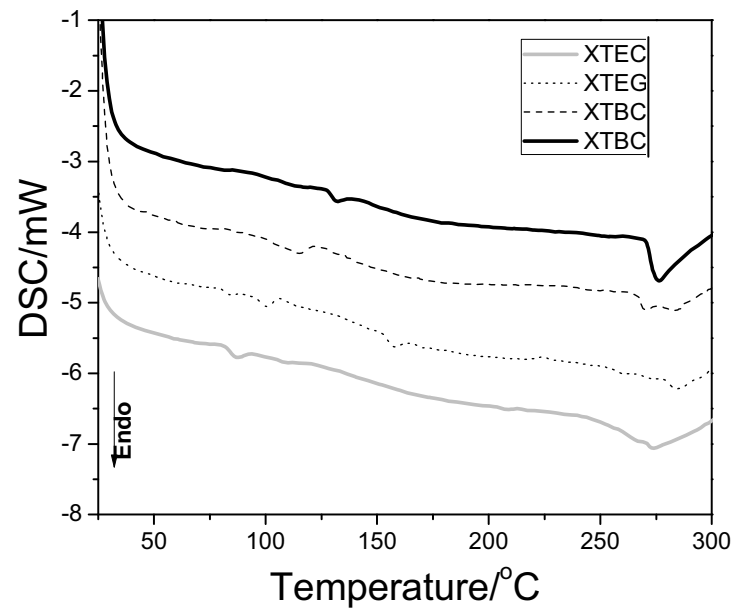


Figure 1: DSC curves for nanocomposite groups.

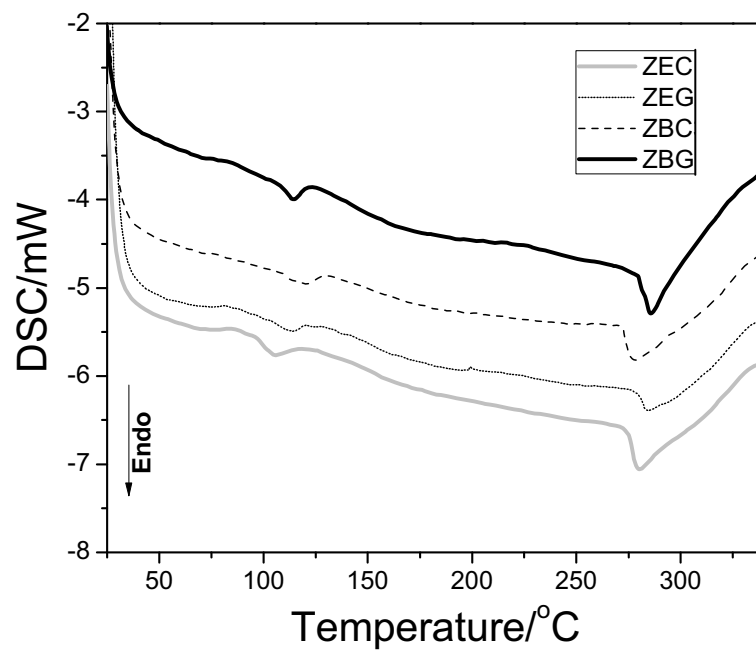


Figure 2: DSC curves for microhybrid groups.

DSC can be used to determine the thermal characteristics of polymers, such as post cure behavior, residual reactivity (amount of unreacted double bonds), and glass transition temperature [40]. Glass transition temperature (T_g) is an important parameter for polymer characterization as it marks a region of dramatic changes in the physical properties of the polymer. The T_g value represents the temperature region at which the polymer is transformed from a glassy material into a rubber like one [17].

Cross-linking density of polymers reduces molecular mobility and thus gives rise to increased apparent T_g . The curing procedure may influence the regularity of the network and the crosslink density, and this may be reflected in the T_g [17, 33]. A lower cross-link density and higher molecular mobility of the composite resins may cause a lower T_g temperature [2, 41].

It can be seen that the Groups investigated in this study presented variations T_g values, to 87 at 120°C, the Filtek™ Z-250 composite resin presented higher T_g value (120°C), while Filtek™ Supreme XT presented lower T_g value (87°C). Despite T_g values present differences, this findings is in agreement with previous observations [42].

The thermal events (T_g and thermal degradation) for the Groups are summarized in Table 4. From the data of Table 4, the Filtek™ Z-250 presented the best thermal stability, corroborating with other studies [42]. The gradual photo-activation method showed higher T_g values or similar to the continuous method, except when Bluephase® C8 LCU was used for cure Filtek™ Z-250 composite resin.

Table 4: Thermal events for the groups obtained from DSC curves.

Composite resins	Light-curing units	Photo-activation method	Glass transition temperature (T _g)	Thermal degradation
Filtek™ Supreme XT	Bluephase® C8	Continuous	115°C	271°C
		Gradual	114°C	286°C
	Elipar Freelight 2™	Continuous	87°C	273°C
		Gradual	100°C	283°C
Filtek™ Z 250	Bluephase® C8	Continuous	120°C	278°C
		Gradual	114°C	289°C
	Elipar Freelight 2™	Continuous	105°C	280°C
		Gradual	114°C	284°C

The Elipar Freelight 2™ LCU provided lower *T_g* values when compared to Bluephase® C8 LCU. These data suggest that thermal properties of composite resins can be influenced by the kind of composite resin, LCU and photo-activation methods. Likewise, thermal degradation was higher for gradual photo-activation methods, regardless of composite resin and LCU.

Ideally, polymerization process of composite resins produces highly cross-linked network systems exhibiting good solvent resistance. However,

strong structural changes may be observed during the polymerization process of multifunctional methacrylate-based composites for dental restorations, which significantly affect the final properties of the materials [43]. Thus, the study of the thermal degradation processes would provide more specific information from the internal structures of the dental composite resins.

With regards the effect of power density on the cross-linking, it has been speculated that a slow start of the polymerization, at low power density, may result in relatively fewer growth centers, which may result in a more linear polymer structure. In the other hand, high power density led to increased cross-links density [25, 44]. However, this observation was not found in this study.

The gradual photo-activation methods displayed by LCUs evaluated in this study consist of the continuous rise of the power density (PD) in the first ten seconds (Elipar Freelight 2TM) and initial PD at 125mW/cm² in the first ten seconds (Bluephase[®] C8). As the PD maximum of the LCU it is raised (996 mW/cm² for Elipar Freelight 2TM), probably the gradual rise in the ten initial seconds allows that the material is most of the time radiated with power density superior to 400mW/cm². This is a PD considered efficient to photo-activate composite resins adequately [45]. In the other hand, LCUs based on LED have a narrow spectral range with a peak around 470 nm, which matches the optimum absorption wavelength for the activation of the camphorquinone photoinitiator. These facts can explain the thermal behavior of the materials when of the use of gradual photo-activation methods evaluated in this study.

As mentioned above, gradual photo-activation methods can change cross-link density of composites. According to Dewaele et al. (2009) [17], comparisons of the continuous and the stepped photo-activation methods (evaluated in this study) are more ambiguous. This statement may be one possible explanation for the fact that gradual photo-activation methods in this study presented higher or similar *Tg* values compared to continuous photo-activation methods.

According to the same authors, the pulse-delay photo-activation method led to polymers of decreased *Tg*. Thus, the decreased *Tg* may be

interpreted as the manifestation of a polymer structure having fewer cross-links. In the pulse-delay curing method, after the short flash of initial light, only few growth centers remain active during the delay. In the present study, pulse-delay photo-activation method was not evaluated.

