ANDRESA CARLA OBICI

AVALIAÇÃO DE PROPRIEDADES FÍSICAS E MECÂNICAS DE COMPÓSITOS RESTAURADORES ODONTOLÓGICOS FOTOATIVADOS POR DIFERENTES MÉTODOS

Tese apresentada à Faculdade de Odontologia de Piracicaba, da Universidade Estadual de Campinas, para a obtenção do Título de Doutor em Materiais Dentários.

PIRACICABA
2003

ANDRESA CARLA OBICI

AVALIAÇÃO DE PROPRIEDADES FÍSICAS E MECÂNICAS DE COMPÓSITOS RESTAURADORES ODONTOLÓGICOS FOTOATIVADOS POR DIFERENTES MÉTODOS

Tese apresentada à Faculdade de Odontologia de Piracicaba, da Universidade Estadual de Campinas, para a obtenção do Título de Doutor em Materiais Dentários.

Orientador: Mário Alexandre Coelho Sinhoreti
Banca Examinadora:
Oscar Fernando Muñoz Chávez
Marcio Grama Hoeppner
Mario Fernando de Góes
Simonides Consani

PIRACICABA
2003

Ficha Catalográfica

Ob3a

Obici, Andresa Carla.
Avaliação de propriedades físicas e mecânicas de compósitos restauradores odontológicos fotoativados por diferentes métodos. / Andresa Carla Obici. -- Piracicaba, SP : [s.n.], 2003.
xviii, 138p. : il.

Orientador : Prof. Dr. Mário Alexandre Coelho Sinhoreti.
Tese (Doutorado) – Universidade Estadual de Campinas, Faculdade de Odontologia de Piracicaba.

1. Materiais dentários. 2. Propriedades mecânicas. 3. Resistência dos materiais. I. Sinhoreti, Mário Alexandre Coelho. II. Universidade Estadual de Campinas. Faculdade de Odontologia de Piracicaba. III. Título.

Ficha catalográfica elaborada pela Bibliotecária Marilene Girello CRB/8–6159, da Biblioteca da Faculdade de Odontologia de Piracicaba - UNICAMP.

DEDICO ESTE TRABALHO

A **Deus**, por ter permeado minha vida com oportunidades
de escolha, sempre iluminando e guiando meus passos.

Aos meus pais, **Laila e Marciano**, exemplos de honestidade e dedicação, cujo incentivo, compreensão e desprendido amor são fundamentais para a minha caminhada.

À minha filha, **Natália**, razão maior da minha existência, que tem tornado tudo significativo.

Aos meus irmãos, **Renata e Juliano**, pela amizade, companheirismo e incentivo nos momentos mais difíceis.

AGRADECIMENTO ESPECIAL

Ao **Prof. Dr. Mário Alexandre Coelho Sinhoreti**, Associado da Área Materiais Dentários, Departamento de Odontologia Restauradora, da Faculdade de Odontologia de Piracicaba, Universidade Estadual de Campinas, pela amizade e compreensão, bem como por expressar com entusiasmo o papel de educador e pesquisador dentro da Odontologia e, acima de tudo pela competente orientação deste trabalho.

AGRADECIMENTOS

À Direção da Faculdade de Odontologia de Piracicaba, da Universidade Estadual de Campinas, na pessoa do seu Diretor **Prof. Dr. Thales Rocha de Mattos Filho** e do Diretor Associado **Prof. Dr. Mario Fernando de Goes**.

Ao **Prof. Dr. Simonides Consani**, Titular da Área Materiais Dentários da Faculdade de Odontologia de Piracicaba, Universidade Estadual de Campinas, pelo incentivo e formação científica.

Ao **Prof. Dr. Mario Fernando de Goes**, Titular da Área Materiais Dentários da Faculdade de Odontologia de Piracicaba, Universidade Estadual de Campinas, pelo exemplo de excelente educador, cujo conhecimento científico contribuiu para minha formação.

Ao **Prof. Dr. Lourenço Correr Sobrinho**, Titular da Área Materiais Dentários da Faculdade de Odontologia de Piracicaba, Universidade Estadual de Campinas, pela amizade, compreensão e grande contribuição em minha formação científica.

À **Profa. Dra. Elisabete Frollini**, Livre Docente do Instituto de Química de São Carlos, Universidade de São Paulo, por permitir a utilização do espectrofotômetro e pela contribuição científica durante a elaboração deste trabalho.

À **Fundação e Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES)**, pelos recursos cedidos, o que possibilitou minha formação do programa de Pós-Graduação.

Ao técnico especializado do laboratório da Área de Materiais Dentários da Faculdade de Odontologia de Piracicaba, Universidade Estadual de Campinas, engenheiro **Marcos Blanco Cangiani**, pela confecção das matrizes utilizados utilizadas neste trabalho, dentre tantas outras contribuições.

Ao técnico especializado da Central de Análises Químicas Instrumentais, do Instituto de Química de São Carlos, da Universidade de São Paulo, **Mauro Roberto Fernandes**, pela valiosa contribuição quanto à análise e o cálculo do grau de conversão.

À **Selma Aparecida Barbosa de Souza Segalla**, técnica da Área de Materiais Dentários da Faculdade de Odontologia de Piracicaba, Universidade Estadual de Campinas, pela amizade e atenção prestadas.

À bibliotecária **Marilene Girello**, da Faculdade de Odontologia de Piracicaba, Universidade Estadual de Campinas, pela orientação nas referências bibliográficas.

Aos colegas de Pós-graduação **Ana Maria, Alysson, Danilo, Gilberto, Janaína, Johnson, Márcia, Marcos, Paulo e Rafael**, pela amizade e companheirismo durante o curso, com os quais espero manter amizade por toda a vida.

Às amigas **Raquel, Ailine e Tatiana**, com as quais morei durante o período de Pós-Graduação.

Às amigas **Juliana S. Rahal, Sueli A. Cardoso, Karina G. Zecchin e Daniela Fernandes**, pela amizade especial.

E a todos os outros que não foram nominados, mas também contribuíram para a realização deste trabalho.

Meus Sinceros Agradecimentos.

EPÍGRAFE

Cuide bem ...

“Cuide bem dos seus pensamentos e sentimentos, porque
eles se transformarão em palavras...
Cuide bem das suas palavras, porque elas se transformarão
em ações...
Cuide bem das suas ações, porque elas se transformarão em
hábitos...
Cuide bem dos seus hábitos, porque eles marcarão o seu
caráter...
Cuide bem do seu caráter, porque ele determinará o seu
destino...”

(Deroni Sabbi)

SUMÁRIO:

RESUMO

Nos últimos anos diversos métodos para a fotoativação de materiais resinosos vêm sendo propostos, no intuito de minimizar a tensão gerada pela contração de polimerização, aumentar o grau de conversão ou reduzir o custo e o tempo clínico do procedimento restaurador. No entanto, muitas dúvidas permanecem com relação às propriedades finais destes materiais quando diferentes técnicas de fotoativação são empregadas. Assim, neste estudo procurou-se avaliar algumas dessas técnicas, sendo que as quatro primeiras empregam a luz halógena, a saber: I- luz contínua (800 mW/cm^2 – 40s); II- luz exponencial (0-800 mW/cm^2 – 40s); III- dupla intensidade de luz (150 mW/cm^2 – 10s; 650 mW/cm^2 – 30s); IV- luz intermitente (600 mW/cm^2 – 2s; 2s sem luz – 80s); V- Arco de Plasma de Xenônio - PAC (1320 mW/cm^2 – 3s); VI- Luz Emitida por Diodo - LED 1 (100 mW/cm^2 – 40s), e; VII- LED 2 (350 mW/cm^2 – 40s). Visando o melhor entendimento dos métodos de fotoativação sobre as propriedades finais dos compósitos restauradores odontológicos a pesquisa foi dividida em cinco trabalhos. O primeiro trabalho avaliou a profundidade de polimerização e a dureza Knoop do compósito P60, cor A3, quando fotoativado pelos métodos I, II, IV – VI. A maior profundidade de polimerização foi obtida com o método de luz intermitente, seguido pela luz contínua, luz exponencial, PAC e LED1. Até a profundidade de 2mm todas as técnicas mostraram valores de dureza similar, porém houve diferenças nas outras profundidades, sendo que o LED1 apresentou os menores valores, seguido pelo PAC. O segundo trabalho investigou o grau de conversão do compósito Z250, cor A3, fotoativado pelos métodos I – VI, dois períodos de armazenagem (24 horas e 20 dias) e duas técnicas de preparo dos corpos-de-prova para FTIR (filme fino de compósito e pastilha com brometo de potássio [KBr]). O grau de conversão não foi estatisticamente

afetado pelos diferentes métodos de fotoativação ou períodos analisados, porém a técnica de preparação do corpo-de-prova alterou significativamente os valores do grau de conversão. O terceiro trabalho investigou o grau de conversão, através da espectroscopia FTIR, do compósito Z250 (cor A3) em diferentes profundidades, usando seis métodos de fotoativação (I – V e VII). Os resultados mostraram que não houve diferenças entre os métodos para a superfície e nas profundidades de 1 e 2mm. Para as regiões mais profundas o PAC obteve os piores resultados e o LED2 os melhores. O quarto trabalho avaliou o grau de conversão e a dureza Knoop do compósito Z250 (cor A3), utilizando todos os sete métodos de fotoativação anteriormente mencionados. Não houve diferença no grau de conversão entre os métodos considerados. Contudo, para a dureza Knoop, os maiores valores foram obtidos para a luz contínua, luz intermitente, luz exponencial e LED2, seguido pelo PAC e com os menores valores o LED1. Finalmente, o quinto trabalho avaliou as propriedades mecânicas de resistência à compressão, tração diametral, flexão e o módulo de elasticidade do compósito Z250, cor A3, fotoativado por seis métodos (I – V e VII). Os maiores valores para resistência à compressão foram obtidos com luz contínua, luz exponencial, luz intermitente e dupla intensidade de luz, seguidos pelo PAC e LED2. Para a resistência à tração diametral, LED2, dupla intensidade de luz, PAC, luz exponencial e luz contínua mostraram os maiores valores, enquanto o menor foi encontrado para a luz intermitente, que diferiu apenas do LED2. Os valores para a resistência à flexão não foram diferentes entre si para os métodos considerados. Os maiores valores para o módulo de elasticidade foram obtidos para LED2, luz exponencial, luz contínua e luz intermitente, enquanto PAC e dupla intensidade de luz alcançaram os menores valores. A partir deste trabalho foi possível concluir que a profundidade de polimerização e as propriedades mecânicas, exceto a resistência à flexão, são significativamente afetadas pelo método de

fotoativação empregado. Por outro lado, o grau de conversão, em profundidade de até 2mm e a resistência à flexão não são significantemente afetados pela técnica de fotoativação.

Palavras Chave:

1- Materiais dentários; 2- Compósitos restauradores odontológicos; 3- Métodos de fotoativação; 4- Profundidade de polimerização; 5- Grau de conversão; 6- Propriedades mecânicas; 7- Dureza Knoop; 8- Resistência à compressão; 9- Resistência à traça diametral; 10- Resistência à flexão; 11- Modulo de elasticidade.

ABSTRACT

In the last years, several photo-activation methods to initiate the reaction of resinous materials have been suggested, in an attempt of minimize shrinkage polymerization stresses, increase the degree of conversion or decrease the restorative procedure time and cost. However, very doubts remain concern to the final properties of these materials when different photo-activation methods are employed. Thus, in this study was to evaluated some of these techniques, which methods of I - IV employed the halogen lamps, as follows: I- continuous light (800 mW/cm^2 – 40s); II- exponential light (0-800 mW/cm^2 – 40s); III- stepped light (150 mW/cm^2 – 10s; 650 mW/cm^2 – 30s); IV- intermittent light (600 mW/cm^2 – 2s; 2s without light – 80s); V- Plasma Arc Curing - PAC (1320 mW/cm^2 – 3s); VI- Light Emitting Diodes - LED 1 (100 mW/cm^2 – 40s), e; VII- LED 2 (350 mW/cm^2 – 40s). This research was divided in five works, in an attempt to improve the knowledge of the photo-activation methods upon the final properties of the restorative composite resins. The first study evaluated the depth of cure and Knoop hardness of in the P60, shade A3, composite resin photo-activated using different methods (I, II, IV – VI). The highest depth of cure was obtained with intermittent light, followed by continuous light, exponential light, PAC and LED1 methods. Up to a depth of 2mm, all methods revealed similar hardness values, but showed differences between them at other depths, where the LED1 demonstrated the lowest values, followed by PAC. The second study investigated the degree of conversion of the Z250 composite, shade A3, using six photo-activation methods (I – VI), two storage periods (24 hours and 20 days) and two preparation techniques of the FTIR specimens (thin resin films and Bromide potassium [KBr] pellet). The DC values were not statically affected by the use of different photo-activation methods or storage periods analyzed.

However, the specimen preparation technique showed significant differences in DC values. The third study evaluated the degree of conversion, by FTIR spectroscopy, of the Z250 composite resin (shade A3) at different depths, using six photo-activation methods (I – V e VII). The results showed that there was no difference between photo-activation methods at a surface and at depths of 1 and 2mm. Concerning the deeper regions, PAC revealed the lowest values and LED2 the highest one. The fourth work investigated the degree of conversion and the Knoop hardness of Z250 composite, shade A3 employing seven photo-activation methods mentioned above. There was no difference in degree of conversion between all photo-activation considered. However, concerning the Knoop hardness, the highest values were obtained to continuous light, intermittent light, and exponential light and LED2, followed by PAC, whilst the lowest values were found to LED1. Finally, the fifth study evaluated the mechanical properties of compressive strength, diametral tensile strength, flexural strength and modulus of elasticity of the Z250 composite resin (shade A3), when photo-activated by six methods (I – V e VII). The highest compressive strength values were obtained to continuous, exponential, intermittent and stepped light methods, followed by PAC and LED2. Conversely, for diametral tensile strength, LED2, stepped light, PAC, exponential and continuous light showed the highest values, whilst the intermittent revealed the lowest values, which differed only to LED2. The flexural strength values were not different between all photo-activation methods considered. The LED2, exponential, continuous and intermittent light techniques demonstrated the highest modulus of elasticity values, whilst PAC and stepped light showed the lowest values. It was possible to conclude in this study that the depth of cure and the mechanical properties, with the exception of flexural strength, are significantly affected by the photo-activation method

employed. Conversely, the degree of conversion, up to a depth of 2mm, and the flexural strength are not significantly affected by the photo-activation technique.

Keywords:

1- Dental materials; 2- Restorative composite resins; 3- Photo-activation methods; 4- Depth of cure; 5- Degree of conversion; 6- Mechanical properties; 7- Knoop hardness; 8- Compressive strength; 9- Diametral tensile strength; 10- Flexural strength; 11- Modulus of elasticity.

INTRODUÇÃO GERAL

A utilização de compósitos restauradores odontológicos fotoativados por luz visível é geralmente preferida tanto para restaurar dentes anteriores quanto posteriores, devido à maior facilidade de manuseio e maior segurança quando comparados aos seus antecessores (BASSIOUNY & GRANT, 1978; RUYTER & OYSAED, 1982). Contudo, diversos fatores podem afetar as propriedades finais destes materiais. Dentre eles, características relacionadas às partículas de carga, matriz resinosa, intensidade de luz e tempo de exposição à luz (ASMUSSEN, 1982; YEARN, 1985; CHUNG & GREENER, 1988; RUEGGEBERG *et al.*, 1993; RUEGGEBERG *et al.*, 1994; KAWAGUCHI *et al.*, 1994).

O tipo, tamanho, quantidade e índice de refração das partículas de carga exercem um papel importante no coeficiente de transmissão da luz através do compósito e, conseqüentemente, nas características de atenuação da luz e na profundidade de polimerização do material (RUEGGEBERG *et al.*, 1993; KAWAGUCHI *et al.*, 1994).

Por outro lado, o sistema de monômeros que compõe a matriz resinosa, também afeta as propriedades finais do material e seu desempenho clínico. Desta forma, as características dos monômeros resinosos, bem como a proporção entre eles resulta em cadeias poliméricas com propriedades distintas. A molécula do BisGMA, principal monômero formador da matriz resinosa da maioria dos compósitos disponíveis comercialmente, apresenta alto peso molecular e reduzida flexibilidade, devido à presença de dois grupos aromáticos no centro da cadeia (PEUTZFELDT, 1997). Ainda, a alta viscosidade do Bis-GMA (1200 Pas a 20ºC), decorrente da quantidade de pontes de hidrogênio intermoleculares (DAVY *et al.*, 1998), limita bastante sua mobilidade, o que por sua vez reduz o grau de conversão (LOVELL *et al.*, 1999). Este conjunto de características torna necessária a diluição do Bis-GMA com monômeros de baixo peso molecular, alta mobilidade e alta flexibilidade, como por exemplo o TEGDMA, o qual é misturado ao BisGMA, de modo a se obter uma consistência favorável à incorporação de carga inorgânica e à utilização clínica (BOWEN, 1963; PEUTZFELDT, 1997). Menores quantidades do monômero diluente, TEGDMA, em relação ao BisGMA proporcionarão um material com propriedades mecânicas superiores e menores valores de contração de polimerização (ASMUSSEN & PEUTZFELDT, 1998; LOVELL *et al.*, 1999; ELLIOTT *et al.*, 2001).

Outros dimetacrilatos vêm sendo desenvolvidos com o intuito de melhorar as propriedades dos compósitos restauradores odontológicos. Dentre eles, podemos destacar os uretanos dimetacrilatos (UDMA), que podem ser utilizados em associação ao BisGMA ou substituindo-o. Estes monômeros apresentam alto peso molecular, semelhante àquele dos Bis-GMA, porém são menos viscosos – 23,1 Pas a 20ºC (DAVY *et al.*, 1998) - e mais flexíveis devido à ligação uretano (PEUTZFELDT, 1997). Ainda, monômeros derivados do próprio BisGMA, como o BisEMA, também vem sendo empregados (PEUTZFELDT, 1997). O monômero Bis-EMA é um homólogo do Bis-GMA sem a presença dos grupos hidroxila, o que promove significativa redução nas pontes de hidrogênio intermoleculares, resultando em maior mobilidade.

A quantidade de duplas ligações, presentes nos monômeros, que são convertidas em ligações simples para formar a cadeia polimérica durante o processo de polimerização é denominada grau de conversão. Tem sido demonstrado que maiores valores de grau de conversão podem ser obtidos pela utilização de altas intensidades de luz, proporcionando propriedades físicas e mecânicas superiores (YEARN, 1985; RUEGGEBERG *et al.*, 1994). Entretanto, também pode resultar em altos valores de tensão gerada pela maior contração de polimerização e maior infiltração marginal (SAKAGUCHI *et al.*, 1992; VENHOVEN, *et al.*, 1993).

Desta forma, diversos pesquisadores têm proposto a utilização programada de baixa e alta intensidade de luz (UNO & ASMUSSEN, 1991; UNTERBRINK & MUESSNER, 1995; FEILZER *et al*, 1995). Isto propiciou o surgimento de uma nova técnica de fotoativação, que utiliza inicialmente baixa intensidade de luz, seguida por alta intensidade de luz. Esta técnica de dupla intensidade de luz tem demonstrado diminuir os valores da tensão gerada pela contração de polimerização, enquanto mantém alto grau de conversão (UNO & ASMUSSEN, 1991; FEILZER *et al*, 1995; SAKAGUCHI & BERGE, 1998; BOUSCHLICHER *et al*, 2000; OBICI *et al.*, 2002).

Desde então, outros métodos de fotoativação, que também utilizam a luz halógena, vêm sendo sugeridos, tal como a fotoativação por luz intermitente (MENIGA, *et al.*, 1997; TARLE *et al.*,1998; OBICI *et al.*, 2002), que alterna luz e ausência de luz e, por fim, a luz exponencial (CALDAS, *et al.*, 2003), cuja intensidade de luz inicia-se em zero e aumenta gradualmente até atingir alta intensidade de luz.

Mais recentemente, outras tecnologias para fotoativação estão sendo disponibilizadas, como o arco de plasma de Xenônio - PAC (HOFMANN *et al.*, 1998; PEUTZFELDT, *et al.*, 2000) e a luz emitida por diodos - LED (FUJIBAYASHI *et al.*, 1998; JANDT *et al.*, 2000; STAHL *et al.*, 2000; KURACHI *et al.*, 2001). Todas estas técnicas objetivam melhorar as características finais dos compósitos, bem como favorecer as situações clínicas como maior facilidade de manutenção e/ou menor tempo de fotoativação. Contudo, muitas dúvidas permanecem a respeito das propriedades finais dos materiais resinosos quando estes métodos são empregados.

Com base no que foi exposto, o objetivo do presente trabalho foi avaliar algumas propriedades físicas e mecânicas de compósitos restauradores odontológicos, fotoativados por diferentes métodos.

PROPOSIÇÃO

Visando o melhor entendimento dos métodos de fotoativação sobre as propriedades finais dos compósitos restauradores odontológicos o estudo foi dividido em cinco trabalhos, cujos objetivos são apresentados:

1- Verificar a profundidade de polimerização e a dureza Knoop do compósito P60 fotoativados por cinco métodos;

2- Avaliar o grau de conversão do compósito Z250, fotoativado por diferentes métodos, dois períodos de armazenagem e duas técnicas de preparo dos corpos-de-prova para FTIR ;

3- Avaliar o grau de conversão, através da espectroscopia FTIR, do compósito Z250 em diferentes profundidades, usando seis métodos de fotoativação;

4- Avaliar o grau de conversão e a dureza Knoop do compósito Z250, utilizando sete métodos de fotoativação;

5- Investigar as propriedades mecânicas de resistência à compressão, tração diametral, flexão e o módulo de elasticidade do compósito Z250 fotoativado por seis métodos.

