



**UNIVERSIDADE ESTADUAL PAULISTA - UNESP
FACULDADE DE ODONTOLOGIA DE ARARAQUARA**

JULIANA MARIA CAPELOZZA BOAVENTURA

**ESTUDO DE DIFERENTES PROPRIEDADES
DE RESINAS COMPOSTAS COMERCIAIS E
EXPERIMENTAL**

Araraquara

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Tese apresentada ao Programa de Pós-Graduação em Ciências Odontológicas, área de concentração Dentística, da Faculdade de Odontologia de Araraquara, como parte dos requisitos para obtenção do título de Doutor em Ciências Odontológicas.

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Araraquara

2012

Boaventura, Juliana Maria Capellozza

Estudo de diferentes propriedades de resinas compostas comerciais e experimental / Juliana Maria Capellozza Boaventura.-- Araraquara: [s.n.], 2012.

150 f. ; 30 cm.

Tese (Doutorado) – Universidade Estadual Paulista, Faculdade de Odontologia

Orientador: Prof. Dr. Marcelo Ferrarezi de Andrade

Co-orientadora: Profa. Dra. Alessandra Nara de Souza Rastelli

**1. Resinas compostas 2. Nanotecnologia 3. Fluorescência
4. Cor 5. Espectroscopia infravermelho transformada de Fourier I. Título**

Ficha catalográfica elaborada pela Bibliotecária Marley C. Chiusoli Montagnoli, CRB-8/5646

Serviço Técnico de Biblioteca e Documentação da Faculdade de Odontologia de Araraquara / UNESP

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Dedicatória

*Primeiramente agradeço a Deus pelo dom da vida,
pela família maravilhosa, amigos e pela
oportunidade de realizar um sonho. Muitos são os
obstáculos, mas só Deus para nos dar força nos
momentos mais difíceis e fazer com que continuemos
caminhando para a vitória com a alegria de missão
cumprida.*

Obrigada meu Deus por estar sempre comigo

Aos meus maravilhosos pais, Antônio e Virgínia, pelo amor e compreensão nos meus momentos de decisão.

Obrigada pelo amor, paciência, carinho e dedicação que sempre tiveram comigo, e, principalmente, por ter acreditado que eu conseguiria vencer. Vocês foram as pessoas mais importantes da minha vida, o qual quero seguir como exemplo

Amo muito vocês

Aos meus queridos irmãos, Raquel, César e Camila pela amizade, apoio e união, além de estarem constantemente presentes em todos os momentos da minha vida.

Aos meus queridos sobrinhos Fábio, Ana Letícia e Gabriel. Muito obrigada pelo carinho e amor que sempre tiveram comigo e pelos momentos de descontração. O sorriso de vocês me reergueu quando estava cansada e desanimada e me fez acreditar que nunca devemos parar de sonhar.

Ao meu querido namorado Luís César, pelo seu amor, paciência e compreensão nos meus momentos de estudo e ausência. Obrigada por sempre me apoiar e incentivar a crescer.

Agradecimentos especiais

Ao meu professor orientador, *Marcelo Ferrarezi de Andrade*, que me acolheu, apoiou e acreditou em mim. Foi amigo e mestre ao mesmo tempo e mostrou que quando trabalhamos juntos, unimos forças e podemos crescer. Obrigada pela sua orientação, dedicação, correção e acima de tudo pela valiosa amizade. Sei que posso contar sempre com a sua ajuda. A caminhada não termina hoje. Meu eterno respeito, admiração e agradecimento.

A minha professora co-orientadora, *Alessandra Nara de Souza Rastelli*, pela paciência e disponibilidade em me ajudar. Tenho muito a agradecer pela direção e pela sua minuciosa correção em todos os trabalhos e pesquisas realizadas, pois muito do que aprendi e conquistei foi fruto da sua colaboração e dedicação. Obrigada pela orientação, confiança e amizade conquistada.

Ao meu *Orientador e Co-orientadora*, que mesmo com a agenda cheia, nunca deixaram de conseguir um tempo

para corrigir o rumo do meu trabalho, orientando como deve fazer um orientador, corrigindo, criticando, elogiando e incentivando.

Obrigada por tudo.

A Professora *María Salete Machado Cândido*

(In Memoriam), minha orientadora do Mestrado e início da caminhada no Doutorado. Com ela adquiri confiança pra continuar nos estudos. Sempre foi uma pessoa dedicada na vida acadêmica e com amor pela profissão, me ensinou muito que sou hoje. Obrigada por ajudar a compreender o valor do estudo, e acima de tudo, o valor da generosidade e honestidade, pois aprendi que para crescer, é necessário respeitar as pessoas com as quais trabalhamos e convivemos.

Aos meus colegas do curso de Pós-Graduação

Andiara Ribeiro Roberto e *William Kabbach* pela amizade e companheirismo nestes anos de Doutorado.

Aos meus amigos de Mestrado e Doutorado, *Esther*

Gomes, Rafael Calixo, Matheus Bandeca, Fernando

Flores, Víctor Clavíjo, Fábio Alvarenga, Janaina, Fabrício, Carlos Borges, Marília Regalado, Fernanda Jassé, Aliny, Mateus Tonetto, Carol, Carol Santezi, Kelly, Taís Cruz, Fabí, Juliana, Marília, Aline, Sabrina, Cris,
pela amizade e ajuda durante o ano que convivi com vocês.

Aos alunos de Graduação e Iniciação Científica,
Jaqueline Ignácio, Aíon Mangino Dias, Nicole Casalle e Ana Carolina Beccí pela colaboração nas pesquisas e a oportunidade de ajudá-los

Agradecimento em especial as amigas *Andiara, Benícia, Esther, Fernanda Jassé, Marília Regalado, Aliny, Carol Santezi e Raquelí* por toda a ajuda, acolhimento, atenção e amizade.

Aos meus *amigos e amigas de Jaú,* que toleraram o meu distanciamento e continuaram de braços abertos para receber quando o meu tempo permitia. A amizade e o carinho de vocês

me ajudaram a crescer e a continuar lutando por aquilo que sonhei.

Corrida para vitória. Obrigada por fazerem parte dessa história.

Agradecimentos

A Faculdade de Odontologia de Araraquara, da Universidade Estadual Paulista, representada pela Senhora Diretora *Profa. Dra. Andreia Affonso Barretto Montandon* e a vice-diretora *Profa. Dra. Elaine Maria Sgavioli Massucato* onde tive a oportunidade de dar um importante rumo ao crescimento científico e profissional.

Ao programa de Pós-Graduação em Ciências Odontológicas, da Faculdade de Odontologia de Araraquara, representado pela *Profa. Dra. Josimeri Hebling* e pelo *Prof. Dr. Edson Alves de Campos*, pela contribuição em minha formação profissional.

Aos professores do Programa de Pós-Graduação do Departamento de Dentística Restauradora, *Osmir Batista de Oliveira Júnior*, *Marcelo Ferrarezi de Andrade*, *José Roberto Cury Saad*, *Maria Salete Machado Candido* (*in memoriam*), *Edson Alves de Campos*, *Sizenando de*

Toledo Porto Neto, Alessandra Nara de Souza Rastelli e Andrea Abi Rached Dantas, pela presteza, competência e experiência transmitidas durante o curso.

Aos funcionários do Departamento de Dentística, *Cida, Wanderlei, Marinho, Priscila e Creusa*, pelo respeito, ajuda, carinho e amizade.

Aos funcionários da seção de pós-graduação, *Serginho, José Alexandre* e em especial a *Mara* por estarem sempre disponíveis, cordiais e solícitos no esclarecimento das dúvidas e prestação dos serviços.

Aos funcionários da Biblioteca, pela atenção e paciência, em especial a *Marley e Ceres*, pela correção e revisão das referências bibliográficas.

Ao Grupo de Óptica e ao Grupo de Crescimento de Cristais e Materiais Cerâmicos, do Instituto de Física em São Carlos (USP) nas pessoas do *Prof. Dr. Vanderlei Salvador*

Bagnato, Prof. Dr. Antonio Carlos Hernandez, Profa. Dra. Maria Inês Basso Bernardi, Geraldo José M. Frigo, Denis Pablo Jacomassi e Vinicius Dantas de Araujo, pela disponibilização de toda estrutura física e laboratorial para realização desta pesquisa, além do apoio técnico-científico para realização deste trabalho.

Ao *Prof. Dr. Renato de Toledo Leonardo* pela atenção, disponibilidade e ajuda no trabalho.

A amiga e *Profa. Dra. Simone Xavier Silva Costa*, pela atenção, conselhos, ensinamento e ajuda.

Ao *Prof. Romeu Magnani*, pela estatística e grande auxílio em todos os artigos. Sua atenção e cuidado foi muito importante para a realização deste trabalho.

As empresas, 3M ESPE representada pela *Eugênia Mara Alexandre* e VOCO pelo *Prof. Dr. Marcelo Balsamo*, pelo auxílio dos materiais utilizados na pesquisa.

À Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (Capes) e PROAP, pelo apoio financeiro concedido e indispensável à realização desta pesquisa e outros trabalhos durante a Pós-Graduação.

A todos que, embora não estejam aqui citados, tenham contribuído direta ou indiretamente para a realização deste trabalho.

Minha eterna gratidão.

"Apesar dos nossos defeitos, precisamos enxergar que somos pérolas únicas no teatro da vida e entender que não existem pessoas de sucesso e pessoas fracassadas.

O que existem são pessoas que lutam pelos seus sonhos ou desistem deles."

Augusto Cury

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Resumo

Boaventura JMC. Estudo de diferentes propriedades de resinas compostas comerciais e experimental [Tese de Doutorado]. Araraquara: Faculdade de Odontologia da UNESP; 2012.

Resumo

O objetivo deste trabalho foi avaliar diferentes propriedades de resinas compostas comerciais e uma resina composta experimental contendo dióxido de zircônia, por meio de 3 estudos: (1): avaliar a fluorescência por meio de imagens conjugadas ao processamento digital e estabilidade de cor após 24 horas de imersão em saliva artificial e envelhecimento acelerado em câmara ultravioleta (UV), (2): avaliar o grau de conversão (GC%) por meio de espectroscopia por FTIR e (3): avaliar sorção de água por meio de imersão em saliva artificial nos períodos de 1, 3, 14, 21, 30 e 60 dias. Para os três estudos, corpos-de-prova para cada resina foram confeccionados em matriz metálica circular com dimensões específicas para cada teste. Para fotoativação, um LED Celalux[®] (Voco, 776 mW/cm²) foi utilizado por 40 segundos. No primeiro estudo, cinco dentes caninos foram utilizados como referência para análise da fluorescência e oito corpos-de-prova para cada resina composta (n=48) foram confeccionados. A análise digital da fluorescência foi realizada com auxílio de câmara CCD conectada a computador, sob iluminação com LED UV. Foram coletadas 16 imagens para cada corpo-de-prova, e estas foram processadas matematicamente, quantificando a intensidade de fluorescência em escala de cinza. Na estabilidade de cor, oito corpos-de-prova para cada resina (n=48) foram submetidos ao envelhecimento artificial, inicialmente por meio de imersão em saliva por 24 horas e depois em câmara ultra-violeta (UV). As mensurações foram obtidas por meio de colorímetro

(Minolta, CM 2600 d, Japão), as quais foram registradas no próprio display do equipamento e transferidos a microcomputador mediante um software específico que registrou os valores de cor de acordo com o Sistema CIE- $L^*a^*b^*$. Os dados para fluorescência e estabilidade de cor foram submetidos à Análise Estatística de Variância (ANOVA) complementada por teste de Tukey ($p < 0,05$). No segundo estudo, foi avaliado o grau de conversão (GC%), para o qual cinco corpos-de-prova ($n=25$) para cada resina, foram triturados, prensados com KBr e analisados em espectrofotômetro FTIR (Nexus-470). Os dados relativos ao GC% foram avaliados estatisticamente por correção de Welch complementado por comparações múltiplas de Games-Howell ($p < 0,05$). No terceiro estudo, o qual avaliou a sorpção de água, 8 corpos-de prova para cada resina ($n=40$) foram pesados diariamente até obter massa constante, para depois serem pesados em intervalos de tempo pré-determinados: 1, 3, 14, 21, 30 e 60 dias. Durante este período, estes foram armazenados em 5 ml de saliva artificial e mantidos em estufa a 37°C ($\pm 1^\circ\text{C}$). Os dados obtidos para sorpção de água foram analisados estatisticamente pela Análise de Variância (ANOVA) e teste de Tukey ($p < 0,01$). Os resultados obtidos para o primeiro estudo mostraram que as resinas compostas FiltekTM Z250 e experimental apresentaram as menores médias de fluorescência. A média para FiltekTM Z350 (0,100; $\pm 0,006$) foi maior que da FiltekTM Z250 (0,084; $\pm 0,006$), mas equivalente à experimental (0,087; 0,008). As outras resinas estabeleceram as seguintes médias de fluorescência: FiltekTM Z350 XT (0,116; $\pm 0,007$) < dente (0,162; $\pm 0,017$) < Grandio[®] (0,210; $\pm 0,010$) < Evolu-X[®] (0,248; $\pm 0,009$). Para estabilidade de cor, não houve diferença significativa para variação de cor (ΔE) após 24 h de imersão em saliva. O ΔE^* foi acentuado após envelhecimento em câmara UV, podendo se estabelecer que FiltekTM Z250 (8,81;

$\pm 0,63$) = Evolu-X[®] (9,66; $\pm 0,70$) \leq Filtek[™] Z350 (10,08; $\pm 0,70$) < Grandio[®] (11,78; $\pm 0,70$) < Filtek[™] Z350XT (15,93; $\pm 0,99$) < experimental (21,64; $\pm 1,07$). Para o segundo estudo, as resinas estabeleceram as seguintes médias de grau de conversão: experimental (47,5%; $\pm 6,0$) < Filtek[™] Z250 (63,9%; $\pm 4,4$) = Filtek[™] Z350 (70,5%; $\pm 2,1$) = Grandio[®] (67,5%; $\pm 2,4$) < Evolu-X[®] (76,5%; 1,5). No terceiro estudo, a resina experimental apresentou aumento significativo de sorção de água como resultado do armazenamento em saliva artificial. Assim, baseados nos resultados apresentados nos três estudos pudemos concluir que as resinas compostas não apresentaram fluorescência semelhante à estrutura dentária e a variação de cor mostrou-se acentuada após envelhecimento em câmara UV, com maior variação para a resina experimental. A composição da resina afeta o GC% e a resina experimental mostrou a maior sorção de água em relação ao tempo de armazenamento em saliva artificial.

Palavras-chaves: Resinas compostas; Nanotecnologia; Fluorescência, Cor; Espectroscopia Infravermelho Transformada de Fourier.



Abstract

Boaventura JMC. Study of the different properties of commercial and experimental composite resins [Tese de Doutorado]. Araraquara: Faculdade de Odontologia da UNESP; 2012.

Abstract

The aim of this study was to evaluate different properties of commercial and experimental composites resins through three studies: (1): to evaluate the fluorescence by digital images and color stability after 24 hours immersion in artificial saliva and accelerated aging in the UV chamber, (2) to evaluate the degree of conversion (DC%) by means of FTIR spectroscopy, and (3): to evaluate water sorption by immersion in artificial saliva at 1, 3, 14, 21, 30 and 60 days. For the three studies, specimens were made in a circular metallic mold with specific dimensions for each test. For photoactivation, a LED Celalux[®] (Voco, 776 mW / cm²) was used for 40 seconds. In the first study, five anterior teeth were used to fluorescence analysis and eight specimens (n=48) were made. The digital fluorescence analysis was performed using a CCD camera (LG) connected to a computer and using a UV LED. For each specimen, 16 images were captured and the mean values were also obtained, which were then converted into gray intensity scale values. For color stability, eight specimens for each composite resin were subjected to artificial aging, initially through immersion in artificial saliva for 24 hours, and in an ultra-violet (UV) chamber. The color measurements were taken with a Minolta colorimeter (CM 2600d, Japan), which were registered in their own display equipment and transferred to a microcomputer through a specific software, which recorded the color values according to the CIE-L * a * b *. Data for fluorescence and color stability were submitted to Analysis of Variance

(ANOVA) followed by Tukey's test ($\alpha=5\%$). For the second study, the degree of conversion (DC%) was evaluated. Five specimens ($n=25$) were pressed with KBr and analyzed by FTIR spectrophotometer (Nexus-470). The data for the DC% were statistically analyzed by Welch's correction and complemented by the Games–Howell multiple comparison test ($p<0.05$). For the third study which evaluated the water sorption, eight specimens for each composite resin ($n=40$) were weighed daily until constant mass, after that they were weighed at predetermined time intervals: 1, 3, 14, 21, 30 and 60 days. During this period they were stored in 5 ml of artificial saliva and maintained in oven at $37^{\circ}\text{C} (\pm 1^{\circ}\text{C})$. The data obtained for water sorption were statistically analyzed by ANOVA and Tukey's test ($p < 0.01$). The results for the first study, show that the FiltekTM Z250 and the experimental composite resins showed the lowest fluorescence mean values. The fluorescence mean value for FiltekTM Z350 (0.100; ± 0.006) was higher than for FiltekTM Z250 (0.084; ± 0.006); however, this value was similar to the experimental composite resin (0.084; ± 0.006). The other composite resins showed the following fluorescence mean values: FiltekTM Z350 XT (0.116; ± 0.007) < Tooth (0.162; ± 0.017) < Grandio[®] (0.210; ± 0.010) < Evolu-X[®] (0.248; ± 0.009). For color stability, there was no significant difference in color changes (ΔE) after 24 h of immersion in saliva. The ΔE^* was pronounced after aging in UV chamber, which can be expressed as follows: FiltekTM Z250 (8.81; ± 0.63) = Evolu-X[®] (9.66; ± 0.70) \leq FiltekTM Z350 (10.08; ± 0.70) < Grandio[®] (11.78; ± 0.70) < FiltekTM Z350XT (15.93; ± 0.99) < experimental (21.64; ± 1.07). In the second study, the following inequality describes the mean values for the degree of conversion of the composite resins: experimental (47.5%; ± 6.0) < FiltekTM Z250 (63.9%; ± 4.4) = FiltekTM Z350 (70.5%; ± 2.1) = Grandio[®] (67.5%; ± 2.4) < Evolu-X[®] (76.5%; ± 1.5). For the third study, the

experimental composite resin showed a significant increase on water sorption as a result of the days of storage in saliva. Thus, based on the results presented in the three studies it was possible to conclude that the composite resins did not show fluorescence similar to dental structure and the color change was greater than after aging in UV chamber, and the greatest change was shown for the experimental resin. The composition of the composite resins affects their DC% and the experimental composite resins showed the greatest influence on water regarding storage time in artificial saliva.

Keywords: Composite resins; Nanotechnology; Fluorescence; Color; Spectroscopy, Fourier Transform Infrared.



Introdução

1 INTRODUÇÃO

A exigência estética da sociedade, o aprimoramento dos materiais, o surgimento de novas técnicas restauradoras e o avanço das pesquisas, permitiram que as resinas compostas evoluíssem e se destacassem dentre os materiais restauradores diretos.

Essa evolução se iniciou por volta da década de 60, por meio das pesquisas de Bowen⁵ que uniu a resina epóxica com a resina acrílica obtendo o Bis-GMA (Bisphenol-A-glicidil metacrilato). O éster glicidil do bisfenol A reage com o metacrilato da resina acrílica, dando origem à resina de Bowen, que é a parte orgânica da resina composta. Esta apresentava um alto grau de manchamento, infiltração marginal, além de alta susceptibilidade a degradação de cor e ao desgaste superficial. Com o objetivo de melhorar essas deficiências, partículas de carga inorgânica unidas à matriz por meio de um agente de união (silano) foram adicionadas (Bowen^{5,6}).

Paralelamente, ocorreu uma grande evolução em relação ao sistema de ativação, e as primeiras resinas compostas fotoativadas foram introduzidas no mercado nos anos 70. Os primeiros materiais eram polimerizados por luz de espectro invisível ultravioleta (UV) e as resinas atuais são polimerizadas por espectro de luz visível (Yoon et al.⁶³). As resinas compostas fotoativadas dependem de uma intensidade de luz suficiente para atingir uma polimerização adequada (Rodrigues Neto et al.⁴³), o que resulta em boas propriedades físicas dos materiais e qualidade clínica das restaurações (Polydorou et al.³⁸).

As resinas compostas atuais são constituídas por matriz orgânica, uma carga inorgânica e um silano como agente de união entre ambos. A maioria das resinas compostas emprega como matriz orgânica o Bis-GMA e/ou UDMA. O Bis-

GMA é um monômero de alto peso molecular e altamente viscoso a temperatura ambiente, o que fez com que monômeros diluentes, de baixa viscosidade como o TEGDMA (trieilenoglicol dimetacrilato) e o EGDMA (etilenoglicol dimetacrilato) fossem incorporados para melhorar a consistência do material e permitir maior adição das partículas de carga. O uso de monômeros de baixo peso molecular não apenas aumenta o grau de conversão das resinas compostas, como também a contração de polimerização, o que limita a quantidade a ser adicionada (Peutzfeldt³⁷).

As partículas inorgânicas como o vidro de bário, boro, zinco, estrôncio, quartzo, sílica, zircônia e o silicato-lítio-alúminio foram adicionadas a matriz orgânica para melhorar as propriedades das resinas, o que permitiu diminuição na contração de polimerização e maior resistência à abrasão e compressão. Para unir as fases, orgânica e inorgânica, as partículas de carga são submetidas a um processo de silanização que torna a superfície destas hidrófobas, prevenindo a penetração de água na interface resina/carga (Peutzfeldt³⁷, Puckett et al.³⁹).

As resinas compostas são classificadas de acordo com os tamanhos das partículas de carga em híbrida, microhíbrida e microparticulada, e com o avanço dos últimos anos e a introdução da nanotecnologia em diversos ramos, surgiu então uma nova classificação para a resina composta, que são as resinas nanohíbridas e nanoparticuladas. A nanotecnologia é conhecida como a produção e a manipulação de materiais e estruturas com tamanho variando aproximadamente entre 0,1 a 100 nm por vários métodos químicos e físicos (da Silva et al.¹²).

A nanotecnologia tem sido alvo de grande interesse nas pesquisas com resinas compostas. Por apresentar partículas de carga mais distribuídas e de tamanho reduzido, maior quantidade pode ser incorporada com conseqüente

redução da contração de polimerização e aumento das propriedades mecânicas, tais como: resistências à tração, compressão e fratura. As resinas compostas à base de nanopartículas conferem ao material, propriedades superiores às dos compósitos híbridos, como melhor polimento, manuseio e capacidade de manter a anatomia por longos períodos, assim como sua alta quantidade de carga faz com que esses materiais tenham resistência adequada para ser indicada em dentes posteriores, bem como propriedades ópticas e lisura semelhantes às resinas compostas microparticuladas (Beun et al.³, Kirk et al.²⁵, Mitra et al.³¹, Moszner, Klapdohr³³, Moszner, Salz³⁴, Terry⁵²).