The physical and mechanical properties of composite resins are directly influenced by the level of conversion attained during polymerization. The degree of conversion (DC) is determined by the proportion of the remaining concentration of the aliphatic C=C double bonds in a cured sample relative to the total number of C=C bonds in the uncured material [46].

Techniques such as Fourier Transform Infra-red spectroscopy (FT-IR) [47-48], spectroscopy RAMAN [42, 49], electron paramagnetic resonance (EPR) [50], nuclear magnetic resonance (NMR) [51], differential scanning calorimetry (DSC) [52] and differential thermal analysis (DTA) [53] have been used to determine the DC. Among these, FT-IR is the most frequently used technique [46].

According to the results presented in Table 5, all photo-activation methods showed no statistical difference among themselves ($p > 0.05$) for DC values. These results indicate that all tested photo-activation methods were able to cure appropriately the Filtek™ Z-250 and Filtek™ Supreme XT (both 3M ESPE) composites, despite the differences (e.g. power density) among them. These results are similar to those found by other studies [2, 6, 13, 26, 34, 54-55].

Table 5: Mean and standard deviation (SD) for degree of conversion (%DC)

Composite resin	LCU	Photo-activation method	Mean	SD	
Filtek™Supreme XT (3M ESPE)	Bluephase® (Ivoclar-Vivadent)	Continuous	52.23	0.72	b
Filtek™Supreme XT (3M ESPE)	Bluephase® (Ivoclar-Vivadent)	Gradual	52.30	1.14	b
Filtek™Supreme XT (3M ESPE)	Elipar Freelight2™ (3M ESPE)	Continuous	52.50	1.65	b
Filtek™Supreme XT (3M ESPE)	Elipar Freelight2™ (3M ESPE)	Gradual	51.75	2.15	b
Filtek™ Z250 (3M ESPE)	Bluephase® (Ivoclar-Vivadent)	Continuous	53.15	1.09	b
Filtek™ Z250 (3M ESPE)	Bluephase® (Ivoclar-Vivadent)	Gradual	54.46	2.39	b
Filtek™ Z250 (3M ESPE)	Elipar Freelight2™ (3M ESPE)	Continuous	50.37	2.03	a
Filtek™ Z250 (3M ESPE)	Elipar Freelight2™ (3M ESPE)	Gradual	48.77	2.76	a

* Different letters indicate statistically significant difference at 5%.

Cunha et al. (2009) [6] demonstrate that photo-activation methods using lower irradiance levels were shown to be effective in reducing the rate of stress generation without compromising the conversion of the restorative composite.

Generally, dental composites reach a DC ranging from 43 to 75%, basically depending on the composite composition, irradiation intensity and exposure time [49, 51, 53, 56-57]. The DC (%) values in this study varied from 48.77% (± 2.76) to 54.46% (± 2.39) which also agrees with the DC observed in other studies [6, 9, 30]. Nevertheless, according Rastelli, Jacomassi, Bagnato (2008) [23] and Soares, Liporoni, Martin (2007) [58] the minimum DC for a clinically satisfactory restoration has not yet been precisely established.

The results presented reveal that there was a significant difference between the composite resins when the Elipar Freelight 2TM LCU (3M ESPE) was used. After 24 hours, using the irradiation time recommended by the manufacturers (20 seconds), FiltekTM Z-250 (3M ESPE) resin provided the lowest values for DC%, either continuous or gradual photo-activation methods displayed by Elipar Freelight 2TM (3M ESPE) (50.37% and 48.77%, respectively). DC of FiltekTM Z-250 and FiltekTM Supreme XT, both 3M ESPE, were statistically different ($p < 0.001$) when the LCU Elipar Freelight 2TM (3M ESPE) was used. Therefore, the results suggested that the LCU and composite resin used had a significant ($p < 0.05$) impact on the DC (Figure 3).

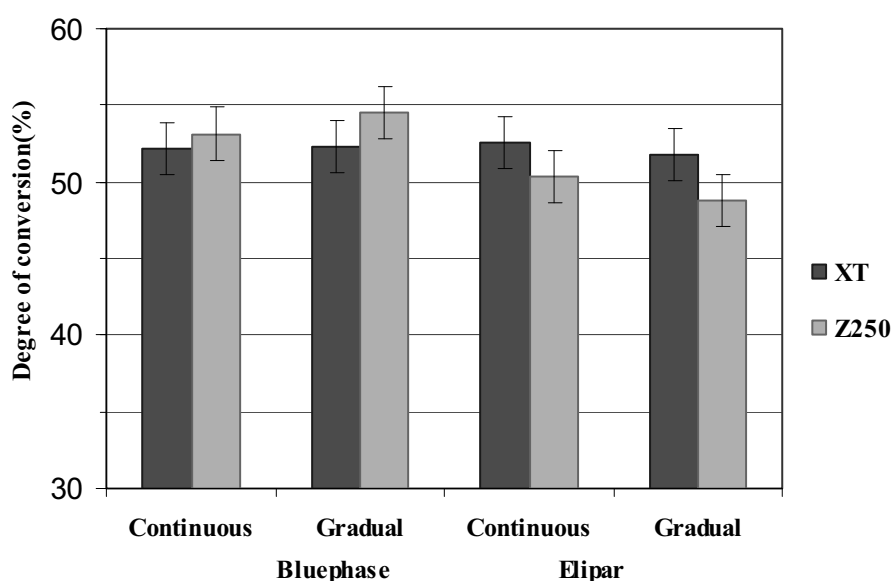


Figure 3: Averages of the %DC depending on the LCU, photo-activation method and composite resin.

Similar results were found by Bala et al (2005) [59]. In the samples photo-activated by Elipar FreelightTM LCU, the lowest DC value was obtained by a microhybrid composite resin FiltekTM Z-250. This can be primarily explained by

the difference in the composition of the resin matrix, filler size, filler volume and filler type of the materials.

Although the organic phase of composite resins evaluated in this study are similar, there are differences in the inorganic phase (size, shape and volume filler content). This difference in composite resins based on urethane dimethacrylates is because of the fact that these materials differ in many other aspects, e.g. amount of filler, initiators and silanation of the filler particles [59]. This statement may explain the results found in this study.

Additionally, in evaluating the percentage of reacted carbon double bonds (DC), differences in filler geometry did not seem to influence the DC of the composites. Notwithstanding, the DC was hindered in composites whose filler particles approached the output wavelength of the curing unit [60]. Previously, this fact was explained by the scattering effect of the penetrating light during photo-activation [61].

Finally, DSC technique allows the direct determination of the rate of polymerization reaction, assuming that the heat produced by the polymerization is proportional to the number of monomer units reacted. Rojas et al (2009) [62] observed a good agreement between the T_g values and degree of conversion. Similar results were observed in this study.

Despite the photo-activation methods had not interfered on the degree of conversion and polymer structure of composite resins in this study, more studies should be performed. In clinical practice, the gradual photo-activation methods are likely to be used to photo-activate composites in preparations with very distinct sizes and geometries. In the literature, however, the studies that analyzed low irradiance techniques generally performed light curing with the composite in direct contact with the photo activator tip, ignoring the conjugated effect of these two light attenuating forms on the restorative cavity [24].