CAPÍTULO I

Evaluation of depth of cure and Knoop hardness in a dental composite photo-activated using different methods

(Brazilian Dental Journal – enviado para publicação)

SUMMARY

The aim of this study was to evaluate the depth of cure and Knoop hardness in the P60 composite resin photo-activated using different methods. A bipartite brass matrix (3mm in diameter X 11mm in height) was filled with the composite and photo-activation was performed using continuous light, exponential light, intermittent light, plasma arc curing – PAC or light-emitting diodes - LED. After opening the matrix, the uncured material was removed with a steel spatula and the polymerized composite was measured using a digital pachimeter. Then, the specimens were included and weared longitudinally and the hardness was measured on the surface and at depths of 1, 2, 3, 4 and 5mm. The data were analysed by ANOVA and Tukey's test (5%). The results showed that the depth of cure was higher with the intermittent light, followed by continuous, exponential light, PAC and LED methods. Up to a depth of 2mm, all methods revealed similar hardness values, but showed differences between them at other depths, where the LED demonstrated the lowest values, followed by PAC.

KEYWORDS: Photo-activation methods, composite resin, depth of cure, Knoop hardness, dental materials

INTRODUCTION

The light-activated composite resins, brought into practice in 1970's, introduced expressive changes that made their satisfactory application in posterior teeth possible. However, characteristics such as composition, light intensity and exposure time can modify the final properties of the material and thus, restrict the clinical applications. Type, size, quantity and refraction index of the fillers into composite exert influence upon light transmission across the material and, consequently, the light attenuation and the depth of cure may be altered [1, 2]. With respect to the organic matrix, the nature of the involved monomer molecules and the degree of conversion obtained in composite resin has an important effect upon mechanical properties [3], where the higher degrees of cure will improve the final properties of the material.

A higher degree of conversion can be obtained by using a high light intensity [4]. However, this higher intensity may result in greater polymerization shrinkage, gap formation and greater marginal leakage [5]. Thus, new photo-activation techniques have been proposed, such the programmed use of low and high intensities that have shown be more effective in decreasing the stress generated by polymerization shrinkage, whilst maintaining a high degree of conversion and satisfactory mechanical properties [6-9]. Since the introduction of this method, other photo-activation methods have been suggested, these include intermittent light [9, 10], plasma arc curing – PAC [11] and, more recently, a new technology employing light-emitting diodes – LED [12, 13]. However, these innovatory techniques require further investigation before they can be effectively applied in dental practice.

The aim of this study was to evaluate the depth of cure and Knoop hardness using different photo-activation methods.

MATERIAL AND METHODS

This study used the Filtek P60 composite resin (3M, St. Paul, MN, USA), shade A3. Composition and batch are listed in Table 1.

The composite was placed in a bipartite brass matrix that presented a central opening of 3 mm in diameter and 11 mm in height. The composite was then covered with a polyester strip and pressed with a glass slab to accommodate the material into the matrix. Photo-activation was performed as follows: a) continuous light; b) exponential light; c) intermittent light; d) PAC, and e) LED.

For the continuous light photo-activation method, the curing tip was positioned close to the brass matrix/restorative composite. The photo-activation was performed for 40 seconds with a high intensity of 800 mW/cm^2, using an Elipar Trilight curing unit (3M-ESPE, Seefeld, D-82229, Germany). For the exponential light technique, the same curing unit was used, however, the light intensity began at zero, increasing gradually to 800 mW/cm^2 in the first 20 seconds, then maintaining this light intensity for an additional 20 seconds, with a total exposure time of 40 seconds. Curing for the intermittent light method was performed using a curing unit developed in the Dental Materials Department, School Dental of Piracicaba, UNICAMP, which provided seconds of light with an intensity of 600 mW/cm^2 and 2 seconds without light. The total time was 80 seconds, of which 40 seconds of light exposure itself. For the PAC technique, the Apollo 95 E curing unit (DMD, Westlake, Village, CA 91362, USA) was used which, according to manufacturer's information, achieved an intensity of 1320 mW/cm^2. The light exposure time was 3 seconds. Finally, for the LED method, a LEC 470 I curing unit (MM Optics, São Carlos-SP 13560-050, Brazil) was used to photo-activate the composite, providing an intensity of 100 mW/cm^2 for 40 seconds. The light intensity of the curing units was measured with a radiometer (Curing Radiometer, model 100, Demetron/Kerr, Danbury, CT 06810, USA), with the exception of the Apollo 95 E curing unit.

After photo-activation, the brass matrix was opened and all uncured material was removed using a steel spatula. The polymerized composite cylinder was measured using a digital pachimeter (Digital pachimeter, model CD-15C, Mitutoyo, Japan), which was positioned in the center of the specimen, determining the depth of cure. Five specimens were prepared for each photo-activation method.

The specimens were then included in self-curing acrylic resin (Artigos Odontológicos Clássico, São Paulo-SP, Brazil) and weared longitunally along the center with grit 80 sandpaper (Carburundum Abrasivos, Recife-PE, Brazil) in a grinding wheel (Arotec, model APL-4, Cotia-SP, Brazil). Finishing and the polishing were then performed with sandpaper (Carburundum Abrasivos, Recife-PE, Brazil) of decreasing grits of 320, 400, 600 and 1000. After 24 ± 1 hour, the Knoop hardness (Micro Hardness Tester, model HMV 2, Shimadzu, Japan) was measured at the surface and at depth of 1, 2, 3, 4 and 5 mm. For Knoop hardness measurement the Micro Hardness Tester was calibrated with a load of 50g for 15 seconds. Five readings were taken for each region and the arithmetic means was calculated for each region of the specimen.

The data were submitted to analysis of variance (ANOVA) and the means were compared by Tukey's test (5% of significance level).

RESULTS

The results of the depth of cure and the Knoop hardness are presented in Tables 2 and 3, respectively.

Table 2 shows that the intermittent light method demonstrated the highest depth of cure (6.70 mm) and was statistically different from the other methods ($p<0.05$). The continuous and exponential light techniques presented intermediate values and there were no significant differences between them ($p>0.05$). The lowest depths of cure values were obtained with the LED and the PAC methods. However, there were statistical differences between them, where the LED demonstrated the lowest depth of cure (4.23 mm).

Table 3 shows that up to a depth of 2 mm, all photo-activation methods presented similar Knoop hardness values ($p>0.05$). At 3 mm, the LED method presented the lowest value and the continuous light technique demonstrated an intermediate value with no statistical difference from the other methods. The intermittent, exponential, continuous light and PAC methods revealed the highest values and with no statistical differences between them ($p>0.05$).

At a depth of 4 mm, the intermittent and continuous light methods presented the highest Knoop hardness values without significant differences between them ($p>0.05$). Furthermore, the continuous light method demonstrated no difference from exponential light and PAC methods. LED revealed the lowest Knoop hardness value, which was significantly different from those of the other methods ($p<0.05$). At 5 mm depth, the LED and the PAC photo-activation methods could not be evaluated, as they did not reach this depth. At this depth, the continuous light method presented an intermediate value with no statistical difference from the other methods. The intermittent light method, however, revealed a statistically higher value than that of the exponential light method ($p<0.05$).

DISCUSSION

The development of new technologies for photo-activation of restorative composite resins has caused great interest among researchers [6-13]. However, the real advantages of these techniques are not yet totally known. Before these methods can be clinically applied, the final properties of the photo-activated composites must be evaluated. Thus, this study evaluated the depth of cure and the Knoop hardness of the P60 composite resin, using different photo-activation methods.

The results of this study showed that the depth of cure is strongly affected by photo-activation methods. The intermittent light demonstrated the highest depth of cure (6.70 mm) and was statistically different from the other methods. The continuous (6.08 mm) and exponential light (5.88 mm) methods demonstrated intermediate values without significant differences between them. The lowest values were obtained with the PAC (4.67 mm) and the LED (4.23 mm) methods, however there were statistical differences between them, although the LED method revealed a lower hardness value than the PAC method.

The intermittent, continuous and exponential light methods supply energy for photo-activation via halogen lamps, which white light must be filtered to emit only the blue spectrum of the visible light. To generate blue light, the lamps must be heated to very high temperatures [14], resulting in the emission of heat through the curing light tip [15, 16]. This heat transmission to the material may be, in part, responsible for the higher depth of cure values achieved using these methods, because the heat may increase the mobility of the monomers, increasing the probability of the occurrence of conversion.

Another factor that may have influenced the depth of cure results and caused the difference between the intermittent light and the continuous and exponential methods is the total amount of energy supplied to the composite for the polymerization. According to

Sakaguchi & Berge [8], maximum light intensity is achieved at 0.55 seconds and then decreases, signifying that, even with the continuous light method (800 mW/cm^2), the amount of energy supplied was not constant. Conversely, the intermittent light method employs 2 seconds of light exposure followed by 2 seconds without light, meaning that the maximum light intensity peak is achieved every time that the light is emitted. Since the polymerization process seems more dependent on the total of energy available for photo-activation than the light intensity property [8, 17], this method may provide a higher amount of energy supplied to the material, which may explain the higher depth of cure values achieved using the intermittent method.

The PAC method employs a different technology, where the light is produced by two electrodes that are placed very close to each other, emitting light when a high voltage is applied rather than by heating a tungsten filament as a halogen lamp [14]. PAC curing light units generate heat and achieve very high light intensity (1320 mW/cm^2) [11, 14]. However, the depth of cure value was lower than that obtained by methods that employ halogen lamps. This result may be due to the reduced photo-activation time used in PAC, representing a lower energy amount [8, 17] and a short time period for the light to reach deeper regions of the material, since part of the light necessary for polymerization is absorbed and scattered by the composite already polymerized [1, 18]. According to Peutzfeldt *et al.* [11], when curing light units are studied, an important parameter is the amount of light energy of appropriate wavelength emitted during the irradiation. This energy is calculated as the product of the output of the curing light unit and the time of irradiation and may be as termed energy density. According these authors, the Apollo 95 E emits less energy in 3 seconds (3.96 J/cm^2) than do the conventional curing light units (approximately 21 - 32 J/cm^2). This could explain the lower depth of cure obtained by this method when compared to methods that use the halogen lamp.

The more recent technology developed for photo-activation of resinous materials, the LED, combines two different semiconductors (p – n junctions). When a voltage is applied, the electrons and ‘holes’ recombine at the LED’s p – n junctions leading, in the case of gallium nitride LEDs, to emission of blue light. The spectral output of gallium nitride blue LED falls conveniently within the absorption spectrum of the camphoroquinone photo-initiator (400 – 500 nm) presented in most of light-activated composite resins, thus no filters are required in LED light curing units [12, 13]. However, the LED demonstrated the lowest depth of cure. This result may be due to the low light intensity (100 mW/cm^2) and lower heat emission with this curing light unit, as well as the lower energy density (4 J/cm^2). The increasing of the exposure time or the light intensity could minimize this problem.

In spite of the differences observed between the photo-activation methods, all provided the minimum depth of cure required by the ISO 4049 regulations [19], i.e., a cure depth of at least 3 mm, when the composite manufacturer’s claims maximum thickness of 2.5 mm.

The Knoop hardness test showed that, at up to a depth of 2 mm, all photo-activation methods provided similar values. This result demonstrates that despite the particular characteristics of each method, the light intensity and the exposure time were enough to adequately polymerize this thickness of composite.

At a depth of 3 mm, the LED demonstrated the lowest hardness value, while the continuous light method revealed an intermediate value with no statistical difference from the other methods. The lower value observed with LED might be due to the low intensity produced by this technique. Even the LED method achieves the maximum irradiation at 466 nm, which according to Nemoto [20] is the most efficient wavelength to excite camphoroquinone, however, the light is absorbed and/or scattered when the thickness increases [1, 18], consequently decreasing the amount of energy for photo-activation. This fact may explain the lower hardness observed at 3 mm depth when LED was used. Despite to this scattering and absorbance of light, all the other methods supplied higher amounts of energy to the composite and, thus, provided higher hardness values at 3 mm depth.

At a depth of 4 mm, the intermittent and continuous light methods demonstrated the highest hardness values without differences between them. The continuous light was similar to the exponential light and PAC, whilst the LED presented the lowest hardness, with statistical differences from the other methods. This result may be due to the total amount of energy that reached the material at this depth. The energy total is related to exposure time and light intensity generated by each method, i.e., the energy density [1, 4, 8, 11].

At a depth of 5 mm, the LED as the PAC methods could not evaluated since they did not achieved a depth of cure of 5 mm. At this depth, the continuous light method presented an intermediate value and was no different to the intermediate and exponential methods. However, the intermittent light revealed a higher hardness value than the exponential technique. Again, the probable explication for this occurrence may be the total amount of energy supplied to the camphoroquinone, even at great depth. It seems that the intermittence method was able to provide a higher amount of energy at this depth, probably due to intermittence itself, where the maximum intensity is achieved at 0.55 seconds and then decreases [8].

Whilst all the photo-activation methods provided depth of cure values that fulfilled the requirements of the ISO 4049 [19], at depths of higher than 2 mm there were differences observed between the methods. These differences were probably due to the characteristics of each method such as the light intensity, exposure time and heat generated. Therefore, in spite of the P60 composite manufacturer's claims of increments of 2.5 mm, thickness of higher than 2 mm should not be used clinically due to differences in the curing light units, possibly resulting in poorly polymerized material at deeper regions of the restoration [1, 4].

It was concluded that the depth of cure is affected by the photo-activation method used, i.e., the intermittent light method provided a higher depth of cure, the continuous and exponential methods presented intermediate values without difference between them and the PAC and LED techniques demonstrated the lowest values, where LED presented a significantly lower depth of cure. Up to a depth of 2 mm, all photo-activation methods demonstrated Knoop hardness with no differences between them. At depth of 3 mm, the continuous light method provided an intermediate value with no significant difference from the other methods. The LED method presented the lowest hardness value which was significantly different from the intermittent, exponential and PAC techniques. At a depth of 4 mm, the continuous and intermittent light methods provided the greatest hardness. The continuous light method was also similar to the PAC and exponential light method, whilst the LED revealed the lowest value. At a depth of 5 mm, the continuous light method presented an intermediate value with no difference from the intermittent and exponential light method, which presented differences between them. The PAC and LED methods did not achieve a depth of 5 mm.

Avaliação da profundidade de polimerização e da dureza Knoop de um compósito odontológico fotoativado por diferentes métodos

RESUMO

O objetivo deste trabalho foi avaliar a profundidade de polimerização e a dureza Knoop do compósito restaurador P60 fotoativado por diferentes métodos. Uma matriz metálica bipartida (3mm de diâmetro X 11mm de altura) foi preenchida com o compósito e fotoativada através da luz contínua, luz exponencial, luz intermitente, plasma de xenônio – PAC ou luz emitida por diodo – LED. Após a abertura da matriz, o material não polimerizado foi removido com o auxílio de uma espátula metálica e o compósito polimerizado medido com um paquímetro digital. Então os espécimes foram incluídos e desgastados longitudinalmente e a dureza foi medida na superfície e nas profundidades de 1, 2, 3, 4 e 5mm. Os dados foram analisados por ANOVA e teste de Tukey (5%). Os resultados mostraram que a profundidade de polimerização foi maior com a luz intermitente, seguida pela luz contínua, luz exponencial, PAC e LED. Acima de 2mm, todos os métodos de fotoativação revelaram valores de dureza similares, porém diferiram a outras profundidades, onde o LED demonstrou os menores valores, seguido pelo PAC.

PALAVRAS-CHAVE - métodos de fotoativação, resina composta, profundidade de polimerização, dureza Knoop.

ACKNOWLEDGEMENTS

The authors thank CAPES for supporting this study.

REFERENCES

1. Rueggeberg FA, Caughman WF, Curtis Jr JW, Davis HC. Factors affecting cure at depths within light-activated resin composites. *Am J Dent* 1993; 6: 91-95.
2. Correr Sobrinho L, de Lima AA, Consani S, Sinhoreti MAC, Knowles JC. Influence of Curing Tip Distance on Composite Knoop Hardness Values. *Braz Dent J* 2000; 11: 11-17.
3. Lovell LG, Lu H, Elliott JE, Stansbury JW, Bowman CN. The effect of cure rate on the mechanical properties of dental resins. *Dent Mater* 2001; 17: 504-511.
4. Rueggeberg FA, Caughman WF, Curtis Jr JW. Effect of light intensity and exposure duration on cure of resin composite. *Operative Dent* 1994; 19: 26-32.
5. Venhoven BAM, de Gee AJ, Davidson CL. Polymerization contraction and conversion of light curing Bis-GMA-based methacrylate resins. *Biomaterials* 1993; 14: 871-875.
6. Uno S, Asmussen E. Marginal adaptation of a restorative resin polymerized at reduced rate. *Scand J Dent Res* 1991; 99: 440-444.
7. Feilzer AJ, Doreen LH, de Gee AJ, Davidson CL. Influence of light intensity on polymerization shrinkage and integrity of restoration-cavity interface. *Eur J Oral Sci* 1995; 103: 322-326.
8. Sakaguchi RL, Berge HX. Reduced light energy density decreases post-gel contraction while maintaining degree of conversion in composites. *J Dent* 1998;

26: 695-700.

9. Obici AC, Sinhoreti, MAC, de Goes MF, Simonides C, Sobrinho LC. Effect of the photo-activation method on polymerization shrinkage of restorative composites. *Operative Dent* 2002; 27: 192-198.
10. Tarle Z, Meniga A, Ristic, M, Sutalo J, Pichler G. The effect of the photopolymerization method on the quality of composite resin. *J Oral Rehabil* 1998; 25: 436-442.
11. Peutzfeldt A, Sahari A, Asmussen E. Characterization of resin composites polymerized with plasma arc curing units. *Dent Mater* 2000; 16: 330-336.
12. Jandt KD, Mills RW, Blackwell GB, Ashworth SH. Depth of cure and compressive strength of dental composites cured with blue light emitting diodes (LEDs). *Dent Mater* 2000; 16: 41-47.
13. Kurachi C, Tuboy AM, Magalhães DV, Bognato VS. Hardness evaluation of a dental composite polymerized with experimental LED-based devices. *Dent Mater* 2001; 17: 309-315.
14. 3M-ESPE. DentNet Masters – 3M ESPErtise SCIENTIFIC – Elipar Freelight: Cordless LED curing unit. Seefeld, 2001.
15. Harrington E, Wilson HJ. Determination of radiation energy emitted by light activation units. *J Oral Rehabil* 1995; 22: 377-385.
16. Loney RW, Prince RB. Temperature transmission of high-output light-curing units through dentin. *Operative Dent* 2001; 26: 516-520.
17. Miyazaki M, Oshida Y, Moore BK, Onose H. Effect of light exposure on fracture toughness and flexural strength of light-cured composites. *Dent Mater*

1996; 12: 328-332.

18. Baharav H, Abraham D, Cardash HS, Helft M. Effect of exposure time on the depth of polymerization of a visible light-cured composite resin. *J Oral Rehabil* 1988; 15: 167-172.
19. INTERNATIONAL ORGANIZATION FOR STANDARDIZATION. *ISO 4049 – Dentistry – Polymer-based filling, restorative and luting materials*. Switzerland, 2000. 27f..
20. Nemoto R. Effect of light wavelength on polymerization of light-cured resins. *Dent Mater J* 1997; 16: 60-73.

Table 1. Composition and batch of the P60 composite resin.

Organic Matrix	**Filler**			**Batch**
	Type	**% (vol)**	**Size (µm)**	
BisGMA, UDMA, BisEMA, camphoroquinone	Zirconia/silica	61	0.19 – 3.3	1KY 2004-04

Table 2. Means of depth of cure according to photo-activation method.

Photo-activation method	**Means [mm]**	
Intermittent light	6.70 (0.26)	a
Continuous light	6.08 (0.18)	b
Exponential light	5.88 (0.07)	b
PAC	4.67 (0.12)	c
LED	4.23 (0.21)	d

Means followed by different letters are statistically different at 5% by Tukey's test.
(   ) Standard deviation

Table 3. Means of Knoop hardness according to region and photo-activation method.

Method	**Surface**	**1mm**	**2mm**	**3mm**	**4mm**	**5mm**
Intermittent	103.65**a**	105.20**a**	104.08**a**	101.43**a**	95.30**a**	80.15**a**
	(11.28)	(7.11)	(7.82)	(5.55)	(3.52)	(4.16)
Continuous	103.65**a**	103.15**a**	99.59**a**	91.80**ab**	79.84**ab**	66.15**ab**
	(5.58)	(5.39)	(6.31)	(5.22)	(5.81)	(4.80)
Exponential	104.21**a**	105.93**a**	102.18**a**	93.85**a**	77.61 **b**	54.96 **b**
	(3.57)	(5.30)	(4.76)	(5.02)	(8.97)	(11.81)
PAC	108.22**a**	107.89**a**	101.08**a**	91.83**a**	70.04 **b**	0.00 **c**
	(5.72)	(9.32)	(5.59)	(4.48)	(6.55)	-
LED	114.88**a**	111.90**a**	101.59**a**	78.93 **b**	37.19 **c**	0.00 **c**
	(10.22)	(9.96)	(9.29)	(6.85)	(35.21)	-

Means followed by different letters, in column, are statistically different at 5% by Tukey's test.
( ) Standard Deviation.