Atualmente, dois tipos de resinas compostas envolvem a tecnologia nanométrica: as resinas nanoparticuladas, cuja composição envolve apenas partículas de proporções nanométricas; e as nanohíbridas, onde há uma mistura de nanopartículas, mas contém também partículas maiores, como as que estão presentes nas resinas microhíbridas. Nas resinas nanoparticuladas, as partículas inorgânicas podem se apresentar na forma dispersa com partículas de sílica, da ordem de 20 nm; e outra aderida com nanocomplexos de sílica-zircônia, que se comportam como uma estrutura única, medindo 75 nm em média. A combinação destas duas formas proporciona um maior percentual de partículas de carga e conseqüente resistência ao material (Mitra et al.³¹, Ward⁵⁷).

As propriedades mecânicas das resinas compostas fotoativadas estão diretamente relacionadas ao seu grau de polimerização. Uma polimerização insuficiente pode alterar a dureza, estabilidade de cor, resistência, além de promover a presença de monômeros residuais que podem contribuir para o aparecimento de cáries secundárias e danos pulpares (Rueggeberg⁴⁶). Há diversos métodos para se verificar o grau de polimerização, como os métodos diretos, que

utilizam a espectroscopia no infravermelho e Raman, e o método indireto, mais utilizado atualmente, representado pelo teste de dureza (Araujo et al.¹, Ferracane et al.¹⁹, Ferracane et al.²⁰).

O termo grau de conversão aplicado às resinas compostas refere-se à conversão de duplas ligações carbônicas monoméricas em polímero de simples ligação carbono, ou seja, é a extensão na qual o monômero é transformado em polímero (Ferracane et al.¹⁹, Ferracane et al.²⁰). Alto grau de conversão significa menor quantidade de monômeros livres e conseqüentemente melhores propriedades físicas e menos danos pulpares. O grau de conversão das resinas compostas pode variar de 43% a 75% dependendo da composição da resina, da intensidade de irradiação e tempo de exposição (Chung, Greener⁸, Ruyter, Oysaed⁴⁵, Silikas et al.⁴⁹). A espectroscopia no infravermelho oferece uma aproximação direta na avaliação de cura das resinas compostas fotoativadas (DeWald, Ferracane¹³), e a técnica determina o grau de conversão baseado na absorção da radiação no intervalo de frequência infravermelho, devido às vibrações moleculares dos grupos funcionais contidos nas cadeias poliméricas (Chung, Greener⁸).

Fatores como, aparelhos fotopolimerizadores, densidade de potência, comprimento de onda corretos, tempo de irradiação, quantidade de cargas inorgânicas, coeficiente de refração da matriz orgânica, tipo e quantidade de fotoiniciador e cor também influenciam fortemente no grau de conversão das resinas compostas (Cook¹⁰, Dlugokinski et al.¹⁴, Vandewalle et al.⁵³). Diversos trabalhos relatam esses fatores, como nos estudos de Rastelli et al.⁴¹ (2008), em que o grau de conversão foi significativamente influenciado pela densidade de potência e tempos de irradiação. Em outro estudo no mesmo ano, os valores de grau de

conversão da resina foram dependentes de diferentes densidades de potências e mudanças na temperatura que ocorre durante a fotoativação da resina composta usando diferentes aparelhos fotopolimerizadores (Rastelli et al.⁴⁰). A luz LED, nos estudos de Saade et al.⁴⁶ (2009), proporcionou uma fotoativação mais uniforme em toda a superfície da resina composta, além de bons valores de dureza. Costa et al.¹¹ (2009), mostrou que o grau de conversão foi influenciado pela fonte de luz, mas não houve diferença quanto ao modo de fotoativação. Para Galvão et al.²¹ (2010), não houve diferença na dureza e grau de conversão da resina composta quando se utilizou LED com diferentes ponteiros.

A resina composta está sujeita a sofrer o processo de sorpção de água quando em contato com a saliva ou outro meio líquido e esse processo leva à expansão com o relaxamento das tensões exercidas pela contração de polimerização. Contudo, a expansão higroscópica e a tensão de contração não ocorrem de maneira uniforme nas restaurações de resina composta, pois a contração ocorre rapidamente e o relaxamento ocorre de forma lenta, podendo durar dias (Yap et al.⁶¹).

Portanto, a reduzida conversão dos monômeros em polímeros decorrentes de uma polimerização deficiente pode levar a sorpção e solubilidade da resina composta, afetando as suas propriedades mecânicas (Pearson, Longman³⁶, Guimarães et al.²²). Em contato com água, a resina primeiramente entumece e ocorre aumento da massa e depois ocorre a lixiviação de componentes não reagidos, como os monômeros residuais, ocasionando perda de massa e redução de propriedades mecânicas (Ferracane¹⁸).

Além das propriedades mecânicas reduzidas, a sorpção de fluidos torna a resina composta mais susceptível a instabilidade de cor, devido à presença de

corantes nos fluidos que são absorvidos levando a um manchamento extrínseco (Schulze et al.⁴⁸), resultado também da pigmentação por cigarros, alimentos, bebidas (Yazici et al.⁶², Güler et al.²³, Domingos et al.¹⁵), além do envelhecimento por várias condições físico-químicas como luz visível e radiação ultravioleta (UV) (Schulze et al.⁴⁸, Lee et al.²⁷). Fatores inerentes ao material, como a matriz resinosa (Reis et al.⁴⁴), tipo de fotoiniciador e alteração da interface matriz/carga pode levar a um manchamento intrínseco do material (Reis et al.⁴², Villalta et al.⁵⁶).

É importante que a resina composta quando inserida e polimerizada na cavidade, não apresente apenas propriedades mecânicas satisfatórias, mas estabilidade de cor ao longo da vida clínica. Além disso, o comportamento óptico deve ser compatível com a estrutura dental (Lee et al.²⁷). A combinação dessas propriedades juntamente com procedimentos técnicos de aplicação resulta no sucesso clínico da restauração (Bin, Yong-Keun⁴). Espera-se que as restaurações de resina composta tenham uma estabilidade de cor que permaneça pelo período de tempo em que se mantiverem funcionais no meio bucal.

Atualmente, as restaurações estéticas não devem reproduzir apenas a cor, mas também a fluorescência, opalescência e translucidez da estrutura dentária. As propriedades ópticas dos materiais são determinadas pela sua composição resultando na diferença entre vários materiais com relação ao índice de reflexão e refração. Nas resinas compostas, o formato, tipo, tamanho e concentração das partículas de carga das diferentes marcas comerciais, assim como a adição de monômeros e pigmentos são fatores responsáveis pelas características de dispersão óptica do material na tentativa de imitar as propriedades ópticas das estruturas dentais (Lee et al.²⁶, Masotti et al.³⁰, Taira et al.⁵¹, Watts, Cash⁵⁸)

Uma dessas propriedades ópticas é a fluorescência. A radiação ultravioleta (UV) em ambiente escuro permite verificar a fluorescência das resinas compostas em comparação a estrutura dentária e podem revelar fluorescência mais clara ou mais escura (Sant'Anna Aguiar Dos Reis et al.⁴⁷). A banda espectral de fluorescência dos dentes naturais varia entre 410 e 500 nm na cor azul (Sant'Anna Aguiar Dos Reis et al.⁴⁷, Wozniak, Moore⁶⁰). Os dentes naturais emitem fluorescência azul quando está sob a ação de uma luz UV, o que torna os dentes mais brancos durante a luz do dia (Lee et al.²⁹, Song et al.⁵⁰). Resinas compostas que não apresentam fluorescência vão apresentar sob a ação de uma luz UV, aspecto mais escuro em relação à estrutura dental. Os componentes básicos das resinas compostas não apresentam fluorescência, e esta propriedade é encontrada por meio da adição de elementos luminescentes como térbio, itérbio e cério, com a finalidade de reproduzir de forma satisfatória a fluorescência das resinas como na dentição natural (Ecker et al.¹⁶, Sant'Anna Aguiar Dos Reis et al.⁴⁷)

Dominar a técnica restauradora, com todos os cuidados necessários durante a sua execução, além de conhecer as propriedades da resina composta, torna-se importante para um bom desempenho do material. Portanto, a combinação de propriedades ópticas como fluorescência, opalescência e cor juntamente com as propriedades de resistência são essenciais para se conseguir o sucesso clínico de uma restauração (Buchalla et al.⁷). Assim esta pesquisa se propôs avaliar diversas propriedades das resinas compostas como fluorescência, estabilidade de cor, grau de conversão e sorpção.



Proposição

2 PROPOSIÇÃO

2.1 Geral

Avaliar uma resina composta nanoparticulada experimental desenvolvida pelo Grupo de Crescimento de Cristais do Instituto de Física de São Carlos-USP e resinas compostas comerciais por meio de fluorescência, estabilidade de cor, grau de conversão e sorção de água.

2.2 Específicas

Esse estudo foi dividido em três capítulos compostos por artigos científicos de acordo com os objetivos propostos:

- Avaliar a fluorescência por meio de imagens conjugadas ao processamento digital e estabilidade de cor após 24 horas de imersão em saliva artificial e envelhecimento acelerado em câmara ultravioleta (UV).**
- Avaliar o grau de conversão (GC%) por meio de espectroscopia por FTIR**
- Avaliar sorção de água por meio de imersão em saliva artificial nos períodos de 1, 3, 14, 21, 30 e 60 dias.**



Capítulos

3 Capítulos

3.1 Capítulo 1

- **How composition of commercial and experimental composite resins influence fluorescence and color stability?**
- **A ser enviado para publicação no periódico Operative Dentistry.**

3.2 Capítulo 2

- **Composition influence on degree of conversion of commercial and experimental composite resins.**
- **A ser enviado para publicação no periódico Journal of Thermal Analysis and Calorimetry.**

3.3 Capítulo 3

- **Water sorption of nanofilled experimental and commercial composite resins after immersion in artificial saliva.**
- **A ser enviado para publicação no periódico Journal of Contemporary Dental Practice.**



Capítulo 1

3.1 Capítulo 1

HOW COMPOSITION OF COMMERCIAL AND EXPERIMENTAL COMPOSITE RESINS INFLUENCE FLUORESCENCE AND COLOR STABILITY?

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Clinical Relevance

Fluorescence and color stability are some of the optical properties of composite resins that are of great interest today. The fluorescence intensity of restorative materials should be as close as possible to that of human enamel and dentin to ensure an acceptable reproduction of these qualities in esthetic restorations. The color of restorative materials should not change during their lifetime in the oral environment. The color change is one of the reasons for replacements of the restorations.

SUMMARY

The purpose of this current study was to evaluate the fluorescence of different composite resins compared to the dental structure by fusing digital images while also evaluating the color stability after artificial aging. Eight specimens (n=48) were prepared for each of the following composite resins: Filtek™ Z250, Filtek™ Z350, Filtek™ Z350 XT (3M ESPE), Grandio® (Voco), Evolu-X® (Dentsply) and an experimental resin with zirconia nanoparticles. Five anterior teeth (n=5) were used for fluorescence analysis. The composite resin specimens were made in a metallic mold with a central orifice (10x1 mm). A Celalux® blue LED (Voco) was used with a power density of 776 mW/cm² and for 40 s. A CCD camera (LG) coupled to an objective lens with a system of LED lamp was used to capture images for the fluorescence measurements. Each specimen was imaged 16 times and mean values were obtained, which were then converted into gray intensity scale. The specimens were subjected to artificial aging to evaluate color stability, initially through immersion in artificial saliva for 24 hours, and then in an ultra-violet (UV) chamber. The color measurements were taken with a

Minolta colorimeter (CM 2600d, Japan), which enabled the evaluation of the overall color change (ΔE) after artificial aging. Data were submitted to Analysis of Variance (ANOVA) followed by Tukey's test ($\alpha = 5\%$). Filtek™ Z250 and the experimental composite resins showed the lowest fluorescence mean values. The fluorescence mean value for Filtek™ Z350 (0.100; ± 0.006) was higher than for Filtek™ Z250 (0.084; ± 0.006); however, this value was similar to the experimental composite resin (0.084; ± 0.006). The other composite resins showed the following fluorescence mean values: Filtek™ Z350 XT (0.116; ± 0.007) < Tooth (0.162; ± 0.017) < Grandio® (0.210; ± 0.010) < Evolu-X® (0.248; ± 0.009). For color stability, there was no significant difference in color changes (ΔE) after 24 h of immersion in saliva. There was significant color changes after accelerated aging in the UV chamber, which can be expressed as follows: Filtek™ Z250 (8.81; ± 0.63) = Evolu-X® (9.66; ± 0.70) \leq Filtek™ Z350 (10.08; ± 0.70) < Grandio® (11.78; ± 0.70) < Filtek™ Z350XT (15.93; ± 0.99) < experimental (21.64; ± 1.07). The different composite resins did not show fluorescence similar to dental structure. Regarding color changes, exposure to UV light for 24 h provided changes in CIE color space coordinates for all of the composite resins, mainly for the experimental composite. UV light showed a higher effect on color stability than artificial saliva.

Keywords: composite resins; nanocomposite resins; fluorescence; color

INTRODUCTION

The growing demand for increasingly aesthetic dental restorations, coupled with good mechanical properties, has resulted in the need for composite resins with improved optical properties. This is because restorations should reproduce not

only the color of the dental structure being restored but also its fluorescence and opalescence.^{1,2}

Today, aggregate composite resins have been designed using nanotechnology in an attempt to combine the properties of resistance and polishing, which are both important in successful restorations.^{3,4} Restorative materials composed of combinations of nanoparticles and larger particles are considered nanohybrids, whereas those with inorganic portions that are solely composed of particles of nanometer-sized dimensions are classified as nanofilled materials.^{5,6} These nanocomposite resins represent a balance between aesthetic and mechanical properties, allowing their use in anterior and posterior restorations. The advantages of these resins include better mechanical and optical properties, smoother surfaces, greater color stability, and reduced wear.^{3,5,6} Stefanski & Dijken (2012) found that nanofilled composite resin showed very good surface characteristics and color matching.⁷

The inorganic particles of composite resins account for approximately 70% of the resin weight. These particles include fillers that are responsible for the resistance of the material and have a direct impact on the surface smoothness of the composite resin.⁸ The organic matrix comprises a mixture of methacrylate coupled with polymerization inhibitors, initiators, and organic dyes. Organic fluorophores can be added to this matrix to provide fluorescence.^{9,10} Unfortunately, composite resin manufacturers are reluctant to reveal the compounds responsible for the fluorescence of their materials.¹¹

Dental structures are naturally fluorescent and emit a strong blue fluorescence under UV light, which makes teeth whiter and brighter in daylight.¹⁰ Fluorescence is the absorption of UV light and concurrent emission of visible light

in the bluish spectrum in response to excitation of molecules through the absorption of electromagnetic radiation.^{1,11-14} As a result, teeth exposed to UV light emit light that is predominantly white with a light blue hue.¹⁵ Thus, dental structures are capable of absorbing light energy at wavelengths below those of visible light and changing the wavelength to within the visible range, resulting in the emission of a blue-white light.¹⁶

Ideal restorative materials should have similar properties of light reflection, scattering, and fluorescence as those of natural teeth. If these properties are absent, the esthetic qualities of the restorations suffer under UV illumination.¹⁰ Fluorescence in a composite resin tends to give a bright iridescence effect, and can be used to brighten dark teeth without negatively affecting the translucency. Furthermore, fluorescence adds to the vitality of a restoration and increases the metameric effect between the teeth and restoration.¹⁷

However, some composite resins have low fluorescence, which causes them to appear darker than the actual dental structure under UV light.¹⁸ Fortunately, many manufacturers are starting to identify the importance of fluorescence and are incorporating additives into their materials that help them fluoresce.¹⁹

In addition, composite resins are continually affected by physical and chemical agents that can change their optical properties after exposure in the oral environment.²⁰ Unsatisfactory color is one of the main reasons for the replacement of composite resin restorations. It is possible that unsatisfactory color can occur due to extrinsic factors related to the absorption of dyes and intrinsic factors in response to changes in the resin matrix and matrix/filler interface.²¹ The aging of composite under several physicochemical conditions, including visible light, UV irradiation, and changes in temperature and humidity, may lead to this

phenomenon.²² Studies have investigated the surface and color changes of composite resins after accelerated aging, an artificial method where the material is submitted to extreme conditions using UV light and changes in temperature and water.²³⁻²⁵

Colorimeters and spectrophotometers are the instruments most commonly used to objectively measure color changes.³ These instruments determine the color by measuring the quantity and spectral composition of light absorbed, transmitted, or reflected in an object³. These devices express their results using CIE L * a * b *, and the colors are determined based on the mixture of red, blue, and green.²⁶

In this current study, commercially available composite resins were compared to an experimental nanofilled composite resin relative to fluorescence and color stability. Thus, this study was conducted to evaluate the fluorescence of different composite resins in comparison to dental structures based on images subjected to digital processing and color stability after artificial aging. The null hypotheses tested were as follows. 1) There would be no differences in fluorescence between the composite resins and the dental structure. 2) There would be no differences in fluorescence between the experimental composite resin and the commercial composite resins. 3) There would be no difference in color stability for all of the resins with regards to artificial aging.

MATERIALS AND METHODS

Commercial and experimental composite resins

The following commercially available composite resins were used in the present study: Filtek™ Z250, Filtek™ Z350, Filtek™ Z350 XT (3M Espe, St Paul, MN, USA), Grandio® (Voco, Cuxhaven, Germany) and Evolu-X® (Dentsply,

Petrópolis, RJ, Brazil) at shade enamel A₂, and a nanofilled experimental composite resin. Table 1 shows the composition of the commercial composite resins (Insert Table 1).

Experimental composite resin

The experimental composite resin is composed of an inorganic form consisting of crystalline nanoparticles of zircônia, Zr₂O₂, an organic form whose matrix resin is composed of Bis-GMA (2,2-bis [4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl] propano) and TEGDMA (triethyleneglycol dimethacrylate), in the proportion of 70/30% respectively with camphoroquinon in addition to DMAEMA as photoinitiating agent (6×10^{-6} mol/g).

Light-curing unit (LCU)

One blue LED LCU, Celalux[®] (Voco, Cuxhaven, Germany), was used with a power density of 776 mW/cm², 390 mW of power and a light tip with a diameter of 8 mm. The power was measured using a powermeter (Fieldsmaster, Coherent Commercial Products Division, model number FM, set n° WX65, part number 33-0506, USA) and the power density was calculated using the formula:

$$I = P/A$$

Where P = power mW (milliwatts) and A= area of the light tip in cm² (centimeter square).

Specimen preparation

Eight specimens were prepared for each composite resin Group (n=48): Filtek[™] Z250 (G1), Filtek[™] Z350 (G2), Filtek[™] Z350 XT (G3), Grandio[®] (G4),

Evolu-X[®] (G5) and the experimental composite resin (G6). A metallic mold, with an internal opening (10 mm diameter and 1 mm thickness), was used. A mylar strip was placed on the glass slide and then the metallic mold was placed on the mylar strip. The composite resins were inserted using a Thompson spatula (Miltex Inc, York, PA, USA) in bulk and then another mylar strip placed on the top surface. A 1 mm glass slide and a 1 kg weight were placed on top to compact and standardize the thickness of the specimens. The weight had a central orifice where the tip of the LCU was adapted and light activated the specimens for 40 s.

The inorganic particles and organic matrix of experimental composite resins are separated, and was held the inorganic (30 mg) and organic portion (100 mg) weighing in analytical balance (model BG Gehaka Ltda - 440) and after mixing the specimens were made in the same way as other composite resins.

After polymerization, the specimens were properly identified and stored in a dry mean at 37 °C (\pm 1°C) until the beginning of the fluorescence analysis. For color stability, the analysis was done immediately after the specimen preparation.

Fluorescence Analysis

Five recently extracted and caries free human canines were selected. The teeth were obtained from the Human Tooth Bank of Araraquara School of Dentistry, Univ. Estadual Paulista UNESP, after approval by the local Human Research Ethics Committee (Protocol number 38/2010). After extraction, the teeth were cleaned, washed and subjected to prophylaxis with pumice paste and water using a slow-speed handpiece. The teeth were analyzed under a stereoscopic lens to check for possible defects and cracks. The selected teeth were stored in distilled

water at room temperature, with the solution being changed every 7 days, until the beginning of the fluorescence measurements.

The teeth were individually analyzed for fluorescence to compare with the composite resins under ultra-violet LED illumination (UV).

In order to obtain the images and fluorescence measurements, a computer with Canware 2.2 software was used. The data were initially obtained by a CCD (LG) camera coupled to an objective lens. The dental structure and composite resin specimens were placed at the center of a black background. The system of illumination used for the experiment was one LED lamp with a centered emission peak at 405 nm (nanometers) and 10 mW (milliwatts) of power.

Figure 1 shows a schematic representation of the image capturing system with its dimensions and angles. The filter-camera system was located at a height of 10.5 cm from the specimen, the energy source was 3 cm in height and 1.5 cm in a horizontal direction from the specimen, forming an angle of 60° from the horizontal plane. The angle of the energy source was used to minimize spreading and to make irradiation as orthogonal as possible. The emitted wavelengths less than 455 nm were physically barred using a filter. This filter was used to avoid some components of the camera becoming fluorescent and compromising data capture without covering up the information, since wavelengths less than 455 nm are not perceptible to the human eye.²⁷

(Insert Figure 1)

The experimental method consisted of obtaining 16 images of each specimen (total images of 848) positioned on a black background. The number of images was used to reduce the errors and numerical fluctuations, and the black background was used because it is considered ideal for reproducing images with low

interference using the capturing system.²⁸ These 16 images were joined together to form a temporal mean. This mean value was converted to the grey color intensity scale. This conversion enabled the measurement of the fluorescence intensity pixel by pixel. The best interface line was chosen among the composite resins and the fluorescence intensities were plotted by positioning the pixels along the absciss axis.

Color Stability Analysis

The color measurements were carried out using a colorimeter (Minolta CM 2600d, Osaka, Japan) with a wavelength ranging from 400 to 700 nm and equipped with a standard light source, type D65 (daylight). This device emits light intensity in a spectral form in order to position the light at a 10° angle in relation to the surface of the specimens. The values obtained were recorded in the display of the equipment and transferred to a microcomputer through a specific software, which recorded the color values according to CIE - $L^* a^* b^*$, as recommended by the CIE (Commission Internationale de l'Eclairage).²⁶ This system determines three parameters: L^* (lightness), which ranges from zero (black) to one hundred (white). The a^* and b^* values are chromaticity measurements, where a^* is related to the red-green axis, ie, when the coordinate a^* is negative ($-a^*$), the color changes to green and when this coordinate is positive ($+a^*$), the color tends to toward red. In contrast, the b^* is related to the blue-yellow axis, in other words, it indicates the direction to blue ($-b^*$) and yellow ($+b^*$).²⁶

Three color measurements were taken for each specimen to determine the color stability: 1- Initial (baseline) measurement (R1 - immediately after preparation of the specimen), 2- Intermediate measurement (R2- 24 hours after

storage in artificial saliva), 3- Final measurement (R3-performed after subsequent artificial aging).

After the first color measurement, the specimens were kept for 24 hours in artificial saliva at 37 °C (± 1 °C). After this period, the specimens were then removed, dried and subjected to the intermediate color measurement. The specimens were then subjected to the artificial aging process for an additional 24 hours. This consisted of exposing the specimens to ultraviolet radiation in a Transilluminator UV chamber (UVP, Upland, CA, USA) with a power density of 3.94 mW/cm² and an irradiation dose of 340.16 J/cm².