CONCLUSIONS

The results obtained for this study indicate that the thermal properties (glass transition temperature and thermal degradation) of composite resins can be influenced by kind composite resin, LCU and photo-activation methods. Microhybrid composite resin presents the best thermal stability. The gradual photo-activation method provided the highest or similar T_g values compare to continuous photo-activation method, and, finally, the Elipar Freelight 2TM LCU provided the lowest T_g values.

The photo-activation method did not influence on the final degree of conversion composite resins. Nevertheless, LCU and composite resin used influenced the degree of conversion. The Elipar Freelight 2TM LCU associated to microhybrid resin presented lowest DC values.

ACKNOWLEDGMENTS

The authors would like to express their gratitude to the University of São Paulo-USP, Physics Institute of São Carlos, especially to the Optics and Cristal Growth and Ceramic Materials Groups by the use of equipments used in this study. Also, the authors would like to thank for 3M ESPE Brazil for providing the composite resins and LCU used in this study. Special thanks to Milko Javier Villarroel Cortes for the availability of the Bluephase C8[®] (Ivoclar/Vivadent) LCU. This study was funded by CAPES and São Paulo State University-UNESP, Araraquara School of Dentistry, Department of Restorative Dentistry.

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Considerações Finais

4 Considerações finais

As propriedades físico-mecânicas e biológicas das resinas compostas estão diretamente relacionadas ao processo de fotoativação. Variações quanto ao tipo de luz, densidade de potência, dose, tempo de irradiação e método de fotoativação têm influência direta sobre as propriedades dos compósitos. Assim, uma adequada polimerização, caracterizada normalmente por elevado grau de conversão dos monômeros em polímeros, tem implicação direta sobre o desempenho clínico e longevidade destes materiais^{4-6,18,66,68,82,105}.

Diferentes métodos de fotoativação, já descritos na introdução deste trabalho, podem ser empregados com o objetivo de minimizar os efeitos deletérios da contração de polimerização dos compósitos. A contração de polimerização é considerada o maior problema associado a estes materiais, pois gera estresses quando o mesmo é aderido às paredes cavitárias, formando microfendas na interface de união e, conseqüentemente, manchamento e infiltração marginal, sensibilidade pós-operatória e recidiva de cárie^{16,34-35,42,48,54,88,99}.

Os métodos de fotoativação graduais foram introduzidos com o objetivo de reduzir a velocidade da reação de polimerização, a qual é, inevitavelmente, acompanhada por contração²⁸. A redução na velocidade de conversão dos monômeros em polímeros permite que a resina composta tenha condições de aliviar as tensões decorrentes desta contração por meio do escoamento do material na sua fase pré-gel^{76,80,106,109}, ou seja, antes que seja alcançada a fase de vitrificação do material^{48,55,78,91}.

A contração de polimerização e o grau de conversão das resinas compostas são propriedades diretamente correlacionadas. Idealmente, os compósitos deveriam apresentar alto grau de conversão, com mínima contração. No entanto, alguns estudos demonstram que o aumento no grau de conversão, implica, necessariamente, no aumento da contração de polimerização^{22,28,80,92,100}.

No primeiro estudo deste trabalho, foi verificado que a contração de polimerização da resina composta nanoparticulada FiltekTM Supreme XT (3M

ESPE) foi influenciada pelo método de fotoativação, independentemente do tipo de luz empregada (halógena ou LED). O método de fotoativação contínuo promoveu os maiores valores de contração de polimerização, corroborando com os resultados encontrados por outros autores^{30,40,49,77,80,103}. No entanto, o método de fotoativação empregado não interferiu no grau de conversão do mesmo material. Por outro lado, o tipo de luz empregada exerceu influência sobre o grau de conversão, sendo os menores valores verificados para o aparelho à base de luz halógena (Optilux 501/Kerr).

As diferenças encontradas no primeiro estudo quanto ao grau de conversão podem estar associadas às diferentes densidades de potência de cada aparelho ($570\text{mW}/\text{cm}^2$ e $860\text{mW}/\text{cm}^2$, para os aparelhos halógeno e LED, respectivamente), uma vez que elevada conversão pode ser obtida quando há exposição do material a altas densidades de potência^{52,75}.

Segundo Obici et al.⁶² (2006), os esforços empregados para maximizar um aspecto envolvido no mecanismo da fotoativação geralmente comprometem ou interferem noutro aspecto. Dessa forma, podemos explicar questões como aumento da contração de polimerização com aumento da densidade de potência, redução na conversão com redução da densidade de potência, dentre outras correlações envolvidas no mecanismo da polimerização.

Este resultado pode estar associado ainda às diferenças existentes na produção de energia luminosa entre a luz halógena e os diodos emissores de luz. As lâmpadas halógenas de quartzo-tungstênio geram energia luminosa através da incandescência do filamento de tungstênio, o qual gera luz na cor branca que será filtrada para produzir luz azul dentro da faixa espectral de 400 a 500nm^{17,74}. De acordo com Rueggeberg⁷³ (1999), apenas 0,5% da energia produzida pela lâmpada halógena é empregada para fotoativação.

Por outro lado, os diodos emissores de luz convertem a energia elétrica diretamente em luz azul por eletroluminescência e por meio dos semicondutores de nitreto de gálio. Estes semicondutores emitem luz na faixa espectral de 450 a 490nm, ou seja, a faixa de maior absorção da canforoquinona, principal fotoiniciador utilizado nas resinas compostas^{29,84-85}. Os aparelhos à base

de LED apresentam seu espectro inteiramente dentro da zona de absorção da canforoquinona, tornando as suas irradiações energeticamente melhor aproveitadas^{2,61}, o que pode justificar os resultados encontrados para o grau de conversão no primeiro estudo.

Considerando estes resultados, os métodos de fotoativação graduais utilizados no primeiro estudo reduziram de forma significativa a contração da resina composta. No entanto, para o aparelho à base de luz halógena (Optilux 501/Kerr), esta redução da contração ocorreu à custa de menor conversão do material, corroborando com resultados provenientes de outros estudos^{37,55,62}. Assim, o método de fotoativação gradual, disponibilizado pelo aparelho LED de 2ª geração, promoveu conversão adequada da resina composta e menor contração.

Apesar dos aparelhos à base de luz halógena ainda serem os mais empregados no consultório odontológico, a utilização dos aparelhos à base de LED de 2ª geração representa uma alternativa efetiva aos tradicionais aparelhos halógenos. Os aparelhos à base de LED reúnem vantagens como portabilidade, maior tempo de vida útil da lâmpada (10.000 horas) e comprimento de onda específico para fotoativação da canforoquinona^{11,60}. Vários estudos têm demonstrado propriedades semelhantes ou até superiores às obtidas com os aparelhos halógenos para as resinas compostas fotoativadas com aparelhos LED de última geração^{8,19,39,45-46,61,94}, o que também foi observado no primeiro estudo deste trabalho. Portanto, as unidades fotoativadoras que utilizam luz halógena tendem a ser substituídas pela tecnologia LED^{46,61,98}.

Reconhecendo que a tecnologia LED representa o futuro para fotoativação dos materiais resinosos, no segundo estudo avaliamos a contração volumétrica das resinas compostas microhíbrida (Filtek™ Z250) e nanoparticulada (Filtek™ Supreme XT), ambas da 3M ESPE, fotoativadas por aparelhos LED de 2ª geração (Bluephase®/Ivoclar-Vivadent e Elipar Freelight 2™/3M ESPE), utilizando os diferentes métodos de fotoativação disponibilizados em cada aparelho.