CAPÍTULO II

Degree of Conversion of Z250 Composite Determined by Fourier Transform Infrared Spectroscopy: Comparison of Techniques, Storage Periods and Photo-activation Methods

(Dental Materials – enviado para publicação)

ABSTRACT

Objectives: The purpose of this study was to evaluate the degree of conversion (DC) of the Z250 composite, using six photo-activation methods, two storage periods and two preparation techniques of the FTIR specimens.

Methods: For the Potassium [KBr] pellet technique, the composite was placed into a metallic mold (6mm in diameter X 2mm in height), and photo-activated as follows: a) continuous light (800mW/cm^2-40s); b). exponential light (0-800mW/cm^2-40s); c). intermittent light (2s-600mW/cm^2; 2s without light-80s); d). stepped light (10s-150mW/cm^2; 30s-650mW/cm^2); e). PAC (1320mW/cm^2-3s); f). LED (100mW/cm^2-40s). The specimens were finely pulverized and pressed with KBr. The measurements were performed in specimens after 24 hours or 20 days. For the thin resin film technique, approximately 0.07g of the composite was pressed between two polyester strips using two glass slabs, photo-activated as above described and analyzed after 24 hours. For each hypothesis tested three specimens were made. A metallic siliceous window was used for the uncured material. The DC was calculated by the standard technique and submitted to ANOVA and Tukey's test (5%).

Results: Regardless the storage period and specimen preparation technique, there were no significant differences between the photo-activation methods ($p>0.05$). In addition no statistical difference was observed between the time periods used ($p>0.05$). The KBr pellet technique, however, presented higher DC values than those of the thin resin films ($p<0.05$).

Significance: The DC values were not statically affected by the use of different photo-activation methods or storage periods analyzed. However, the specimen preparation technique employed significantly affected the DC values.

Keywords: Dental materials, dental composite, degree of conversion, FTIR, photo-activation methods, depth of cure.

INTRODUCTION

The restorative composite resins are composed by a resinous matrix (organic phase), in which are dispersed sillanized fillers. This matrix is typically a mixture of at least two dimethacrylate monomers. In general, one of the monomers is relatively viscous, nominated the base monomer, whilst the other presents a low viscosity, the diluent monomer. The dimethacrylates frequently employed as base monomers in Dentistry are Bis-GMA and UDMA and TEGDMA is used as a diluent monomer. This combination results in a material with good handling properties.

The base monomers decrease polymerization shrinkage by virtue of their relatively large molecular volume and, in the case of Bis-GMA, the stiffness of the molecule results in increased elastic modulus of the polymer. Conversely, the diluent monomer improves copolymer conversion due to its greater flexibility, lower molecular volume and lower viscosity, which provides greater mobility to the system [1, 2].

Concerning to the photo-polymerizable composites, the final properties of the material depend upon light curing, becoming the choice of the ideal curing method difficult. Although optimization of the mechanical and physical properties of a composite is desirable, it is important to minimize polymerization shrinkage, in order to preserve the tooth/restoration interface integrity [3, 4].

Some researchers have found better integrity of the bond to the cavity wall of a tooth when the cure rate is reduced [3, 5]. This finding suggested an increased ability for flow, providing partial relaxation of polymerization shrinkage [6, 7]. However, a significant problem that arises when using low intensities is lower degree of conversion (DC) and a reduced curing depth [8, 9]. Thus, longer curing times [9 – 11] or post curing at higher intensity [12 – 14] can compensate this problem.

Several technologies have been suggested to initiate the polymerization reaction. The halogen lamp with a high intensity is the most common and well known [8, 11]. Some variations in technique may be performed in an attempt to reduce polymerization shrinkage, whilst maintaining the DC. Such variations include stepped light [12 – 15], exponential light [16] and intermittent light [14, 17, 18]. Another method employs the plasma arc curing (PAC) lamps, which provide a high intensity in a short time [19, 20]. Finally, the light emitting diode (LED) can also be used to initiate the photo-activation process in the composite resin [21 – 24].

Independently of the photo-activation method, the DC should be 100%. However, Bis-GMA and UDMA based dental composites exhibit incomplete conversion of double bond, ranging between 43 – 85 % [15, 19, 25 – 28], due to the complex reaction mechanism.

FTIR spectroscopy has been extensively used to determine the DC of dental composites [25, 27 – 31]. However, the techniques for FTIR analysis and the time periods required after specimen preparation are not well established. The literature reports two techniques for FTIR analyze: potassium bromide (KBr) pellet [25, 27] and thin resin films [19, 27 – 31]. Time periods reported can range from immediately after specimen preparation up to some days after [25, 27 – 33].

The purpose of this study was to evaluate the DC of the Z250 composite resin, using six photo-activation methods, two time periods (24 hours and 20 days), and two preparation techniques of the FTIR specimens (Potassium Bromide [KBr] pellet and thin resin film).

MATERIALS AND METHODS

In the present study was used the Z250 composite resin (3M, St. Paul, MN, USA), shade A3. Composition and bath are listed in Table 1. The samples analyzed by FTIR spectroscopy were prepared by two techniques: potassium bromide (KBr) pellet and thin resin films. Concerning the KBr pellet technique the FTIR analysis were performed with specimens submitted by two storage periods: 24 hours and 20 days.

For the KBr pellet technique, the composite was placed in a circular brass matrix of 6 mm in diameter and 2 mm in height. The composite was then covered with a polyester strip and pressed with a glass slab to accommodate the material into the matrix. Photo-activation was performed as follows: a) continuous light; b) exponential light; c) intermittent light; d) stepped light, e) PAC, or; f) LED. For the continuous light photo-activation method, the curing tip was positioned close to brass matrix/restorative composite. The photo-activation was performed for 40 seconds with a light intensity of 800 mW/cm^2, using an Elipar Trilight curing unit (3M-ESPE, Seefeld, D-82229, Germany). For the exponential light technique, the same curing unit was used, however, the light intensity began at zero, increasing gradually to 800 mW/cm^2 in the first 20 seconds, then maintaining this light intensity for an additional 20 seconds, with a total exposure time of 40 seconds. Curing with the intermittent light method was performed using a curing unit developed in the Dental Materials Department, School Dental of Piracicaba, UNICAMP, which provided 2 seconds of light with intensity of 600mW/cm^2 and 2 seconds without light. The total time was 80 seconds, of which 40 seconds of light exposure itself. The stepped light method was performed using a XL 2500 curing unit (3M-ESPE, Seefeld, D-82229, Germany), which provided an initial 10-second exposure to the activating light with an intensity of approximately 150 mW/cm^2, maintaining a distance of nearly 2.0 cm from the curing tip. The curing tip was then positioned close to the brass matrix/restorative composite, resulting in an increased light intensity of 650 mW/cm^2, which was maintained for an additional 30 seconds. For the PAC technique, the Apollo 95 E curing unit was used (DMD, Westlake, Village, CA 91362, USA) which, according to manufacturer's information, achieved an intensity of 1320 mW/cm^2. The light exposure time was 3 seconds. Finally, for the LED method, a LEC 470 l curing unit (M M Optics, São Carlos – SP 13560-050, Brazil) was used to photo-activate the composite, providing an intensity of 100 mW/cm^2 for 40 seconds. The light intensity of the curing units was measured with a radiometer (Curing Radiometer, model 100, Demetron/Kerr, Danbury, CT 06810, USA), with the exception of the Apollo 95 E curing unit.

After photo-activation, the polymerized composite resin was pulverized into fine powder with a hard tissue-grinding machine (Marconi, model MA590, Piracicaba – SP, Brazil). The pulverized composite was maintained in a dark room until the moment of the FTIR analyzes. Ten milligrams of the ground powder was mixed with one hundred milligrams of KBr powder salt. This mixture was placed into a pelleting device (Aldrich, Milwaukee, WI, USA) and then pressed in a hydraulic press (Carver Laboratory Press, model 3648, Wabash, St. Morris, USA) with a load of eight tons, to obtain a pellet. This pellet was then placed into a holder attachment within the spectrophotometer (Bomem, model MB-102, Quebec – Canada) for analysis. For this technique specimens were made and analyzed after two storage periods, 24 ± 1 hour and 20 days. For the thin resin film technique, approximately 0.07g of the composite was placed between two polyester strips and pressed by two plain glass slides, one either side of the material. The thin resin film (60

– 70 μm) was photo-activated by the methods described above. After 24 ± 1 hours, the thin films were separated from the polyester strips and then analyzed by the FTIR spectrophotometer. The uncured composite resin was analyzed using a metallic siliceous window. The measurements were recorded in absorbance, with a FTIR spectrometer (Bomem, model MB-102, Quebec, Canada) operating under the following conditions: 300–4000 cm^{-1} wavelength; 4 cm^{-1} resolution; 32 scans. The percentage of unreacted carbon-carbon double bonds (% C=C) was determined from the ratio of absorbance intensities of aliphatic C=C (peak at 1638 cm^{-1}) against internal standard before and after curing of the specimen: aromatic C$^{\cdots}$C (peak at 1610 cm^{-1}) and urethane N$^{\cdots}$H (peak at 1537 cm^{-1}). The degree of conversion was determined by subtracting the % C=C from 100%. All experiments were carried out in triplicate. The data were analyzed by ANOVA and the means were compared by Tukey's test (5% of significance level).

RESULTS

The results of this study are presented in Tables 2 and 3.

Table 2 reveals that there was no statistical difference between the specimens stored for 24 hours and 20 days. ($p>0.05$).

Table 3 shows that the specimens analyzed by KBr pellet technique demonstrated the highest DC values (66.25 – 59.61%) for all photo-activation methods and were statistically different than those obtained for the samples prepared using the thin resin films (52.84 – 46.9 %), according to Tukey's test ($p<0.05$).

Independently of the FTIR technique used and storage period considered, no statistically significant difference in DC values was observed for samples submitted to the different photo-activation methods utilized ($p>0.05$) (Tables 2 and 3).

DISCUSSION

The photo-activated composite resins cure by a free radical polymerization mechanism, produced when light of an appropriate wavelength is absorbed by an α-diketone, usually the camphoroquinone, and in its excited state reacts with an amine reducing agent. The free radicals formed initiate the polymerization process of the methacrylate groups of monomer molecules to produce a cross-linked polymeric matrix. Some factors such as energy density, as well as type and concentration of the monomer and initiator systems may affect the final DC of the composite resin [8, 34]. This study investigated the DC by FTIR analysis of a proprietary composite resin, Z250, using six different photo-activation methods, two techniques for specimen preparation, aiming the FTIR analysis and two storage periods after specimen preparation.

According to the results presented in Tables 2 and 3, all photo-activation methods showed no statistically significant difference between them ($p>0.05$) for DC values, independently of FTIR technique and period of storage considered. These results indicate that all methods tested were able to cure the Z250 composite of similar manner, despite the differences (e.g. energy density) between them. Several factors may be responsible for the lack of significant differences between photo-activation methods, including spectral distribution of the light emitted by the curing unit, the polymerization process itself and the nature of the monomer system.

The energy density is the product of the output of the curing unit and the time of irradiation, and is an important parameter of the curing unit [4, 19, 35]. The energy densities of the photo-activation methods tested in this study varied greatly, ranging between 3.96 - 32 J/cm^2. However, this variation did not affect, significantly, the DC values for Z250 composite. Variations in DC may be the consequence of other factors that affect the conversion of the material (spectral distribution of light, the polymerization reaction itself, monomer system and exposure time), as well as the variations in the property measurements of the output of the curing unit obtained. Mills *et al.*[36] showed that the output of the curing unit differs greatly when it is measured using a commercial dental radiometer designed for practice use or when measured with a power meter, which shows the distribution of the light output across the spectrum. Differences also exist among commercial radiometers and these measurement variations result in different density energies. In this study was employed a headpiece radiometer to obtain the light intensity (Demetron/Kerr).

Camphoroquinone presents an absorption peak at a wavelength of 468 nm. Hence, the closer the wavelength of the curing unit to this absorption peak, the greater its ability to active camphoroquinone and, thus, to initiate the polymerization process. Although LED devices usually achieve lower light intensity (and lower energy density) than halogen curing units, the wavelength peak of the LED curing unit is 466 nm [21], i.e. very close to the camphoroquinone absorption peak. According to Nemoto [37], the narrow wavelength spectrum emitted by LED devices lies within the 450 – 490 nm range, a range which appropriately polymerizes the composites use camphoroquinone as the initiator. Thus, the LED light curing device achieves an almost ideal light source emission.

PAC units are characterized by a very high output (approximately 1320 mW/cm^2, according to manufacturer's information) in a rather narrow range of wavelengths around 470 nm, however, the exposure time is just a few seconds. This results in lower energy density, however the peak absorption wavelength is near to that of camphoroquinone.

Although the LED and PAC curing units provided the lowest energy densities (4 J/cm^2 and 3.96 J/cm^2, respectively), the DC values were not statistically different to those of the halogen light sources. This finding may be explained by the wavelength peak, emitted by these curing units, which active camphoroquinone more efficiently (at approximately 468 nm). The halogen curing units exhibit higher energy density, however, they also present a wide wavelength range of between 380 – 510 nm, with a wavelength peak at 484 nm [21]. Yet, the halogen lamps generate heat, becoming extremely hot (near to 400ºC), resulting in a 70% loss of output. However, the light intensity decreases to 10% when a cut-off filter is used to obtain the optimal wavelength range required for curing composite resins. Thus, the final ratio of available wavelength range for the polymerization process is only 1% of the total energy output of the halogen lamps [21]. Despite these variations in curing units and photo-activation methods no significant differences in DC values were observed, as it was already mentioned.

The cross-linked nature of the composite resins makes the photo-polymerization of the dimethacrylate monomers a complex process. Different behaviors are exhibited during the reaction, such as autoacceleration, autodeceleration, termination processes controlled by reaction diffusion, formation of structural heterogeneities (microgels) and limiting functional groups conversion. Firstly, monomer molecules are incorporated into chains as units containing pendent bonds. Further propagation can proceed by addition of the next molecule (growing polymeric chain), by an intramolecular attack of the radical site on the pendent double bond (primary cyclization) or by an intermolecular linkage (cross-linking) that leads to network formation. The apparent reactivity of pendent double bonds on the same chain is initially enhanced as compared to the monomeric double bond due to their larger concentration near the radical site. This leads to an extensive primary cyclization reaction, which creates microgels, leading to heterogeneity in the polymer network [26, 38, 39]. Cyclization will promote higher local conversion since it does not decrease the mobility of the system as much as cross-linking. However, cyclization can lead to a reduction in the effective cross-linking density, reducing the mechanical and physical properties [26, 38]. This density reduction occurs due to many of the uncured pendent double bonds becoming entrapped in the microgel regions, making further reaction inaccessible [39]. Cyclization can proceed if chain flexibility allows for ring formation. On the other hand, a very stiff or long bridge between two unsaturations will prevent intramolecular cross-linking [39]. Network formation causes the reaction diffusion mechanism to be more pronounced and setting in at lower conversions. All these phenomena limit final conversion of double bonds to well below 100%.

In addition, network formation highly decreases the mobility of macroradicals from the very beginning of the polymerization, which is the main cause for another phenomenon: the onset of autoacceleration (gel effect) in the initial stages of the polymerization. Autoacceleration causes a rapid increase in the polymerization rate despite monomer consumption. At higher conversions, the gel effect appears to stop and the polymerization rate reaches its maximum value, then, the reaction proceeds with a decreasing rate reaching limited conversion due to vitrification. In general, for dimethacrylate monomers, the polymerization rate reaches its maximum between 20 and 40% conversion [39]. The decrease in the polymerization rate after its maximum polymerization rate may result from factors, such as a reduction in monomer concentration, difficulties in monomer diffusion through the solidifying medium, reduced mobility of uncured pendant double bonds and decreasing dissociation efficiency of the photo-initiator in the viscous medium [39]. At higher conversions, however, both propagation and termination processes become diffusion controlled, leading to a rapid drop in the rate of reaction, the autodeceleration. Thus, the final conversion of the polymerization is controlled by the diffusion limitations of the reacting medium and not by the amount of uncured monomer or pendant double bonds in the system [39, 40].

According to Lovell *et al.* [40], the nature of the monomer molecule plays an important role in the final DC values. The viscosity of the system, when BisGMA is homo-polymerized, is so high that autoacceleration is immediate, leading to final conversion values of below 30%. The incorporation of monomers to reduce the viscosity of the system will strongly contribute to the achievement of higher DC values.

The high viscosity of the BisGMA monomer (1200 Pas at 20ºC) is the consequence of strong intermolecular hydrogen bonding. This occurs because the hydroxyl groups are positioned diametrically across the rigid bisphenol core structure of the molecule, becoming them unable to interact intramolecularly, resulting in intermolecular hydrogen bonding [41]. The stiffness of BisGMA is also related to the bulky, aromatic groups of the central part of the molecule, further inhibiting rotation about the bonds [1]. This stiffness limits early cyclization as well as decreasing the cyclization reactions in general [38]. A significant reduction in intermolecular hydrogen bonding can be obtained with some derivatives of BisGMA, such as the BisEMA monomer, which is a non-hydroxylated homologous monomer of BisGMA [1]. This reduction in the intermolecular hydrogen bonding provides the BisEMA monomer with more mobility, since it presents a rigid core due to the aromatic groups.

Another group of monomers used in commercial composite resins is the urethane dimethacrylates (UDMA). These monomers have molecular weights similar to that of BisGMA, but are less viscous due to a greater flexibility of the urethane linkage [1]. The viscosity of the UDMA monomer is 23.1 Pas at 20ºC [41]. Stansbury and Dickens [2] found higher DC values in UDMA-based resins when compared to BisGMA-based resins for a given irradiation interval. This can be explained due to the fact that the UDMA/TEGDMA resins, used in that study, reach a higher maximum polymerization rate and the maximum rate occurs at a later stage of conversion than in BisGMA/TEGDMA resins. The higher final DC for UDMA-based resins is related to the lower viscosity in the uncured stage when compared to the viscosity of the BisGMA [2].

BisGMA, BisEMA and UDMA compose the organic matrix of the Z250 composite resin used in this study. All these monomers present high molecular weight, but different mobilities, providing satisfactory DC values. The results found in this study are in agreement with those mentioned in the literature [15, 19, 25 – 28]. Limited final conversion is a phenomenon inherent of the polymerization process, as mentioned earlier. Although there are great differences among the photo-activation methods used, the irradiance supplied was sufficient to reach the conversion characteristic for these dimethacrylate monomer systems.

Photo-polymerization of multifunctional monomers exhibits a marked post-curing effect. After irradiation has been interrupted, the photo-induced reactions continue to proceed over a time scale of seconds, minutes or even hours. The extent of the dark reactions depends on the amount of initiating radicals generated by the irradiation step, storage temperature, as well on the reactivity of the polymerizable function [39, 40].

Table 2 shows that there was no statistical difference between two periods of storage that the samples were submitted, 24 hours and 20 days ($p>0.05$). During the storage time, the specimens were maintained at room temperature and in a dark ambient to avoid further photo-activation. Thus, the absence of differences between the storage periods considered may be explained due to atmospheric oxygen, which reduces the extent of post-polymerization at room temperature due to the scavenging of carbon free radicals by diffusing oxygen with the formation of peroxy and hydroperoxy radicals. These radicals are much less reactive towards double bond, than those of carbon, thereby reducing the efficiency of initiation and post-polymerization [39].

The results presented in Table 3 reveal that there was a significant difference between the two FTIR analysis techniques. The use of KBr pellet technique lead to higher DC values than those found when the thin resin film technique was used ($p<0.05$). Two probable explanations for this are: (1) the negative effect of oxygen inhibition on the polymer surface which leads to the scavenging of the free radicals in this region, which probably occurs in a more intensive way on the surface of the resin prepared as thin film and (2) the exothermic nature of the polymerization reaction, what possibly caused a higher localized heating in the composite resin tested *via* the KBr pellet technique by virtue of higher quantity of material polymerizing at the same time [27, 39, 42, 43]. The temperature rise during the polymerization provides more mobility to the components of reaction medium, causing higher conversions, as well reducing oxygen inhibition due to a decrease in the solubility of oxygen in the polymerizing medium [39, 40].

Hence, it was possible to determine that the DC of the Z250 composite resin was not affected by photo-activation methods used or by the storage periods considered. The FTIR analysis technique used, however, showed significant differences in DC values.

ACKNOWLEDGEMENTS

The authors thank CAPES for supporting this study.

REFERENCES

1. Peutzfeldt A. Resin composites in Dentistry: the monomers systems. *Eur J Oral Sci* 1997; 105:97-116.
2. Stansbury JW and Dickens SH. Network formation and compositional drift during photo-initiated copolymerization of dimethacrylates monomers. *Polymer* 2001; 42:6363–6369.
3. Feilzer AJ, Dooren LH, de Gee AJ and Davidson CL. Influence of light intensity on polymerization shrinkage and integrity of restorative-cavity interface. *Eur J Oral Sci* 1995; 103:322–326.
4. Sakaguchi RL and Berge HX. Reduced light energy density decreases post-gel contraction while maintaining degree of conversion in composites. *J Dent* 1998; 26:695-700.
5. Uno S and Asmussen E. Marginal adaptation of a restorative resin polymerized at reduced rate. *Scand J Dent Res* 1991; 99:440-444.
6. Davidson CL and de Gee AJ. Relaxation of polymerization contraction stresses by flow in dental composites. *J Dent Res* 1984; 63:146-148.

7. Feilzer AJ, de Gee AJ and Davidson CL. Quantitative determination of stress reduction by flow in composite restorations. *Dent Mater* 1990; 6:167-171.