The difference between the color values of the initial and intermediate measurements (ΔE_{R1-R2}) represented the first reading of color stability, illustrating the clinical behavior of a newly installed restoration in the oral cavity. The difference between the initial and the final measurement (ΔE_{R1-R3}) represented the second reading of color stability, illustrating the color changes of the composite resins when subjected to clinical conditions.

The final color stability of each specimen was given by the formula:

$$\Delta E = [(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2]^{1/2} \quad (1)$$

The formula was applied twice, one for the color difference between R1 and R2 and another for the color difference between R1 and R3, as follows:

$$\Delta E_{R1-R2} = [(L_{R1} - L_{R2})^2 + (a_{R1} - a_{R2})^2 + (b_{R1} - b_{R2})^2]^{1/2} \quad (2) \quad \text{and}$$

$$\Delta E_{R1-R3} = [(L_{R1} - L_{R3})^2 + (a_{R1} - a_{R3})^2 + (b_{R1} - b_{R3})^2]^{1/2} \quad (3)$$

According to the individual ability of the human eye to appreciate differences in colors, three different intervals were used to distinguish color change values: $\Delta E < 1$ imperceptible by the human eye; $1.0 < \Delta E < 3.3$ - considered

observable only for a skilled person, still considered clinically acceptable and, $\Delta E > 3.3$ - easily observed, these color change values are not clinically acceptable.²⁹

Statistical analysis

The Analysis of Variance (ANOVA), complemented by Tukey test, was applied in the fluorescence evaluation and Analysis of Variance (ANOVA) of repeated measurements was applied for color stability. The variance homogeneity conditions, as well as the residual normality of the analysis of variance, were proved respectively by Levene's and Shapiro-Wilk tests. All statistical analyses were performed at a 5% significance level.

RESULTS

Fluorescence

Table 2 shows the fluorescence mean values and standard deviations (sd) for the different composite resins and the teeth. The Analysis of Variance showed a significant difference between the fluorescence mean values ($p < 0.001$). For this reason, Tukey multiple comparison test was performed to identify the different fluorescence mean values.

(Insert Table 2)

Filtek™ Z250 and the experimental composite resin showed the lowest fluorescence mean values. Filtek™ Z350 (0.100; ± 0.006) presented a fluorescence mean value that was higher than Filtek™ Z250 (0.084; ± 0.006); however, the fluorescence of Filtek™ Z350 was similar to the experimental composite resin (0.087; ± 0.008). The other composite resins showed the following mean values of

fluorescence: Filtek™ Z350 XT (0.116; ±0.007) < Tooth (0.162; ±0.017) < Grandio® (0.210; ±0.010) < Evolu-X® (0.248; ±0.009).

The fluorescence mean values are shown in Figure 2 with 95% confidence intervals for the mean population. These intervals enable an estimation of the accuracy of the mean values obtained.

(Insert Figure 2)

Color stability

The mean values and standard deviations of the L*, a* and b* color components obtained for the composite resins used at the beginning of the experiment are shown in Table 3. Table 4 shows the mean and standard deviations of ΔE and the color change components: ΔL*, Δa* and Δb*, after 24 hours of storage in artificial saliva and aging in the UV chamber in relation to the initial values. The Analysis of Variance (ANOVA) of ΔE showed a statistical significance among material and time, as well as a statistical significance for the interaction between them (p<0.001 for all effects).

(Insert Table 3 and 4)

Table 4 shows the color changes for the different composite resins stored for 24 hours in artificial saliva. There was no significant difference among the materials, leaving the average ΔE within the range of 1-2 units, which is considered clinically acceptable. After UV aging, the color changes were significant, as follows: Filtek™ Z250 (8.81; ±0.63) = Evolu-X® (9.66; ±0.70) ≤ Filtek™ Z350 (10.08; ±0.70) < Grandio® (11.78; ±0.70) < Filtek™ Z350XT (15.93; ±0.99) < experimental (21.64; ±1.07).

The mean change of the L^* , a^* and b^* color components enables a clear interpretation of the color change (ΔE). It can be noted that the ΔE^* and Δb^* mean values were very close to each other, whether after 24 hours in saliva or after aging in the UV chamber. This essentially shows that the variation in b^* determined the overall change in ΔE . There may have been an influence of both ΔL and Δa on the color change of Filtek Z350TM XT ($\Delta L = -5.52$; $\Delta a = 3.04$) and the experimental composite resins ($\Delta L = -4.59$) only.

A graphical illustration of the sample mean values of ΔE can be seen in Figure 3, with 95% confidence intervals for the mean population. These intervals indicate the precision of the mean values of ΔE .

(Insert Figure 3)

DISCUSSION

Composite resins have largely been able to meet the requirement of producing restorations that have optical properties similar to natural teeth.³⁰ Along with improvements in restorative techniques, advances in light curing sources and in the mechanical and adhesive properties of the resins, the changes to aesthetic properties, such as fluorescence, opalescence and color, need to be highlighted.

The fluorescence in composite resins and dental structures occurs through absorbed energy at certain wavelengths, which is reemitted as light with longer wavelengths. When these fluorescent materials are excited under UV light, they emit blue fluorescence, thus making them whiter and brighter in black light.^{1,12,31}

In this current study, a digital camera was used to simulate the situation of composite resin restorations that are exposed to artificial illumination with black light (UV) bulbs to quantify the fluorescence of composite resins and teeth. Additionally, the digital camera also enabled the capturing of digital data to quantify the level of light detected in each region, pixel by pixel, through a purely optical method.

In this present study, Evolu-X[®] showed the highest fluorescence intensity, followed by Grandio[®], both of which were greater than dental structure. Some authors^{10,30} have said that these composite resins are useful in restorative cases where the aim is to mask a darker dentin or provide light in small thicknesses, and therefore have clinical merit.

Both the experimental composite resin (0.087; \pm 0.008) and Filtek[™] Z250 (0.084; \pm 0.006) showed low fluorescence intensities, with no significant differences found between them. Filtek[™] Z350 (0.100; \pm 0.006) and Filtek[™] 350 XT (0.116; \pm 0.007) presented intermediate values of fluorescence. A study by Lee & You¹ demonstrated that Filtek[™] Z350 showed low fluorescence, with a fluorescence value below the wavelength of 440-450 nm. Although Filtek[™] Z350 XT presents higher fluorescence than Filtek[™] Z350 resin in the current study, it was still found to be below that for the fluorescence of dental structure.

None of the composite resins presented statistically significant fluorescence mean values when compared to dental structure. The fluorescence of dental structure occurs by the absorption of light in the ultraviolet range (350-365 nm) and the emission of light in the visible range (400 nm).³² Radiation close to this wavelength is found in natural sunlight and from the light of some camera flashes, black light lamps and UV lamps.³³

In this current study, only composite resins with enamel colors were used, since the last layer of composite is crucial in the restoration of fluorescence. Additionally, intact teeth were used to simulate the final clinical result with more precision. The components that provide fluorescence in composite resins remain unknown because the manufacturers do not provide information about their specific luminophorous agents. The Europium elements of terbium, ytterbium and cerium are the ones commonly used by manufacturers to give fluorescence to composite resins.^{18,33}

Another property widely studied is the color of the composite resin, which is undoubtedly one of their main advantages; however, it is hoped that composite resin presents color stability and retains its original color over time. In order to analyze the color change, an accelerated aging methodology³⁴ was used, which excludes extrinsic staining due to the lack of available pigmentation, but promotes intrinsic staining, which demonstrates the oxidative nature of the color change.

In this current study, no significant difference was found among the materials when the color change was analyzed 24 hours after storage in artificial saliva. However, a color change was observed after storage in a UV chamber for all composite resins. According to other studies,^{23,35-38} ΔE less than or equal to 3.3 is considered a clinically acceptable for the color change of composite resins. After storage in artificial saliva for 24 hours, all composite resins showed ΔE values below 3.3 and above 1.0. Domingos et al.³⁹ found the same result, with slightly noticeable color changes when the composite resins were immersed in artificial saliva.

Initially, the mean values and standard deviation of the color changes of the components L^* , a^* and b^* were calculated; however, the experimental composite

resin does not present a specific color as do the commercial resins, which were all shade A₂. For the experimental composite resin, the hue a* presented a negative mean value which indicates a tendency to green, the hue b*, on the other hand, tended to yellow and was found to be close to zero when compared to the other composite resins. This difference in b* had a result of presenting a lighter color in the immediate assessment of the experimental resin; however, this did not affect the final result, as the evaluation was based on how far the color changed after 24 hours of storage in artificial saliva and in a UV aging chamber when compared to the immediate color.

It can be observed that Δb^* , after 24 hours in artificial saliva or UV accelerated aging, showed mean values closest to ΔE for all composite resins, indicating that this value influenced the final color change.

After UV accelerated aging, all of the composite resins presented ΔE mean values far above 3.3, which indicates a visually and clinically remarkable color change. In this current case, the change of b* values were higher after UV exposure than after 24 hours in artificial saliva, which shows the influence of Δb^* in the final color decision, with a tendency to yellow. For Filtek™ Z350 XT resin, the Δa^* value showed the greatest change (three units toward the red). For the experimental composite resin, the ΔL^* value was close to -5, which indicates the greatest darkening, although all of the composite resins presented a decrease in brightness. Therefore, for these resins, the Δb^* was not only determinant of the final color, but also ΔL^* and Δa^* , where Filtek™ Z350 XT and the experimental composite resin showed the highest ΔE values.

Many authors^{8,39-41} have pointed out that the yellowing of the composite resins may be influenced by camphoroquinone, which is the photoinitiator used to

start the light-curing process and is present in most composite resins. When the irradiation is not enough, a small amount of camphoroquinone may remain inactive, and may lead to yellowing of the composite resin, changing the final color. This can be one of the reasons that led to the significant color change in this present study, since there was a wide color change of b^* after accelerated aging; however, this cannot be precisely verified since a single curing light source and a single type of photoinitiator were used. Vichi et al.²⁹ (2004) attributed the color change of composite resins to the size and distribution of the filler particles and the composition of the organic matrix. Fontes et al.³⁶ (2004) reported that composite resins with a lower amount of inorganic fillers presented more color change due to the greater resin matrix volume, which allows for greater water sorption.

FiltekTM Z350 XT and the experimental nanofilled composite resin showed low color stability among all of the composite resins, which is in agreement with other authors,^{3,34,42} who claimed that the size of the inorganic particles exerted a great influence on the maintenance of the color after accelerated aging. The explanation may be related to the greater water sorption capacity of the matrix/filler interface, a typical characteristic of nanoresins, especially in those that present nanoclusters of silica/zirconia. These composite resins have a low resistance to color change when compared to the microhybrid resins, a fact that was observed in this present study.

The organic matrix of the composite resins also exerts an influence on color stability.^{29,36,42-44} FiltekTM Z250, a microhybrid containing an organic composition of Bis-GMA, UDMA and Bis-EMA, was used in this present study. TEGDMA is present in the composition of the other evaluated composite resins, which is a hydrophilic monomer and may be responsible for increased staining and water

absorption, according to Ertas et al.⁴² (2006). Although Evolu-X[®] contains the TEGDMA monomer, no statistical difference was found when comparing it to Filtek[™] Z250 after UV accelerated aging, with the explanation potentially due to the effectiveness of the matrix/filler silanization.⁴⁵

A resin with higher or lower fluorescence was found to have no effect on color stability; therefore, color stability is due to the combination of both properties and will determine the best optical features in the restorative materials. This study is only a preliminary evaluation, it is necessary to evaluate new formulations and perform other studies with the experimental composite resin.

CONCLUSIONS

The composite resins evaluated in this study did not show fluorescence similar to dental structure. The experimental composite resin showed fluorescence equivalent to Filtek[™] Z250 and Filtek[™] Z350. The composite resins showed color changes above the clinically acceptable limit after accelerated aging by UV, where the experimental nanofilled composite resin showed the greatest change.

ACKNOWLEDGMENTS

The authors would like to thank CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brazil) for the support in this study. Also the authors would like to express their gratitude to 3M Espe Brazil and Voco Brazil for providing the composite resins and the light-curing unit (LCU).

References

1. Yu B & Lee YK (2008) Differences in color, translucency and fluorescence between flowable and universal resin composites *J Dent* 36 (10) 840-846.
2. Yu B, Ahn JS, Lim JL & Lee YK (2009) Influence of TiO₂ nanoparticles on the optical properties of resin composites *Dent Mater* 25 (9) 1142-1147.
3. Schmitt VL, Puppim-Rontani RM, Naufel FS, Nahsan FP, Sinhoreti MAC & Baseggio W (2011) Effect of the polishing procedures on color stability and surface roughness of composite resins *ISRN Dent* 617672.
4. da Silva EM, Almeida GS, Poskus LT & Guimarães JG (2008). Relationship between the degree of conversion, solubility and salivary sorption of a hybrid and a nanofilled resin composite *J Appl Oral Sci* 16(2) 161-166.
5. Mitra SB, Wu D & Holmes BN (2003) An application of nanotechnology in advanced dental materials *J Am Dent Assoc* 134 (10) 1382-1390.
6. Ward DH (2005) Esthetic restoration of tooth structure using a nanofill composite system *Compend Contin Educ Dent* 26 (4) 252 254 256-7.
7. Stefanski S & van Dijken JW (2012) Clinical performance of a nanofilled resin composite with and without an intermediary layer of flowable composite: a 2-year evaluation *Clin Oral Invest* 16(1) 147–153
8. Pires-de-Souza FdeC, Garcia Lda F, Hamida HM & Casemiro LA (2007) Color stability of composites subjected to accelerated aging after curing using either a halogen or a light emitting diode source *Braz Dent J* 18(2) 119-123.
9. Rattle CN & Bush MA (2009) Fluorescence and structural degradation in composite resins as a function of temperature *J Forensic Sci* 54(2) 433-388.
10. Lee YK, Lu H & Powers JM (2005) Fluorescence of layered resin composites *J Esthet Restor Dent* 17(2) 93–101.

11. Takahashi MK, Vieira S, Rached RN, de Almeida JB, Aguiar M & de Souza EM (2008) Fluorescence intensity of resin composites and dental tissues before and after accelerated aging: a comparative study *Oper Dent* 33(2) 189-195.
12. Lim YK & Lee YK (2007) Fluorescent emission of varied shades of resin composites *Dent Mater* 23(10) 1262-1268.
13. McLaren EA (1997) Luminescent veneers *J Esthetic Dent* 9 (1) 3–12.
14. Zena R (2001) Evolution of dental ceramics *Compend Cont Educ Dent* 22 (12) 12–4.
15. Spitzer D & Bosch JJ (1976) The total luminescence of bovine and human dental enamel *Calcif Tissue Res* 20(2) 201–208.
16. Chu SJ & Ahmad I (2003). Light dynamic properties of a synthetic, low-fusing, quartz glass-ceramic material *Pract Proced Aesthet Dent* 15(1) 49-56.
17. Leinfelder KF (2000) Porcelain esthetics for the 21st century *J Am Dent Assoc* 131 47S–51S.
18. Sant'Anna Aguiar Dos Reis R, Casemiro LA, Carlino GV, Lins EC, Kurachi C, Bagnato VS, Pires-De-Souza Fde C & Panzeri H (2007) Evaluation of fluorescence of dental composites using contrast ratios to adjacent tooth structure: a pilot study *J Esthet Restor Dent* 19 (4) 199–206 discussion 207.
19. Miller M (2004) Composite resin fluorescence *J Esthet Restor Dent* 16(6) 335.
20. Soares LE, Cesar IC, Santos CG, De Cardoso AL, Liporoni PC, Munin E & Martin AA (2007) Influence of coffee on reflectance and chemistry of resin composite protected by surface sealant *Am J Dent* 20(5) 299-304.
21. Villalta P, Lu H, Okte Z, Garcia-Godoy F & Powers JM (2006) Effects of staining and bleaching on color change of dental composite resins *J Prosthet Dent* 95(2) 137-142.

22. Wilson NH, Burke FJ & Mjör IA (1997) Reasons for placement and replacement of restorations of direct restorative materials by a selected group of practitioners in the United Kingdom *Quintessence Int* 1997 28(4) 245-248.
23. Schulze KA, Marshall SJ, Gansky SA & Marshall GW (2003). Color stability and hardness in dental composites after accelerated aging *Dent Mater* 19(7) 612-619.
24. Lee YK, Lu H & Powers JM (2006) Changes in opalescence and fluorescence properties of resin composites after accelerated aging *Dent Mater* 22(7) 653-660.
25. ISO - Standards (2000) ISO 7491 Dental Materials—Determination of colour stability Geneva: *The International Organization for Standardization* 2nd edition 1-4.
26. Commission Internationale de L'Eclairage (1986) Colorimetry, Vienna: *Central Bureau of the CIE* Publication 15(2).
27. Watson AB (1993) *Digital images and human vision* MIT Press Cambridge, USA
28. Gonzalez RC & Wintz P (1987) *Digital Image Processing* Addison Wesley, USA.
29. Vichi A, Ferrari M & Davidson CL (2004) Color and opacity variations in three different resin-based composite products after water aging *Dent Mater* 20(6) 530-534.
30. Lee YK, Lu H & Powers JM (2006) Influence of fluorescent and opalescent properties of resin composites on the masking effect *J Biomed Mater Res B Appl Biomater* 76(1) 26–32.
31. Rattle CN & Bush MA (2009) Fluorescence and structural degradation in composite resins as a function of temperature *J Forensic Sci* 54(2) 433-438.
32. Vanini L (1996) Sistema composito microibrido universale: fluorescence e opalescence *Dent Cadmos* 8 36-48

33. Ecker GA, Moser JB, Wozniak WT & Brinsdsen GI (1985) Effect of repeated firing on fluorescence of porcelain-fused-to-metal porcelains *J Prosthet Dent* 54(2) 207–214.
34. Mundim FM, Garcia Lda F & Pires-de-souza Fde C (2010) Effect of staining solutions and repolishing on color stability of direct composites *J App Oral Sci* 18 (3) 249-254.
35. Abu-Bakr N, Han L, Okamoto A & Iwaku M (2000) Color stability of compomer after immersion in various media *J Esthet Dent* 12(5) 258-263.
36. Fontes ST, Fernández MR, de Moura CM & Meireles SS (2009) Color stability of a nanofill composite: effect of different immersion media *J App Oral Sci* 17(5) 388-391.
37. Catelan A, Briso AL, Sundfeld RH, Goiato MC & dos Santos PH (2011) Color stability of sealed composite resin restorative materials after ultraviolet artificial aging and immersion in staining solutions *J Prosthet Dent* 105(4) 236-241.
38. Valentini F, Oliveira SG, Guimarães GZ, Barbosa RP & Moraes RR (2011) Effect of surface sealant on the color stability of composite resin restoration *Braz Dent J* 22(5) 365-368.
39. Domingos PA, Garcia PP, Oliveira AL & Palma-Dibb RG (2011) Composite resin color stability: influence of light sources and immersion media *J Appl Oral Sci* 19(3) 204-211.
40. Janda R, Roulet JF, Latta M, Steffin G & Rüttermann S (2005) Color stability of resin-based filling materials after aging when cured with plasma or halogen light *Eur J Oral Sci* 113(3) 251-257.

41. Kolbeck C, Rosentritt M, Lang R & Handel G (2006) Discoloration of facing and restorative composites by UV-irradiation and staining food *Dent Mater* 22(1) 63-68.
42. Ertas E, Güler AU, Yücel AC, Köprülü H & Güler E (2006) Color stability of resin composites after immersed in different drinks *Dent Mater J* 25(2) 371-376.
43. Güler AU, Güler E, Yücel AC & Ertaş E (2009) Effects of polishing procedures on color stability of composite resins *J App Oral Sci* 17(2) 108-112.
44. Dietschi D, Campanile G, Holz J & Meyer JM (1994) Comparison of the color stability of ten new-generation composites: An in vitro study *Dent Mater* 10(6) 353-362.
45. Rueggeberg FA & Craig RG (1988) Correlation of parameters used to estimate monomer conversion in a light-cured composite *J Dent Res* 67(6) 932-937.

TABLE CAPTIONS

Table 1: Classification and composition of the commercial composite resins

Table 2: Mean values and standard deviations (sd) of the fluorescence. Means followed by the same letter are not significantly different at the 5% level by the Tukey test

Table 3: Mean values and standard deviations (sd) of the color components

Table 4: Mean values and standard deviations (sd) of the color changes

FIGURE CAPTIONS

Figure 1. Image capturing system.

Figure 2. Mean values (columns) of fluorescence and confidence intervals for 95% of the mean population.

Figure 3. Mean values of ΔE color change and confidence intervals for 95% of the mean population.