Os resultados encontrados demonstraram diferenças significativas entre os métodos de fotoativação e as resinas compostas. Os métodos de

fotoativação contínuo e a resina composta nanoparticulada Filtek™ Supreme XT (3M ESPE) demonstraram maior contração volumétrica. Assim como no primeiro estudo, os resultados demonstraram que os métodos graduais de fotoativação, agora aplicados exclusivamente à tecnologia LED, são efetivos para minimizar as tensões decorrentes da contração de polimerização.

Como vimos, a contração volumétrica foi influenciada também pelo tipo de resina composta e os maiores valores foram observados para a resina nanoparticulada, independentemente do aparelho empregado. Segundo Ernst et al.³¹⁻³², o tipo de resina composta empregada tem influência direta sobre o método de fotoativação gradual, estando os melhores resultados associados às resinas híbridas, o que pode explicar os resultados apresentados no segundo estudo.

Outra provável explicação para este resultado está na relação existente entre a composição química da resina composta e seu comportamento visco-elástico. Propriedades como módulo de elasticidade e contração de polimerização têm relação direta com a geração de estresses^{23,49}, afinal, a capacidade que o material tem de escoar durante a polimerização, compensa a contração e esta propriedade está correlacionada à composição química do material⁶⁴.

A contração de polimerização, isoladamente, não representa o principal agente causal do insucesso das restaurações de resina composta, mas sim as tensões desenvolvidas quando a resina está aderida às paredes cavitárias⁷¹. Há uma relação direta entre tensão e rigidez (módulo de elasticidade) de um material, assim, quanto maior o módulo de elasticidade da resina composta, maiores as tensões desenvolvidas a partir da contração⁸⁹.

De acordo com os resultados do segundo estudo, sugere-se que a resina microhíbrida Filtek™ Z250 (3M ESPE) possa apresentar menor rigidez que a resina nanoparticulada Filtek™ Supreme XT (3M ESPE). Novos estudos que correlacionem o tipo de resina composta, o módulo de elasticidade e a contração volumétrica devem ser realizados para melhor elucidação desta questão.

Outro ponto a ser destacado no segundo estudo diz respeito ao método empregado para mensuração da contração volumétrica. O método

empregado, diferentemente do que foi utilizado no primeiro estudo, capta a contração do material através de um mecanismo que utiliza vídeo e imagem (Acuvol[®]/Bisco).

No primeiro estudo foi empregada uma metodologia para aferição das forças de contração de polimerização proposta por Castañeda-Espinosa²⁰ (2005). Esta metodologia baseou-se no estudo de Feilzer, De Gee, Davidson³³ (1987), porém apresentou pequenas modificações, especialmente no que diz respeito à configuração e volume dos corpos-de-prova. Nesta metodologia, as forças de contração de polimerização são determinadas a partir da deformação da célula de carga acoplada à máquina de ensaios universal.

De acordo com Peutzfeldt⁶⁵ (1997), em laboratório, o total do percentual de redução volumétrica só pode ser determinado quando o compósito fotoativado não estiver aderido a nenhuma superfície capaz de impedir a sua contração. Atendidas estas condições no teste, determina-se a contração volumétrica livre dos materiais⁹. Assim, a metodologia empregada no primeiro estudo capta as forças decorrentes da contração (MPa) do material que são transmitidas às células de carga, enquanto a metodologia do segundo estudo determina a contração volumétrica livre (%). Portanto, em cada um dos estudos aqui apresentados, foram verificadas diferentes características para as resinas compostas submetidas a diferentes métodos de fotoativação (forças de contração e contração volumétrica livre).

Dentre as vantagens associadas ao equipamento Acuvol[®] (Bisco), a principal está na capacidade que o equipamento possui para acompanhar o processo de polimerização do material em sua totalidade^{14,79,93}. Neste método, a contração volumétrica é registrada durante o período determinado pelo operador para mensuração e os valores são dados (%), para cada segundo, em um computador contendo um *software* específico (MIOD *Detection Technologies*). Este *software*, além de possibilitar o cálculo automatizado da contração volumétrica, em tempo real, permite que o operador veja a superposição das imagens antes e após a fotoativação, o que permite a visualização direta do quanto o material contraiu^{13-14,79,93}.

Devido a esta possibilidade, os resultados demonstraram que num tempo total de dez minutos de mensuração, os valores mais significativos de contração dos materiais foram verificados no primeiro minuto, contrariando os estudos que demonstram haver forças de contração significativas minutos após cessar a irradiação do material^{26,40,78,83,110}. No entanto, antes de evidenciarmos esta contradição, devem ser consideradas as diferenças existentes entre os métodos empregados para mensuração da contração nas diversas pesquisas.

Não foi encontrado na literatura estudos que tenham utilizado o equipamento Acuvol[®] (Bisco) para avaliação da contração de polimerização, considerando as diferenças existentes entre os períodos pré, durante e pós fotoativação para compararmos aos nossos resultados. Há a necessidade, portanto, de uma maior exploração desta particularidade metodológica associada ao aparelho Acuvol[®] (Bisco), a qual poderá trazer informações bastante relevantes a cerca do mecanismo de polimerização.

Diante dos resultados obtidos no segundo estudo tem-se que os métodos de fotoativação graduais, disponibilizados pelos aparelhos LED de 2ª geração, promovem menor contração, especialmente quando empregada a resina composta microhíbrida.

Apesar de promover a redução da contração de polimerização, os métodos graduais de fotoativação podem tornar os materiais resinosos mais susceptíveis à degradação em meio úmido^{4-5,10,105}. De acordo com Asmussen, Peutzfeldt⁴⁻⁵ a análise do grau de conversão, isoladamente, não traduz completa caracterização do polímero, uma vez que polímeros com graus de conversão semelhantes podem apresentar diferentes graus de reticulação (quantidade de ligações cruzadas e lineares). Idealmente, o processo de polimerização deve produzir polímeros com alta quantidade de ligações cruzadas na sua estrutura final, o que caracteriza um material com boa resistência à ação dos solventes presentes na cavidade oral¹⁰².

A explicação para estes achados pode estar associada à possibilidade dos métodos de fotoativação graduais promoverem a formação de menores centros de crescimento durante a polimerização, resultando em um

polímero mais linear, com diminuição da quantidade de ligações cruzadas. O aumento da concentração de ligações cruzadas tem sido associado com aumento da estabilidade polimérica e melhores propriedades físicas^{4,27,90}.

Tem sido demonstrada na literatura que uma das formas de avaliação do grau de reticulação de um polímero é a medida da temperatura de transição vítrea (T_g)^{3,90}. A T_g é um parâmetro importante para a caracterização dos polímeros, pois representa uma região de mudanças dramáticas nas propriedades físicas do material²⁷. O grau de reticulação de um polímero reduz a mobilidade molecular, o que dá origem a um material com maiores valores de T_g ^{38,72}.

Assim, no terceiro estudo, avaliamos o comportamento térmico e o grau de conversão das mesmas resinas compostas, aparelhos fotoativadores e métodos de fotoativação empregados no segundo estudo. O comportamento térmico foi avaliado pelo método da calorimetria exploratória diferencial para determinação das temperaturas de transição vítrea (T_g) e de degradação dos materiais. O grau de conversão, assim como no primeiro estudo, foi avaliado pelo método da espectroscopia infravermelha transformada de Fourier. Esta metodologia apresenta alta sensibilidade para análise da profundidade de cura e conversão dos materiais resinosos^{59, 92,108}, além de ser a técnica mais empregada para análise da taxa de conversão^{80,86}.