8. Yearn JA. Factors affecting cure of visible light activated composites. *Inter Dent J* 1985; 35:218–225.

9. Rueggeberg FA, Caughman WF, Curtis Jr JW and Davis HC. Factors affecting cure at depth within light-activated resin composites. *Am J Dent* 1993; 6:91-95.

10 Baharav H, Abrahan D, Cardash HS and Helft M. Effect of exposure time on the depth of polymerization of the visible light-cured composite resin *J Oral Rehabil* 1988; 15:167-172.

11 Rueggeberg FA, Caughman WF and Curtis Jr JW. Effect of light intensity and exposure duration on cure of resin composite. *Operat Dent* 1994; 19:26-32.

12 Koran P and Kürschner R. Effect of sequential versus continuous irradiation of light-cured resin composite on shrinkage, viscosity, adhesion, and degree of polymerization. *Am J Dent* 1998; 11:17-22.

13 Burgess JO, Goes MF, Walker R and Ripps AH. An evaluation of four light-curing units comparing soft and hard curing. *Pract Period Aesthc Dent* 1999; 11:125-132.

14 Obici AC, Sinhoreti MAC, Goes MF, Consani S and Sobrinho LC. Effect of photo-activation method on polymerization shrinkage of restorative composites. *Operat Dent* 2002; 27:192-198.

15 Bouschicher MR, Rueggeberg FA and Boyer D. Effect of stepped light intensity on polymerization force and conversion in a photo-activated composite. *J Esthet Dent* 2000; 12:23-32.

16 Caldas DB, de Almeida JB, Correr-Sobrinho L, Sinhoreti MAC and Consani S. Influence of curing tip distance on resin composite knoop hardness number, using three different light curing units. *Operat Dent.* 2003; 28:315-320.

17 Meniga A, Tarle Z, Ristic M, Sutalo and Pichler G. Pulsed blue laser curing of hybrid composite resins. *Biomaterials* 1997; 18:1349-1354.

18 Tarle Z, Meniga A, Ristic M, Sutalo J, Pichler and Davidson CL. The effect of photopolymerization method on the quality of composite resin. *J Oral Rehabil* 1998; 25:436-442.

19 Peutzfeldt A, Sahari A and Asmussen E. Characterization of resin composites polymerized with plasm arc curing units. *Dent Mater* 2000; 16:330-336.

20 Hofmann N, Hugo B, Schubert K and Klaiber B. Comparison between a plasma arc light source and conventional halogen curing units regarding flexural strength, modulus, and hardness of photoactivated resin composites. *Clin Oral Invest* 2000; 4:140-147.

21 Fujibayashi K, Ishimaru K, Takahashi N and Kihno A. Newly developed curing unit using blue light-emitting diodes. *Dentistry in Japan* 1998; 34:49-53.

22 Jandt KD, Mills RW, Blackwell GB and Ashworth SH. Depth of cure and compressive strength of dental composites cured with blue light emitting diodes (LEDs). *Dent Mater* 2000; 16:41-47.

23 Stahl F, Ashworth SH, Jandt KD and Mills RW. Light-emitting diode (LED) polymerization of dental composite: flexural properties and polymerization potential. *Biomaterials* 2000; 21:1379-1385.

24 Kurachi C, Tuboy AM, Magalhães DV and Bognato VS. Hardness evaluation of a

dental composite polymerized with experimental LED-based devices. *Dent Mater* 2001; 17:309-315.

25 Imazato S, McCabe JF, Tarumi H, Ehara A and Ebisu S. Degree of conversion of composites measured by DTA and FTIR. *Dent Mater* 2001; 17:178-183.

26 Ruyter IE and Svendsen SA. Remaining methacrytate groups in composite restorative materials. *Acta Odontol Scand.* 1978; 36:75-82.

27 Ferracane JL and Greener EH. Fourier Transform Infrared analysis of degree of polymerization in unfilled resins – methods comparison. *J Dent Res* 1984; 63:1093-1095.

28 Guerra RM, Duran I and Ortiz P. FTIR monomer conversion analysis of UDMA-based dental resins. *J Oral Rehabil* 1996; 23:632-637.

29 Chung H and Greener EH. Degree of conversion of seven visible light-cured posterior composites. *J Oral Rehabil.* 1988; 15:555-560.

30 Rueggeberg FA and Craig RG. Correlation of parameters used to estimate monomer conversion in a light-cured composite. *J Dent Res* 1988; 67:932-937.

31 Silikas N, Eliades G and Watts DC. Light intensity effects on resin-composite degree of conversion and shrinkage strain. *Dent Mater* 2000; 16:292-296.

32 Rueggeberg FA, Caughman WF and Chan DCN. Novel approach to measure composite conversion kinetics during exposure with stepped or continuous light-curing. *J Esthet Dent.* 1999; 11:197-205.

33 Stansbury JW and Dickens SH. Determination of double bond conversion in dental resins by near infrared spectroscopy. *Dent Mater* 2001; 17:71-79.

34 Venhoven BAM, de Gee AJ and Davidson CL. Light initiation of dental resin:

dynamics of the polymerization. *Biomaterials* 1996; 17:2313-2318.

35 Miyazaki M, Oshida Y, Moore BK and Onose H. Effect of light exposure on fracture toughness and flexural strength of light-cured composites. *Dent Mater* 1996; 12:328-332.

36 Mills RW, Jandt KD and Ashworth SH. Dental composite depth cure with halogen and blue light emitting diode technology. *Brit Dent J* 1999; 186:388-391.

37 Nemoto R. Effect of wavelength on polymerization of light-cured resins. *Dent Mater J* 1998; 16:60-73.

38 Elliott JE, Lovell LG and Bowman CN. Primary cyclization in the polymerization of BisGMA and TEGDMA: a modeling approach to understanding the cure of dental resins. *Dent Mater* 2001; 17:271-279.

39 Andrzejewska E. Photopolymerization kinetics of multifunctional monomers. *Prog Polymer Sci* 2001; 26:605-665.

40 Lovell LG, Newman SM and Bowman CN. The effects of light intensity, temperature, and comonomer composition on the polymerization behavior of dimethacrylate dental resins. *J Dent Res* 1999; 78:1469-1476.

41 Davy KWM, Kalachandra S. Padain MS and Braden M. Relationship between composite matrix molecular structure and properties. *Biomaterials* 1998; 19: 2007-2014.

42 Reinhardt KJ. [Unconverted double bonds and interface phenomena in composite materials] *Dtsch Zahnartl Z* 1991; 46: 204–208. (Article in German)

43 Shortall AC and Harrington E. Temperature rise during polymerization of light-activated resin composites. *J Oral Rehabil* 1998; 25:908-913.

Table 1. Composition of organic matrix and filler of the Z250 composite resin.

Organic Matrix	Filler			Batch
	Type	% (vol)	Size (µm)	
Bisphenol-glycidyl methacrylate (BisGMA), urethanethyl dimethacrylate (UDMA) and Bisphenol-polyethylene glycol dimethacrylate (BisEMA). Camphoroquinone (initiator)	Zirconia/silica	60	0.19 – 3.3	1NL 2004-08

Table 2. Means of DC according to analyzed storage periods and photo-activation methods.

Photo-activation method	DC after 24 hours [%]				DC after 20 days [%]			
Continuous light	66.25	(2.55)	a	A	62.64	(1.98)	a	A
Intermittent light	63.74	(2.37)	a	A	59.14	(5.24)	a	A
Stepped light	62.94	(4.92)	a	A	62.17	(6.26)	a	A
LED	62.14	(10.15)	a	A	58.05	(3.5)	a	A
PAC	60.01	(1.13)	a	A	59.64	(2.14)	a	A
Exponential light	59.61	(5.85)	a	A	60.37	(1.79)	a	A

Means followed by same small letters are not statistically different in columns at the 5% significance level, by Tukey's test.

Means followed by same capital letters are not statistically different in row at the 5% significance level, by Tukey's test.

(   ) Standard deviation.

Table 3. Means of DC according to FTIR technique analyzed and photo-activation methods used.

Photo-activation method	**KBr pellet [%]**				**Thin film [%]**			
Continuous light	66.25	(2.55)	a	A	52.84	(4.32)	b	A
Intermittent light	63.74	(2.37)	a	A	46.9	(2.41)	b	A
Stepped light	62.94	(4.92)	a	A	59.5	(2.3)	b	A
LED	62.14	(10.15)	a	A	51.07	(4.23)	b	A
PAC	60.01	(1.13)	a	A	49.7	(4.23)	b	A
Exponential light	59.61	(5.85)	a	A	47.89	(3.67)	b	A

Means followed by same small letters are not statistically different in row at the 5% significance level, by Tukey's test.

Means followed by same capital letters are not statistically different in columns at the 5% significance level, by Tukey's test.

( ) Standard deviation.

CAPÍTULO III

Evaluation of Degree of Conversion by FTIR at different depths using six photo-activation methods

(Operative Dentistry – enviado para publicação)

CLINICAL RELEVANCE

Different photo-activation methods may result in dissimilar degree of conversion at deeper regions from the surface for a same material. Hence, thicknesses higher than 2mm (or even 1mm) are not recommended.

SUMMARY

The purpose of this study was to evaluate the degree of conversion (DC), by FTIR spectroscopy, of the Z250 composite resin at different depths, using six photo-activation methods. The material was placed into a silicon matrix (7mm in diameter X 5mm in height) and then covered with a polyester strip and pressed with a glass slab. Photo-activation was performed as follows: a) continuous light (800mW/cm^2-40s); b) exponential light (0-800mW/cm^2-40s); c) intermittent light (2s-600mW/cm^2; 2s without light-80s); d) stepped light (10s-150mW/cm^2; 30s-650mW/cm^2); e) PAC (1320mW/cm^2-3s); f) LED (350mW/cm^2-40s). The cured composite cylinders were transversally cut into slices with thickness of 300μm obtained from the cylinder surface and in the regions corresponding to 1, 2, 3, 4 and 5mm in depth. Each material disc was finely pulverized and, after 24 ± 1 hours, pellets were made with KBr and analyzed by FTIR. A metallic siliceous window was used for the uncured material. The DC was calculated by standard technique and then submitted to ANOVA and Tukey's test (5%). Results demonstrated that for the surface and depths of 1 and 2 mm, the methods were not statistically different. At 3 and 4 mm, the LED, intermittent, stepped, exponential and continuous light techniques presented the highest DCs, whilst PAC attained the lowest (although only statistically different from LED). At 5 mm, there was no difference between the methods, with the exception of PAC,

which did not reach this depth. The LED technique presented similar DC values at the surface and depths of 1, 2 and 3 mm, without significant difference between them. Values obtained at 4 mm were not statistically from those obtained at other depths, with the exception of 1 mm. The DC obtained at 5 mm with the LED technique was statistically different from those obtained at the depths of 1, 2 and 3 mm. For the continuous light method, the highest values were obtained at the surface and at 1 and 2 mm, with no significant difference between them. The DC at the surface also was similar to those at 3 and 4 mm, differing only from that at 5 mm, which presented the lowest value and was not different from that at 4 mm. The intermittent, stepped and exponential light methods showed similar results. The highest DC values for these methods were found at the surface, and at 1, 2 and 3 mm without significant difference. At 4 mm, the values were not statistically different from those at the other depths, with the exception of 1 and 2 mm. PAC attained the highest DC at the surface and at 1 mm with no statistical difference. In addition, there were no differences between the surface and 2mm, however the DC at 2mm was lower than that at 1mm. At 3mm, the DC values were statistically similar to those of 2 and 4mm, although the 2mm value was higher than that of 4mm. For this technique, the composite did not polymerize at a depth of 5mm. It was concluded that the method of photo-activation affects the DC in the deeper regions of the material.

INTRODUCTION

Visible light-activated composite resins were introduced in Dentistry as direct restorative materials over 25 years ago, replacing with superiority their antecessors. However, several factors can limit depth of cure and the final degree of conversion (DC) of the composite. Some variations are related to the composition of the material, whilst others are related to the light source. With respect to the composite, factors such as resin formulation, type and concentration of catalyst system, shade and translucency of organic matrix, type and loading of filler may exert an important effect upon the final depth of cure as well as the DC at each corresponding depth (Yearn, 1985; Rueggeberg & others, 1993; Kawaguchi, Fukushima & Miyazaki, 1994). Type, size, quantity and refraction index of the fillers, and shade and translucency of resin may cause a light attenuation across the bulk of the material, limiting the depth of cure (Yearn, 1985; Kawaguchi & others, 1994), and consequently, the DC values at deeper regions. Conversely, characteristics related to the light source, such as light intensity, exposure time, correct wavelength, spectral distribution and energy density may also alter the final properties of the material (Yearn, 1985; Rueggeberg & others, 1993, Rueggeberg, Caughman & Curtis Jr, 1994).

According to several researchers, the DC is an important parameter to determine the final physical, mechanical and biological properties of the composite resin (Ruyter & Svendsen, 1978; Asmussen, 1982; Pearson & Longman, 1989; Peutzfeldt & Asmussen, 2000; Lovell & others, 2001). Higher DC values may be obtained when high light intensity is applied (Yearn, 1985; Rueggeberg & others, 1994; Lovell, Newman & Bowman, 1999). However, higher light intensity also correlates with increased shrinkage polymerization, which may result in gap formation around the margins of the restoration due to stress produced in these areas, in turn, disrupting the bond of the composite to dental tissues (Unterbrink & Muessner, 1995; Feilzer & others, 1995; Silikas, Eliades & Watts, 2000). Efforts to maximize one side of the balance usually result in compromising the other.

In an attempt to maintain the DC values and reduce the polymerization shrinkage several photo-polymerization techniques have been suggested to initiate the material cure reactions. Traditionally, halogen lamps are used with high intensity (Yearn, 1985;

Rueggeberg & others, 1994; Silikas & others, 2000) and are nominated as the continuous light method. These lamps, however, can also be applied in different manners. For example, stepped light employs an initial low intensity followed by a higher intensity (Unterbrink & Muessner, 1995; Feilzer & others, 1995; Silikas & others, 2000; Obici & others, 2002). Exponential light, begins zero intensity and increases gradually to higher intensity (Caldas & others, 2003; Obici & others, 2003) and intermittent light that alternates light and darkness (Meniga & others, 1997; Tarle & others, 1998; Obici & others, 2002). Another method employs plasma arc curing (PAC), which provides a high intensity in a short time (Peutzfeldt, Sahari & Asmussen, 2000; Hofmann & others, 2000), and finally, the light emitting diode (LED) that supplies a lower intensity, but with a range wavelength, which is more specific for camphoroquinone (Fujibayashi & others, 1998; Jandt & others, 2000; Stahl & others, 2000; Kurachi & others, 2001). It is essential that adequate polymerization results from any curing method used, especially in deeper regions of the bulk material.

The aim of this study was to evaluate the DC, by FTIR spectroscopy, at different depths, using six photo-activation methods.

MATERIAL AND METHODS

For this study, the Filtek Z250 composite resin (3M, St. Paul, MN, USA), shade A3, was used, the composition and bath of which are listed in Table 1. The evaluation of degree of conversion was performed using a Potassium Bromide (KBr) pellet analyzed by FTIR spectroscopy.

The composite resin was placed into a cylindrical silicon matrix of 7 mm in diameter and 5 mm in height. The material was then covered with a polyester strip and pressed with a glass slab to accommodate the composite into the matrix. Photo-activation was performed as follows with: a) continuous light; b) exponential light; c) intermittent light; d) stepped light; e) PAC, or; f) LED.

For the continuous light photo-activation method, the curing tip was positioned close to brass matrix/restorative composite. The photo-activation was performed for 40 seconds with a light intensity of 800 mW/cm^2, using an Elipar Trilight curing unit (3M-ESPE, Seefeld, D-82229, Germany). For the exponential light technique, the same curing unit was used, however, the light intensity began at zero, increasing gradually to 800 mW/cm^2 in the first 20 seconds, then maintaining this light intensity for an additional 20 seconds, with a total exposure time of 40 seconds. Curing with the intermittent light method was performed using a curing unit developed in the Dental Materials Department, School Dental of Piracicaba, UNICAMP, which provided 2 seconds of light with intensity of 600mW/cm^2 and 2 seconds without light. The total time was 80 seconds, of which 40 seconds of light exposure itself. The stepped light method was performed using a XL 2500 curing unit (3M-ESPE, Seefeld, D-82229, Germany), which provided an initial 10-second exposure to the activating light with an intensity of approximately 150 mW/cm^2, maintaining a distance of nearly 2.0 cm from the curing tip. The curing tip was then positioned close to the brass matrix/restorative composite, resulting in an increased light intensity of 650 mW/cm^2, which was maintained for an additional 30 seconds. For the PAC technique, the Apollo 95 E curing unit was used (DMD, Westlake, Village, CA 91362, USA) which, according to manufacturer's information, achieved an intensity of 1320 mW/cm^2. The light exposure time was 3 seconds. Finally, for the LED method, an Elipar Freelight curing unit (3M-ESPE, Seefeld, D-82229, Germany) was used to photo-activate the composite, providing an intensity of 350 mW/cm^2 for 40 seconds. The light intensity of the curing units was measured with a radiometer (Curing Radiometer, model 100, Demetron/Kerr, Danbury, CT 06810, USA).

After photo-activation, the cylinder of the cured composite was transversally cut, according to depths: surface, 1, 2, 3, 4 and 5 mm. Each material disc presented a thickness of approximately 300μm (representing each depth) and was finely pulverized with a hard tissue-grinding machine (Marconi, model MA590, Piracicaba – SP, Brazil). The pulverized composite was maintained in a dark container for 24 ± 1 hour. 10 mg of the ground powder was then mixed with 100 mg of KBr powder salt. This mixture was placed into a pelleting device (Aldrich, Milwaukee, WI, USA) and pressed in a hydraulic press (Carver Laboratory Press, model 3648, Wabash, St. Morris, USA) with a load of 8 tons, to obtain a pellet. This pellet was then placed into a holder attachment within the spectrophotometer (Bomem, model MB-102, Quebec – Canada) for analysis by the infrared beam. The uncured composite resin was analyzed using a metallic siliceous window.

The measurements were recorded in absorbance, with a FTIR spectrometer (Bomem, model MB-102, Quebec, Canada) operating under the following conditions: 300–4000 cm^{-1} wavelength; 4 cm^{-1} resolution; 32 scans. The percentage of unreacted carbon-carbon double bonds (% C=C) was determined from the ratio of absorbance intensities of aliphatic C=C (peak at 1638 cm^{-1}) against internal standard before and after curing of the specimen: aromatic $C \cdots C$ (peak at 1610 cm^{-1}) and urethane $N \cdots H$ (peak at 1537 cm^{-1}). The degree of conversion was determined by subtracting the % C=C from 100%.

All experiments were carried out in triplicate. The data were analyzed by two-way ANOVA and the means were compared by Tukey's test (5% of significance level).

RESULTS

The results of this study are presented in Table 2. The DC values at the surface and at 1 and 2mm for all photo-activation methods showed no statistical difference between them ($p>0.05$). At the depths of 3 and 4mm, the highest values of DC was found with LED, intermittent light, stepped light, exponential light and continuous light without significant difference between them ($p>0.05$). The intermittent light, stepped light, exponential light, continuous light and PAC methods also showed no significant difference between them ($p>0.05$). However, the LED technique revealed statistically higher DC values than the PAC method ($p<0.05$). All photo-activation methods revealed no significant differences between them at a depth of 5 mm ($p>0.05$), with the exception of the PAC technique, which did not reach this depth ($p<0.05$).

When each photo-activation method was analyzed separately, the results showed that the continuous light presented the highest DC values at the surface and at the depths of 1 and 2mm without significant difference between them ($p>0.05$). In addition, there was no statistical difference between the DCs at the surface, 2 and 3mm ($p>0.05$), however, at a depth of 1mm the DC was significantly higher than that at 3mm ($p<0.05$). Furthermore, there were no differences between DCs at the surface, 3 and 4mm ($p>0.05$), however at 4mm the DC was lower than at 1 and 2mm ($p<0.05$). The lowest DC values were obtained at a depth of 5mm, which were not statistically different from those obtained at 4mm ($p>0.05$), however they were significantly different from those at the other depths ($p<0.05$).

The intermittent light, stepped light and exponential light techniques demonstrated the highest values at depths of surface, 1, 2 and 3mm without significant difference between them ($p>0.05$). At a depth of 4mm, an intermediate DC value was obtained, which was not significantly different from those at the surface, 3 and 5mm ($p>0.05$), but differed to those at 1 and 2mm ($p<0.05$). The DC values at a depth of 5mm were significantly lower than those at the surface, 1, 2 and 3mm ($p<0.05$).

For the LED, results demonstrated that the highest values were obtained at the surface, and at 1, 2 and 3mm without significant differences ($p>0.05$). Furthermore, there were no differences between the surface, 2, 3 and 4mm ($p>0.05$), but a depth of 4mm the DC value was lower than that at 1mm ($p<0.05$). At 4 and 5mm, no significant difference was observed ($p>0.05$), however, at 5mm the DC differed from the surface, 1, 2 and 3mm values ($p<0.05$).

Finally, the PAC method demonstrated the highest values at surface and 1mm without statistical difference ($p>0.05$). There were no differences between surface and 2mm ($p>0.05$), but at a depth of 2mm the DC was lower than at 1mm ($p<0.05$). At 3mm, the DC values were statistically similar to those of 2 and 4mm ($p>0.05$), however at 2mm the DC was higher than at 4mm ($p<0.05$). For this technique, the composite did not polymerize at a depth of 5mm.