TABLES

Table 1

Material	Classification	Organic matrix	Filler type loading	% Load	Manufacturer
Filtek™ Z250	Microhybrid	Bis-GMA Bis-EMA UDMA	Zirconium/Silica with an average particle size of 0.6 µm.	82% weight 60% vol	3M Espe, St. Paul, MN, USA
Filtek™ Z350	Nanofilled	Bis-GMA Bis-EMA UDMA TEGDMA	Aggregates of zirconium/silica matrix with an average size of 0.6-1.4 µm with the size of a primary particle in the range of 5-20 nm and silica incorporation of 20 nm.	78.5% weight 84.5% vol	3M Espe, St. Paul, MN, USA
Filtek™ Z350 XT	Nanofilled	Bis-GMA Bis-EMA UDMA TEGDMA PEGDMA	A non-agglomerated silica of 20 nm, non-agglomerated zirconia ranging from 4 to 11 nm and a combined load aggregate of silica/zirconia.	78.5% weight 63.3% vol	3M Espe, St. Paul, MN, USA
Grandio®	Nanohybrid	Bis-GMA TEGDMA	Silicon dioxide spheres within the range of 20-50 nm and thin particles of ceramic glass.	87% weight 71.4 % vol	Voco, Cuxhaven Germany
Evolu-X®	Nanohybrid	Modified Bis-GMA TEGMA	Silanized barium aluminum borosilicate glass, silanized barium fluoroaluminum borosilicate glass nanoparticulated silica.	75-77% weight 58% vol	Dentsply, Petrópolis, RJ, Brazil

Table 2

Groups	Mean values	Standard deviations(sd)	
Filtek™ Z250	0.084	0.006	a
Filtek™ Z350	0.100	0.006	b
Filtek™ Z350 XT	0.116	0.007	c
Grandio®	0.210	0.010	e
Evolu-X®	0.248	0.009	f
Experimental	0.087	0.008	ab
Tooth	0.162	0.017	d

Table 3

Composite resins (Groups)	L*	a*	b*
	Mean (sd)	Mean (sd)	Mean (sd)
Filtek™ Z250	73.53 (1.03)	1.31 (0.34)	18.22 (0.91)
Filtek™ Z350	75.93 (1.21)	3.26 (0.13)	19.25 (0.65)
Filtek™ Z350 XT	75.33 (1.57)	1.34 (0.28)	17.12 (0.78)
Grandio®	75.55 (0.83)	2.73 (0.24)	19.25 (0.89)
Evolu-X®	74.73 (0.97)	3.44 (0.43)	17.11 (0.88)
Experimental	81.61 (1.26)	-0.13 (0.15)	8.41 (0.38)

Table 4

Composite resins	ΔL	Δa	Δb	ΔE		
	Mean (SD)	Mean (SD)	Mean (SD)	Mean(SD)		
24h	Filtek™ Z250	0.15 (0.35)	0.10 (0.07)	1.15 (0.58)	1.24 (0.50)	a
	Filtek™ Z350	0.37 (0.45)	0.08 (0.06)	0.96 (0.17)	1.07 (0.37)	a
	Filtek™ Z350 XT	0.06 (0.79)	0.07 (0.03)	0.90 (0.29)	1.17 (0.32)	a
	Grandio®	0.31 (0.25)	0.06 (0.04)	1.22 (0.41)	1.27 (0.44)	a
	Evolu-X®	0.40 (0.35)	0.30 (0.09)	0.83 (0.37)	1.03 (0.34)	a
	Experimental	0.90 (0.63)	0.53 (0.12)	1.56 (0.39)	1.96 (0.44)	a
UV	Filtek™ Z250	-0.49 (0.52)	0.62 (0.14)	8.76 (0.64)	8.81 (0.63)	b
	Filtek™ Z350	-1.07 (0.63)	0.73 (0.23)	9.98 (0.70)	10.08(0.70)	c
	Filtek™ Z350 XT	-5.52 (1.03)	3.04 (0.32)	14.61 (0.72)	15.93(0.99)	e
	Grandio®	-1.61 (0.55)	0.24 (0.14)	11.65 (0.68)	11.78(0.70)	d
	Evolu-X®	-0.02 (0.54)	-0.19 (0.14)	9.65 (0.70)	9.66 (0.70)	bc
	Experimental	-4.59 (1.02)	0.73 (0.26)	21.12 (0.93)	21.64(1.07)	f

Mean values in the column with the same letters does not have significant difference (Tukey's test $p < 0.05$)

FIGURES

Figure 1

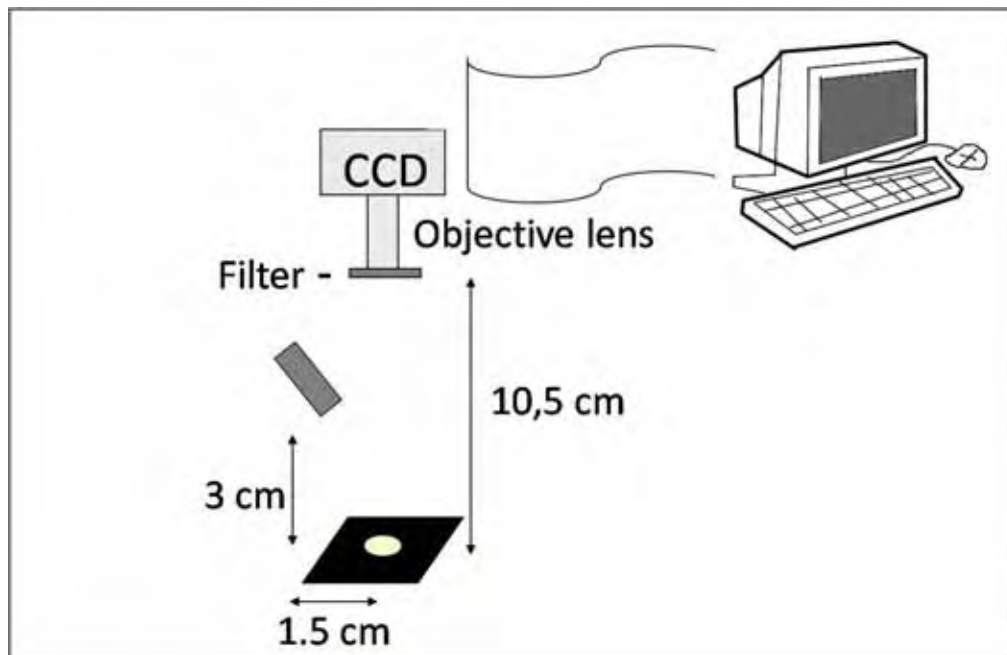


Figure 2

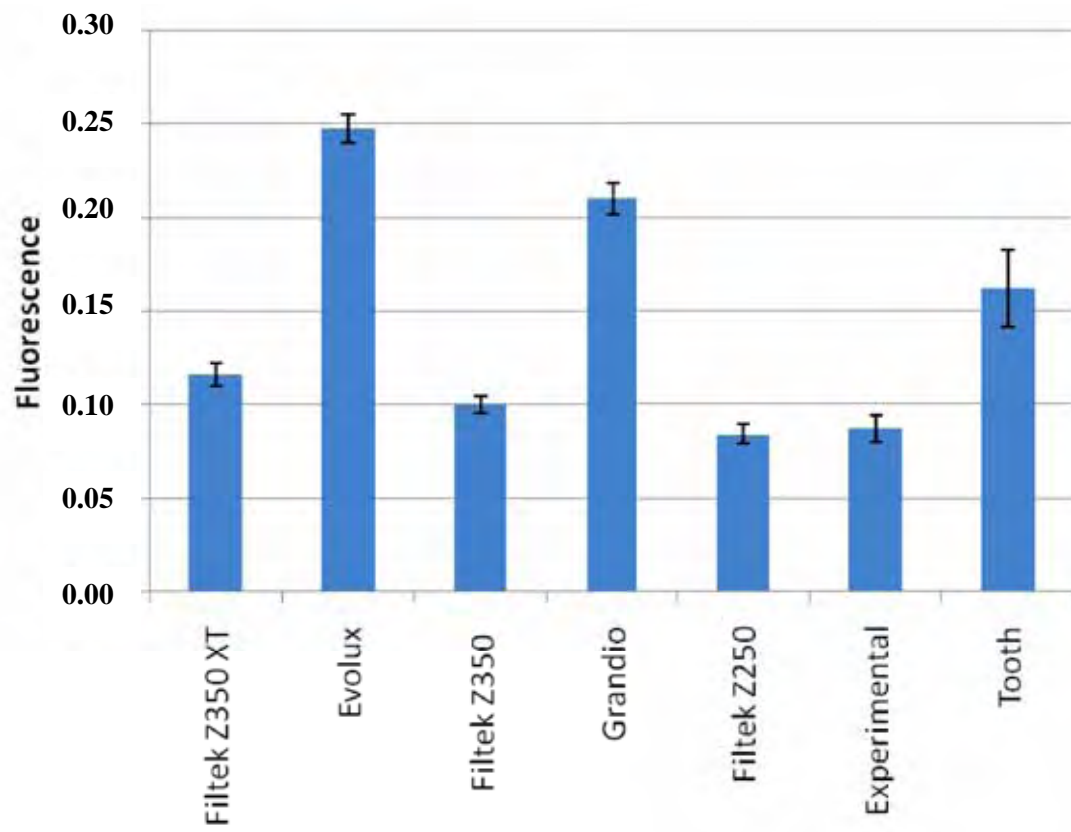
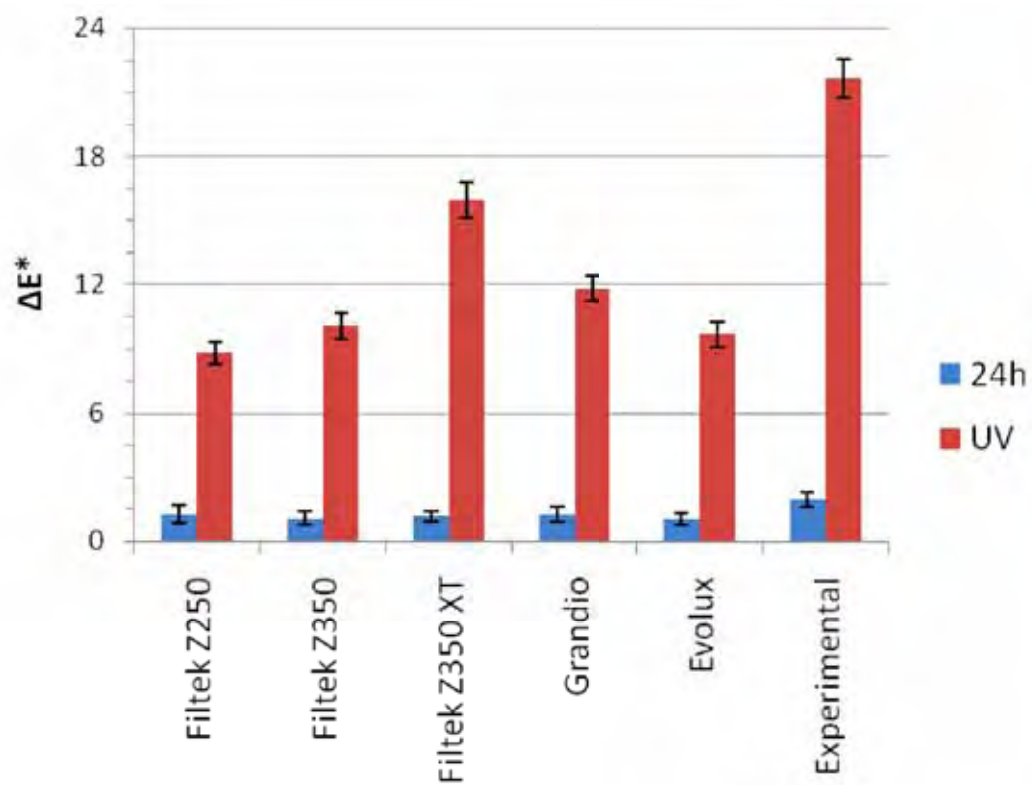


Figure 3





Capítulo 2

3.2 Capítulo 2

Composition influence on degree of conversion of commercial and experimental composite resins

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Abstract

Composite resins containing nanosized particles are currently attracting increasing interest as restorative nanomaterials for dental restorations. In this study, we evaluated the degree of conversion (DC%) of four commercial and one experimental composite resins containing nanoparticles. Five specimens ($n = 25$) for each group were made using a metallic mold (4 mm diameter \times 2 mm thickness) using the composite resins FiltekTM Z250 (3M Espe), FiltekTM Z350 (3M Espe), Grandio[®] (Voco), Evolu-X[®] (Dentsply), and an experimental composite resin containing zirconium dioxide. Photoactivation of the specimens was achieved using one Celalux[®] (Voco) LED with a power density of 776 mW/cm² for 40 s. Absorbance spectra were obtained using an FT-IR spectrophotometer (Nexus 470) equipped with a TGS detector, using diffuse reflectance (32 scans, resolution of 4 cm⁻¹) coupled with computer. The percentage of unreacted carbon-carbon double bonds (% C=C) was determined from the ratio of the absorbance intensities of the aliphatic C=C peak (1638 cm⁻¹) against the internal standard before and after curing of the specimen to that of the aromatic C-C peak (1608 cm⁻¹). The mean values and standard deviations were calculated and the Welch correction was applied, complemented by the Games-Howell multiple comparison test ($p < 0.05$). The DC% values obtained for the composite resins were: FiltekTM Z250, 63.9 % (± 4.4); FiltekTM Z350, 70.5 % (± 2.1); Grandio[®], 67.5% (± 2.4); Evolu-X[®], 76.5% (± 1.5); and experimental composite resin, 47.5% (± 6.0). The following inequality describes the mean values for the degree of conversion of the composite resins: Experimental $<$ (FiltekTM Z250 = FiltekTM Z350 = Grandio[®]) $<$ Evolu-X[®]. It is concluded that the composition of the composite resins affects their DC%.

Keywords: Composite resins, Degree of conversion, Spectroscopy Fourier Transform Infrared.

Introduction

Advancements in the field of composite resins have brought major changes in their physical properties with the addition of inorganic particles together with improvements in coupling agents (silanes) [1]. The evolution of composites, or more precisely, the size of the inorganic particles, allows for the classification of the composite resins into hybrid (0.04 to 5 μm), microhybrid (0.04 to 0.7 μm), and microfilled (0.04 to 0.4 μm) categories [2]. Recently, with the introduction of nanotechnology incorporated in composite resins, two new classifications have emerged: nanohybrid and nanofilled resins [3]. Nanohybrid resins are combinations of larger particles (0.7 μm) with nanoparticles of around one hundred nanometers. Nanofilled resins contain nanometer particles below 100 nm in size (usually between 20 to 75 nm), and these resins are also silanized [2,4,5]. Thus, this resin, with smaller and better-distributed particles, allows for a greater load to be incorporated, resulting in improved strength and polishing [2,6,7].

Monomers such as bis-GMA, TEGDMA, and UDMA are most commonly found in the resin matrix [8] these go through the process of polymerization, and are transformed into the polymer matrix, which is a large molecule made up of smaller monomer units [9]. Therefore, the extent by which the monomer is converted into the polymer, called the degree of conversion (DC%), will influence the physical and mechanical properties of the composite resins [10,11].

The greater part of commercial composite resins use bisphenylglycidyl dimethacrylate (BisGMA) as the base monomer of the resin matrix [9]. Nevertheless, this monomer has a high viscosity and as a result of its high viscosity, the use of diluent co-monomers becomes necessary to allow incorporation of the inorganic filler [12,13]. The co-monomer most commonly used is triethylene glycol

dimethacrylate (TEGDMA). On the other hand, the increased conversion granted by TEGDMA causes a clinically undesirable increase in polymerization shrinkage [14]. For this reason, monomers with low viscosity and high molecular weight, such as ethoxylated bisphenol-A dimethacrylate (BisEMA), are present in several commercial formulations, partially or totally replacing TEGDMA.

The mechanical performance of composite resins is directly related to their formulation [15,16]. The molecular backbone characteristics of the co-monomers involved will determine the hydrophilicity, mobility, and kinetic parameters, which, in turn will influence the DC [17,18].

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 [19]. Usually, the composite resins reach a DC ranging from 43 to 75%, mainly depending on the composite composition, power density of light curing units and exposure time [20].

The degree of conversion depends on factors related to curing, such as the irradiation time, light distance and wavelength, and material composition [21-23]. Inadequate polymerization leads to inferior physical properties, leaving the dental restorations susceptible to microleakage, the emergence of secondary caries, and consequently pulp irritation, as well as the possibility of unconverted monomers being released into the mouth and causing allergic reactions [24-26].

Techniques such as Fourier Transform Infrared (FTIR) spectroscopy [25,27-32], RAMAN spectroscopy [33], Electron Paramagnetic Resonance (EPR) [34], Nuclear Magnetic Resonance (NMR) [35], Differential Scanning Calorimetry

(DSC) [30,36,37] and Differential Thermal Analysis (DTA) [38] have been used to determine the DC. But, among these, FTIR is the most frequently used technique [19].

Different factors related to the composition of composite resins may affect the mechanical properties of the material, such as the type and concentration of the monomer that is used [39], or the size, type, and quantity of the filler that is present in the materials [5,40]. Therefore, nanoparticles were inserted into composites in order to enhance their mechanical properties and to promote greater esthetic value to the restorations performed with these materials [2], as well as to increase packing of fillers and thus to reduce polymerization shrinkage.

As there is a new experimental composite resin in this study, we aimed to evaluate the degree of conversion (DC%) of the commercial composite resins and experimental nanofilled composite resin using infrared spectroscopy (FTIR). It was hypothesized that the experimental nanofilled composite resin would present a degree of conversion similar to those of the commercial composite resins.

Experimental

The dental composite resins used in this study were: Filtek™ Z250 (3M Espe, Dental Products St. Paul, MN, USA); Filtek™ Z350 (3M Espe, Dental Products St. Paul, MN, USA); Grandio® (Voco, Cuxhaven, Germany); Evolu-X® (Dentsply, Petrópolis, RJ, Brazil) at color enamel A₂; and the experimental nanofilled composite resin.

Table 1 summarizes the dental composite resins and batch numbers.

Table 1: Main characteristics of commercial composite resins used

Composite resins	Classification	Polymeric matrix	Filler type loading	% Load	Batch number
Filtek™ Z250	Microhybrid	Bis-GMA, Bis-EMA UDMA	Zirconium/Silica with an average particle size of 0.6 µm.	82% weight 60% vol	8FF
Filtek™ Z350	Nanofilled	Bis-GMA, Bis-EMA UDMA, TEGDMA	Aggregates of zirconium/silica matrix with an average size of 0.6-1.4 µm with the size of a primary particle in the range of 5-20 nm and silica incorporation of 20 nm.	78,5% weight 84,5% vol	7HL
Grandio®	Nanohybrid	Bis-GMA, TEGDMA	Silicon dioxide spheres within the range of 20-50 nm and thin particles of ceramic glass.	87% weight 71.4 vol	0809115
Evolu-X®	Nanohybrid	Bis-GMA modified TEGMA	Silanized barium aluminum borosilicate glass, silanized barium fluoroaluminum borosilicate glass nanoparticulated silica.	75 a 77%weight 58% vol	131522B

The experimental composite resin is composed of an inorganic form consisting of crystalline nanoparticles of zircônia, Zr_2O_2 , an organic form whose matrix resin is composed of Bis-GMA (2,2-bis [4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl] propano) and TEGDMA (triethyleneglycol dimethacrylate), in the proportion of 70/30% respectively with camphoroquinon in addition to DMAEMA as photoinitiating agent (6×10^{-6} mol/g).

Sample preparation

For the analysis of the degree of conversion (DC%), five samples of composite resins were made using a metallic mold of 4 mm internal diameter and 2 mm thickness (ISO 4049) [41].

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 a thickness of 1 mm was positioned, and a 1-kg weight was used to pack the composite resin. Subsequently, the top surface of the sample was placed in contact with the light-curing tip.

The composite resins were photoactivated for 40 s by irradiation using one Celalux[®] (Voco, Germany) LED with a power density of 776 mW/cm², a power of 390 mW, and an active tip of 8 mm in diameter. The power output was measured using a powermeter (Fieldmaster, Coherent Commercial Products Division, model No. FM, set No. WX65, part No. 33-0506, Santa Clara, CA, USA), and the power density was determined from the equation: $I = P/A$, where P is the power (mW) and A is the area of the light tip (cm²).

The inorganic particles and organic matrix of experimental composite resins are separated, and was held the inorganic (30 mg) and organic portion (100 mg) weighing in analytical balance (model BG Gehaka Ltda - 440) and after mixing the specimens were made in the same way as other composite resins.

After polymerization, the samples were properly identified and stored in a dry mean ate 37°C (±1°C) for 24 h.

Degree of conversion (DC%)

The samples for the determination of DC% were prepared, and were analyzed 24 h after photoactivation. The composite resins were pulverized into a fine powder. The composite powder (5 mg) was thoroughly mixed with KBr (bromide potassium) power salt (100 mg). This mixture was placed into a pelleting

device and then compressed in a press with a load of 10 t for 1 min to obtain a pellet.

The number of carbon double bonds that are converted into single bonds provides the degree of conversion (DC%) of the composite resin. For the measurement of the degree of conversion, the pellet was placed into a holder attachment in the spectrophotometer (Nexus 470 FTIR, Thermo Nicolet). The Fourier-transform infrared (FTIR) spectra of both the uncured and cured samples were analyzed using the diffuse reflectance accessory. The absorbance measurements were taken under the following conditions: 32 scans, a resolution of 4 cm^{-1} , and a wavelength of $300\text{--}4000\text{ cm}^{-1}$. The percentage of unreactive carbon-carbon double bonds (% C=C) was determined from the ratio of the absorbance intensities of the aliphatic C=C peak (1638 cm^{-1}) against an internal standard before and after the curing of the specimen to the aromatic C-C peak (1608 cm^{-1}). DC% was determined by subtracting % C=C from 100%, according to the following formula:

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

Statistical analysis

The DC% data were analyzed by analysis of variance. Not being able to assume the homogeneity of variances between groups using the Levene test, in this analysis we used the Welch correction, which was complemented by the Games-Howell multiple comparison test. It is noteworthy that there was evidence of approximate normality of the waste from the Shapiro-Wilk test. In statistical tests, it was adopted a significance level of 5%.

Results

Table 2 shows the mean values and standard deviations of the degree of conversion (%) obtained in samples of Filtek™ Z250, Filtek™ Z350, Grandio®, and Evolu-X® composite resins, and the experimental composite resin. The accentuated discrepancy between the standard deviations justified the methodology adopted. The analysis of variance provided evidence of a significant difference between the mean values of the degree of conversion ($p < 0.001$). Then, the Games–Howell multiple comparisons test, which was appropriate in this case, was applied for the identification of the mean values of the degree of conversion; the results are summarized in Table 2.

Table 2 – Mean and standard deviation of degree of conversion (different letters indicate statistically significant difference at 5% by according to Games–Howell test)

Composite resins	Mean values	Standard deviations
Filtek™ Z250	63.9 ^b	4.4
Filtek™ Z350	70.5 ^b	2.1
Grandio®	67.5 ^b	2.4
Evolu-X®	76.5 ^c	1.2
Experimental	47.5 ^a	6.0

The experimental composite resin and Evolu-X® composite resin presented the lowest and highest mean values, respectively, for the degree of conversion. The other composite resins presented equivalent and intermediate mean values. The following inequality describes the degree of conversion mean values of the composite resins: Experimental < (Filtek™ Z250 = Filtek™ Z350 = Grandio®) < Evolu-X®.

A graphical representation of the sample mean values of the degree of conversion (DC%) can be seen in Figure 1, as well as the 95% confidence intervals for the mean population. These intervals indicate the precision of the mean values obtained.

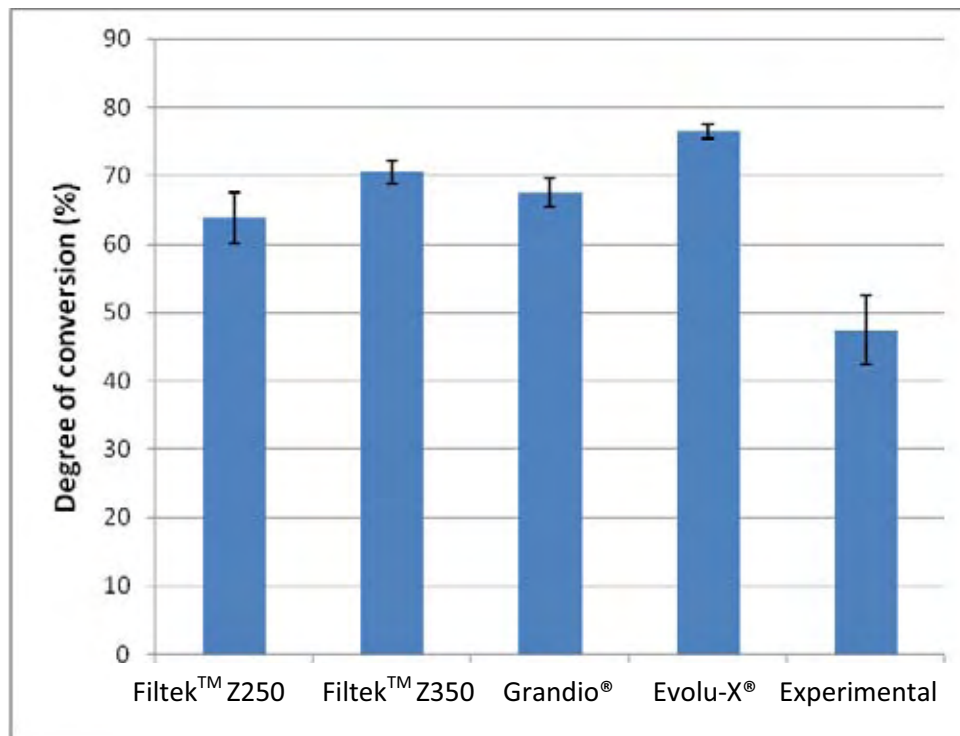


Figure 1 – Sample means (columns) of degree of conversion and 95% confidence intervals for the population means (vertical bars).