A resina composta microhíbrida Filtek™ Z250 (3M ESPE) apresentou a melhor estabilidade térmica. Resultado semelhante foi verificado em outro estudo que avaliou o comportamento térmico e estrutural das resinas compostas Filtek™ Supreme XT (3M ESPE), Filtek™ Z250 (3M ESPE) e TPH3 (Dentsply), onde a resina Filtek™ Z250 (3M ESPE) apresentou o melhor desempenho¹².

Os métodos de fotoativação não tiveram influência sobre o comportamento térmico dos materiais. Quando os métodos de fotoativação graduais foram empregados, a temperatura de transição vítrea (T_g) e de degradação foram equivalentes ou até superiores aos métodos de fotoativação contínuo. De acordo com alguns trabalhos na literatura^{4-5,10}, como discutido

anteriormente, a utilização destes métodos pode estar associado a uma estrutura mais linear do polímero formado, com menor concentração de ligações cruzadas, favorecendo a maior degradação do material, o que não foi observado no terceiro estudo. Uma explicação para estes resultados, que contrariam os achados da literatura, pode estar associada ao tipo de luz empregada na utilização dos métodos graduais de fotoativação.

A grande maioria dos estudos que avaliam a influência dos métodos de fotoativação graduais sobre a estrutura polimérica das resinas compostas emprega aparelhos fotoativadores à base de luz halógena^{1,4-5,10,15,27,37,50,81-82}. Nestas pesquisas, a influência do método de fotoativação sobre a densidade de ligações cruzadas das resinas compostas foi avaliada pela temperatura de transição vítrea (T_g), utilizada no nosso estudo, e/ou microdureza com armazenamento em etanol.

Como já discutido anteriormente, os aparelhos LED apresentam seu espectro estreito, dentro da zona de absorção da canforoquinona (470nm), tornando as suas irradiações energeticamente melhor aproveitadas^{2,61}. Portanto, com o maior aproveitamento da energia luminosa, a utilização dos métodos de fotoativação graduais nos aparelhos LED pode ser mais efetiva e não interferir na estrutura polimérica das resinas compostas. No entanto, o número de estudos que avaliaram a influência da utilização dos métodos de fotoativação graduais com os aparelhos LED sobre a estrutura polimérica das resinas é escasso para afirmarmos esta questão com segurança.

Yap et al.¹⁰⁷ (2004) avaliaram a influência da utilização de diferentes métodos de fotoativação sobre a estrutura polimérica da resina composta Z-100 (3M ESPE), utilizando aparelhos à base de luz halógena e LEDs. O método para avaliação da densidade de ligações foi o de microdureza, antes e após armazenamento em etanol a 75%. Os resultados demonstraram que os espécimes submetidos aos métodos de fotoativação graduais foram mais susceptíveis à degradação em etanol, com menores valores de microdureza após o armazenamento. Estes resultados não podem ser comparados aos da nossa

pesquisa, pois outra metodologia foi empregada para avaliação da estrutura polimérica final.

Os menores valores T_g foram encontrados nos grupos fotoativados com o aparelho Elipar Freelight 2™ (3M ESPE), demonstrando correlação com os resultados verificados para o grau de conversão que serão discutidos adiante.

Com relação ao grau de conversão, também não foi observada influência exercida pelo método de fotoativação. No entanto, os menores valores do grau de conversão foram verificados para as amostras confeccionadas com a resina microhíbrida, fotoativada com o aparelho Elipar Freelight 2™ (3M ESPE).

Corroborando com estes resultados, Bala et al.⁸ (2005) também verificaram os valores mais baixos para o grau de conversão quando a resina microhíbrida Filtek™ Z-250 foi fotoativada com o aparelho Elipar Freelight, ambos da 3M ESPE. Os autores avaliaram o grau de conversão de resinas híbridas (Esthet-X/Dentsply e Filtek Z-250/3M ESPE), compactáveis (Filtek P60/3M ESPE, Prodigy Condensable/Kerr, Surefil/Dentsply e Solitaire/Heraeus-Kulzer) e uma resina à base de ORMOCER (Admira/Voco), associando o resultado obtido principalmente às diferenças encontradas na composição dos materiais (matriz orgânica, tipo, tamanho e volume da carga inorgânica).

As matrizes orgânicas das resinas compostas utilizadas no terceiro estudo são semelhantes, todavia, existem diferenças com relação à porção inorgânica das mesmas. Ainda neste contexto, Turssi et al.⁹⁵ (2005) verificaram que o tamanho e a forma das partículas de carga têm influência direta sobre a resistência ao desgaste e o grau de conversão dos compósitos. Os autores mencionam que esta questão está associada à possibilidade de dispersão da luz de acordo com a forma e tamanho das partículas de carga.

No entanto, no terceiro estudo, a resina microhíbrida apresentou os menores valores do grau de conversão apenas quando o aparelho Elipar Freelight 2™ (3M ESPE) foi empregado. Nas mesmas condições, quando fotoativada pelo aparelho Bluephase® (Ivoclar-Vivadent), esta resina apresentou valores semelhantes aos da resina nanoparticulada. Dessa forma, estudos adicionais são

necessários para verificar a influência exercida pelo tipo de aparelho fotoativador e categoria da resina composta sobre o grau de conversão dos materiais resinosos.

De acordo com estes resultados, os métodos de fotoativação graduais, disponibilizados pelos aparelhos LED de 2ª geração, promovem conversão adequada sem provocar alterações na cadeia polimérica das resinas compostas que possam ser detectadas pelas temperaturas de transição vítrea (T_g) e de degradação. Contudo, o comportamento térmico e o grau de conversão dos compósitos podem ser influenciados pela categoria de resina composta e tipo de aparelho fotoativador.

A justificativa para a disponibilidade dos métodos graduais de fotoativação nos aparelhos LED de última geração está associada ao aumento da densidade de potência verificada nos últimos anos. O aumento da densidade de potência nos aparelhos LED permitiu a obtenção de propriedades semelhantes às obtidas com os aparelhos halógenos, contudo, trouxe repercussão direta sobre a contração de polimerização^{25, 49, 97} e o aumento da temperatura^{6-7, 36, 46, 68-69}.

De acordo com os resultados verificados nos três estudos aqui apresentados e discutidos, pode-se concluir que a utilização dos métodos graduais de fotoativação, seja com luz halógena ou LED, diminui os estresses provenientes da contração de polimerização. Todavia, o aparelho de luz halógena foi responsável pelas menores taxas de conversão. Os aparelhos LED de 2ª geração e seus respectivos métodos de fotoativação graduais proporcionaram adequado grau de conversão sem alterar a configuração polimérica final das resinas compostas microhíbrida e nanoparticulada. No entanto, o tipo de aparelho LED empregado e a categoria da resina composta podem interferir no comportamento térmico e estrutural dos materiais.