DISCUSSION

When light of an appropriate wavelength reaches the composite resins, photo-activation initiates the polymerization of the methacrylate groups of monomer molecules to produce a densely cross-linked polymeric matrix. The light emitted from a light-curing tip must be able to achieve and adequately polymerize deeper regions of the material. However, as the light passes through the composite, it is absorbed and scattered, attenuating the intensity and reducing the effectiveness of the light to initiate the polymerization in deeper regions (Rueggeberg & others, 1993; Kawaguchi & others, 1994; Rueggeberg & others, 1994; Obici & others, 2003). Adequate polymerization is a crucial factor in obtaining optimal physical, mechanical and biological properties (Ruyter & Svendsen, 1978; Asmussen, 1982; Pearson & Longman, 1989; Peutzfeldt & Asmussen, 2000; Lovell & others, 2001), making the description of the properties of different light sources clinically very important. Hence, the present study evaluated the DC of Z250 composite resin at different depths from the surface, by FTIR spectroscopy analysis, following six different photo-activation methods.

According to the results presented in Table 2, the DC values at depths of surface, 1 and 2 mm showed no significant difference between photo-activation methods. At a depth of 3 and 4 mm, the highest values were obtained for LED, followed by intermittent light, stepped light, exponential light and continuous light without statistical differences between them. At these depths, the lowest value was found for PAC, which differed only from the LED technique. At a depth of 5 mm, all photo-activation methods demonstrated no significant difference between them, with exception of the PAC, which did not reach this depth.

Several factors concerning the light source may affect the DC of the composites, such as: energy density, spectral distribution of light emitted by a curing unit and choice of correct wavelength (Fujibayashi & others, 1998; Nemoto, 1997; Mills, Jandt & Ashworth, 1999; Peutzfeldt & others, 2000). In addition, the characteristics of the material for light attenuation will also exert influence on the depth of cure and, consequently, on the DC at deeper regions (Baharav & others, 1988; Rueggeberg & others, 1993; Kawaguchi & others, 1994; Rueggeberg & others, 1994). As the composite resin used was the same for all hypotheses tested, only the characteristics of each light source will be considered in this study.

Although there was no statistical difference between DC values at the surface and at 1 mm, the DC at the surface was slightly lower than those at a depth of 1mm for all photo-activation methods. This occurrence is probably the consequence of the negative effect of oxygen inhibition on the polymer surface, which leads to the scavenging of free radicals in this region, thereby reducing the efficiency of initiation and decreasing the final DC (Andrzejewska, 2001). However, in a clinical situation, during the finishing and polishing procedures, this layer would be removed, exposing the inner part of material, which was polymerized in greater extension (Reinhardt, 1991).

The energy density is the product of the light output of the curing unit and the time of irradiation (Peutzfeldt & others, 2000). The results of the present study showed that in the regions nearer to the surface (surface, 1 and 2 mm), since the light curing units that emitting lower energy density were able to cure the Z250 composite, without significant difference. This may be explained by the fact that the light did not yet suffer significant reduction in intensity due to the light attenuation caused by the material.

Conversely, in deeper regions from the surface irradiated, the energy density exerted a great influence on DC values. The lowest value was found for the PAC method, which also presents the lowest energy density (3.96 J/cm^2) of all the photo-activation methods. However, the DCs obtained for the PAC method did not differ significantly from those of the other methods, with exception of the LED technique. The energy density of these methods, employing halogen lamps, ranged around 20 – 32 J/cm^2, whilst the LED supplied 14 J/cm^2. This signifies that other properties of the light source influenced the polymerization process in deeper regions, such as spectral distribution of light and appropriate wavelength emitted by the curing unit.

Although statistically some values are similar, it is possible to evaluate the tendency of DC towards the increase of depth from the surface, as it is shown in Figure 1, which considerate all photo-activation methods used in the present work. According to Fig. 1, and the previous discussion, it can be observed a tendency of the DC decreasing, when the distance from surface increase, for all the photo-activation method used. However, while the samples submitted to intermittent, exponential, continuous, and stepped lights showed a similar behavior, those submitted to LED and PAC can be considered apart from others. Samples submitted to LED showed the softer DC diminution, when compared to the others, whilst those submitted to PAC showed the stronger DC decreases, as the distance from the surface increase.

The photo initiator present in the Z250 composite is camphoroquinone (Table 1), which exhibits an absorption peak at a wavelength of 468 nm (Fujibayashi & others, 1998; Nemoto, 1997). Thus, the closer the wavelength of the curing unit to this absorption peak, the greater its ability to activate the camphoroquinone. Although the photo-activation methods that employ halogen lamps exhibit higher energy density, they also present a wide wavelength range of between 380 – 510 nm, with a wavelength peak at 484 nm (Fujibayashi & others, 1998). The LED presents a narrow wavelength spectrum that lies within 450 – 490 nm (Nemoto, 1997), and a wavelength peak at 466 nm (Fujibayashi & others, 1998). Hence, at deeper regions, where significant light attenuation occurs, the curing unit that emits light at more specific wavelength and with high enough intensity will provide higher DC in these regions. This could to explain the results obtained in the present study.

When each photo-activation method was analyzed, individually, for each depth of cure, the results showed that the LED presented similar DC values at the surface and at 1, 2 and 3 mm without significant difference between them. At 4 mm, the values were not statistically different from the other depths, with the exception of at 1 mm. At 5 mm, the DC was statistically different from the DCs of the surface and at 1, 2 and 3 mm. For continuous light, the highest values were obtained at the surface and at 1 and 2 mm with no significant difference between them. The DC at the surface was also similar those at 3 and 4 mm, differing only from that at 5 mm, which demonstrated the lowest value and was no different from 4 mm. The intermittent, stepped and exponential light methods showed similar results. The higher DC values were found at the surface, 1, 2 and 3 mm without significant difference. At 4 mm, the values were not statistically different from those at the other depths, with the exception of 1 and 2 mm. PAC showed the highest DC at the surface and 1 mm with no statistical difference. In addition, there were no differences between the surface and 2mm, but at the depth of 2mm the DC was lower than at 1mm. At 3mm, the DC values were statistically similar to those at 2 and 4mm, however at 2mm, the DC was higher than at 4mm. For this technique, the composite did not polymerize at a depth of 5mm.

According to manufacturer's information, the Z250 composite, in shade A3, may be applied in a maximum thickness of 2.5 mm and photo-activated by high light intensity. ISO 4049 regulations (2000) recommend that a composite resin must present a depth of cure of at least 0.5 mm higher than that of the manufacturer's information. Although all specimens for all photo-activation methods considered achieved depths of cure of higher than 3 mm, at a depth of 2 mm for PAC and 3 mm for the continuous light technique, the DC values were statistically lower.

These results may be explained by the characteristics of each source light. PAC units are characterized by a more symmetric light distribution and a rather narrow range of wavelength of around 470 nm than the halogen lamps, at a very high light intensity (Peutzfeldt & others, 2000; Lovell & others, 2003). Although the PAC technique presents the highest light intensity of all photo-activation methods considered in this study (1320 mW/cm^2 according to manufacturer's information), the exposure time much shorter, just 3 seconds, representing a lower energy density and, hence, the lower DC values achieved at deeper regions, as mentioned above and showed in Fig. 1.

The continuous light technique presents the highest energy density (32 J/cm^2), however, at a depth of 3 mm the DC values were statistically different to those at 1 mm, whilst the LED, intermittent, stepped and exponential light methods (with lower energy densities) did not present any differences until the depth of 3mm. A possible explanation for this occurrence may be the polymerization process itself, which results in a polymeric densely cross-linked matrix.

The photo-polymerization of dimethacrylate monomers is a complex process, involving different behaviors during the reaction, such as the autoacceleration (gel effect) and autodeceleration. As the network formation highly decreases the mobility of the macroradicals from the very beginning of the polymerization, the autoacceleration occurs at the initial stages of the reaction, causing a rapid increase in the polymerization rate or a runaway reaction. At higher conversions, the gel effect stops and the polymerization reaches its maximum value, the reaction then proceeds at a decreasing rate reaching limited conversion due to vitrification (Decker, 1996; Andrzejewska, 2001). At this point, both propagation and termination processes become diffusion controlled, leading to a rapid drop in the rate of reaction, termed autodeceleration. For dimethacrylate monomers, the polymerization rate reaches its maximum between 20 and 40% (Andrzejewska, 2001), and then decreases. Thus, the final conversion of double bonds is limited to well bellow 100%

(Andrzejewska, 2001, Elliott, Lovell & Bowman, 2001). In general, the DC of dimethacrylate monomers used in dental composites is not higher than 70% (Ruyter & Svendsen, 1978; Peutzfeldt & others, 2000; Andrzejewska, 2001; Imazato & others, 2001).

When high light intensity is supplied to the system, more molecules of the photo-initiator are activated at the same time and it is probable that the autoacceleration occurs immediately after the onset of photo-activation. According to Decker (1996), an adequate compromise must be found between cure speed and cure depth, providing a uniform, but slow deep-through cure for low absorption by the photo-initiator or a rapid, but differential through-cure for high absorption. This could explain the limited DC at deeper regions for the PAC and continuous light methods due to the greater absorption of the light by material in regions nearer to surface and an earlier beginning of the autoacceleration.

Another explication for these results is that the creation of the excited state of the photoinitiator reduces the concentration of excitable molecules and therefore the efficiency of absorption declines. The photoinitiator system may rapidly become saturated when the irradiance is increased and then, no further improvement in the rate of polymerization initiation is possible. Furthermore, at high rates of generation of free radical, leads to mutual annihilation and reduced reaction chain length and thus poorer network formation and poorer mechanical properties. It is possible that over-exposure to be detrimental, whether a high-irradiance lamp is chosen (Musanje & Darvell, 2003). Lovell *et al.* (2003) examined the effect of initiation rate, using different type of light sources, on the conversion and flexural strength of a model resin mixture that did not contain filler particles. The authors found that though the specimens exposed to similar absorbed photon fluxes (controlled by the use of appropriate filters), had polymerization rate no equivalent. This suggests that mutual annihilation and reduced reaction chain length really occur.

The other photo-activation methods present alternative mechanisms for decreasing the initial light intensity or alternating light and darkness, and thus, reducing the polymerization reaction speed. These methods may delay the onset of autoacceleration, providing more mobility to the system in earlier stages of the polymerization, possibly resulting in higher DC values at deeper regions, when compared with techniques that supply initial high light intensity. This phenomenon may explain the results obtained in this study.

Hence, several factors are involved in the polymerization process, making the description of the ideal photo-activation method difficult. The results obtained in this work can only be taken as an indication that the use of LED as the source of light, can lead to a more homogeneous cured composite. On the other hand, there is an indication that the use of PAC can lead to a less homogeneous cured composite, considering DC values in different depths, as a function of material used. Although the manufacturers of the Z250 composite recommends increments of 2.5 mm, thickness of 2 mm (or even 1 mm), depending on the characteristics of the light source, should not be used clinically, since they result in lower DCs in deeper regions.

CONCLUSIONS

- All photo-activation methods showed similar DC values, between them, at the surface and at depths at 1 and 2 mm, but they presented differences between them at other depths.
- The LED, stepped, exponential and intermittent light techniques provided the highest DC values at the surface and at depths of 1, 2 and 3mm. The continuous

light presented similar DC values at the surface and at 1 and 2mm, whilst the PAC revealed the highest values at surface and at 1mm.

- The photo-activation method employed can significantly affect the DC value at deeper regions.
- Thickness higher than 2mm (or even 1mm) should not be utilized in clinical situations.

ACKNOWLEDGEMENTS

The authors thank CAPES for supporting this study.

REFERENCES

1. Andrzejewska E (2001) Photopolymerization kinetics of multifunctional monomers. *Progress in Polymer Science* 26(4) 605-665.
2. Asmussen E (1982) Restorative resins: hardness and strength vs. quantity of remaining double bonds. *Scandinavian Journal of Dental Research* 90(6) 484-489.
3. Baharav H, Abrahan D, Cardash HS & Helft M (1988) Effect of exposure time on the depth of polymerization of the visible light-cured composite resin *Journal of Oral Rehabilitation* 15(2) 167-172.
4. Caldas DB, de Almeida JB, Correr-Sobrinho L, Sinhoreti MAC & Consani S (2003) Influence of curing tip distance on resin composite knoop hardness number, using three different light curing units. *Operative Dentistry* 28(3) 315-320.

5. Decker C (1996) Photoinitiated crosslinking polymerization. *Progress in Polymer Science* 21(4) 593-650.

6. Elliott JE, Lovell LG & Bowman CN (2001) Primary cyclization in the polymerization of BisGMA and TEGDMA: a modeling approach to understanding the cure of dental resins. *Dental Materials* 17(3) 271-279.

7. Feilzer AJ, Dooren LH, de Gee AJ & Davidson CL (1995) Influence of light intensity on polymerization shrinkage and integrity of restorative-cavity interface. *European Journal of Oral Science* 103(5) 322–326.

8. Fujibayashi K, Ishimaru K, Takahashi N & Kihno A (1998) Newly developed curing unit using blue light-emitting diodes. *Dentistry in Japan* 34(1) 49-53.

9. Hofmann N, Hugo B, Schubert K & Klaiber B (2000) Comparison between a plasma arc light source and conventional halogen curing units regarding flexural strength, modulus, and hardness of photoactivated resin composites. *Clinical of Oral Investigation* 2000; 4(3) 140-147.

10. Imazato S, McCabe JF, Tarumi H, Ehara A & Ebisu S (2001) Degree of conversion of composites measured by DTA and FTIR. *Dental Materials* 17(2) 178-183.

11. INTERNATIONAL ORGANIZATION FOR STANDARDIZATION. *ISO 4049 – Dentistry – Polymer-based filling, restorative and luting materials*. Switzerland, 2000. 27f.

12. Jandt KD, Mills RW, Blackwell GB & Ashworth SH (2000) Depth of cure and compressive strength of dental composites cured with blue light emitting diodes (LEDs). *Dental Materials* 16(1) 41-47.

13. Kawaguchi M, Fukushima T & Miyazaki K (1994) The relationship between cure

depth and transmission coefficient of visible-light-activated resin composites. *Journal of Dental Research* 73(2) 516-521.

14. Kurachi C, Tuboy AM, Magalhães DV & Bognato VS (2001) Hardness evaluation of a dental composite polymerized with experimental LED-based devices. *Dental Materials* 17(4) 309-315.
15. Lovell LG, Lu H, Elliott JE, Stansbury JW & Bowman CN (2001) The effect of cure rate on the mechanical properties of dental resins. *Dental Materials* 17(6): 504 – 511.
16. Lovell LG, Newman SM & Bowman CN (1999) The effects of light intensity, temperature, and comonomer composition on the polymerization behavior of dimethacrylate dental resins. *Journal of Dental Research* 78(8) 1469-1476.
17. Lovell LG, Newman SM, Donaldson MM & Bowman CN (2003) The effect of light intensity on double bond conversion and flexural strength of a model, unfilled dental resin. *Dental Materials* 19(6) 458 – 465.
18. Meniga A, Tarle Z, Ristic M, Sutalo & Pichler G (1997) Pulsed blue laser curing of hybrid composite resins. *Biomaterials* 1997; 18(20) 1349-1354.
19. Mills RW, Jandt KD & Ashworth SH (1999) Dental composite depth cure with halogen and blue light emitting diode technology. *British Dental Journal* 186(8) 388-391.
20. Musanje L & Darvell BW (2003) Polymerization of resin composite restorative materials: exposure reciprocity. *Dental Materials* 19 (6): 531 – 541.
21. Nemoto R (1997) Effect of wavelength on polymerization of light-cured resins. *Dental Materials Journal* 16(1) 60-73.

22. Obici AC, Sinhoreti MAC, Goes MF, Consani S & Sobrinho LC (2002) Effect of photo-activation method on polymerization shrinkage of restorative composites. *Operative Dentistry* 27(2) 192-198.
23. Obici AC, Sinhoreti MAC, Sobrinho LC, Goes MF & Consani S (in press) Evaluation of depth of cure and Knoop hardness in a dental composite photo-activated using different methods. *Brazilian Dental Journal* in press.
24. Pearson GJ & Longman CM (1989) Water sorption and solubility of resin-based materials following inadequate polymerization by a visible-light curing system. *Journal of Oral Rehabilitation* 16(1) 57-61.
25. Peutzfeldt A & Asmussen E (2000) The effect of postcuring on quantity of remaining double bond, mechanical properties, and in vitro wear of two resin composites. *Journal of Dentistry* 28(6) 447 – 452.
26. Peutzfeldt A, Sahari A & Asmussen E (2000) Characterization of resin composites polymerized with plasm arc curing units. *Dental Materials* 16(5) 330-336.
27. Reinhardt KJ (1991) [Unconverted double bonds and interface phenomena in composite materials] *Dtsch Zahnartl Z* 46(3) 204–208. (Article in German)
28. Rueggeberg FA, Caughman WF & Curtis Jr JW (1994) Effect of light intensity and exposure duration on cure of resin composite. *Operative Dentistry* 19(1) 26-32.
29. Rueggeberg FA, Caughman WF, Curtis Jr JW & Davis HC (1993) Factors affecting cure at depth within light-activated resin composites. *American Journal of Dentistry* 6(2) 91-95.
30. Ruyter IE & Svendsen SA (1978) Remaining methacrytate groups in composite

restorative materials. *Acta Odontologica Scandicavica* 36(2) 75-82.

31. Silikas N, Eliades G & Watts DC (2000) Light intensity effects on resin-composite degree of conversion and shrinkage strain. *Dental Materials* 16(4) 292-296.
32. Stahl F, Ashworth SH, Jandt KD & Mills RW (2000) Light-emitting diode (LED) polymerization of dental composite: flexural properties and polymerization potential. *Biomaterials* 21(13) 1379-1385.
33. Tarle Z, Meniga A, Ristic M, Sutalo J, Pichler & Davidson CL (1998) The effect of photopolymerization method on the quality of composite resin. *Journal of Oral Rehabilitation* 25(6) 436-442.
34. Unterbrink GL & Muessner R (1995) Influence of light intensity on two restorative systems *Journal of Dentistry* 23(3) 183-189.
35. Yearn JA. (1985) Factors affecting cure of visible light activated composites. *International Dentistry Journal* 35(3) 218–225.

Table 1. Composition of the Z250 composite resin (according to manufacturer's information).

Organic Matrix	Filler			Batch
	Type	% (vol)	Size (µm)	
Bisphenol-glycidyl methacrylate (BisGMA), urethanethyl dimethacrylate (UDMA) and Bisphenol-polyethylene glycol dimethacrylate (BisEMA). Camphoroquinone (initiator)	Zirconia/silica	60	0.19 – 3.3	1NL 2004-08

Table 2. Means of DC for all photo-activation methods according to depth of cure.

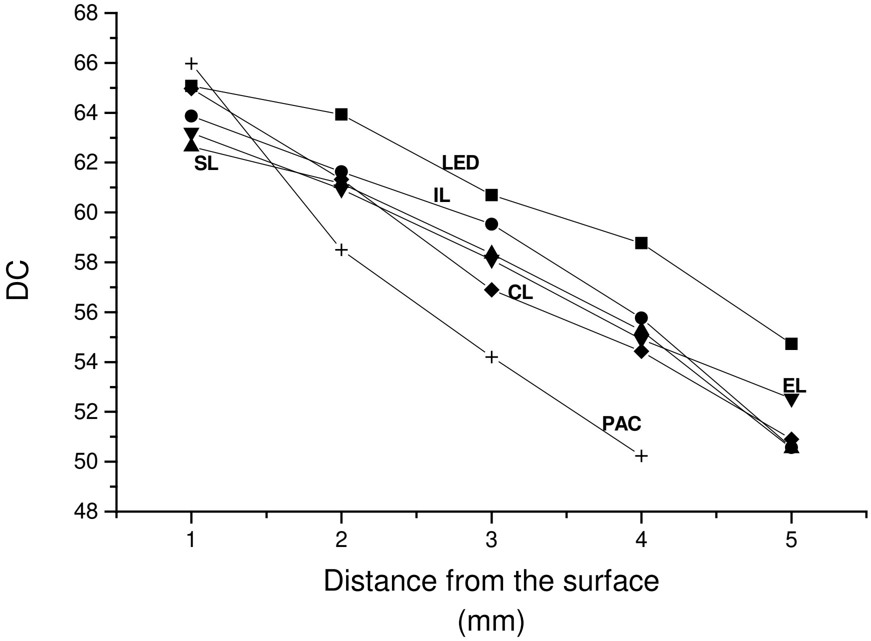
Methods	Surface		1 mm		2 mm		3 mm		4 mm		5 mm	
LED	60.7	A	65.07	A	63.93	A	60.7	A	58.77	A	54.73	A
	(1.73)	ab	(0.32)	a	(1.07)	ab	(1.93)	ab	(0.58)	bc	(2.34)	c
Intermittent light	59.17	A	63.87	A	61.63	A	59.53	AB	55.77	AB	50.57	A
	(1.29)	ab	(2.86)	a	(1.88)	a	(1.1)	ab	(3.43)	bc	(2.12)	c
Stepped light	58.43	A	62.63	A	61.17	A	58.33	AB	55.27	AB	50.53	A
	(0.58)	ab	(0.86)	a	(0.74)	a	(0.81)	ab	(0.15)	bc	(2.93)	c
Exponential light	60.4	A	63.2	A	60.93	A	58.1	AB	54.9	AB	52.53	A
	(4.18)	ab	(4.0)	a	(2.21)	a	(1.56)	ab	(1.56)	bc	(0.65)	c
Continuous light	59.93	A	64.97	A	61.33	A	56.9	AB	54.43	AB	50.9	A
	(4.44)	abc	(4.28)	a	(3.2)	ab	(1.22)	bc	(2.3)	cd	(2.02)	d
PAC	61.47	A	65.97	A	58.5	A	54.2	B	50.23	B	----	---
	(3.87)	ab	(1.27)	a	(2.96)	bc	(2.79)	cd	(1.85)	d	----	---

Means followed by same small letters are not statistically different in row at the 5% significance level, by Tukey's test.