Discussion

An ideal composite resin is considered to exhibit a high degree of conversion (DC) and minimal polymerization shrinkage [14]. However, DC and polymerization shrinkage vary generally antagonistically, that means a relatively higher DC, goes along with higher volume shrinkage and vice versa [42,43].

With the evolution of composites, especially for use in posterior teeth, it is important that the materials provide adequate strength to support occlusal stress,

and have satisfactory aesthetic properties and good biological characteristics. The strength of the material may be related to the extent of polymerization, because a higher degree of crosslinking results in better mechanical properties [44]. There are several factors influencing the degree of conversion, such as the matrix resin, the concentrations of photoinitiator and amine, the shape and quantity of inorganic particles, the wavelength and intensity of the light source, the irradiation time, and the distance between the light source and the resin surface [25,26,28-30,45]. In the words, the physical and biological properties of composite resins are directly influenced by the degree of conversion attained during polymerization, thus DC is one of the important factors that affects clinical performance of composites [19].

Among several methods to determine the degree of conversion (DC) of composites, Fourier Transformation Infrared Spectroscopy (FTIR) has been proven to be a great technique and has been widely used as a reliable method as it detects the C=C stretching vibrations directly before and after curing of materials [38]. In this study, the methodology used was infrared absorption spectroscopy (FTIR), which is one of the main methods used to study the degree of conversion.

In the present study, a single curing unit was used because the objective was to verify the degree of conversion in the experimental nanofilled composite resin and in other commercial composite resins, without considering the influence of the device type, irradiation time, or power density. These variables, which have been taken into account in other studies [28-30], influence the final conversion of the material. According to Peutzfeld (1997) [9], the degree of conversion can be influenced by both the resin matrix and its filler particles.

The composite resin Filtek™ Z350, being a nanofilled composite resin, showed no statistical difference in comparison with the microhybrid composite resin Filtek™ Z250 and the nanohybrid composite resin Grandio®, which showed the highest degree of conversion, but showed a significant difference from the experimental nanofilled composite resin. Findings by other authors may disagree, Atai & Motevasselian (2009) [46] and Gaglianone et al. (2012) [47] found that the microhybrid composite resin promoted better conversion than the nanofilled composite resin. Halvorson et al. (2003) [20], da Silva et al. (2008) [3] and Ribeiro et al. (2012) [48] showed in their studies that the nanofilled composite resin exhibited the lowest degree of conversion, which does not agree with the results for Filtek™ Z350 in our study. The reason for this may be the non-agglomerated silica nanoparticles found by the authors [3], which had an average size of 20 nm, and may have caused a light-scattering effect. This dispersion effect would cause a reduction in light intensity, consequently leading to a lower conversion. However, the particle size does not seem to be the only factor, as there was a difference between Filtek™ Z350 and the experimental nanofilled composite resin. These resins differ in the composition of their organic matrices.

The composite Filtek™ Z350 contains the monomers bis-GMA and TEGDMA, the base resin matrix exhibit UDMA (urethane dimethacrylate) and bis-EMA (bisphenol A dimethacrylate polyethylene glycol diether). This type of resin has a molecular weight greater than conventional basic bis-GMA and TEGDMA, and consequently, it has fewer double bonds per unit weight, which allows the material to achieve a higher degree of conversion when exposed to light [49]. The composite Evolu-X® showed the highest degree of conversion of all the

resins evaluated, perhaps because of the presence of glass particles in its inorganic portion, unlike other resins that contain a combination of silica and zirconia.

For the resins, the average degree of conversion should be between 43% and 75% [20]; this is in agreement with the results of our study, in which the values were found to range from approximately 47.5% to 76.5%. Ideally, the resins should achieve a high conversion of the monomers into polymers, but several studies have shown that high conversion results in higher polymerization shrinkage of the composite resin [42,43]. Authors [21] also report that the minimum degree of conversion for a satisfactory restoration has not been precisely established, but a low conversion of composite resin affects the longevity of restorations, as unreacted monomers can be released, causing tissue irritation and microleakage, and leading to allergic reactions and pulp damage [21].

The degree of conversion is only one of the methods used to determine the degree of polymerization of a resin. Further studies are needed to analyze the behavior of the experimental resin by comparison with commercial resins, such as hardness tests [10,11] which are commonly used as an indirect method to verify the degree of polymerization of composite resins, and thermal analysis by scanning calorimetry [30,36-38].

Conclusions

It is concluded that the composition of a composite resin affects its DC% value. All composites showed a degree of conversion within the minimum recommended values (43 a 75%). The experimental nanofilled composite resin showed a lower degree of conversion than the commercial composite resins. More

studies are needed to evaluate the performance of this new experimental composite resin.

Acknowledgements

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 for permitting us to use the equipments used in this study. This study was funded by CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brazil) and São Paulo State University-UNESP, and the Department of Restorative Dentistry, Araraquara School of Dentistry.

References

- 1- Bowen RL. Properties of silica-reinforced polymer for dental restorations. *J Am Dent Assoc.* 1963; 66: 57- 64.
- 2- Mitra SB, Wu D, Holmes BN. An application of nanotechnology in advanced dental materials. *J Am Dent Assoc.* 2003; 134: 1382-1390.
- 3- da Silva EM, Almeida GS, Poskus LT, Guimarães JG. Relationship between the degree of conversion, solubilty and salivary sorption of a hybrid and a nanofilled resin composite: Influence of the light –activation mode. *J Appl Oral Sci.* 2008; 16: 161-166.
- 4- Ward D H. Esthetic restoration of tooth structure using a nanofill composite system. *Compend Contin Educ Dent.* 2005; 26: 252-257.
- 5- Beun S, Glorieux T, Devaux J, Vreven J, Leloup G. Characterization of nanofilled comparated to universal and microfilled composites. *Dent Mater.* 2007; 23: 51-59.

- 6- Moszner N, Klapdohr S. Nanotechnology for dental composites. *Int J Nanotechnol.* 2004; 1: 130-156.
- 7- Moszner N, Salz U. New developments of polymeric dental composites. *Prog Polym Sci.* 2001; 26: 535-576.
- 8- Puckett A, Fitchie JG, Kirk PC, Gamblin J. Direct composite restorative materials. *Dent Clin N Am.* 2007; 51: 659-675.
- 9- Peutzfeldt A. Resins composites in dentistry: the monomer systems. *Eur J Oral Sci.* 1997; 105: 97-116.
- 10- Ferracane JL, Mitchem JC, Condon JR, Todd R. Wear and marginal breakdown of composites with various degrees of cure. *J Dent Res.* 1997; 76: 1508-1516.
- 11- Ferracane JL, Moser JB, Greener EH. Ultraviolet light – induced yellowing of dental restorative resins. *J Prosthet Dent.* 1985; 54: 483-487.
- 12- Dickens S, Stansbury J, Choi K, Floyd C. Photopolymerization kinetics of methacrylate dental resins. *Macromolecules* 2003; 36: 6043–6053.
- 13- Rueggeberg FA. From vulcanite to vinyl, a history of resins in restorative dentistry. *J Prosthet Dent* 2002; 87(4): 364–379.
- 14- Dewaele M, Truffier-Boutry D, Devaux J, Leloup G. Volume contraction in photocured dental resins: the shrinkage–conversion relationship revisited. *Dent Mater* 2006; 22: 359–365.
- 15- Asmussen E, Peutzfeldt A. Influence of UEDMA BisGMA and TEGDMA on selected mechanical properties of experimental resin composites. *Dent Mater* 1998; 14: 51–56.
- 16- Gonçalves F, Kawano Y, Pfeifer C, Stansbury JW, Braga RR. Influence of Bis-GMA, TEGDMA, and Bis-EMA contents on viscosity, conversion, and flexural

- strength of experimental resins and composites. *Eur J Oral Sci* 2009;117: 442-446.
- 17- Floyd CJ, Dickens SH. Network structure of Bis-GMA- and UDMA-based resin systems. *Dent Mater* 2006; 22: 1143–1149.
- 18- Lemon MT, Jones MS, Stansbury JW. Hydrogen bonding interactions in methacrylate monomers and polymers. *J Biomed Mater Res A*. 2007; 83: 734–746.
- 19- Moraes LG, Rocha RS, Menegazzo LM, de Araújo EB, Yukimito K, Moraes JC. Infrared spectroscopy: a tool for determination of the degree of conversion in dental composites. *J Appl Oral Sci* 2008; 16: 145-149.
- 20- Halvorson RH, Erickson RL, Davidson CL. The effect of filler and silane content on conversion of resin-based composite. *Dent Mater*. 2003; 19: 327-333.
- 21- Porto IC, Soares LE, Martin AA, Cavalli V, Liporoni PC. Influence of the photoinitiator system and light photoactivation units on the degree of conversion of dental composites. *Braz Oral Res*. 2010; 24: 475-481.
- 22- Palin WM, Senyilmaz DP, Marquis PM, Shortall CA. Cure width potencial for MOD resin composite molar restorations. *Dent Mater*. 2008; 24: 1083-1094.
- 23- Halvorson RH, Erickson RL, Davidson CL. Energy dependent polymerization of resin-based composite. *Dent Mater*. 2002; 18: 463-469.
- 24- Hansel C, Leyhausen G, Mai UE, Geurtsen W. Effects of various resin composite (co) monomers and extracts on two caries-associated microorganisms in vitro. *J Dent Res*. 1998; 77: 60-6

- 25- Rastelli ANS, Jacomassi DP, Bagnato VS. Effect of Power densities and irradiation times on the degree of conversion and temperature increase of a microhibrid dental composite resin. *Laser Phys.* 2008; 18: 1074-1079.
- 26- Rasteli ANS, Jacomassi DP, Bagnato VS. Changes in the temperature of a dental light-cured composite resin by different light-curing units. *Laser Phys.* 2008; 18: 1003-1007.
- 27- DeWald JP, Ferracane JL. A comparison of four modes of evaluating depth of cure of light-activated composites. *J Dent Res.* 1987; 66: 727-730.
- 28- Costa SXS, Martins LM, Franscisoni PAS, Bagnato VSV, Saad JRC, Rastelli ANS et al. Influence of different light sources and photo-activation methods on degree of conversion and polymerization shrinkage of a nanocomposite resin. *Laser Phys.* 2009; 19:1-9.
- 29- Galvão MR, Costa SXS, Victorino KR, Ribeiro AA, Menezes FCH, Rastelli ANS et al. Influence of light guide tip used in the photo-activation on degree of conversion and hardness of one nanofilled dental composite. *Laser Phys.* 2010; 20: 2050-2055.
- 30- Costa SXS, Galvão MR, Jacomassi DP, Bernardi MIB, Hernandes AC, Rastelli ANS et al. Continous and gradual photo-activation methods: influence on degree of conversion and crosslink density of composite resin. *J Thermal Anal Calor.* 2010; 1: 1-9.
- 31- Silikas N, Eliades G, Watts DC. Light intensity effects on resin composite degree of conversion and shrinkage strain. *Dent Mater.* 2000; 16: 292-296.
- 32- Stansbury JW, Dickens SH. Determination of double bond conversion in dental resins by near infrared spectroscopy. *Dent Mater.* 2001; 17: 71-79.

- 33- Gauthier MA, Stangel I, Ellis TH, Zhu XX. A new method for quantifying the intensity of the C=C band of dimethacrylate dental monomers in their FTIR and Raman spectra. *Biomaterials*. 2005; 26: 6440-6448.
- 34- Sustercic D, Cevc P, Funduk N, Pintar MM. Determination of curing time in visible-light-cured composite resins of different thickness by electron paramagnetic resonance. *J Mater Sci Mater Med*. 1997; 8: 507-510.
- 35- Morgan DR, Kalachandra S, Shobha HK, Gunduz N, Stejskal EO. Analysis of a dimethacrylate copolymer (Bis-GMA and TEGDMA) network by DSC and ¹³C solution and solid-state NMR spectroscopy. *Biomaterials*. 2000; 21: 1897-1903.
- 36- Rojas SS, Frigo GJM, Bernardi MIB, Rastelli ANS, Hernandez AC, Bagnato VS. Thermal and structural properties of commercial dental resins light-cured with blue emitting diodes (LEDs). *J Thermal Anal Calor*. 2010; 99: 263-268.
- 37- Bernardi MIB, Rojas SS, Andreta MRB, Rastelli ANS, Hernandez AC, Bagnato VS. Thermal analysis and structural investigation of different dental composite resins. *J Thermal Anal Calor*. 2008; 94: 791–6.
- 38- Imazato S, McCabe JF, Tarumi H, Ehara A, Ebisu S. Degree of conversion of composites measured by DTA and FTIR. *Dent Mater*. 2001;17: 178-183.
- 39- Asmussen E, Peutzfeldt A. Influence of selected components on crosslink density in polymer structures. *Eur J Oral Sci*. 2001; 109: 282-285.
- 40- Lu H, Lee YK, Oguri M, Powers JM. Properties of a dental resin composite with a spherical inorganic filler. *Oper Dent*. 2006; 31: 734-740.
- 41- International Organization for Standardization. ISO 4049: Dentistry polymer – based filling, restorative and luting materials. Geneve : ISO ; 2000.

- 42- Amirouche-Korichi A, Mouzali M, Watts DC. Effects of monomer ratios and highly radiopaque fillers on degree of conversion and shrinkage-strain of dental resin composites. *Dent Mater.* 2009; 25: 1411–1418.
- 43- Stansbury JW, Trujillo-Lemon M, Lu H, Ding X, Lin Y, Ge J. Conversion-dependent shrinkage stress and strain in dental resins and composites. *Dent Mater.* 2005; 21: 56–67.
- 44- Sideridou I, Tserki V, Papanastasiou G. Effect of chemical structure on degree of conversion in light-cured dimethacrylate-based dental resins. *Biomaterials.* 2002; 23: 1919-1823.
- 45- Vandewalle KS, Ferracane JL, Hilton TJ, Erickson RL, Sakaguchi RL. Effect of energy density on properties and marginal integrity of posterior resin composite restorations. *Dent Mater.* 2004; 20: 96-106.
- 46- Atai M, Motevasselian F. Temperature rise and degree of photopolymerization conversion of nanocomposites and conventional dental composites. *Clin Oral Investig.* 2009; 13: 209-216.
- 47- Gaglianone LA, Lima AF, Araújo LS, Cavalcanti AN, Marchi GM. Influence of different shades and LED irradiance on the degree of conversion of composite resins. *Braz Oral Res.* 2012; 26: 165-169.
- 48- Ribeiro BCI, Boaventura JMC, de Brito-Gonçalves J, Rastelli ANS, Bagnato VS, Saad JRC. Degree of conversion of nanofilled and microhybrid composite resins photo-activated by different generations of LEDS. *J Appl Oral Sci* 2012; 20: 212-217.
- 49- Lindberg A, Emami N, Van Dijken JWV. A Fourier transform Raman spectroscopy analysis of the degree of conversion of a universal hybrid resin

composite cured with light-emitting diode curing units. Swed Dent J. 2005; 29: 105-112.



Capítulo 3

3.3 Capítulo 3

WATER SORPTION OF NANOFILLED EXPERIMENTAL AND COMMERCIAL COMPOSITE RESINS AFTER IMMERSION IN ARTIFICIAL SALIVA.

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Abstract

Aim: Evaluate the water sorption of one nanofilled experimental and different commercial composite resins as function of time.

Methods and Materials: The commercial composite resins used were: FiltekTM Z250 (3M Espe), FiltekTM Z350 (3M Espe), Grandio[®] (Voco) and Evolu-X[®] (Dentsply) and a nanofilled experimental composite resin. Eight samples (n=40) were prepared for each composite resin using a metallic mold (8 mm diameter and 2 mm of thickness). One blue LED Celalux[®] (Voco, Germany) with a power density of 776 mW/cm² was used during 40 s. All samples were dried at 50°C, immersed in artificial saliva at 37°C and weighed at suitable time intervals (1, 3, 14, 30 until 60 days). Data of water sorption were evaluated with two-way ANOVA and post hoc Tukey's test (p<0.01).

Results: The nanofilled experimental composite resin had a significant increase on water sorption as a result of the days of storage in saliva. Considering the storage time separately for each composite resin, the highest mean water sorption occurred in the period of 60 days, for the nanofilled resins.

Conclusion: The nanofilled experimental composite resin was the one that suffered the greatest influence on water sorption in relation to storage time in artificial saliva

Keywords: Composite resins; Dental nanocomposites; Water sorption

Introduction

Most composites present the Bis-GMA (bisphenol-A-glycidyl dimethacrylate) and/or UDMA (urethane dimethacrylate) as organic matrix besides the solvent monomers such as the TEGDMA (Triethylene glycol dimethacrylate) and EGDMA (ethyleneglycol dimethacrylate), but they can differ in terms of the inorganic particles, which may be glass barium, boron, zinc, strontium, quartz, silica, zirconium and lithium-aluminum-silicate.^{1,2} According to the size of these filler particles, the resins are classified as hybrid, microhybrid and microfilled. Recently, with the advent of nanometric technology, a new classification was created, which includes nanohybrid and nanofilled resins.³

The nanohybrid composite resins present not only a mixture of nanoparticles, but also larger particles as those found in the microhybrid resins. The nanofilled resins are presented in a dispersed form with silica particles of the order of 20 nm and the other one attached to clusters of silica-zirconium, which behave as a single structure, measuring 75 nm in average.⁴⁻⁶ The combination of these two forms provides a higher percentage of filler particles, allowing better resistance and polishing of the material.^{4,7,8}

In order to combine the organic and inorganic phases, the filler particles are subjected to a silanization process making their surface hydrophobic, preventing water penetration at the interface resin/filler.^{1,2} The water penetration at the interface leads to the sorption phenomenon, where there is an increase in the material weight, which may lead to the loss of union between the filler and matrix, degradation of the particles,⁹ the instability of color,¹⁰ lower mechanical properties and reduced longevity of the composite resin restorations.^{11,12} The water sorption is also dependent on the crosslink density of the polymer bonds through its

diffusion and entrapment in the spaces between the polymer, which shows that a deficient polymerization is more susceptible to this phenomenon.^{11,13}

Different immersion media can be used for water sorption analysis, such as distilled water, ethanol, artificial saliva. In oral environment, composite resins are exposed continuously to chemical agents found in saliva which may contribute to the chemical degradation.¹⁴ Rahin et al.¹⁵ (2012) found that the sorption for some composite resins were significantly increased after exposure in acidic solutions, and beyond the immersion media, other factors can play an important role to determine water sorption characteristics such as filler loading, filler size, filler type and polymer matrix.

Hydrophilic monomers will have a high water sorption and chemical reactions between filler particles and water can result in a mass increase of composite resins.¹⁵ Örtengren et al.⁹ showed that with increased storage time, the filler surface and/or filler-matrix bond will be affected and will occur the water sorption.

The purpose of this study was to evaluate the water sorption of one experimental nanofilled and different brands of composite resins by means of water sorption over 60 days. The tested hypothesis was that the material type and storage time have an influence on water sorption.

Materials and Methods

Commercial composite resins

The tested composite resins, compositions and their manufacture's are listed on Table 1.

(Insert Table 1)

In order to perform this study, the following brands of composite resins were used: Filtek™ Z250 (3M Espe, St. Paul, MN, USA), Filtek™ Z350 (3M Espe, St. Paul, MN, USA), Grandio® (Voco, GmbH Cuxhaven, Germany) and Evolu-X® (Dentsply, Petrópolis, RJ, Brazil) at color A₂, and one nanofilled experimental composite resin.

Experimental composite resin

The experimental composite resin is composed of an inorganic form consisting of crystalline nanoparticles of zircônia, Zr₂O₂, an organic form whose matrix resin is composed of Bis-GMA (2,2-bis [4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl] propano) and TEGDMA (triethyleneglycol dimethacrylate), in the proportion of 70/30% respectively with camphoroquinon in addition to DMAEMA as photoinitiating agent (6×10^{-6} mol/g).

Light curing unit (LCU)

One blue LED Celalux® (Voco, Cuxhaven, Germany) LCU was used with a power density of 776 mW/cm², 390 Mw of power and light tip of 8 mm diameter. The power of this device was measured using a powermeter (Fieldsmaster, Coherent Commercial Products Division, model number FM, set n° WX65, part number 33-0506, USA) and the power density was calculated using the formula:

$$I = P/A$$

Where P = power mW (milliwatts) and A = area of the light tip in cm² (centimeter square).

Specimen preparation

Eight specimens (n=40) were prepared for each composite resin Group: Filtek™ Z250 (G1), Filtek™ Z350 (G2), Grandio® (G3), Evolu-X® (G4) and experimental nanofilled composite resin (G5). A metallic mold with an internal opening (8 mm diameter and 2 mm thickness) was placed on a mylar strip on a glass slide and then, the composite resins were packed into the mold. A second mylar strip with a glass slide was placed onto the composite resin. Sufficient pressure was made using a 1 kg weight in order to standardize the thickness of the specimens. The weight has a central orifice where the LCU tip was adapted. The specimens were photo-activated during 40 s.

The inorganic particles and organic matrix of experimental composite resins are separated, and was held the inorganic (30 mg) and organic portion (100 mg) weighing in analytical balance (model BG Gehaka Ltda - 440) and after mixing the specimens were made in the same way as other composite resins.

Water sorption evaluation

After preparation, the specimens for each group were stored in oven drying at 50°C (\pm 1°C) and their masses were measured daily and individually using analytical balance with a precision 0.001 g (BG 440 Gehaka Ltda, São Paulo, SP, Brazil). This cycle was repeated until making a constant mass (initial mass - m1) for 3 consecutive days.

After determining the initial mass, the specimens were then individually placed in a sealed plastic container containing about 5 mL of artificial saliva in an oven at 37°C (\pm 1°C), which was changed once a week to avoid microbial activity. Water evaporation during the storage period was completed in order to keep the

specimens continuously immersed in 5 mL of artificial saliva. After that, the specimens were weighed after 1, 3, 14, 21, 30 and 60 days (m_2 – final mass). Before the each weight, the specimens were washed during 1 min, dried to remove excess liquid with filters paper, weighed on using analytical balance in order to determine the corresponding mass according to the periods previously established and returned to the artificial saliva bath. The dry weight (the weight of the specimens after drying in the stove to obtain a constant mass and before immersion in saliva) were subtracted from their wet weight (the weight of the specimens after their immersion in artificial saliva) to determine water gain. The average water gain of the materials at each storage interval was recorded and divided by the total volume of the specimens to calculate the water sorption ($\mu\text{g}/\text{mm}^3$) according to the formula:

$$\text{Water sorption} = \frac{m_2 - m_1}{V}$$

The data of water sorption obtained were statistically analyzed using two-way ANOVA. This analysis was complemented with multiple comparisons using the Tukey's test at 5% significance level.

Results

The mean values and standard deviations of the resins water sorption are shown in Table 2, according to the number of days of storage in saliva. The analysis of Variance indicated a significant effect of the interaction between the composite resins and the storage period ($p < 0.001$), leading to the application of the Tukey for multiple comparisons between all of the means, at the 5% significance level.