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5 Referências*

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Anexos

6 Anexos

Material e métodos

Experimento 1

6.1 Análise do grau de conversão por espectroscopia infravermelha transformada de Fourier (FT-IR)

Neste trabalho foram executados cinco corpos-de-prova (CP) para cada grupo avaliado, utilizando matriz metálica contendo orifício central de 4mm de diâmetro e 2 mm de espessura (Figura 1-ISO 4049). Sobre uma placa de vidro foi posicionada uma lamínula de vidro e a matriz metálica. As resinas compostas foram inseridas em único incremento no orifício da matriz, e, em seguida, posicionados uma tira de poliéster e um peso metálico de 1 kg, o qual continha uma abertura para adaptação e posicionamento da ponta do aparelho fotoativador (Figura 2). Os materiais foram então fotoativados de acordo com o grupo em questão.



FIGURA 1-Matriz metálica contendo orifício central (4mm de diâmetro e 2mm de espessura), conforme normas ISO 4049.

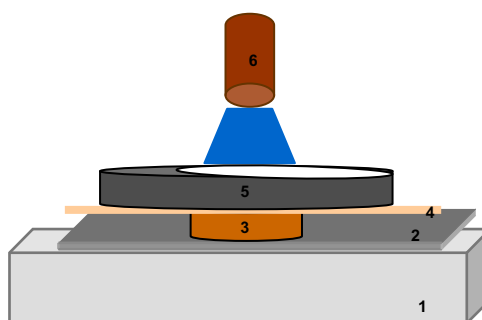


FIGURA 2- Desenho esquemático representando a confecção dos corpos-de-prova (1=placa de vidro; 2=lâmina de vidro; 3=matriz metálica; 4=tira de poliéster; 5=peso metálico e 6=ponta do fotoativador).

Após a confecção dos CP houve o armazenamento dos mesmos em água destilada, à temperatura de 37°C, durante vinte e quatro horas, em recipientes plásticos escuros. Logo após, os CP foram moídos em grau e pistilo de ágata até a obtenção de um pó e, em uma balança de precisão (Mettler Toledo), foram pesados para utilização de 5 mg. Os CP moídos foram misturados a 100mg de brometo de potássio (KBr) e, após a homogeneização, colocados em pastilhador metálico (Figura 3) para serem levados à prensa (SKAY, São José do Rio Preto, SP, Brasil), com pressão de 10 toneladas, durante 1 minuto, para obtenção de uma pastilha (Figura 4). Em seguida, as pastilhas obtidas foram posicionadas e avaliadas no espectrofotômetro (Nexus 470 FT-IR/Thermo Nicolet/USA) do Instituto de Física de São Carlos (Figura 5) para obtenção dos picos de absorbância.

Após a obtenção dos picos de absorbância no espectrofotômetro, o percentual de duplas ligações carbônicas não convertidas (%C=C) foi determinado pela taxa de intensidade de absorção entre ligações duplas de carbono alifáticas (1.638cm⁻¹) e ligações simples de carbono aromáticas (1.608 cm⁻¹). O grau de conversão (GC) correspondente foi calculado pela subtração desta taxa de 100%, como explicitado na fórmula:

$$(\%) \text{ GC} = 1 - \frac{(1638\text{cm}^{-1}/1608\text{cm}^{-1})_{\text{resina curada}}}{(1638\text{cm}^{-1}/1608\text{cm}^{-1})_{\text{resina não-curada}}} \times 100$$



FIGURAS 3 e 4-Partes constituintes do pastilhador metálico e pastilha sendo removida do pastilhador.



FIGURA 5-Espectrofotômetro Nexus 470 FT-IR.

6.2 Análise da contração de polimerização

As forças da contração de polimerização foram avaliadas utilizando uma máquina de ensaios universal (Emic DL 500 BF-NO5775-NS168) do Departamento de Materiais Odontológicos da Faculdade de Odontologia de Bauru. Nesta máquina foram adaptadas duas bases retangulares metálicas (50mm de altura, 6mm de largura e 2mm de profundidade), sendo a superior acoplada a uma célula de carga de 10kg e a inferior fixada na base transversal da máquina

(Figura 6). As bases metálicas foram posicionadas uma acima da outra, de forma paralela e com seus longos eixos posicionados verticalmente (Figura 7).

Uma vez posicionadas as bases metálicas na máquina de ensaios, o braço móvel foi movimentado até apresentar íntimo contato entre as bases. Nesta posição a máquina foi zerada e o braço móvel novamente movimentado até a obtenção de uma distância de 1mm, configurando assim o espaço para inserção da resina composta.

Incrementos únicos das resinas compostas foram inseridos e adaptados entre as bases metálicas retangulares, e, em seguida, houve a fotoativação de acordo com o grupo avaliado, conforme ilustrado nas Figuras 8, 9 e 10.