Means followed by same capital letters are not statistically different in columns at the 5% significance level, by Tukey's test.

( ) Standard deviation.

Fig.1- DC (%) as a function of depth from the surface, considering samples cured using different photo-activation methods: LED, Intermittent light (IL), Stepped light (SL), Exponential light (EL), Continuous light (CL), PAC.



CAPÍTULO IV

Degree of Conversion and Knoop hardness of Z250 composite using different photo-activation methods

(American Journal of Dentistry – enviado para publicação)

ABSTRACT: *Purpose:* The aim of this study was to evaluate the degree of conversion (DC) by FTIR spectroscopy and the Knoop hardness (KHN) of Z250 composite resin, using seven photo-activation methods**.** ***Materials and Methods:*** For both tests, the material was placed into a metallic mold (6mm in diameter X 2mm in height), and photo-activated as follows: a) continuous light (800mW/cm^2-40s); b) exponential light (0-800mW/cm^2-40s); c) intermittent light (2s-600mW/cm^2; 2s without light-80s); d) stepped light (10s-150mW/cm^2; 30s-650mW/cm^2); e) PAC (1320mW/cm^2-3s); f) LED1 (100mW/cm^2-40s); g) LED2 (350mW/cm^2-40s). For FTIR spectroscopy analysis, the specimens were finely pulverized and, after 24±1 hour, pressed with KBr in a proportion of 1:10 and then analyzed by spectrophotometer. The DC was calculated by standard technique. For Knoop hardness test, the specimens were included and weared longitudinally. The hardness was measured on the surface and at depths of 1 and 2 mm. The data were analysed by ANOVA and Tukey's test (5%). *Results:* The results showed that there was no statistical difference in DC values between the photo-activation methods. The highest Knoop hardness value was obtained for continuous light, followed by stepped, exponential and LED2 with no difference between them. For intermittent light, no difference was observed compared with stepped, exponential LED2 and PAC, however, the KHN for PAC was lower than those of stepped and exponential light. LED1 demonstrated the lowest KHN, which was statistically different to those of the other methods.

CLINICAL SIGNIFICANCE:

Although DC values are not statically affected by different photo-activation methods, in specimens with 2mm of thickness, the Knoop hardness showed significant differences, signifying that the polymeric matrixes formed were dissimilar, when different photo-activation were employed.

INTRODUCTION

Degree of conversion (DC) is one of the most important factors affecting the clinical performance of composite resins. Optimal physical, mechanical and biological properties are related to high DC, which in a photo-activated composite is dependent on the total light energy, at a correct wavelength, supplied to the photoinitiator [1-4]. Although high light intensity provides higher DC values, it also produces greater polymerization shrinkage, which may cause gap formation and further microleakage, compromising the longevity of the restoration [5-7].

Traditionally, the composites are photo-activated by halogen lamps with a high light intensity. However, several photo-activation methods have been suggested to initiate the composite cure reactions, maintaining the DC values similar to that found using high light intensity, whilst reducing the polymerization shrinkage. In this context, alternative methods that employ halogen lamps, such as stepped light [5-8], exponential light [9, 10] and intermittent light [5, 11], as well as other technologies that utilize plasma arc curing – PAC [10, 12, 13] or a light emitting diode – LED [14-16] can be used.

Independently of the photo-activation method applied, the DC must be as high as possible, ensuring that the material possesses the best properties. Studies in the literature demonstrating a good correlation between DC and hardness of composites and, thus, hardness is utilized as an indicator of DC [3, 17, 18].

The purpose of this study was to evaluate the degree of conversion and Knoop hardness number of a single composite resin using different photo-activation methods.

MATERIAL AND METHODS

In the present study, the Filtek Z250 composite resin [a], shade A3, was utilized. The composition and batch of the resin are listed in Table 1. The evaluation of degree of conversion was performed directly by FTIR spectroscopy, using a Potassium Bromide (KBr) pellet or, indirectly, by measurement of Knoop Hardness Number (KHN).

For both techniques, the composite was placed in a circular brass matrix of 6 mm in diameter and 2 mm in height. The material was then covered with a polyester strip and pressed with a glass slab to accommodate the material into the matrix. Photo-activation was performed as follows: a) continuous light; b) exponential light; c) intermittent light; d) stepped light, e) PAC, f) LED1, or g) LED2.

For the continuous light photo-activation method, the curing tip was positioned close to brass matrix/restorative composite. The photo-activation was performed for 40 seconds with a light intensity of 800 mW/cm^2, using an Elipar Trilight curing unit [b]. For the exponential light technique, the same curing unit was used, however, the light intensity began at zero, increasing gradually to 800 mW/cm^2 in the first 20 seconds, then maintaining this light intensity for an additional 20 seconds, with a total exposure time of 40 seconds. Curing with the intermittent light method was performed using a curing unit developed in the Dental Materials Department, School Dental of Piracicaba, UNICAMP, which provided 2 seconds of light with intensity of 600mW/cm^2 and 2 seconds without light. The total time was 80 seconds, of which 40 seconds of light exposure itself. The stepped light method was performed using a XL 2500 curing unit [b], which provided an initial 10-second exposure to the activating light with an intensity of approximately 150 mW/cm^2, maintaining a distance of nearly 2.0 cm from the curing tip. The curing tip was then positioned close to the brass matrix/restorative composite, resulting in an increased light intensity of 650 mW/cm^2, which was maintained for an additional 30 seconds. For the PAC technique, the Apollo 95 E curing unit was used [c], which, according to manufacturer's information, achieved an intensity of 1320 mW/cm^{2}. The light exposure time was 3 seconds. Finally, for the LED1 method, a LEC 470 l curing unit [d] was used to photo-activate the composite, providing an intensity of 100 mW/cm^{2} for 40 seconds, whilst for the LED2 technique, an Elipar Freelight curing unit [b] was used, which presented an intensity of 350 mW/cm^{2} for 40 seconds. The light intensity of the curing units was measured with a radiometer [e], with the exception of the Apollo 95 E curing unit.

After photo-activation, the specimens prepared for FTIR spectroscopy analysis were finely pulverized with a hard tissue-grinding machine [f]. The pulverized composite was maintained in a dark container until the moment of the FTIR analyzes. After 24±1 hour, 10 mg of the ground powder were mixed with 100 mg of KBr powder salt. This mixture was placed into a pelleting device [g] and then pressed in a hydraulic press [h] with a load of 8 tons, to obtain a pellet. This pellet was then placed into a holder attachment within the spectrophotometer [i] for analysis. The uncured composite resin was analyzed using a metallic siliceous window.

The measurements were recorded in absorbance, with a FTIR spectrometer [i] operating under the following conditions: 300–4000 cm^{-1} wavelength; 4 cm^{-1} resolution; 32 scans. The percentage of unreacted carbon-carbon double bonds (% C=C) was determined from the ratio of absorbance intensities of aliphatic C=C (peak at 1638cm^{-1}) against internal standard before and after curing of the specimen: aromatic $C^{\cdots}C$ (peak at 1610cm^{-1}) and urethane $N^{\cdots}H$ (peak at 1537cm^{-1}). The degree of conversion was determined by subtracting the % C=C from 100%. All experiments were carried out in triplicate.

After photo-activation, the specimens that there were prepared for analysis of Knoop hardness were included in self-curing acrylic resin [j] and then weared longitunally along the center with grit 80 sandpaper [k] in a grinding wheel [l]. Finishing and the polishing were performed with sandpaper [k] of decreasing grits of 320, 400, 600 and 1000. The specimens were maintained in a dark container until the moment of the hardness test. After 24 ± 1 hour, the Knoop hardness [m] was measured at the surface and at the depths of 1 and 2 mm, with a load of 50g for 15 seconds. Five readings were taken for each region and the arithmetic mean was calculated for the specimen. Five specimens were made for each photo-activation method.

The data were analyzed by ANOVA and the means were compared by Tukey's test (5% of significance level).

RESULTS

The results of this study are presented in Tables 2 and 3.

Table 2 shows that there was no statistical difference in DC values between photo-activation methods considered ($p>0.05$).

Conversely, Table 3 reveals statistical difference in Knoop hardness between photo-activation methods. The highest values were obtained for continuous light, stepped light, exponential light and LED2, without significant differences between them ($p<0.05$). Intermittent light technique presented a KHN, which was statistically similar to, stepped light, exponential light and LED2, however, this method demonstrated lower values than those of continuous light. No statistical difference was found, however, between LED2, intermittent light and PAC ($p>0.05$). Finally, the LED1 presented the lowest KHN, which was statistically different from those of the other methods ($p<0.05$).

DISCUSSION

The final physical, mechanical and biological properties of composite resins are strongly influenced by the DC, achieved by the organic matrix. Thus, the light source features for photo-activation of these resins are crucial for the final characteristics of the material. This study investigated the Knoop hardness and DC by FTIR spectroscopy of Z250 composite resin, using seven photo-activation methods.

According to the results presented in Table 2, there was no statistical difference in DC values between the photo-activation methods considered, demonstrating that all techniques were able to polymerize the Z250 composite to a thickness of 2 mm. Since great differences exist between photo-activation methods tested in this study, several factors may be responsible for these results, including energy density, spectral distribution of the light emitted by the curing unit and the polymerization process itself.

An important parameter for curing units is the amount of light energy of appropriate wavelength emitted during the irradiation. This energy is calculated as the product of the output of the curing unit and the time of irradiation and is named energy density. Although the photo-activation methods tested present great variation in energy density (3.96 – 32 J/cm^2), the DC results did not differ statistically between them. This finding demonstrates that other factors are important for determining the conversion of the composite. In this context, the spectral distribution of the light of each photo-activation method exerts a significant effect upon the DC of resinous materials.

The Z250 composite utilizes camphoroquinone as a photoinitiator (Table 1), which demonstrates the most effective frequency band between 460 nm and 480 nm [19], with an absorption peak at 468 nm [20]. Thus, the light curing unit that emits the wavelength closest to this absorption peak will present the greatest ability to activate camphoroquinone and, hence, to initiate the polymerization process.

Halogen lamps used in conventional curing units are referred as incandescent lights, emitting a spectrum that is continuous over the visible range, especially towards the red end of the spectrum. Thus, approximately 98 – 99% of this radiation does not contribute to polymerization and must be filtered [13, 14]. According to Fujibayashi *et al.* (1998) and Mills et al. (1999) the wavelength of light emitted by halogen lamps range between 380 nm and 510 nm, with a peak at 484 nm (already filtered). PAC light sources also emit continuous frequency bands, however, these bands are much narrower than those of incandescent lights. Therefore, less radiation of undesired wavelength must be filtered. The Apollo 95E emits light between 440 nm and 500 nm, with a peak at 470 nm [12, 13]. Finally, the LED devices use junctions of doped semiconductors (p-n junctions) for the generation of light. When a voltage is applied, electrons from the n-doped and holes from the p-doped recombine, resulting in the emission of blue light, in the case of the LEDs, which contain gallium nitride [15]. These LEDs are characterized by a narrow wavelength spectrum that lies within 450 nm and 490 nm [21], with a wavelength peak at 466 nm [14, 22]. Although the photo-activation methods considered in this study presented great differences between them, the DC values were not statistically different. This probably occurred as the consequence of the sum of the characteristics of each technique. Whilst photo-polymerization methods that employ halogen lamp supply a higher energy density, they also present a larger spectral distribution with a wavelength peak at a region more distant to that of camphoroquinone, whilst the situation is inversed for the PAC and LED methods.

During the polymerization process of the dimethacrylate monomers that compose the composite resins, different phenomena occur, such as autoacceleration, autodeceleration, termination processes controlled by reaction diffusion, formation of structural heterogeneities (microgels or microregions) and limiting functional groups conversion, making this reaction very complex. Initially, monomer molecules are incorporated into polymer chains as units that contain pendent bonds. The apparent reactivity of these pendent bonds within the same chain is initially enhanced when compared to the monomeric double bond, leading to an extensive primary cyclization reaction, which creates microgels or microregions, causing the heterogeneity in the polymer network [23-25]. Cyclization will promote higher local conversion and not decrease mobility of the system as much as cross-linking. Conversely, it can lead to a reduction in the effective cross-linking density, decreasing the mechanical and physical properties [23, 25], due to many of the uncured pendent double bonds becoming entrapped into microgels, making further reaction inaccessible [24].

In addition, network formation highly decreases the mobility of macroradicals from the very beginning of the polymerization, which is the main cause for the onset of autoacceleration (gel effect or reaction runaway) in the initial stages of the polymerization. Autoacceleration causes a rapid increase in the polymerization rate, achieving a maximum polymerization rate at higher conversions, it then stops, and the reaction proceeds with a decreasing rate reaching limited conversion due to vitrification. At this point, both propagation and termination processes become diffusion controlled, leading to a rapid drop in the rate of reaction, the autodeceleration [24, 4]. The decrease in the polymerization rate at higher conversions may result from factors, such as a reduction in monomer concentration, difficulties in monomer diffusion through the solidifying medium, reduced mobility of uncured pendent bonds and decreasing dissociation efficiency of the photoinitiator in the viscous medium [24]. All these phenomena limit final conversion of double bonds to well below 100%. Thus, since for a light curing unit that supply high energy density, with an adequate wavelength, the degree of conversion will not reach 100%. In general, the DC of dental composites ranges between 43 – 75% [12, 23, 26]. However, only approximately one-tenth of these uncured methacrylate groups are presented as residual monomer [27]. The results of DC obtained in the present study show this limited DC in dimethacrylate monomers, independently of photo-activation method considered.

With respect to the Knoop hardness results (Table 3) found in this study, it was possible to observe statistical differences between photo-activation methods. The highest values were obtained for continuous light, stepped light, exponential light and LED2, without significant differences between them. The intermittent light technique presented a KHN statistically similar to those of stepped light, exponential light and LED2, however, this method demonstrated lower values than those of the continuous light technique. Furthermore, no statistical difference was found between LED2, intermittent light and PAC. Finally, the LED1 presented the lowest KHN and was different from the other methods.

Knoop hardness is a punctual mechanical property that not describes the behavior of the material as a bulk. The differences between photo-activation methods may be due to the heterogeneity inherent of the polymerization process of the composite resins. Inside the microgel, polymerization occurs at a higher rate because of a local gel effect, resulting in a higher cross-linking density than the densities of the regions between each microregion [23].

If the light source supplies lower energy density or allows flow of the material by the intermittence, the initial stages of polymerization that antecede the autoacceleration could be prolonged, resulting in greater primary cyclization, reducing the effective cross-linking density and, consequently, the mechanical properties. This may not represent a significant decrease in DC, affecting only the mechanical properties, possibly explaining the results found in the present study.

Considering the samples with different hardness, the following cure parameters can be conceived: light source type, wavelength range, light intensity and exposure time. Following this sequence and adding the mean hardness values first (table 3), we have: 101.65 - continuous light, 380-510 nm (peak at 484 nm), 800 mW/cm^2, 40 s; 93.95 - PAC, 440-500 nm (peak at 470 nm), 1320 mW/cm^2, 3s; 89.57 - LED1, 450-490 nm (peak at 466 nm), 100 mW/cm^2, 40 s. In this set of source light, LED1 has the narrowest wavelength range, the closest absorption peak to that of camphoroquinone and then, at first, should be the most efficient to initiate the reaction. However, despite these favorable properties, the sample submitted to continuous light, with the same exposure time to that submitted to LED1, showed higher KHN. This result can indicates that the light intensity (and, energy density) was the main parameter that defined the cross-linking density. Concern to the sample submitted to PAC, although the light intensity was the highest, the lower exposure time leaded to a sample of lower KHN than that submitted to continuous light. In this case, besides the light intensity, it seems that the exposure time played an important role. These findings corroborate with studies previous [2, 12], which claim that the polymerization process seems dependent upon the energy density.

Conversely, although the exposure time supplied with LED1 was higher than that submitted to PAC, the lowest light intensity of LED1 apparently lead to a sample less cross-linked. When the results obtained with LED1 are compared to that obtained with LED2 (450-490 nm, peak at 466 nm, 350 mW/cm^2, 40 s), which showed a KHN value of 98.04, statistically different from LED1 (Table 3), again comes out the importance of light intensity, the only parameter that differentiates both sources.

This could not represent a significant change in the respective DC, because the dimethacrylate monomers can be incorporated to the growing chains, nearly with the same extension, independently of the photo-activation method used, but the cross-linking density can be affected by parameters as light intensity and exposure time, what could explain the results found in the present study.

Hence, it was possible to verify that DC values of Z250 composite resin was not affected by the photo-activation methods considered, however the Knoop hardness was dependent on some parameters linked to the light source and exposure time. The results of the present work calls for the fact that care must be taken when hardness is considered as an indicative of DC, because in some cases samples with similar DC can have different cross-linking density, which in turn can affect hardness.

a. (3M, St. Paul, MN, USA)
b. (3M-ESPE, Seefeld, D-82229, Germany)
c. (DMD, Westlake, Village, CA 91362, USA)
d. (M M Optics, São Carlos – SP 13560-050, Brazil)
e. (Curing Radiometer, model 100, Demetron/Kerr, Danbury, CT 06810, USA)
f. (Marconi, model MA590, Piracicaba – SP, Brazil)
g. (Aldrich, Milwaukee, WI, USA)
h. (Carver Laboratory Press, model 3648, Wabash, St. Morris, USA)

i. (Bomem, model MB-102, Quebec – Canada)

j. (Artigos Odontológicos Clássico, São Paulo-SP, Brazil)

k. (Carburundum Abrasivos, Recife-PE, Brazil)

l. (Arotec, model APL-4, Cotia-SP, Brazil)

m. (Micro Hardness Tester, model HMV 2, Shimadzu, Japan)

ACKNOWLEDGEMENTS

The authors thank CAPES for supporting this study.

REFERENCES

1. Yearn JA. Factors affecting cure of visible light activated composites. *Inter Dent J* 1985; 35: 218–225.
2. Sakaguchi RL, Berge HX. Reduced light energy density decreases post-gel contraction while maintaining degree of conversion in composites. *J Dent* 1998; 26: 695-700.
3. Ferracane JL, Greener EH. The effect of resin formulation on the degree of conversion and mechanical properties of dental restorative resins. *J Biomed Mater Res* 1986; 20: 121 – 131.
4. Lovell LG, Newman SM, Bowman CN. The effects of light intensity, temperature, and comonomer composition on the polymerization behavior of dimethacrylate dental resins. *J Dent Res* 1999; 78: 1469-1476.
5. Obici AC, Sinhoreti MAC, Goes MF, Consani S, Sobrinho LC. Effect of photo-activation method on polymerization shrinkage of restorative composites.

Operat Dent 2002; 27: 192-198.

6. Feilzer AJ, Dooren LH, de Gee AJ, Davidson CL. Influence of light intensity on polymerization shrinkage and integrity of restorative-cavity interface. *Eur J Oral Sci* 1995; 103: 322–326.
7. Silikas N, Eliades G, Watts DC. Light intensity effects on resin-composite degree of conversion and shrinkage strain. *Dent Mater* 2000; 16: 292-296.
8. Unterbrink GL, Muessner R. Influence of light intensity on two restorative systems *J Dent* 1995; 23: 183-189.
9. Caldas DB, de Almeida JB, Correr-Sobrinho L, Sinhoreti MAC, Consani S. Influence of curing tip distance on resin composite knoop hardness number, using three different light curing units. *Operat Dent.* 2003; 28: 315-320.
10. Obici AC, Sinhoreti MAC, Sobrinho LC, Goes MF, Consani S. Evaluation of depth of cure and Knoop hardness in a dental composite photo-activated using different methods. *Brazilian Dent J* 2003; in press.
11. Tarle Z, Meniga A, Ristic M, Sutalo J, Pichler, Davidson CL. The effect of photopolymerization method on the quality of composite resin. *J Oral Rehabil* 1998; 25: 436-442.
12. Peutzfeldt A, Sahari A, Asmussen E. Characterization of resin composites polymerized with plasm arc curing units. *Dent Mater* 2000; 16: 330-336.
13. Hofmann N, Hugo B, Schubert K, Klaiber B. Comparison between a plasma arc light source and conventional halogen curing units regarding flexural strength, modulus, and hardness of photoactivated resin composites. *Clin Oral Invest* 2000; 4: 140-147.

14. Fujibayashi K, Ishimaru K, Takahashi N, Kihno A. Newly developed curing unit using blue light-emitting diodes. *Dentistry in Japan* 1998; 34: 49-53.

15. Jandt KD, Mills RW, Blackwell GB, Ashworth SH. Depth of cure and compressive strength of dental composites cured with blue light emitting diodes (LEDs). *Dent Mater* 2000; 16: 41-47.

16. Kurachi C, Tuboy AM, Magalhães DV, Bognato VS. Hardness evaluation of a dental composite polymerized with experimental LED-based devices. *Dent Mater* 2001; 17: 309-315.