In general, there was no significant difference in water sorption for composite resins, except for the experimental composite resin. In the final period of 60 days, the mean water sorption of this resin was greater than that of the mean water sorption of the Filtek™ Z250, Grandio® and Evolu-X® composite resins, but equivalent to the increase water sorption in the Filtek™ Z350 composite resin.

On the other hand, considering the storage time for each composite resin separately, significant increases in water sorption were just observed for the experimental composite resin. It was observed that the first increase in water sorption, without a significant difference, occurred between 1 to 21 days, the second between 3 to 30 days and, finally, the third increase occurred between the periods of 21, 30 and 60 days.

Discussion

When the composite resin is exposed to humid conditions such as water and saliva, the sorption phenomenon will initially occur in which there is an increase in mass and then the solubilization of the components such as the particles and residual monomer.¹⁶⁻¹⁸ Factors like: changes in composition and hydrophilicity of the matrix resin, size and distribution of filler particles,^{3,19} effectiveness of their silanization,²¹⁻²³ besides the type of polymerization employed^{24,25} may exert an influence thereby leading to the occurrence of these phenomena. In the present study, a single light-curing unit and the same method of polymerization were used, stored in a single medium, the artificial saliva, which shows that the water sorption was influenced by the composite restorative material. Several studies have shown that the sorption is highly dependent on the material and is present at the interface between the filler particles and the resin matrix.^{21,23}

The properties of composite resins can also be influenced by the degree of the cross-linked polymer bonds. The cross-links that occur between the polymer chains lead to a decrease in the permeability of the polymer to water, since the free volume between the chains is reduced, hindering the swelling as a result of the water accumulation. Therefore, the higher the number of cross-links, the smaller the space for the expansion to occur, once the absorption is reduced due to resistance to degradation with regard to a liquid medium.^{13,18}

The composite resins absorb water and are able to expand does not mean that they always have beneficial effect as reported by some authors,²⁶ who say that the polymerization shrinkage is compensated due to the relaxation of the stress generated. The absorption is insufficient to cause a linear expansion capable of compensating the polymerization shrinkage, because you can not completely seal the gap formed at the resin/dentin interface thereby causing microfractures and compromising the mechanical properties of the material. Several studies have shown that the expansion partially offsets the polymerization shrinkage.²⁷⁻³⁰

In this present study, all the composite resins were stored in artificial saliva and kept at 37° C (\pm 1°C) to simulate the condition of oral cavity after presenting the stabilized weight. Several authors^{3,24,31,32,33} have used solution of artificial saliva to analyze the sorption of composite resins. Sideridou et al.²⁴ (2011) compared the sorption of composite resins in saliva and water, and both showed the same effect in terms of physical properties of the resins evaluated. However, it is known that the intra-oral conditions are clearly more complex than those obtained by means of water, artificial saliva or any other solution in the laboratory.

The composite resins were weighed in pre-determined periods to compare if there was an increase in water sorption with regard to the initial period, and if

there was a significant difference in the final periods and among the composites. The period was extended to 60 days for being more clinically relevant as reported by Sakaguchi³⁴ in 2005. According to studies by Martin et al.³² (2003), the period of analysis up to 7 days may indicate only 50% of the dimensional changes of the composite resins and it is impossible to verify the actual behavior of the material. It can be observed in our study that all the composite resins presented an water sorption increase in relation with the initial period is concerned, though this is not always significant. The experimental composite resin was therefore the one that showed water sorption higher than the other composite resins have following 21 days of storage in saliva, increasing further until the end of the experiment.

Grandio[®] and Evolu-X[®] composite resins present glassy particles in their composition, while the others present silica and the combination silica-zirconia, which may be responsible for a less effective silanization²⁰ for not being adequately covered by the silane, and present the possibility of greater sorption. The Bis-EMA monomer (bisphenol A polyethylene glycol dimethacrylate diether), which is being used in the current resins for creating more rigid bonds as compared to TEGDMA, absorbs less water and releases fewer unreacted monomers¹³. The Evolu-X[®] and Grandio[®] composite resins do not present the Bis-EMA in their organic form, which shows that not only the composition of the monomer may interfere, but also the quantity³⁵. The experimental resin presents a higher quantity of organic matrix in comparison to the other evaluated resins and it was the only one that had greater water absorption among the evaluated periods and at the end of 60 days. The same was found to have occurred in the studies of Sarret et al.³⁶ (1991), where the microfilled resin evaluated had a greater amount of the organic matrix and the highest water sorption.

The results showed a significant increase of water sorption as a result the days of storage in saliva, only for experimental composite resin. The greatest increase sorption occurred for nanofilled composite resins, however it is not significant for Filtek™ Z350 composite resin.

In the analysis of storage time for each composite resin separately, the highest mean water sorption occurred in the period of 60 days, for the nanofilled experimental and Filtek™ Z350 composite resins, however, the Filtek Z350 did not present significant difference in relation the other commercial composite resins. Therefore, the type of composite resin and the storage period may influence the water sorption of the composite.

Silva et al.³ (2009) reported that the nanofilled composite resins presented higher sorption than the hybrid resins, perhaps owing to the fact that the silica nanoclusters of 20 nm allow greater accumulation of water in the load-matrix interface. Santos et al.³⁷ showed that the presence of porosity and formation of filler particle aggregates increased the water uptake into composites.

The methodology used in our study has shown so simple and fast, the amount of water absorbed by the composite resin for artificial saliva immersion in due time, however, the results should not be extrapolated because various factors like type and light curing time and other immersion media can influence in water sorption of the material.

Conclusion

Under the tested conditions, the following conclusions can be drawn:

- 1- The type of composite resin and the storage period may influence the water sorption of the composite

- 2- **The nanofilled experimental composite resin presented water sorption increase in relation to the initial period;**
- 3- **For the period of 60 days, the nanofilled experimental and Filtek™ Z350 composite resins presented the highest water sorption.**

Acknowledgments

The authors would like to thank CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brazil) for the financial support. Also the authors would like to express their gratitude to 3M Espe Brazil and Voco Brazil for providing the composite resins and the light-curing unit (LCU), respectively.

References

1. **Peutzfeldt A. Resin composites in dentistry: the monomer systems. Eur J Oral Sci. 1997; 105: 97-116.**
2. **Puckett AD, Fitchie JG, Kirk PC, Gamblin J. Direct composite restorative materials. Dent Clin N Am. 2007; 51: 659-675.**
3. **da Silva EM, Almeida GS, Poskus LT, Guimarães JGA. Relationship between the degree of conversion, solubility and salivary sorption of a hybrid and a nanofilled resin composite: Influence of the light –activation mode. J Appl Oral Sci. 2008; 16: 161-166.**
4. **Mitra SB, Wu D, Holmes BN. An application of nanotechnology in advanced dental materials. J Am Dent Assoc. 2003; 134: 1382-1390.**
5. **Ward DH. Esthetic restoration of tooth structure using a nanofill composite system. Compend Contin Educ Dent. 2005; 26: 252-257.**

6. Beun S, Glorieux T, Devaux J, Vreven J, Leloup G. Characterization of nanofilled compared to universal and microfilled composites. *Dent Mater.* 2007; 23: 51-59.
7. Moszner N, Klapdohr S. Nanotechnology for dental composites. *Int J Nanotechnol.* 2004; 1: 130-156.
8. Moszner N, Salz U. New developments of polymeric dental composites. *Prog Polym Sci.* 2001; 26: 535-576.
9. Örtengren U, Andersson F, Elgh U, Terselius B, Karlsson S. Influence of Ph and storage time on the sorption and solubility behaviour of three composite resin materials. *J Dent.* 2001; 29: 35-41.
10. Ferracane JL, Berge HX, Condon JR. In vitro aging of dental composites in water. Effect of degree of conversion, filler volume, and filler/matrix coupling. *J Biomed Mater Res.* 1998; 42: 460-472.
11. Yap AU, Soh MS, Han TT, Siow KS. Influence of curing lights and modes on cross-link density of dental composites. *Oper Dent.* 2004, 29: 410-415.
12. Peutzfeldt A, Asmussen E. Resin composite properties and energy density of light cure. *J Dent Res.* 2005; 84: 659-662.
13. Sideridou I, Terski V, Papanastasiou G. Study of water sorption, solubility and modulus of elasticity of light-cured dimethacrylate-based dental resins. *Biomaterials.* 2003; 24: 655-665.
14. Santos PAD, Garcia PPNS, Oliveira ALBMD, Chinelatti MA, Palma-Dibb RG. Chemical and morphological features of dental composite resin: influence of light curing units and immersion media. *Microsc Res Tech* 2010; 73:176–81.

15. **Rahim TN, Mohamad D, Md Akil H, Ab Rahman I. Water sorption characteristics of restorative dental composites immersed in acidic drinks. Dent Mater. 2012; 28: 63-70.**
16. **Pearson GJ, Longman CM. Water sorption and solubility of resin-based materials following inadequate polymerization by a visible-light curing system. J Oral Rehabil. 1989; 16: 57-61.**
17. **Yap AU, Wee KE. Effects of cyclic temperature changes on water sorption and solubility of composite restoratives. Oper Dent. 2002; 27(2): 147-153.**
18. **Ferracane JL. Hygroscopic and hydrolytic effects in dental polymer networks. Dent Mater. 2006; 22: 211- 222.**
19. **Malacarne J, Carvalho RM, de Goes MF, Svizero N, Pashley DH, Tay FR et al. Water sorption/solubility of dental adhesive resins. Dent Mater. 2006; 22: 973-980.**
20. **Karabela MM, Sideridou ID. Synthesis and study of properties of dental resin composites with different nanosilica particles size. Dent Mater. 2001; 27: 825-835.**
21. **Mohsen NM, Craig RG. Hydrolytic stability of silanated zirconia-silica-urethane dimethacrylate composites. J Oral Rehabil. 1995; 22: 213-220.**
22. **Toledano M, Osorio R, Osorio E, Fuentes V, Prati C, Garcia-Godoy F. Sorption and solubility of resin-based restorative. Dent Mater. 2003; 31: 43-50.**
23. **Karabela MM, Sideridou ID. Effect of the structure of silane coupling agent on sorption characteristics of solvents by dental resin-nanocomposites. Dent Mater. 2008; 24: 1631-1639.**

24. Sideridou ID, Karabela MM, Vouvoudi EC. Physical properties of current dental nanohybrid and nanofill light-cured resin composites. *Dent Mater.* 2011; 27: 598-607.
25. Lopes LG, Jardim Filho Ada V, de Souza JB, Rabelo D, Franco EB, de Freitas GC. Influence of pulse-delay curing on sorption and solubility of a composite resin. *J Appl Oral Sci.* 2009; 17: 27-31.
26. Feilzer AJ, de Gee AJ, Davidson CL. Relaxation of polymerization contraction shear stress by hygroscopic expansion. *J Dent Res.* 1990; 69: 36-39.
27. Suliman AH, Boyer DB, Lakes RS. Polymerization shrinkage of composite resins: comparison with tooth deformation. *J Prosthet Dent.* 1994; 71: 7-12.
28. Carvalho RM, Pereira JC, Yoshiyama M, Pashley DH. A review of polymerization contraction: the influence of stress development versus stress relief. *Oper Dent.* 1996; 21: 17-24.
29. Armstrong SR, Keller JC, Boyer DB. The influence of water storage and C - factor on the dentin - resin composite microtensile bond strength and debond pathway utilizing a filled and unfilled adhesive resin. *Dent Mater.* 2001; 17: 268-276.
30. Rüttermann S, Krüger S, Raab WH, Janda R. Polymerization shrinkage and hygroscopic expansion of contemporary posterior resin-based filling materials - A comparative study. *J Dent.* 2007, 35: 806-813.
31. Musanje L, Shu M, Darvell BW. Water sorption and mechanical behavior of cosmetic direct restorative materials in artificial saliva. *Dent Mater.* 2001; 17: 394-401.

32. Martin N, Jedynakiewicz NM, Fisher AC. Hygroscopic expansion and solubility of composite restoratives. *Dent Mater.* 2003; 19: 77-86.
33. Carvalho AA, Moreira Fdo C, Fonseca RB, Soares CJ, Franco EB, Souza JB, Lopes LG. Effect of light sources and curing mode techniques on sorption, solubility and biaxial flexural strength of a composite resin. *J Appl Oral Sci.* 2012; 20: 246-252.
34. Sakagushi RL. Review of the current status and challenges for dental posterior restorative composites: clinical, chemistry, and physical behavior considerations. Summary of discussion from the Portland Composites Symposium (POCOS) June 17-19, 2004, Oregon Health and Science University, Portland, Oregon. *Dent Mater.* 2005; 21: 3-6.
35. Archegas LR, Caldas DB, Rached RN, Vieira S, Souza EM. Sorption and solubility of composites cured with quartz-tungsten halogen and light emitting diode light-curing units source. *J Contemp Dent Pract.* 2008; 9: 73-80.
36. Sarrett DC, Söderholm KJ, Batich CD. Water and abrasive effects on three-body wear of composites. *J Dent Res.* 1991. 70: 1074-1081.
37. Santos C, Clarke RL, Braden M, Guitian F, Davy KWM. Water absorption characteristics of dental composites incorporating hydroxyapatite filler. *Biomaterials.* 2002; 23: 1897-19.

TABLE CAPTIONS

Table 1 – Classification and composition of commercial composite resins used

Table 2- Mean values (m) and standard deviations (sd) of water sorption variations for each period, in $\mu\text{g}/\text{mm}^3$ (mean values followed by the same capital letter in the same column or small letter on the same line are not significantly different according to the Tukey test at the 5% level)

TABLES

Table 1

Material	Classification	Organic matrix	Filler type loading	% Load	Manufacturer
Filtek™ Z250	Microhybrid	Bis-GMA Bis-EMA UDMA	Zirconium/Silica with an average particle size of 0.6 µm.	82% weight 60% vol	3M Espe, St. Paul, MN, USA
Filtek™ Z350	Nanofilled	Bis-GMA Bis-EMA UDMA TEGDMA	Aggregates of zirconium/silica matrix with an average size of 0.6-1.4 µm with the size of a primary particle in the range of 5-20 nm and silica incorporation of 20 nm.	78.5% weight 84.5% vol	3M Espe, St. Paul, MN, USA
Grandio®	Nanohybrid	Bis-GMA TEGDMA	Silicon dioxide spheres within the range of 20-50 nm and thin particles of ceramic glass	87% weight 71.4 % vol	Voco, Cuxhaven Germany
Evolu-X®	Nanohybrid	Modified Bis-GMA TEGMA	Silanized barium aluminum borosilicate glass, silanized barium fluoroaluminum borosilicate glass nanoparticulated silica.	75-77% weight 58% vol	Dentsply. Petrópolis, RJ, Brazil

Table 2

Composite resins		Storage Time (days)					
		1	3	14	21	30	60
Filtek™ Z250	m	-0.31	1.87	2.18	0.00	2.80	4.04
	sd	1.59	2.90	1.59	1.88	1.59	7.51
		aA	aA	aA	aA	aA	aA
Filtek™ Z350	m	4.35	3.11	3.42	5.28	7.46	7.15
	sd	4.56	2.90	1.29	2.08	5.48	1.59
		aA	aA	aA	aA	aA	aAB
Grandio®	m	1.55	1.24	0.93	2.18	2.18	1.87
	sd	1.29	1.88	2.28	2.08	2.46	1.15
		aA	aA	aA	aA	aA	aA
Evolu-X®	m	0.62	1.87	3.11	1.55	3.11	1.87
	sd	4.36	8.69	10.01	9.85	8.38	11.94
		aA	aA	aA	aA	aA	aA
Experimental	m	4.97	7.46	7.77	10.26	10.57	15.54
	sd	2.66	1.88	1.59	2.80	3.19	3.45
		aA	abA	abA	abcA	bcA	cB



*Considerações
Finais*

4 CONSIDERAÇÕES FINAIS

A nanotecnologia incorporada aos materiais restauradores, mais precisamente nas resinas compostas permitiu melhora nas suas propriedades mecânicas e ópticas, sendo de fundamental importância para o sucesso restaurador. A nanotecnologia é capaz de gerar resinas com partículas de tamanhos menores e permitir que maior quantidade de carga seja incorporada (Beun et al.³, Terry⁵²).

No primeiro estudo deste trabalho, foi verificado que a fluorescência das resinas compostas não foram similares a estrutura dental. As resinas compostas Grandio[®] e Evolu-X[®], ambas resinas compostas nanohíbridas apresentaram fluorescência acima do encontrado para a fluorescência dentária. Alguns autores (Lee et al.^{28,29}) afirmam que resinas compostas com maior fluorescência apresentam mérito clínico, pois podem ajudar a mascarar uma dentina mais escura ou fornecer luminosidade em pequenas espessuras.

As resinas compostas Experimental e FiltekTM Z250 demonstraram menores valores de fluorescência. A resina composta FiltekTM Z350 XT, que foi introduzida no mercado com a finalidade de melhores propriedades ópticas, embora apresente maior fluorescência que a FiltekTM Z350, ainda encontra-se abaixo dos valores de fluorescência para a estrutura dentária.

Em relação à resina composta nanoparticulada experimental, esta apresenta menor fluorescência, mas não foi encontrado diferença significativa em relação às resinas compostas comerciais FiltekTM Z250 e FiltekTM Z350. Apesar de não apresentar diferença em relação às respectivas resinas compostas, ainda assim encontra-se abaixo dos valores de fluorescência dentária, e maior atenção por parte dos fabricantes para essa propriedade se faz necessário.

Nas resinas compostas comerciais usadas, os fabricantes não informam quais agentes luminóforos estão presentes, e por isso os componentes que proporcionam fluorescência permanecem desconhecidos. Os elementos térbio, itérbio e cério são os geralmente usados para dar fluorescência à resina composta (Ecker et al.¹⁶, Sant'Anna Aguiar Dos Reis et al.⁴⁷).

A importância da fluorescência fica bem evidente quando dente e material restaurador ficam expostos a certas situações, como a luz UV presente em discotecas, boates e casas noturnas. O dente natural exposto à luz UV exibe fluorescência com faixa de emissão de espectro que vai desde o branco intenso até o azul claro. Esses raios UV situam-se entre 350 – 400 nm (Vanini⁵⁴). Radiações próximas a esse comprimento de onda podem ser encontradas em lâmpadas de luz negra, luz solar e lâmpadas de alguns flashes para fotografia.

Nesse estudo, câmera digital foi utilizada para quantificar a fluorescência das resinas compostas e estrutura dentária, de forma a simular a mesma situação das restaurações de resina composta que são expostas a ambientes iluminados artificialmente com lâmpadas de luz negra, além de permitir que dados digitais quantifiquem pixel a pixel o nível de luz detectada em cada região, através de um método puramente óptico.

Outra propriedade avaliada no primeiro estudo foi a cor, que é de extrema importância na longevidade da restauração, principalmente quando do seu uso em dentes anteriores. A resina composta deve apresentar estabilidade de cor, o que evitaria trocas de restaurações apenas por manchamento.

Sabe-se que alguns alimentos e bebidas como café, refrigerantes a base de cola, vinho, influenciam em um menor ou maior grau no manchamento extrínscico da restauração, fato comprovado por diversos estudos (Yazici et al.⁶², Güler et

al.²³). Já o manchamento intrínseco, pode ser resultado da alteração da matriz resinosa e interface matriz/carga (Villalta et al.⁵⁷). O envelhecimento do compósito sob várias condições físico-químicas como luz visível, irradiação UV, alteração da temperatura e umidade podem levar a essa mudança de cor (Wilson et al.⁵⁹).

As resinas compostas avaliadas no estudo quanto à estabilidade de cor, 24 horas após a fotoativação e armazenamento em saliva artificial, ilustra o comportamento clínico de uma restauração recém instalada na cavidade bucal. Como resultado não houve alteração significativa de cor, porém após envelhecimento acelerado em câmara UV, todas as resinas mostraram mudança de cor e valores de ΔE^* acima do limite clinicamente aceitável ($\Delta E \leq 3.3$).

As resinas nanoparticuladas FiltekTM Z350 XT e experimental apresentaram menores estabilidade de cor dentre todas as resinas. A explicação pode estar na maior capacidade de sorção de água presente na interface matriz/carga, característico de resinas nanométricas, principalmente naquelas que apresentam nanoaglomerados de sílica/zircônia como na FiltekTM Z350 XT. As partículas inorgânicas assim como a matriz orgânica exercem influência na estabilidade de cor (Ertas et al.¹⁷, Güler et al.²³, Mundim et al.³⁵, Vichi et al.⁵⁵).

No segundo e terceiro estudo foi analisado o grau de conversão e sorção de água das mesmas resinas compostas com exceção da resina FiltekTM Z350 XT. O grau de conversão está relacionado com a extensão de polimerização. Uma polimerização insuficiente pode alterar as propriedades mecânicas e estabilidade de cor, além da presença de monômeros residuais que podem contribuir para o aparecimento de cáries secundárias e danos pulpares (Rueggeberg⁴⁴).

O termo grau de conversão aplicado às resinas compostas refere-se à conversão de duplas ligações carbônicas monoméricas em polímero de simples

ligação carbono, ou seja, é a extensão na qual o monômero é transformado em polímero (Ferracane et al.¹⁹, Ferracane et al.²⁰). O grau de conversão das resinas compostas pode variar de 43 a 75% dependendo da composição da resina, da intensidade de irradiação e tempo de exposição (Chung, Greener⁸, Ruyter, Oysaed⁴⁵, Silikas et al.⁴⁹). Em nosso estudo todas as resinas compostas apresentaram grau de conversão dentro dessa faixa. A resina composta nanoparticulada experimental apresentou menor conversão, e a resina FiltekTM Z350, ao contrário de outro estudo (da Silva et al.¹²) apresentou conversão mais alta. A justificativa para as resina nanoparticulada apresentar conversão mais baixa, é devido ao espalhamento da luz que ocorre pelo tamanho das nanopartículas. Esse efeito de dispersão faz com que a intensidade de luz seja reduzida, levando conseqüentemente a uma menor conversão (da Silva et al.¹²). Em nosso estudo, como a resina composta nanoparticulada FiltekTM Z350 apresentou um grau de conversão maior, não apenas o tamanho das partículas de carga exerce influência na conversão, mas também a matriz orgânica, e para esse estudo foi usado outro tipo de fonte de luz LED.

Já a resina composta nanohíbrida Evolu-X[®] foi a que apresentou maior conversão dentre todas as resinas compostas avaliadas, e a explicação pode ser pela presença de partículas de vidro na sua composição orgânica, diferentemente das outras resinas que possuem um combinado sílica/zircônia.

A sorção de água, propriedade avaliada no terceiro estudo é um processo de difusão controlada que ocorre principalmente na matriz resinosa. A presença de porosidades e espaços intermoleculares faz com que a água penetre a rede polimérica e acumula-se na interface carga/matriz resinosa (Peutzfeldt³⁷, Pucket et al.³⁹) o que pode ocasionar degradação hidrolítica, instabilidade de cor,

propriedades mecânicas inferiores e redução da longevidade das restaurações de resina (Bagheri et al.²).