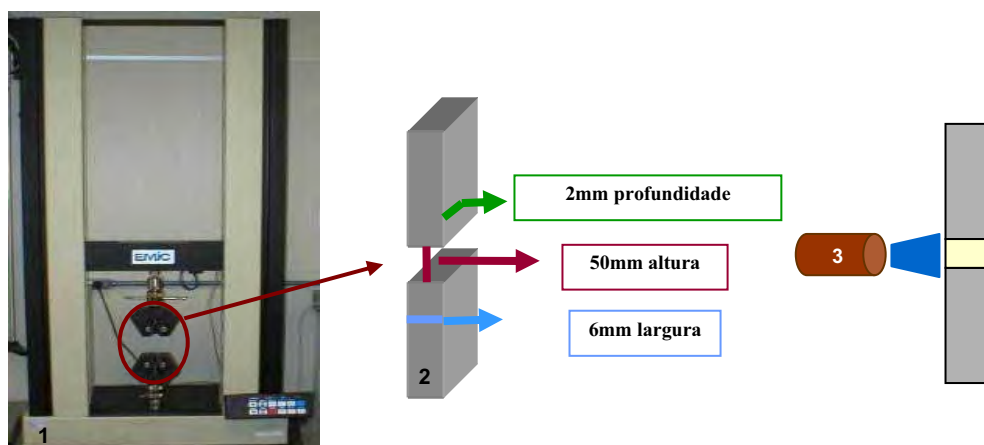
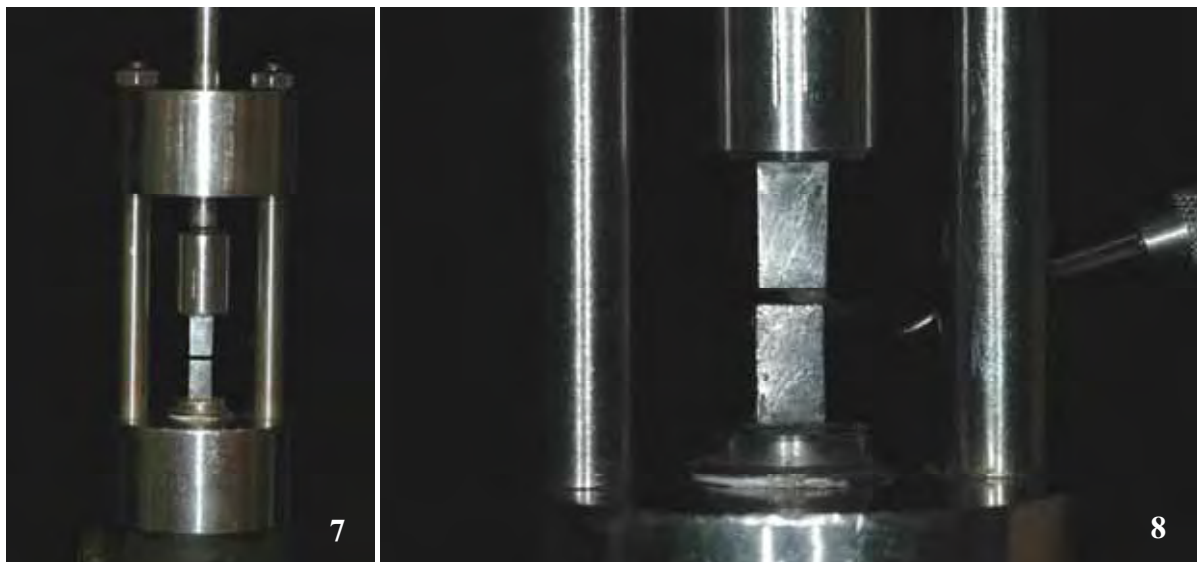
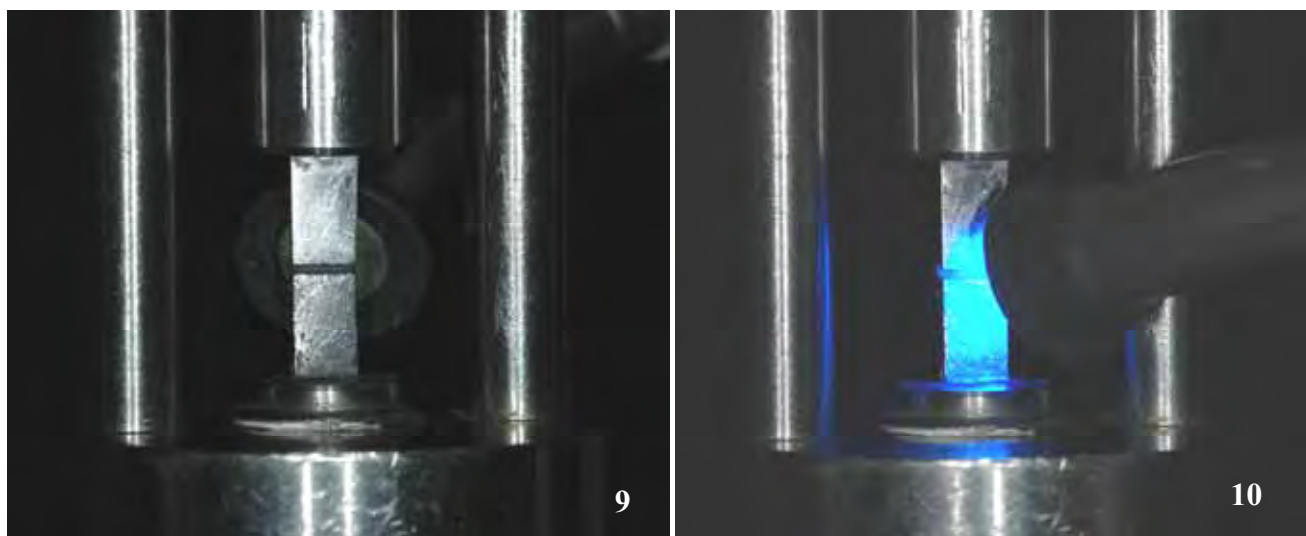


FIGURA 6-Máquina de ensaios universal Emic DL 500 (1), notar que na região destacada foram adaptadas as bases metálicas (2) para inserção e fotoativação do material (3).



FIGURAS 7 e 8-Bases metálicas acopladas à célula de carga (superior) e à base transversal da máquina (inferior). Notar o espaço pré-definido entre as bases e a inserção do incremento de resina composta.



FIGURAS 9 e 10-Incremento de resina composta inserido, adaptação da ponta do aparelho fotoativador e fotoativação.

Os dados obtidos foram registrados no computador que estava acoplado à máquina a partir do início da fotoativação até o tempo de dois minutos, pois, de acordo com Lim et al.⁴⁸ (2002), a maior parte das forças de contração ocorrem neste intervalo de tempo.

O registro das forças de contração foi realizado utilizando o *software* padrão da máquina de ensaios. O método empregou o teste de tração, porém a máquina de ensaios foi mantida imóvel durante a mensuração. As forças de contração foram transmitidas da base metálica superior à célula de carga, originando mínima deformação, a qual foi traduzida novamente como força no programa da máquina de ensaios. Cada corpo-de-prova (n=10) descreveu no programa uma curva relacionando força, expressa em Newton (N), com o tempo transcorrido, expresso em segundos (s).

Experimento 2

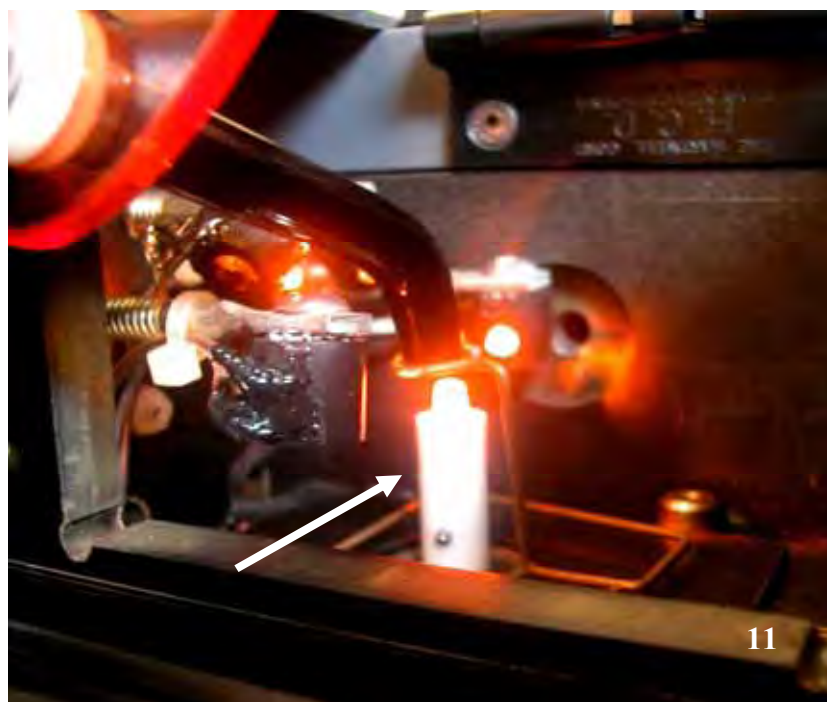
6.3 Análise da contração volumétrica

A porcentagem da contração volumétrica foi determinada por meio de um mecanismo de vídeo e imagem (AcuVol[®]/Bisco) do Laboratório de Pesquisas do Departamento de Estomatologia da Universidade Federal de Santa Catarina. Tal dispositivo contém em seu interior uma câmera de vídeo (Sony XC75-X), responsável por filmar a amostra de resina composta em tempo real, acoplada a um microcomputador dotado de um *software* específico (MIOD *Detection Technologies*). Este *software* captura e digitaliza as imagens das amostras nos períodos antes, durante e após a fotoativação, registrando o percentual de contração volumétrica a cada segundo, durante o tempo pré-estabelecido pelo operador.