17. Rueggeberg FA, Craig RG. Correlation of parameters used to estimate monomer conversion in a light-cured composite. *J Dent Res* 1988; 67: 932-937.

18. Tirtha R, Fan RL, Dennison JB, Powers JM. "*In vitro*" depth of cure of photo-activated composites. *J Dent Res* 1982; 61: 1184 – 1187.

19. McCabe JF, Carrick TE. Output from visible-light activation units and depth of photo-activated composites. *J Dent Res* 1989; 68: 1534 – 1539.

20. Taira M, Urabe H, Hirose T, Wakasa K, Yamaki M. Analysis of photoinitiators in visible-light-cured dental composite resins. *J Dent Res* 1988; 67: 24 – 28.

21. Nemoto R. Effect of wavelength on polymerization of light-cured resins. *Dent Mater J* 1998; 16: 60-73.

22. Mills RW, Jandt KD, Ashworth SH. Dental composite depth cure with halogen and blue light emitting diode technology. *Brit Dent J* 1999; 186: 388-391.

23. Ruyter IE, Svendsen SA. Remaining methacrytate groups in composite restorative materials. *Acta Odontol Scand.* 1978; 36: 75-82.

24. Andrzejewska E. Photopolymerization kinetics of multifunctional monomers. *Prog*

Polymer Sci 2001; 26: 605-665.

25. Elliott JE, Lovell LG, Bowman CN. Primary cyclization in the polymerization of BisGMA and TEGDMA: a modeling approach to understanding the cure of dental resins. *Dent Mater* 2001; 17: 271-279.
26. 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.
27. Ferracane JL. Elution of leachable components from composites. *J Oral Rehabil* 1994; 21: 441 – 452.

Table 1. Composition of organic matrix and filler of the Z250 composite resin (according to manufacturer's information).

Organic Matrix	**Filler**			**Batch**
	Type	**% (vol)**	**Size (μm)**	
Bisphenol-glycidyl methacrylate (BisGMA), urethanethyl dimethacrylate (UDMA) and Bisphenol-polyethylene glycol dimethacrylate (BisEMA). Camphoroquinone (initiator)	Zirconia/silica	60	0.19 – 3.3	1NL 2004-08

Table 2 – Results of DC values, according to photo-activation methods analyzed.

Photo-activation methods	**Degree of conversion (%)**		
Continuous light	66.2	(2.5)	a
Intermittent light	63.7	(2.4)	a
Stepped light	62.9	(4.9)	a
PAC	60.0	(1.1)	a
LED 2 (3M-ESPE)	59.8	(3.0)	a
Exponential light	59.6	(5.8)	a
LED 1 (MMOptics)	58.6	(4.9)	a

Means followed by different letters are statistically different at 5% by Tukey's test.

(   ) Standard deviation

Table 3 – Results of Knoop Hardness Number, according to photo-activation methods analyzed.

Photo-activation methods	**Knoop Hardness Number (KHN)**		
Continuous light	101.65	(3.52)	a
Stepped light	100.1	(3.67)	ab
Exponential light	98.23	(4.13)	ab
LED 2 (3M-ESPE)	98.04	(2.36)	abc
Intermittent light	96.57	(2.4)	bc
PAC	93.95	(5.6)	c
LED 1 (MMOptics)	89.57	(9.51)	d

Means followed by different letters are statistically different at 5% by Tukey's test.

( ) Standard deviation

CAPÍTULO V

Evaluation of mechanical properties of Z250 composite resin photo-activated by different methods

(Journal of Dentistry – enviado para publicação)

SUMMARY

Objectives: This study evaluated some mechanical properties of Z250 composite resin using different photo-activation methods. Methods: Ten specimens were prepared for each group, with different dimensions according to the test, as follows: compression strength - d = 3 mm, h = 6 mm; diametral tensile strength - d = 6 mm, h = 3 mm; flexural strength and modulus of elasticity - l = 25 mm, w = 2 mm, h = 2 mm. Photo-activation was performed by: a). continuous light (800mW/cm^2-40s); b). exponential light (0-800mW/cm^2-40s); c). intermittent light (2s-600mW/cm^2; 2s without light-80s); d). stepped light (10s-150mW/cm^2; 30s-650mW/cm^2); e). PAC (1320mW/cm^2-3s); f). LED (350mW/cm^2-40s). After 24 ± 1 h, the specimens were loaded at a cross-head speed of 0.5 mm/min until fracture. The mechanical properties were calculated and analyzed statistically by ANOVA and Tukey's test (5%). Results: Results showed that, for compressive strength, the highest values were found with the continuous, exponential, intermittent and stepped light methods, whilst the PAC and LED obtained the lowest values. The LED, stepped light, PAC, exponential and continuous light demonstrated the highest values for diametral tensile strength, whilst the intermittent light showed the lowest value, which differed statistically only from the LED. The results of flexural strength did not differ between all photo-activation methods. Finally, for modulus of elasticity the highest values were obtained for LED, exponential, continuous and intermittent light, whilst PAC and stepped light showed the lowest values. Conclusions: The mechanical properties are differently affected by photo-activation methods employed.

INTRODUCTION

The light-cured composite resins are an important group of restorative material in Dentistry and can be utilized in restorations of anterior and posterior teeth. The mechanical properties of a restorative material are a crucial factor in their clinical performance. Strength data usually provided by the manufacturers includes compressive, tensile and/or flexural strength. These properties are strongly related to the composition (filler content, organic matrix) of the material (1 - 5) and may be altered depending on the characteristics of the light source (6 - 9).

Dimethacrylate monomers are widely used as an essential ingredient of organic matrix of composite resins, which reacts via an addition polymerization, forming highly cross-linked structures, when light of appropriate wavelength and intensity is supplied (4, 10). The addition of inert filler to dimethacrylate resins can significantly improve certain properties, such as compressive and flexural strength, hardness and modulus of elasticity (5, 11, 13). For this to occur, an efficient coupling must occur between the filler and matrix resin (5, 12, 13). However, factors concerning resin composition are determined by the manufacturers and cannot be altered by the clinicians. Thus, light irradiation is the factor most available for control by the dentist and may determine the final properties of the material and, hence, the clinical success. Several studies have demonstrated that the degree of conversion of double bonds is a co-determinant of the mechanical properties of the resulting polymer and, in it turn, the degree of conversion is dependent on the total light incident on the material with appropriate characteristics to activate the photo-initiator (1 – 4, 8, 9, 14, 15).

The main light curing units available on the market today include: halogen lights, plasma arc lights (PAC) and the light emitting diode (LED). These technologies present great differences between them, with respect to the light intensity, exposure time and spectral emission. Halogen lamps used in conventional curing units generate a white light when the tungsten filament is heated to high temperatures, this light must be filtered to emit only the blue spectrum, the visible light. Traditionally, these lamps are used to supply a high intensity (6, 10). In recent years, alternative photo-polymerization methods have been suggested, utilizing these lamps, such as stepped light or step-cure (14, 16, 17), exponential light or ramp-cure (18, 15) and intermittent light or pulse-cure (16, 19). PAC source also emits continuous light, but at a very high intensity (> 1000 mW/cm^2). However, the PAC light has a more symmetric light distribution of around 470 nm, when compared to halogen lamps. Due to the high light intensity emitted by these sources, the manufacturers recommend exposure times of between 1 and 3 seconds (8, 9, 15, 20). Finally, the LED devices present a narrow and symmetric wavelength spectrum (21 – 24), but supply a lower light intensity than the halogen and PAC lamps.

The inherent differences between each photo-activation method may provide different initiation and polymerization rates, as well as result in polymeric matrixes with dissimilar densities of cross-linking (9, 15, 25). As a consequence, variations in the final mechanical properties are possible.

The aim of this study was to evaluate the effects of different photo-activation methods upon the several mechanical properties of a universal composite resin.

MATERIALS AND METHODS

The composite resin used in this investigation was Filtek Z250, shade A3, the composition and batch of which is listed in Table 1.

The composite was tested for compressive strength, diametral tensile strength, flexural strength and modulus of elasticity. For the compressive and diametral tensile strength testing, the composite was placed into silicon matrixes (compressive strength: h = 6 mm, d = 3 mm; and diametral tensile strength: h = 3 mm, d = 6 mm), with increments between 1.5 – 2.0 mm in thickness, which were irradiated individually. The matrix was placed upon a glass slab with a clear polyester strip for placing the material. The last increment was also covered with a polyester strip and pressed with a glass slide to accommodate the composite into the matrix. For flexural strength and modulus of elasticity testing, the material was placed into an acrylic matrix (l = 25 mm, h = 2 mm, w = 2 mm), which was placed upon a metallic base and a polyester strip, and then covered by another polyester strip and pressed with a glass slide. The light irradiation was initially performed at the center, and then moved to the next section until all specimens had been irradiated. Photo-activation methods employed in this study were: a) continuous light; b) exponential light; c) intermittent light; d) stepped light; e) PAC, or; f) LED.

For the continuous light photo-activation method, the curing tip was positioned close to brass matrix/restorative composite. The photo-activation was performed for 40 seconds with a light intensity of 800 mW/cm^2, using an Elipar Trilight curing unit (3M-ESPE, Seefeld, D-82229, Germany). For the exponential light technique, the same curing unit was used, however, the light intensity began at zero, increasing gradually to 800 mW/cm^2 in the fist 20 seconds, then maintaining this light intensity for as additional 20 seconds, with a total exposure time of 40 seconds. Curing with the intermittent light method was performed using a curing unit developed in the Dental Materials Department, School Dental of Piracicaba, UNICAMP, which provided 2 seconds of light with intensity of 600mW/cm^2 and 2 seconds without light. The total time was 80 seconds, of which 40 seconds of light itself. The stepped light method was performed using a XL 2500 curing unit (3M-ESPE, Seefeld, D-82229, Germany), which provided an initial 10-second exposure to the activating light with an intensity of approximately 150 mW/cm^2, maintaining a distance of nearly 2.0 cm from the curing tip. The curing tip was then positioned close to the brass matrix/restorative composite, resulting in an increased light intensity of 650 mW/cm^2, which was maintained for an additional 30 seconds. For the PAC technique, the Apollo 95 E curing unit was used (DMD, Westlake, Village, CA 91362, USA) which, according to manufacturer's information, achieved an intensity of 1320 mW/cm^2. The light exposure time was 3 seconds. Finally, for the LED method, an Elipar Freelight curing unit (3M-ESPE, Seefeld, D-82229, Germany) was used to photo-activate the composite, providing an intensity of 350 mW/cm^2 for 40 seconds. The light intensity of the curing units was measured with a radiometer (Curing Radiometer, model 100, Demetron/Kerr, Danbury, CT 06810, USA), with the exception of the Apollo 95 E curing unit.

After photo-activation, the specimens of each group were separated from the matrix and stored in a dark container during 24 ± 1 hour. The compressive and diametral tensile specimens were then subjected to a compressive force in a Universal Testing Machine (Model 4411, Instron Corp., Canton, MA, USA) at a cross-head speed of 0.5 mm/min until failure. The compressive strength (CS) was calculated by dividing the failure load (F) by the cross-sectional area, i.e.: $CS = F/\pi R^2$, where R is the ray of the cross-sectional of the specimen. The diametral tensile strength (DTS) was calculated using the equation: $DTS = 2F/\pi Dt$, where F is the failure load, D the diameter, and t the height of the specimen.

For the flexural strength (σ), the bar-shaped specimens were placed on two supports that were 20 mm apart. A force was applied at mid-span at a cross-head speed of 0.5 mm/min until failure and the flexural strength calculated: $\sigma = 3Fl/2bh^2$, where F is failure load, l the distance between the supports, b the width, and h the height of the specimen. The modulus of elasticity (ε) was calculated from the results of the tree-point bending test, utilizing the value of load and deformation of the specimen before the fracture. Ten replicates were made for each mechanical property, with the exception of the modulus of elasticity test, which was calculated from tree-point bending test, as earlier mentioned.

The data were submitted to analysis of variance (ANOVA) and compared by Tukey's test at a significance level of 5%.

RESULTS

The results of this investigation are presented in Tables 2, 3, 4 and 5.

Table 2 shows the results of the compression strength of Z250 composite resin. Continuous, exponential, intermittent and stepped light methods revealed the highest compression strength values, without statistical difference between them ($p>0.05$). The lowest values were demonstrated by the PAC and LED techniques, which were not statistically different from each other ($p>0.05$), but were lower than those of the other methods ($p<0.05$).

The results for diametral tensile strength are listed in Table 3 and show that there was no statistical difference between the LED, stepped light, PAC, exponential light and continuous light methods ($p>0.05$), which revealed the highest values. The lowest value was found for the intermittent light, which differed only from LED ($p<0.05$).

The flexural strength values showed no statistical difference between all photo-activation methods ($p>0.05$), according to Table 4. Finally, Table 5 presents the results of the modulus of elasticity test, which demonstrate that the LED, exponential, continuous and intermittent light methods obtained the highest values, without significant differences between them ($p>0.05$). The lowest values were found for PAC and stepped light, which did not differ between them ($p>0.05$), but were statistically different from the other methods ($p<0.05$).

DISCUSSION

Light-cured composite resins are basically composed by a resin matrix, inorganic fillers and a coupling agent. Thus, characteristics concerning the composition of this material exert an influence upon their final properties, and obviously, upon the clinical performance. The filler content, size, type and the distribution of the filler particles, as well as an efficient coupling agent are factors that determine some properties such as strength and modulus of elasticity (5, 11, 13). However, the degree of conversion of double bonds, for a given monomer system, is a co-determinant of the mechanical properties of the resulting polymeric matrix (1 - 4). As the degree of conversion of double bonds is dependent upon the characteristic of the light incident, the choice of light curing unit may have an important effect upon the final properties. Thus, the present study investigated four mechanical properties: compressive strength, diametral tensile strength, flexural strength and modulus of elasticity, using different photo-activation methods to activate the polymerization process of Z250 composite.

Three light sources and six light-curing techniques were used: 1). halogen lamps, which were employed in four techniques: 1.a- continuous light, 1.b- stepped light, 1.c- intermittent light and, 1.d- exponential light; 2). PAC, and 3). LED.

The results presented in this study (Tables 2 – 5) show the mechanical properties for Z250 composite when photo-activated by different methods. The compressive strength values demonstrated no statistical difference for continuous, exponential intermittent and stepped light methods, which were higher than those for PAC and LED (Table 2). The explanation for this result may be related to energy density, which is the product of the output of the curing unit and the time of irradiation (20). The energy density is an indication of the total light energy to which the material is exposed (15). The PAC and LED devices present the lowest energy densities, 3.96 and 14 J/cm^2, respectively. However, there is a great difference between the energy densities of these two methods. Yet, these methods represent the two extremes of the relationship between light intensity and exposure time. While the PAC presents a very high light intensity (1320 mW/cm^2) for a few seconds (3 s), the LED supplies a lower intensity (350 mW/cm^2), but at longer exposure time (40 s). The highest compressive strength values were found for the photo-activation methods that employ the halogen lamps, which supply an intermediate light intensity, but provide higher energy densities due to exposure time (21 – 32 J/cm^2). These results corroborate with previous studies in the literature, which suggest that light intensity does not significantly affect the composite resin properties as long as a constant energy application is used (9, 27, 28).

The highest value for diametral tensile strength was obtained for LED, followed by stepped light, PAC, exponential and continuous light, without difference between them, whilst the lowest value was found for intermittent light, which differed only from the LED

(Table 3). This finding demonstrates a difference in the behavior of the Z250 composite in relation to compressive strength *vs.* diametral tensile strength, when photo-activated by different methods. Previous studies have already demonstrated no correlation between these mechanical properties (15, 29, 30). According to Brosh et al. (1999) high compressive strength cannot predict the ability of the material to withstand tensile strength. When tensile stress develops in a restoration, opening or sliding of cracks and flaws within the material occurs, resulting in failure of the restoration.

In the present study, the specimens for compressive and diametral tensile strengths were prepared utilizing silicon molds, which did not offer resistance to the displacement of the specimen, preventing the formation of cracks and flaws within the material during the their preparation. As the same material was used in all conditions tested, characteristics concerning the light source and polymerization process itself might explain these differences.

Although light intensity and energy density are usually related to higher degree of conversion and mechanical properties (6, 29, 1, 2, 4, 27, 28), these properties are not specific related to spectral emission. Thus, each light source may exert dissimilar influences upon the Z250 composite, the photo-initiator of that is camphoroquinone, which has an absorption peak at a wavelength of 468 nm (21). The light curing units used in this study present great differences in relation to spectral emission. The halogen lamps are characterized by a wide wavelength that ranges between 380 – 510 nm, with a wavelength peak at 484 nm (21). These light sources emit a significant quantity of energy towards the red end of the spectrum, i.e., generate heat (9, 8). The PAC curing units supply high light intensity, at a narrow and symmetric wavelength of around 470 nm (440 – 500 nm), but they are utilized for just a few seconds (9). Finally, the LEDs present a narrow and symmetric wavelength that lies between 450 – 490 nm, with a wavelength peak at 466 nm, however they supply a low light intensity (21).

Since that the molar absorption of camphoroquinone is a function of wavelength, different emission profiles will have non-equivalent effects on the initiator (9). In fact, the energy is not the main issue, but the correct wavelength that is supplied to the photo-initiator. This energy requires no more than one photon, in a correct wavelength, to achieve the excitation of the camphoroquinone. The efficiency of absorption clearly varies with wavelength and is never 100%, thus, the efficiency of the creation of free radicals will also be less than 100% (26). However, the creation of the excited state of the photo-initiator reduces the concentration of excitable molecules and, therefore, the efficiency of absorption declines. The photo-initiator system may rapidly become saturated when the irradiation is increased and, as a consequence, no further improvement in the rate of polymerization initiation is possible. Furthermore, at high rates of generation of free radicals, mutual annihilation and reduced reaction chain length occur, leading to poorer network formation and poorer mechanical properties (26). It is possible that over-exposure may be detrimental, if a high-irradiation lamp is chosen (26). Lovell *et al.* (2003) examined the effect of initiation rate, using different types of light sources, on the conversion and flexural strength of a resin mixture model that did not contain filler particles. The authors found that, although the specimens were exposed to similar absorbed photon fluxes (controlled by the use of appropriate filters), the polymerization rates were not equivalent. This may have occurred due to nature of the light sources utilized in the study: a PAC curing unit that supplies a high light intensity (1800 mW/cm^2) for a few seconds (1 – 18 s); and a halogen lamp, which emitted a filtered light between 440 – 510 nm (200 mW/cm^2) at various exposure times (3 – 80 s). These findings suggested that mutual annihilation and reduced reaction chain length really occur.

Compressive and tensile stresses form the basis of flexural tensions. Hence, the flexural strength might be able predict more clearly the characteristics of the material from a practical point of view. The results of this study indicated that flexural strength values were not affected by the curing light sources (Table 4). However, the modulus of elasticity, which was calculated from the three-point bending test, showed higher values for LED, exponential, intermittent and continuous light than those for PAC and stepped light (Table 5). This finding may signify that the modulus of elasticity of the Z250 composite being a more sensitive indicator of the differences between photo-activation methods than flexural strength.

According to Miyazaki et al (1996), if the final degree of conversion of a material is maintained, the mechanical properties will be the same. In an earlier study, the effect of photo-activation method upon the degree of conversion of the Z250 composite was studied. The authors showed that there were no differences in degree of conversion values (31). However, the claims of Miyazaki et al (1996) can be compared only to the flexural strength values in the present study.

The lowest modulus of elasticity values were obtained for the PAC and stepped light, signifying that there were probably significant differences in the kinetics of the polymerization and network formation when these two methods were employed. The PAC source supply a high intensity, which, theoretically, may has been caused two problems: firstly, the photo-initiator system may rapidly become saturated by the high light intensity supplied, causing no improvement in the initiation rate, as well as mutual annihilation of the free radicals (26), as above mentioned; secondly, the faster polymerization rates produced by high intensity might result in shorter chains with lower molecular weight and less cross-linking. Higher molecular weight may be an important factor since it may yield tie molecules (25, 20). For the stepped light, another phenomenon may have occurred: the low intensity supplied in the initial 10 seconds (which presents wide wavelength) provides the lowest polymerization rate, which may result in more linear polymeric chains with reduced density of cross-linking. However, lower initiation and polymerization rate in the initial stages of the reaction may lead to an extensive primary cyclization, creating microgels, which promote higher local conversion, but can lead to a reduction in the effective cross-linking density, thus reducing the mechanical properties (32, 33).

Finally, in terms of mechanical properties, the results of this study are not conclusive. The findings showed that each property revealed a different behavior as a function of the photo-activation method considered. Unfortunately, the macroscopic testing performed in this study cannot confirm all hypotheses mentioned, they only describe the behavior of the material as a function of the photo-activation method. Since the complexity of this subject is great, microscopic testing which can discern the network structure as a function of polymerization conditions might be performed.

ACKNOWLEDGEMENTS

The authors thank CAPES for supporting this study.

REFERENCES

1. Asmussen E. Restorative resins: hardness and strength *vs*. quantity of remaining double bonds. *Scandinavian Journal of Dental Research* 1982; **90**: 484 – 489.