No terceiro estudo, a resina composta nanoparticulada experimental e Filtek™ Z350 apresentaram maior sorpção de água na análise do período de 60 dias. A sorpção avaliada para diferentes resinas compostas em períodos pré estabelecidos (1,3,14, 21, 30 e 60 dias), não apresentou diferença significativa ao longo do tempo com exceção da resina composta experimental. Autores mostraram que as resinas nanoparticuladas apresentaram maior sorpção do que as resinas híbridas, talvez pelo fato de nanoaglomerados de sílica de 20 nm permitirem maior acúmulo de água na interface matriz-carga (Mohsen, Craig³², Karabela, Sideridou²⁴)

Em nosso estudo, o tipo de resina composta e o período de armazenamento podem influenciar a sorpção de água do compósito e a resina composta experimental apresentou um aumento de sorpção de água em relação ao período inicial.

De acordo com os resultados verificados nos três estudos aqui apresentados e discutidos, pode-se concluir que as resinas compostas comerciais e experimental apresentam valores de fluorescência menor e maior que a estrutura dentária, o envelhecimento do compósito em câmara UV promoveu alteração significativa da cor sendo maior para as resinas Filtek™ Z350 XT e experimental. Na análise do grau de conversão, todas as resinas compostas apresentaram-se dentro dos valores recomendados (43 a 75%), mas com diferença para as resinas compostas, sendo maior para a resina composta Evolu-X® e menor para a resina composta nanoparticulada experimental. Na avaliação de sorpção, a resina composta experimental apresentou um aumento de sorpção de água em relação ao período

inicial, e o período de 60 dias de armazenamento da resina composta em saliva promoveu maior aumento de sorção para a resina composta experimental e Filtek Z350. Diante dos resultados encontrados, faz se necessário analisar as propriedades avaliadas para a resina composta experimental já que está se encontra em fase laboratorial e em estudo.



Referências

5 Referências*

- 1. Araújo CSA, Schein MT, Zuchi CH, Rodrigues Jr SA, Demarco FF. Composite resin microhardness: the influence of light curing method, composite shade, and depth of cure. J Contemp Dent Pract. 2008; 9: 43-50.**
- 2. Bagheri R, Burrow MF, Tyas MJ. Surface characteristics of aesthetic restorative materials – an SEM study. J Oral Rehabil. 2007; 34:68-76.**
- 3. Beun S, Glorieux T, Devaux J, Vreven J, Leloup G. Characterization of nanofilled compared to universal and microfilled composites. Dent Mater. 2007; 23: 51-9.**
- 4. Bin Y, Yong-Keun L. Differences in color, translucency and fluorescence between flowable and universal resin composites. J Dent. 2008; 36: 840-6.**
- 5. Bowen RL. Dental filling material comprising vinyl silane treated fused silica and a binder consisting of the reaction product of bisphenol and glycidyl acrylate. US Patent 3066112.1962**
- 6. Bowen RL. Properties of silica-reinforced polymer for dental restorations. J Am Dent Assoc. 1963; 66: 57-64.**
- 7. Buchalla W, Attin T, Hilgers RD, Hellwig E. The effect of water storage and light exposure on the color and translucency of a hybrid and a microfilled composite. J Prosthet Dent. 2002; 87: 264-70.**
- 8. Chung KH, Greener HE. Degree of conversion of seven visible light-cured posterior composites. J Oral Rehabil. 1988; 15: 555-60.**
- 9. Commission Internationale de L'Eclairage. Colorimetry Central Bureau of the CIE. Vienna: CIE; 1986.**

*De acordo com o estilo Vancouver. Disponível em <http://www.nlm.nih.gov/bsd/uniform.requirements.html>.

10. Cook WD. Factors affecting the depth of cure of UV- polymerized composites. *J Dent Res.* 1980; 59: 800-8.
11. Costa SXS, Martins LM, Francisconi PAS, Bagnato VSV, Saad JRC, Rastelli ANS et al. Influence of different light sources and photo-activation methods on degree of conversion and polymerization shrinkage of a nanocomposite resin. *Laser Phys.* 2009; 19:1-9.
12. da Silva EM, Almeida GS, Porkus LT, Guimarães JGA. Relationship between the degree of conversion, solubility and salivary sorption of a hybrid and a nanofilled resin composite: influence of the light –activation mode. *J Appl Oral Sci.* 2008; 16: 161-6.
13. DeWald JP, Ferracane JL. A comparison of four modes of evaluating depth of cure of light-activated composites. *J Dent Res.* 1987; 66: 727-30.
14. Dlugokinski MD, Caughman WF, Rueggeberg FA. Assessing the effect of extraneous light on photoactivated resin composites. *J Am Dent Assoc.* 1998; 129: 1103-9.
15. Domingos PA, Garcia PP, Oliveira AL, Palma-Dibb RG. Composite resin color stability: influence of light sources and immersion media. *J Appl Oral Sci.* 2011; 19: 204-11.
16. Ecker GA, Moser JB, Wozniak WT, Brindsen GI. Effect of repeated firing on fluorescence of porcelain-fused-to-metal porcelains. *J Prosthet Dent.* 1985; 54: 207–14.
17. Ertas E, Güler AU, Yücel AC, Köprülü H, Güler E. Color stability of resin composites after immersed in different drinks *Dent Mater J.* 2006; 25: 371-6.
18. Ferracane JL. Hygroscopic and hydrolytic effects in dental polymer networks. *Dent Mater.* 2006; 22: 211-2.

19. Ferracane JL, Mitchem JC, Condon JR, Todd R. Wear and marginal breakdown of composites with various degrees of cure. *J Dent Res.* 1997; 76: 1508-16.
20. Ferracane JL, Moser JB, Greener EH. Ultraviolet light – induced yellowing of dental restorative resins. *J Prosthet Dent.* 1985; 54: 483-7.
21. Galvão MR, Costa SXS, Victorino KR, Ribeiro AA, Menezes FCH, Rastelli ANS, et al. Influence of light guide tip used in the photo-activation on degree of conversion and hardness of one nanofilled dental composite. *Laser Phys.* 2010; 20: 2050-5.
22. Guimarães FBR, Gomes HR, Fonseca RS, Barros LM, Marinho VA, Freitas ABDA. Influência do tempo de fotopolimerização de diferentes resinas compostas na sorpção de água. *Rev Odonto Ciênc.* 2008; 21: 67-71.
23. Güler AU, Güler E, Yücel AC, Ertaş E. Effects of polishing procedures on color stability of composite resins. *J Appl Oral Sci.* 2009; 17: 108-12.
24. Karabela MM, Sideridou ID. Effect of the structure of silane coupling agent on sorption characteristics of solvents by dental resin-nanocomposites. *Dent Mater.* 2008; 24: 1631-9.
25. Kirk RE, Othmer DF, Kroschwitz J, Howe-Grant M. *Encyclopedia of chemical technology.* 4 th ed. New York: Wile; 1991. p. 397.
26. Lee YK, Kim SH, Powers JM. Changes in translucency of resin composites after storage in salivary esterase. *J Esthet Restor Dent.* 2005; 17: 293-9.
27. Lee YK, Lu H, Powers JM. Changes in opalescence and fluorescence properties of resin composites after accelerated aging. *Dent Mater.* 2006; 22: 653-60.

28. Lee YK, Lu H, Powers JM. Fluorescence of layered resin composites J Esthet Restor Dent. 2005; 17: 93–101.
29. Lee YK, Lu H, Powers JM. Influence of fluorescent and opalescent properties of resin composites on the masking effect. J Biomed Mater Res B Appl Biomater. 2006; 76: 26 - 32.
30. Masotti AS, Onófrío AB, Conceicao EN, Spohr AM. UV-vis spectrophotometric direct transmittance analysis of composite resins. Dent Mater. 2007; 23: 724-30.
31. Mitra SB, Wu D, Holmer BN. An application of nanotechnology in advanced dental materials. J Am Dent Assoc. 2003; 134: 1382-90.
32. Mohsen NM, Craig RG. Hydrolytic stability of silanated zirconia-silica-urethane dimethacrylate composites. J Oral Rehabil. 1995; 22: 213-20.
33. Moszner N, Klapdohr S. Nanotechnology for dental composites. Int J Nanotechnol. 2004; 1: 130-56.
34. Moszner N, Salz U. New developments of polymeric dental composites. Prog Polym Sci. 2001; 26: 535-76.
35. Mundim FM, Garcia LF, Pires-de-Souza FC. Effect of staining solutions and repolishing on color stability of direct composites. J Appl Oral Sci. 2010; 18: 249-54.
36. Pearson GJ, Longman M. Water sorption and solubility of resin-based materials following inadequate polymerization by a visible-light curing system. J Oral Rehabil. 1989; 16: 57-61.
37. Peutzfeldt A. Resin composites in dentistry: the monomer systems. Eur J Oral Sci 1997; 105: 97-116.

38. Polydorou O, Manolakis A, Hellwig E, Hahn P. Evaluation of the curing depth of tow translucent composite materials using a halogen and two LED curing units. *Clin Oral Investig.* 2008; 1: 45-51.
39. Puckett A, Fitchie JG, Kirk PC, Gamblin J. Direct composite restorative materials. *Dent Clin North Am.* 2007; 51: 659-75.
40. Rasteli ANS, Jacomassi DP, Bagnato VS. Degree of conversion and temperature increase of a composite resin light cured with an argon laser and blue LED. *Laser Phys.* 2008; 18: 1570-5.
41. Rasteli ANS, Jacomassi DP, Bagnato VS. Effect of power densities and irradiation times on the degree of conversion and temperature increase of a microhibrid dental composite resin. *Laser Phys.* 2008; 18: 1074-9.
42. Reis AF, Giannini M, Lovadino JR, Ambrosano GM. Effects of various finishing systems on the surface roughness and staining susceptibility of packable composite resins. *Dent Mater.* 2003; 19: 12-8.
43. Rodrigues Neto E, Elossais AA, Muñoz Chavez OF, Pereira NRS, Silva PG, Saad JRC. Estudo comparativo de aparelhos fotopolimerizadores para determinar o grau de conversão de resinas compostas utilizando o espectrofotômetro de infravermelho. *RGO.* 2007; 55: 357-61.
44. Rueggeberg FA. Precision of hand-held dental radiometers. *Quintessence Int.* 1993; 24: 391-6.
45. Ruyter IE, Oysaed H. Conversion in different depths of ultraviolet and visible light actived composite materials. *Acta Odontol Scand.* 1982; 40: 179-92.
46. Saade EG, Bandeca MC, Rastelli ANS, Bagnato VS, Porto-Neto ST. Influence of pre-heat treatment and different light-curing units on vickers hardnessof a microhybrid composite resin. *Laser Phys.* 2009; 19:1-6.

47. Sant'Anna Aguiar Dos Reis R, Casemiro LA, Carlino GV, Lins EC, Kurachi C, Bagnato VS, et al. Evaluation of fluorescence of dental composites: a pilot study. *J Esthet Restor Dent.* 2007; 19: 199-206; discussion 207.
48. Schulze KA, Marshall SJ, Gansky As, Marshall GW. Color stability and hardness in dental composites after accelerated aging. *Dent Mater.* 2003; 19: 612-9.
49. Silikas N, Eliades G, Watts DC. Light intensity effects on resin-composite degree of conversion and shrinkage strain. *Dent Mater.* 2000; 16: 292-6.
50. Song SH, Yu B, Ahn JS, Lee YK. Opalescence and fluorescence properties of indirect and direct resin materials. *Acta Odontol Scand.* 2008; 66: 236-42.
51. Taira M, Okazaki M, Takahashi J. Studies on optical properties of two commercial visible-light-cured composite resins by diffuse reflectance measurements. *J Oral Rehabil.* 1999; 26: 329-37.
52. Terry DA. Direct applications of a nanocomposites resin system: Part 1 - The evolution of comtemporany composite materials. *Pract Proced Aesthet Dent.* 2004; 16: 417-22.
53. Vandewalle KS, Ferracane JL, Hilton TJ, Erickson RL, Sakaguchi RL. Effect of energy density on properties and marginal integrity of posterior resin composite restorations. *Dent Mater.* 2004; 20: 96-106.
54. Vanini L. Sistema composito microibrido universale: fluorescencia e opalescencia. *Dent Cadmos.* 1996; 8: 36-48.
55. Vichi A, Ferrari M, Davidson CL. Color and opacity variations in three different resin-based composite products after water aging. *Dent Mater.* 2004; 20: 530-4.

56. Villalta P, Lu H, Okte Z, Garcia-Godoy F, Powers JM. Effects of staining and bleaching on color change of dental composite resins. *J Prosthet Dent.* 2006; 95: 137-42.
57. Ward DH. Esthetic restoration of tooth structure using a nanofill composite system. *Compend Contin Educ Dent.* 2005; 26: 252-7.
58. Watts DC, Cash AJ. Analysis of optical transmission by 400-500 nm visible light into aesthetic dental biomaterials. *J Dent.* 1994; 22: 112-7.
59. Wilson NH, Burke FJ, Mjör IA. Reasons for placement and replacement of restorations of direct restorative materials by a selected group of practitioners in the United Kingdom. *Quintessence Int.* 1997; 28: 245-8.
60. Wozniak WT, Moore BK. Luminescence spectra of dental porcelains. *J Dent Res.* 1978; 57: 971-4.
61. Yap AU, Wang HB, Siow KS, Gan LM. Polymerization shrinkage of visible-light-cured composites. *Oper Dent.* 2000; 25: 98-103.
62. Yazici AR, Celik C, Dayangaç B, Özgünaltay G. The effect of curing units and staining solutions on the color stability of resins composites. *Oper Dent.* 2007; 32: 616-22.
63. Yoon TH, Lee YK, Lim BS, Kim CW. Degree of polymerization of resin composites by different light sources. *J Oral Rehabil.* 2002; 29: 1165-73.



Apêndice

6 APÊNDICE

METODOLOGIA

Resinas compostas comerciais e experimental

Para os diferentes estudos foram utilizadas as resinas compostas comerciais: Filtek™ Z250 (3M Espe), Filtek™ Z350 (3M Espe), Filtek™ Z350 XT (3M Espe), Grandio® (Voco) e Evolu-X® (Dentsply) todas na cor A₂, e resina composta nanoparticulada experimental. A Tabela 1 mostra as características das resinas compostas comerciais que foram utilizadas no estudo.

Tabela 1 – Classificação e composição das resinas compostas utilizadas

Material	Classificação	Matriz orgânica	Porção inorgânica	% de carga	Fabricante
Filtek™ Z250	Microhíbrida	Bis-GMA Bis-EMA UDMA	Zircônia/Sílica com tamanho médio das partículas de 0,6 µm	82% peso 60% vol	3M Espe, St. Paul, MN, USA
Filtek™ Z350	Nanoparticulada	Bis-GMA Bis-EMA UDMA TEGDMA	Agregados da matriz de zircônia/sílica com um tamanho médio de 0,6 a 1, 4 micron com tamanho de partícula primária de 5 a 20 nm e uma incorporação de sílica de 20 nm	78,5% peso 84,5% vol	3M Espe, St. Paul, MN, USA
Filtek™ Z350 XT	Nanoparticulada	Bis-GMA Bis-EMA UDMA TEGDMA PEGDMA	Sílica de 20 nm não aglomerado, Zircônia de 4 a 11 nm não aglomerado, e carga combinada de sílica/zircônia agregada	78,5% peso 63,3% vol	3M Espe, St. Paul, MN, USA
Grandio®	Nanohíbrida	Bis-GMA TEGDMA	Dióxido de silício esférico de 20-50 nm e partículas finas de vidro cerâmico	87% peso 71,4 % vol	Voco, Cuxhaven Alemanha
Evolu-X®	Nanohíbrida	Bis-GMA modificado TEGMA	Vidro de bário alumínio borossilicato silanizado, vidro de bário fluor alumínio borossilicato silanizado e sílica nanoparticulada	75 a 77% peso 58% vol	Dentsply. Petrópolis, RJ, Brasil

Resina composta experimental

Como composição da resina composta experimental, há a porção inorgânica composta de nanopartículas cristalinas de zircônia, Zr_2O_2 , e a porção orgânica cuja matriz resinosa é composta de Bis-GMA (2,2-bis [4-(2-hydroxy-3-methacryloxypropoxy)-phenyl] propano) e TEGDMA (triethyleneglycol dimethacrylato), na proporção de 70/30%, respectivamente, com canforoquinona + DMAEMA como agente fotoiniciador (6×10^{-6} mol/g).

Aparelho fotoativador

Foi utilizado aparelho LED Celalux[®] (Voco, Alemanha) com intensidade de luz de 776 mW/cm², potência de 390 mW e ponta ativa com 8 mm de diâmetro. A potência óptica desse aparelho foi aferida utilizando potenciômetro (Fieldsmaster, Coherent Commercial Products Division, model number FM, set n^o WX65, part number 33-0506, USA) e a irradiância foi calculada por meio da fórmula: $I = P/A$, onde P= potência mW (milliwatts); A= área da ponta de luz em cm² (centímetro quadrado).



FIGURA 1 - Aparelho LED utilizado na fotoativação dos corpos-de-prova (Celalux[®], Voco, Alemanha).

Confecção dos corpos-de-prova

Os corpos-de-prova foram confeccionados utilizando-se de uma matriz metálica com dimensões de acordo com os tipos de testes utilizados. Para o teste de fluorescência e estabilidade de cor foi utilizada uma matriz com orifício interno 10 mm de diâmetro e 1 mm de espessura. Para os outros testes foram utilizadas matrizes com dimensões específicas. Para o teste de grau de conversão, a matriz contém orifício interno de 4 mm de diâmetro e 2 mm de espessura de acordo com a norma ISO 4049 (International Organization for Standardization³), e para a análise de sorção de água, a matriz apresenta orifício interno de 8 mm de diâmetro e 2 mm de espessura. Cabe ressaltar que para todos testes, os corpos-de-prova foram confeccionados da mesma maneira. As figuras 2, 3 e 4 correspondem as dimensões das matrizes utilizadas nos estudos.

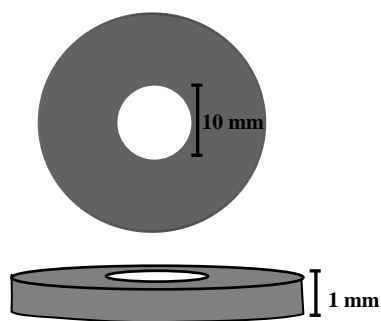


FIGURA 2 - Matriz de 10 mm x 1 mm.

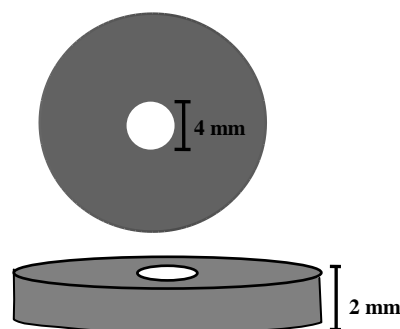


FIGURA 3 - Matriz de 4 mm x 2 mm.

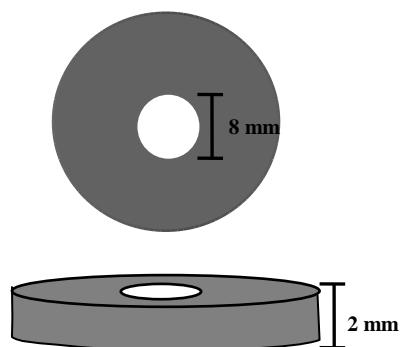


FIGURA 4- Matriz de 8 mm x 2 mm.

Portanto, para a sua confecção, a matriz metálica foi colocada sobre placa de vidro e tira de poliéster para promover lisura da superfície da base dos corpos-de-prova. As resinas foram levadas com auxílio de espátula Thompson (Miltex Inc, York, PA, USA) em um único incremento até completar todo o orifício, e em seguida foi posicionada nova tira de poliéster sobre o topo da resina composta. Logo após, foi colocada uma lâminula de vidro de 1 mm e peso de 1 kg para compactar e padronizar a espessura dos corpos-de-prova. O peso apresenta um orifício central para adaptação e posicionamento da ponta do aparelho fotoativador que em contato com lamínula foi acionado por 40 segundos

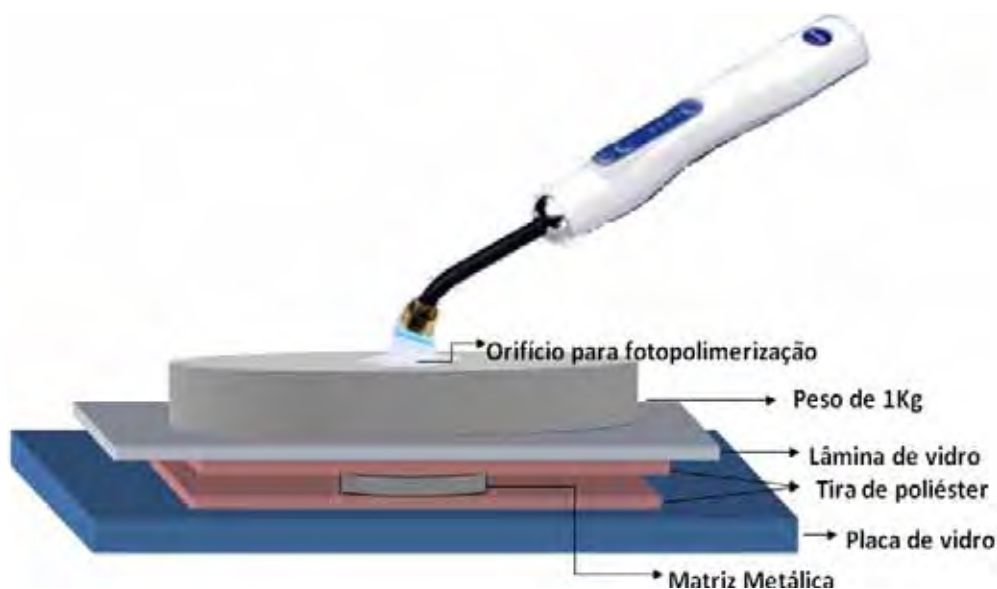


FIGURA 5 - Seqüência para a confecção dos corpos-de-prova.

As porções inorgânicas e orgânicas da resina composta experimental encontram-se separadas, e foi realizada a pesagem da porção inorgânica (30 mg) e orgânica (100 mg) em balança analítica (Gehaka Ltda- modelo BG 440) e após a mistura, procedeu a confecção dos corpos-de-prova, da mesma forma que as outras resinas compostas.

Após a fotoativação, os corpos-de-prova devidamente identificados em frascos, foram armazenados em estufa a 37°C ($\pm 1^\circ\text{C}$) por 24 horas com exceção para a análise de sorção e estabilidade cor, em que os corpos-de-prova foram analisados imediatamente após a sua confecção.

A seguir, será detalhada a metodologia de cada artigo de acordo com os testes empregados:

METODOLOGIA – ARTIGO 1

How composition of commercial and experimental composite resins influence fluorescence and color stability?

Após a confecção dos corpos-de-prova, foram realizadas as análises de Fluorescência e Estabilidade de cor.

Fluorescência

Para esse estudo foram utilizados oito corpos-de-prova para cada grupo de resina composta e 5 dentes caninos (n=53), conforme descrição do Quadro 1.