Foram confeccionados cinco corpos-de-prova (CP) com 15 μ l (\pm 1) de volume (verificado através do *software*). Cada incremento de resina composta foi retirado diretamente da bisnaga e posicionado em um pedestal no interior da máquina, focalizado a 10 cm da lente da câmera de vídeo (Figura 11). Essa imagem foi capturada e digitalizada pelo *software* e, após 2 minutos de escoamento do material, o perímetro do CP foi contornado por uma linha virtual pontilhada e essa dimensão ficou armazenada no programa como volume inicial da amostra. Logo após, o incremento de resina composta foi fotoativado, de acordo com grupo em questão, estando a ponta do fotoativador distante 1 mm da superfície do CP. Esta distância foi padronizada pela colocação de um dispositivo para inserção da ponta do fotoativador (Figura 12).

Ao final do período de mensuração (10min), outra linha pontilhada virtual contornou o perímetro do volume final apresentado pelo material. Considerando que as linhas (inicial e final) estavam representadas na mesma imagem, foi possível visualizar a contração da amostra por meio da diferença entre a linha virtual pontilhada inicial e a linha pontilhada final. O percentual de

contração volumétrica, calculado de forma automatizada pelo *software*, foi registrado numericamente a cada segundo, durante o tempo de 10 minutos.



FIGURAS 11 e 12-Pedestal de teflon (seta) localizado no interior do equipamento Acuvol® (Bisco) onde é inserido o incremento de resina composta. Notar o dispositivo confeccionado para padronizar a distância ponta do fotoativador/incremento de resina.

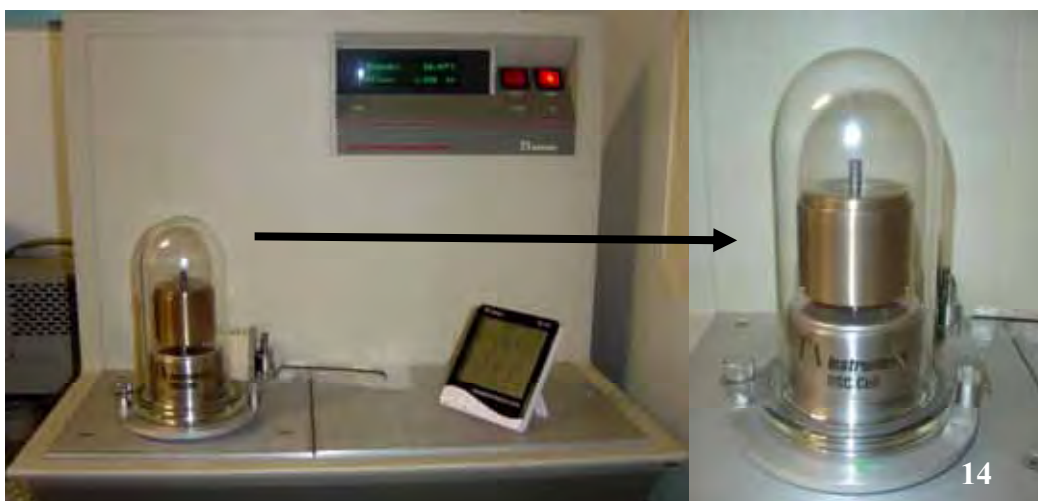
Experimento 3

6.4 Análise por calorimetria exploratória diferencial

A análise da estrutura polimérica das resinas compostas foi realizada pelo método da calorimetria exploratória diferencial ou *Differential Scanning Calorimetry* (DSC). Os corpos-de-prova (CP) foram confeccionados seguindo os mesmos parâmetros da análise do grau de conversão. Após o tempo de armazenagem de vinte e quatro horas, os CP foram triturados e pesados em balança analítica de precisão (Mettler AJ150) para utilização de 18mg.

As medidas DSC foram realizadas para o acompanhamento da variação de energia e massa envolvida durante o processo de aquecimento dos CP sob atmosfera dinâmica do ar (60 mL min^{-1}). As medidas foram realizadas em aparelho calibrado com padrão de índio (DSC 2910/TA Instruments), acoplado a um microcomputador servidor, do Grupo de Crescimento de Cristais e Materiais Cerâmicos do Instituto de Física de São Carlos (Figuras 13 e 14).

Para tal, dispositivos denominados “cadinho” e suas respectivas coberturas (*hermetic pan e hermetic lid*) foram utilizados (Figura 15) para colocação do fragmento de resina composta (Figuras 16 e 17). Em seguida, estes dispositivos foram levados à prensa para fechamento hermético (Figura 18) e, depois, posicionados no aparelho DSC 2910 (Figuras 19 e 20). As amostras foram aquecidas a $10^\circ\text{C}/\text{min}^{-1}$, numa faixa de temperatura de 10°C a 350°C , sob nitrogênio a 40 mL min^{-1} para observar a temperatura de transição vítrea (T_g) e de degradação dos materiais. Os resultados obtidos foram processados no programa *Origin 7.5* e as respectivas temperaturas foram obtidas nos gráficos gerados.



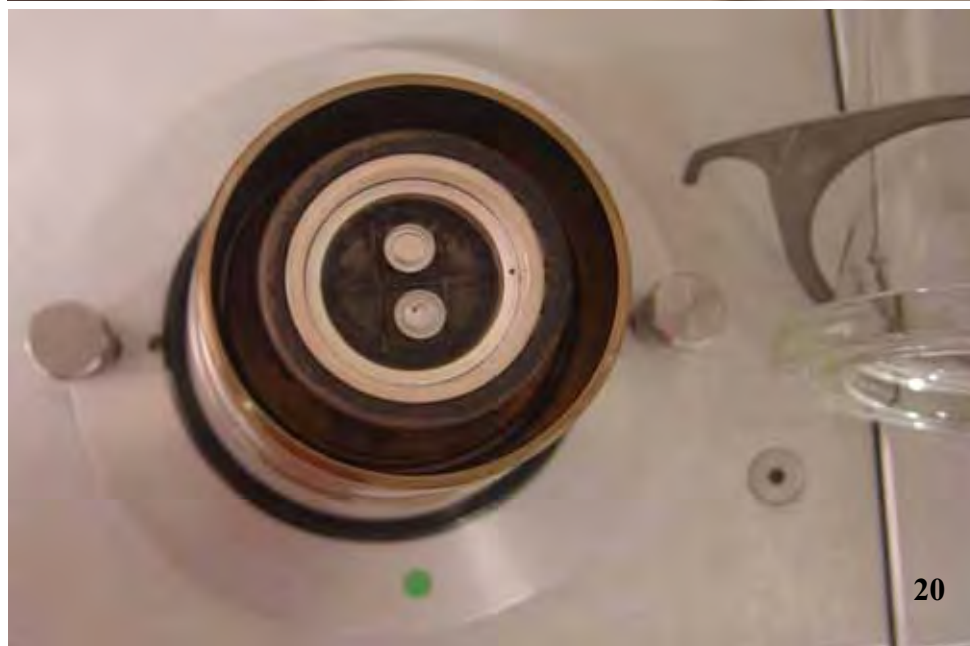
FIGURAS 13 e 14-Aparelho DSC 2910/*Instruments*. Notar a cápsula onde são posicionados os CP para submissão às temperaturas programadas.



FIGURAS 15, 16, 17 e 18-Dispositivos para colocação dos CP (*Hermetic Pan e Lid*), CP sendo posicionado no dispositivo e, em seguida, levado à prensa.



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FIGURAS 19 e 20-Cápsula do aparelho DSC 2910/*Instruments* desmontada para colocação dos CP e vista superior da região onde serão posicionados os CP.

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Araraquara, 19 de abril de 2010.

Simone Xavier Silva Costa