2. Ferracane JL, Greener EH. The effect of resin formulation on the degree of conversion and mechanical properties of dental restorative resins. *Journal of Biomedical Materials Research* 1986; **20**: 121 – 131.
3. Rueggeberg FA, Craig RG. Correlation of parameters used to estimate monomer conversion in a light-cured composite. *Journal of Dental Research* 1988; **67**: 932 – 937.
4. Lovell LG, Lu H, Elliott JE, Stansbury JW, Bowman CN. The effect of cure rate on the mechanical properties of dental resins. *Dental Materials* 2001;**17**:504-511.
5. Ikejima I, Nomoto R, McCabe JF. Shear punch strength and flexural strength of model composites with varying filler volume fraction, particle size and silanation. *Dental Materials* 2003; **19**: 206 – 211.
6. Rueggeberg FA, Caughman WF, Curtis Jr JW and Davis HC. Factors affecting cure at depth within light-activated resin composites. *American Journal of Dentistry* 1993; **6**: 91-95.
7. Silikas N, Eliades G and Watts DC. Light intensity effects on resin-composite degree of conversion and shrinkage strain. *Dental Materials* 2000; **16**:292-296.
8. Hofmann N, Hugo B, Schubert K and Klaiber B. Comparison between a plasma arc light source and conventional halogen curing units regarding flexural strength, modulus, and hardness of photoactivated resin composites. *Clinical of Oral Investigation* 2000; **4**:140-147.
9. Lovell LG, Newman SM, Donaldson MM, Bowman CN. The effect of light intensity on double bond conversion and flexural strength of a model, unfilled

dental resin. *Dental Materials* 2003; **19**: 458 – 465.

10. Yearn JA. Factors affecting cure of visible light activated composites. *International Dental Journal* 1985; **35**:218–225.
11. Braem M, Finger W, Van Doren VE, Lambrechts P, Vanherle G. Mechanical properties and filler fraction of dental composites. *Dental Materials* 1989; **5**: 346 – 349.
12. Mohsen NM, Craig RG. Effect of silanation of fillers on their dispersability by monomer system. *Journal of Oral Rehabilitation* 1995; **22**: 183 – 189.
13. Bowen RL. Properties of a silica-reinforced polymer for dental restoration. *Journal of American Dental Association* 1963; **66**: 57 – 64.
14. Asmussen E, Peutzfeldt A. two-step curing: influence on conversion and softening of a dental polymer. *Dental Materials* 2003; **19**: 466- 470.
15. St-Georges AJ, Swift Jr EJ, Thompson JY, Heymann HO. Irradiance effects on the mechanical properties of universal hybrid and flowable hybrid composite resin. *Dental Materials* 2003; **19**: 406 –413.
16. Obici AC, Sinhoreti MAC, Goes MF, Consani S and Sobrinho LC. Effect of photo-activation method on polymerization shrinkage of restorative composites. *Operative Dentistry* 2002; **27**:192-198.
17. Uno S and Asmussen E. Marginal adaptation of a restorative resin polymerized at reduced rate. *Scandinavian Journal of Dental Research* 1991; **99**:440-444.
18. Caldas DB, de Almeida JB, Correr-Sobrinho L, Sinhoreti MAC and Consani S. Influence of curing tip distance on resin composite knoop hardness number, using three different light curing units. *Operative Dentistry.* 2003; **28**:315-320.

19. Tarle Z, Meniga A, Ristic M, Sutalo J, Pichler and Davidson CL. The effect of photopolymerization method on the quality of composite resin. *Journal of Oral Rehabilitation* 1998; **25**:436-442.

20. Peutzfeldt A, Sahari A and Asmussen E. Characterization of resin composites polymerized with plasma arc curing units. *Dental Materials* 2000; **16**:330-336.

21. Fujibayashi K, Ishimaru K, Takahashi N and Kihno A. Newly developed curing unit using blue light-emitting diodes. *Dentistry in Japan* 1998; **34**:49-53.

22. Jandt KD, Mills RW, Blackwell GB and Ashworth SH. Depth of cure and compressive strength of dental composites cured with blue light emitting diodes (LEDs). *Dental Materials* 2000; **16**:41-47.

23. Stahl F, Ashworth SH, Jandt KD and Mills RW. Light-emitting diode (LED) polymerization of dental composite: flexural properties and polymerization potential. *Biomaterials* 2000; **21**:1379-1385.

24. Mills RW, Jandt KD and Ashworth SH. Dental composite depth cure with halogen and blue light emitting diode technology. *British Dental Journal* 1999; **186**:388-391.

25. Rueggeberg FA. Contemporary issue in photocuring. *Compendium Continued of Education Dentistry* 1999; **20** (Suppl): 4 – 15.

26. Musanje L, Darvell BW. Polymerization of resin composite restorative materials: exposure reciprocity. *Dental Materials* 2003; **19**: 531 – 541.

27. Miyazaki M, Oshida Y, Moore B K, Onose H. Effect of light exposure on fracture toughness and flexural strength of light-cured composites *Dental Materials*

1996; **12**:328-332.

28. Sakaguchi R L, Berge H X. Reduced light energy density decreases post-gel contraction while maintaining degree of conversion in composites *Journal of Dentistry* 1998; **26**:695-700.
29. Chung KH, Greener EH. Correlation between degree of conversion, filler concentration and mechanical properties of posterior composite resins. *Journal of Oral Rehabilitation* 1990; **17**: 487 – 494.
30. Brosh T, Ganor Y, Belov I, Pilo R. Analysis of strength properties of light-cured resin composites. *Dental Materials* 1999; **15**: 174 – 179.
31. Obici AC, Sinhoreti MAC, Frollini E, Sobrinho LC, Consani S. Degree of conversion of Z250 composite determined by Fourier Transform Infrared Spectroscopy: comparison of techniques, storage periods and photo-activation methods *Dental Materials* (in press).
32. Andrzejewska E. Photopolymerization kinetics of multifunctional monomers. *Progress in Polymer Science* 2001; **26**:605-665.
33. Elliott JE, Lovell LG and Bowman CN. Primary cyclization in the polymerization of BisGMA and TEGDMA: a modeling approach to understanding the cure of dental resins. *Dental Materials* 2001; **17**:271-279.

Table 1. Composition of the Z250 composite resin (according to manufacturer’s information).

Organic	Filler			Batch
Matrix	Type	% (vol)	Size (µm)	
Bisphenol-glycidyl methacrylate (BisGMA), urethanethyl dimethacrylate (UDMA) and Bisphenol-polyethylene glycol dimethacrylate (BisEMA). Camphoroquinone (initiator)	Zirconia/silica	60	0.19 – 3.3	2XX 2005-09

Table 2- Means of compression strength of Z250 composite resin.

Photo-activation method	**Compression strength (Mpa)**			
Continuous light	298.32	(20.98)	a	
Exponential light	282.9	(28.50)	a	
Intermittent light	280.6	(30.11)	a	
Stepped light	269.44	(36.55)	a	
PAC	225.12	(38.54)		b
LED	213.91	(38.30)		b

Means followed by different letters are statistically different at 5% by Tukey's test.

( ) Standard Deviation.

Table 3- Means of diametral tensile strength of Z250 composite resin.

Photo-activation method	**Diametral tensile (Mpa)**			
LED	66.35	(12.36)	a	
Stepped light	63.52	(9.95)	a	b
PAC	59.73	(13.77)	a	b
Exponential light	58.88	(10.85)	a	b
Continuous light	57.91	(12.97)	a	b
Intermittent light	49.95	(10.53)		b

Means followed by different letters are statistically different at 5% by Tukey's test.

( ) Standard Deviation.

Table 4- Means of flexural strength of Z250 composite resin.

Photo-activation method	**Flexural Strength (Mpa)**		
Intermittent light	172.97	(19.63)	a
Exponential light	168.78	(12.79)	a
LED	164.36	(14.25)	a
Stepped light	163.16	(31.44)	a
PAC	155.23	(15.87)	a
Continuous light	154.1	(23.4)	a

Means followed by different letters are statistically different at 5% by Tukey's test.

( ) Standard Deviation.

Table 5- Means of modulus of elasticity of Z250 composite resin.

Photo-activation method	**Modulus of Elasticity (Gpa)**		
LED	11.57	(1.14)	a
Exponential light	11.0	(0.89)	a
Continuous light	10.9	(0.92)	a
Intermittent light	10.68	(1.82)	a
PAC	9.04	(0.94)	b
Stepped light	8.92	(1.03)	b

Means followed by different letters are statistically different at 5% by Tukey's test.

( ) Standard Deviation.

CONCLUSÕES GERAIS

Com base nos resultados obtidos dos cinco trabalhos, pôde-se concluir que:

1- O método de fotoativação altera a profundidade de polimerização e os valores de dureza Knoop a profundidades maiores do que 2 mm, o que pode resultar em material deficientemente polimerizados em regiões mais profundas da restauração. Portanto, incrementos maiores do que 2 mm não são recomendados clinicamente.

2- O grau de conversão do compósito Z250, em espessura de 2 mm, não foi estatisticamente afetado pelo uso de diferentes métodos de fotoativação ou períodos de armazenamento considerados. Entretanto, a técnica de preparo do corpo-de-prova significativamente afetou os valores de grau de conversão para este material.

3- Até a profundidade de 2 mm, não houve diferença no grau de conversão do compósito Z250 quando fotoativado por diferentes métodos. A maiores profundidades foi observado que o grau de conversão foi significativamente afetado pelo método de fotoativação. Os métodos de LED, dupla intensidade de luz, luz exponencial e luz intermitente não mostraram diferenças significativas no grau de conversão na superfície e nas profundidades de 1, 2 e 3 mm. Já a luz halógena contínua apresentou valores de grau de conversão similares para a superfície, 1 e 2 mm, enquanto o PAC revelou os maiores valores para a superfície e 1 mm.

4- O grau de conversão do compósito Z250 não foi estatisticamente afetado pelos diferentes métodos de fotoativação, em corpos-de-prova que apresentavam 2 mm de espessura. Entretanto, os valores de dureza Knoop mostraram significantes diferenças entre os métodos de fotoativação.

5- As propriedades mecânicas foram diferentemente afetadas pelos métodos de fotoativação. Para a resistência à compressão, os maiores valores foram encontrados com os métodos de luz contínua, luz exponencial, luz intermitente e dupla intensidade de luz, enquanto PAC e LED mostraram os menores valores. Os maiores valores para a resistência à tração diametral foram observados para o LED, dupla intensidade de luz, PAC, luz exponencial e luz contínua, enquanto a luz intermitente obteve os menores valores, diferindo apenas do LED. Os métodos de fotoativação não causaram diferenças significativas nos valores de resistência à flexão do compósito Z250. E, finalmente, os maiores valores do módulo de elasticidade foram obtidos com LED, luz exponencial, luz contínua e luz intermitente, já o PAC e a dupla intensidade de luz mostraram os menores valores.

REFERÊNCIAS BIBLIOGRÁFICAS *

1. Asmussen E, Peutzfeldt A. Influence of UDMA, BisGMA and TEGDMA on selected mechanical properties of experimental resin composites. ***Dent. Mater.*** 1998 Jan., 14(1): 51-56.
2. Asmussen, E. Restorative resins: hardness and strength *vs.* quantity of remaining double bonds. ***Scand. J. Dent. Res.***, 1982 Dec., 90(6): 484 – 489.
3. Bassiouny MA, Grant, AA. A visible light-cured composite restorative. ***Brit. Dent. J.*** 1978 Dec.; 145(11): 327-330.
4. Bouschlicher MR, Rueggeberg FA, Boyer D. Effect of stepped light intensity on polymerization force and conversion in a photoactivated composite. ***J. Esthet. Dent.*** 2000 Jan., 12(1): 23-32.
5. Bowen RL. Properties of a silica-reinforced polymer for dental restorations. ***J. Am. Dent. Ass.*** 1963 Jan., 66(1): 57-64.
6. Caldas DB, de Almeida JB, Correr-Sobrinho L, Sinhoreti MAC, Consani S. Influence of curing tip distance on resin composite knoop hardness number, using three different light curing units. ***Operat Dent.*** 2003 May/Jun., 28(3): 315-320.
7. Chung K, Greener EH. Degree of conversion of seven visible light-cured posterior composite. ***J. Oral Rehabil.*** 1988 Nov., 15(6): 555-560.

---

* De acordo com a norma utilizada na FOP/UNICAMP, baseada no modelo Vancouver. Abreviatura dos periódicos em conformidade com o Medline.

* Referências pertinentes à Introdução Geral do trabalho.

8. Davy KWM, Kalachandra S, Padain MS, Braden M. Relationship between composite matrix molecular structure and properties. ***Biomaterials***, 1998 Nov., 19(22): 2007-2014.
9. Elliott JE, Lovell LG, Bowman CN. Primary cyclization in the polymerization of BisGMA and TEGDMA: a modeling approach to understanding the cure of dental resins. ***Dent. Mater.*** 2001 May, 17(3): 271-279.
10. Feilzer AJ, Dooren LH, de Gee AJ DavidsonCl. Influence of light intensity on polymerization shrinkage and integrity of restoration-cavity interface. ***Eur. J. Oral Sci.*** 1995 Oct., 103(5): 322-326.
11. Fujibayashi K, Ishimaru K, Takahashi N, Kihno A. Newly developed curing unit using blue light-emitting diodes. ***Dentistry in Japan*** 1998 Mar., 34:49-53.
12. Hofmann N, Hugo B, Schubert K, Klaiber B. Comparison between a plasma arc light source and conventional halogen curing units regarding flexural strength, modulus, and hardness of photoactivated resin composites. ***Clin Oral Invest*** 2000 Sept.; 4(3): 140-147.
13. Jandt KD, Mills RW, Blackwell GB, Ashworth SH. Depth of cure and compressive strength of dental composites cured with blue light emitting diodes (LEDs). ***Dent. Mater.*** 2000 Jan., 16 (1): 41-47.
14. Kawaguchi M, Fukushima T, Miyazaki K. The relationship between cure depth and transmission coefficient of visible-light-activated resin composites. ***J. Dent. Res.*** 1994 Feb., 73(2): 516 – 521.
15. Kurachi C, Tuboy AM, Magalhães DV, Bognato VS. Hardness evaluation of a dental composite polymerized with experimental LED-based devices. ***Dent. Mater.***

2001 Jul., 17(4): 309-315.

16. Lovell LG, Newman SM, Bowman CN. The effects of light intensity, temperature, and comonomer composition on the polymerization behavior of dimethacrylate dental resins. ***J. Dent. Res.*** 1999 Aug., 78(8): 1496-1476.
17. Meniga A, Tarle Z, Ristic M, Sutalo J, Pichler G. Pulsed blue laser curing of hybrid composite resins. ***Biomaterials*** 1997 Oct., 18(20): 1349-1354.
18. Obici AC, Sinhoreti MAC, Goes MF, Consani S, Sobrinho LC. Effect of photo-activation method on polymerization shrinkage of restorative composites. ***Operat. Dent.*** 2002 Mar./Apr., 27(2): 192-198.
19. Peutzfeldt A, Sahari A, Asmussen E. Characterization of resin composites polymerized with plasma arc curing units. ***Dent. Mater.*** 2000 Sept., 16(5): 330-336.
20. Peutzfeldt A. Resin composites in dentistry: the monomer systems. ***Eur. J. Oral Sci.*** 1997 Mar./Apr., 105(2): 97-116.
21. Rueggeberg FA, Caughman WF, Curtis Jr JW, Davis HC. Factors affecting cure at depth within light-activated resin composites. ***Am. J. Dent.*** 1993 Jan, 6(1): 91-95.
22. Rueggeberg FA, Caughman WF, Curtis Jr JW. Effect of light intensity and exposure duration on cure of resin composite. ***Operat. Dent.*** 1994 Jan., 19(1): 26-32.
23. Ruyter IE, Oysaed H. Conversion in different depths of ultraviolet and visible light activated composite materials. ***Acta. Odontol. Scand.***, 1982 June, 40(3): 179-192.
24. Sakaguchi RL, Berge HX. Reduced light energy density decreases post-gel

contraction while maintaining degree of conversion in composites. ***J. Dent.*** 1998 Nov./Dec., 26(6): 695-700.

25. Sakaguchi RL, Douglas WH, Peters MCRB. Curing light performance and polymerization of composite restorative materials. ***J. Dent.*** 1992 Mar., 20(3): 183-188.
26. Stahl F, Ashworth SH, Jandt KD, Mills RW. Light-emitting diode (LED) polymerization of dental composite: flexural properties and polymerization potential. ***Biomaterials*** 2000 Jul., 21 (13): 1379-1385.
27. Tarle Z, Meniga A, Ristic M, Sutalo J, Pichler, Davidson CL. The effect of photopolymerization method on the quality of composite resin. ***J Oral Rehabil*** 1998 Dec., 25(6): 436-442.
28. Uno S, Asmussen E. Marginal adaptation of a restorative resin polymerized at reduced rate. ***Scand. J. Dent. Res.*** 1991 Sept./Oct., 99(5): 440-444.
29. Unterbrink GL, Muessner R. Influence of light intensity on two restorative systems. ***J. Dent.*** 1995 May/June, 23(3): 183-189.
30. Venhoven BAM, de Gee AJ, Davidson CL. Polymerization contraction and conversion of BisGMA-based methacrytate resins. ***Biomaterials*** 1993 Sept., 14(11): 871-875.
31. Yearn JA. Factors affecting cure of visible light activated composites. ***Inter. Dent. J.*** 1985 Sept.; 35(3): 218–225.

APÊNDICES

Apêndice 1: Carta de aceitação do trabalho referente ao Capítulo I.

Universidade de São Paulo
Faculdade de Odontologia de Ribeirão Preto
BRAZILIAN DENTAL JOURNAL
e-mail: bdj@forp.usp.br
e-mail: pecora@forp.usp.br

Via do Café s/n 14040-904 Ribeirão Preto, SP, Brasil. Fax 55-16-633-0999

Ribeirão Preto, 03 de novembro de 2003.

Prezados Professores,

O trabalho BDJ 570 **EVALUATION OF DEPTH OF CURE AND KNOOP HARDNESS IN A DENTAL COMPOSITE PHOTO-ACTIVATED USING DIFFERENT METHODS** dos autores Andresa Carla OBICI (andresaobici@yahoo.com ou andresa@unipar.br); Mário Alexandre Coelho SINHORETI (sinhoret@fop.unicamp.br); Lourenço CORRER SOBRINHO; Mario Fernando de GÓES; Simonides CONSANI (consani@fop.unicamp.br), foi aceito no mérito científico para publicação.

No entanto, deve-se ressaltar alguns aspectos que precedem a publicação final do trabalho em questão. O artigo será submetido à apreciação do *technical editor*, após o que, poderão ser necessárias alterações e ou adequações para a sua publicação, sem que isso implique na sua recusa. Ainda mais, devido ao grande número de artigos já aprovados pelo corpo editorial e outros vários em processo de avaliação, a publicação do presente artigo não se dará antes 18 meses, o que pode deixar de interessar a Vossa Senhoria. Por fim, em função das questões econômicas, o custo da revisão do inglês e a correção formal do artigo será repassado para os autores.

Dessa forma, aguardamos a vossa manifestação quanto ao interesse em publicar o seu artigo científico.

Atenciosamente,

Prof. Dr. Manoel D. Sousa Neto
Editor

Apêndice 2: Carta de envio do trabalho referente ao Capítulo II.

UNICAMP
UNIVERSIDADE ESTADUAL DE CAMPINAS
FACULDADE DE ODONTOLOGIA DE PIRACICABA

Piracicaba, 25 de agosto de 2003.

Dr. David C. Watts - Editor of Dental Materials
University of Manchester Dental School
Higher Cambridge Street - Manchester, M15 6FH – UK

Dear Dr. Watts

We are submitting a manuscript "**Degree of Conversion of Z250 Composite Determined by Fourier Transform Infrared Spectroscopy: Comparison of Techniques, Storage Periods and Photo-activation Methods"** to Dental Materials.

Sincerely,

Andresa Carla Obici

Dr. Mário Alexandre Coelho Sinhoreti

Apêndice 3: Carta de recebimento do trabalho referente ao Capítulo III.

Dear Dr Sinhoreti

Thank you for submitting your LABORATORY RESEARCH manuscript 03-237 *Evaluation of Degree of Conversion by FTIR at Different Depths Using Six Photo-Activation Methods*. We appreciate your considering our journal for the publication of your work.

Copies of your paper will be sent to our referees for review. Once their reviews have been received and a decision has been made regarding publication, we will notify you. This process usually takes from twelve to fourteen weeks.

If you have any questions, please feel free to contact our office. Thank you again for submitting your manuscript to *Operative Dentistry*.

Sincerely

Joan Matis
Editorial Assistant/Subscription Manager
Operative Dentistry
email: jmatis@indy.rr.comfax
fax: USA 317-852-3162

Apêndice 4: Carta de recebimento do trabalho referente ao Capítulo IV.

Dr. Sinhoreti

I received your paper and will send it to two reviewers for their comments.

Immediately after I hear from them I will contact you.

Sincerely,

Prof. Dr. Franklin Garcia-Godoy
Editor

College of Dental Medicine
Nova Southeastern University
3200 South University Drive
Fort Lauderdale, FL 33328, U.S.A.

Apêndice 5: Carta de envio do trabalho referente ao Capítulo V.

UNIVERSIDADE ESTADUAL DE CAMPINAS
FACULDADE DE ODONTOLOGIA DE PIRACICABA

Piracicaba, 20 de outubro de 2003.

Dr. Joanne Frankland,
Administrative Editor
Journal of Dentistry
Oxford - UK

I would like to submit my manuscript: **Evaluation of mechanical properties of Z250 composite resin photo-activated by different methods** " to Journal of Dentistry. This manuscript has not been published in any form or any language and is only submitted to the Journal of Dentistry.

Sincerely,

Andresa Carla Obici

Dr. Mário Alexandre Coelho Sinhoreti