Quadro 1- Descrição dos grupos para fluorescência

Grupos	Resinas compostas
G1	Filtek™ Z250
G2	Filtek™ Z350
G3	Filtek™ Z350 XT
G4	Grandio®
G5	Evolu-X®
G6	Experimental
G7	Dentes caninos

Foram selecionados 05 caninos humanos hígidos, recém extraídos, isentos de lesão cariiosa, o qual foi aprovado pelo Comitê de Ética em Pesquisa em Seres Humanos da Universidade Estadual Paulista “Júlio de Mesquita Filho”, da

Faculdade de Odontologia de Araraquara, sob Processo nº 38/2010 (Anexo). Após a extração, estes foram lavados, limpos e se realizou a profilaxia com pedra pomes e água. Os dentes foram analisados em lupa estereoscópica para verificar possíveis trincas e defeitos. Em seguida, foram armazenados em água destilada, a temperatura ambiente, solução a qual foi renovada a cada sete dias até o início do experimento.

Após a confecção e fotoativação das resinas compostas, os corpos-de-prova devidamente identificados ficaram armazenados em meio seco sob estufa a 37°C ($\pm 1^\circ\text{C}$) até o momento do experimento (24 horas).

Os dentes caninos selecionados, foram avaliados individualmente quanto a sua fluorescência, de forma a serem utilizados como referência, para se comparar a fluorescência da estrutura dentária e material restaurador sob iluminação LED ultra-violeta (UV).

Para obtenção das imagens e medidas de fluorescência, foi utilizado um computador com hardware específico para aquisição de imagens e um software de análise digital Camware 2.2. A obtenção inicial dos dados foi realizada por meio de câmera CCD (LG) acoplada à lente objetiva (Figura 6). Os corpos-de-prova e os caninos foram posicionados em fundo preto ao centro, pois para a análise empregada, este é o fundo que apresenta a menor interferência na imagem da fluorescência. Foi utilizada uma lanterna LED com pico de emissão centrada em 405 nm (nanômetros) e 10 mW (miliwatts) de potência para excitação (Figura 7).

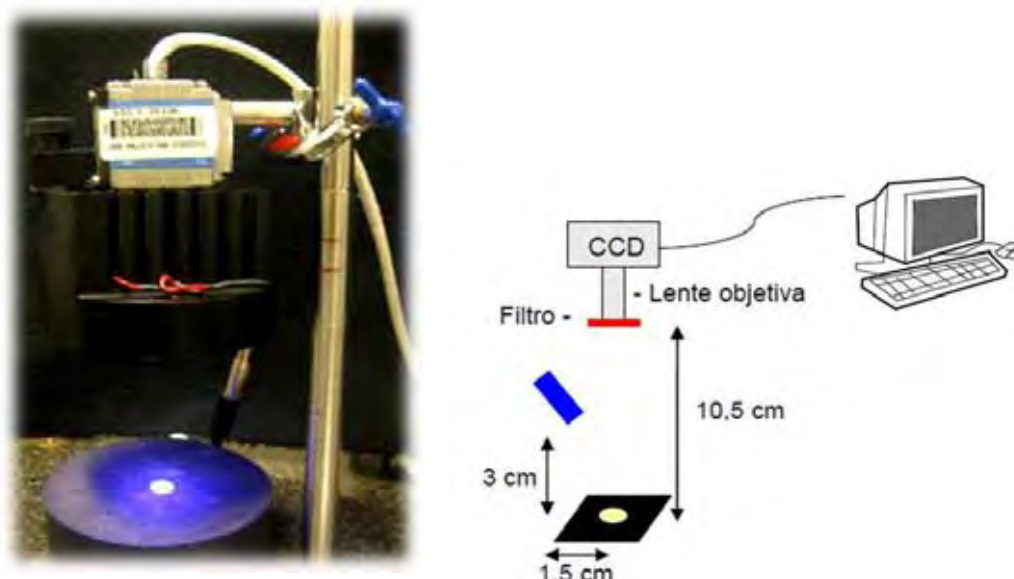
Na Figura 8, observa-se a representação esquemática do sistema de captura das imagens com suas dimensões e angulações. O sistema câmera-filtro está a uma altura de 10,5 cm do espécime; a fonte de luz a 3 cm de altura e 1,5 cm em distância horizontal do espécime, perfazendo uma angulação de 60° com o plano horizontal. Quanto ao ajuste do setup experimental, a angulação em que as fontes de luz se

encontram, visa minimizar o espalhamento e tornar a irradiação mais ortogonal possível. Os comprimentos de onda inferiores a 455 nm foram barrados fisicamente com o uso de um filtro. Este filtro tem a finalidade de evitar que alguns componentes da câmera fluoressam e comprometam a captura de dados sem, contudo, camuflar a informação, uma vez que comprimentos de onda menores que 455 nm não são perceptíveis pelo olho humano (Watson⁶).

O algoritmo de captura consistiu, primeiramente, na obtenção de 16 imagens de cada corpo-de-prova (resina composta e estrutura dental, n=53), posicionados em fundo preto, totalizando em 848 imagens. O número de imagens é dito como ótimo para a minimização de erros e flutuações numéricas (Gonzalez²), enquanto o fundo preto é o que pode produzir menor interferência seguindo esse sistema de captura. Essas 16 imagens foram reunidas perfazendo uma média temporal. Essa média foi transportada para a escala de intensidade de cinza. Dessa forma foi possível quantificar pixel a pixel a intensidade de fluorescência. Então, foi escolhida a melhor linha de interface entre as resinas compostas e foram plotadas as intensidades de fluorescência pelo posicionamento dos pixels no eixo das abscissas.



FIGURA 6 - Detalhe da câmera analógica CCD.



FIGURAS 7 e 8 - Sistema de captura de imagens com detalhe para corpo de prova posicionado ao centro em fundo preto.

Estabilidade de cor

As mensurações de cor foram obtidas através do colorímetro (Minolta, CM 2600d, Japão) (Figuras 9 e 10), com comprimento de onda variando entre 400 a 700 nm, equipado com fonte de luz padrão tipo D65 (luz do dia). Este aparelho emite intensidade de luz de forma espectral de maneira a incidir a luz em um ângulo de 10° com a superfície dos corpos-de-prova.



FIGURAS 9 e 10 - Vista lateral e frontal do colorímetro Minolta (CM 2600d, Japão).

Os valores obtidos pelo colorímetro foram registrados no próprio display do equipamento e, em seguida, transferidos a um microcomputador acoplado ao colorímetro mediante um software específico, o qual registrou os valores de cor de acordo com o Sistema CIE- $L^*a^*b^*$ recomendado pela CIE (Commission Internationale de l'Eclairage¹).

Esse sistema determina os três parâmetros: L^* (luminosidade), o qual varia de zero (preto) a cem (branco), seguindo do preto puro ao branco puro respectivamente. Os valores a^* e b^* são medidas de cromaticidade, em que a^* relaciona-se com o eixo verde-vermelho, ou seja, quando a coordenada a^* for negativa ($-a^*$), a cor do objeto tende ao verde e quando esta coordenada for positiva ($+a^*$), a tendência é a direção para o vermelho. Quando estas duas coordenadas aproximam-se do valor zero, estamos próximos de uma área acromática (cinza neutro)¹.

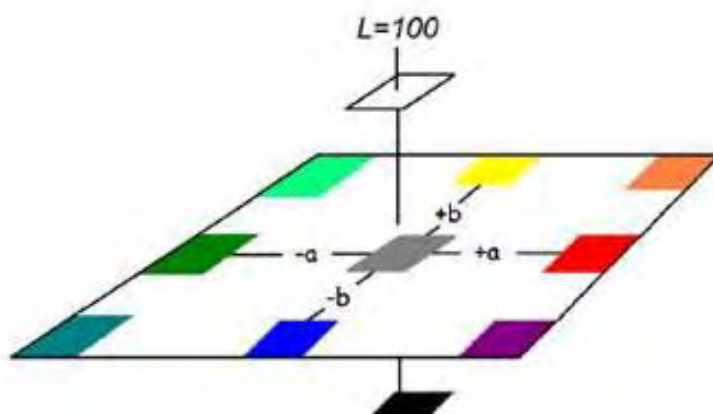


FIGURA 11 - Sistema CIE- $L^*a^*b^*$.

Para a análise de estabilidade de cor, os grupos foram divididos em 6, com oito corpos-de-prova para cada resina composta ($n=48$) de acordo com o Quadro 2.

Quadro 2 - Descrição dos grupos para estabilidade de cor

Grupos	Resinas compostas
G1	Filtek™ Z250
G2	Filtek™ Z350
G3	Filtek™ Z350 XT
G4	Grandio®
G5	Evolu-X®
G6	Experimental

Foram realizados 3 registros de cor para cada um dos corpos-de-prova a fim de se determinar a estabilidade de cor de cada um deles, a saber:

- 1- Registro inicial (R1) - imediatamente após a confecção dos corpos-de-prova;
- 2- Registro intermediário (R2) - 24 horas após o armazenamento em saliva artificial;
- 3- Registro final (R3) - realizada após subsequente envelhecimento artificial.

Após o primeiro registro de cor, os corpos-de-prova foram mantidos por 24 horas em saliva artificial em estufa regulada para a temperatura de 37°C (\pm 1°C), em frascos plásticos devidamente identificados. Após este período, os corpos-de-prova foram retirados, secos e submetidos ao registro de cor intermediária. A seguir, os corpos-de-prova foram submetidos ao processo de envelhecimento artificial por mais 24 horas. Este consiste na exposição dos corpos-de-prova a radiação ultravioleta, em câmara UV Transilluminator (UVP, Upland, CA, USA)

com intensidade de potência de $3,94 \text{ mW/cm}^2$ e dose de irradiação de $340,16 \text{ J/cm}^2$ (Figura 12).



FIGURA 12 - Câmara UV Transilluminator (UVP, Upland, CA, USA) com os corpos-de-prova.

A diferença entre os valores de cor do registro inicial e a intermediário (ΔE^*) representou a primeira leitura de estabilidade de cor e ilustra o comportamento clínico de uma restauração recém instalada na cavidade bucal. Já a diferença entre o registro inicial e o registro final representou a segunda leitura de estabilidade de cor e ilustra a degradação das propriedades ópticas das resinas quando submetidas a condições clínicas.

A estabilidade de cor final de cada um dos corpos-de-prova foi dada pela formula: $\Delta E = [(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2]^{1/2}$, onde 1 corresponderá a primeira leitura e 2 a segunda leitura realizada, ou seja, a fórmula foi aplicada duas vezes, uma para a diferença de cor entre R1 e R2 e outra vez para a diferença de cor entre R1 e R3. Sendo, então, aplicada da seguinte forma:

$$\Delta E_{R1-R2} = [(L_{R1} - L_{R2})^2 + (a_{R1} - a_{R2})^2 + (b_{R1} - b_{R2})^2]^{1/2}$$

e

$$\Delta E_{R1-R3} = [(L_{R1} - L_{R3})^2 + (a_{R1} - a_{R3})^2 + (b_{R1} - b_{R3})^2]^{1/2}$$

De acordo com a habilidade individual do olho humano em apreciar diferença nas cores, três diferentes intervalos foram usados para distinguir alteração de cor (Vichi et al.⁵): $\Delta E < 1$ - imperceptível ao olho humano; $1,0 < \Delta E < 3,3$ – considerado observável somente por uma pessoa experiente (calibrada), mas ainda considerado clinicamente aceitável; $\Delta E > 3.3$ – facilmente observado, alterações de cor não são clinicamente aceitáveis.

METODOLOGIA - ARTIGO 2

Composition influence on degree of conversion of the commercial and experimental composite resins

Para as análises de Grau de Conversão (GC%), cinco corpos-de-prova (n=25) foram confeccionados respectivamente para cada Grupo, conforme descrição no Quadro 3.

Quadro 3 - Descrição dos grupos para análise de grau de conversão

Grupos	Resinas compostas
G1	Filtek™ Z250
G2	Filtek™ Z350
G3	Grandio®
G4	Evolu-X®
G5	Experimental

Grau de Conversão (GC%)

Após obtenção dos corpos-de-prova, 24 horas após a fotopolimerização e estar armazenado em estufa a 37°C (± 1) sob meio seco, cada corpo-de-prova foi triturado em grau e pistilo de ágata até a obtenção de um fino pó (Figuras 13 e 14). Desse pó da resina composta, foram pesados 5 mg em balança analítica AB204-S (Mettler Toledo), que posteriormente foram misturados a 100 mg da substância translúcida, brometo de potássio (KBr – Merk, Darmstadt, Alemanha) (Figura 15). Após homogeneização, o pó misturado foi colocado em pastilhador metálico

(figuras 16 e 17), e em seguida levado à prensa (Figura 18), com pressão de 10 toneladas durante 1 minuto para obtenção de uma pastilha (figura 19). Cada pastilha foi colocada em um frasco escuro coberto por sílica com a finalidade de se evitar umidade do corpo-de-prova (Figura 20). Foram também confeccionadas pastilhas das resinas compostas não curadas, no qual uma pequena porção de cada resina composta foi triturada e homogeneizada com 100 mg de KBr. Essas pastilhas foram levadas ao espectrofotômetro e o grau de conversão de monômeros em polímeros foi obtido por meio de espectroscopia de infravermelho (FTIR).

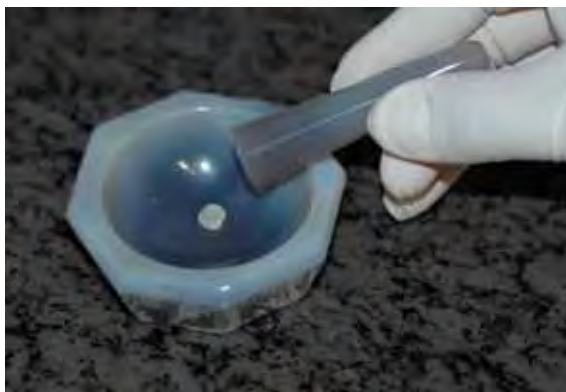


FIGURA 13 - Corpo-de-prova de resina composta.

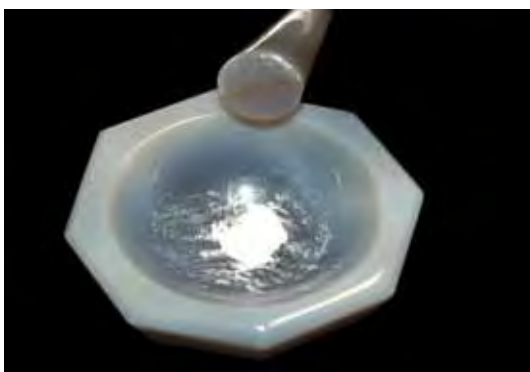


FIGURA 14 - Corpo-de-prova triturado em gral e pistilo de ágata.



FIGURA 15 - Mistura de 5 mg de resina composta com 100 mg de Kbr.



FIGURA 16 - Partes constituintes do pastilhador.



FIGURA 17 - Mistura levada ao pastilhador.



FIGURA 18 - Pastilhador posicionado na prensa hidráulica.



FIGURA 19 - Pastilha confeccionada.



FIGURA 20 - Frasco com sílica onde será colocada a pastilha de resina confeccionada.

Para obtenção dos espectros na região do infravermelho, foi empregado espectrofotômetro (Nexus-470 FT-IR, Thermo Nicolet) (Figura 21), equipado com

detector TGS na faixa espectral de $4000 - 300 \text{ cm}^{-1}$, utilizando acessório de refletância difusa com resolução de 4 cm^{-1} acoplado a microcomputador servidor, operando com 32 scans. Os espectros foram obtidos pela técnica de transmissão observando-se os picos de absorbância.



FIGURA 21 - Espectrofotômetro Nexus 470 FT-IR (Thermo Nicolet).

Após a obtenção dos picos de absorbância, o percentual de duplas ligações carbônicas não convertidas (%C=C) foi determinado pela taxa de intensidade de absorção entre ligações C=C em 1638 cm^{-1} e ligações C-C em 1608 cm^{-1} , antes e após a polimerização (Figura 22). O grau de conversão (GC) foi calculado pela fórmula:

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

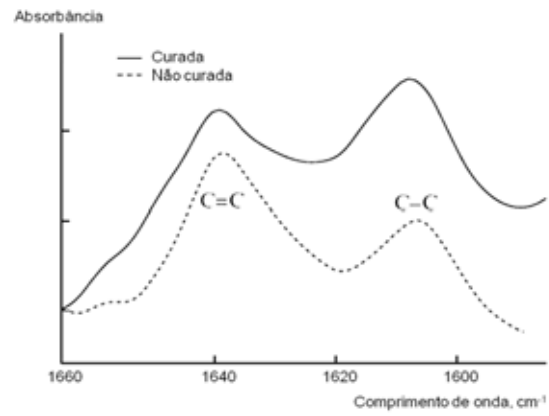


FIGURA 22 - Gráfico demonstrativo dos picos de absorvância para ligações C=C e C-C antes e após polimerização da resina composta. (Rastelli et al.⁴).

METODOLOGIA – ARTIGO 3

Water sorption of nanofilled experimental and commercial composite resins after immersion in artificial saliva

Para esse estudo, foram utilizados oito corpos-de-prova para cada Grupo (n=40), de acordo com a descrição no Quadro 4.

Quadro 4 - Descrição dos grupos para sorção

Grupos	Resinas compostas
G1	Filtek™ Z250
G2	Filtek™ Z350
G3	Grandio®
G4	Evolu-X®
G5	Experimental

Após a confecção dos corpos-de-prova, estes foram pesados diariamente e individualmente em balança analítica BG 440 (Gehaka Ltda, São Paulo, SP, Brasil), até o momento em que massa de cada um dos grupos de resina se apresentasse constante (massa inicial – m1), ou seja, cada corpo-de-prova apresentou por 3 dias consecutivos a mesma massa e para isso, durante todo esse período, os corpos-de-prova ficaram armazenados em recipientes individuais (figura 23) sob meio seco em estufa a 50°C (± 1°C).

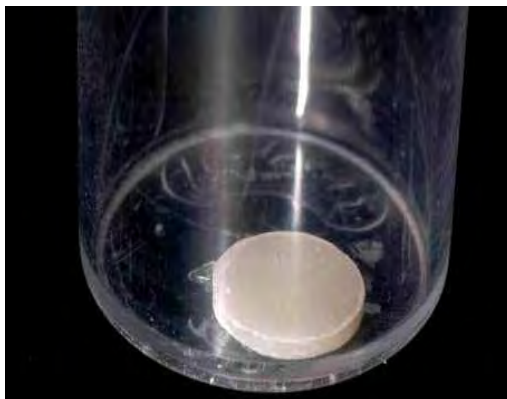


FIGURA 23 - Corpo-de-prova armazenado em recipiente sob meio seco.

Determinado a massa inicial, os corpos-de-prova foram armazenados individualmente em 5 ml de saliva artificial (Figura 24) em estufa a $37^{\circ}\text{C} (\pm 1^{\circ}\text{C})$, o qual foi trocada semanalmente. Após o primeiro dia dos corpos-de-prova apresentarem a massa constante e estarem armazenados em saliva, esses foram pesados nos tempos de 1, 3, 14, 21, 30 e 60 dias (m_2 – massa final). A cada pesagem, os corpos-de-prova eram lavados em água corrente por 1 minuto (Figura 24), secados em papel absorvente (Figura 25) e pesados novamente em balança analítica para determinar a massa correspondente de acordo com os períodos estabelecidos (Figura 27). O peso seco (o peso dos corpos-de-prova após obter a massa constante e antes da imersão em saliva) foi subtraído do peso úmido (o peso dos corpos-de-prova após imersão em saliva artificial) para determinar o ganho de água. A média do ganho de água dos materiais para cada período de armazenameto foi dividido pela volume total dos corpos-de-prova para cacular a sorpção de água ($\mu\text{g}/\text{mm}^3$) de acordo com a fórmula:

$$\text{Sorpção de água} = \frac{m_2 - m_1}{V}$$



FIGURA 24 - Corpo-de-prova armazenado em 5 ml de saliva artificial.



FIGURA 25 - Lavagem do corpo-de-prova em água corrente por 1 minuto.

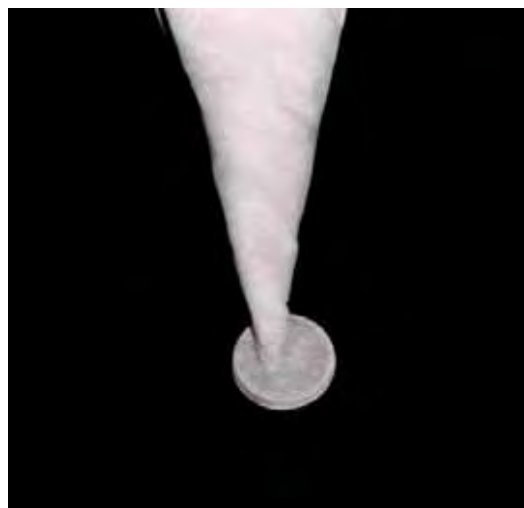


FIGURA 26 - Secagem do corpo-de-prova com papel absorvente.



FIGURA 27 - Pesagem do corpo-de-prova de acordo com os períodos estabelecidos.

REFERÊNCIAS* (METODOLOGIA)

- 1- Commission Internationale de L'Eclairage. Colorimetry Central Bureau of the CIE. Vienna: CIE; 1986.**
- 2- Gonzalez RC, Wintz P. Digital image processing. 2nd ed AddisonWesley, USA, 1987**
- 3- International Organization for Standardization. ISO 4049: Dentistry polymer – based filling, restorative and luting materials. Geneve : ISO ; 2000.**
- 4- Rastelli ANS, Jacomassi DP, Bagnato VB. Effect of power densities and irradiation times on the degree of conversion and temperature increase of a microhybrid dental composite resin. Laser Phys. 2008; 18: 1074-9.**
- 5- Vichi A, Ferrari M, Davidson CL. Color and opacity variations in three different resin-based composite products after water aging. Dent Mater. 2004; 20: 530-4.**
- 6- Watson A. Digital imagens and human vision. Cambridge: Bradford Book, 1993.**

*De acordo com o estilo Vancouver. Disponível em <http://www.nlm.nih.gov/bsd/uniform.requirements.html>.



ANEXO

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Comitê de Ética em Pesquisa

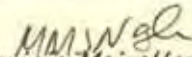


Certificado

Certificamos que o projeto de pesquisa intitulado "*COMO DIFERENTES RESINAS COMPOSTAS PODEM INTERFERIR NA FLUORESCÊNCIA*", sob o protocolo nº **38/10** e o relatório final de responsabilidade do Pesquisador (a) **MARCELO FERRAREZI DE ANDRADE** estão de acordo com a Resolução 196/96 do Conselho Nacional de Saúde/MS, de 10/10/96, tendo sido aprovado pelo Comitê de Ética em Pesquisa-FOAr.

Certify that the research project titled "*HOW DIFFERENT COMPOSITE RESINS CAN INFLUENCE ON FLUORESCENCE*", protocol number **38/10**, and final technical report, under **MARCELO FERRAREZI DE ANDRADE** responsibility, is under the terms of Conselho Nacional de Saúde/MS resolution # 196/96, published on May 10, 1996. This research has been approved by Research Ethic Committee, FOAr-UNESP.

Araraquara, 9 de agosto de 2011.


Prof. Dr. Mauricio Meirelles Nagle
Coordenador

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Araraquara, 31 de julho de 2012

JULIANA MARIA CAPELOZZA BOAVENTURA